URBAN SODICITY IN A HUMID SUBTROPICAL CLIMATE: IMPACT ON BIOGEOCHEMICAL CYCLING

A Dissertation

by

MEREDITH KATE STEELE

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

August 2011

Major Subject: Soil Science

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ABSTRACT

Urban Sodicity in a Humid Subtropical Climate: Impact on Biogeochemical Cycling.

(August 2011)

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Understanding the mechanisms of non-point source carbon and nutrients in urban watersheds will help to develop policies to maintain surface water quality and prevention of eutrophication. The purpose of this dissertation is to investigate the impact of sodium on carbon and nutrient leaching from the two main contributors; soil and leaf litter, and calculate the sodium exports in a humid subtropical urban river basin.

The first chapter reviews the current literature on urbanization in watersheds. Chapter II quantifies the carbon and nutrient in intact soil core leachates and in water extractable solution from urban soils collected from 26 towns and cities across the state of Texas. Chapter III investigates the impact of sodicity and salinity on water extractable organic carbon and nitrogen from vegetation. Chapter IV investigates the export of sodium and chloride from the upper Trinity River basin. The results derived from this study indicate that sodium exports are elevated in urban watersheds and that sodium in irrigation water elevates the loss of carbon and nutrients from both watershed soil and senesced vegetation, and that this may contribute to high concentrations in urban freshwaters.

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NOMENCLATURE

ALK	Alkalinity
ALK_{iw}	Alkalinity of irrigation water
C_S	Total soil carbon
DDW	De-ionized distilled water
DOC	Dissolved organic carbon
DON	Dissolved organic nitrogen
EC_{iw}	Electrical conductivity of irrigation water
ECs	Electrical conductivity of saturated past soil extract
ESP	Exchangeable sodium percentage
pHs	pH of saturated past soil extract
POM	Particulate organic matter
SAR	Sodium adsorption ratio
SAR_{iw}	Sodium adsorption ratio of the irrigation water
SARs	Sodium adsorption ratio of saturated past soil extract
SMB	Soil microbial biomass
SOM	Soil organic matter
UTRB	Upper Trinity River Basin
WEDOC	Water extractable dissolved organic carbon
WEDON	Water extractable dissolved organic nitrogen
WWTF	Wastewater treatment facility

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CHAPTER I

INTRODUCTION: PROBLEM STATEMENT AND REVIEW OF LITERATURE*

Problem Statement

Urban and suburban watersheds in the in Bryan/College Station region have extremely high dissolved organic carbon (DOC) concentrations which are strongly related to urban open area land use (Aitkenhead-Peterson et al. 2009). Problems associated with high DOC in surface waters include: a) the loss of terrestrial sequestered carbon pools, providing a substrate for microbial growth, and b) the formation of the carcinogenic trihalomethane compounds if the water is chlorinated for drinking supplies. In addition, elevated phosphorus and nitrate are also listed as concerns based on screening levels for Carters Creek (TCEQ 2008). Elevated concentrations of nitrogen (N) and phosphorus (P) in surface waters can lead to eutrophication and designated beneficial use impairment (Sharpley and Withers 1994).

The municipal water supplies in the Bryan/College Station region have high concentrations of sodium (~200 mg L^{-1}) and bicarbonate (~450 mg L^{-1}). Aydemir et al.

This dissertation follows the style of Biogeochemistry.

*Chapter I is reprinted with permission from Steele MK, McDowell WH, Aitkenhead-Peterson JA (2010) Chemistry of urban, suburban, and rural surface waters. Urban Ecosystem Ecology. Eds. JA Aitkenhead-Peterson and A Volder. Agronomy Monograph 55. p. 297-339.

measured soil irrigated with municipal water supplies high in sodium in south Texas. Of the variables tested, they reported the sodicity of the irrigation water was the best single predictor of sodium accumulation in the soil (Aydemir et al. 2005).

In a broad perspective, many municipal water sources across the United States are sodic presenting a severe risk of causing water infiltration problems through the soil matrix. As urban and suburban development expands into areas that were previously utilized for agriculture, irrigation of homeowner landscapes, commercial aesthetic landscaping and newly constructed sports parks and golf courses with sodic water may well mobilize P that was previously applied to the soil as fertilizers and manure in an agricultural setting. In addition to sodic water sources already in use, pressure on existing water supplies may increase the use of treated effluent and grey water for irrigating recreational green space (Hayes et al. 1990; Mancino and Pepper 1992) and home owner gardens (Finley et al. 2009) in urban areas. These alternative water sources typically contain more sodium than the original municipal tap water because of the addition of detergents, cleaning agents and other inputs to wastewater treatment facilities. Understanding the relationship between urban sodicity and biogeochemical cycling will help us understand and protect our nation's surface water.

Urbanization and Surface Water Biogeochemistry

Throughout the world, the number of people living in cities is growing. Within the next several decades 60% of the people on the planet will live in urban areas, with 85% of the population in developed nations (UNPD 2003). Rapid population growth in urban areas causes both more extensive and more intensive development. This development and the activities that occur post-development have a significant impact on the chemistry surface water within and downstream of cities. The National Water Quality Inventory: 2000 Report to Congress identified runoff within urban ecosystems as a leading source of water quality impairment to surface waters, ranking it fourth for rivers and streams, third for lakes, and second for estuaries (USEPA 2002). Pathogens, sediments, toxic chemicals, heavy metals, nutrients, salinity, and carbon are potential impairments caused by urbanization. Bernhardt and Palmer (2007) described the state of urban streams as “gutters”, simplified channels that carry high loads of water and other elements away from urban centers. Both intentionally and unintentionally, people have used the natural process of collection and removal provided by streams and rivers to simply carry away wastes and residues. This collection system integrates human activities and natural process on the land and in the water, resulting in what has been called a “distinct urban biogeochemistry” (Kaye et al. 2006). Almost every object and organism in a city interacts with water at some point in its existence, from cradle or manufacturing to its grave or disposal. Water has been termed the universal solvent, and thus every interaction has the potential to alter water chemistry and quality. However, the system is robust and generally the most common activities and objects in cities that have the largest impact.

Cities are often characterized by a large fraction of impervious surfaces, and almost all of the urban impacts that manifest themselves as water quality changes have some connection to increases in impervious surfaces. Impervious surfaces are relatively smooth, reduce infiltration to soil, and are designed to shed water as quickly as possible. These conditions create an ideal situation for water to transport anything on the surface. The other common attribute of urban systems that impacts stream chemistry is wastewater treatment facilities (WWTF). Changes in impervious surface are typically considered to be non-point or diffuse sources of pollution, while WWTF are technically considered to be point sources because they provide a single, easily identified input to surface waters. The actual impacts of WWTF on water quality are more complicated; however, as leaks in the sewer lines can discharge raw sewage into surface waters as an effective non-point source, and for combined sewer systems, the runoff from impervious systems can be treated and thus can act to reduce non-point source inputs to surface waters.

The concentrations and loads of nitrogen and phosphorus in surface waters have received enormous attention over the past several decades (e.g. Grimm et al. 2000; Paul and Meyer 2001; Bernhardt et al. 2008). Interest in these two elements is due to their key roles as limiting nutrients for aquatic biota and the eutrophication of lakes, estuaries, rivers, and streams (Huisman et al. 2005; Diaz et al. 2008). Eutrophication of surface water is considered one of the leading causes of dead zones in estuaries, where the high nutrient concentrations increase algal primary productivity and result in a depletion of oxygen when algal biomass is subsequently decomposed. Previously nitrogen was thought to control dead zones in marine environments, while phosphorus was more important in controlling freshwater eutrophication; however, new evidence suggests that a dual approach of considering nitrogen and phosphorus together may reduce impacts throughout a drainage network and provide a more permanent solution (Conley et al. 2009). While much research has been aimed at quantifying agricultural contributions to nutrient loads, urbanization has been recognized for some time as a cause of high loads and concentrations of nitrogen and phosphorus in surface waters (USEPA 2002).

The first portion of this chapter describes terrestrial and aquatic sources and sinks, the resulting concentrations and/or loads in surface runoff, and the in-stream processes that regulate the retention or loss in surface waters of nutrients (nitrogen and phosphorus), carbon, and major anions and cations in urban ecosystems. The second part of this chapter focuses on the effects of sodium in urban and rural soils and biogeochemical cycles.

Urban Nitrogen Cycling

Reactive nitrogen is an important component of life and its abundance controls the rate of many biological processes. Reactive nitrogen refers to inorganic nitrogen, such as ammonium and nitrate, as well as organic forms of nitrogen such as amino acids. Both forms can be utilized by the majority of living organisms. Henceforth, the term "nitrogen" (N) will be used to refer to reactive nitrogen. Humans require N and consume it in the form of plant and animal products. Human alteration of the landscape by agriculture has increased the delivery of N to surface waters (Boyer et al. 2002) both by increases in coverage of N-fixing crops (legumes and rice in association with cyanobacteria) and by the synthesis of inorganic nitrogen fertilizers (Galloway et al. 2004). In combination with fossil fuel combustion, the amount of reactive nitrogen produced by humans approximately equals the amount produced naturally and is expected to exceed natural production by the year 2050 (Galloway et al. 2004; IPCC 2007). Nitrogen fertilizers have revolutionized agriculture during the 20th century and altered the N cycle in large areas of the earth. Urban centers indirectly concentrate much of this N fertilizer in the form of food shipped in from agricultural areas, dispersed throughout the population, and re-concentrated at wastewater treatment facilities (Groffman et al. 2004). Food is not the only source of N inputs to urban ecosystems and is only one of the pathways N takes through the urban environment. Like N cycling in pristine regions, urban nitrogen cycling is complex. Several components make up the nitrogen cycle for a given area; inputs, transformations, storage, and outputs (or losses).

Inputs of N

In a natural terrestrial ecosystem, the primary inputs of reactive N are from atmospheric deposition of N_2 fixed by lightning, and fixation by naturally occurring leguminous plants. The amount of reactive nitrogen produced by lightning globally ranges from 3 to 10 Tg N yr^{-1} (Prather et al. 2001; Galloway et al. 2004). Nitrogen inputs into urban watersheds are very complex and few studies have attempted N budgets for urban watersheds as almost every commodity has some N component (Van Breeman et al. 2002; Bernhardt et al. 2008). The importation of water into urban areas is an important N input. Large volumes of water imported from outside the watershed can act as an N loading mechanism. The concentration of N in this water is generally low; however, the volumes are very high resulting in high input loads to the watershed (Kennedy et al. 2007; Wolf et al. 2007). For example, Warren-Rhodes and Koenig

(2001) found that 8 tons of N which represented 3% of all imported N annually, was imported within water to Hong Kong in 1997.

Food is another N import to an urban watershed. Groffman et al. (2004) used an assumed human N consumption (and excretion) rate of 12 g of N per capita per day based on the findings by Bleken and Bakken (1998). This major flux of nitrogen to most cities, estimated by Bernhardt et al. (2008) to contribute 13 to 90% of imported N based on five urban watershed mass balance studies conducted to date (Baker et al. 2001; Faerge et al. 2001; Warren-Rhodes and Koenig 2001; Groffman et al. 2004; Wollheim et al. 2005). Pet food may be a particularly important part of the total food load because N in food is released as waste from the animal and is more likely to be deposited onto lawns and other green spaces and subject to leaching and runoff, rather than entering the wastewater stream with human wastes (Baker et al. 2001). For the Baltimore LTER, pet waste–derived N can be a larger annual input (17 kg N ha^{-1} yr^{-1}) than either fertilizer application or atmospheric deposition (Baker et al. 2001; Groffman et al. 2004).

Fertilizer applications and fossil fuel combustions may also be a significant input. Groffman et al. (2004) estimated that lawn fertilization in Baltimore (14.4 kg N ha^{-1} yr^{-1}) was greater than atmospheric deposition. In Hong Kong the estimate for lawn fertilization was about 8 kg N ha^{-1} yr^{-1} (Warren-Rhodes and Koenig 2001). A survey of home owners found application rates were highly variable; however, rates (in mass per area) were similar for areas with low population density area (and typically larger lawn areas) and high density areas with less total lawn area (Law et al. 2004). Localized deposition of N from fossil fuel combustion may be a significant contributor of ammonia

(NH_3) to surface runoff when NH_3 is given off as a by-product of catalytic conversion of NO_x compounds (Maestre and Pitt 2005; Bernhardt et al. 2008). Baker et al (2001) estimate that dry deposition in Phoenix, AZ is 15 kg NO_x-N ha^{-1} and 3.5 kg NH_3-N ha^{-1} annually in urban areas, compared to the 1.9 kg N ha^{-1} y^{-1} received via wet deposition in Phoenix, AZ. Many other sources of N get deposited onto impervious surfaces (e.g. excrement dropped by migrating birds) or funneled into the waste water treatment system (e.g. industrial byproducts) and contribute to loading; however, our knowledge of these is still limited.

Movement, Retention, and Storage

The majority of N inputs in undisturbed or agricultural ecosystems first make contact with vegetation or soil. This is an important difference between “natural” N cycles and urban N cycles, because contact with soil and vegetation provides an increased opportunity for N to be immobilized by plants and microbes. N_2 converted to ammonia can either be taken up directly by plants or transformed in the soil to nitrate and then immobilized in the form of organic nitrogen compounds by plants. If nitrogen is limiting, then most of the N will be scavenged by plants and microbes. The majority of organic nitrogen compounds returned to the soil will be mineralized to ammonia, transformed back to nitrate, and re-adsorbed by plants. Nitrate not adsorbed has several possible fates: leaching to ground and surface waters in aerobic conditions, and reduced to volatile N_2O and N_2 compounds in anaerobic conditions.

Nitrogen loads in urban ecosystem are less likely to make contact with the soil and vegetation. Urban ecosystems have a greater chance of N being deposited on impervious surfaces, thus reducing the chance that the N is immobilized. Gobel et al. (2007) estimated average concentration ranges from rainwater and roofs and trafficked impervious surfaces to contain 0.10 to 3.39 mg l^{-1} of ammonium and 1.54 to 5.00 mg l^{-1} nitrate. N on impervious surfaces is a result of atmospheric deposition, NO_x release from fossil fuel combustion, excreta from urban animals, dust settling, and fertilizer overspray. Furthermore, the N brought into an urban ecosystem in the form of food bypasses the outside environment almost entirely. The majority of N in food is consumed and concentrated at WWTF, and waste food is delivered to landfills. Food N thus does not come into contact with the environment or soil until it is discharged as wastewater effluent. Where on-site waste disposal is practiced (typically in low-density urban areas), however, a portion of the N in food will be filtered through the soil, taken up by plants, or may end up percolating through to groundwater. Hatt et al. (2004) found that river N concentrations were directly related to septic tank density in Melbourne, Australia; however; the total loads of N in urban streams were more directly related to the amount of effective impervious surfaces. Nitrogen delivered to WWTF undergoes treatment before its release to surface waters. In 2004, approximately 70% of wastewater treatment facilities treated waste by primary and secondary treatment, which entails settling out solids and aerobic biological digestion; few use tertiary treatment which enables the removal of the majority of N from the wastewater stream (USEPA 2002). N released in effluent after secondary treatment is generally in inorganic form (primarily nitrate) and the effect on surface waters in urban ecosystems is a reduction in the ratio of dissolved organic nitrogen to total dissolved nitrogen (DON:TDN) relative to surface waters in urban ecosystems that do not contain a WWTF (Aitkenhead-Peterson et al. 2009).

Little information is available on the sinks of N in urban ecosystems. Depending on the soil type, climate, and hydrology, lawns and green spaces have less runoff than impervious surfaces and are predicted to be one of the N sinks (Bernhardt et al. 2008). Fertilized green spaces such as lawns, athletic fields, and golf courses may not function as sinks because of the high N inputs from fertilizer. King et al. (2007) investigated N loss from a golf course in Austin, TX and found that 3% of applied N fertilizer was lost in storm water. While not a large proportion, it does indicate that these spaces are less likely to function as sinks. Landfills are also predicted to be sinks, as they accumulate the majority of solid waste from municipalities (Bernhardt et al. 2008). The infrastructure itself may become a sink for N as it becomes enriched in N-containing consumer products (Kennedy et al. 2007). In a Baltimore LTER study, the overall N retention was found to be 75% of all inputs for suburban areas, only slightly less than agricultural ecosystems with 77% retention but much lower than a forested catchment which retained 95% of N inputs (Groffman et al. 2004). Baker et al. (2001) suggested that the majority of N input to Phoenix, AZ is lost through denitrification to the atmosphere. Losses other than those to surface water include aerosolized and volatilized N, dust loss, and N transported out of the watershed by humans in various products or wastes.

Nitrogen Loss to Surface Waters

Bernhardt et al. (2008) compared five nitrogen budgets for urban watersheds in Phoenix, AZ (Baker et al. 2001), Baltimore (Groffman et al. 2004), Boston (Wollheim et al. 2005), Bangkok (Faerge et al. 2001) and Hong Kong (Warren-Rhodes and Koenig 2001) and suggested that despite the greater likelihood that N deposited on the landscape will end up in surface waters, the percentage of total nitrogen inputs lost to surface water is relatively small with only 3% of N inputs (Phoenix, AZ), 10% of N inputs (Baltimore, MD), and 15% of N inputs to a small catchment in the suburbs of Boston are exported to stream waters (Baker et al. 2001; Groffman et al. 2004; Wollheim et al. 2005). These values are lower than might be expected due to the fact that most N in the waste stream is exported out of these basins and thus does not enter surface waters. Impacts to surface waters are greater in developing urban areas with less comprehensive wastewater treatment and more localized or limited treatment; for example, 90% of N inputs to Bangkok province and approximately 50% of N inputs to the city of Hong Kong were lost as outputs to surface waters (Faerge et al. 2001; Warren-Rhodes and Koenig 2001).

The percent of inputs lost to surface waters by urban watersheds is relatively low in industrialized cities; the total export of N from urban and suburban watersheds through surface waters is higher than exports from less populated watersheds. Groffman et al. (2004) found that total N exports from three suburban and one urban watershed ranged from 4.9 to 11.2 kg N ha^{-1} yr^{-1} from 1999 to 2001, substantially larger exports compared to the range of 0.51 to 0.48 kg N ha^{-1} yr^{-1} for a forested reference watershed for the same period. A study of 42 watersheds around the world by Peierls et al. (1991) found that watershed nitrate concentrations and exports were strongly correlated with population density in the watershed. However, agriculture has a significant effect on the N exports in large watersheds that include both the production and consumption of food. Investigations on the Mississippi watershed show that the largest contributor to N enrichment of the watershed and the Gulf of Mexico is agriculture (Mitsch et al. 2001; Robertson et al. 2009).

A range of N species concentrations have been reported in the literature. Overall, total dissolved nitrogen (TDN) and dissolved organic nitrogen (DON) concentrations show no trend with increasing percentage of urban land use in watersheds without wastewater treatment effluent affecting stream N. However both nitrate-N and ammonium-N are both weakly positively correlated with increasing urban land use (Figure 1.1). Treated and untreated effluent had a significant impact on the concentrations of all N species regardless of percent urban land use (Table 1.1). Surface water impacted by untreated sewage has significantly higher ammonium than nitrate concentrations (Bhatt and McDowell 2007).

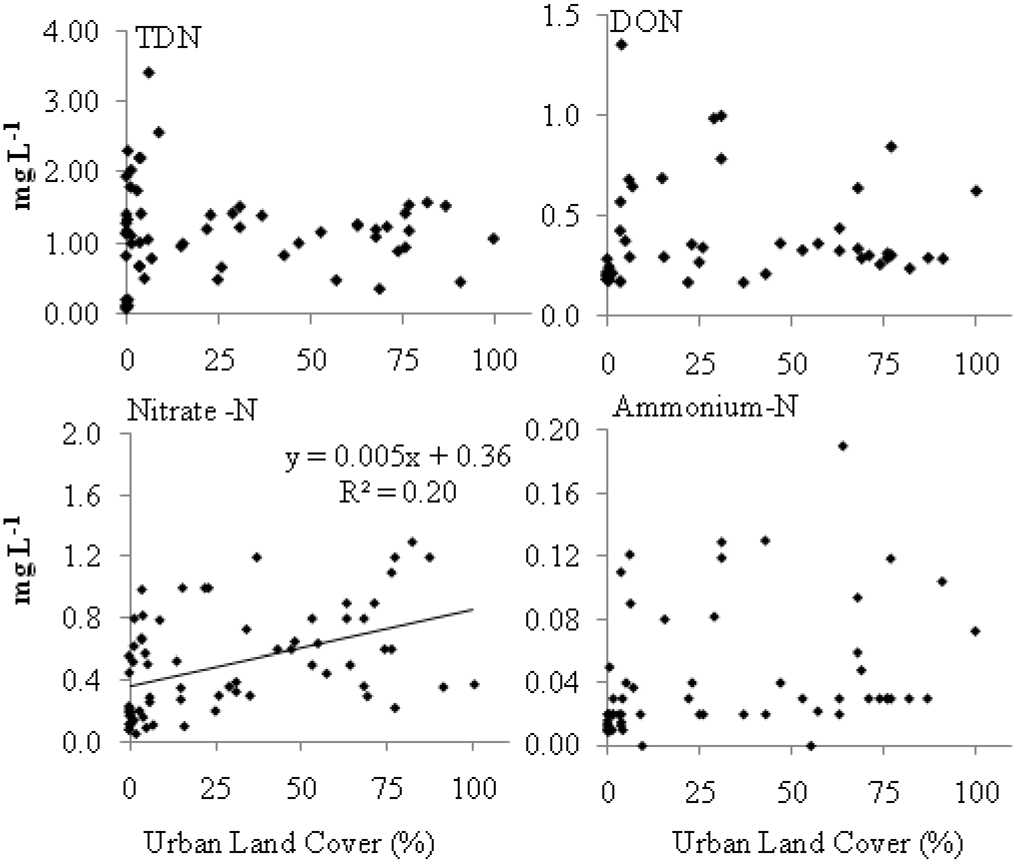

Figure 1.1 Relationship between surface water concentrations of total dissolved nitrogen (TDN), dissolved organic nitrogen (DON), nitrate nitrogen (Nitrate-N), and ammonium nitrogen (ammonium-N) and the percent urban land cover in watersheds reported in the literature. Regressions lines are significant at $\alpha < 0.10$. Source data are obtained from the following references: Aitkenhead-Peterson et al. 2009; Bahar and Yamamuro 2008; Bedore et al. 2008; Bhatt and McDowell 2007; Brett et al. 2005; Chang and Carlson 2005; Chea et al. 2004; Cunningham et al. 2009; Daniels et al. 2002; Fitzpatrick et al. 2007; Lewis et al. 2007; Lui et al. 2000; Rose and Peters 2001; Schoonover et al. 2005; Smart et al. 1985; Von Schiller et al. 2008; Zampella et al. 2007.

Table 1.1 Chemistry of urban surface waters directly receiving wastewater treatment effluent and those not directly receiving effluent.

	No effluent	Effluent
pH	7.66	7.67
Electrical conductivity (µS cm^{-1})	444	790
Sodium (mg L^{-1})	36.3	104.1
Potassium (mg L^{-1})	3.46	7.99
Magnesium (mg L^{-1})	10.6	11.5
Calcium (mg L^{-1})	29.2	32.8
Chloride (mg L^{-1})	26.8	84.2
Sulfate (mg L^{-1})	27.4	28.0
Total dissolved nitrogen (mg L^{-1})	1.08	12.60
Ammonium-N (mg L^{-1})	0.04	5.30
Nitrate-N (mg L^{-1})	0.51	5.38
Bicarbonate (mg L^{-1})	128	193
Phosphate-P (mg L^{-1})	0.07	1.43
Dissolved organic nitrogen (mg L^{-1})	0.42	1.88
Dissolved organic carbon (mg L^{-1})	10.3	19.0

Data Sources: Aitkenhead-Peterson et al. 2009; Bahar and Yamamuro 2008; Bedore et al. 2008; Bhatt and McDowell 2007; Brett et al. 2005; Chang and Carlson 2005; Chea et al. 2004; Cunningham et al. 2009; Daniels et al. 2002; Fitzpatrick et al. 2007; Lewis et al. 2007; Lui et al. 2000; Rose and Peters 2001; Schoonover et al. 2005; Smart et al. 1985; Von Schiller et al. 2008; Zampella et al. 2007.

Riparian and In-Stream Nitrogen Processing

Nitrogen cycling in streams is altered by urbanization due to changes in stream hydrology, biology, riparian zone function, and rates of N delivery that accompany urbanization. These changes result in alteration of the uptake, transformation and release of nitrogen. Increases in urban impervious surface area and storm water drainage infrastructure increase the surface runoff loading, peak discharges, and annual water export of receiving streams (McMahon and Cuffney 2000; Rose and Peters 2001; Walsh et al. 2005).

Most of the N entering urban streams bypasses riparian zones, as it is delivered directly to the stream through storm water drainage systems and wastewater treatment facilities. Natural riparian zones are the interface between the surface water and terrestrial systems. Vegetation along riparian zones has the capacity to take up and immobilize nutrients before they enter the stream channel. Roughness from vegetation and its litter slows down overland flow, encouraging infiltration. Riparian zones, with water tables close to the soil surface, tend to be more saturated with water for longer time periods inducing reducing conditions. Saturation reduces oxygen availability, and nitrate inputs to riparian zones are likely to undergo denitrification resulting in production of volatile N_2O and N_2 compounds. Bypassing these natural filters, where they would otherwise be present in the urban landscape, results in more N being added directly to the stream. Even when water does pass through riparian zones in urban ecosystems, they may no longer be effective filters for N. Groffman et al. (2002) found that urban streams were highly incised and had lower water tables. These lower water tables created more aerobic soils and reduced the riparian zone capacity for denitrification, possibly contributing to the increased concentrations of nitrate in urban streams (Groffman et al. 2002).

Changes to ecosystem processes within the stream channel may alter N cycling and increase N concentrations. Industrial and municipal waste and high chloride concentrations have been shown to decrease the denitrification potential in streams

(Richards and Knowles 1995; Hale and Groffman 2006). A study of denitrification across a large land cover gradient found no significant relationship between land cover and denitrification, possibly due to the wide range of conditions that occur within land covers (Mulholland et al. 2009). However, the efficiency of denitrification decreased as nitrate levels increased (Mulholland et al. 2009). This result suggests that surface waters receiving effluent high in nitrate will export a higher fraction than those that receive lower-concentration waste water treatment effluents (Table 1.1).

Urban streams often have altered courses and hardened banks to prevent the stream from meandering. This can homogenize the streambed and reduce the ability of streams to store carbon, decreasing the potential for N to be metabolized (Meyer et al. 2005). A study by Hall et al. (2009) found that a structural equation model based on ecosystem metabolism, hydraulic parameters and N concentrations was able to explain 79% of the variability in log uptake length of nitrate. Uptake length increased with discharge and increasing nitrate concentrations, where land use indirectly correlated with uptake length via gross primary productivity (Hall et al. 2009). Increases in dissolved organic carbon (DOC) concentration in the Sacramento River, California have also been attributed to upstream WWTF discharge into the River (Sickman et al. 2007). The few studies on urban stream metabolism have variable results from very low to high metabolisms (Meyer et al. 2005; Grimm et al. 2005). A study by Von Schiller et al. (2008) found that ammonium demand (measured as uptake velocity) decreased along the forested to urban gradient in response to increases in ammonium, DON, and DOC. One of the primary concerns with high N loading in urban ecosystems is the potential for eutrophication of fresh and estuarine waters.

In addition to the complex factors that are already known to affect N cycling in urban aquatic ecosystems, additional effects on N cycling may also be occurring due to the host of contaminants entering urban systems. Polynuclear aromatic hydrocarbons (PAHs), pharmaceuticals, personal care chemicals, and metals all have potential effects on N metabolism in streams, but they have barely begun to be investigated (Bernhardt et al. 2008). Nitrogen concentrations and loads transported from urban areas are also dependent on levels of available phosphorus in the water (Paerl et al. 2004). If phosphorus is limiting biotic growth then the excess N will not be utilized and transported downstream (Paerl 2009). Problems with eutrophication and low oxygen can be displaced further downstream of significant sources where the two nutrients are both found in excess quantities (Paerl 2009).

Urban Phosphorus

Surface water in urban catchments around the world generally has higher phosphorus concentrations than surface water in rural catchments (Meybeck 1998; Winter and Duthie 2000; Bhatt and McDowell 2007). For example, a 10 year record of catchments in the greater Seattle area found stream water phosphorus concentrations were correlated with urban land cover; and most urban streams had on average 95% higher total phosphorus and 122% higher soluble reactive phosphorus than the most forested streams (Brett et al. 2005). Even where the percentage of urbanized land in a catchment is relatively low (< 10%), urban areas can still have significant impacts on P concentrations and loads (Osborne and Wiley 1988). In a mid-western USA catchment, urbanization was a dominant factor even though urban areas constituted only 5% of the area, yet urban land use controlled dissolved phosphorus concentration throughout the year (Osborne and Wiley 1988).

High concentrations generally lead to higher loads and exports from the watershed and phosphorus loads generated in urban areas can influence downstream reaches and discharge points. Inputs of P to an urban watershed include; fertilizers, human and pet food, atmospheric deposition, and P-containing consumer and industrial products (Davis and Gentry 2000). Fewer detailed budgets of P loading are currently available compared to N budgets. Davis and Gentry (2000) found that 35% of the annual P input into the urbanized Illinois River watershed was lost through river exports to the greater Mississippi River watershed. Part of this exported P was generated from sewage discharged from WWTFs in the Chicago area that contributed an estimated 70% of P load in the Illinois River and ~5% of the P load to the Gulf of Mexico from the Mississippi River watershed (Davis and Gentry 2000). The proportion of inputs of P into an urbanized region lost through surface water is variable. In another P budget of the upper Potomac River Basin, Jaworski et al. (1992) found that over less than 40% of the imported P was lost from the watershed.

Sources of P

Wastewater Treatment Facilities and Septic Systems

Discharge of wastewater to urban surface waters has been found to be a major contributor to the total P loads (LeValle 1975; Davis and Gentry 2000; Bowes et al. 2005). In the state of Illinois, USA, WWTF effluent contributed 47% of the total P load to the state's rivers (Davis and Gentry 2000). A study of WWTF P inputs found that introducing an 80% reduction in P load from the seven largest WWTF in the English Warwickshire Avon catchment resulted in an estimated decrease in TP export of 378 metric tons year^{-1} (52% of the total load) (Bowes et al. 2005). However, because of the extremely high nutrient loadings that exist in many UK rivers, nutrient removal from these large WWTF's alone are unlikely to reduce P concentrations to a desired concentration of 0.2 mg L^{-1}. This would require tertiary treatment at not only large, but also medium and smaller facilities (Bowes et al. 2005). In a multiple regression analysis of 24 catchments in the Windsor Ontario area, 76% of the variation in stream orthophosphate concentrations was explained by the percentage of watershed households connected to city sewers, while garden fertilizer use and precipitation phosphate content accounted for 4 and 2% of the variation, respectively (La Valle 1975). Jarvie et al. (2006) argued that point discharge of effluent is a greater threat to urban water quality than diffuse sources from urban and agricultural runoff. They reasoned that WWTF effluent contains the primary soluble reactive P (SRP- <0.45 µm, molybdate reactive), and because SRP is more easily utilized by aquatic organisms, streams receiving effluent are at a larger risk for eutrophication than those with P loads primary from particulate sources (Jarvie et al. 2006). Bans on P-based detergents, which reduced the SRP in WWTF effluent, were successful in decreasing algal blooms in the freshwater portions of the Neuse River, North Carolina (Paerl et al. 2004).

In a properly functioning septic system, soils also adsorb P from the system's leach field and therefore reduce the potential for septic systems to contribute significantly to P loading in urban streams. Several studies have concluded that septic systems do not contribute to P loading in urban surface waters (Hoare 1984; Hatt et al. 2004; Jarvie et al. 2006). Where P was filtered out by the soil, nitrate has been connected to surface water concentrations (Hoare 1984; Hatt et al. 2004). Gerritse et al. (1995) also found that stream concentrations were unaffected by septic systems; however, they found a minimum travel time of P was between 1 and 8 years based on column leaching which suggests that over time there is a potential for P from septic systems to reach groundwater or surface water in older communities. Studies have found that the potential for leaching P from soil increases in soil with greater than 10% degree of soil P saturation (Heckrath et al. 1995; Hooda et al. 2000). In Ireland, evidence suggests that septic systems, primarily poorly maintained systems, contributed to high P loading in high density rural populations (Arnscheidt et al. 2007). Similarly, Jarvie et al. (2006) found a correlation between SRP during high flow in catchments where no WWTF exists, and concluded that the SRP was most likely from septic systems and small plants which discharge onto the floodplain being washed in as the water table rises.

Impervious Surfaces

Impervious surfaces have been implicated as a source of many contaminants in urban environments, and are among the main sources for dissolved P in many northern climates (Bannerman et al. 1993; Hatt et al. 2004). Hatt et al. (2004) found strong correlations between P loads and impervious surface and connectivity of impervious surfaces and streams via stormwater drainage systems. Phosphorus from natural sources such as pollen deposition from trees, leaching of P from plant tissue, and airborne particulate deposition, as well as anthropogenic sources such as road sand, or misapplied fertilizer can accumulate on impervious surfaces, making their impact on urban water resources critical to assess (Sharpley 1981; Dorney 1985; Banks and Nighswander 1999; Hu et al. 2001; Ahn and James 2001; Burian et al. 2002; Easton 2007).

Fertilization

The resulting build up of P in agricultural soil from over fertilization with either chemical fertilizers or manures has been a recognized problem for water quality and the prevention of cultural eutrophication (Sharpley et al. 1994). Similar problems occur in urban ecosystems where over fertilization with chemical fertilizers, biosolids used in sod production or manures from pets can lead to nutrient buildups in soil compared to less human impacted systems (Baker et al. 2001; Pouyat et al. 2007). Fertilizer use in urban catchments has been found to contribute to the elevated phosphorus concentrations in streams (LaValle 1975; Waschbusch et al. 1999). For example, lawns and streets were found to be the primary source of phosphorus to urban streams in Madison, Wisconsin. As a result of fertilizer application, lawns were estimated to contribute between 49 and

61% of the total P load in urban streams (Waschbusch et al. 1999). Influencing the amount and timing of P fertilization in urban ecosystem through education and extension may be more difficult than in agriculture due to greater number of residents in any given urban watershed. Working with lawn care companies may provide a more effective avenue to influence a greater area of fertilized turf and horticultural areas in a city.

Groundwater

The exchange of water between ground and surface waters has a strong influence on the stream chemistry and nutrient fluxes (Pionke et al. 1988; Fiebig et al. 1990; Triska et al. 1993; Sonoda and Yeakley 2007). However, less is known about the nature of this relationship in urban ecosystems. A study on the urbanizing Johnson Creek in Portland, OR, USA did conclude that in both less disturbed and urban streams groundwater contributed to the total P load; however, in urban systems the relationship between stream and groundwater P concentrations can be masked by other inputs and overall P concentrations are more closely related to land-use patterns than groundwater (Sonoda and Yeakley 2007). A study by Meross (2000) on the same watershed found that sections of Johnson Creek were altered through channelization and re-routing due to urban development, but that only 6% of the precipitation was hydrologically disconnected from the creek; therefore could not explain the lack of influence groundwater had on urban stream chemistry in this watershed (Sonoda and Yeakley 2007). Stream alterations such as channeling, armoring, and the connectivity between ground and surface water are highly variable within and among urban centers, and therefore further research is needed on the influence that these alterations may have on concentrations of groundwater P and on stream P loads. Because riparian zones function as interfaces between groundwater and surface waters in urban ecosystems as well as other more natural environments, they likely play a key role in regulating the relationship between ground and surface water concentrations and load of P.

Erosion

Urban activities and stream hydrology increase erosion of sediments from upland soils and stream channels (Wolman and Schick 1967; Trimble 1997; Nelson and Booth 2002; Maniquiz et al. 2009). Sediments washed into urban streams and stream beds are more likely to be coarser textured and therefore more likely to release adsorbed P to the water column (Finkenbine et al. 2000; Pizzuto et al. 2000; McDowell and Sharpley 2001). Due to their increased adsorption capacity, erosion of stream banks and finer materials into urban surface water have less potential to contribute to high P in the water column and may act as a sinks for P in rivers and streams (McDowell and Sharpley 2001). However, erosion of these materials may increase eutrophication downstream in lakes and reservoirs and as oxygen decreases eroded sediments may release P to the water column (McDowell and Sharpley 2001).

"Chemical Time Bombs"

Several scenarios in urban ecosystems may result in high levels of P being released in short periods of time. Phosphorus is often stored within the soil matrix due to over fertilization or adsorption of P from septic systems, or saturation of riparian soils. P can be mobilized by changes in land-management practices, particularly those that increase water and wind erosion and release P to surface waters in large quantities

(Bennett et al. 1999; Conley et al. 2002). This effect has been called the "chemical time bomb" (Stigliani et al. 1991) and is of particular concern when previously agricultural land is cleared for urban growth and large amounts of sediments have been mobilized (Bennett et al. 1999; Maniquiz et al. 2009). Riparian zones are an example of another type of "time bomb" that exists when soils with high P concentration become anaerobic and chemically reduced. These soil conditions have the potential to release large amounts of P when they become saturated and reducing conditions occur (Patrick and Khalid 1974). Remobilization of P under hypoxic conditions in lakes and the annual variation in sediment has long been known to release P in quantities up to an order of magnitude greater than other, more controllable P sources (Mortimer 1941; Ingall et al. 1993; Conley et al 2002).

Characterization and P In-Stream Processing

Phosphorus in streams is present in several metabolically available forms and can be immobilized by chemical, adsorptive, and biotic processes. Based on measurements in streams of Missouri's Ozark Plateau, USA Smart et al. (1985) found urbanization increased total phosphorus as a result of increased particle-associated phosphorus and dissolved phosphorus levels. Removal and sequestration of P within an urban stream may be affected by the concentration of other dissolved ions; however this has not always been shown to be true in urban catchments. In Chicago area streams, for example, 79% of the total P was found in the dissolved form despite the high levels of Ca present (Bedore et al. 2008). Bedore et al. (2008) suggested that removal of P from the water column of these streams was inhibited by the high concentrations of dissolved

P in the presence of Ca^{+2} and Mg^{+2}. Although the presence of Ca with P is generally considered to aid removal of P from the water column, dissolved P concentrations greater than 0.61 mg P L^{-1} inhibit calcite nucleation and disrupt crystal growth, resulting in co-precipitation of Ca and P only at low to moderate initial concentrations of dissolved P (House and Donaldson 1986). The majority of dissolved P removal from the water column may occur through adsorption to sediments during both high and low flows (Gibson and Meyer 2007; House and Denison 2002). Antecedent weather conditions are also important in regulating P adsorption to sediments, because they control the pool of fine sediment and associated P available for remobilization during storm pulses (House and Denison 2002). McDowell and Sharpley (2001), compared bank sediments, and reported that sandier bed sediments released P more readily and supported a higher P concentration in the water. Several studies have found adsorption of P were correlated with Fe and organic matter concentrations and P in sediments were adsorbed on Fe and organic complexes (McDowell and Sharpley 2001; Bedore et al. 2008).

Phosphorus is also removed from the water column and temporarily stored by biotic activity. McDaniel and David (2009) found biotic activity contributed to a mean range of 26% to 40% of total P uptake in Illinois rivers, and was correlated with sediment organic matter content. Haggard et al. (1999) reported a similar average of 38% uptake by the biotic community in Oklahoma streams. Dissolved P more easily supports microbial metabolic activity than organic P; therefore the presence of high dissolved P has also been suggested to inhibit the mineralization of organic P in the water column, increasing the potential for organic P to accumulate in the sediment and be transported downstream (Bedore et al. 2008). The persistence and cycling within a stream reach is an important indicator of utilization by aquatic organisms and the amount of P that will be transported downstream (Peterson et al. 2001). Small streams across biomes are efficient at retaining and cycling nutrients; however, small streams receiving point-source inputs are typically less efficient than less disturbed streams (Haggard et al. 2001, 2005; Marti et al. 2004; Peterson et al. 2001; Pollock and Meyer 2001). In Vermont, USA, Meals et al. (1999) used a P associated with a dye tracer to spike the LaPlatt River, a eutrophic river fed by a WWTF in the fall and winter seasons. In the fall, thirty-nine percent of the added P was retained over 12 hours and at the end of 48 hours 38% of added P (4 mg P m^{-2}) was still retained in the stream reach. However, during the winter all the P added was exported from the reach within 24 hours (Meals et al. 1999). Phosphorus retention and uptake lengths can be influenced by many different factors including; flow, temperature, concentration gradient, total suspended solids, and biological activity (Meals et al. 1999; Gibson and Meyer 2007). In the large, urbanized Chattahoochee River in Atlanta Georgia, P uptake lengths (the distance traveled by a P molecule before being removed from the water column) were highly variable with some measured dates having no uptake and others indicating a release of soluble reactive phosphorus within the river reach, but on average the uptake lengths for P were many kilometers (Gibson and Meyer 2007). Several studies suggest that short- and medium-term P uptake and release is a function of biotic activity and bioavailable P, rather than sediment sorption (McDowell et al. 2003; McDaniel et al. 2009).

Carbon

Total carbon in surface and ground waters consists of natural organic compounds derived primarily from the decomposition of plants and animals, inorganic carbon that can be in the form of CO_2, HCO_3^- or CO_3^{2-}, and novel or man-made organic carbon. This section will discuss natural organic carbon.

The biogeochemical cycling of organic carbon is arguably the most important process in aquatic ecosystems because of its central role in regulating many other elemental cycles and providing food for consumer organisms (Chrost 1989; Findley and Sinsabaugh 1999; Harbott and Grace 2005). Important ecosystem functions of organic carbon (OC) include providing energy to microbial consumers and subsequently to higher trophic levels, as well as regulating the availability of dissolved nutrients and metals (Chrost 1989; Findlay and Sinsabaugh 1999). Despite its important role, however, the amounts, sources, quality, and functions of carbon in urban aquatic ecosystems are poorly understood compared to less disturbed aquatic ecosystems (Paul and Meyer 2001).

The sources of organic carbon in urban surface waters include both point source discharges and non-point sources. Sickman et al. (2007) found point source urban wastewater discharges made up about 60% of DOC inputs to the Sacramento River; the remaining 40% was contributed through non-point sources. Other studies have found that DOC was not significantly greater in urban streams receiving WWTF effluent (Daniels et al. 2002; Aitkenhead-Peterson et al. 2009). Several studies have shown increasing concentrations of dissolved organic carbon (DOC) with high flow and storm events, indicating that carbon sources in the surface water were not the result of high carbon levels in the groundwater that contributes to base flow (Chang and Carlson 2005; Hook and Yeakley 2005). Non-point sources of organic carbon in urban regions are most often related to the amount of remaining vegetation within cities. Positive relationships between DOC concentration and the percentage of remaining forested cover within urban areas have suggested that leaf litter may contribute to DOC concentrations in urban streams (Chang and Carlson 2005). During storm events, Hook and Yeakley (2005) found that 70-74% of DOC export was contributed by remnant riparian areas. Carbon dating analysis suggests that DOC in non-point source carbon in the Sacramento River is derived primarily from leaching of older soil organic matter (Sickman et al. 2007). However, in an urban to rural gradient in South Central Texas, DOC concentrations were not related to remaining forest, but were more closely associated with urban open areas such as golf courses, sports parks and neighborhood lawns (Aitkenhead-Peterson et al. 2009). Novel organic compounds washed from impervious surfaces during storm events also contribute to the total organic carbon loads in urban watersheds (Eganhouse et al. 1981; Xian et al. 2007). In a single storm event sampling of the Los Angeles River, 60% of the total extractable organics was estimated to be hydrocarbons of anthropogenic origin (Eganhouse et al. 1981). Streams without a WWTF are often depleted of organic carbon in the benthic material. In a comparison of 2 forested and 4 urban catchments, average organic matter standing stocks were significantly lower in urban streams near Atlanta, Georgia, caused by scouring of the highly mobile sandy substrates in urban channels as a result of more severe high flow events (Paul 1999). More research is needed on DOC sources in urban areas with a variety of climates, urban land uses, and water chemistries.

Despite the critical role of DOC in aquatic ecosystems, limited work has been done on DOC quality in urban stream ecosystems (Eganhouse et al. 1981; Paul and Meyer 2001). Storm events can increase both dissolved and particulate organic carbon concentrations, however, less is known about the baseflow proportions of particulate and dissolved organic carbon (McConnell 1980; Paul and Meyer 2001). In an urbanized creek, carbohydrate concentrations in particulate organic matter (POM) were higher than that in POM of a nearby forested reference stream, suggesting that urbanization affects the nature of transported organic matter (Sloane-Richey et al. 1981). The carbon associated with sewage effluent is generally more labile than dissolved organic carbon from natural sources, causing high biological oxygen demand and oxygen deficits associated with storms in urban environments (McConnell 1980; Faulkner et al. 2000; Ometo et al. 2000).

Bioavailability and metabolism of different types of DOC in urban surface water affect both the concentrations of DOC and the microbial communities supported by them. Results from analysis of relative extracellular enzyme activity (EEA) rates by Harbott and Grace (2005) in streams with roughly similar DOC concentrations show that there was a shift in DOC bioavailability depending origin of organic substrates in each stream. Large variations in EEA suggest diverse sources of DOC from urban areas (Harbott and Grace 2005). A study by Paul (1999) also found that leaf litter from different tree species decayed at different rates in an urban Atlanta, Georgia stream compare to a rural one. Compared to forested streams, all coarse and fine particles released in urban Atlanta streams traveled much further before leaving the water column (Paul 1999). These findings, combined with decrease in organic matter storage, indicate that urban streams retain less organic matter, and suggests that secondary production could be limited (Paul 1999). A comparison of three rivers in Michigan by Ball et al. (1973) found the urban river had higher gross primary production and community respiration than the forested river.

Cations and Anions

Many other cations and anions are elevated in urban streams, including chloride, sulfate, calcium, sodium, potassium, and magnesium and overall electrical conductivity (Figures 1.2 and 1.3) (McConnell 1980; Smart et al. 1985; Zampella 1994; Ometo et al. 2000; Paul and Meyer 2001). A breakdown of urban land uses in the Shimousa Upland, Japan revealed significant positive correlations base cation concentrations and land use. K^+, Mg^{2+}, and Ca^{2+} concentrations were correlated with residential area in a watershed, Mg^{2+} and Ca^{2+} were correlated with commercial areas, and Ca^{2+} was correlated with urban developing areas (Bahar and Yamamoto 2008). In contrast, a literature review shows that calcium and magnesium concentrations both tend to decline with the fraction of land use in a basin (Figure 1.2). Similarly, Fitzpatrick et al. (2007) found biogeochemical fingerprints of human impact differed between agricultural and urban land uses for major cations (Urban: Na, K, Cl /Agriculture: Ca, Mg). Bhatt and McDowell (2007) demonstrated strong relationships between many ion concentrations and the human population density adjacent to the Baghmati River, in Nepal where untreated sewage had a significant impact on the water chemistry. The combined effect of increases in ion concentrations is an increase in electrical conductivity. These increases in ions are so common that some have suggested using chloride concentration or electrical conductivity as an indicator of urban impacts on water chemistry (Wang and Yin 1997; Herlihy et al. 1998; Paul and Meyer 2001). Sources of cation and anions in urban stream water include: wastewater effluent, irrigation runoff, deposition to impervious surfaces (atmospheric, dust, vehicle exhaust, and animal waste), infrastructure dissolution, spills, and sediment erosion. Irrigation runoff in urban areas may impact surface water chemistries if the source water for potable use is significantly different than the surface water.

Measuring and assessing the impact of urbanization on ion concentrations may be more difficult than at first expected. Jackson et al. (2008) assessed the density driven flow in the Chicago River and found that increased salinity from deicing salts and WWTF effluent were the likely cause of reversing the flow direction due to the increased density of the underflow (Jackson et al. 2008). They suggested that water quality assessments of the Chicago River may underestimate (or overestimate) water quality impairment because standard monitoring practices do not account for density driven underflows (or overflows) and do not adjust their depth of sampling to accommodate this (Jackson et al. 2008).

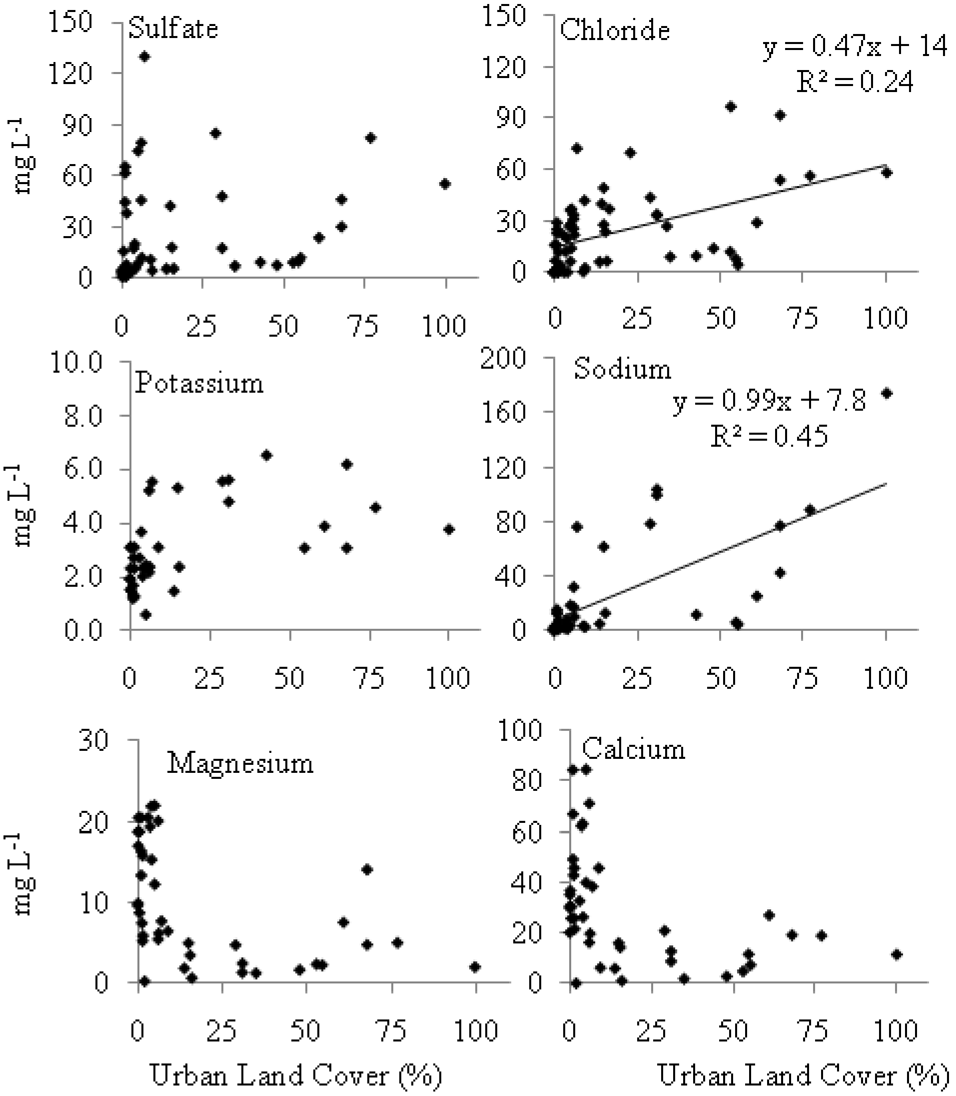

Figure 1.2 Relationship between surface water concentrations of chloride, sulfate, potassium, sodium, magnesium and calcium and the percent urban land cover in watersheds reported in the literature. Regressions are significant at α<0.10. Source data are obtained from the following references: Aitkenhead-Peterson et al. 2009; Bahar and Yamamuro 2008; Bedore et al. 2008; Bhatt and McDowell 2007; Brett et al. 2005; Chang and Carlson 2005; Chea et al. 2004; Cunningham et al. 2009; Daniels et al. 2002; Fitzpatrick et al. 2007; Lewis et al. 2007; Lui et al. 2000; Rose and Peters 2001; Schoonover et al. 2005; Smart et al. 1985; Von Schiller et al. 2008; Zampella et al. 2007.

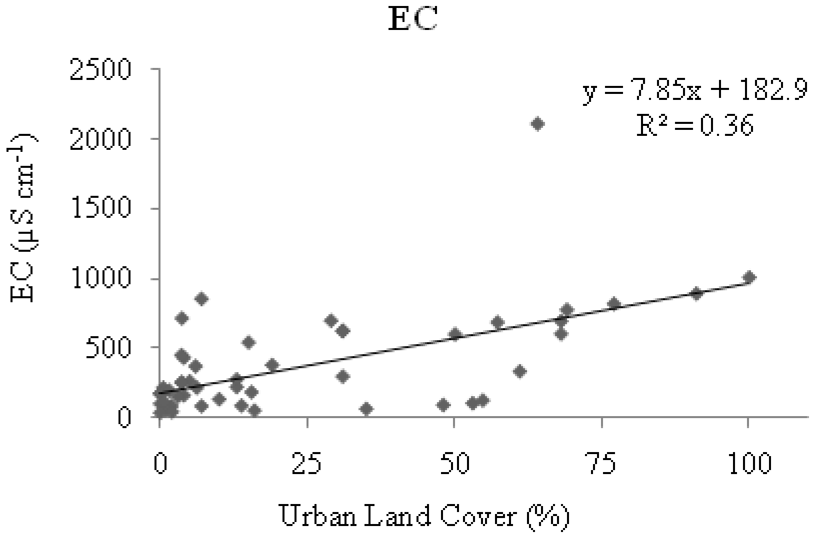

Figure 1.3 Relationship between surface water electrical conductivity and the percent urban land cover in watersheds reported in the literature. Regression is significant at $\alpha = 0.008$. Source data is obtained from the following references: Aitkenhead-Peterson et al. 2009; Bahar and Yamamuro 2008; Bedore et al. 2008; Bhatt and McDowell 2007; Brett et al. 2005; Chang and Carlson 2005; Chea et al. 2004; Cunningham et al. 2009; Daniels et al. 2002; Fitzpatrick et al. 2007; Lewis et al. 2007; Lui et al. 2000; Rose and Peters 2001; Schoonover et al. 2005; Smart et al. 1985; Von Schiller et al. 2008; Zampella et al. 2007.

Sodium and Chloride

Although total salinity can have negative impacts on ecosystem function and aquatic health in streams and rivers, there are certain ions that can be particularly detrimental. Sodium and chloride are naturally occurring constituents of surface waters. Sources in surface waters include saline groundwater, geologic weathering and soil exchange processes, marine aerosols, salt water intrusion and atmospheric deposition. Ecological problems with sodium and chloride concentrations generally only occur in freshwater ecosystems, and include toxicity to plants, invertebrates and fish. Human health concerns relate to the impacts of salt intake on hypertension (Howard and Haynes 1993; Forman and Alexander 1998; Wegner and Yaggi 2001).

Some surface waters are naturally enriched in sodium; however, recent findings have indicated a strong anthropogenic enrichment of sodium and chloride in surface waters through the use of deicing salts and wastewater treatment effluent (Kaushal et al. 2005; Novotny et al. 2009; Steele and Aitkenhead-Peterson 2011). The Salt Institute (2004) estimated that eighteen million Mg (1 Mg =1 metric ton) of NaCl is spread on paved surfaces for deicing annually. Deicing salts are used in cooler climates to prevent and treat roads and sidewalks to make vehicle and pedestrian traffic safer. A study in Toronto found that 45% of the salt applied to the catchment is removed through runoff and the remainder is stored temporarily in shallow subsurface waters (Howard and Haynes 1993). Salt stored in shallow subsurface waters is released as base flow throughout the year; and the authors predicted that if continued at the present, rate the average chloride concentrations in groundwater discharging as springs will increase three-fold (Howard and Haynes 1993). Kaushal et al. (2005) found the largest increases in the winter months in chloride concentrations in urban streams when salt was being applied in three Northeastern cities; however, chloride concentrations did not return to base level during the summer demonstrating an increasing trend over several decades. In the colder climate of New Hampshire, USA, chloride concentrations were typically highest during summer low flows, suggesting that pervasive groundwater contamination with road salt has occurred (Daley et al. 2009). Chloride concentrations were found in some Maryland locations to be 25% those of sea water and increasing, rendering many potential drinking water sources non-potable within the next century (Kaushal et al. 2005). Similarly, thirteen lakes in the Twin Cities metropolitan area of Minnesota, USA had sodium and chloride concentrations that were 10 to 25 times higher than non-urban lakes; this increase in concentrations was correlated with road salt applications (Novotny et al. 2008).

Both sodium and chloride are relatively mobile in the soil and deeper geologic environment compared to other major ions, although chloride is somewhat more mobile than sodium due to some ion exchange or adsorption of sodium (Shanley 1994; Jackson and Jobbagy 2005; Daley et al. 2009). The change in the ratio of Na:Cl may allow researchers to determine the relative importance or contribution of direct inputs of salts, via direct surface drainage, or those that have an indirect underground flow path (Jackson and Jobbagy 2005). For streams affected by surface runoff or drainage systems, the ratio of Na:Cl should be roughly similar to the source material (0.65:1 mass ratio); however, if the dominant flow path involves transport through soils or bedrock, then the ratio of Na:Cl will be lower. Sodium will gradually displace Ca, Mg, K, and protons in the soil, altering soil fertility and uncoupling the flow of Na from Cl (Norrstrom and Bergstedt 2001; Jackson and Jobbagy 2005). The ratio of Na:Cl in surface waters impacted by extensive road salt application also can be expected to increase over time due to the exhaustion of exchangeable cations in watershed soils.

While the majority of research on aquatic sodium and chloride has been conducted in colder regions where deicing salts were likely to have a major impact;

population density also appears to be significantly correlated to increased concentrations and loading. In a study of 56 basins across the United States, Peters (1984) reported that population density was a significant predictor, accounting for 13% of sodium and 20% of chloride loading. In the urban Chattahoochee River basin, Rose (2007) attributed increases in sodium and chloride to leaking sewage infrastructure. Sources of Na^+ and Cl^- in urban stream water other than de-icing salts might include: wastewater effluent, landfill seepage, septic systems, irrigation runoff, atmospheric deposition, impervious surface deposition (dust, vehicle exhaust, and animal feces), infrastructure dissolution, spills, and sediment erosion.

Sodium and Soil

Surface water chemistry is often linked to watershed soil attributes and processes in temperate climates (e.g. Aitkenhead-Peterson et al. 2003; Aitkenhead-Peterson and Alexander 2005). It is logical then that in sub-tropical and arid climates where irrigation with ground or recycled water is the norm that sodium accumulation in soil can impact soil physical and chemical properties and therefore also impact surface water chemistry albeit indirectly. Large areas of the world's arable lands have been affected by salinization and sodification through natural processes; however, irrigation practices have significantly contributed to the problem (Szbolcs 1989). The increase in salt-affected soils due to irrigation practices is considered to be one of the most urgent problems facing irrigated soils in arid and semi-arid regions (Bui et al. 1998). In urban environments, irrigation is used to enhance green spaces as well as in recreational facilities. Pressure on existing water supplies may increase the use of treated effluent and grey water for irrigating green space in urban areas (Hayes et al. 1990; Mancino and Pepper 1992). These alternative water sources typically contain more sodium than the original municipal tap water because of the addition of detergents, cleaning agents and other inputs to wastewater treatment facilities. The relationship between sodium and soil is of great interest to society because of the strong affect it has on soil properties. Accumulation of sodium in urban soils through irrigation or deicing salts causes the soils to display "sodic" properties. Sodium in irrigation water has been categorized by the USDA based on the risk of negatively altering soil properties (Table 1.2).

Table 1.2 Classification of irrigation water quality for infiltration risk based on sodium adsorption ratio (SAR) and electrical conductivity (EC). Adapted from FAO recommendations (Ayers and Westcot 1994).

	Risk (Electrical Conductivity - dS m^{-1})		
SAR	None	Slight to moderate	Severe
0 to 3	> 0.7	0.7 – 0.2	< 0.2
3 to 6	> 1.2	1.2 – 0.3	< 0.3
6 to 12	> 1.9	1.9 – 0.5	< 0.5
12 to 20	> 2.9	2.9 – 1.3	< 1.3
20 to 40	>5.0	5.0 – 2.9	< 2.9

What Is A Sodic Soil?

The first report of sodic soils in the United States was made by Hilgard (1877) and was believe to be caused by the accumulation of salts. In 1917, Beazeale (1917) recognized the impact of various sodium salts on pH and organic matter eluviations. It was not until the late 1930's that the role of adsorbed Na and the balance between exchangeable Na and the equilibrium electrolyte concentration was confirmed by investigating the influence of electrolyte concentrations on soil water permeability (Bodman 1937; Fireman and Bodman 1939; Huberty and Pillsbury 1941; Fireman 1944). In 1954, the USDA adopted a classification system that recognized four categories of salt affected soil based on the measurements of exchangeable sodium percentage (ESP) and the electrical conductivity (EC) (Table 1.3). The use of 15% ESP as the boundary between sodic and non-sodic soils is somewhat arbitrary and a number of studies have demonstrated significant decreases in permeability at much lower ESP values (Quirk and Schofields 1955; Martin and Richards 1959). Due to low soluble materials, in Australia the boundary between sodic and non-sodic soils is considerably lower, when ESP > 6% (Rengasamy and Olsson 1991).

Table 1.3 Classification of saline and sodic soils (adapted from USSL Staff 1954)

	Nonsaline Nonsodic	Sodic Nonsaline	Saline Sodic	Saline Nonsodic
ESP (%)	< 15	≥15	≥15	<15
EC (dS m^{-1})	<4	<4	≥4	≥4

Modified in 1979, the definition of sodic soil accepted by the Soil Science Society of America is:

> A non-saline soil (undefined) containing sufficient exchangeable Na to adversely affect crop production and soil structure under most conditions of the soil and plant type. The lower limit of SAR of such soils is conventionally set at 13. (Glossary of Soil Science Terms 1979)

While ignoring that many soils respond to lower concentrations of sodium, this definition uses SAR instead of ESP as the diagnostic criterion to eliminate the numerous potential errors in traditional CEC and ESP determinations (Sumner et al. 1998). Modified from the Gapon equation, SAR is based on a paste extract (USSL Staff 1954) and is calculated as in Eq. 1.1,

$$\text{Eq. 1.1}\quad \mathrm{SAR} = \mathrm{Na^{+}} / [(\mathrm{Ca^{2+}} + \mathrm{Mg^{2+}})/2]^{1/2},$$

where Na^{+}, Ca^{2+}, Mg^{2+} are soluble ionic concentrations in $\mathrm{mmol_c\ L^{-1}}$. SAR estimates the sodium ratios in the soil solution and is also used to estimate the quality of irrigation waters.

Sodic soils are also classified based on soil pH as an indicator of carbonates. Though the USSL Staff (1954) classifications included the term “alkali” as those soils with pH > 8.5, the term had fallen out of favor until Gutpa and Abrol (1990) reintroduced the term to refer to sodic soils with ESP > 15, containing free Na_2CO_3 indicated by pH >8.4 and having a Na/(Cl +SO_4) ratio greater than 1 (Sumner et al. 1998).

Nitrogen, Phosphorus, and Organic Carbon in Sodic Soils

Nitrogen cycling can be affected by the soil’s physical and chemical changes as sodium accumulates in exchange sites. Low rates of mineralization of organic nitrogen may occur due to decreased availability of mineralizable organic N (Cairn et al. 1962; Cairns 1963). However, Laura (1976) examined N and C mineralization rates with a soil amended with *Delonix regia* leaves and found steadily increasing rates of C mineralization as soil ESP increased; however, N mineralization remained constant for

ESP 2 to 49 and increased only at the highest levels of ESP. Due to dispersion of soil, water logging and reduction in oxygen availability the conversion of ammonia to nitrate through nitrification was inhibited and ammonia was found to accumulate in soils (Laura 1976).

As a result leaching losses of nitrate are likely to be very small; however, losses due to volatilization of NH_3 and denitrification are likely to be the primary mechanisms for N losses. Several studies in Australia have found significant rates of denitrification in sodic B horizons as water logging and leaching of organic matter from the topsoil occurs (McGarty and Myers 1986; Myers and McGarity 1972). Furthermore, high nitrous oxide flux from urban turfgrass (e.g. Bremer 2006; Livesley et al. 2010) is also indicative that many urban lawns and green spaces may be displaying the redox tendencies of wetlands or riparian zones that traditionally have higher C. Nitrous oxide fluxes tend to increase if precipitation occurs within 3 days of fertilizer application to turfgrass according to Bremer (2006). In soils with high pH, Gupta and Abrol (1990) found NH_3 volatilization was the major pathway for N loss.

Numerous studies have demonstrated that P tends to have greater solubility and thus greater availability to plants in sodic soils (Pratt and Thorne 1948; Chhabra 1985; Gutpa et al. 1990; Curtin et al. 1992). Phosphorus is generally adsorbed by the plant as orthophosphate ions ($H_2PO_4^-$ and HPO_4^{-2}). In most soils, the concentration of PO_4-P in solution is controlled through abiotic adsorption and desorption (Syers and Curtin 1989). However, in negatively charged soils which are saturated with Na, less P is adsorbed compared to soils saturated with divalent cations (Curtin et al. 1987; Smillie et al. 1987;

Sharpley et al. 1988). The lack of P adsorption in sodic soils is most likely due to a decrease in the electrostatic potential which decreases the attraction between surfaces and P ions (Barrow 1985). In sodic soils, the adsorption of P is also highly pH dependent, decreasing sharply as pH increases (Barrow 1984; Curtin et al. 1993; Gupta et al. 1990). Increases in P solubility are often coupled with decreases in plant demand for P due to poor root growth, attributed to physical growing conditions induced by high salt concentrations (Curtin and Naidu 1998). In addition, soil tests for P may be insensitive to the effects of P solubility under sodic conditions and underestimate the availability resulting in unnecessary fertilization (Rimmer et al. 1992; Curtin et al. 1993).

Sodic soils are most frequently associated with poor soil structure and the loss of permeability to water and air. However, in addition to physical changes, sodic soils also affect nutrient availability, organic matter, and general soil chemistry. While there is a large body of literature individually, the interaction between sodicity and soil organic matter is less well understood (Emerson 1983; Emerson et al. 1986; Mullins et al. 1990; Churchman et al. 1993; Nelson and Oades 1998). Soils with high organic matter generally resist Na adsorption due to increased hydrophobicity of organic matter and resist changes in hydraulic conductivity (Rengasamy and Olsson 1991). In Australia however, sodic soils have some of the lowest total organic carbon contents (Spain et al. 1983). In general, a negative correlation is found between soil organic carbon content and ESP (Nelson and Oades 1998). The cause of the low organic matter contents of sodic soils can be generalized by low vegetative input and high losses (mineralization, erosion, and leaching).

The presence of Na^+, particularly in combination with high pH and low electrolyte concentration, increases the solubility of organic matter (Breazeale 1917; Greenland 1965). A large portion of soil organic matter is comprised of negatively charged colloids and compounds. Polyvalent cations link anionic organic matter to mineral surfaces through water bridges, while monovalent cations link colloid surfaces to organic matter by direct ion dipoles (Nelson and Oades 1998). In sodium dominated soils, the weaker monovalent linkages allow for greater organic matter solubility. Na^+ salts of simple organic acids are more soluble than the Ca^{2+} salts and ionize more readily (Nelson and Oades 1998). Ultimately the dissolution or dispersion of organic molecules and organomineral complexes can increase the concentration of complexed metals in solution (Sholkovitz and Copland 1981).

In addition to the chemical mechanisms, the physical dispersion of aggregates during wetting can increase the accessibility of previously protected organic matter to microbes (Oades 1984). Solubilization of organic matter increases the mass of easily decomposable substrate which may alleviate sodium stress on microbial populations (McCormick and Wolf 1980; Pathak and Rao 1998; Jandl and Sollins 1997). Wong et al. (2008) in a study measuring soil microbial biomass (SMB) over a 12 week incubation period in soils treated with a range of salinity and sodicity attributed higher SMB in the high salinity treatment to increases in dispersed or dissolved organic matter. In a similar 12 week incubation study, Wong et al. (2009) reported increased

SMB and respiration following the incorporation of organic material to a highly saline-sodic soil. Microbial populations can become adapted to high salt environments (Polonenko et al. 1981; Zahran 1997). Using fatty acid methyl ester profiles, Pankhurst et al. (2001) reported lower ratios of fungal to bacterial fatty acids in high salinity soils, indicating a shift in communities which may be less diverse and active. In a 9 year plot study in Hisar, India, Chander et al. (1994) report decreases in microbial biomass and activity due to irrigation water with increasing SAR. Because there was no accumulation of residue or organic matter, they hypothesized that this smaller microbial population was no less effective at organic matter decomposition (Chander et al. 1994). However, they did not take into account other losses, such as leaching or erosion, which may also have been higher under sodic irrigation water.

Leaching of, N, PO_4, and DOC

Very little information is available on the leaching losses of DOC, DON, and PO_4-P from sodic soils. Higher solubility and subsequent mobility can result in leaching losses of soil organic matter (quantified as DOC) and P (Jacquin et al. 1979; Skene and Oades 1995). Skene and Oades (1995) combined soil in solutions with SARs ranging from 1 to 10 and observed the greatest clay dispersion at high SAR and low EC. They also observed positive correlations between clay dispersion and total organic carbon and PO_4-P in the solution (Skene and Oades 1995). In a study examining leachate from Brown Chernozemic soil columns in Saskatchewan, Canada, Curtin et al. (1992) reported increased concentrations of PO_4-P in leachate as the SAR increased and the EC decreased in soil.

Sodic Soils and Surface Water N, PO_4, and DOC

The extent to which surface waters are affected by the leaching of DOC and P due to sodic soil conditions is not well understood. In Australia, observed accumulation and staining of organic matter at the top of the B horizon in Solonetz soils and suggested that organic matter leaching from the surface horizon was the most likely cause (Nelson and Oades 1998). In southern Australia, Naidu et al. (1993) found high concentrations of DOC in streams draining acidic sodic soils in the Warren Reservoir Catchment. Characterized by a significant increase in soil clay content, leachate from these Duplex soils is thought to move laterally as throughflow over the B horizon across the landscape before draining into streams (Naidu et al. 1993). At the same study site in southern Australia, Skene and Oades (1995) reported correlations between DOC concentration (ranging from 2 to 25 mg L^{-1}) and stream SAR values (1 to 4). Stream concentrations of DOC, N and P were also correlated with turbidity (Skene and Oades 1995). Aitkenhead-Peterson et al. (2009) also found strong correlations ($R^2 = 0.94$) between SAR and DOC in rural and urban streams; concentrations of DOC were much higher than those reported by Skene and Oades (1995) and Naidu et al. (1993) with DOC stream annual average concentrations ranging from 5 to 55 mg L^{-1} and SAR from 5 to 17. In the United States, increases in organic matter mobility have been found as a result of road salt application (Amrhein et al. 1992) and a study in Scotland inferred that road salt was responsible for the reduction in soil carbon along roadside splash zones (Green et al. 2009, 2008).

Study Objectives

This study has four main objectives: a) determine if a municipal water supply with high SAR increases leaching of PO_4-P, N, and DOC from soil obtained from under irrigated and non-irrigated turfgrass or landscaping in College Station under common soil management practices and model water extractable DOC, N, and PO_4-P in irrigated soil from municipalities in Texas with a range of SARs in their municipal water supplies (Chapter II); b) compare the effect of sodium and salinity on the loss of DOC from cool season and warm season turfgrass, mulch, ornamental post oak, and mixed riparian leaf litter (Chapter III); and c) quantify sodium and chloride exports from a humid subtropical gradient and compare exports to urban centers in northern climates (Chapter IV).

CHAPTER II

THE EFFECT OF IRRIGATION SODICITY ON THE LEACHING OF DISSOLVED ORGANIC CARBON, NITROGEN AND ORTHOPHOSPHATE FROM URBAN SOIL UNDER TURFGRASS

Introduction

Human activities that occur on the watershed landscape can significantly affect dissolved organic carbon (DOC), nitrogen, and phosphorus concentrations in surface water impacting aquatic ecosystem health and causing impairment for human uses. Sources of DOC from urban watersheds are still the subject of ongoing research; however, suggested inputs of DOC to urban surface waters include wastewater treatment effluent (Sickman et al. 2007), runoff of hydrocarbons from impervious surfaces (Eganhouse et al. 1981; Xian et al. 2007), soil organic matter (Sickman et al. 2007), leaf litter (Chang and Carlson, 2005) and remnant riparian areas (Hook and Yeakley 2005). Elevated concentrations of nitrogen are frequently associated with wastewater discharge, turfgrass and landscape fertilization, and impervious surface runoff (Steele et al. 2010). Human activities associated with urban land use known to be contributors of orthophosphate to urban surfaces waters include; wastewater treatment plants (e.g. LaValle 1975, Davis and Gentry 2000, Bowes et al. 2005), poorly maintained septic systems (e.g. Arnscheidt et al. 2007; Jarvie et al. 2006), fertilization (e.g. Waschbusch et al. 1999), erosion (e.g. Finkenbine et al. 2000), and impervious surfaces (e.g. Bannerman et al. 1993, Hatt et al. 2004). With the exception of wastewater treatment effluent and impervious surface runoff, which bypass the watershed soil and discharge directly to the waterway, the remaining potential sources of DOC, N and P that are likely to be associated with the soil environment; and include water leached from the soil *in situ* and eroded soil particles, leaf litter, fertilizers and failing septic systems. Aitkenhead-Peterson et al. (2009) found DOC concentrations in an urban to rural gradient in south-central Texas to be closely associated with urban open area land uses, including parks, golf courses, and home lawns. Thus supporting studies by Sickman et al. (2007) who determined that soil was the most likely contributor of non-point source organic matter in a Sacramento watershed by carbon dating the DOC in the river which was found to be > 2000 years in age. Therefore, soil retention and release of DOC, N, and P may control a significant portion of non-point sources.

Urbanization has been shown to increase the overall salinity of urban surface waters, particularly increases in sodium (e.g. Fitzpatrick et al. 2007). Deicing salts, wastewater effluent, irrigation water and septic systems have all been cited as sources of sodium in urban watersheds and have the potential to contribute to the accumulation of salts in soil (Mullaney et al. 2009; Novotny et al. 2009; Aitkenhead-Peterson et al. 2009; Steele and Aitkenhead-Peterson 2011). The accumulation of Na^+ in soil has significant impacts on soil carbon and nutrient cycling (Skene and Oades 1995; Curtin et al. 1992). The presence of Na^+, particularly in combination with high pH and low electrolyte concentration, increases the solubility of organic matter (Breazeale 1917; Greenland 1965). A large portion of soil organic matter is comprised of negatively charged colloids and molecules. Polyvalent cations link anionic organic matter to mineral surfaces through water bridges, while monovalent cations link colloid surfaces to organic matter by direct ion dipoles (Nelson and Oades 1998). In sodium-dominated soils where sodium occupies significant percentages of the adsorption sites, the weaker monovalent linkages allow for greater organic matter solubility.

Numerous studies have demonstrated that P tends to have greater solubility and thus availability to plants in sodic soils (Pratt and Thorne 1948; Chhabra 1985; Gutpa et al. 1990; Curtin et al. 1992). In most soils, the concentration of PO_4^{3-} in solution is controlled through abiotic adsorption and desorption (e.g. Syers and Curtin 1989). However, in negatively charged soils that are saturated with Na^+, less phosphate is adsorbed compared to soils saturated with divalent cations (Curtin et al. 1987; Smillie et al. 1987; Sharpley et al. 1988). The lack of phosphate adsorption in sodic soils is most likely due to a decrease in the electrostatic potential which decreases the attraction between surfaces and phosphate ions (Barrow 1985). In sodic soils, the adsorption of phosphate is also highly pH dependent, decreasing sharply as pH increases (Barrow 1984; Curtin et al. 1993; Gupta et al. 1990). Increases in P solubility are often coupled with decreases in plant demand for P due to poor root growth, physical growing conditions and high salt concentrations (Curtin and Naidu 1998).

Studies on the impact of sodium on soil nitrogen cycling have reported mixed results. For example, Cairns et al. (1962) and Cairns (1963) reported that sodium can impact the nitrogen cycle by slowing nitrogen mineralization rates. Laura (1976), however, found no impact on N mineralization except under the highest soil exchangeable sodium percentages (ESP) where nitrification was completely inhibited in a study where soil was treated with sodium bicarbonate and amended with leaf litter. In contrast large releases of nitrate were observed in a study examining an acidic soil impacted by NaCl deicing salts after spiking the soil with ammonium-N (Green et al. 2008). Several other studies have found that under conditions of high sodium and high pH that ammonia volatilization is a major pathway for N loss from soils (Gutpa and Abrol 1990).

Turf irrigated with sodic water may have a significant impact on the leaching rates of DOC and nutrients from soil. The presence of the growing vegetation itself may have multiple and competing affects on DOC and P leaching. Root and microbial respiration during organic matter decomposition can cause soil acidification through the release of CO_2 into the soil. Increased acidity may counter the increasing pH induced by sodic irrigation water and promote retention of DOC, NH_4-N, and PO_4-P (Gupta et al. 1989; Gutpa and Abrol 1990; Robbins 1986). The addition of organic matter from vegetation in the form of litter or root exudate can prevent dispersion of aggregates and losses of occluded SOM (Tisdall and Oades 1982). Green manures have proven effective at remediating sodic soils by stimulating CO_2 production which will in turn lower soil pH (Chorom and Rengasamy 1997). Independent of pH effects, Nelson et al. (1993) found that soil salinity and sodicity retarded litter decomposition, depleted the labile C pool and increased the mineralization of SOM. The rate of phosphorus release from soils and nitrogen leaching will also be affected by plant uptake which may decrease its losses. While the effects of growing vegetation are proven to improve soil infiltration and pH, it is unknown how organic matter inputs from vegetation will impact the leaching of DOC, phosphorus or nitrogen under sodic soil conditions.

Mulching soil around trees and ornamental vegetation is a common management practice in urban areas to help retain soil moisture, prevent weed growth, and protect roots. While no known studies investigate the effects of mulching on DOC and P loss in soils irrigated with sodic water, Wright et al. (2008) investigated the impacts of composting turf on soil sodicity and water extractable DOC on a Boonville series soil in College Station, TX. They reported that compost applications decreased soil Na^+, EC and pH relative to unamended soil, and suggested these chemical changes were likely due to the organic matter and the Ca^{2+}, Mg^{2+}, and K^+ inputs in the compost occupying exchange sites and organic matter coating soil particles allowing for greater leaching of salts (Wright et al. 2008). In an earlier paper in the same location, Wright et al. (2005) found a significant increase in DOC and extractable PO_4-P with compost application compared to unamended soil.

Another management practice to increase the quality of alkali-sodic irrigation waters is to acidify water before application, usually with the addition of sulfuric acid or granular sulfur. Acidification decreases the bicarbonate fraction of inorganic carbon and prevents the formation of carbonate minerals. Chorom et al. (1994) found that clay dispersion was reduced 3-fold when the pH was reduced from 9 to 7. It has long been established that elevated pH in “black alkali” soils increases the release of organic matter from soil, for example Breazeale (1917) investigated the effects of various sodium salts on organic matter solubility. Thus reductions in pH should decrease the rate of both

DOC and PO_4-P leaching. Because of the cost associated with acidification, the most common users of this management technique in urban ecosystems are golf courses. Local municipalities do not have the resources to treat irrigation waters in parks and athletic fields (College Station Parks and Recreation Interview, October 2007).

Irrigation is the most common cause of salinity and sodicity problems in agricultural ecosystems worldwide (Bui et al. 1998). Irrigation in an urban ecosystem is primarily used to maintain turf and trees in homeowner and commercial lawns, sports fields, and golf courses. Aydemir et al. (2005) reported an accumulation of sodium in soils under turfgrass from irrigation with municipal water supplies high in sodium in south Texas. Of the variables tested, they reported the sodicity of the irrigation water was the best single predictor of sodium accumulation in the soil (Aydemir et al. 2005). Based on their findings, the solubility and mobility of DOC, N and PO_4-P in urban irrigated soil may be the result of the sodium adsorption ratio (SAR) and chemistry of the municipal tap water used for irrigation thereby controlling the potential for non-point source runoff of DOC and P to urban surface waters. This study had two main objectives: 1) compare the impact of common urban land management practices on the leaching of DOC, N-species (NO_3-N, NH_4-N and DON), and PO_4-P from intact soil cores under a) short term high intensity irrigation and b) long-term under moderate irrigation rates, and 2) compare the water extractable DOC, N, and P from irrigated soil under turfgrass from municipalities across Texas having a large range of municipal tap water chemistry.

Materials and Methods

Soil Core Leaching

Cores from under previously rain-fed turfgrass were collected from Lemontree and Gabbard recreational parks, College Station, TX. Soil from Gabbard (Site A) is from the Zack series a fine, smectitic, thermic Udertic Paleustalf and the soil from Lemontree (Site B) is from the Boonville series a fine, smectitic, thermic Chromic Vertic Albaqualf. Soil texture for both soils is a fine sandy loam for the upper horizons which overlay clayey B horizons. The two soils are common to Brazos County with the Zach series found in upland positions while the Boonville is found in lowland positions nearer to surface waters. Vegetation at the two park locations vary, but was dominated by Bermuda grass (*Cynodon dactylon* L.) and a variety of forbes.

Twenty four 6 cm diameter undisturbed cores were collected from a depth of 0 to 7 cm from each park for a total of 48 cores. Existing vegetation was removed by clipping. Soil cores were air dried in the laboratory and weighed. Pore volumes were determined using the air dried bulk density and the volume of the soil on four random soil cores. The mean pore volume of the cores was 85 ml (standard deviation = 3.9 ml) Cores were contained in HPDE bottles of a similar diameter with the bottom sawed off so that the top of the core was open and the bottom sat on the smaller end were the screw top was. A ball of tulle was placed in the bottom opening to allow water to flow out but prevent soil loss. Soil cores were maintained indoors at an average room temperature of 20°C. Three composite soil samples of six cores each were also taken from the same depths using a 2 cm diameter stainless steel push probe for soil texture measured by particle size analysis following the methods of Gee and Bauder (1986) and carbon and nitrogen analysis. The composite samples were air dried, crushed, and passed through a 2 mm sieve to remove gravel and large organic debris.

Undisturbed soil cores were treated with a combination of management practices common in urban landscapes. Soil management practices included were maintaining growing turf or mulching to cover soil and were compared to a bare control soil. Irrigation management included irrigating with a pH neutralized water to reduce the alkalinity or irrigating with rain water only, simulated here by using distilled water; these were compared to using a highly sodic tap water. These management practices were combined for a total of 8 treatments (Table 2.1). Each treatment was replicated on three cores from each site. Perennial ryegrass (*Lolium perenne* L.) was established and grown for four weeks on 18 (9 from each park) of the soil cores before leaching treatment was started (Table 2.1; treatments 4, 5 and 6). During turf establishment, these cores were irrigated with 5 mL of distilled water daily. Soil cores without ryegrass were slowly rewetted by adding 5 ml portions of distilled water 3 times a day for 1 week to wet the soil but not allow leaching. Hardwood landscaping mulch was applied at a rate of 2.5 cm on a further 6 cores from each site (Table 2.1 treatments 7 and 8) and 9 cores from each site were left bare (Table 2.1; treatments 1, 2 and 3).

Upon initiation of irrigation treatments, all soil cores were irrigated with 85 mL (the mean pore volume of soil cores) at a rate of 100 mL hr^{-1} from a single drip source using intravenous tubing hanging approximately 1 cm above the soil surface. Soil cores were irrigated with one of either: distilled water (DDW), tap water, or neutralized tap water (Table 2.1). The tap water had the following chemistry: pH = 8.65, EC = 0.93 dS m^{-1}, Na = 235 mg L^{-1}, Ca = 2.5 mg L^{-1} and alkalinity = 353 mg L^{-1}. To neutralize the tap water, concentrated sulfuric acid (36 N) was added until pH stabilized at 6.5 (approximately 0.2 ml per L tap water). Soils were irrigated daily for 16 days with one pore volume of solution each day. Approximately 70 to 75 ml was released as leachate and to normalize data all masses were reported by the output volume. To simulate a rain event, distilled water was used to irrigate all treatments every fifth day (pore volumes 6, 11, and 16). Seven of the 16 pore volumes were collected and analyzed (pore volumes 2, 3, 7, 10, 11, 15, and 16).

Table 2.1 The eight treatment combinations used to simulate soil management scenarios in urban landscapes.

Treatment	Soil Cover	Irrigation water
1	Bare	Distilled
2	Bare	Municipal
3	Bare	Neutralized
4	Perennial Ryegrass	Distilled
5	Perennial Ryegrass	Municipal
6	Perennial Ryegrass	Neutralized
7	Mulched	Distilled
8	Mulched	Municipal

A second set of cores from both sites A and B were irrigated with untreated tap water for 15 pore volumes for a period of four months (120 days) to evaluate a less intensive irrigation regime over the long-term. Soil was collected in the same manner, undisturbed cores 6 cm in diameter from a depth of 0 to 7 cm using a beveled edge soil corer were collected and maintained in the lab environment. Cores were leached with municipal tap water. Every fourth leaching distilled water was used to simulate a rain event. Cores were leached once a day for the first 12 days, after which they were leached 2 times per week. During each leaching 50 mL of water was applied at a rate of 100 mL per hour through a single drip source using intravenous tubing hanging approximately 1 cm above the soil surface. Every leaching in this second set was collected and analyzed for carbon and nutrients.

Collection of Irrigated Urban Soils from Texas

Thirty three composite soil samples (7 cores to a depth of 10 cm) were retrieved from irrigated urban turfgrass sites from twenty-eight cities across Texas (Figure 2.1). Samples were from a broad range of climates, soil types, and management practices and furthermore included a wide range of municipal water quality in terms of sodium concentration (Table 2.2). Four cities were chosen to sample more than one location but the same water source was utilized to evaluate inter-city variability (College Station, Bryan, Houston, and San Antonio). Depending on the availability and accessibility at each city, soil samples were collected from several different types of irrigated turf, including: athletic fields, commercial lawns, and apartment complex lawns (Table 2.2). Based on the results of Aydemir (2005) who reported that changes in soil sodicity were negligible after five years of irrigation, all sites selected for this study had been irrigated for at least five years based on the age of the property or park. At each city, municipal tap water samples were taken from establishments close to the soil sampling site, or in

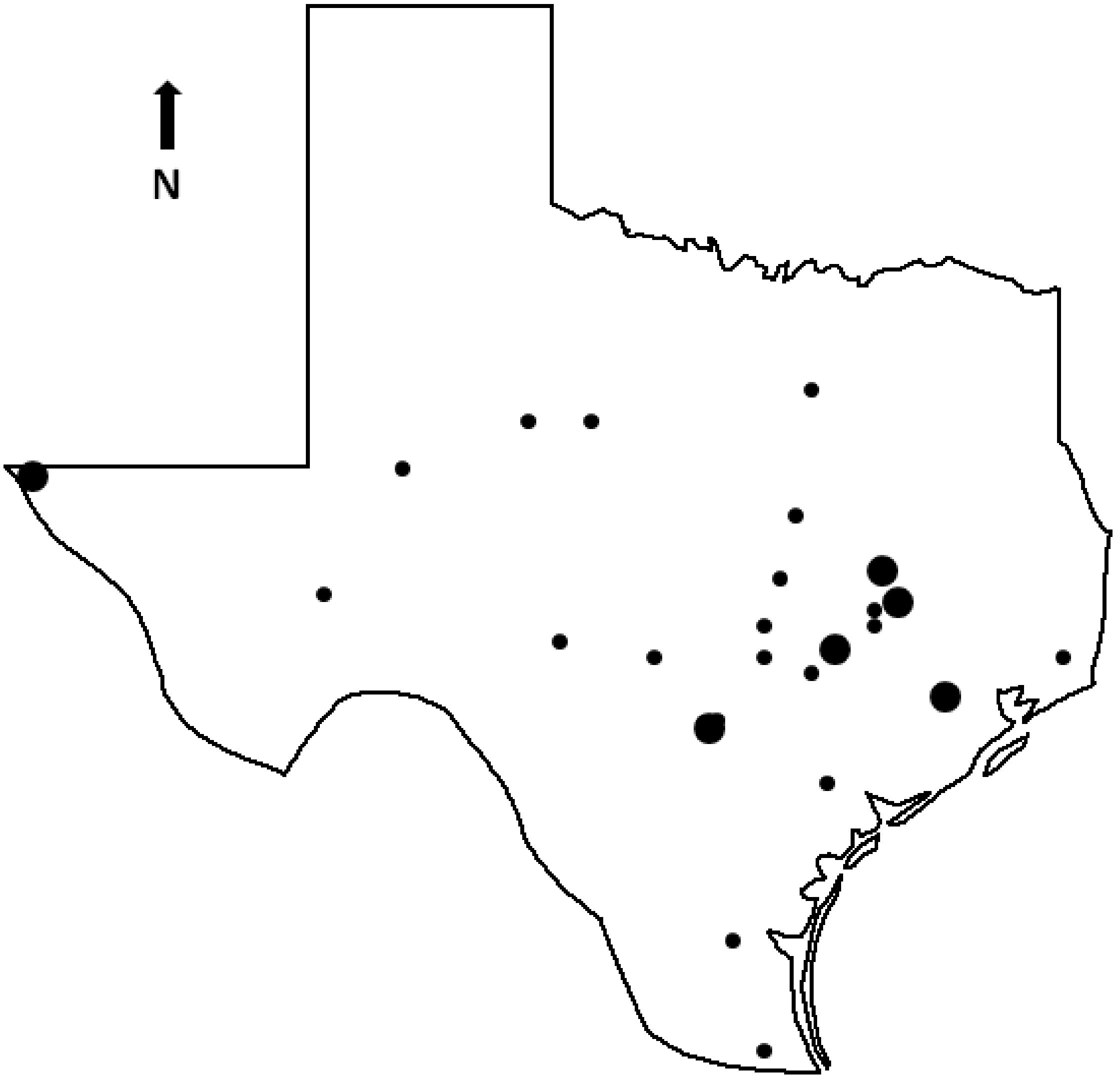

Figure 2.1 Location of cities sampled in Texas. Large circles indicate that two locations were sampled per city. Smaller dots indicate one sample per city was collected.

Table 2.2 The identification number, city, site type, site name, and location of sample sites across Texas: AF = Athletic Field, CL = Commercial Lawn, AL = Apartment Complex Lawn, GL = Government Building Lawn, MP = Municipal Park.

ID	City	Land Use	Site Name	Latitude	Longitude
1	Abilene	AF	Will Hair Park	32°28'20.47"N	99°43'19.34"W
2	Austin	CL	Holiday Inn	30°13'0.55"N	97°41'33.70"W
3	Bastrop	CL	Comfort Inn	30°6'21.27"N	97°20'9.41"W
4	Beaumont	AF	Beaumont Athletic Facility	30°3'52.98"N	94°9'53.56"W
5	Bryan	AL	Woodtrails Apartment	30°40'30.28"W	96°21'1.72"W
6	Bryan	AL	Reveille ranch	30°37'46.32"W	96°21'31.70"W
7	College Station	AL	Gateway Apartments	30°35'37.85"W	96°20'4.84"W
8	College Station	AL	Trails at WP Creek	30°37'3.38"W	96°18'3.18"W
9	El Paso	GL	TAMU Center	31°41'50.16"N	106°16'56.40"W
10	El Paso	GL	TAMU North Loop	31°39'21.95"N	106°16'14.42"W
11	Falfurrias	MP	Municipal park	27°13'51.13"N	98°8'32.38"W
12	Fort Stockton	AF	James Rooney Park	30°53'1.37"N	102°52'23.30"W
13	Fredericksburg	AF	Old Fair Park	30°16'7.22"N	98°52'22.65"W
14	Giddings	CL	Ramada Inn	30°10'34.52"N	96°53'51.07"W
15	Giddings	CL	Bank	30°10'34.73"N	96°53'52.01"W
16	Grand Prairie	AF	Charlie Taylor Park	32°44'24.88"N	96°59'48.71"W
17	Houston	CL	Citibank	29°44'2.92"N	95°25'46.76"W
18	Houston	MP	Levy Park	29°43'59.10"N	95°25'26.60"W
19	Junction	AF	Schrier Park	30°29'28.99"N	99°45'41.99"W
20	Midland	AF	Rusk Park	32°0'43.62"N	102°7'49.49"W
21	Navasota	CL	BBS Bank	30°23'25.28"N	96°5'7.20"W
22	Round Rock	CL	Candlewood Suites	30°30'22.19"N	97°41'1.51"W
23	San Antonio	AL	Conemerra Estates	29°34'51.20"N	98°26'50.53"W
24	San Antonio	AL	Three Fountains	29°27'47.19"N	98°38'44.57"W
25	San Marcos	CL	Tangier Outlets	29°49'33.67"N	97°59'9.21'W
26	Snook	CL	First Bank of Snook	30°29'36.24"N	96°28'7.27"W
27	Somerville	CL	Americas Best Value Inn	30°20'19.25"N	96°31'26.43"W
28	Somerville	GL	ISD Administration	30°20'27.66"N	96°32'6.89"W
29	Sweetwater	AF	Newman Park	32°29'8.38"N	100°24'39.08"W
30	Temple	CL	Holiday Inn	31°4'59.98"N	97°24'26.15"W
31	Victoria	AF	Riverside Stadium	28°48'47.50"N	97°1'23.51"W
32	Waco	CL	Residence Inn	31°33'21.32"N	97°7'27.87"W
33	Weslaco	CL	Prime Outlets	26°9'41.29"N	97°53'21.53"W

the case of athletic fields, from their irrigation water faucet. Soil and water samples were collected at the end of the summer irrigation season during the months of August and September 2010. Soils were air dried, crushed, and passed through a 2-mm sieve. Two 3.5 g subsamples from each soil sample were extracted using a 1:10 soil to water ratio with distilled water and shaken for 24 hours. Samples were centrifuged at 7500 g-force for 10 minutes and the supernatant removed. The pH and conductivity were measured on unfiltered samples and supernatant was filtered prior to being diluted 2:1 with ultra-pure water and frozen until analysis.

The percent sand content, saturated paste extract conductivity (ECs), sodium adsorption ratio (SARs), $CaCO_3$ equivalents, total carbon and total nitrogen content were quantified on all soils. Preliminary evaluation of the extract data revealed that carbon and nutrient in extract solutions was better related to the sand content reported by the USDA soil survey than to any other textural component. Therefore, percent sand content was measured following the procedures of Gee and Bauder (1986): where 10 g soil was combined with 100 ml of 20 g L^{-1} sodium hexametaphosphate and shaken for 12 hours. The solution was then passed through a 47µm sieve (#300 mesh) and rinsed repeatedly. What remained on the sieve was oven dried at 105°C for 24 h, removed and cooled prior to weighing. Percent sand was calculated based on the organic matter-free weight of the soil. Calcium carbonate was estimated by measuring the CO_2 evolution after soil acidification modified from the methods of Holmgren (1973). The Dumas method for total carbon and nitrogen analysis of the soil was performed at the Texas A&M AgriLife Environmental Quality Center, in Vernon, Texas, USA using a Vario Max Elementar

C/N Combustion Analyzer. Soil pH, conductivity, Na^+, Ca^{2+}, Mg^{2+}, and K^+ were measured on saturated paste extracts according to the methods described by Rhoades (1996). Deionized, distilled water was added to 150 g of soil (not to saturation) and allowed to sit in an air tight container for 2 hours; after which more water was added to the saturation point and soaked for a further 2 hours prior to weighing. The solution was then vacuum-filtered through an 8 cm diameter funnel fitted with a Whatman Grade No. 5 cellulose filter paper.

Solution Chemistry

The soil core leachates and extract solutions were analyzed in the same manner. Electrical conductivity and pH were determined immediately on unfiltered aliquots of the solution and the remainder of the sample was syringe filtered through ashed (400° C for 5 hours) Whatman GF/F filters (0.7 μm nominal pore size). Samples were stored in acid washed, ultra-pure water rinsed (Barnstead Nanopure Diamond water filtration system) HDPE bottles and frozen until analysis.

Dissolved organic carbon, total dissolved nitrogen, nitrate-N, ammonium-N, PO_4-P alkalinity, Na^+, Ca^{2+}, Mg^{2+} were quantified in the leachate from soil cores, the soil extracts and the municipal tap water solutions. Dissolved organic carbon, measured as non-purgeable organic carbon, and total nitrogen were quantified using high temperature Pt-catalyzed combustion with a Shimadzu TOC-V_{CSH} and total measuring unit TNM-1; following US EPA method 415.1 which entails acidifying the sample and sparging for 4 min with C-free air. Sample replicates, blanks, NIST traceable and check standards were run every 12th sample to monitor instrument precision (coefficient of variance (CV) < 2%) and accuracy (CV < 5%). Ammonium-N was analyzed using the phenate hypochlorite method with sodium nitroprusside enhancement (US EPA method 350.1). Nitrate-N was analyzed using Cd-Cu reduction method (US EPA method 353.3). Alkalinity was measured using the methyl orange method (US EPA method 310.2), and PO_4-P was measured using the ammonium molybdate and antimony potassium with ascorbic acid (US EPA method 365.1) method. All colorimetric methods were performed with a Westco Scientific Smartchem Discrete Analyzer (Westco Scientific Instruments Inc. Brookfield CT, USA).

Aliqouts were filtered through 0.2 µm Pall filters prior to analysis by ion chromatography for Ca^{2+}, Mg^{2+}, K^+ and Na^+. Ion chromatography was performed using a DIONEX ICS 1000 with Ionpac CS16 analytical and Ionpac CG16 guard column for separation and 20 mM methanosulfonic acid as eluent at a flow rate of 1 mL min^{-1} and injection volume of 10 µL (DIONEX Corp. Sunnyvale, CA, USA). Sample replicates, blanks, NIST traceable and check standards were run every 10th sample to monitor instrument precision (coefficient of variance (CV) < 2%) and accuracy (CV < 5%).

The measured Na^+, Ca^{2+}, and Mg^{2+} of all irrigation water, leachates and soil extracts was converted to mmol (+) per liter prior to calculating the sodium adsorption ratio using the following calculation:

$$\text{Eq. 2.1} \quad SAR = Na^+ / [(Ca^{2+} + Mg^{2+})/2]^{1/2}.$$

Statistical Analysis

Leaching from Soil Cores

Data from each pore volume of the leaching study were analyzed using a factorial univariate analysis of variance with irrigation water (DDW, tap water, and neutralized tap water), soil cover (bare, mulch, and ryegrass) and location (site A and B) as fixed factor effects. Post-hoc pair wise comparisons using LSD were used to determine differences between treatments at alpha ≤ 0.05. Retention or release of cations was determined by subtracting the mass of Na^+, Ca^{2+}, K^+, and Mg^{2+} in the soil leachate from the initial mass added by the irrigation water. Positive values indicated retention, while negative values represented the release of cations. The second study evaluated the change in carbon and nutrient leaching with a less intense irrigation regime. Changes in leaching were quantified by regression analysis between the mass of C or nutrients leached extrapolated to m^2 and the number of pore volumes.

Irrigated Urban Soils

The mean of the two replicate measurements on each soil sample was used for all statistical analyses. Each sample site was treated as an independent unit for a total of 34 sites from 24 cities. Individual relationships between water extractable DOC, PO_4-P, TDN, NO_3-N, NH_4-N, and DON and irrigation water chemistry (sodium, calcium, SAR, %Na^+, EC, SAR/EC, pH) and measured properties (percent sand, total soil C, total soil N) were determined using regression analysis. For the multiple regression analysis DOC, DON, SAR, and alkalinity (ALK) were natural log transformed to achieve a normal distribution. A new parameter was also added to the regression analysis: the

SAR was divided by the EC in dS m^{-1} (SAR/EC). The severity of sodicity in soils was expected to be dependent on the inverse relationship between these two parameters, as SAR increases and EC decreases the more severe the effects of sodicity on soil properties. Stepwise multiple regression analysis was used to model relationship between each water extractable C, N, and P and the irrigation water chemistry (lnSAR, lnEC, lnALK, SAR/EC), environmental factors (precipitation), and soil properties (percent sand, total soil C, and total soil N).

For each multiple regression model the residuals were plotted to test for outliers and normal distributions. In addition, to evaluate the models' accuracy, the original data for each analyte (DOC, DON, NH_4-N, NO_3-N and PO_4-P) was plotted with the value predicted by the model and the two were compared using a zero intercept regression with observed values as the independent variable and predicted values as the dependent variable. The closer the resulting y value and R^2 are to 1, the better the model.

The regression models for each analyte were also validated by the "Leave *n* Out Cross Validation" method (Shao 1993), where five observations were randomly removed from the data set and a new regression model was generated. The new regression equation was then used to predict the values of the removed data. This process was repeated 10 times. Regression analysis was then used to compare the resulting predictions from the re-sampled models with the original predicted values to generate a slope (y′) and R^2 value. The closer y and R^2 is to 1 the more robust the model (table on p. 86). All analyses were performed using SPSS v. 16.

Results

Irrigation and Management Impacts on the Leaching of C, N, and P

Irrigation water had a significant effect on the leaching of DOC from soil starting at three pore volumes. The mean rate of DOC loss by leaching from the municipal tap water treatment was 932 ± 109 mg C m^{-2} and remained relatively constant over the 16 pore volumes (Figure 2.2). The mean rate of the DOC loss over the study period from the DDW and neutralized treatments were 787 ± 227 mg C m^{-2} and 687 ± 181 mg C m^{-2} respectively. The DDW and neutralized tap water treatments were initially high in DOC loss but had a decreasing trend as the number of pore volumes increased (Figure 2.2). Release of DOC from the untreated tap water treatment was significantly higher than both DDW and neutralized tap water during pore volumes 7, 10, 11, 15 and 16. After day 7 (i.e. >7 pore volumes), the second simulated rain event (pore volume 11) resulted in the neutralized tap water treatment releasing more DOC than the DDW treatment, otherwise there were no significant differences between those treatments.

The type of cover had a significant impact on DOC leaching during pore volumes 3 through 10 and again at pore volume 16. During these periods the ryegrass treatment released significantly lower DOC than the mulch and the bare soil treatments with a mean of 727 ± 402 mg C m^{-2} soil during the whole treatment period compared to 1021 ± 542 mg C m^{-2} for bare soil and 1000 ± 384 mg C m^{-2} for mulch. No significant interactions were found between soil cover and irrigation water. Soil type had no impact on DOC leaching losses.

Similar results were found for DON leaching (Figure 2.3). However, the impact of irrigation water began at 7 pore volumes instead of 3. Tap water caused significantly greater leaching of DON with a mean loss of 78 ± 12 mg N m^{-2} after 7 pore volumes compared to 38 ± 5.4 mg N m^{-2} for DDW and 33 ± 7.9 mg N m^{-2} for neutralized tap water. DON also displayed different trends over the treatment period compared to DOC. Both the DDW and tap water treatments increased DON leaching over the study period whereas for DOC, losses either decreased or were maintained (Figures 2.2 and 2.3). Soil cover only had a significant impact on DON leaching during pore volumes 7 and 15. In both cases the ryegrass treatment had significantly less DON loss to leaching compared to the other two treatments. No other effects or interactions were found.

Both cover and irrigation water treatments had a significant impact on the leaching of NH_4-N and NO_3-N (Figures 2.4 and 2.5). Soil cover impacted NH_4-N leaching between pore volumes one through seven. The bare soil leached significantly higher amounts of ammonium-N than ryegrass during that period with the mulch treatment falling in the middle. Beginning at pore volume seven the irrigation water type had a significant impact on the leaching of NH_4-N with tap water leaching a mean of 73 ± 20 mg N m^{-2} between pore volumes 7 to 16. Neutralized tap water leached 74 ± 18 mg N m^{-2}, and distilled water leached a mean of 54 ± 21 mg N m^{-2} over the same period. The effects of soil cover and irrigation water on NO_3-N leaching were less consistent than on other nutrients or DOC (Figure 2.4). As is commonly found after a disturbance which will aerate the soil, large amounts of NO_3-N were released during the

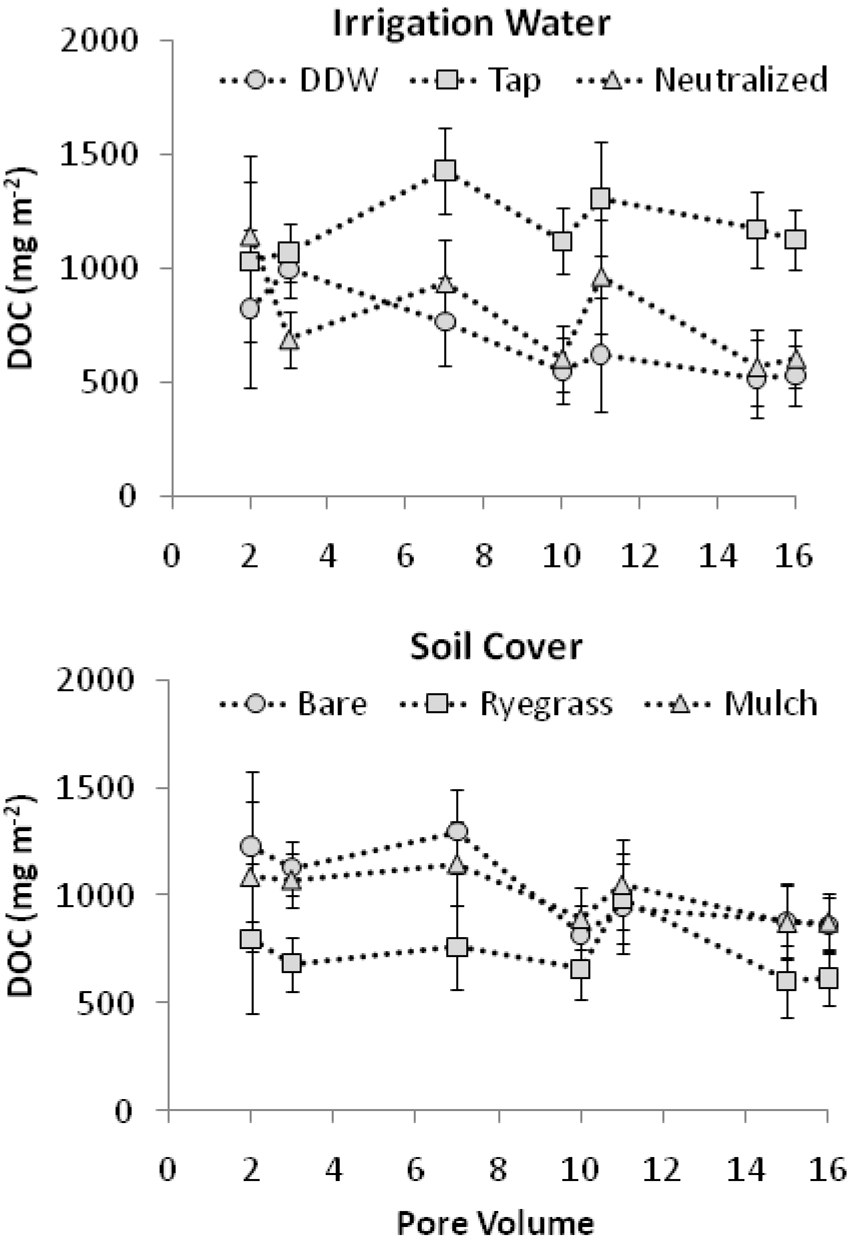

Figure 2.2 Mean release of dissolved organic carbon (DOC) in leachate during each pore volume under irrigation water treatments (top), distilled water (DDW), sodic municipal tap water (Tap), and neutralized tap water (Neutralized), over all soil cover treatments. The mean release of DOC from three soil cover treatments (bottom) bare, mulch, and ryegrass overall irrigation treatments. Error bars represent the least significant difference (LSD) values for a 95% confidence interval.

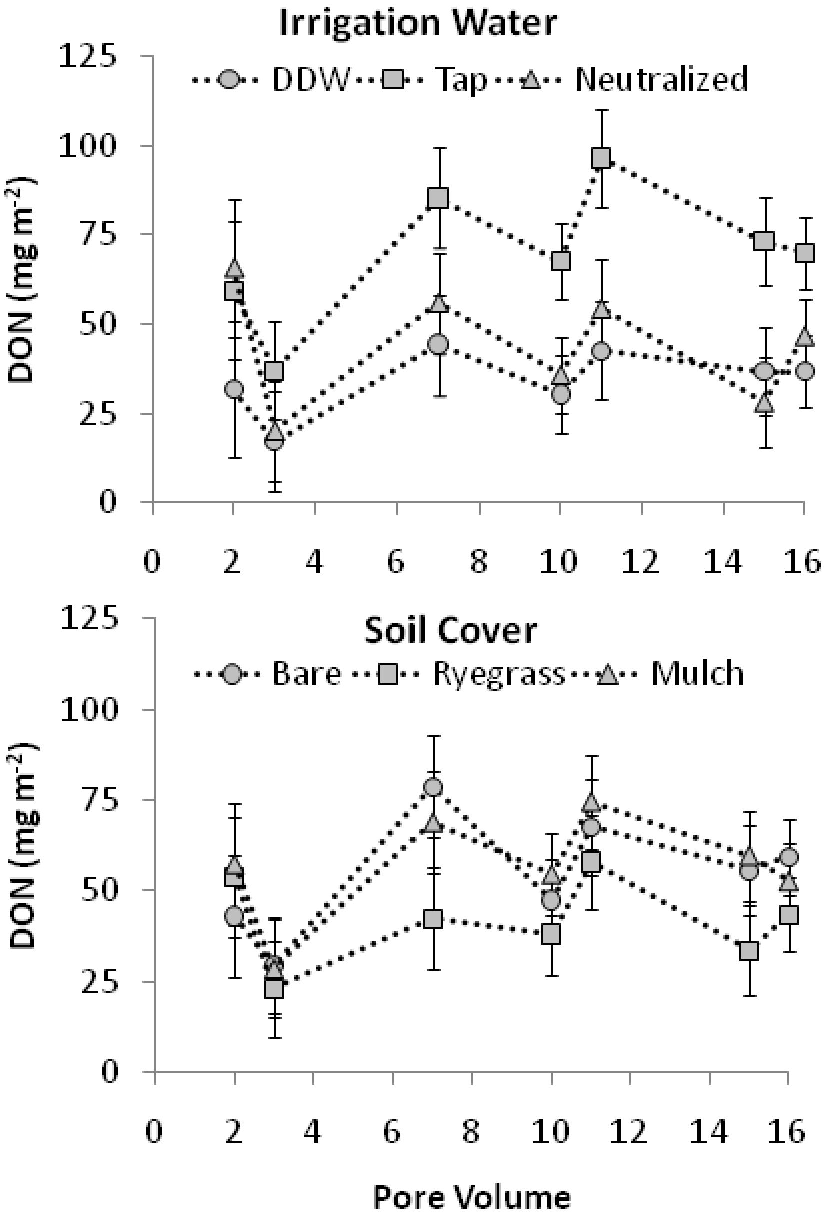

Figure 2.3 Mean release of dissolved organic nitrogen (DON) in leachate during each pore volume under irrigation water treatments (top), distilled water (DDW), sodic municipal tap water (Tap), and neutralized tap water (Neutralized), over all soil cover treatments. The mean release of DON from three soil cover treatments (bottom) bare, mulch, and ryegrass overall irrigation treatments. Error bars represent the least significant difference (LSD) values for a 95% confidence interval.

first three pore volumes after which they began to stabilize. Irrigation water had a significant impact on nitrate leaching at pore volumes 3 and also between 11 through 16. The DDW treatment leached significantly less NO_3-N than either the tap water or neutralized treatments. Soil cover had a significant effect on NO_3-N leaching during pore volumes 3, 10 and 15; here the mulch treatment leached significantly lower NO_3-N than either the bare soil or ryegrass treatments.

Unlike DOC or nitrogen, significant differences due to location were found to impact the leaching of orthophosphate-P (Figure 2.6). Soil from Site B leached significantly more orthophosphate at all pore volumes than did Site A. Soil at site A was fairly similar to soil at site B. Both were fine sandy loams with 68% sand, 20 % silt, 12% clay and 1.41% carbon in Soil A and 69% sand, 13% silt, 18% clay, and 2.19% carbon in the soil at B. Otherwise no other treatment effects were found during the study period due to the high variability within each treatment. The release of P was fairly constant over the study period (Figure 2.6).

Decreasing the irrigation volume and frequency in the second core leaching experiment yielded similar results as the first, more intensive leaching experiment. Mass of DOC, NH_4-N and NO_3-N leached from soil cores increased over the 15 pore volumes rather than remaining constant as in the more intense irrigation treatment in the first experiment. Leachates were within a similar range indicating that drier conditions did not decrease or increase the release of carbon and nutrients from the soil (Figure 2.7). DON was the only N species that remained constant over the 15 pore volumes, which differed from experiment one, where there appeared to be a pattern of increasing losses

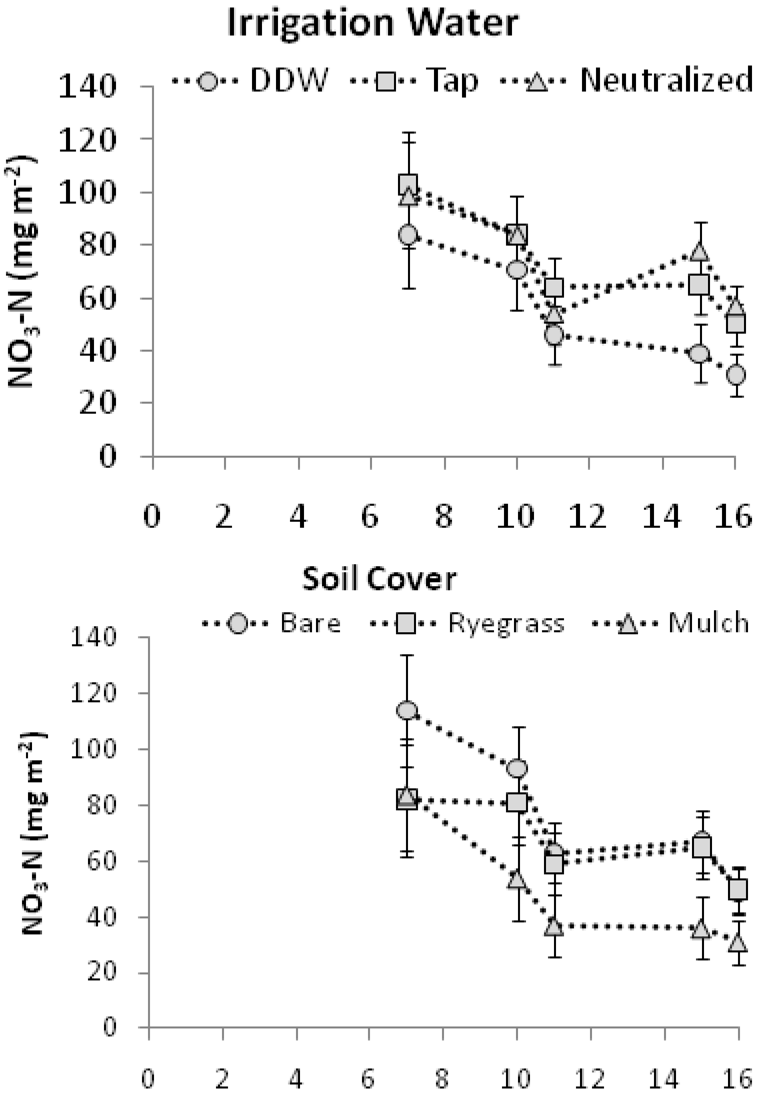

Figure 2.4 Mean release of NO_3-N in leachate during each pore volume under irrigation water treatments (top), distilled water (DDW), sodic municipal tap water (Tap), and neutralized tap water (Neutralized), over all soil cover treatments. The mean release of NO_3-N from three soil cover treatments (bottom) bare, mulch, and ryegrass overall irrigation treatments. Error bars represent the least significant difference (LSD) values for a 95% confidence interval. The NO_3-N graphs only show pore volumes 7 through 16 so that a better view of the treatment effects could be obtained.

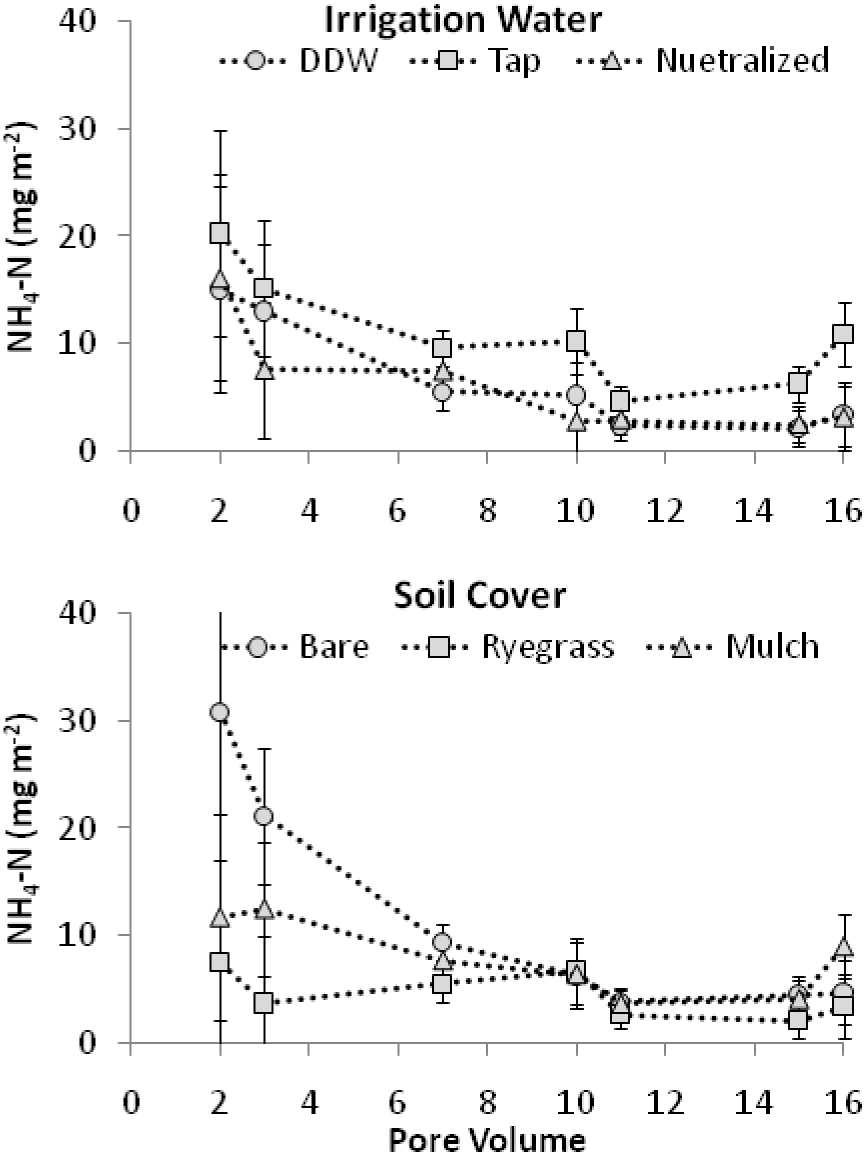

Figure 2.5 Mean release of NH_4-N in leachate during each pore volume under irrigation water treatments (top), distilled water (DDW), sodic municipal tap water (Tap), and neutralized tap water (Neutralized), over all soil cover treatments. The mean release of NH_4-N from three soil cover treatments (bottom) bare, mulch, and ryegrass overall irrigation treatments. Error bars represent the least significant difference (LSD) values for a 95% confidence interval.

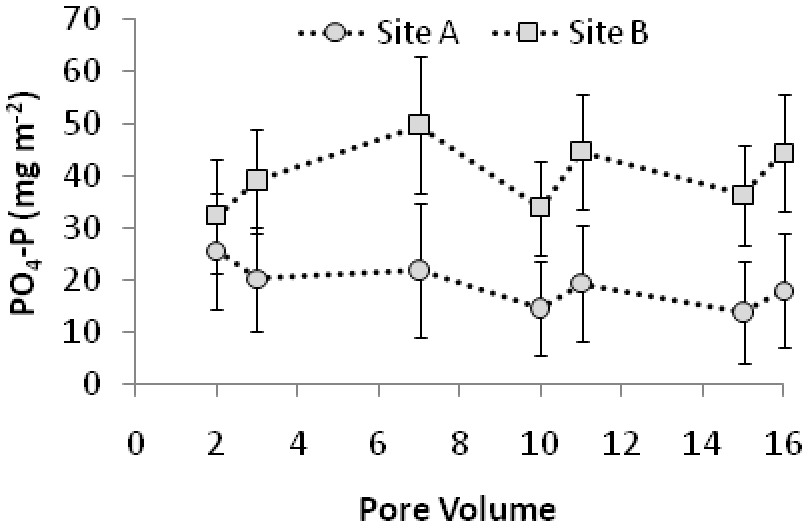

Figure 2.6 Mean release of orthophosphate (PO_4-P) in leachate from two sampling locations (Site A and Site B) over all irrigation and soil cover treatments. Error bars represent the standard error of the mean. Error bars represent the least significant difference (LSD) values for a 95% confidence interval.

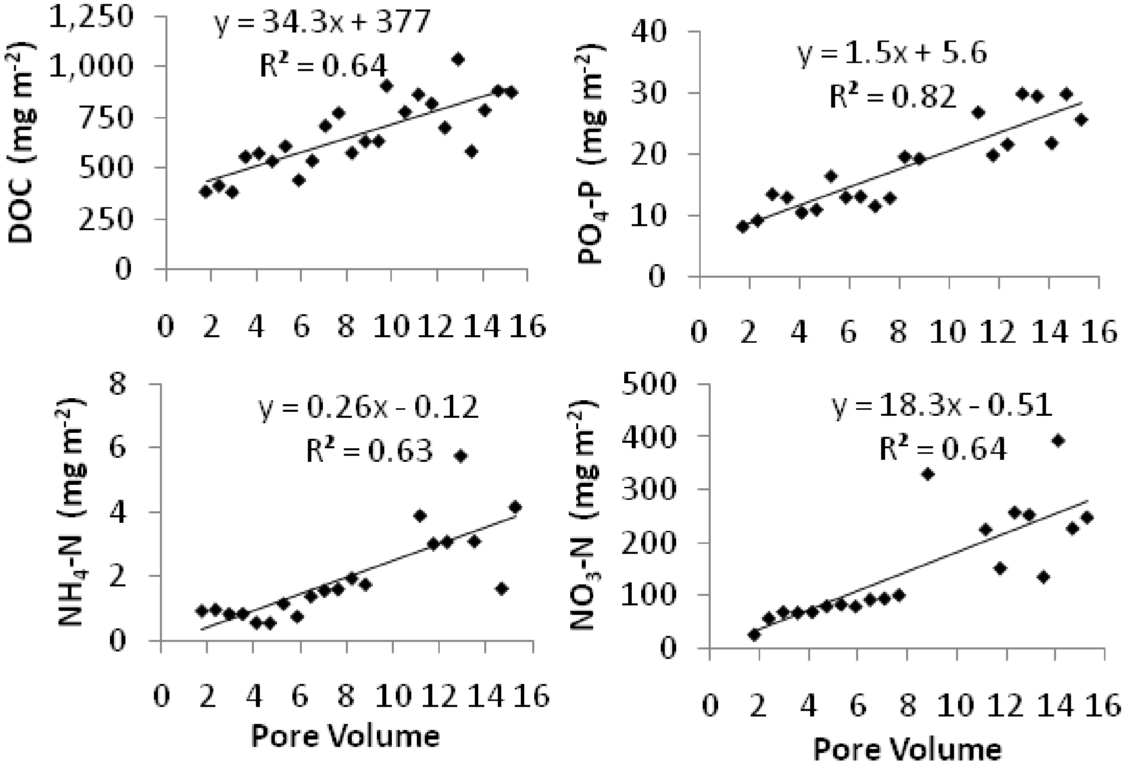

Figure 2.7 The release of dissolved organic carbon (DOC), orthophosphate-P (PO_4-P), ammonium-N (NH_4-N) and nitrate (NO_3-N) in leachate from soil cores irrigated with municipal tap water with decreased irrigation volume and frequency. All relationships are significant at $\alpha = 0.05$. Note difference in y-axis scales.

(Figures 2.3). Under the intense irrigation regime there was no significant impact of irrigation water treatment on PO_4-P, however, under the less frequent leaching regime there was a positive relationship between the number of pore volumes passed through the soil and the release of PO_4-P (Figure 2.7). In addition, the mean pH of the soil leachate was much higher by pore volume 15 (pH = 8.75) than was the pH of the untreated tap water treatment under more intense irrigation regime (pH = 7.97).

Release and Retention of Cations

Irrigation water quality, soil series, and soil cover all affected the retention or release of sodium in the soil (Figure 2.8). Of the two treatments types, irrigation water quality had the greatest impact. Retention was highest in the earlier rounds and decreased through the study period for both untreated and neutralized tap water (Figure 2.8). The opposite pattern was observed in the DDW treatment which released small amounts of Na throughout the study period. At pore volumes 7 and 15 tap water retained significantly more Na^+ than both neutralized tap water and distilled water. During pore volumes 3 and 10 there was a significant interaction between the water treatment and the soil cover treatment. The following differences were observed in Na^+ retention for the two treatment combinations: (tap+bare) > (tap+mulch) = (tap+ryegrass) = (neutralized+ryegrass) > (neutralized+bare) >>> (DDW+all). During pore volume 10 the following treatment differences were observed: (tap+bare) = (tap+mulch) > (tap+ryegrass) > (neutralized+all) >> (DDW+all). It appeared that the mulch and ryegrass cover were able to reduce the retention of Na^+ during these pore volumes, their effects were not consistent however. During pore volumes 10 and 15 site affected Na^+ retention with the soil at site A retaining significantly more Na^+ than soil at site B.

Both soil cover and irrigation water affected the release of K^+ from soil cores. Ryegrass cover significantly decreased K^+ release compared to both bare and mulched soil during pore volumes 3, 10, and 15. The effects of irrigation water quality were not as consistent as soil cover on K^+ release. Neutralized tap water decreased K^+ release

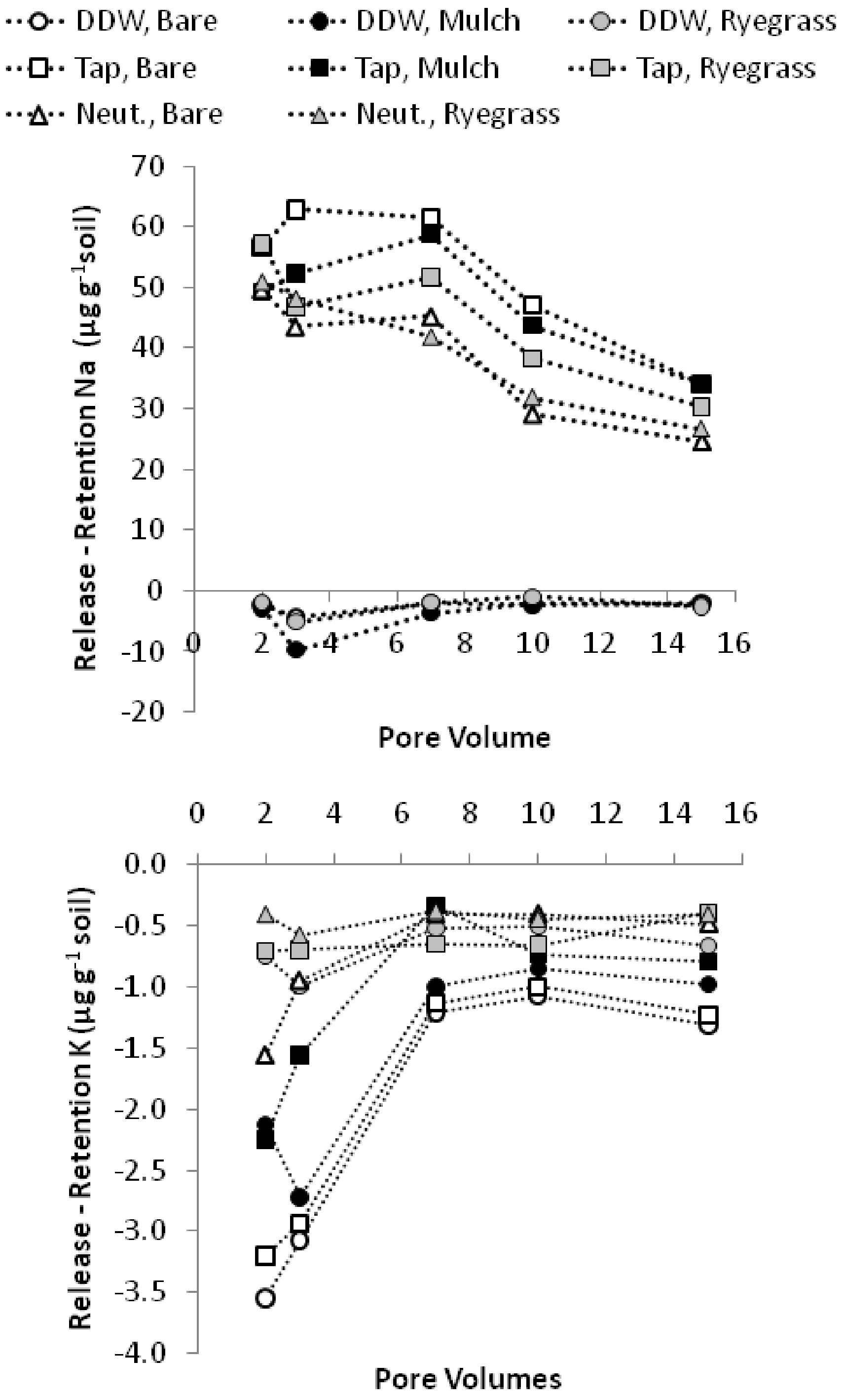

Figure 2.8 The retention and release of sodium (Na) and potassium (K) from soil irrigated with distilled water (DDW), untreated tap water (Tap), or neutralized tap water (Neut.). Soil cores had one of three soil cover treatments bare, mulch, or ryegrass (R). Positive values indicate retention while negative values indicate release.

compared to DDW during pore volume 3 and decreased release compared to both DDW and Tap water during pore volume 15.

Irrigation water quality affected the release of Ca^{2+} beginning in pore volume 7 (Figure 2.9). The neutralized tap water treatment released the most calcium (11.0 ± 0.4 µg Ca g^{-1} soil), followed by the untreated tap water (6.9 ± 0.2 µg Ca g^{-1} soil), and distilled water which released the least (4.0 ± 0.9 µg Ca g^{-1} soil). The retention or release of calcium was affected by soil type starting at pore volume 3 and continuing through pore volume 16. The release of calcium for soil at site B (12.2 ± 5.8 µg Ca g^{-1} soil) during those pore volumes was significantly higher than site A (8.3 ± 4.8 µg Ca g^{-1} soil). There were no significant interactions between irrigation water treatments and the location. Soil cover only impacted Ca^{2+} release during pore volume three where the ryegrass treatment was significantly lower than both the bare soil ($p = 0.007$) and mulch ($p = 0.019$) treatments.

The release of Mg^{2+} was also impacted by both irrigation water and soil cover treatments with no difference between the locations (Figure 2.9). Irrigation water affected the release of Mg^{2+} during pore volume 7 through 10 where Mg^{2+} release from greatest to least was: neutralized tap water > untreated tap water > distilled water. Soil cover affected Mg^{2+} release during pore volumes 3 and 10; however, there was no consistent pattern across pore volume. For example, during pore volume 3, ryegrass released significantly less magnesium than both mulch and bare soil, whereas during pore volume 7, mulch released less magnesium than the other treatments. During pore

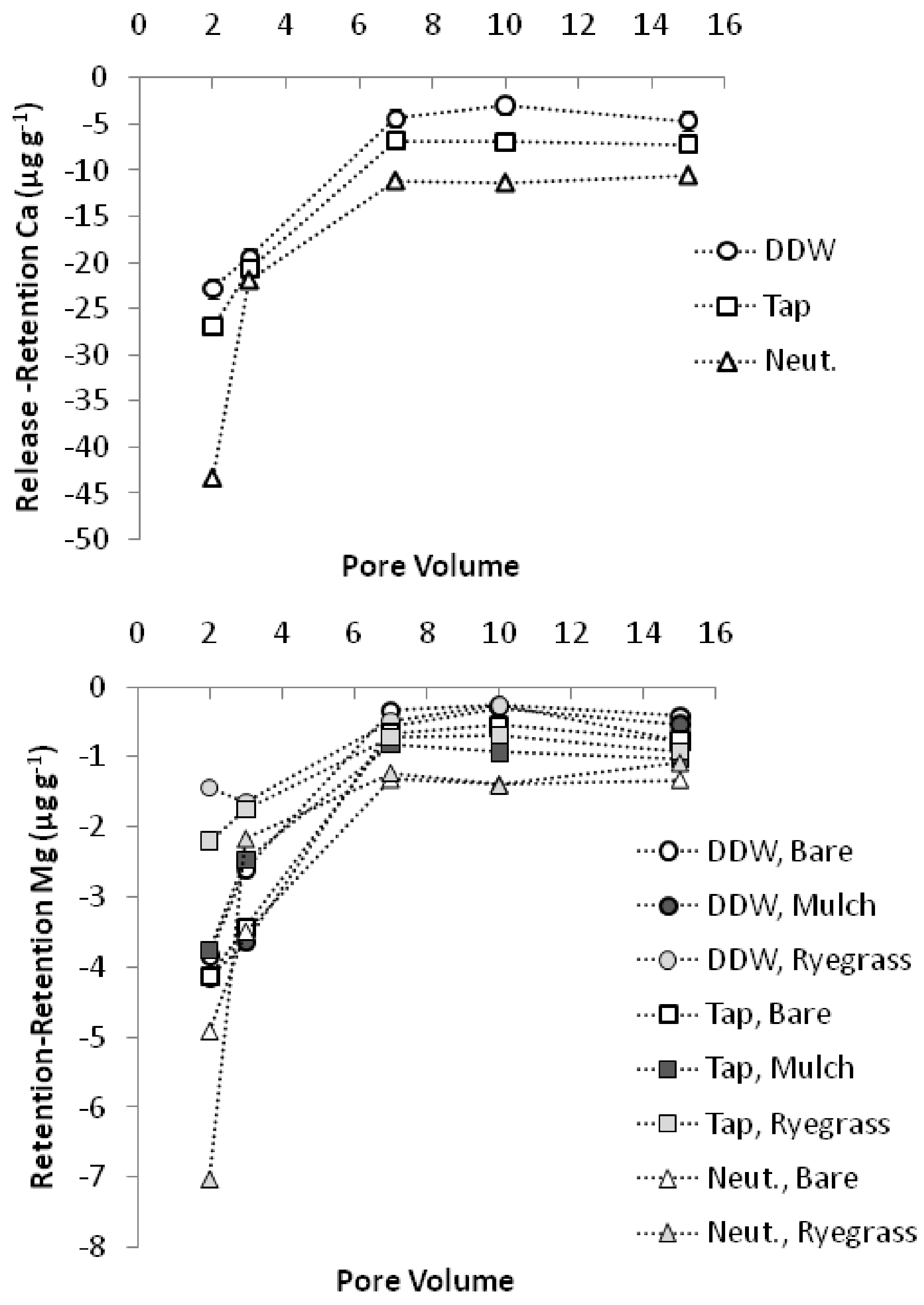

Figure 2.9 The retention or release of calcium (Top) and magnesium (Bottom) from soil cores irrigated with three water types, distilled (DDW), untreated tap water (Tap), or neutralized tap water (Neut.). There was no significant impact of soil cover on Ca therefore the means include all soil cover treatments. The mean of the three soil cover treatments were bare soil, mulch, or ryegrass are shown for magnesium. Negative values indicate release. Note differences in y-axis scales.

volume 15 there were significant interactions between irrigation water quality and soil cover ($p < 0.001$). The following treatment effects on Mg^{2+} release were observed during pore volume 15: (neutralized+bare soil) > (neutralized+ryegrass) = (tap+mulch) = (tap+ryegrass) > (tap+bare) = (DDW+ryegrass) > (DDW+mulch) = (DW+bare).

Solubility of Carbon and Nutrients in Irrigated Urban Soils

The soil samples collected represented 23 soil series from across the state of Texas, USA and five major soil orders: Mollisols, Entisols, Vertisols, Alfisols, and Aridisols (Table 2.3). All soils were alkaline and ranged from of 7.4 to 8.6 with a median of 8.14 pHs (saturated paste pH; Table 2.4). A wide range of textures were represented in the samples collected, percent sand ranged from 16.3 to 88% (Median = 56.2%). The total soil carbon ranged from 0.89 to 7.88% and total nitrogen ranged from 0.04% to 0.34% (Table 2.4). Similarly a wide range of irrigation waters were sampled. The EC_{iw} ranged from 0.18 to 2.43 dS m^{-1} (median = 0.57 dS m^{-1}), the SAR_{iw} ranged from 0.38 to 54.9 (median = 2.89), and the $alkalinity_{iw}$ ranged from 54.6 to 393 mg L^{-1} (median = 154.5) (Table 2.4).

Preliminary analysis revealed some correlations between irrigation water and soil properties. Several of the irrigation water chemistries were correlated with the percent sand. SAR was significantly correlated with $alkalinity_{iw}$ ($r = 0.52$) and percent sand ($r = 0.53$). The EC_{iw} and $alkalinity_{iw}$ were correlated with percent sand ($r = 0.53$ and 0.44 respectively). As is often found in soils, the total carbon was correlated with total nitrogen ($r = 0.59$).

Table 2.3 The series and taxonomic classification of the 33 soils sampled under irrigated urban turf from across the state of Texas, USA.

ID	Series	Taxonomic Classification
1	Gageby	Fine-loamy, mixed, superactive, thermic Cumulic Haplustolls
2	Patrick	Clayey over sandy or sandy-skeletal,carbonatic, thermic Typic Calciustolls
3	Bosque	Fine-loamy, mixed, superactive, thermic Cumulic Haplustolls
4	League	Fine, smectitic, hyperthermic Oxyaquic Dystruderts
5	Zack	Fine, smectitic, thermic Udertic Paleustalfs
6	Zack	Fine, smectitic, thermic Udertic Paleustalfs
7	Boonville	Fine, smectitic, thermic Chromic Vertic Albaqualfs
8	Zack	Fine, smectitic, thermic Udertic Paleustalfs
9	Bluepoint	Mixed, thermic Typic Torripsamments
10	Glendale	Fine-silty, mixed superactive, calcareous, thermic Typic Torrifluvents
11	Czar	Fine-loamy, mixed, superactive, hyperthermic Pachic Argiustolls
12	Hoban	Fine-silty, mixed, superactive, thermic Ustic Haplocalcids
13	Pedernales	Fine, mixed, active, thermic Typic Paleustalfs
14	Tabor	Fine, smectitic, thermic Oxyaquic Vertic Paleustalfs
15	Zack	Fine, smectitic, thermic Udertic Paleustalfs
16	Houston Black	Fine, smectitic, thermic Udic Haplusterts
17	Urban Land	N/A
18	Urban Land	N/A
19	Frio	Fine, smectitic, thermic Cumulic Haplustolls
20	Amarillo	Fine-loamy, mixed, superactive, thermic Aridic Paleustalfs
21	Chazos	Fine, smectitic, thermic Udic Paleustalfs
22	Sunev	Fine-loamy, carbonatic, thermic Udic Calciustolls
23	Eckrant	Clayey-skeletal, smectitic, thermic Lithic Haplustolls
24	Houston Black	Fine, smectitic, thermic Udic Haplusterts
25	Houston Black	Fine, smectitic, thermic Udic Haplusterts
26	Burleson	Fine, smectitic, thermic Udic Haplusterts
27	Rader	Fine-loamy, mixed, semiactive, thermic Aquic Paleustalfs
28	Rader	Fine-loamy, mixed, semiactive, thermic Aquic Paleustalfs
29	Colorado	Fine-loamy, mixed, superactive, calcareous, thermic Typic Ustifluvents
30	Heiden	Fine, smectitic, thermic Udic Haplusterts
31	Sinton	Fine-loamy, mixed, superactive, hyperthermic Cumulic Haplustolls
32	Bastsil	Fine-loamy, siliceous, active, thermic Udic Paleustalfs
33	Hidalgo	Fine-loamy, mixed, active, hyperthermic Typic Calciustolls

Table 2.4 Soil and irrigation water characteristics for 33 sites sampled and the precipitation (Precip.). The pH (pH_S), electrical conductivity (EC_S), and sodium adsorption ratio (SAR_S) are based on saturated paste soil extracts. The total carbon (C_S) and total nitrogen (N_S) are for the whole soil. The irrigation water electrical conductivity (EC_{iw}), sodium adsorption ratio (SAR_{iw}) and alkalinity (Alk_{iw}) correspond to each site. Dashes indicate no measurement was made due to a lack of sample.

ID	pH_S	EC_S (dS m^{-1})	SAR_S	C_S (%)	N_S (%)	Sand (%)	EC_{iw} (dS m^{-1})	SAR_{iw}	Alk_{iw} (mg L^{-1})	Precip. (mm)
1	8.17	0.93	0.74	2.26	0.18	44.8	0.821	2.83	113	606
2	8.08	1.02	0.50	4.15	0.23	57.1	0.290	1.79	54.6	843
3	8.13	1.33	0.94	3.71	0.04	57.6	0.701	1.03	223	965
4	7.94	0.83	2.63	1.87	0.15	58.1	0.254	2.95	141	1429
5	8.14	1.28	8.86	1.62	0.16	56.7	0.848	30.0	369	1000
6	-	-	-	1.13	0.09	50.5	0.848	30.0	369	1000
7	7.98	1.78	2.78	1.45	0.11	47.8	0.887	38.5	393	1000
8	-	-	-	2.34	0.18	59.4	0.887	38.5	393	1000
9	8.06	0.57	1.04	0.89	0.04	71.5	0.670	3.70	102	219
10	8.16	1.93	2.35	1.49	0.12	85.7	0.620	5.00	114	219
11	8.33	1.42	3.33	0.96	0.08	78.7	1.23	5.96	189	645
12	8.00	1.33	2.72	7.88	0.32	27.1	0.570	3.10	125	357
13	8.27	1.81	1.17	2.57	0.19	66.6	0.808	1.03	236	803
14	8.37	3.58	27.6*	1.52	0.12	88.7	0.740	54.9	298	911
15	-	-	-	2.44	0.16	65.0	0.820	69.0	475	911
16	8.09	1.23	0.78	3.64	0.23	38.7	0.337	2.28	61.9	905
17	7.42	1.17	1.38	1.66	0.13	33.1	0.437	1.88	98.7	1307
18	8.23	1.01	1.81	4.64	0.29	55.7	0.437	1.91	98.6	1307
19	8.16	1.72	0.88	6.17	0.23	39.4	0.180	1.90	284	446
20	7.82	4.57†	6.67	1.54	0.16	72.0	2.43	4.82	74.3	374
21	8.54	1.99	13.8*	2.03	0.20	65.8	1.070	10.5	169	1000
22	8.42	1.44	0.91	4.99	0.15	32.6	0.380	0.93	144	924
23	8.04	1.28	0.46	3.90	0.19	20.1	0.570	0.50	190	749
24	8.05	1.16	0.79	7.50	0.21	16.3	0.570	0.50	190	749
25	8.07	0.73	0.55	4.95	0.22	50.5	0.510	0.38	165	844
26	8.39	1.71	9.66	1.93	0.18	73.7	0.350	37.2	224	1000
27	8.64	1.20	6.81	1.52	0.09	52.7	0.575	32.7	212	1000
28	-	-	-	3.50	0.34	54.9	0.575	32.7	212	1000
29	8.19	1.89	1.36	2.19	0.16	60.1	0.760	0.96	126	596
30	7.93	1.35	1.22	5.87	0.09	32.4	0.440	0.99	144	909
31	8.16	1.42	0.88	5.69	0.24	66.2	0.425	1.00	110	939
32	7.89	1.11	0.70	4.88	0.30	41.6	0.319	1.27	95.5	917
33	8.21	1.14	3.27	1.61	0.09	59.1	1.075	3.36	68.9	583

* Indicates soil would be classified as Sodic, Non-Saline according to Glossary of Soil Science Terms (1979)

† Indicates soil would be classified as Non-Sodic, Saline according to the USSL Staff (1954)

Regression analysis showed several significant relationships between the irrigation water and soil nutrients and carbon. The water extractable dissolved organic carbon (WEDOC) was positively related to sodium in the irrigation water and negatively related to the calcium concentrations (Figure 2.10 A and B). In addition to evaluating concentrations, several methods of characterizing the relationship between sodium and other cations in the irrigation water were evaluated (Figure 2.10 C and D). Both SAR and the percentage of charge contributed by sodium (Na^{+}_{iw}) were able to explain more of variation in WEDOC than was sodium concentrations alone. WEDOC was also significantly related to the alkalinity of the irrigation water solution. WEDOC was not significantly related to any of the soil properties (sand, $CaCO_3$ equivalents, total soil carbon, or total soil nitrogen).

Similar relationships were found between water extractable dissolved organic nitrogen (WEDON) and irrigation water chemistry. WEDON was positively related to sodium concentrations and negatively related to calcium concentration in the irrigation water (Figure 2.11 A and B). Again, SAR and Na^{+}_{iw} accounted for more of the variability in WEDON between samples than did sodium concentrations alone (Figure 2.11 C and D). Like WEDOC, WEDON was positively related to alkalinity (Figure 2.11 E). DON was not significantly related to any soil properties.

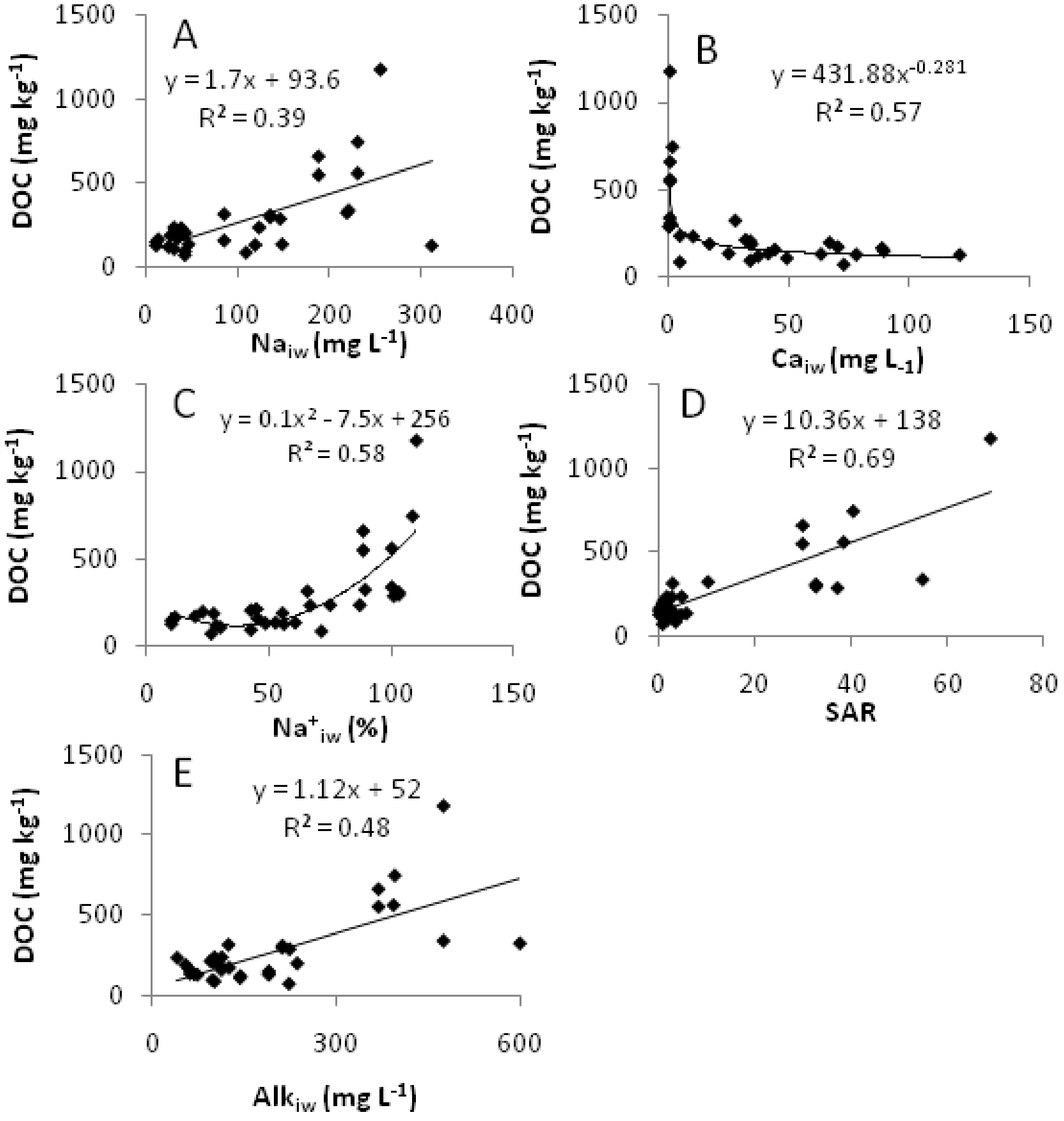

Figure 2.10 Relationships between water extractable dissolved organic carbon (DOC) in urban soils of Texas and irrigation water chemistry: sodium (A) and calcium (B) concentrations, the percentage of sodium charge in irrigation water (C), SAR (D), and alkalinity (E). All regressions are significant at $\alpha < 0.05$.

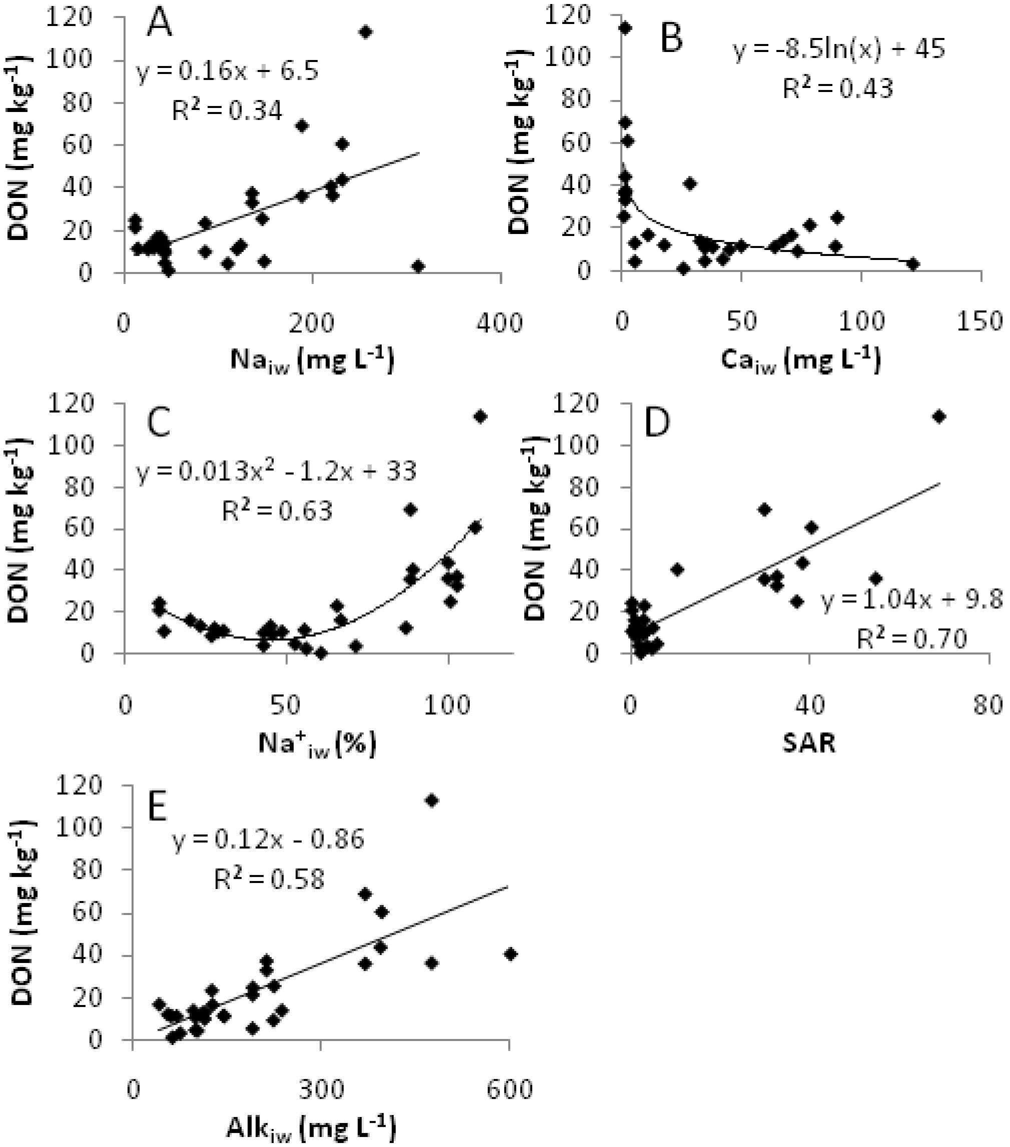

Figure 2.11 Relationships between water extractable dissolved organic nitrogen (DON) in urban soils of Texas and irrigation water chemistry: sodium (A) and calcium (B) concentrations, the percentage of sodium charge in irrigation water (C), SAR (D), and alkalinity (E). All regressions are significant at $\alpha < 0.05$.

Relationships between irrigation waters and soil properties were very different between the two inorganic nitrogen components, NH_4-N and NO_3-N. Similar to WEDOC and WEDON, the water extractable NH_4-N was positively related to sodium and alkalinity of irrigation waters, but was not related to the irrigation water calcium concentrations (Figure 2.12 A and C). The SAR and Na^{+}_{iw} only accounted for slightly more variability in NH_4-N than the sodium concentrations alone (Figure 2.12 B and D). NH_4-N was not significantly related to any soil properties. NO_3-N, however, was not related to any of the irrigation water characteristics. NO_3-N was only positively related to total soil nitrogen, but no other soil properties (Figure 2.13).

Water extractable phosphorus (PO_4-P) was significantly related to both irrigation water and soil properties. Like WEDOC, WEDON, and ammonium, PO_4-P was positively related to sodium concentrations and alkalinity in irrigation water; both SAR and Na^{+}_{iw} were able to explain more of the variation than sodium concentrations alone (Figure 2.14 A, C, D, and F). PO_4-P was also positively related to the percent sand in soil and negatively related to the $CaCO_3$ in soil (Figure 2.14 B and E).

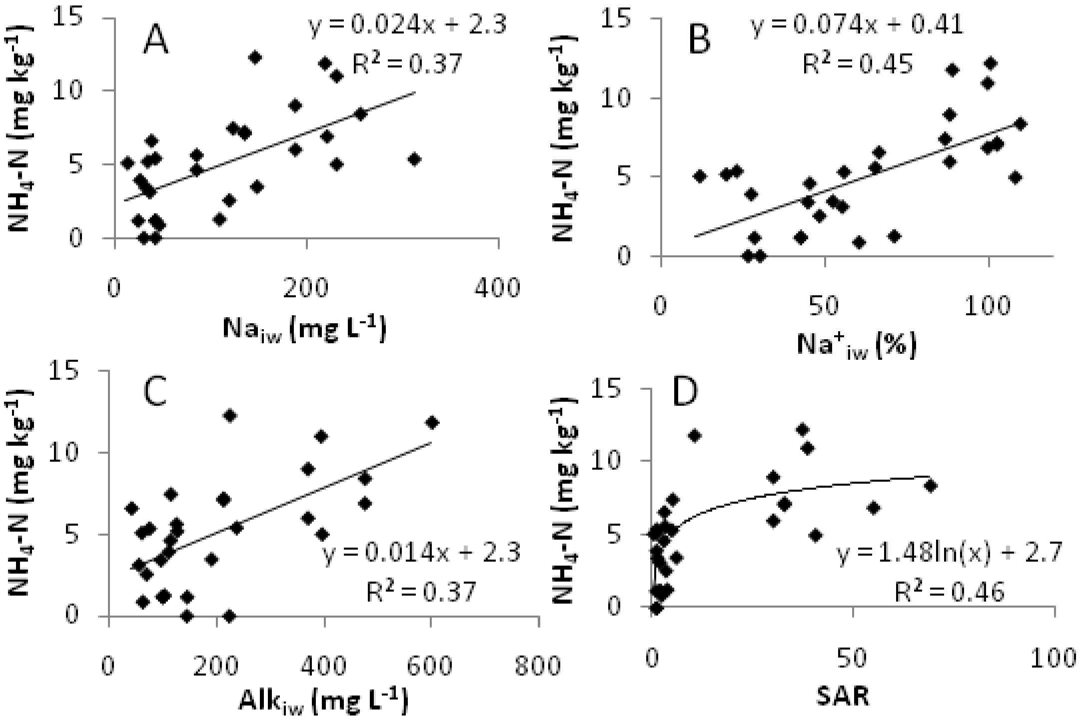

Figure 2.12 Relationships between water extractable ammonium (NH_4-N) in urban soils under turfgrass and irrigation water chemistry: sodium concentrations (A), the percentage of sodium charge in irrigation water (B), alkalinity (C), and SAR (D). All regressions are significant at $\alpha < 0.05$.

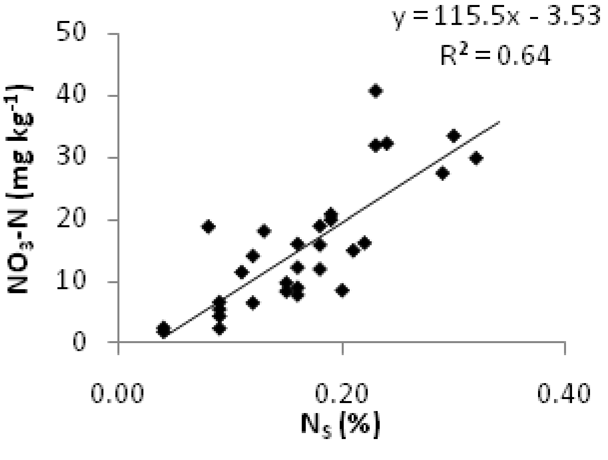

Figure 2.13 Relationships between water extractable nitrate (NO_3-N) in urban soils under turfgrass and total soil nitrogen. Regressions are significant at $\alpha < 0.05$.

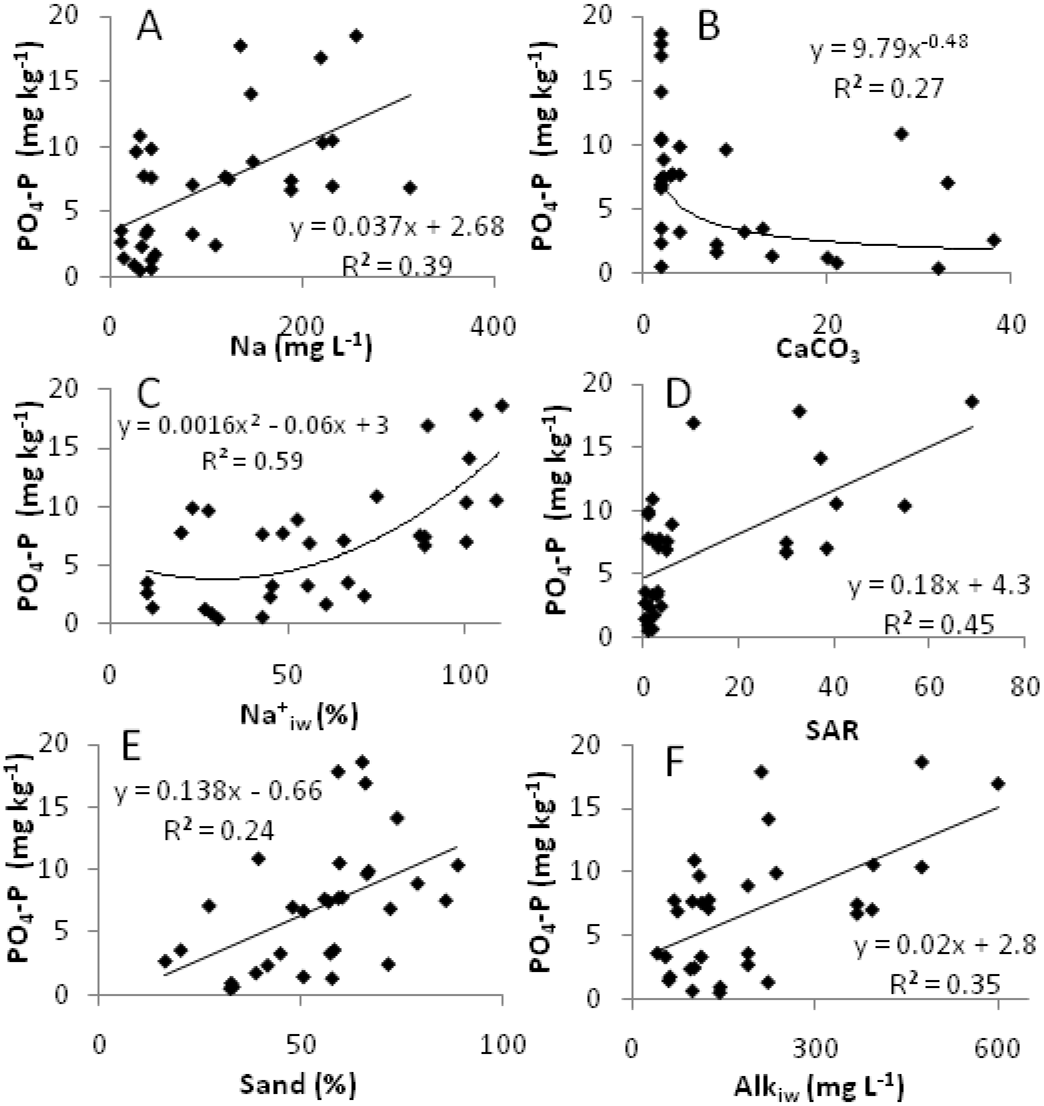

Figure 2.14 Relationships between water extractable orthophosphate (PO_4-P) in urban soils under turfgrass and irrigation water chemistry: sodium concentrations (A) and calcium carbonate equivalents (B), the percentage of sodium charge in irrigation water (C), SAR (D), percentage of sand in soil (E) and alkalinity (F). All regressions are significant at $\alpha < 0.05$.

Multiple regression analysis identified a number of significant relationships between the water extractable carbon and nutrients and the quality of irrigation water (Table 2.5). Only NO_3-N was unrelated to irrigation water quality, but the natural log of NO_3-N was related to soil carbon and nitrogen (adj. $R^2 = 0.74$) (Table 2.5). The $\ln(SAR_{iw})$, N_S, and Alk_{iw} were significant predictors of water extractable DOC (WEDOC) with an adjusted R^2 of 0.82. Slopes of the predicted vs. observed and cross validation (Table 2.5) for ln(WEDOC) were 0.88 and 1.09 respectively. Visual observation of the relationship between irrigation water $\ln(SAR_{iw})$ and WEDOC indicated a change in slope at approximately $SAR_{iw} = 5$. To investigate this phenomenon further, the samples were divided into two groups, $SAR_{iw}<5$ and $SAR_{iw} \geq 5$. The mean WEDOC in those soils exposed to $SAR_{iw}<5$ was 160 mg C kg^{-1} soil and at $SAR_{iw} \geq 5$ the mean WEDOC was 379 mg C kg^{-1} soil, more than double the losses when $SAR_{iw}<5$. While WEDOC was not significantly correlated to SAR_{iw} when $SAR_{iw}<5$it was strongly correlated with total soil nitrogen (Figure 2.15). Water extractable DOC in those samples where $SAR_{iw} \geq 5$ were significantly correlated with SAR_{iw} but not with total soil nitrogen (Figure 2.15). Seventy seven percent of the variability in WEDON was explained by irrigation water and soil attributes (SAR_{iw}, N_S, and Alk_{iw}). The mean WEDON in regions where $SAR_{iw}<5$ was 11.9 mg N kg^{-1} soil and for regions where $SAR_{iw} \geq 5$ the mean WEDON was 36.7 mg N kg^{-1} soil, representing a threefold increase.

Multiple regression analysis found that SAR_{iw}/EC_{iw} was a significant predictor of water extractable PO_4-P and NH_4-N. SAR_{iw}/EC_{iw} and sand content appeared to be the best predictors of water extractable orthophosphate, explaining 54% of the variability in samples (Table 2.5). The mean water extractable PO_4-P in those soils where irrigation water $SAR_{iw}<5$ was 4.2 mg P kg^{-1} soil and for regions where irrigation water $SAR_{iw} \geq 5$, water extractable PO_4-P was10.2 mg P kg^{-1} soil. Irrigation water SAR_{iw}/EC_{iw} and annual precipitation were able to explain 59% of the variability in water extractable NH_4-N. The mean water extractable NH_4-N was 3.25 mg N kg^{-1} soil in regions where $SAR_{iw}<5$ and 8.0 mg N kg^{-1} soil in regions where $SAR_{iw} \geq 5$. In short, water extractable soil C, N and P was two to three times higher in those regions in Texas where the municipal tap water used for irrigation had a SAR greater than 5.

Table 2.5 Results of the stepwise multiple regression for water extractable dissolved organic carbon (WEDOC), orthophosphate (PO_4-P), nitrate (NO_3-N), ammonium (NH_4-N) and dissolved organic nitrogen (WEDON) and associate factors: sodium adsorption ratio (SAR_{iw}), total soil nitrogen (N_S), alkalinity (Alk_{iw}), SAR/EC ratio, percent sand, and precipitation (Precip.) and the cross validation results (Leave *n* out method) of each model.

				Adj.	Std. Error of	Cross Validation	
		Coefficient	*p*-value	R^2	the Estimate	y'	R^2
ln(WEDOC)	$\ln(SAR_{iw})$	0.273	<0.001	0.82	0.253	1.09	0.99
	N_S	3.895	<0.001				
	Alk_{iw}	0.002	0.001				
	Constant	3.895	<0.001				
PO_4-P	SAR/EC	0.076	0.001	0.54	2.47	1.11	0.97
	Sand	0.093	0.003				
	Constant	-0.262	0.864				
ln(NO_3-N)	N_s	11.816	<0.001	0.74	0.428	0.93	0.98
	C_s	-0.151	0.01				
	Constant	1.066	<0.001				
NH_4-N	SAR/EC	0.104	<0.001	0.59	2.06	0.93	0.68
	Precip	-0.003	0.039				
	Constant	5.497	<0.001				
WEDON	Alk_{iw}	0.089	0.002	0.77	8.11	1.14	0.89
	SAR	0.506	0.013				
	N_s	22.14	0.031				
	Constant	-8.88	0.115				

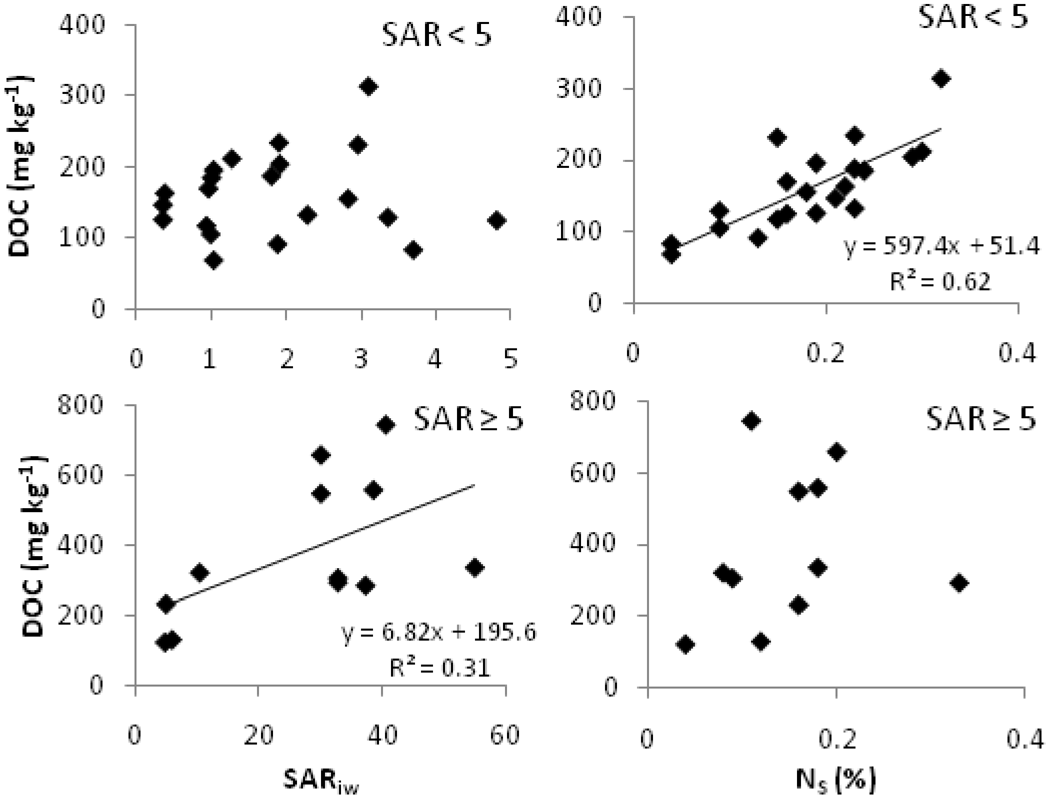

Figure 2.15 Relationships between water extractable dissolved organic carbon (DOC), SAR of irrigation water (SAR_{iw}), and total soil nitrogen (N_s) for soils with irrigation water SAR < 5 (top row) and soils with irrigation water SAR ≥ 5 (bottom row). Relationships are significant at $\alpha = 0.05$. Note differences in x-axis scales in left column.

Discussion

Impacts of Irrigation Water Chemistry and Management on Leaching

The solubility and its subsequent leaching of organic matter, ammonium, and nitrate will increase due to irrigation with high sodium water (Green et al. 2008; Greenland 1965; Holgate et al. 2011; Laura 1976; Skene and Oades 1995). This study indicated that the leaching of intact soils with different irrigation water chemistry had significant impacts on the leaching of DOC and nitrogen from soil thus supporting the findings reported in other studies conducted in USA, Great Britain, Australia and India. Compared to irrigation with DDW, the sodic municipal tap water used in the core leaching study approximately doubled the release of DOC, DON, NO_3-N and NH_4-N after seven pore volumes. DON in sodic soils is a nitrogen species that is not widely examined except with respect to mineralization rates (Green et al. 2009; Laura 1976) or soil leaching losses in forested and urban ecosystems (e.g. Kalbitz et al. 2004; Aitkenhead-Peterson et al. 2011a,b; Holgate et al. 2011). Because DON is a subset of molecules thought to be from the same pool as DOC based on strong relationships between the two (Aitkenhead-Peterson et al. 2003), it is reasonable to assume that those mechanisms that alter DOC retention in soil such as adsorption to minerals (pH, EC, anion competition, dispersion) will also impact DON (e.g. Kaiser and Zech 1998). Although both DOC and DON release were found to be elevated in both the short term, high intensity leaching study and the water extractable soil organic matter (SOM) survey of urban soils, DOC and DON were not tightly coupled. For example, in the first leaching experiment, DOC release stayed relatively stable for the 16 pore volumes while DON appeared to be increasing (Figure 2.1). The decoupling of DOC and DON due to salt accumulation has been suggested by Green et al. (2009) who studied an acid soil impacted by road salt and due to N-saturation in forested ecosystems by McDowell (2003). Both high sodium from the irrigation water and high N from municipality fertilization regimes and domestic and wildlife animal feces may well be a reason for the decoupling of DOC and DON in this study.

Previous studies have documented increased P release as soil sodicity increases (Curtin et al. 1992, Curtin et al. 1987; Smillie et al. 1987; Sharpley et al. 1988). Unlike the results reported by Curtin et al. (1992), the irrigation water sodicity in this study had no impact on orthophosphate leaching in the high intensity, short term leaching study (Figure 2.3). The soil core replicates had a large amount of variability in the amount of PO_4-P leached. Phosphorus is naturally highly variable in soils. The two municipal parks where the soil was collected are in the middle of residential neighborhoods of both single and multi-family homes, walking paths, and are likely frequented by domesticated animals whose defecation may have contributed to the soil P variability. However, when the irrigation volume and frequency were decreased from daily to two times per week the increase in P leaching was evident. Several mechanisms may be contributing to the increase P release under less frequent irrigation. One, the increase may be a result of the wetting and drying cycles enhancing dispersion of aggregates and exposure of P therein. Two, the concentration of ions in solution likely became more concentrated around soil particle surfaces as a result of the soil drying. This concentration would have promoted the competition between anions and increased the negative charge of the exchange surface. Three, pH has a strong impact on the solubility of P as the electrostatic potential of the surfaces decrease (Barrow 1985). The mean pH of the leachate solution was almost a full unit higher (pH= 8.74) under the less intense irrigation regime compared to the more frequent irrigations (7.97) which may explain the increased P leaching. These results indicate that homeowners who are more likely than businesses and athletic fields to irrigate less frequently may actually have a higher potential to release P from the soil.

To the best of my knowledge no previous studies have investigated the impact of acidifying an alkaline irrigation water to reduce carbon and nutrient leaching, which would be logical when one considers that organic matter in acidic sodic soils is known to be less soluble than in alkaline sodic soils (Nelson and Oades 1998). Results from the soil management treatments tested in this study indicated positive results for retarding the release of carbon and nitrogen from soil. Of these, acidifying the municipal irrigation water with sulfuric acid (neutralized tap water) to pH = 6.5 was the most effective. The leaching of DOC and N when irrigated with neutralized tap water was no different from irrigating with DDW for most of the treatment period; suggesting that at least in the short term, acidification of irrigation water will reduce the solubility and leaching of carbon and nitrogen from the soil. Interestingly, the pH of the leachates under the neutralized water treatment were similar to those of untreated tap water (pH = 7.97 and 7.95 respectively) and increased compared to the pH of the DDW treatment (pH = 7.17) despite having been reduce to a pH of 6.5 indicating the neutralized tap water was still contributing some bicarbonate to the soil. The relationships between soil DOC and pH are complex. In soil organic horizons, numerous laboratory studies have shown a positive correlation between pH and DOC solubility (Tipping and Woof 1990; Whitehead et al. 1981; Hay et al. 1985; Tipping and Hurley 1988; Kennedy et al. 1996; You et al. 1999). This is suggested to be caused by the protonation of functional groups which occurs as pH decreases thus reducing solubility due to changing steric conformation and more effective van der Waals forces and proton bridging. Since the leachate pH of the neutralized and untreated tap water treatments were virtually identical, it is unlikely that pH is the mechanism controlling the release or retention of DOC and DON. The acidification of tap water reduced the alkalinity and the total amount of bicarbonate present in the irrigation water solution. Bicarbonate can impact pH and neutralize the protonation of functional groups allowing for a more mobile steric conformation. Nodvin et al. (1998) identified several anions which act as competitors with DOC, which is primarily anionic, for positively charged sites. Typically PO_4^{3-} and F^- sorp to soil minerals most strongly, but there tends to be competition between DOC, DON and SO_4^{2-} for exchange sites and NO_3^- and Cl^- do not compete well for sites (Nodvin et al. 1986). Preliminary data (*Aitkenhead-Peterson, unpublished data*) indicated that bicarbonate is also an anion competitor of DOC for exchange sites in urban soils. While solubility of organic matter in sodic soils is often thought to be a function of the very high pH (pH =10), based on the data generated in this study, organic matter loss occurs long before those pH extremes are reached and an anion competition mechanism would likely explain the increase in DOC leaching observed in this study while pH levels were still relatively low.

In addition, to reducing the release of DOC and DON, neutralization of tap water also reduced the retention of Na^+ in the soil relative to using untreated tap water. Acidification of the tap water increased the total salt concentration from 0.93 dS m^{-1} in the tap water to 1.05 dS m^{-1}. The slight increase in total salt concentration may have helped to decrease dispersive forces in the soil which prevented Na^+ exchange and DOC and DON release. As expected, the soil still retained large amounts of sodium in both the untreated and neutralized tap water treatments compared to the distilled water treatment in which there was a release of all cations. Despite the reduction Na^+ retention, the neutralized tap water still released significantly more Ca^{2+} and Mg^{2+} than untreated tap water. As stated, neutralization increased the electrical conductivity of solution and the concentration of sulfate in the water. It is possible then that the increase in H^+ ions were able to replace more Ca^{2+} and Mg^{2+} on exchange sites causing the increase in divalent cation release (e.g. Johnson et al. 1994). These divalent cations can be released to maintain the electroneutrality of leachate solution. Though acidifying irrigation water may be beneficial in reducing nitrogen, phosphorus and carbon leaching which may ultimately help to prevent infertility and loss of physical structure, the sustained loss of divalent cations may negate those benefits in the long term.

The impact of organic matter additions on the amelioration of alkaline sodic conditions has been widely studied (Robbins 1986; Ahmad et al. 1988; More 1994). In this study soil cover had an effect on the leaching of carbon and nutrients for all irrigation water treatments. The effect of soil cover on leaching was primarily observed in the earlier pore volumes and not as pronounced as was observed in the acidification of the irrigation water. The ryegrass cover generally reduced the leaching of DOC, DON, and NH_4-N from soil compared to both mulch and bare soil even though the grass would have increased the available soil organic matter. Plant roots and their debris exude labile compounds which include polysaccharides and acidic functional groups (Oades 1978). For example, Norway spruce roots produce between 4 and 8 mg C g^{-1} dry root and this is highly biodegradable ranging from 37 – 69% degradability depending upon N addition (Aitkenhead-Peterson and Kalbitz 2005). The fate of root contributed DOC is more likely to be mineralization and stable humification of the remaining C (Aitkenhead-Peterson and Kalbitz 2005) rather than loss to leachate. The roots and their associated mucilages and microbial colonies can also provide the foundation for stable aggregates (Oades and Waters 1991). The addition of organic matter from the roots of growing ryegrass plants may have contributed to the maintaining the stability of aggregates, preventing dispersion and thereby reducing DOC and DON leaching. Carbon dioxide is continually produced by roots and other soil biota which reacts with water forming a weak acid, H_2CO_3, which dissociates readily at high pH (Nelson and Oades 1998). The acidity neutralizes sodium carbonates and dissolves precipitated $CaCO_3$. In addition to enhancing aggregate stability the ryegrass plants may have also taken up a portion of the smaller DON molecules (e.g. Jones et al. 2005). Alternatively the root may have created preferential flow paths that allowed irrigation water to bypass soil, reducing solution residence time and thereby reducing the leaching of carbon and nutrients.

Nitrate losses to leachate are typically much less from soils with a cover crop relative to soils left fallow (e.g. Beckwith et al. 1998). Nitrate is also considered a conservative ion that does not adsorp to soil exchange sites (Nodvin et al. 1986). Soil cover in this study had a very different effect on nitrate leaching compared to the other N species. Nitrate leaching was lowest under the mulch treatment compared to either the bare soil or the ryegrass treatment. Nitrate leaching under ryegrass would have been expected to decrease due to plant uptake, yet it was found to be no different from bare soil. This may be due to the N uptake preferences of ryegrass which has been shown to take up both nitrate and ammonium in equal proportions until the lesser is exhausted (Bailey 1998). In this study, ammonium was found in much lesser concentrations and ryegrass decreased the amount of ammonium released by leaching suggesting an N preference for ammonium. The amount of nitrate taken up by ryegrass may well have been undetectable compared to the overall concentrations. Several mechanisms may have been responsible for the decrease in nitrate leached under mulch. One, the very low N coupled with high C rendered little N available for ammonification and heterotrophic microbial uptake of C and even though the C was high it may not have been in a bioavailable form. Another potential mechanism is that the mulch cover may have decreased the evaporation of water and oxygen diffusion from the soil surface and maintained a higher water content resulting in anaerobic conditions which may have led to denitrification losses of nitrate, or alternatively dampened the conversion of ammonium to nitrate through nitrification; however, no corresponding build up of NH_4-N was observed to support this theory and since all treatments were irrigated daily and kept at room temperature it is assumed that there was minimal evaporation from any of the treatments.

Impacts of Irrigation Water Chemistry in Urban Soils

The effects of sodic irrigation water on the leaching of carbon, nitrogen, and phosphorus observed in the laboratory experiments of this study were also observed in the soils collected from cities across Texas. SAR_{iw}, total soil nitrogen, and ALK_{iw} were the best predictors of water extractable soil DOC and DON. It is important to note that neither the concentration of sodium or calcium in irrigation water were related to the DOC and DON solubility through water extraction, but the relationship between the monovalent and divalent cations, as measured by SAR or $\%Na^{+}_{iw}$, was a better predictor. Green et al. (2009) measured DOC and DON losses in de-icing salt affected soils and evaluated them based on the soil sodium concentration rather than the SAR, which led to somewhat contradictory results between sodium concentrations and DOC leaching. My study suggests that SAR will give a more accurate prediction of the DOC and DON solubility and potential movement than sodium or calcium alone.

When the data set was broken into two groups: SAR ≥ 5 and SAR < 5, it was observed that total soil nitrogen was the best predictor of water extractable DOC when SAR < 5. The opposite was found for soils with irrigation water SAR ≥ 5 where soil nitrogen was not a good predictor of WEDOC. This breaking point at SAR 5 likely represents a shift from one set of mechanisms controlling DOC release to another. While the Soil Science Society of America (SSSA) defines a sodic soil based on saturated paste extract SAR of 13 and the USDA based on ESP of 15% (Glossary of Soil Science Terms 1979; USSL Staff 1954), the Australians define a sodic soil at an ESP of 6% (Rengasamy and Olsson 1991); thereby recognizing the effects of sodicity at much lower ESP values. Similar to the Australian studies, the results of my studies indicate that the impacts of sodic irrigation water on carbon and nutrient solubility begin much lower than SAR = 13. Based on the SSSA definition of soil sodicity, only two of the soils sampled across the state of Texas would be classified as sodic whereas six of the sampled soils would be classified as sodic under the Australian system.

The SAR/EC parameter was a significant predictor of water extractable PO_4-P and NH_4-N from soil. The ratio was constructed based on the theory that it would give a more accurate indicator of the two main mechanisms controlling soil dispersion, sodicity and ionic strength, and the inverse relationship between them. As SAR or the related exchangeable sodium percentage (ESP) of soil increases and the ionic strength of soil solution decreases there is an increase in soil dispersion. Curtin et al. (1992) established that leaching solution SAR had no effect on P concentrations in the leachate when EC = 10 dS m^{-1} or greater; however leachate solution values of less than 10 SAR did impact P leaching. The adsorption and desorption of P is the most susceptible to mechanisms that are affected by increases in ESP. Barrow (1985) suggested that increase in sodium decreases the electrostatic potential of the soil mineral surfaces causing those surfaces to become more negative and less attractive to P ions. It is plausible that this effect is increased under low EC which may explain why the ratio of SAR/EC was the best predictor of extractable PO_4-P rather than SAR or EC independently. In addition, calcium phosphate precipitation and dissolution may control the solubility of P; however, it is unlikely under field conditions that concentrations will be low enough to induce dissolution of calcium phosphate (Sharpley et al. 1988; Nelson and Oades 1998).

The ratio of SAR/EC was also the best predictor of water extractable ammonium NH_4-N. Several studies have documented the buildup and loss of ammonium through leaching and ammonia volatilization under alkaline conditions (Gutpa and Abrol 1990;

Rao and Batra 1983; Rao and Ghai 1986; Rao 1987). Waterlogging can decrease the oxygen availability necessary for conversion of ammonium to nitrate via nitrification resulting in a buildup of ammonium in the soil solution (Laura 1976; McCormick and Wolf 1980). In addition, ammonium ions may be displaced from exchange sites by Na^+ (Duckworth and Cresser 1990). Thus, the SAR/EC may be the best indicator of dispersion and the resulting limitation of oxygen.

The nitrate results generated by this study contradict the findings by Green et al. (2008) who documented large amounts of nitrate in response to ammonium additions to an acidic soil exposed to road salt runoff. They suggested that road salt exposure may release large pulses of nitrate to watersheds. Nitrate in the urban soils of Texas, which were neutral to alkaline, had no relationship with the sodicity of the irrigation water and were best related to the total soil nitrogen and soil carbon. Though DOC, phosphate, and nitrate are all negatively charged, of the three, nitrate has the least potential to be adsorped by soil (Nodvin et al. 1986). Because sodicity impacts solubility by changing the adsorption mechanisms of soils (Barrow 1985), sodic soils have little impact on already very soluble nitrate.

Environmental Implications

The relationship between water extractable carbon and nutrients and the quality of irrigation water has significant implications for the loss of C, N and P to surface and ground waters. The increase in solubility and release due to irrigation water quality documented in both the laboratory and urban field studies indicated that soil sodicity may be a potential non-point source of carbon and nutrients to urban surface waters. There are many factors which may impact the contribution of carbon and nutrients from sodic irrigation other than irrigation chemistry. These include: the total area irrigated in a watershed, the presence of impeding layers causing subsurface lateral flow, and the irrigation rates in terms of intensity and frequency. The strong correlation between DOC and SAR in urban streams reported by Aitkenhead-Peterson et al. (2009) coupled with the findings in my study confirms that leaching of soil carbon with sodic irrigation water can impact the surface water chemistry.

The highest SAR values in municipal waters were found in Central Texas and were sourced from groundwater. The sodium and bicarbonate in the groundwater is naturally occurring in the Coastal Plain Sediments as a result of the weathering of albite to kaolinite or montmorillonite (Bui et al. 1998). Fortunately, while high sodium municipal water supplies do occur throughout the nation, they do not currently represent the majority of municipal water. That being said, the increase in sodium is one of the most common impacts on surface water chemistry in both northern and southern cities due to deicing salts, wastewater treatment effluent, and other non-point sources (Kaushal et al. 2005; Fitzpatrick et al. 2007; Mullaney et al. 2009, Steele and Aitkenhead-Peterson 2011). Users downstream of urbanized watersheds are likely to have higher concentrations of sodium and higher SAR values in their water supplies if their municipal source water is surface water. While the rise in salt concentrations in urban freshwaters has been well documented, there is currently little research on freshwater SAR values and how they change due to urbanization (Aitkenhead-Peterson et al. 2009).

In addition, alternative water sources being developed to supplement water supply for urban irrigation such as wastewater treatment effluent, industrial return water, and more saline water have the potential to contain more sodium than the original municipal water supply. Because the increase in nutrient solubility appears to begin at lower irrigation water SAR levels, I suggest that when evaluating alternative sources for irrigation use, a SAR value of less than five should be used as a guide to limit the risk of increasing solubility and loss of nutrients from soil to surface waters. The core leaching experiment indicated that acidification of alkaline tap waters may also help prevent the loss of soil carbon and nutrients. My results indicate that sodicity has a significant impact on the non-point sources of carbon and nutrients and more research is necessary in a broader range of climates in the nation.

Conclusions

Results from both the laboratory leaching study indicate there is increased risk of leaching of carbon and nutrients due to irrigation water with high sodium. Water solubility of DOC, DON, nitrate, ammonium and phosphorus in urban soils across the state of Texas with a range of uses and management were related to the sodicity of irrigation water. These findings indicated irrigation water quality may have a significant impact on the cycling and losses of carbon and nutrient to surface waters and further may result in losses of carbon sequestered in urban soils from prior land use.

CHAPTER III

IMPACTS OF SALINITY AND SODICITY ON THE LEACHING OF DISSOLVED ORGANIC CARBON AND NITROGEN FROM URBAN VEGETATION

Introduction

Increases in riverine dissolved organic carbon (DOC) in the northern hemisphere since the early 1990's and observed increased sodium in streams are currently important topics in surface water chemistry (Daley et al. 2009; Driscoll et al. 2003; Kaushal et al. 2005; Monteith et al. 2007). A few of studies have linked these two phenomena and suggested that increases in salt exposure is conducive to the leaching organic matter from soils thus contributing to DOC concentrations in surface waters (Aitkenhead-Peterson et al. 2009; Green et al. 2009; Skene and Oades 1995). There has not, however, been any study examining the effects of sodium and dissolved salts on the leaching of organic carbon or nitrogen from leaf litter, a large contributor to allochthonous DOC in surface waters. Surface water sodicity and salinity across the globe is naturally variable due to geologic factors. In addition, human activities commonly increase the sodium concentrations in freshwaters, attributed to: the use of road salts applied to roads to melt ice and keep roads clear (Kaushal et al. 2005; Mullaney et al. 2009; Novotny et al. 2009) and to sodic irrigation water (Aitkenhead-Peterson et al. 2011a). More recently, Steele and Aitkenhead-Peterson (2011) reported that exports of sodium and chloride in the upper Trinity River basin, a sub-tropical ecosystem with little road salt use, were similar to those reported in northern cities. They suggested that perhaps northern researchers should examine other sources of sodium loading to their watersheds; particularly because between 47% and 67% of the sodium loading in the upper Trinity basin was from waste water effluent.

The impacts of increased sodium on DOC cycling at the watershed scale are poorly understood. Skene and Oades (1995) and Aitkenhead-Peterson et al. (2009) recognized a link between increased streamwater DOC concentrations and increased sodium adsorption ratio (SAR) in the Mt. Lofty Ranges in Australia and in turfgrass irrigated with high sodium bicarbonate water in sub-tropical urban watersheds in USA. Green et al. (2009) also observed the DOC-sodium link and suggested that splash and drainage from winter salted roads in northern England's Lake District solubilized soil C releasing it into surface water as DOC.

Typically, allochthonous sources of DOC and DON include precipitation, throughfall, stemflow, leaf litter, root exudates and decay and contributions from organic and mineral soil layers (Aitkenhead-Peterson et al. 2003). These allochthonous sources of DOC and DON usually have a strong linear relationship and are tightly coupled because they are both derived from the same organic pool (Aitkenhead-Peterson et al. 2003); though decoupling of the two has been observed with no consensus as to why (McDowell 2003). Water from precipitation moving through the terrestrial ecosystem increases in DOC as it passes through the vegetated canopy as throughfall and through the organic matter rich horizon of soils (e.g. Aitkenhead-Peterson et al. 2003). McDowell and Likens (1988) reported that throughfall contributed 47 kg DOC ha^{-1} yr^{-1}

in the Hubbard Brook Valley in New Hampshire, USA. Of the allochthonous DOC sources in urban watersheds, leaf litter is important as it represents an energy source for microbial communities in aquatic ecosystems (Fisher and Likens 1973; Suberkropp and Klug 1976; Cummins and Klug 1979; Meyer et al. 1998) and is a major contributor to the development of organic matter which also provides a substrate for soil microbes (e.g. McDowell et al. 2006).

Abscessed leaf litter is also a significant contributor to leached DOC from the forest floor and soil. For example, within 24 hours of submersion, up to 30% of an abscessed leaf's dry weight can be lost (Petersen and Cummin 1974; McDowell and Fisher 1976). Qualls et al. (1991) examined DOC losses in water extracts of freshly fallen litter and reported releases of 27% of the carbon. The fates of the large quantities of DOC leached from leaf litter and organic horizons include adsorption by soil minerals as solution infiltrates through soil horizons (Cronan 1990; Qualls et al. 1991; Kaiser and Zech 1998), mineralization by the soil microbial community (McDowell et al. 2006) , infiltration through soil horizons to the ground water or runoff as throughflow or Hortonion overland flow contributing to aquatic DOC.

Leaf litter also contributes to aquatic particulate organic carbon (POC) when leaf litter and other organic debris are transported to the stream channel as particulate matter. Once particulate matter reaches the aquatic system, DOC is released through leaching and microbial decomposition (Meyer 1990; Meyer et al. 1998). Meyer et al. (1998) estimated that 30% of daily DOC export was generated by leaf litter stored in-stream in an Appalachian forested headwater stream in North Carolina.

The majority of research on the contribution of leaf litter to aquatic DOC has been conducted on small headwater streams in north-eastern mixed forest watersheds (e.g McDowell and Fisher 1976); however, the source of DOC in urban watersheds and the role of leaf litter and cut vegetation such as turfgrass is less understood. Non-point sources of organic carbon in urban watersheds are often related to the amount of remaining vegetation within cities (Chang and Carlson 2005; Hook and Yeakley 2005) or to created urban open areas such as neighborhood gardens and city parks (Aitkenhead-Peterson et al. 2009). Positive relationships between DOC concentration and the percentage of remaining forested cover within urban areas have suggested that leaf litter may contribute to DOC concentrations in urban streams (Chang and Carlson 2005). During storm events, Hook and Yeakley (2005) found that 70-74% of DOC export was contributed by remnant riparian areas. However, when comparing two forested and four urban catchments near Atlanta, Georgia, Paul (1999) reported that the average organic matter stocks were significantly lower in urban streams, and that this was due to scouring of the highly mobile sandy substrates in urban channels as a result of more severe high flow events.

In an urban to rural gradient in south-central Texas, DOC concentrations were not related to remaining forest, but were more closely associated with urban open areas such as golf courses, sports parks and neighborhood lawns (Aitkenhead-Peterson et al. 2009). Turfgrass is an important component in urban landscaping. Senesced and cut turf grass vegetation can be blown into storm drains or road gutters and transported to streams by storm water and contribute to the particulate carbon and DOC directly or

DOC can reach streams via leaching from turf grass during runoff from irrigation or high intensity storms.

A positive relationship between leaf decay and nutrient content and nutrient additions has been well established (Kaushik and Hynes 1971). The classic conceptual model of litter decomposition has all water soluble materials leaching very quickly and the remaining decomposition controlled by microbial processes (Kalbitz et al. 2000) with no consideration given to the chemical environment in which leaching occurs. Despite this, leaf litter stored in rivers and streams are subjected to a wide range of aquatic chemistries both temporally and spatially. No known study to date has investigated the impact of water sodicity and salinity on the leaching of DOC from senesced vegetation in aquatic environments. Based on the affects of salinity and sodicity on soil and live plant material it may also impact the dissolution of DOC in senesced plant material. A larger portion of vegetation exposed to more saline or sodic irrigation water in urbanized watersheds may shift the carbon and nitrogen fractions from the particulate to the dissolved phase and contribute more DOC per gram of dry vegetation than DOC leached from vegetation in less saline headwater streams. The objective of this study was to investigate the impact of salinity and sodicity on the leaching rates of dissolved organic carbon and dissolved organic nitrogen from five types of urban vegetation found in south-central Texas, USA.

Materials and Methods

Five types of urban vegetation common to south-central Texas were examined in this leaching experiment: abscessed live oak (*Quercus fusiformis*) leaves, abscessed leaves from mixed shrub and woody riparian vegetation, annual ryegrass (*Lolium multiflorum* Lam.) clippings, St. Augustine (*Stenotaphrum secundatum (*Walter) Kuntze) clippings and commercial wood mulch (Natural Earth Hardwood Mulch,). Live oak leaves were collected from a recreational park in College Station, TX. Mixed shrub and woody leaves were collected from the riparian zone of an urban stream in College Station, TX; species included Winged Elm (*Ulmus alata*), Pecan (*Carya illinoensis*) and American Beech (*Fagus grandifolia*). Live oak leaves and riparian litter were collected during the spring of 2010 at the end of the ryegrass growing season. Annual ryegrass was cut from a lawn on the Texas A&M University campus. St. Augustine was cut from a homeowner lawn in Bryan, TX in late summer at the end of its growing season. Grass clipping were approximately three inches in length when cut and both turfgrass sites were irrigated with municipal water. All vegetation types were collected, air dried in a thin layer at room temperature and stored in the dark until analysis.

Vegetation was soaked in three sets of salt solutions. 1) Thirty extraction solutions were created by mixing series of NaCl-$CaCl_2$ solutions with sodium adsorption ratio (SAR) values of 2, 10, or 30 and electrical conductivity (EC) values of 0.1, 0.3, 0.7, 1.0, 2.0, or 3.0 dS m^{-1}. The range of SAR and EC was based on reported salinities and SAR values of streams impacted by salts (Aitkenhead-Peterson et al. 2009; Kaushal et al. 2005). 2) Six solutions of $NaHCO_3$-$CaCl_2$ solution with SAR = 30 and increasing EC values of 0.1, 0.3, 0.7, 1.0, 2.0, or 3.0 dS m^{-1} to compare the effect of sodium bicarbonate to sodium chloride at high SAR levels. 3) To test impact of SAR of stream water on the release of DOC and DON live oak and riparian litters were soaked in stream water from four watersheds in Bryan and College Station, TX with a range of sodium concentrations and salinity (Table 3.1) as well as de-ionized, distilled water (DDW) typically used in extraction experiments. Only live oak and riparian leaf litters were chosen because they are most likely to come into contact with stream water by falling or being blown into streams and rivers. All 41 solutions were replicated three times for each vegetation type used in the extraction.

Table 3.1 The electrical conductivity (EC), sodium adsorption ratio (SAR), alkalinity, and pH of stream water from four watersheds in Bryan and College Station, TX. The percentage of urban land cover of each watershed is from the 2001 Nation Land Cover Dataset (NLCD).

Solution	2001 Urban (%)	EC (dS m^{-1})	SAR	pH	Alkalinity (mg L^{-1})
Wolf Pen Creek	100.0	1.406	19.2	8.64	488
Carters Creek	67.4	0.977	17.5	8.35	229
Hudson Creek	30.7	0.840	19.3	8.65	254
Wickson Creek	6.3	0.645	4.7	8.31	189

The following procedure was used for all solution extractions. Leaves and grass clippings were combined with at a 1:20 ratio of vegetation to solution for 24 hours at laboratory temperature. The extraction period was chosen because of the large amounts of carbon that can be released within a short period of time (Petersen and Cummin 1974; McDowell and Fisher 1976; Qualls et al. 1991) and because microbial breakdown has been found to be non-significant when extraction periods are 24 hrs or less (Nykvist 1959). Because of the short extraction period time, no antimicrobial agent was used. Leaves and mulch were extracted whole; 1.75 ± 0.1 g of whole vegetation was combined with 35 ml of extracting solution in 40 ml centrifuge tubes and capped. Tubes were inverted four times over a 24 hour period for mixing. After a 24 hour leaching period, leachate solutions were strained from the mixture. Electrical conductivity and pH were determined immediately on unfiltered aliquots of the extraction and the remainder of the sample was syringe filtered through ashed (400° C for 5 hours) Whatman GF/F filters (0.7 μm nominal pore size). All vegetation types, except the mulch, were diluted 10:1 with distilled water. A 3:1 dilution was used for mulch due to the much lower DOC concentrations in solution (assessed by solution color). Samples were stored in acid washed, ultra-pure water rinsed (Barnstead Nanopure Diamond water filtration) HDPE bottles and analyzed immediately or refrigerated until analysis within 24 hours.

Dissolved organic carbon and DON were quantified in the vegetation extracts, stream water and the municipal tap water used for extraction. Dissolved organic carbon was measured as non-purgeable organic carbon, and total nitrogen was quantified using high temperature Pt-catalyzed combustion with a Shimadzu TOC-V_{CSH} and total measuring unit TNM-1; following USEPA method 415.1 which acidifies the sample and sparges for 4 min with C-free air. Sample replicates, blanks, National Institute of Standards and Technology traceable and check standards were run every 12th sample to monitor instrument precision (coefficient of variance (CV) < 2%) and accuracy (CV < 5%). Ammonium was analyzed using the phenate hypochlorite method with sodium nitroprusside enhancement (USEPA method 350.1). Nitrate was analyzed using Cd-Cu reduction method (USEPA method 353.3). All colorimetric methods were performed with a Westco Scientific Smartchem Discrete Analyzer (Westco Scientific Instruments Inc. Brookfield CT, USA). Ca^{2+}, Mg^{2+}, and Na^{+} were measured in municipal tap and stream waters by filtering aliquots of the original solution through 0.2 µm Pall filters prior to quantification by ion chromatography using a DIONEX ICS 1000 with Ionpac CS16 analytical and Ionpac CG16 guard column for separation and 20 mM methanosulfonic acid as eluent at a flow rate of 1 mL min^{-1} and injection volume of 10 µL (DIONEX Corp. Sunnyvale, CA, USA). Dissolved organic nitrogen is the product of TDN – (NH_4-N + NO_3-N). Sample replicates, blanks, NIST traceable and check standards were run every 10th sample to monitor instrument precision (coefficient of variance (CV) < 2%) and accuracy (CV < 5%). The Dumas method for total carbon and nitrogen analysis of the leaves was performed at the Texas A&M AgriLife Environmental Quality Center, in Vernon, Texas, USA using a Vario Max Elementar C/N Combustion Analyzer.

Data Analysis

To normalize DOC and DON the mass loss of DOC and DON per gram of vegetation was calculated from the concentration data. The sodium adsorption ratio in stream waters was determined using Eq. 3.1 using concentrations in the form of mmol(+) L^{-1},

$$\text{Eq. 3.1} \qquad SAR = [Na^{+}] / (([Ca^{2+}] + [Mg^{2+}])/2)^{0.5}.$$

To calculate the release of DOC from vegetation extracted with stream water (Extraction 3), the measured mass of DOC in the stream water was subtracted from the final mass.

SPSS v.16 was used for all statistical analyzes. Data from the NaCl extraction were analyzed using univariate analysis of variance (ANOVA) to determine main effects of SAR, and EC on DOC and DON for each vegetation type. A least significant difference (LSD) mean comparison analysis was performed after to compare differences in treatments. To determine the effect of HCO_3^- on leaching, data from the $NaHCO_3$ extraction were compared to the NaCl data for SAR = 30 by ANOVA with two levels, salt type and EC for each vegetation type. For extraction three, an ANOVA with LSD mean comparison analysis was used to determine differences between DOC and DON released by each stream water and DDW. No interactions were found between vegetation and stream water and therefore the two vegetation types were combined in a correlation between analysis mean DOC release from the stream water solutions (extraction 3) and the initial SAR of the stream water. The impact of vegetation type on the final pH and conductivity of the solution post-extraction was determined using ANOVA with LSD post hoc analysis. Correlation analysis was also used to analyze the coupling of DOC and DON in the NaCl extraction series.

Results

Solution pH and EC

Final pH (pH_F) of extraction solutions ranged from 4.70 to 5.61 in NaCl solutions and 5.69 to 7.17 in $NaHCO_3^-$ solutions. The pH_F was lower than in the initial extraction solutions for all vegetation types and vegetation type had a significant effect on pH_F (Table 3.2). Mulch had the least impact on pH_F, while live oak decreased pH_F the most. pH_F of the $NaHCO_3$ extractions where higher due to the neutralization of acidity by bicarbonate and ranged from 5.69 to 7.1. The final EC (EC_F) was also significantly higher than in the initial extract solutions for all vegetation types. Both St. Augustine (5.73 dS m^{-1}) and ryegrass (4.18 dS m^{-1}) released two to three times more solutes compared to the senesced leaf litter, live oak (1.42 dS m^{-1}) and riparian litter (1.72 dS m^{-1}), and four times as the mulch (1.18 dS m^{-1}). A similar EC_F pattern was observed in the $NaHCO_3$ extraction series. The pH of $NaHCO_3$ extractions where higher due to the neutralization of acidity by bicarbonate and ranged from 5.7 to 7.1.

Table 3.2 The mean initial pH and conductivity of NaCl and $NaHCO_3$ extraction solutions and after 24 hours for each vegetation type. Letters represent significant differences ($\alpha<0.05$) between vegetation types.

	NaCl (SAR 2 to 30)		$NaHCO_3$ (SAR = 30)	
	pH	EC (dS m^{-1})	pH	EC (dS m^{-1})
Initial solution	6.19	1.01	9.02	1.01
Final solution				
St. Augustine	5.31^b	4.18^b	6.31^a	4.24^a
Ryegrass	5.25^b	5.73^a	5.69^b	3.91^a
Live Oak	4.70^c	1.42^d	6.08^{ab}	1.18^{bc}
Riparian	5.61^a	1.72^c	6.41^a	1.57^b
Mulch	5.25^b	1.18^d	7.17^c	1.03^c

Impacts of SAR and Salinity on DOC and DON

Overall, SAR had a significant effect on the amount of dissolved organic carbon released from vegetation within 24 hours, while the effect of salinity on DOC released was minimal. For woody plant leaves and mulch, elevated SAR significantly increased the amount of dissolved organic carbon leached; between SAR =2 and SAR = 30 the mass of DOC leached increased 64% for live oak leaves, 47% for riparian litter, and 37% for hardwood mulch (Table 3.3). The percentage of total carbon leached in 24 hours from vegetation increased with SAR: live oak 2.4 to 4.0%, riparian litter 2.7 to 3.7%, and mulch 0.56 to 0.77% of the total carbon contained in vegetation between SAR 2 and 30 (Table 3.4). The LSD mean comparison analysis, however, showed that there was no significant difference in the mass of DOC leached between SAR = 2 and SAR = 10 for riparian litter and mulch; but the mass of DOC leached when SAR = 30 was significantly increased compared to both SAR = 2 and 10 (Figure 3.1). Significant differences between the amounts of DOC released at all three SAR values were found in live oak leaves (Figure 3.1). Total salinity, measured as EC from 0.1 dS m^{-1} to 3 dS m^{-1}, did not impact the mass of DOC leached from woody vegetation at any level of sodicity.

Similar results were found for the mass of DOC leached from grass clippings. Compared to the woody vegetation species, the percentage of total carbon leached in 24 hours was overall greater for St. Augustine (3.6 to 8.0%) and ryegrass (13.2 to 16.9%) (Table 3.4). The grasses also had lower C:N ratios than the woody vegetation. A significant interaction was found between SAR and EC for both St. Augustine and ryegrass (Table 3.2; Figure 3.2). In both grass types, at SAR = 2, DOC release increased as salinity (EC) increased; however at SAR = 10 and 30, as EC increased the mass of DOC released decreased (Figure 3.2). This pattern was variable over the EC range and was more strongly pronounced for St. Augustine than for ryegrass. For all values of

Table 3.3 Results for main effects of sodium adsorption ratio (SAR) and electrical conductivity (EC) and interactions for dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) release for five types of vegetation: St. Augustine, ryegrass, live oak, riparian litter, and hardwood mulch. Asterisk (*) indicates results are significant at α= 0.05. For each vegetation type measured percentage of dry weight (%DW) carbon and nitrogen.

		DOC		DON	
Vegetation		F value	p value	F value	p value
St. Augustine	SAR	246.5	<0.001*	59.9	<0.001*
	EC	5.28	0.001*	2.16	0.076
	SAR*EC	2.39	0.027*	1.32	0.257
Ryegrass	SAR	35.1	<0.001*	4.63	0.016*
	EC	5.83	<0.001*	2.59	0.042*
	SAR*EC	6.96	<0.001*	6.25	<0.001*
Live Oak	SAR	33.7	<0.001*	16.7	<0.001*
	EC	1.83	0.131	0.879	0.505
	SAR*EC	0.560	0.835	0.827	0.606
Riparian Litter	SAR	37.8	<0.001*	25.2	<0.001*
	EC	2.35	0.06	4.26	0.004*
	SAR*EC	0.830	0.603	3.71	0.002*
Mulch	SAR	5.37	0.009*	2.43	0.102
	EC	0.134	0.983	0.495	0.778
	SAR*EC	0.243	0.989	0.260	0.986

Table 3.4 The dry weight (DW) percentage of carbon and nitrogen and C:N ratio of the five vegetation types. The calculated mean percentage of carbon and total dissolved nitrogen lost during a 24 period at SAR = 2, 10, and 30 (standard deviation) from vegetation.

				Percentage lost in 24 hours		
Vegetation	C:N		% DW	SAR 2	SAR 10	SAR 30
St. Augustine	23.6	C	41.3	3.6(0.5)	5.8(0.6)	8.0(0.8)
		N	1.75	14.3(3.2)	20.4(1.6)	25.9(3.4)
Ryegrass	11.2	C	40.3	13.2(0.8)	13.4(0.4)	16.9(0.9)
		N	3.59	35.6(4.2)	36.4(1.6)	37.6(3.3)
Live Oak	42.5	C	43.8	2.4(0.3)	3.2(0.4)	4.0(0.2)
		N	1.03	2.9(0.5)	3.1(0.7)	4.2(0.4)
Riparian Litter	24.4	C	41.5	2.7(0.2)	2.6(0.3)	3.7(0.4)
		N	1.70	5.5(0.5)	4.9(0.5)	5.6(0.9)
Mulch	99.0	C	22.8	0.56(0.05)	0.63(0.04)	0.77(0.05)
		N	0.23	1.8(0.3)	2.5(0.5)	4.8(4.3)

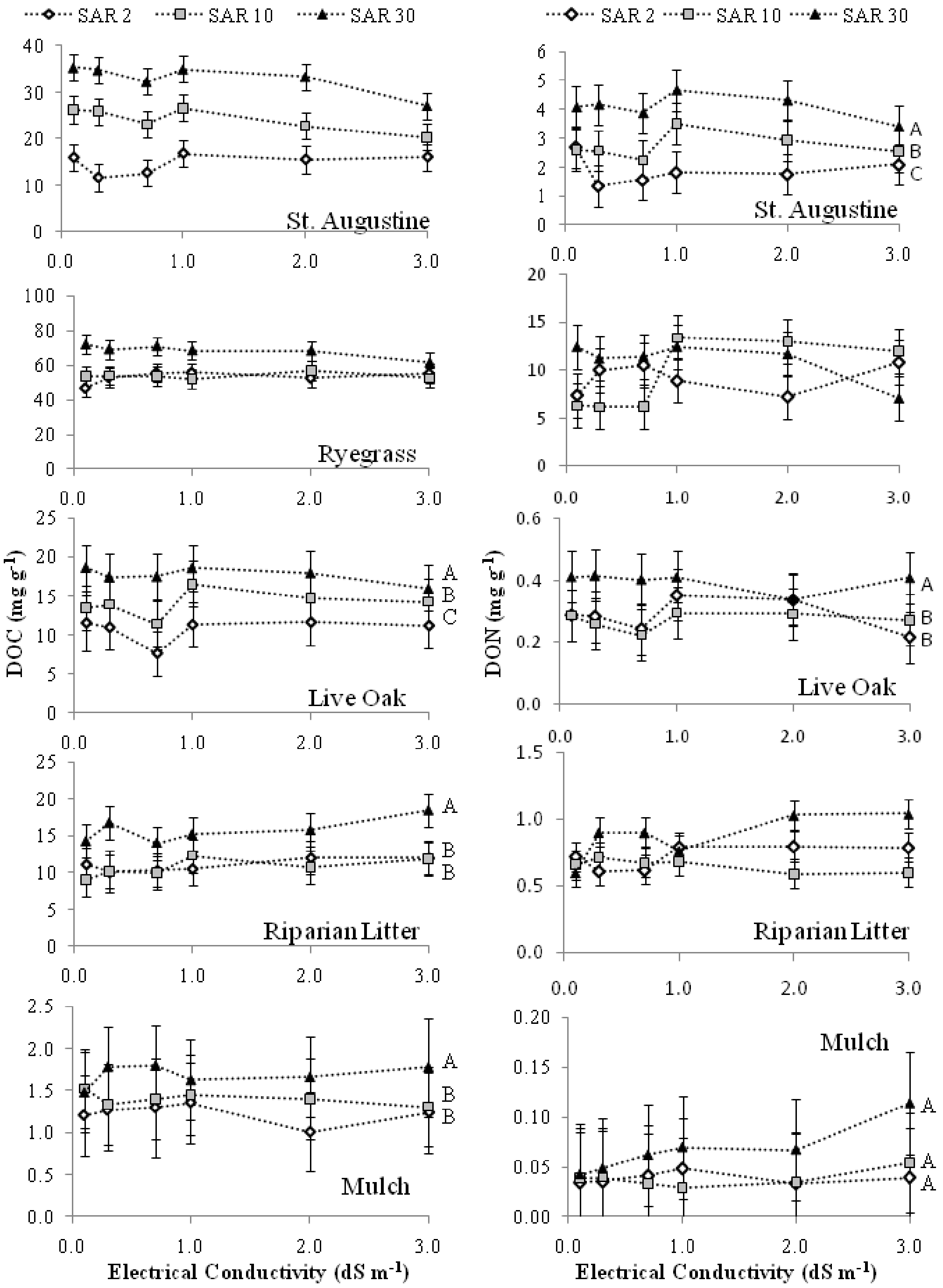

Figure 3.1 Dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) leached from five types of vegetation in NaCl solutions with sodium adsorption ratios (SAR) = 2, 10, and 30 and electrical conductivity = 0.1, 0.3, 0.7, 1.0, 2.0, and 3.0 dS m^{-1} in 24 hours. Letters represent significant differences in DOC and DON leaching between SAR 2, 10, and 30 at $\alpha<0.05$. Bars represent the least significant difference (LSD). Note different values on y-axis.

EC, the mass of DOC released from St. Augustine increased incrementally for each SAR value; however, for ryegrass only at SAR = 30 was the mass of DOC increased relative to SAR = 2 and 10.

The percentage of total nitrogen leached from vegetation over 24 hours was variable in each species: St. Augustine 14.3 to 25.9%, ryegrass 35.6 to 37.6%, live oak 2.9 to 4.2%, riparian litter 4.9 to 5.6%, and mulch 1.8 to 4.8% of total vegetation nitrogen (Table 3.4). Salinity and sodicity had similar general impacts on DON but with some key differences. Neither SAR nor EC had an effect on the mass of DON released from mulch. Significant differences were found due to the solution SAR, but not EC for St. Augustine and live oak leaves (Table 3.2). For St. Augustine, where SAR 2 < SAR 10 < SAR 30 there was a 117% increase in the mass of DON released between SAR 2 and 30 (Figure 3.3). For live oak, SAR 2 = SAR 10 < SAR 30 with a 39% increase in the mass of DON released between SAR 2 and 30 (Figure 3.1). Significant interactions were found between SAR and EC in ryegrass and riparian litter (Table 3.2). SAR 30 had elevated DON release compared to SAR 2 and 10 for both ryegrass and riparian litter. While differences were found in DON across the EC gradient there were no clear patterns in either vegetation type (Figure 3.1).

The effect of $NaHCO_3$ relative to NaCl on the mass release of DOC at SAR = 30 depended upon vegetation type. No significant differences were found for either salt type or EC for mulch. DOC mass release decreased with $NaHCO_3$ ($p<0.001$) relative to NaCl and varied with EC ($p<0.001$) for ryegrass. Significant interactions between salt type*EC were found for the other vegetation types (Figure 3.3). Mass of DOC leached

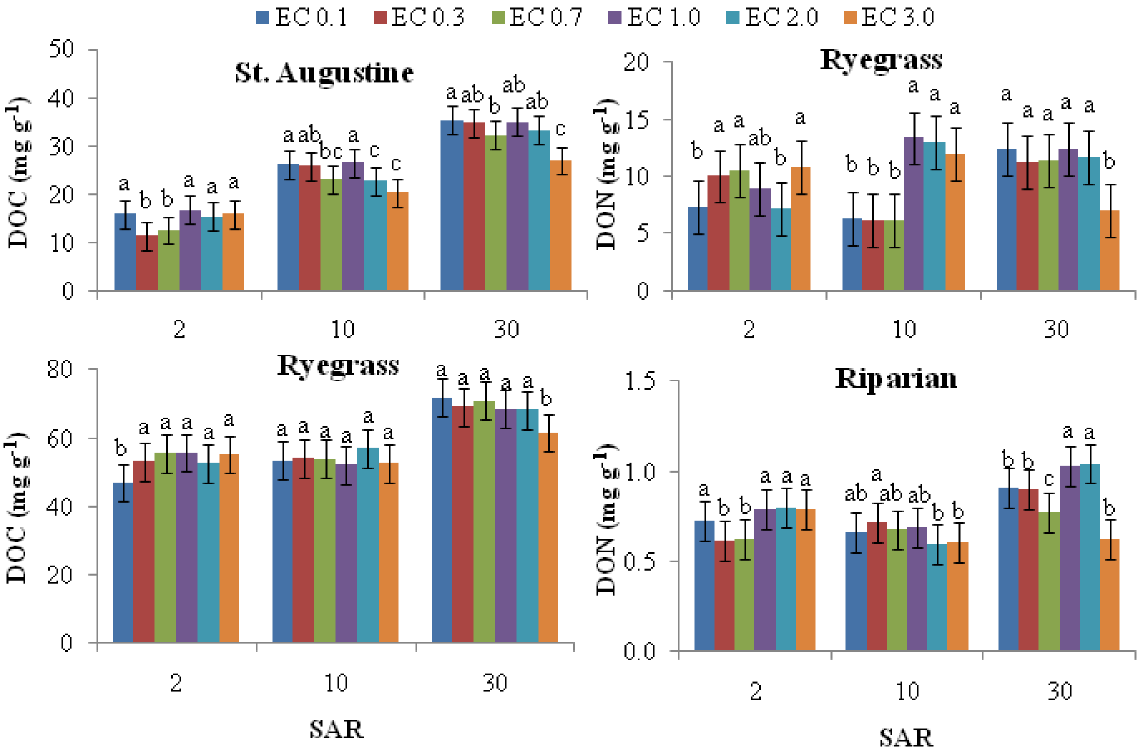

Figure 3.2 Dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) leached from vegetation in NaCl solutions with sodium adsorption ration (SAR) = 2, 10, and 30 and electrical conductivity = 0.1, 0.3, 0.7, 1.0, 2.0, and 3.0 dS m^{-1} in 24 hours. Letters represent significant differences in DOC and DON leaching between solutions with electrical conductivity = 0.1, 0.3, 0.7, 1.0, 2.0, 3.0 dS m^{-1} at $\alpha<0.05$ within SAR levels 2, 10, and 30. Bars represent the least significant difference between means. Note differences in y-axis ranges.

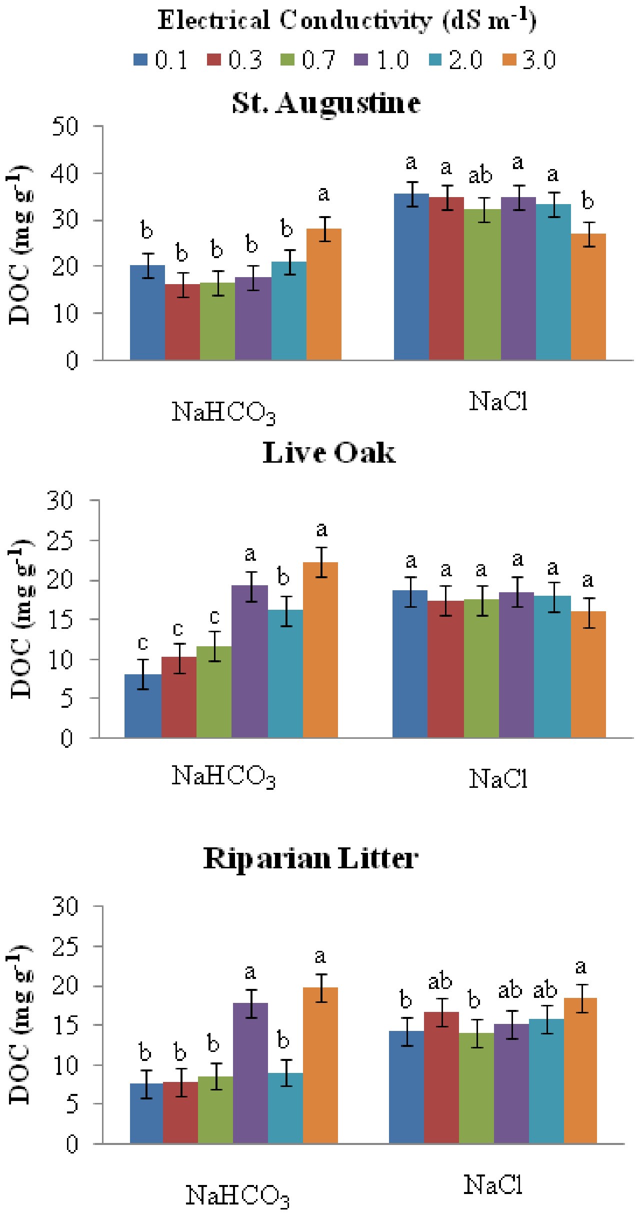

Figure 3.3 Dissolved organic carbon (DOC) leached from vegetation in $NaHCO_3$ and NaCl solutions with sodium adsorption ratio = 30 and Electrical Conductivity = 0.1, 0.3, 0.7, 1.0, 2.0, and 3.0 dS m^{-1} in 24 hours. Letters represent significant differences in DOC and DON leaching between solutions with electrical conductivity (dS m^{-1}) = 0.1, 0.3, 0.7, 1.0, 2.0, 3.0 at $\alpha<0.05$ within salt type. Bars represent the least significant difference between means. Note differences in y-axis ranges.

increased as salinity (EC) increased, but was overall lower than the amount released by NaCl at SAR = 30 for St. Augustine grass, live oak, and riparian leaves (Figure 3.3).

Analysis of r values from a series of 2-tailed Pearson bivariate correlations between DOC and DON revealed a wide variability in the strength of the correlation (Table 3.5). When all the vegetation types were combined (Table 3.5 “All”) a good relationship between DOC and DON leaching was found through all subsets of the data. These correlations were likely driven by the differences between the nutrient content of each vegetation type, for example ryegrass always leached very high concentrations of both DOC and DON compared to mulch or live oak. DOC and DON coupling within each vegetation type varied. The weakest couplings between DOC and DON were found in ryegrass and riparian litter at higher salinities (Table 3.5). For most vegetation types, changes in electrical conductivity affected DOC and DON coupling more at SAR = 10 and 30 than at SAR = 2. Changes in SAR also had an effect on DOC and DON coupling at electrical conductivities > 1.0 dS m^{-1}.

Impact of Stream Water on DOC and DON Leaching

Differences in stream water chemistry had a significant impact on the mass loss of DOC from riparian and live oak leaves compared to leaves leached with DDW (Figure 3.4). While there was a significant difference in the mass of DOC leached between live oak and riparian litter (p = 0.003), no significant interactions were found between stream water and vegetation type therefore the combined means were analyzed. There was a significant correlation between SAR of the stream water and the variation in mass of DOC released from vegetation, with SAR explaining 88% of the variance in DOC mass loss among the streams (Figure 3.4). No significant relationship was found between DON and SAR in stream water.

Table 3.5 Pearson correlation r values between DON and DOC for all data (All) and each vegetation type (St. Augustine, ryegrass, live oak, riparian, mulch). Data are further broken into correlations between DOC and DON for each level of SAR and each level of EC for all data and each vegetation type. Values are from a 20:1 solution:vegetation, 24 h leaching with NaCl. Asterisks indicates correlations are significant at $\alpha<0.05$.

	All	St. Augustine	Ryegrass	Live Oak	Riparian Litter	Mulch
	Pearson Bivariate Corrrelation Coefficent					
All	0.93*	0.93*	0.57*	0.80*	0.61*	0.82*
SAR						
2	0.97*	0.87*	0.78*	0.49*	0.83*	0.78*
10	0.89*	0.49*	0.18	0.73*	-0.08	0.77*
30	0.94*	0.98*	0.73*	0.89*	0.67*	0.84*
EC						
0.1	0.96*	0.76*	0.86*	0.83*	0.89*	0.97*
0.3	0.96*	0.94*	0.77*	0.86*	0.84*	0.59*
0.7	0.96*	0.95*	0.78*	0.73*	0.84*	0.88*
1.0	0.93*	0.99*	0.51	0.50	0.23	0.85*
2.0	0.95*	0.99*	0.62	0.53	0.76*	0.86*
3.0	0.85*	0.97*	0.20	0.89*	0.30	0.65*

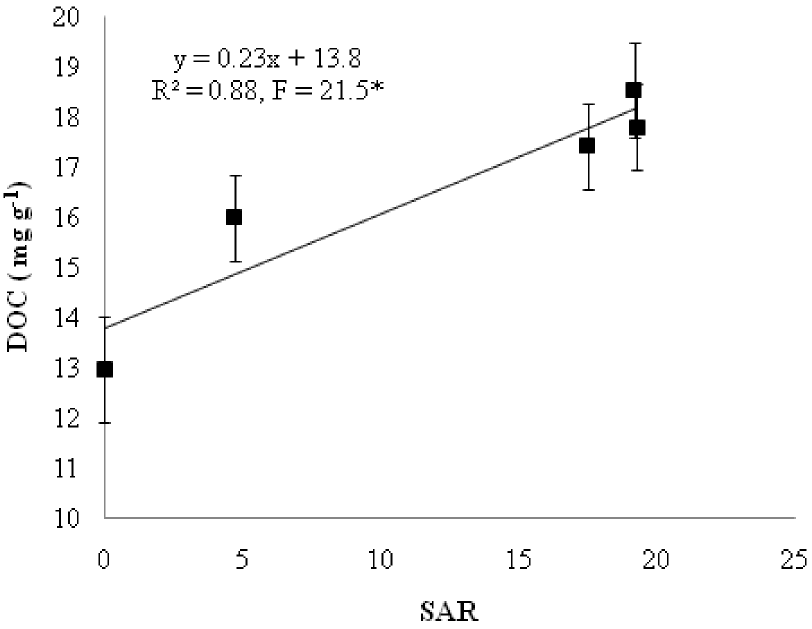

Figure 3.4 Dissolved organic carbon leached from vegetation with distilled water and four stream waters (Carter, Hudson, Wickson, and Wolfpen) and their relationship with stream sodium adsorption ratio (SAR). Asterisks indicate significance at $\alpha<0.05$. Bars represent the least significant difference between means.

Discussion

As the SAR ratio in urban streams increases so does DOC concentration (Aitkenhead-Peterson et al. 2009). Recognizing the nationwide increases in riverine sodium and DOC, this study sought to test the hypothesis that increases in sodic and saline water, either through irrigation, wet or dry deposition, or in-stream chemistry, would leach large volumes of DOC and DON from watershed and in-stream vegetation. This study found similar quantities of carbon were lost from vegetation where between 0.5 and 17% of the carbon in vegetation was leached over 24 hours at SAR values ranging from 2 to 30. There large losses of carbon from vegetation litter upon exposure to water and its contribution to DOC concentration and exports have been reported in numerous studies (e.g. Petersen and Cummin 1974; McDowell and Fisher 1976, Meyer et al. 1998). All of these studies were conducted in, or with respect to, relatively undisturbed northern forests, and to the best of my knowledge, no study has considered the impacts of water sodicity or salinity on leaching of DOC or DON from vegetation in urban ecosystems. Petersen and Cummin (1974) reported 24 hour carbon leaching loss rates of 5 to 27% of dry weight C content when leaf packets were soaked in stream waters in Michigan, USA. McDowell and Fisher (1976) also reported carbon leaching rates of 2 to 25% of total dry weight C, dependent upon species, when leaves were soaked in stream water in New Hampshire, USA. While neither study reported solution sodicity, McDowell and Fisher (1976) reported a stream EC range of 0.064 to 0.126 dS m^{-1}. The high SAR values in my study streams, most of which is likely contributed by sodic irrigation water derived from groundwater wells of the Carrizo Wilcox aquifer (Aitkenhead-Peterson et al. 2011a), increased the mass of DOC released by 13% between SAR values of 5 and 20.

The chemistry of solution to which vegetation is exposed has an effect on the amount of carbon leached. In this study, increases in SAR values had a positive impact on the dissolution of carbon for all vegetation types, whereas changes in total salt content (salinity) of the solution induced some changes, but a pattern of increasing or decreasing carbon was not clear and varied with vegetation type and SAR value. At a SAR of 30, all vegetation types responded to increased sodium concentrations at all levels of conductivity; but DOC leaching only significantly increased at all three values (SAR = 2, 10, and 30) for St. Augustine and live oak. While the exact reason for this is unknown, there are several possible explanations for this pattern. Live oak and St. Augustine leaves were thicker and broke apart less readily compared to the ryegrass and riparian litter. It may be that the more ridged cellular structure, instead of preventing carbon loss, rendered the cellular compartments more likely to burst due to changes in osmotic pressure and thereby lose more carbon at lower sodium concentrations. Another potential reason is that some vegetation is known to leach some Na^+, Ca^{2+}, and Mg^{2+} from the leaves (Nykvist 1959). It may be that ryegrass and riparian litter leached more Ca^{2+} into the extract solution thereby decreasing the SAR from its initial value. However, my data does not support this theory considering the initial concentrations of Na^+ used in the experiment were very large in the high EC treatments compared to the potentially small amount of Ca^{2+} leached from the vegetation and should not therefore substantially impact SAR levels. Ultimately it is unclear why live oak and St Augustine grass were more sensitive to changes in SAR.

The lack of response to changes in total salt content (EC) was unexpected. While no studies have investigated DOC leached from senesced vegetation with respect to SAR and EC, in soil there is a strong relationship between SAR and EC in the development of sodic soil properties (Bodman 1937; Fireman and Bodman 1939; Huberty and Pillsbury 1941; Fireman 1944; Ayers and Westcot 1994). Risk to soil physical and chemical properties are greatest under high SAR and low electrolyte concentrations due to the effect on colloid dispersion. This pattern of increasing DOC loss due to decreasing EC was documented at SAR = 10 and 30 for St. Augustine and SAR = 30 for ryegrass and was not particularly strong (Figure 3.2). At SAR = 2, there was a slight pattern of increasing DOC loss as EC increased (Figure 3.2). Response to changes in EC may also have been muted due to the large amount of total solutes that were released from the vegetation into the solution during the extraction (Table 3.3). The final concentration of solutes (as measured by EC) differed by vegetation type and had increased considerably compared to the initial extraction solution. This increase in concentration may have affected the leaching response to EC. In streams, the ratio of water to the mass of vegetation is considerably more than the 20:1 ratio used in this experiment and therefore EC of the water may have a greater impact when the solutes are diluted.

DOC and DON are often tightly coupled in the natural environment but have become decoupled in some human-dominated ecosystems (McDowell 2003). DOC and DON have been found to be frequently coupled in natural watershed surface water and soils as they are measuring two fractions of the same pool; however, instances of decoupling have been documented (Andersson et al. 1999; Hood et al. 2002; Kaushal and Lewis 2003; Willet et al. 2004; McDowell et al. 2004; Wiegner and Seitzinger 2004). The actual mechanism causing decoupling of DOC and DON is unknown (McDowell 2003). Similar results were found for both DON and DOC mass loss in the NaCl extracts suggesting that NaCl does not cause a decoupling of DOC and DON. In contrast, SAR increased the mass of DON leached from all vegetation types except for the mulch, suggesting that the relative contribution of sodium compared to calcium and magnesium in solution may be responsible for decoupling of DOC and DON. Compared to the other plant materials, the mulch had extremely low concentrations of DON and high variability within the mulch treatments may have made differences difficult to detect. While total salinity did impact the quantity of DON leached from leaf and grass vegetation; there were no clear patterns of increasing or decreasing DON with EC. Perhaps more importantly, DON leachate patterns did not always couple closely with DOC leachate patterns (Table 3.4). Green et al. (2009) reported changing DOC:DON ratios in soil extracts with a range of NaCl concentrations. My data indicated that changes in salinity and sodicity may be another reason for decoupling of DOC and DON in vegetation leachate.

The substitution of bicarbonate (HCO_3^-) for chloride (Cl^-) (i.e. $NaHCO_3$ vs. NaCl) affected the mass loss of DOC from vegetation. At SAR 30, the HCO_3^- mass of DOC lost decreased at most values of EC compared to the mass of DOC lost under the sodium chloride treatment; however, there was a more prominent pattern of increased DOC loss with increasing salinity (Figure 3.4). The final pH of bicarbonate extracts ranged between 5.69 and 7.17, whereas the chloride extracts were more acidic, ranging from 4.70 to 5.61. Humic substances generally become more soluble as pH increases (Kipton et al. 1992). On the contrary I found that the release of carbon decreased with increasing pH in this experiment with sodium chloride extracting more DOC.

Ecological Implications

Stream waters extract a greater volume of DOC from vegetation relative to ultra-pure water. The DOC results from the created extraction solutions were supported when using stream water from local watersheds with a range of sodicity and salinity. Compared to extractions with distilled water all stream waters extracted more DOC and similar amounts of DOC as the prepared extracts with a SAR of 30. The strong correlation between stream water SAR and carbon extracted indicated that for every unit increase in SAR an additional 0.23 mg C g^{-1} of C substrate would be moved into the dissolved fraction from the vegetation. Changes in cation chemistry are common in urban streams (Steele et al. 2010) and have not yet been considered by the biogeochemistry community as a mechanism for changing in-stream organic matter dynamics. For streams with elevated sodium such as those downstream from wastewater treatment plants (e.g. Novotny et al. 2009; Steele and Aitkenhead-Peterson 2011), those receiving deicing salts (e.g. Kaushal et al. 2005), or streams in sub-tropical climates receiving high sodium irrigation runoff (e.g. Aitkenhead-Peterson et al. 2009, 2011a), this may be responsible for greater transfer of carbon as DOC from the particulate organic carbon in streams and substrates to the water column and a depletion of carbon stocks from within benthic organic matter.

The study was designed to examine a small piece of the puzzle, namely the observed increased stream and river sodicity, salinity and DOC; however, the findings were relatively clear-cut and have very broad implications. Increased solution SAR, resulting from irrigation water, road salts or waste water treatment plants, is likely to cause increases in DOC released from watershed and in-stream senescent vegetation contributing to an overall increase in DOC observed in first and second order streams.

Conclusions

Increasing SAR values had a significant impact on the leaching of dissolved organic carbon and dissolved organic nitrogen from abscessed and cut vegetation at both very low (0.1 dS m^{-1}) salinity and very high salinity (3 dS m^{-1}) increasing the amount of carbon leached by 37% to 65% between SAR = 2 to SAR =30. Some changes in the release of DOC and DON due to EC were found; however, and patterns inconsistently varied. The substitution of sodium bicarbonate for sodium chloride caused decreases in the mass of DOC lost by leaching. Stream waters with a range of salinity and sodicity resulted in similar changes in the mass of DOC leached from vegetation. These results indicated that the salinity and sodicity of streams, high sodium irrigation water, road splash and runoff in northern climates, and atmospheric wet deposition may all play an important role in the biogeochemical cycling of C and N. Further work is needed at the watershed scale to test the impact of surface water sodicity and salinity on the contributions of DOC and DON from vegetation on surface water concentrations.

CHAPTER IV

LONG-TERM SODIUM AND CHLORIDE SURFACE WATER EXPORTS FROM THE DALLAS/FORT WORTH REGION*

Introduction

Increasing salinity is one of the many impacts urbanization has on surface water quality. Increased concentrations of chloride, sulfate, calcium, sodium, potassium, and magnesium plus overall electrical conductivity due to urbanization and human activity have been reported in several studies (McConnell 1980; Ometo et al. 2000; Paul and Meyer 2001; Smart et al. 1985; Zampella 1994). Sodium and chloride concentrations and exports have, however, been more closely associated with urban land cover and population density compared to other ions (Fitzpatrick et al. 2007; Peters 1984). Increasing concentrations and yields of sodium and chloride have been associated with both general urbanization parameters and specific human activities. For example, Fitzpatrick et al. (2007) reported that the biogeochemical fingerprint in streams of human impacts were different between agricultural and urban land uses for major cations; where urban land use resulted in greater sodium and potassium and agricultural land use resulted in greater calcium and magnesium concentrations. Negative impacts of elevated sodium and chloride include toxicity to aquatic plants and fish and groundwater

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contamination. Furthermore, when surface water is used as a drinking water source, human health may also be affected by high salt intake leading to hypertension and other problems such as stroke and cardiovascular disease (Forman and Alexander 1998; Howard and Haynes 1993; Strazzullo et al. 2009; Wegner and Yaggi 2001).

The majority of research on surface water salinity has concentrated on the effects of deicing salts (Demers and Sage 1990; Lofgren 2001; Kaushal et al. 2005; Kelly et al. 2008; Mason et al. 1999; Mullaney et al. 2009). Sodium chloride, an inexpensive deicing salt used on paved surfaces in large areas of the northern United States has been identified as a major source of salts to urban watersheds in northern latitudes. In three north-eastern USA cities, Kaushal et al. (2005) reported that the largest increases in chloride concentrations in urban streams occurred during the winter months when deicing salt was being applied. Interestingly stream chloride concentrations did not return to base levels during the summer thereby contributing to a pattern of increasing chloride over several decades. Similarly, thirteen lakes in the Twin Cities metropolitan area of Minnesota, USA had increased sodium and chloride concentrations which were 10 to 25 times higher than those observed in non-urban lakes; this increase was correlated with road salt applications (Novotny et al. 2008). Mullaney et al. (2009) measured chloride concentrations and yields in surface waters of 100 basins in 15 northern states from 1991 to 2004 and found increases in chloride concentrations during the winter and spring months; the estimated annual yields of chloride were greater in urban dominated basins (30.8 Mg km^{-2}) compared to agricultural (5.4 Mg km^{-2}) and forest dominated (2.2 Mg km^{-2}) basins. Multiple regression analysis indicated that the density of major roads, potential evapotranspiration, number of major wastewater discharges and the percentage of overland runoff were significant factors affecting chloride concentrations and loading (Mullaney et al. 2009). From their statistical analysis they attributed high chloride concentrations and yields to deicing salts, wastewater discharges, septic systems, and saline groundwater plumes from landfills and salt storage areas (Mullaney et al. 2009).

While the majority of research on aquatic sodium and chloride has been conducted in colder regions where deicing salts were likely to have a major impact; urbanization has also been reported to impact salinity in warmer watersheds. For example, a study of 56 basins across the United States, Peters (1984) reported that population density was a significant predictor, accounting for 13% of sodium and 20% of chloride loading. This link between population density and chloride is not surprising when one considers that based on the recommended salt intake, the average person releases 1.3 kg yr^{-1} of chloride into their local watershed (Mullaney et al. 2009). Further support for link between sodium and chloride and sewage effluent was found in the urban Chattahoochee River basin, where Rose (2007) attributed increases in sodium and chloride to leaking sewage infrastructure. Besides food, other materials utilized in a watershed can contain and release salts. For example, water softeners from private septic systems have been found to contribute to the salt loading of watersheds (Panno et al. 2006). Chloride is also present in artificial fertilizers (Panno et al. 2006), and supporting this Zobrist and Reichart (2006) estimated a contribution of 8.7 kg km^{-2} yr^{-1}

chloride from extensive agriculture in eleven watersheds in Switzerland. These may all contribute to loads and exports through non-point sources.

The release of effluent from a wastewater treatment plant is a point source in the waste stream. Fitzpatrick et al. (2007) reported elevated concentrations of chloride (92 ± 8.5 mg L^{-1}) in urban streams relative to concentrations in agricultural (19.9 ± 8.6 mg L^{-1}) and forested (6.3 ± 3.9 mg L^{-1}) streams in Michigan; the contribution from sewage effluent (161 mg L^{-1}) to the urban streams was responsible for this increased concentration. Chloride concentrations in sewage effluent can be high; for example, Novotny et al. (2009) observed a range of chloride concentrations from 227 to 387 mg L^{-1} in four wastewater treatment plants in the Twin Cities Metropolitan area of Minnesota and suggested that 72% of the chloride in rivers was contributed by wastewater treatment plants. Differences in the concentrations of chloride in treated effluent may be due to differences in disinfection techniques and differences in chloride concentrations in the municipal tap water.

The Dallas – Fort Worth Metroplex, a large urban center located in a humid-subtropical climate in the upper portion of the Trinity River basin provided an opportunity to examine sodium and chloride fluxes with minimal influence of deicing salts. The use of deicing salts in this region is limited compared with northern regions. In the Dallas /Fort Worth region municipalities use 90 to 100% sand with 0 to 10% sodium chloride (NaCl) mixture and magnesium chloride for ice and traction control. Effluent from wastewater treatment facilities is a large contributor to stream flow in the basin, particularly during the dry summer months. The major objective of this study was to compare long-term average annual and seasonal fluxes of sodium and chloride and land cover and land use parameters associated with urbanization for two decadal periods: 1980’s and 1990’s based on availability of National Land Cover Data (NLCD) 2001 (USGS, 2003) and NLCD 1992 (USGS, 2000) in an effort to identify potential sources of sodium and chloride in five watersheds in the upper Trinity River basin. My secondary objective was to compare average annual and seasonal fluxes of sodium and chloride over three decadal periods; the 1980’s, 1990’s and 2000’s.

Materials and Methods

Site Description

The Trinity River Basin is located in the east-central portion of Texas in the south-central United States (Figure 4.1). The most northern latitude of the study area is 33° 43’ 33”N and the most southern is 32° 21’46”N, with the western longitude at 98° 43’23”W and the eastern at 96°13’11”W. The total area covered by the upper Trinity River Basin (UTRB) is 21,101 km^2. South of the study area, the Trinity River supplies many downstream municipalities and agricultural operations with surface water before draining into the Gulf of Mexico. The climate of UTRB is described as humid-subtropical with a mean annual temperature of 18.3°C (NOAA 2010). The mean annual precipitation changes over the UTRB from 736 mm in the northwest to 1092 mm in the north eastern portion (Figure 4.2).

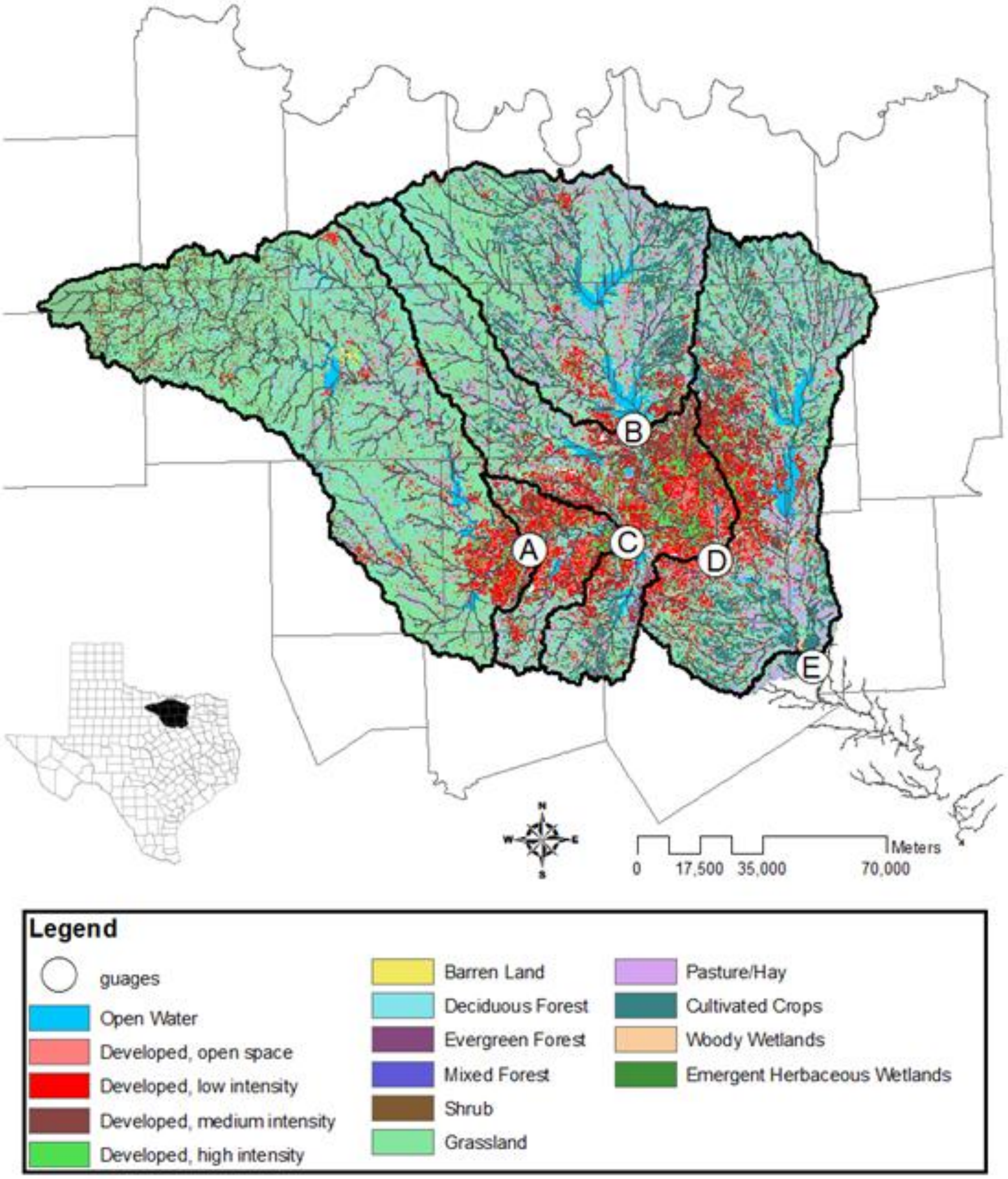
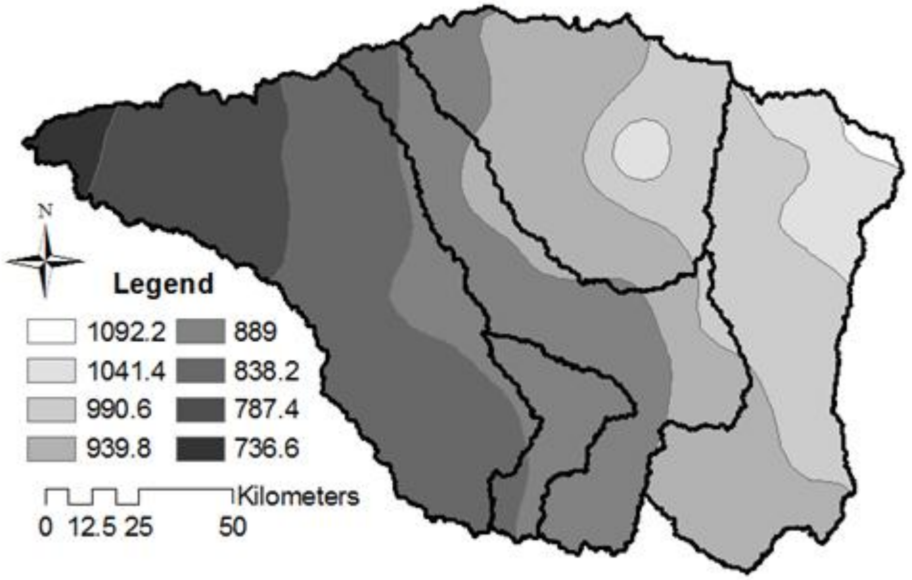


Figure 4.1 The land cover of the five designated watersheds of the upper Trinity River Basin (A, B, C, D, E) covering Dallas, Fort Worth, and surrounding municipalities from the 2001 National Land Cover Database (USGS, 2003). Letters are located at gauge site with catchment upstream.

Mean Annual Precipitation (mm)



Major and Minor Aquifers

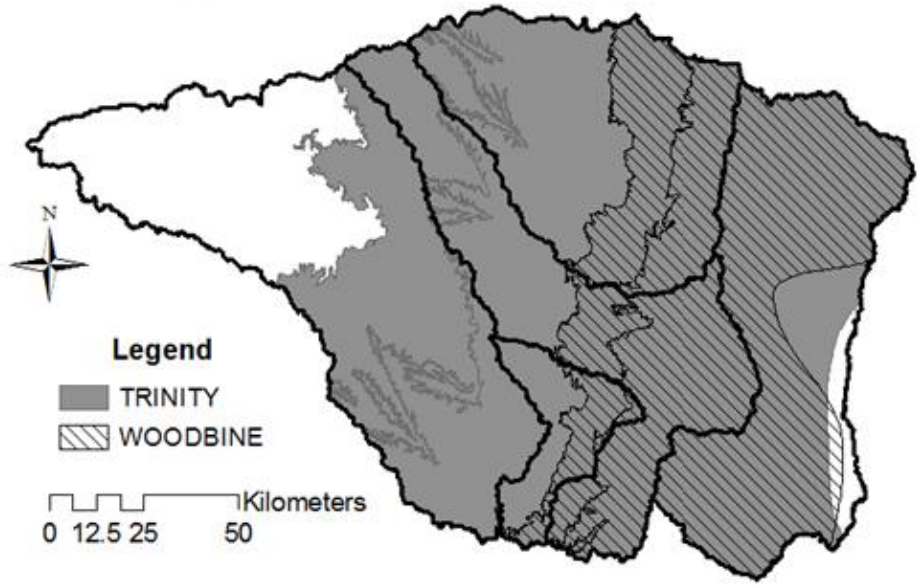


Figure 4.2 The mean annual precipitation (mm) and the major, Trinity, and minor, Woodbine, Aquifers of the upper Trinity River Basin watersheds. Source data from Texas Water Development Board (TWDB 2010b).

The Trinity River Basin is a modified sedimentary landform comprising six Integrated Land Resources Units (ILRU); the North Central Prairie, the Western Cross Timbers, Grand Prairie, Eastern Cross Timbers, the Blackland Prairie, and Bottomlands. Three soil orders are represented; Alfisols, Mollisols, and Vertisols. Major geologic formations include the Trinity Group and the Woodbine Group and include the Trinity and Woodbine aquifers (Figure 4.2; Ulery et al. 1993). The Trinity aquifer is characterized by moderately to severely hard water, while the Woodbine aquifer contains appreciable amounts of sodium and chloride. There are several major reservoirs located within the study area that are major sources of drinking water within the region; however, based on drinking water quality reports furnished by the municipalities, at least one, Grand Prairie, does supplement with water from the Trinity Aquifer (City of Grand Prairie 2009).

The UTRB was selected based on its climate and the positioning and availability of water quality data at USGS gauges around the Dallas/Fort Worth area. Five gauges were identified that divided the UTRB into five watersheds with a range of urban land cover classifications and other land covers (Figure 4.1). Water chemistry and discharge data were available for the majority of the gauges from the USGS database for the period of 1980 until 2010 (USGS 2010).

Long-Term Sodium and Chloride Loads

Sodium and chloride concentration data and discharge data were obtained from the USGS database for each gauge (USGS 2010). USGS has maintained long-term water quality sampling at locations across the country since 1965. The integrity and continuity of those measurements have been reported elsewhere (e.g. Alexander et al. 1998). Procedures were updated in 1995 by USGS to ensure better reporting based on updated minimum detection limit (MDL) criteria; however, since concentration at all gauges in this study are well above MDL limits I have no reason to believe the continuity of data was compromised over the study year period. All USGS measurements were made on filtered samples according to the procedures detailed by the USGS for dissolved sodium (code 00930) (ICP-AES) and chloride (code 00940). To ensure reliable regression coefficients for all available years while still attaining a detailed analysis of changes over the 30 year period, sodium and chloride concentrations from 1980 to 2009 were divided into two year increments, so that for most periods the chemistry for 12 water samples were available. For each 2-year period, regression coefficients were calculated for the power law form of the exponential relationship between ion concentration and discharge on the day the sample was collected (Eq. 4.1)

$$\text{Eq. 4.1} \quad \log C = m (\log Q) + b,$$

where: C = ion concentration (mg L^{-1}), Q = discharge (L sec^{-1}), m = slope and = y intercept. Only regressions with $R^2 \geq 0.6$ values were used to estimate the average daily concentration based on the average daily discharge. The predicted daily concentrations (mg L^{-1}) were then multiplied by daily discharge (L s^{-1}) and time (86,400) to generate daily loads (mg d^{-1}).

Because the watersheds are nested (Figure 4.1), in order to estimate daily and annual loads for watersheds I made the assumption that there was a low probability of in-stream uptake or sediment retention of sodium and chloride and that the entire load leaving the upstream gauge would still be present at the downstream gauge. To calculate loads and exports of individual watersheds the upstream gauge loads were subtracted from the downstream gauge loads using the following equations:

Eq. 4.2 $C_{\text{watershed}} = C_{\text{gauge load}} - A_{\text{gauge load}}$

Eq. 4.3 $D_{\text{watershed}} = D_{\text{gauge load}} - (C_{\text{gauge load}} + B_{\text{gauge load}})$

Eq. 4.4 $E_{\text{watershed}} = E_{\text{gauge load}} - D_{\text{gauge load}}$.

For those years with a regression $R^2 < 0.6$, the slope and intercept were estimated based on the average slope and intercepts of all periods. The daily loads were summed into two time periods, monthly loads and annual loads. The monthly loads were used to evaluate seasonal changes in exports while the yearly loads were used to evaluate patterns over the 30 year period. Annual data are based on the calendar year. To standardize loads by watershed area, annual and monthly loads were divided by watershed area (Mg km^{-2} yr^{-1}).

Seasonal atmospheric deposition data were obtained for the period from 1984 to 2008 from the National Atmospheric Deposition Programs (NADP 2010). Data were obtained from station TX56 located in the L.B.J. National Grasslands in Wise County, Texas at an elevation of 312 m in the rural northwest portion of the study area near the border of watersheds A and B. Annual sodium and chloride deposition was summed from seasonal values and these totals were assumed to be a reasonable estimate of wet and dry atmospheric deposition across the study area. The contribution of wastewater effluent to 2009 loads was calculated by attaining the mean annual effluent discharge reported through the Permit Compliance System to the U.S. Environmental Protection Agency and accessed through "Envirofacts" during the period of 2007 to 2009 for every permitted treatment plant in the study region (EPA 2011). The sum of all annual permitted wastewater treatment plant sodium and chloride loads were calculated for each sub-watershed. Concentrations of sodium and chloride were obtained through personal communication with laboratory personnel from the three largest wastewater treatment plants in the upper Trinity River basin: Southside Wastewater Treatment Plant, Trinity River Authority (TRA) Central Region Wastewater Treatment Plant, and Village Creek Wastewater Treatment Plant. Of these, only one (TRA Central Region WWTP) measured sodium in the effluent which averaged 95.0 mg L^{-1}. The mean chloride concentration from the three plants from 2007 to 2010 is 79.2 mg L^{-1} (standard deviation = 11.2 mg L^{-1}). Effluent concentrations of sodium and chloride were similar to the concentrations in the most urbanized watersheds at lowest measured flows during the summer, which are known to be effluent dominated. Estimates of annual deicing salt use were obtained from the street divisions of Fort Worth and Dallas and inputs were standardized by area.

Watershed Delineation and Land Cover Analysis

ArcGIS version 9.3 (ESRI 2009) was used to delineate the watershed for each gauge and to calculate population (numbers and density), land cover and impervious surface for each watershed. Watershed delineation was performed using the hydrology function under the Spatial Analyst Toolbox. Input data were 30 x 30 m digital elevation model (DEM) raster data from the National Elevation Dataset (http://ned.usgs.gov) publically available from the U.S. Geologic Survey through the National Map Seamless Server. Population density, impervious surface area and urban land cover percentages for each watershed were calculated from the 2000 Census Data (TNRIS 2009), and National Land Cover Data (NLCD) 2001 (USGS 2003) and NLCD 1992 (USGS 2000) by using the *zonal statistics* calculator in the *Spatial Analyst* which sums the pixels for each land cover within the watershed boundaries.

Field Measurements

Starting in late 1990s the USGS stopped collecting and publishing water quality measurements for three of the five watersheds (table on p. 140); therefore, to ensure the accuracy of the published data and acquire the latest exports, grab samples were collected at each gauge for a one year period from June 2009 to May 2010. Grab samples (mid channel) were collected monthly in sterile Whirlpak® bags from bridges to facilitate ease of sampling at each of the five river gauge sites. Electrical conductivity and pH were quantified on unfiltered aliquots, and the remainder of the sample was syringe filtered through ashed (400° C for 5 hours) Whatman GF/F filters (0.7 µm nominal pore size). Samples were stored frozen in acid washed, ultra-pure water rinsed HDPE bottles until analysis. Subsample aliquots were filtered through 0.2 µm Pall filters prior to analysis by ion chromatography. Sodium was quantified using an Ionpac CS16 analytical and Ionpac CG16 guard column for separation and 20 mM methanosulfonic acid as eluent at a flow rate of 1 mL min and injection volume of 10 µL

(DIONEX Corp., Sunnyvale, CA, USA). Chloride was quantified using Ionpak AS20 and Ionpak AG20 analytical and guard columns for separation with 35 mM KOH as eluent at a flow rate of 1 mL min and an injection volume of 25 µL (DIONEX Corp., Sunnyvale, CA, USA). Sample replicates, blanks, NIST traceable and check standards were run every 10th sample to monitor instrument precision (Coefficient of Variation (CV) <2%) and accuracy (CV < 5%). Machine detection limits were 0.002 mg L^{-1} for sodium and 0.1 mg L^{-1} for chloride. Concentrations of sodium and chloride obtained from field sampling and discharge at the USGS gauges at the time of collection were used to estimate loads and exports for my defined 2009 water year (June 2009 to May 2010).

Data Analysis

Data were analyzed using SPSS v. 16.0. Regression analysis was used to determine change in predicted annual exports over time (1980 to 2008) for the USGS data combined with collected samples for the 2009 water year. The decadal mean of annual exports was calculated for three decades: 1980 to 1989, 1990 to 1999, and 2000 to 2009. These decadal means were compared to available land cover data which is only published once a decade, NLCD 1992 and 2001. The most recent land cover data is not available and therefore the 2000 to 2009 data could not be used. Regression analysis was used to determine relationships between estimated decadal mean of the annual sodium and chloride exports for the periods of 1980 to 1989 and 1990 to 1999 (separately and combined) and the associated land cover (percent urban land cover, and impervious surface area). The combined decadal regression model was validated using the "leave-one-out" cross-validation method (e.g. Aitkenhead-Peterson and Kalbitz 2005; Aitkenhead-Peterson et al. 2007). Paired students t- tests were used to determine changes in the mean monthly export during each season between 1980 to 1989 and 1990 to 1999 for four seasons: Winter = December through February, Spring = March through May, Summer = June through August, and Fall = September through November. Seasons were chosen based changes in temperature and precipitation. The 2000 to 2008 period was left out of this analysis due to a lack of USGS data (table on page 141).

Results

Annual Concentrations, Loads, and Exports

For most years there was a strong relationship between sodium and chloride concentrations and discharge (Table 4.1). There was good continuity in measured and predicted concentrations across the study period with no apparent jumps or breaks and the 2009 measurements fell in a reasonable range. Watersheds A and B, which had smaller discharge volumes and were less urbanized than watersheds C, D, and E, had concentrations less strongly related to discharge than watersheds with higher discharge (C, D, E). The mean annual predicted concentrations of the UTRB ranged from 19.6 to 65.5 mg L^{-1} chloride and 20.2 to 73.4 mg L^{-1} sodium (Table 4.2). The annual mean chloride concentration of the initial measured USGS sample concentrations obtained from their database fluctuated somewhat, but nevertheless remained relatively constant over the study period. The concentrations of sodium, however, showed a distinct decrease for three of my watersheds between 1980 and 1985 which was reflected in the sodium:chloride ratio of these watersheds. The mean difference between the mean annual predicted concentrations and the mean annual measured USGS concentrations was 3.5 mg L^{-1} for chloride and 3.3 mg L^{-1} sodium.

Table 4.1 Mean slope, intercept, and R^2 of regression models of the long-term USGS stream chemistry and discharge data from all available periods. The units for "x" are the log discharge in m^3 s^{-1}. The units for "y" are mg L^{-1}.

	Mean Slope		Mean Intercept		Mean R^2	
Watershed	Sodium	Chloride	Sodium	Chloride	Sodium	Chloride
A	-0.4509	-0.4065	2.2215	2.2029	0.81	0.68
B	-0.4967	-0.4724	2.4964	2.4341	0.91	0.88
C	-0.4455	-0.4721	2.4762	2.4505	0.87	0.85
D	-0.1642	-0.1455	1.5157	1.4588	0.63	0.53
E	-0.102	-0.185	1.44	1.589	0.56	0.54

The mean annual export of chloride from my watersheds in 2009 ranged from 5.47 in my least urbanized (B) to 26.6 Mg km^{-2} yr^{-1} in my most urbanized (C) watersheds and sodium ranged from 6.97 in my least urbanized (B) to 27.0 Mg km^{-2} yr^{-1} on my most urbanized (C) watersheds (Table 4.2). There was a large amount of variation in the annual exports due to changes in annual discharge which may be related to the amount precipitation received during the period, but overall, urban watersheds displayed an increase in chloride and sodium export between 1980 and 2009 (Table 4.2). The watershed with the highest percentage of urban land cover (C) had significant

Table 4.2 The decadal mean of the annual chloride and sodium exports and concentrations. Sodium and chloride concentrations based on USGS data and my empirical model predicted concentrations and exports for the periods of 1980 to 1989, 1990 to 1999, and 2000-2008. Estimates for 2009 were based on collected samples from this study. Dashes indicate there was insufficient data available for these periods to make predictions.

Site	Years	**Chloride**			**Sodium**		
		Concentration mg L^{-1}		Export Mg km^{-2} yr^{-1} Mean/ Median	Concentration mg L^{-1}		Export Mg km^{-2} yr^{-1} Mean/ Median
		Observed	Predicted		Observed	Predicted	
A	1980 - 89	41.5	40.65	1.04/0.37	35.3	32.5	0.84/0.35
	1990 - 99	33.1	-	-	27.3	26.4	2.10/1.28
	2000 - 08	-	-	-	-	-	-
	2009	26.2	24.9	2.42/ -	20.74	20.2	1.78/ -
B	1980 - 89	25.9	23.1	2.72/1.32	26.6	23.2	2.61/1.25
	1990 - 99	22.1	19.6	3.38/2.41	18.7	22.8	3.65/2.91
	2000 - 08	-	-	-	-	-	-
	2009	24.8	28.2	5.47/ -	28.5	24.4	6.97/ -
C	1980 - 89	70.4	64.0	14.1/13.8	80.4	73.4	15.5/15.7
	1990 - 99	63.4	56.1	-	60.3	53.6	20.4/20.4
	2000 - 08	65.5	64.3	-	63.5	62.3	-
	2009	60.5	58.3	26.6/ -	51.9	51.7	27.0/ -
D	1980 - 89	60.7	53.4	8.36/7.76	74.3	63.5	9.70/9.03
	1990 - 99	46.3	46.6	7.91/7.27	48.2	48.9	9.79/9.20
	2000 - 08	51.0	55.2	-	-	-	-
	2009	47.9	46.1	15.7/ -	46.1	44.3	15.0/ -
E	1980 - 89	47.5	44.7	2.50/2.04	50.6	52.9	3.32/2.27
	1990 - 99	43.0	40.2	5.75/4.76	47.3	43.7	6.67/5.36
	2000 - 08	53.2	57.8	6.42/4.14	52.7	56.3	-
	2009	49.1	47.4	7.99/ -	46.8	44.9	7.15/ -

increasing exports from the period of 1980 to 2010 for both sodium and chloride (Table 4.3, Table 4.4). Watershed E also had significant increases in sodium exports during the study period (Table 4.3). Watersheds with the lowest percentage of urbanization (A and B) displayed no significant increase in exports of sodium and chloride over the thirty year study period.

Table 4.3 Area of watershed, estimated population density in 2000 (TNRIS 2000) percentage of total urban land cover (combining low, medium, and high density) calculated from National Land Cover Data 1992 and 2001, and results of regression analysis of sodium and chloride exports for the five watersheds (A, B, C, D, E) of the upper Trinity River across the 30 year study period. NS is not statistically significant at $\alpha < 0.05$. Units for "x" are year and units for "y" are Mg km^{-2} yr^{-1}.

Water-shed	Area (km^2)	Population Density (persons per km^{-2})	Urban (%) 1992	Urban (%) 2001	Element	Slope	Intercept	Adjusted R^2	p value
A	6954	607	3.15	5.32	Na	0.044	-86.7	0.036	NS
					Cl	0.051	-101.0	0.112	NS
B	4333	478	5.45	6.22	Na	0.072	-140.2	-0.030	NS
					Cl	0.051	-97.6	0.052	NS
C	984	960	39.0	41.5	Na	0.331	-638.5	0.480	0.034
					Cl	0.474	-924.6	0.621	0.022
D	3982	899	22.3	28.0	Na	0.174	-336.4	0.330	NS
					Cl	0.194	-375.9	0.092	NS
E	4846	802	12.7	16.3	Na	0.234	-460.7	0.340	0.008
					Cl	0.065	-123.6	-0.019	NS

Table 4.4 Annual sodium and chloride exports (Mg km^{-2}) from studies in northern states, USA with percent urban land cover and reported watershed areas. Dashes indicate data were not reported in publication. Exports from this study are from grab samples collected from June 2009 to May 2010. Percent urban land cover from this study is from the 2001 National Land Cover Dataset.

Source	Export Na^+	Export Cl^-	Urban %	Area (km^2)	Location	Year
Mullaney et al. (2009)	_	30.8	44‡	141	Northern States, USA	1994 to 2001
Kelly et al. (2008)	9.6	19.2	9	62.4	Wappinger Creek, New York	1986 to 2005
Peters and Turk (1981)	4.94	7.3	6†	9103	Mohawk River, New York	1951 to 1974
Godwin et al. (2003)	6.51	10.2	6	9103	Mohawk River, New York	1990 to 1998
Novotny et al. (2009)	-	28.9	-	4150	Minneapolis/St. Paul, Minnesota	2000 to 2007
This Study: A	1.78	2.42	5.32	6945	Trinity River, Texas	2009
B	6.97	5.47	6.22	4333	Trinity River, Texas	2009
C	27.0	26.6	41.5	984	Trinity River, Texas	2009
D	15.0	15.7	28.0	3982	Trinity River, Texas	2009
E	7.15	7.9	16.3	4846	Trinity River, Texas	2009

‡ personal communication with JR Mullaney (Mullaney et al. 2009);

†Estimate based on land cover from Godwin et al. 2003

Seasonal Concentrations and Exports

Sodium and chloride concentrations followed a seasonal pattern with increased concentrations during the summer months when precipitation was low and decreased concentrations during the fall, winter and spring when precipitation increased (Figure 4.3). Highest sodium and chloride concentrations were observed in the moderately to highly urbanized watersheds (C, D, and E). Concentrations of both sodium and chloride remained fairly constant between the two decades for the two rural watersheds (A and B); however, the more urbanized watersheds displayed greater seasonal changes in concentrations between decades.

The change in mean monthly exports for each season between period from 1980 to 1998 and 1990 to 1999 was variable across the watershed (Figure 4.4). Paired student t-tests comparing the mean monthly seasonal sodium exports during the period from 1980 to 1989 to the period of 1990 to 1999 indicated that in only the most urbanized watershed (C) were there significant increases in sodium exports during all four seasons. Watershed A had increased exports during the winter and spring seasons, and watershed E had increased exports during the winter, spring, and fall seasons (Figure 4.4). Due to the lack of USGS chloride data for the period between 1990 and 1999, only the three of the five watersheds (B, D, and E) were available for comparison; however, similar patterns were also found in seasonal chloride exports for available watersheds (Figure 4.4).

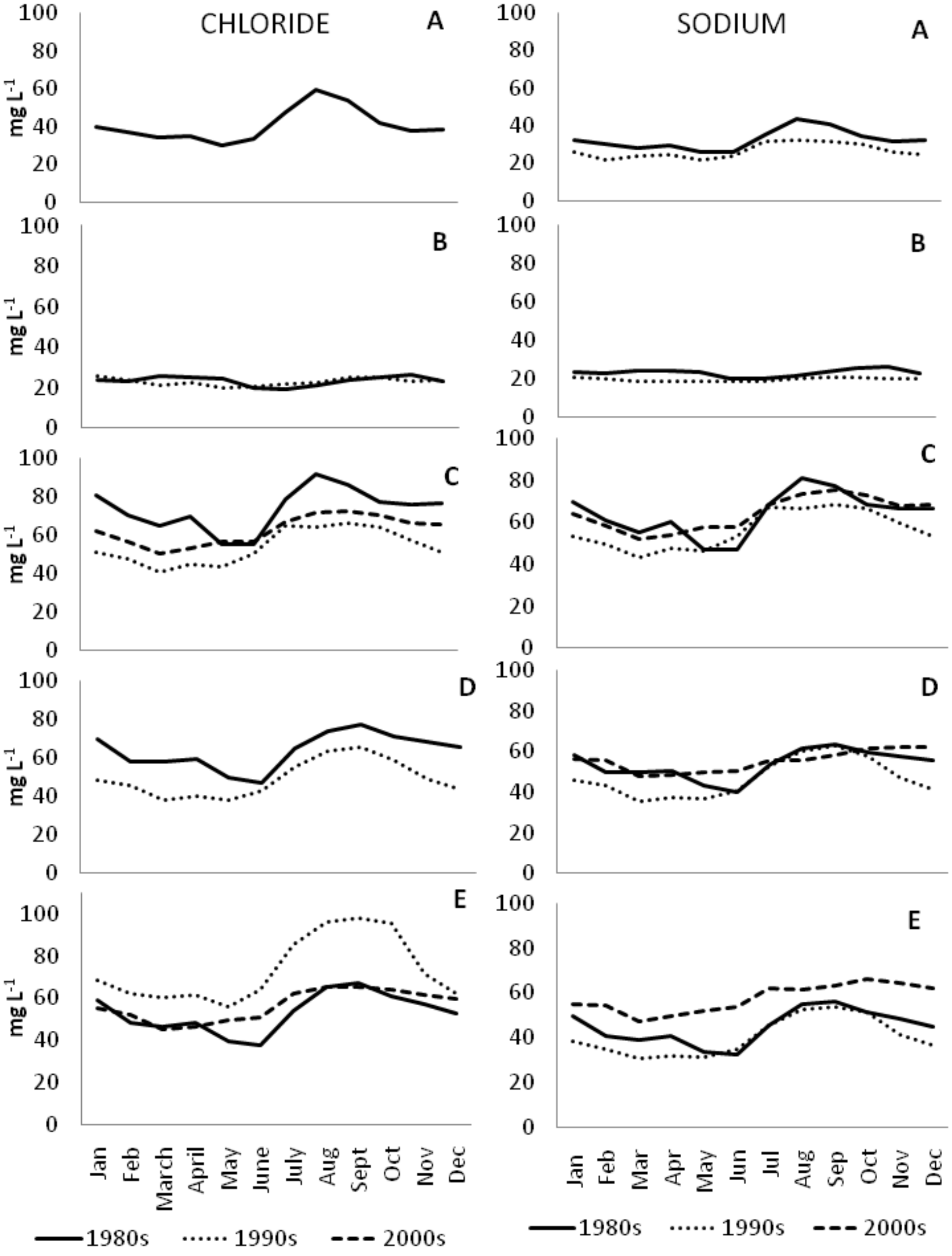


Figure 4.3 Predicted decadal mean of the mean monthly concentration of sodium and chloride of watersheds A, B, C, D, and E of the upper Trinity River.

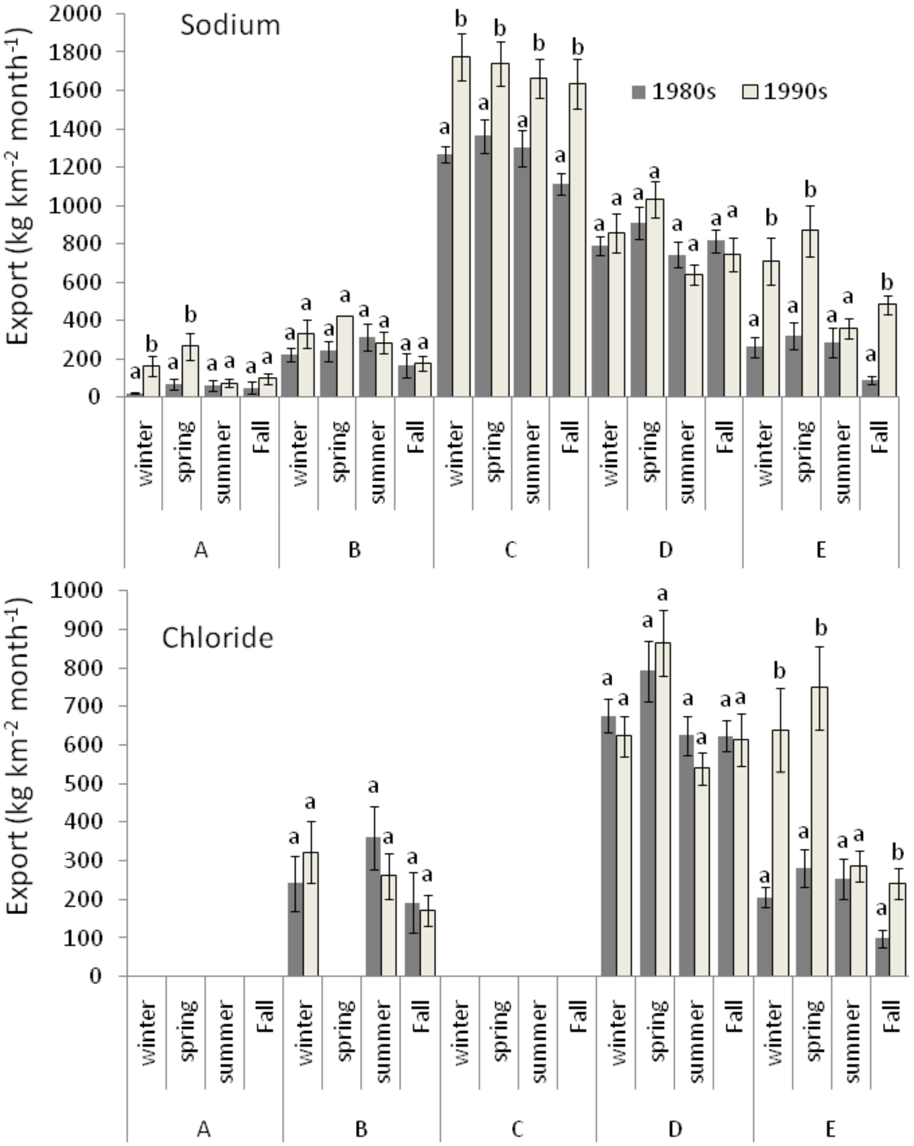


Figure 4.4 Results of paired t-test of seasonal mean monthly exports of sodium and chloride between the 1980s and the 1990s. Letters above bars indicate significant difference ($p < 0.05$) between decades within each season and watershed. Letters at bottom the graphs refer to the watershed ID (A, B, C, D, and E). Winter: December-February, Spring: March-May, Summer: June-August, and Fall: September-November. Error bars represent the standard error of the monthly mean.

Sodium:Chloride Ratios

Most of the watersheds within the upper Trinity River basin have sodium to chloride molar ratios (Na:Cl) at or above 1 (Figure 4.5). The most rural watershed (A) had the smallest average ratio (Na:Cl = 1.29), while watersheds B (Na:Cl = 1.68) and D (Na:Cl = 1.71) had the highest ratios. Only watershed A had no visible change in its Na:Cl ratio over the 30 year study period. During most of the period from 1980 to 1990, the three most urbanized watersheds (C, D, and E) had declining Na:Cl ratios (Figure 4.5). Watershed B, sampled just downstream of a major reservoir, was the only watershed to show a pattern of increasing ratios over the entire 30 year study period. Based on the dissociation ratios, molar ratios should be approximately equal to one if all of the watershed sources of sodium and chloride are from NaCl and not other forms of sodium or chloride.

Relationships Between Exports and Land Cover

Strong, positive relationships were found between sodium and chloride export and my measures of urbanization for the two decades studied (Figure 4.6). I found some co-correlation between the percentage of total urban area and percentages of high, medium, and low intensity urban land cover. A log linear relationship was also found between population density and urban land cover ($R^2 = 0.91$). When mean annual exports of sodium and chloride from the two decades are combined, the relationship between urban land cover and salts was still strong, predicting an increase in sodium of

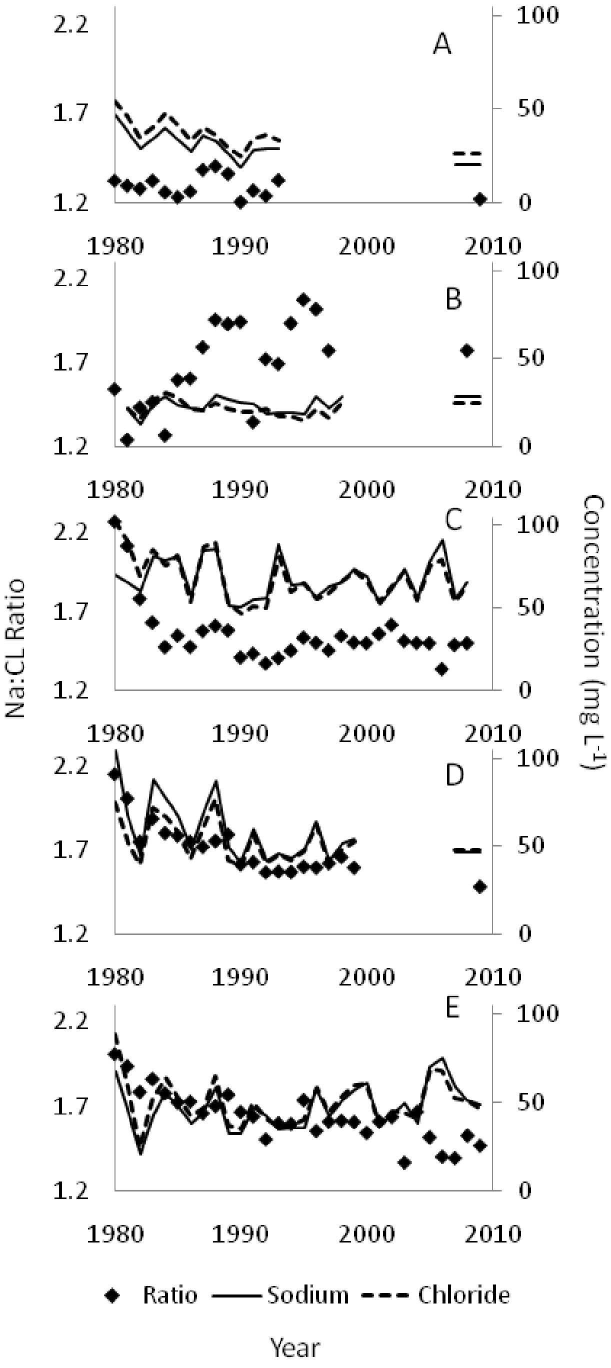


Figure 4.5 Mean annual measured sodium and chloride concentrations (right axis) and molar ratios (left axis) for watersheds of the upper Trinity River (A, B, C, D, E) over from 1980 to 2009. The 1980 to 2008 data source is USGS, breaks in data result from a lack of available data for the time period. Data for 2009 is from this study's sampling.

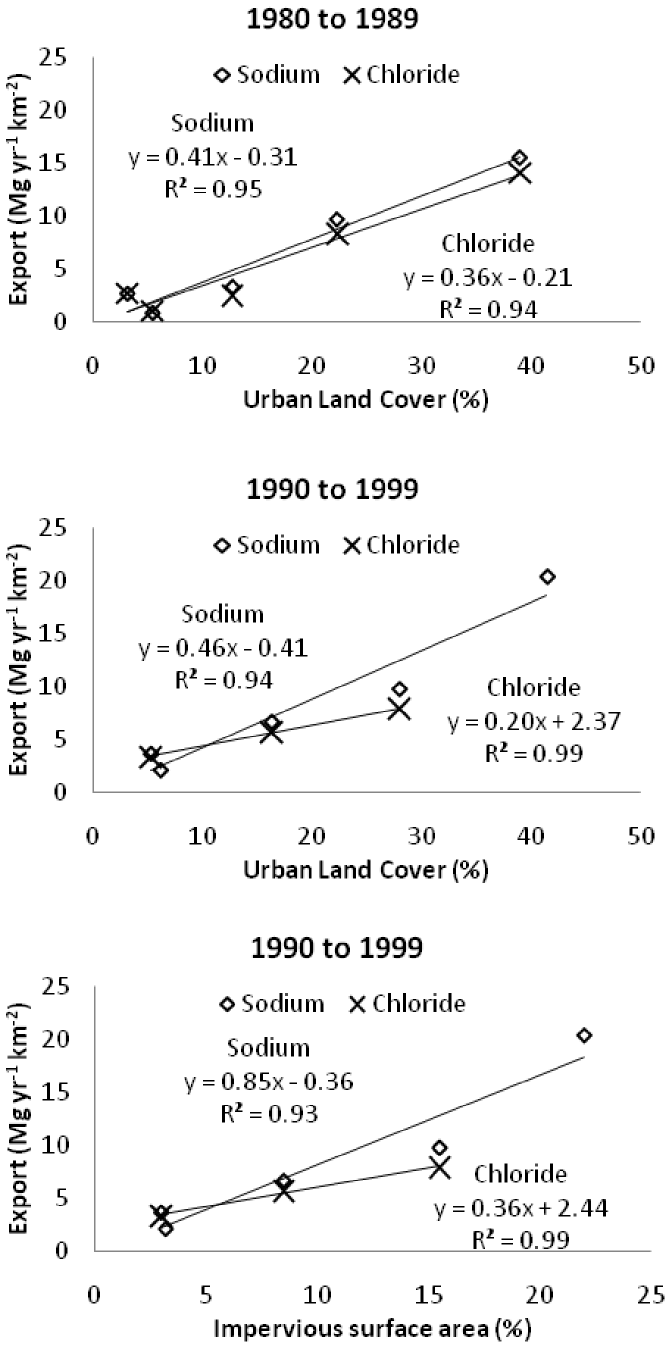


Figure 4.6 Relationships between percent area of urban land cover and the decadal mean of the annual exports of sodium and chloride for periods of 1980 to 1989 (1980s) and 1990 to 1999 (1990s) and impervious surface area for 1990 to 1999 (1990s).

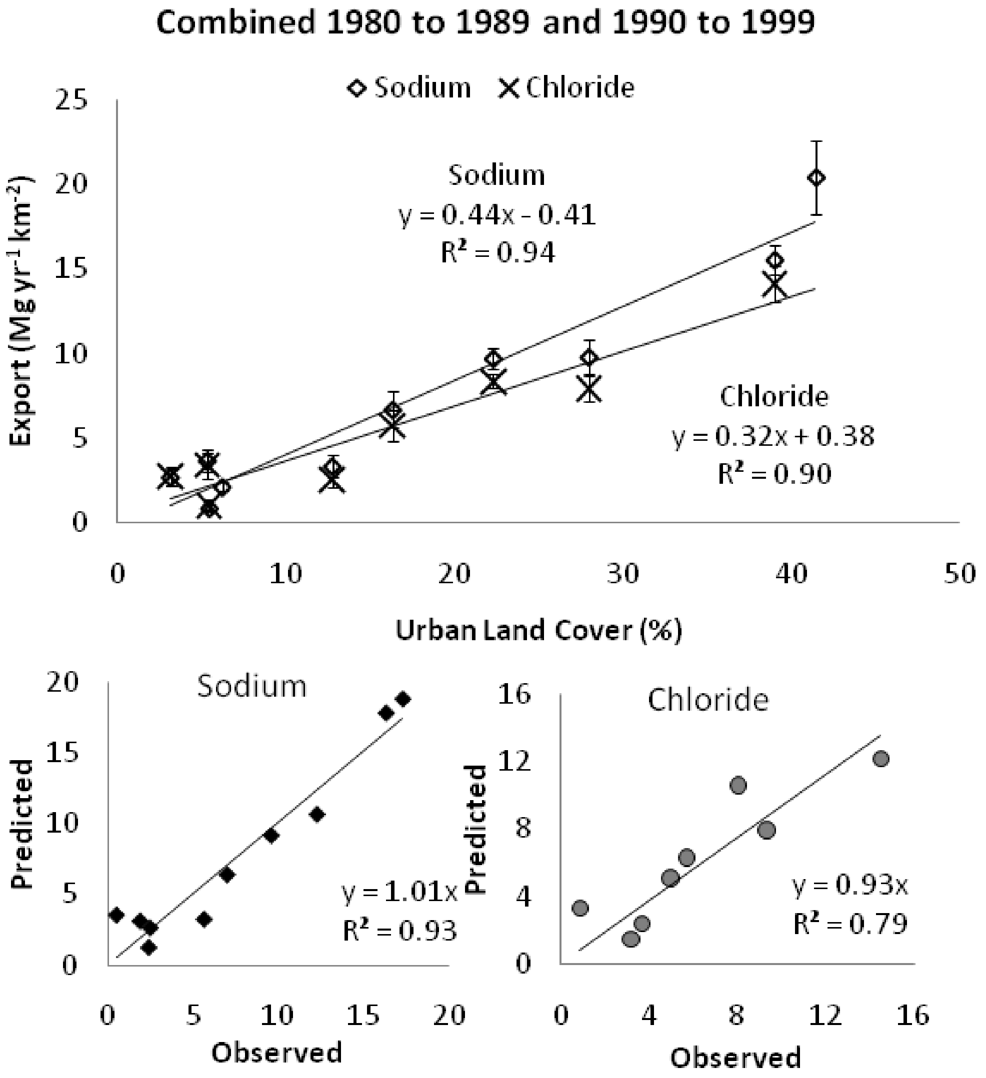


Figure 4.7 Relationship between percent area of urban land cover and the decadal mean of the annual exports of sodium and chloride for the combined periods of 1980 to 1989 (1980s) and 1990 to 1999 (1990s). Error bars represent the standard error of the decadal mean.

0.436 Mg km^{-2} yr^{-1} and an increase in chloride of 0.323 Mg km^{-2} yr^{-1} for every 1% increase in urban land cover within the watershed (Figure 4.7).

Discussion

Streams and rivers in northern cities have high sodium and chloride concentrations attributed to deicing salts (e.g. Kaushal et al. 2005; Mullaney et al. 2009). Despite being located in warmer latitudes and not subject to the extensive use of deicing salts, the exports of sodium and chloride from watersheds in the Dallas –Fort Worth Metroplex are still relatively large. Mullaney et al. (2009) reported that the average urban export of chloride is 30.8 Mg km^{-2} yr^{-1}. The basins in the Mullaney et al. (2009) study had a wide range of urbanization, but the median lumped NLCD urban land cover was 44.7% (Table 4.4; Mullaney, *personal communication*). Novotny et al. (2009) did not report the percent urban land cover for Minneapolis/St. Paul; however, their chloride exports were similar to those of Mullaney et al. (2009) at 28.9 Mg km^{-2} yr^{-1}. In the Dallas/Fort Worth region my calculated export of chloride from watershed C in 2009 was 26.6 Mg km^{-2} yr^{-1} and had an urban land cover of 40.6%, very similar to the results from the northern cities. Because the chloride export from an urban, sub-tropical watershed was so similar to those reported from watersheds in humid temperate climates, three questions need to be answered: a) if the UTRB does not utilize as high a mass of deicing agents as northern cities, then what is the source of riverine sodium and chloride? b) is the source unique to Dallas or do other cities in warmer climates also have high sodium and chloride exports? and c) is the increased riverine exports of sodium and chloride in northern climates caused primarily by deicing agents or could there be another source?

Table 4.5 Estimated inputs from deicing agents from municipalities in the upper Trinity River Basin, Texas. Source data from municipalities' street divisions.

	Dallas	Fort Worth
Sand/Salt ratio	90%/10%	95% / 5%
Annual Use (Mg)	3229	907-1810
Salt input (Mg)		
$NaCl$	323	43.35-90.7
Na^+	127	15.2-31.7
Cl^-	196	28.2-58.9
Land Area (km^2)	997	780
Loading ($Mg\ km^{-2}\ yr^{-1}$)		
Na^+	0.127	0.019-0.041
Cl^-	0.196	0.036-0.075

Point Sources of Sodium and Chloride

Wastewater Treatment Plants

Wastewater treatment facilities are often cited as contributors to salt loads in urban watersheds (Peters 1984; Mullaney et al. 2009; Novotny et al. 2009). The concentrations of sodium and chloride reported by the Dallas/Fort Worth wastewater treatment plants, 95 and 79.2 mg L^{-1} for sodium and chloride, were lower than those observed by Fitzpatrick et al. (2007) and Novotny et al. (2009). Yet for year 2009 I estimated wastewater effluent supplied approximately half of the sodium and chloride loads generated by the three most urbanized watersheds (Table 4.6). Novotny et al. (2009) also found very large proportions of the chloride exports were contributed by wastewater effluent in Minneapolis/St. Paul, (87000 Mg of the 120000 Mg or 72.5%).

The mean Na:Cl ratio of wastewater effluent from the three largest wastewater treatment plants in the Dallas/Fort Worth region was 1.26, which was similar to the Na:Cl ratios of the urbanized watersheds C, D, and E.

I believe these high exports are a result of the loading of urban watersheds by industrial and consumptive products such as food, detergents, water softeners and the importation of municipal water that ends up released to the watershed through the waste stream in urban environments (e.g. Steele et al. 2010). Kelly et al. (2008) estimated very small sodium chloride contributions from sewage (4%) and water softeners (3%) in a small basin in New York. Mullaney et al. (2009) estimated that 1.3 kg of chloride was released per person per year based on the daily recommended intake of sodium (2300 mg day^{-1}). Using the Mullaney et al. (2009) estimate and the population of 5.6 million residing in the upper Trinity Basin counties, this would result in 7280 Mg of chloride released annually or 11.6% of the total estimated load contributed by the wastewater effluent. At this time it is not possible to draw any conclusion on the contributions of the other various users of the wastewater system and further research is needed.

Table 4.6 The estimated mean volume of wastewater effluent discharged in to each sub-watershed and the calculated mass of sodium and chloride exported to the watershed by the treatment plants. The calculated percentage of total watershed exports in 2009 contributed by wastewater treatment effluent.

Watershed	Wastewater Effluent Volume (m^3 yr^{-1})	Wastewater Exports (Mg yr^{-1})		Percentage of watershed 2009 exports	
		Sodium	Chloride	Sodium	Chloride
A	$3.86*10^6$	4580	3860	15.2	16.3
B	$4.82*10^7$	367	309	2.96	1.83
C	$1.46*10^8$	13900	11700	52.2	44.7
D	$3.37*10^8$	32000	26900	53.7	43.1
E	$2.73*10^8$	23600	19900	68.1	51.3

Non-Point Sources of Sodium and Chloride

While approximately half of the exports of sodium in chloride in 2009 resulted from effluent discharge into the rivers, the other half of these substantial exports were likely a result of non-point sources found in the watershed landscape.

Deicing Salts

Dallas/Fort Worth averages 6.4 cm of snowfall annually (NOAA 2010). Municipalities of the UTRB use a sand/sodium chloride mixture and magnesium chloride to increase traction and prevent icing of roads, bridges and sidewalks. Across the DFW municipalities, the mass of sodium ranges from 0 to 10% of the total weight applied to surfaces. Based on interviews with local authorities, municipalities apply approximately 907-3229 Mg of the sand-salt deicing mixture per year, resulting in 28-196 Mg of chloride and 15-127 Mg of sodium added to the watersheds (Table 4.5). The salt loading from deicing salts to my watersheds is therefore only a very small proportion of the exports; an average 1.8% of chloride and 0.9% of sodium is accounted for by deicing materials. These estimates do not take into account potential homeowner or business use of deicing salts (i.e. sodium chloride, magnesium chloride, or calcium chloride) to prevent freezing on sidewalks, driveways and parking lots, but it is assumed to be small compared to use in colder climates. Based on my estimates, deicing salts are not considered a large contributor to sodium and chloride exports in the UTRB.

Sodium:chloride ratios for urbanized watersheds in this study were close to or > 1. Cherkauer (1975) also found Na:Cl ratios higher than 1.0 in urban impacted watersheds and suggested that, because the main salt source in that study was sodium chloride, the increased ratios were a result of sodium saturation of substrate clays in the stream bed during the winter months and the subsequent release of sodium from clays when water column solution concentrations decrease causing the enrichment of sodium in the water column compared to chloride. In contrast, other studies in colder regions impacted by deicing salts have observed decreases in Na:Cl ratios (Bowser 1992; Mattson and Godfrey 1994). Rhoades et al. (2001) reported that molar ratios, which should be 1 for sodium chloride, have decreased in watersheds impacted by road salt in Massachusetts, USA. They reported a 15% increase in chloride for highly impacted and 10% increase for moderately impacted watersheds. They further suggested that the decrease in sodium relative to chloride was the result of adsorption of sodium to soil and clay particles in watershed soils (Rhoades et al. 2001).

It is interesting to note that in my study and that of Novotny et al. (2009), point sources contributed a relatively consistent large proportion of the total exports in highly urbanized watersheds and both studies found increases in non-point source exports correlated with seasonal highs in precipitation. Novotny et al. (2009) attributed this to a mobilization of the large amounts of deicing salts applied to the urban landscape and stored until precipitation flushed the watershed during the spring. In my watersheds no known large mass application of salts occurs during the winter and therefore the source of the similar spring flush is unclear.

Septic Systems and Leaking Infrastructure

Septic systems have been also been proposed as a loading mechanism for sodium and chloride (Rose 2007; Mullaney et al. 2009). In addition to septic systems, Lerner (2002) estimated that in cities throughout the world, approximately 10 to 30% of sewer pipes leak and may contribute to groundwater recharge in urban settings. In a study of the Chattahoochee River basin which contains the large city of Atlanta, Rose (2007) reported correlations between stream sodium, chloride, and potassium and the presence of underground pipes in a watershed suggesting that leaking pipes and septic tanks may be contributing to shallow groundwater. If sodium chloride were leaking from the waste stream through buried pipes it is possible that the soil would retain sodium and the Na:Cl ratio should then be less than one; however, in the UTRB ratios of Na:Cl were greater than one for my urbanized watersheds during the 30 year study period indicative that the majority of sodium is not being transported through watershed soils and that leaking pipes are unlikely to be a contributor.

Wet and Dry Deposition

Atmospheric deposition of sodium and chloride contributes to river exports. Estimates of this contribution to exports with minimal urbanization range from 26 to 46% of sodium exports and 28 to 55% of chloride exports from watersheds located across the United States including, but not limited to, those impacted by sea salt (e.g. Conway 1942; Livingston 1963; Garrels and Mackenzie 1971; Peters 1984). Atmospheric deposition of sodium ranged from 0.22 to 0.33 Mg km^{-2} yr^{-1}and averaged 0.12 Mg km^{-2} yr^{-1} in my study region. Deposition of chloride ranged from 0.06 to 0.36

Mg km^{-2} yr^{-1} and averaged 0.19 Mg km^{-2} yr^{-1} from the period of 1984 to 2008. If, however, I assume that 100% of the atmospheric deposition was contributing to my river exports, it would account for only 25% of the sodium and 27% of the chloride in my least urbanized watershed (A) during the 1980s which is a similar contribution to those watersheds reported with minimal urbanization (e.g. Conway 1942; Livingston 1963; Garrels and Mackenzie 1971; Peters 1984). In my most urbanized watershed (C), 100% atmospheric deposition would only account for an average of 0.7% of the sodium export and 1.3% of the chloride export from the period of 1990 to 1999.

Stormwater discharge resulting from impervious surface runoff may also impact sodium and chloride concentrations in urban streams. Apel and Hudak (2001) measured Na^+ and Cl^- concentrations during the winter and spring in Pecan Creek watershed, an ephemeral drainage system in Denton, TX a suburb north of Dallas in watershed B of this study. From all five measured sites they found no change between first flush concentrations and the remainder of the rain event and the median concentration in the runoff of four measured storms was 18.7 mg L^{-1} sodium and 12 mg L^{-1} chloride. The concentrations of sodium (0.16 mg L^{-1}) and chloride (0.26 mg L^{-1}) in atmospheric deposition (NADP 2010) are low in comparison to the runoff concentrations reported by Apel and Hudak (2001) and indicate that precipitation is gaining salts from the urban surface. The source of salts gained from the urban surface may include deposition of dusts, irrigation over spray, and spills. In addition to deposition, the dissolution of the surface itself may have contributed to the concentrations of sodium and chloride observed by Apel and Hudak (2001). For example, sodium concentrations in concrete pore water can be extremely high and can be readily leached from concrete (Andersson et al. 1989; Reardon 1992; Barna et al. 1994) and this factor can be important when considering that a larger percentage of roads in southern cities are constructed with concrete rather than the asphalt found in northern cities. Furthermore, numerous concrete manufacturers are located within the watershed which may also provide a source to surface waters.

Another source of salts resulting in impervious surface deposition may be the overspray and runoff from urban turf irrigation. The majority of drinking water for my study region is sourced from 11 reservoirs, ten of which are located in the Trinity River watershed, and of which eight are located inside the boundaries of this study. Of those eight, six reservoirs are located in the two rural watersheds (A and B), watersheds D and E each contain one, and none are found in watershed C. Water imported through the municipal water system from the rural to urban watersheds may result in an additional loading of salts. In 2007, counties of the UTRB used 90%, or 1467.8 million m^3 of water, of the total water use in the region, with Dallas County consuming approximately half of that (TWDB 2007). While a large portion of those salts may be released into the watershed via the wastewater treatment plants, irrigation can be a significant portion of the total water municipal water use and may release a significant amount of salt into watersheds soils and onto impervious surfaces. According to the Texas Water Development Board, approximately 35% of residential water used is for watering lawns, which would result in approximately 513 million cubic meters of water applied to the landscape as irrigation (TWDB 2010a). The average water sprinkler system is 75%

efficient (Connellan 2002). Thus at a efficiency 75% rate, irrigation would result in 128 million m^3 of water lost to runoff, evapotranspiration and evaporation resulting in approximately 2565 Mg yr^{-1} sodium (assuming an average Na^+ municipal water concentration of 20 mg L^{-1}). Evaporation of irrigation water from the soil and vegetation will leave salts behind; these salts may then be mobilized during the next precipitation event. Because it is not possible at this point to determine the distribution of water between my watersheds and the area of irrigated land in each watershed is unknown, it is not possible to make any further estimates on how the 2565 Mg might have been distributed among my watersheds.

Oil and Gas Industry

Another potential contributor to non-point source loading within the UTRB is the oil and natural gas industry. The average sodium concentration of oil-field brine is approximately 30,000 mg L^{-1} (Collins 1975). Leifeste and Hughes (1967) identified brine contamination in four watersheds within the Trinity River basin. Since the early 1970s discharge of oil-field brines has come under strict regulation (Van Metre and Callender 1996). Van Metre and Callender (1996) reported decreasing concentrations of sodium in the sediment of Lake Livingston in the lower segment of the Trinity River Basin between the years 1962 to 1992. This regulation may explain the decrease in my sodium concentrations and Na:Cl ratios during the early 1980s (Figure 4.5).

There is significant drilling activity in the Barnett Shale which covers most of the eastern counties of the Upper Trinity River Basin. Almost 10,000 oil and gas wells have been introduced into the region since 1989, a large number of which lie north and east of

Dallas-Fort Worth (Limerick et al. 2008). Currently, the primary method of disposal of recovered hydraulic fracturing solution or "produced water" defined as highly saline water returned from the drilled well is to use deep well injection into the Ellenburger Formation below the Barnett Shale (Chesapeake Energy 2011). Surface casing of wells is utilized to prevent contamination of the Paluxy and Trinity Aquifers (Chesapeake Energy 2011). The location of the majority of wells are concentrated in the rural watersheds (A and B) of this study, and because of their low sodium and chloride exports relative to the urban watersheds, it is doubtful that they are contributors to the higher exports observed in the urban watersheds. The upstream location of watersheds A and B, however, also means that sodium and chloride migration cannot be ruled out. At this time it is not possible determine the impact that these wells may have on watershed salt exports and more research on the impact of produced water on surface waters is needed.

Potential Environmental Implications

Large exports of sodium and chloride in the UTRB associated with urban land use and growth indicate there is significant loading and loss of salts from urban watersheds to surface waters. Long-term concentrations of sodium have declined and concentrations remain lower than the 250 mg L^{-1} limit for chronic toxicity, indicating there is minimal risk to aquatic ecosystem health. The presence of such large quantities of sodium and chloride may pose greater risk for downstream users who abstract water for irrigation and municipal use.

Conclusions

The purpose of this study was to investigate the impact of urbanization on exports of sodium and chloride from watersheds in a humid subtropical climate where the use of deicing salts was minimal. Concentration and exports of both sodium and chloride from the upper Trinity River Basin increased with percentage of urbanized land. The results of this study have the potential to alter the perspective on salt loads in urban streams. Surprisingly, the magnitude of the exports from UTRB was comparable to exports from urban centers in colder climates. Exports were strongly related to the percentage of urbanized land cover, and wastewater effluent discharges contributed approximately half of the total loads for watersheds with high areas of urban development. Atmospheric deposition and deicing salts contributions were very small compared to total exports. There are other potential non-point sources which include deposition of dusts and imported water through irrigation onto impervious surfaces, failing septic systems or sewage pipes, oil and gas industrial by-products and leaching of cement infrastructure, all of which require further investigation into their contribution to salt loads to urban watersheds. Further research is needed on salt exports from cities in milder climates and my results from the Dallas/Fort Worth Region may indicate the need for a re-evaluation of sources in northern cities.

CHAPTER V

CONCLUSIONS

The objective of this research was to investigate sodium in a humid subtropical climate and its potential impacts on the biogeochemical cycling in urban environments. Through a series of experiments on multiple scales, this research has found that A) sodicity of irrigation water increases the solubility and leaching of dissolved organic carbon, ammonium, dissolved organic nitrogen and phosphate from soil, B) irrigation water sodicity in municipal tap water explained the variability in the solubility of carbon and nutrients in 26 cities across Texas, C) sodicity increased the leaching of dissolved organic carbon and dissolved organic nitrogen from cut leaves and leaf litter, and D) the export of sodium and chloride from the Upper Trinity Watershed was related to urbanization and were of similar magnitude to northern cities despite the lack of deicing salts.

These results suggest that non-point sources of carbon and nutrients may be related to soil and solution chemistry under elevated salt conditions due to deicing salts, irrigation water with naturally occurring sodium, or irrigation with alternative waters such as wastewater treatment effluent. Numerous urban watersheds in the nation and around the world need to consider if the concentrations of sodium in irrigation and surface waters may be contributing to high carbon and nutrient loading from watersheds.

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APPENDIX A

Appendix A Results from soil core leaching over pore volumes (PV) 2 through 16 with different irrigation waters, distilled water (DDW), municipal tap water (tap), and neutralized tap water (N) and three soil cover treatments, bare soil (bare), mulch, and ryegrass (rye). In leachate: electrical conductivity (EC), pH, Na, Ca, Mg, and K retention or release, and release of dissolved organic carbon (DOC), nitrate-N, ammonium –N, dissolved organic nitrogen (DON), and phosphate-P.

PV	Water	cover	site	EC (dS m^{-1})	pH	Na (mg g^{-1})	Ca (mg g^{-1})	Mg (mg g^{-1})	K (mg g^{-1})	DOC (mg m^{-2})	NO_3-N (mg m^{-2})	NH_4-N (mg m^{-2})	DON (mg m^{-2})	PO_4-P (mg m^{-2})
2	DDW	Bare	A	0.17	6.72					752.3	22.7	397.8	37.7	36.4
2	DDW	Bare	A	0.42	6.53	-5.1	-14.0	-1.7	-2.5	762.6	16.3	850.5	7.4	26.5
2	DDW	Bare	A	0.00		-1.3	-9.8	-1.7	-4.4	1023.2	19.7	735.4	32.8	19.7
2	DDW	mulch	A	0.51	6.89	-4.8	-14.0	-2.5	-2.3	664.7	11.9	1042.9		12.1
2	DDW	mulch	A	0.05	7.61	-2.4	-2.2	-0.3	-1.3	368.4	5.7	104.9	35.1	6.1
2	DDW	mulch	A	0.66	7	-2.6	-23.4	-4.8	-3.8	608.0	19.6	1730.5		20.6
2	DDW	rye	A	0.35	6.97	-2.7	-15.8	-2.6	-0.8	398.3	3.6	1176.6	25.2	14.6
2	DDW	rye	A	0.18	7.05	-1.6	-7.9	-1.5	-1.0	224.1	3.8	582.2	15.1	9.3
2	DDW	rye	A	0.15	7.25	-0.7	-6.4	-0.6	-0.7	312.2	2.2	380.6	15.5	13.1
2	Tap	Bare	A	0.94	7.94	44.6	-13.0	-2.4	-2.3	957.6	32.7	655.8	71.9	13.8
2	Tap	Bare	A	0.84	6.76	56.0	-18.4	-3.3	-7.0	1245.5	37.0	932.5	26.5	11.6
2	Tap	Bare	A	0.87	7.56	70.7	-25.9	-3.7	-3.2	1353.4	46.3	854.6	49.1	10.7
2	Tap	mulch	A	0.98	8.2	40.9	-18.3	-3.0	-1.6	1415.7	15.3	860.5	105.7	11.6
2	Tap	mulch	A	0.79	7.86	56.6	-14.5	-2.7	-2.2	1457.1	22.7	714.1	95.6	8.8
2	Tap	mulch	A	0.90	7.6	48.3	-23.9	-4.5	-1.7	1195.4	7.5	1387.3	57.0	29.6
2	Tap	rye	A	0.68	8.07	50.6	-12.5	-2.0	-1.1	860.4	11.5	588.8	38.9	13.2
2	Tap	rye	A	0.79	8.26	53.7	-16.8	-2.0	-1.4	705.0	3.8	233.3	40.2	15.7
2	Tap	rye	A	0.77	7.83	58.1	-13.0	-2.3	-0.1	689.8	3.0	552.4	29.6	13.3
2	N	Bare	A	1.02	7.36	76.4	-49.7	-4.6	-1.0	916.2	4.0	694.2	52.3	66.0
2	N	Bare	A	1.12	7.62	42.4	-15.8	-3.2	-1.9	1087.6	38.7	749.4	59.9	10.8

PV	Water	cover	site	EC (dS m^{-1})	pH	Na (mg g^{-1})	Ca (mg g^{-1})	Mg (mg g^{-1})	K (mg g^{-1})	DOC (mg m^{-2})	NO$_3$-N (mg m^{-2})	NH$_4$-N (mg m^{-2})	DON (mg m^{-2})	PO$_4$-P (mg m^{-2})
2	N	Bare	A	1.39	7.84	59.6	-48.0	-8.6	-1.0	1256.7	6.0	1990.8		34.5
2	N	rye	A	1.08	7.77	-547.7	-174.1	-29.1	-21.0	4733.7	72.7	3658.3	214.8	171.3
2	N	rye	A	0.93	7.85	51.8	-14.4	-2.2	-0.2	312.0	2.4	570.8		12.1
2	N	rye	A	1.10	7.87	51.5	-38.9	-3.3	0.0	667.1	3.7	728.5	78.5	33.3
2	DDW	Bare	B	1.05	6.93	-1.8	-40.1	-4.1	-2.0	1408.2	21.1	2587.5		14.2
2	DDW	Bare	B	0.19	7.45					563.7	8.7	497.3	41.0	30.6
2	DDW	Bare	B	1.40	6.46	-1.5	-45.6	-7.9	-5.3	2927.9	101.6	3198.5		43.0
2	DDW	mulch	B	0.74	7.77	-2.2	-2.8	-0.4	-1.5	370.1	14.5	201.8	27.0	15.7
2	DDW	mulch	B	1.07	7.06	-2.1	-48.4	-5.9	-2.2	1012.0	8.0	3407.9		40.7
2	DDW	mulch	B	0.21	6.6	-3.8	-97.5	-10.9	-1.7	1718.6	3.3	6582.6		79.5
2	DDW	rye	B	0.47	7.49	-3.0	-17.4	-2.0	-0.6	582.7	2.7	1090.8	37.0	43.7
2	DDW	rye	B	0.35	7.79	-1.9	-12.9	-1.1	-0.7	600.1	2.6	595.8	58.5	24.7
2	DDW	rye	B	0.15	6.99	-1.4	-6.9	-0.8	-0.7	546.5	4.3	309.9	32.2	57.2
2	Tap	Bare	B	0.70	7.8	48.9	-21.0	-1.9	-0.6	1065.3	9.1	642.7	81.9	8.2
2	Tap	Bare	B	1.65	7.07	62.5	-44.9	-8.0	-2.5	1458.9	74.1	3373.8		30.0
2	Tap	Bare	B	1.45	7.77	56.2	-45.1	-5.6	-3.6	1905.3	61.3	2730.4	16.0	48.2
2	Tap	mulch	B	0.91	7.61	52.7	-20.8	-3.0	-4.8	1796.4	22.8	1120.1	67.6	24.2
2	Tap	mulch	B	0.21	8.16	36.4	-85.9	-5.8	-1.6	948.0	4.1	5787.2		16.9
2	Tap	mulch	B	0.90	8.25	60.2	-31.3	-3.5	-1.7	1494.8	5.0	638.7	94.2	43.2
2	Tap	rye	B	0.82	8.35	56.4	-19.4	-1.8	-0.7	665.5	2.6	440.2	31.5	19.5
2	Tap	rye	B	1.05	8.3	53.4	-28.4	-2.6	-0.8	687.7	3.7	890.9	66.2	29.3
2	Tap	rye	B	0.70	8.07	70.5	-31.8	-2.6	-0.2	1044.8	2.5	526.2	65.8	85.6
2	N	Bare	B	1.29	7.64	42.9	-27.4	-5.9	-2.4	1149.2	39.3	1510.5	34.8	15.4
2	N	Bare	B	1.23	7.95	40.6	-47.2	-3.9	-1.6	1283.9	8.8	1182.2	57.3	11.5
2	N	Bare	B	1.47	7.96	36.1	-40.5	-3.4	-1.6	985.0	7.2	1826.7	17.3	16.7
2	N	rye	B	1.11	7.95	39.7	-19.5	-2.1	-0.6	434.6	3.7	408.3	20.1	23.2

PV	Water	cover	site	EC (dS m^{-1})	pH	Na (mg g^{-1})	Ca (mg g^{-1})	Mg (mg g^{-1})	K (mg g^{-1})	DOC (mg m^{-2})	NO_3-N (mg m^{-2})	NH_4-N (mg m^{-2})	DON (mg m^{-2})	PO_4-P (mg m^{-2})
2	N	rye	B	0.94	7.86	61.1	-24.7	-2.6	-0.2	459.3	2.6	456.8	16.9	33.4
2	N	rye	B	1.03	7.47	51.0	-18.6	-2.9	-1.0	472.5	4.3	585.3	34.3	23.8
3	DDW	Bare	A	0.37	6.75	-3.3	-9.0	-1.3	-4.3	939.6	11.7	607.0	39.8	31.6
3	DDW	Bare	A	0.43	6.77	-3.2	-14.7	-1.9	-2.8	908.2	10.6	874.1	3.0	25.7
3	DDW	Bare	A	0.19	6.7	-2.7	-9.3	-1.2	-4.0	945.3	12.6	516.4	20.5	16.3
3	DDW	mulch	A	0.51	6.39	-6.0	-16.0	-2.5	-2.3	799.6	9.8	956.6	4.7	17.4
3	DDW	mulch	A	0.43	6.65	-1.9	-16.2	-1.9	-1.7	747.2	17.3	902.4		10.4
3	DDW	mulch	A	0.94	5.43	-7.1	-38.8	-8.6	-6.3	889.8	25.8	3027.2		44.7
3	DDW	rye	A	0.44	6.95	-10.5	-14.3	-2.4	-0.7	462.9	2.1	1048.7		20.4
3	DDW	rye	A	0.16	7.05	-6.1	-7.6	-1.4	-1.1	322.2	7.1	497.5	8.4	13.6
3	DDW	rye	A	0.18	7.16	-8.1	-11.3	-1.1	-1.2	648.3	10.2	544.0	20.2	28.2
3	Tap	Bare	A	0.79	7.92	42.4	-12.7	-2.1	-1.8	951.6	25.2	473.5	16.3	11.7
3	Tap	Bare	A	0.59	6.81	78.1	-16.4	-2.7	-7.3	1250.6	38.9	527.6	42.8	18.2
3	Tap	Bare	A	0.69	7.67	57.2	-18.8	-2.4	-2.9	1251.2	38.4	415.1	30.0	13.3
3	Tap	mulch	A	0.80	8.27	59.0	-13.8	-2.0	-0.6	912.3	6.1	458.6		9.1
3	Tap	mulch	A	0.72	8.07	51.8	-8.8	-1.7	-2.4	1178.4	15.6	364.5	50.9	10.2
3	Tap	mulch	A	0.77	7.76	57.3	-16.4	-2.9	-1.2	1031.3	8.8	624.4	33.5	23.9
3	Tap	rye	A	0.71	8.27	43.7	-8.7	-1.6	-1.0	916.1	7.1	211.1	52.7	12.9
3	Tap	rye	A	0.00		36.2	-12.0	-1.4	-1.3	793.3	2.7	166.3	27.3	16.2
3	Tap	rye	A	0.75	7.89	43.3	-11.6	-1.8	-0.1	836.1	2.4	348.7	10.2	13.5
3	N	Bare	A	0.97	7.71	50.0	-30.2	-2.9	-0.6	645.3	3.4	235.9	8.9	50.7
3	N	Bare	A	1.11	7.79	34.7	-16.9	-3.4	-1.4	934.6	29.5	780.7		9.5
3	N	Bare	A	1.01	7.66	56.1	-30.1	-5.4	-0.4	1209.0	5.1	611.0	65.2	30.6
3	N	rye	A	0.90	7.72	52.4	-14.3	-2.5	-1.3	534.8	4.5	304.4	7.3	14.3
3	N	rye	A	1.05	7.81	34.6	-13.7	-2.0	-0.7	414.9	3.2	333.1	5.3	15.9
3	N	rye	A	1.05	8.01	56.6	-27.6	-2.3	0.1	681.0	2.7	443.2	15.3	28.8

PV	Water	cover	site	EC (dS m^{-1})	pH	Na (mg g^{-1})	Ca (mg g^{-1})	Mg (mg g^{-1})	K (mg g^{-1})	DOC (mg m^{-2})	NO_3-N (mg m^{-2})	NH_4-N (mg m^{-2})	DON (mg m^{-2})	PO_4-P (mg m^{-2})
3	DDW	Bare	B	0.65	6.89	-1.7	-24.2	-2.6	-1.9	1343.8	9.4	1510.6		14.5
3	DDW	Bare	B	1.11	7.08	-6.6	-35.0	-3.7	-0.8	1224.4	6.6	2983.4		47.3
3	DDW	Bare	B	0.98	6.3	-8.5	-34.5	-4.9	-4.6	2073.7	55.5	2795.0		17.8
3	DDW	mulch	B	1.03	7.66	-29.9	-20.2	-1.9	-2.1	1027.5	16.7	1787.4		32.4
3	DDW	mulch	B	0.84	7.41	-3.9	-29.9	-3.5	-3.0	1159.5	16.7	2434.7		38.2
3	DDW	mulch	B	0.66	7.11	-10.1	-29.4	-3.4	-0.9	1812.4	14.6	1568.2		112.2
3	DDW	rye	B	0.45	7.56	-1.2	-19.4	-2.7	-1.2	877.6	3.1	904.7	11.5	64.2
3	DDW	rye	B	1.69	4.41	-3.5	-11.6	-1.1	-0.9	666.2	2.0	357.1	26.7	25.9
3	DDW	rye	B	0.12	7	-1.7	-8.8	-1.1	-0.9	1106.6	3.3	346.7	47.0	139.1
3	Tap	Bare	B	0.63	7.76	65.2	-13.2	-1.2	-0.2	809.7	5.3	269.0	34.6	5.7
3	Tap	Bare	B	1.65	6.83	63.7	-40.6	-6.8	-2.2	1549.5	75.0	3670.6		25.1
3	Tap	Bare	B	1.17	7.33	70.2	-45.2	-5.3	-3.3	1794.0	18.9	2592.8		72.9
3	Tap	mulch	B	0.77	7.66	51.7	-12.6	-1.7	-3.3	1345.9	12.4	602.2	18.9	21.4
3	Tap	mulch	B	1.84	8.3	43.8	-55.3	-3.9	-0.8	698.6	2.7	1070.6	####	15.5
3	Tap	mulch	B	0.84	8.33	49.5	-24.0	-2.6	-1.0	1268.9	3.1	301.6	58.7	51.0
3	Tap	rye	B	0.82	8.29	50.1	-18.3	-1.6	-0.8	827.9	3.9	307.0	41.9	24.2
3	Tap	rye	B	0.85	8.36	47.1	-23.5	-2.2	-0.6	716.4	2.7	606.2		36.1
3	Tap	rye	B	0.65	8.23	59.8	-21.1	-1.8	-0.4	1106.1	3.0	221.4	50.7	88.8
3	N	Bare	B	1.20	7.61	34.6	-22.3	-4.6	-1.7	1044.3	28.3	1096.2		13.3
3	N	Bare	B	1.16	8.24	47.1	-29.7	-2.4	-0.6	760.6	4.8	303.2	24.4	6.7
3	N	Bare	B	1.31	8.2	38.6	-26.0	-2.2	-0.9	678.0	2.2	826.8		12.8
3	N	rye	B	1.12	7.97	39.0	-15.6	-1.4	-0.4	407.5	2.5	264.1	8.4	21.8
3	N	rye	B	0.95	7.91	57.5	-17.1	-1.8	-0.2	396.8	1.4	208.3	15.9	28.1
3	N	rye	B	0.00		49.3	-18.7	-2.9	-1.0	561.6	3.2	471.5	3.7	26.3
7	DDW	Bare	A	0.06	6.94	-2.2	-1.7	-0.2	-1.7	494.1	4.4	73.0	25.3	27.1
7	DDW	Bare	A	0.08	6.9	-2.6	-3.5	-0.4	-1.2	814.7	4.4	87.2	39.4	14.0

PV	Water	cover	site	EC (dS m^{-1})	pH	Na (mg g^{-1})	Ca (mg g^{-1})	Mg (mg g^{-1})	K (mg g^{-1})	DOC (mg m^{-2})	NO_3-N (mg m^{-2})	NH_4-N (mg m^{-2})	DON (mg m^{-2})	PO_4-P (mg m^{-2})
7	DDW	Bare	A	0.06	6.76	-2.5	-2.7	-0.3	-1.7	634.1	5.3	84.7	31.7	14.4
7	DDW	mulch	A	0.06	6.86	-4.7	-7.4	-0.9	-0.6	902.8	6.5	39.8	47.7	17.2
7	DDW	mulch	A	0.07	6.87	-1.4	-3.3	-0.3	-0.7	724.0	9.5	88.8	28.0	6.1
7	DDW	mulch	A	0.08	6.09	-0.9	-4.8	-0.7	-2.2	949.7	7.7	123.2	52.6	59.4
7	DDW	rye	A	0.06	7.23	-1.2	-3.7	-0.4	-0.6	542.4	4.6	140.2	28.0	28.0
7	DDW	rye	A	0.07	7.44	-0.5	-2.4	-0.4	-0.4	274.1	4.1	127.5	10.2	14.5
7	DDW	rye	A	0.08	7.5	-4.8	-6.8	-0.6	-0.4	639.8	4.0	96.9	32.2	27.3
7	Tap	Bare	A	0.61	7.89	47.2	-3.3	-0.6	-1.0	878.1	14.3	76.6	38.0	13.2
7	Tap	Bare	A	0.33	7.33	69.4	-4.2	-0.4	-3.0	1849.2	11.0	110.8	111.5	30.5
7	Tap	Bare	A	0.44	7.7	68.3	-6.9	-0.7	-0.9	1586.5	14.8	86.3	76.7	9.1
7	Tap	mulch	A	0.53	7.95	62.3	-8.0	-1.0	-0.1	1448.5	6.8	107.0	83.9	14.9
7	Tap	mulch	A	0.45	7.75	61.2	-4.9	-0.7	-0.7	1729.8	20.2	53.4	114.8	9.6
7	Tap	mulch	A	0.52	7.7	58.3	-6.1	-1.0	-0.5	1378.1	8.0	101.0	92.5	24.8
7	Tap	rye	A	0.51	8.07	50.8	-3.2	-0.4	-0.4	1099.1	7.6	46.1	43.7	12.7
7	Tap	rye	A	0.73	8.27	44.6	-7.6	-0.8	-0.7	974.4	5.7	66.2	56.0	21.8
7	Tap	rye	A	0.60	7.93	48.7	-5.1	-0.8	-0.4	869.7	7.0	66.4	37.1	17.8
7	N	Bare	A	0.66	8.11	55.6	-11.8	-0.9	-0.3	1308.6	7.7	122.8	84.6	57.6
7	N	Bare	A	0.83	7.82	44.8	-8.0	-1.5	-0.5	978.1	13.3	196.6	65.5	13.1
7	N	Bare	A	0.66	7.8	51.7	-9.3	-1.6	0.0	1455.3	6.6	84.5	95.8	27.0
7	N	rye	A	0.77	7.64	45.9	-9.6	-1.4	-1.0	719.3	7.8	50.2	28.4	15.6
7	N	rye	A	0.98	7.54	30.5	-7.5	-1.2	-0.5	565.8	6.1	95.9	21.4	24.3
7	N	rye	A	0.83	8.02	44.9	-11.7	-1.0	0.1	982.4	5.7	111.0	57.3	25.2
7	DDW	Bare	B	0.08	6.9	-1.9	-4.4	-0.4	-0.8	836.9	4.9	96.1	56.6	12.0
7	DDW	Bare	B	0.11	7.28	0.0			0.0	1234.9	5.2	105.8	95.8	70.9
7	DDW	Bare	B	0.07	6.71	-0.7	-3.7	-0.5	-1.8	1112.6	10.4	123.3	60.6	25.2
7	DDW	mulch	B	0.17	8.307	-8.7	-4.6	-0.4	-1.0	722.9	4.2	68.5	38.7	37.8

PV	Water	cover	site	EC (dS m^{-1})	pH	Na (mg g^{-1})	Ca (mg g^{-1})	Mg (mg g^{-1})	K (mg g^{-1})	DOC (mg m^{-2})	NO_3-N (mg m^{-2})	NH_4-N (mg m^{-2})	DON (mg m^{-2})	PO_4-P (mg m^{-2})
7	DDW	mulch	B	0.07	7.89	-1.0	-5.2	-0.5	-0.6	863.8	5.7	53.7	48.8	35.7
7	DDW	mulch	B	0.07	7.42	-5.5	-6.7	-0.6	-0.8	1210.3	5.8	37.9	97.0	176.7
7	DDW	rye	B	0.08	7.81	-4.5	-5.6	-0.7	-0.8	696.4	4.4	65.6	43.5	81.2
7	DDW	rye	B	0.09	7.97	-0.4	-5.6	-0.5	-0.5	488.8	4.0	48.4	29.0	37.0
7	DDW	rye	B	0.05	7.51	-0.6	-2.9	-0.3	-0.4	644.5	4.1	51.5	31.3	111.1
7	Tap	Bare	B	0.61	8.02	53.4	-7.7	-0.6	-0.1	983.8	5.4	73.0	59.0	6.8
7	Tap	Bare	B	0.34	6.79	66.9	-5.1	-0.7	-0.8	3642.9	25.0	228.5	241.8	65.5
7	Tap	Bare	B	0.48	7.43	64.0	-9.4	-1.0	-1.0	2331.4	10.9	229.5	150.5	122.3
7	Tap	mulch	B	0.44	7.57	79.1	0.8	0.1	0.6	1581.0	7.5	88.8	82.6	19.5
7	Tap	mulch	B	0.78	8.33	45.3	-16.2	-1.2	-0.6	1049.4	5.2	205.1	66.4	22.7
7	Tap	mulch	B	0.73	8.4	46.2	-10.1	-1.0	-0.7	1187.4	6.4	44.8	73.1	57.4
7	Tap	rye	B	0.60	8.35	51.9	-9.1	-0.9	-0.3	836.8	6.3	85.5	44.4	26.2
7	Tap	rye	B	0.69	8.45	58.0	-4.6	-0.5	-2.0	992.7	5.4	117.7	58.6	44.0
7	Tap	rye	B	0.55	8.38	55.7	-11.5	-0.9	0.0	1323.0	5.4	68.8	104.2	96.3
7	N	Bare	B	0.00	7.51	43.5	-7.5	-1.4	-0.6	1317.3	13.0	144.3	75.6	17.9
7	N	Bare	B	0.85	8.13	37.9	-15.5	-1.2	-0.3	995.2	6.4	41.7	53.3	10.4
7	N	Bare	B	0.90	8.24	37.6	-15.8	-1.4	-0.7	862.0	5.9	92.9	53.0	20.8
7	N	rye	B	0.95	8.07	45.8	-11.8	-1.1	-0.1	576.0	4.6	85.3	40.5	24.1
7	N	rye	B	0.80	7.98	43.7	-12.6	-1.2	-0.2	779.3	5.5	69.0	50.5	37.4
7	N	rye	B	0.84	7.58	40.4	-12.4	-1.5	-0.6	711.2	7.0	94.4	44.3	38.6
10	DDW	Bare	A	0.09	6.73	-2.7	-1.6	-0.2	-1.4	378.9	1.8	80.4	19.4	17.7
10	DDW	Bare	A	0.08	6.68	-2.4	-2.2	-0.2	-1.1	458.9	2.1	69.5	21.3	9.6
10	DDW	Bare	A	0.07	6.64	-2.4	-2.1	-0.2	-1.5	450.8	2.7	74.8	22.3	7.2
10	DDW	mulch	A	0.06	6.95	-2.1	-2.2	-0.2	-1.0	682.9	2.7	36.5	37.0	13.0
10	DDW	mulch	A	0.05	7.13	-1.4	-1.7	-0.1	-0.4	567.9	4.2	18.6	23.9	4.8
10	DDW	mulch	A	0.06	6.39	-0.9	-2.7	-0.3	-1.6	693.4	3.7	57.9	40.9	50.6

PV	Water	cover	site	EC (dS m^{-1})	pH	Na (mg g^{-1})	Ca (mg g^{-1})	Mg (mg g^{-1})	K (mg g^{-1})	DOC (mg m^{-2})	NO_3-N (mg m^{-2})	NH_4-N (mg m^{-2})	DON (mg m^{-2})	PO_4-P (mg m^{-2})
10	DDW	rye	A	0.03	7.6	-0.9	-2.0	-0.2	-0.3	394.2	1.7	33.9	19.2	16.6
10	DDW	rye	A	0.05	7.32	-1.0	-1.8	-0.2	-0.3	290.5	1.7	87.6	10.4	11.6
10	DDW	rye	A	0.06	7.51	-0.9	-2.9	-0.3	-0.3	476.6	21.3	58.6	17.6	17.7
10	Tap	Bare	A	0.75	8.15	41.9	-2.6	-0.3	-0.6	741.8	7.3	32.6	36.7	9.2
10	Tap	Bare	A	0.58	7.61	52.6	-3.8	-0.5	-3.0	1185.2	4.5	88.4	73.3	21.8
10	Tap	Bare	A	0.61	7.92	55.3	-4.9	-0.7	-1.1	1094.8	12.7	48.1	49.6	5.8
10	Tap	mulch	A	0.71	8.2	50.9	-8.6	-1.2	-0.1	1158.8	11.1	123.6	74.9	13.2
10	Tap	mulch	A	0.70	7.12	45.1	-5.9	-0.9	-0.6	1106.3	13.2	43.3	78.2	6.1
10	Tap	mulch	A	0.65	7.87	44.7	-7.1	-1.0	-0.6	1220.2	8.6	69.6	76.1	18.0
10	Tap	rye	A	0.71	8.4	35.1	-3.0	-0.4	-0.3	862.5	4.6	50.3	43.6	9.0
10	Tap	rye	A	0.84	8.44	35.8	-5.9	-0.6	-0.5	757.0	13.9	75.4	42.5	19.2
10	Tap	rye	A	0.69	8.55	38.7	-4.6	-0.5	0.0	1103.9	11.6	52.2	58.5	9.4
10	N	Bare	A	1.05	8.35	39.1	-12.6	-1.0	-0.2	628.1	2.2	69.6	35.3	30.6
10	N	Bare	A	0.99	8.18	33.7	-9.9	-1.5	-0.3	585.1	5.7	130.6	27.2	5.8
10	N	Bare	A	1.04	8.07	33.7	-11.3	-1.9	-0.2	839.0	2.3	85.3	52.8	12.7
10	N	rye	A	0.99	7.88	33.5	-9.9	-1.6	-0.9	499.3	3.0	57.9	23.2	11.7
10	N	rye	A	0.99	7.83	32.8	-8.0	-1.3	-0.5	452.5	2.1	79.8	19.0	13.2
10	N	rye	A	1.07	8.06	31.7	-14.3	-1.4	0.0	643.1	2.1	107.2	34.2	16.7
10	DDW	Bare	B	0.10	6.6	-2.8	-2.4	-0.2	-0.8	460.0	5.8	102.6	22.5	7.5
10	DDW	Bare	B	0.10	7	-2.2	-5.7	-0.5	-0.5	901.5	2.4	120.9	65.7	52.3
10	DDW	Bare	B	0.07	6.7	-1.6	-3.4	-0.3	-1.2	605.2	4.2	140.8	31.8	20.4
10	DDW	mulch	B	0.13	7.77	-5.5	-3.6	-0.3	-1.0	515.4	1.8	58.2	28.7	21.6
10	DDW	mulch	B	0.05	7.87	-1.7	-2.8	-0.3	-0.6	572.0	2.5	45.4	28.3	23.5
10	DDW	mulch	B	0.08	7.54	-1.0	-5.0	-0.5	-0.5	908.4	12.7	52.4	73.4	123.0
10	DDW	rye	B	0.08	7.59	-0.5	-4.3	-0.4	-0.3	547.1	3.6	67.0	34.8	42.6
10	DDW	rye	B	0.08	7.96	-0.7	-3.8	-0.3	-0.4	390.0	12.2	103.6	18.2	21.5

PV	Water	cover	site	EC (dS m^{-1})	pH	Na (mg g^{-1})	Ca (mg g^{-1})	Mg (mg g^{-1})	K (mg g^{-1})	DOC (mg m^{-2})	NO_3-N (mg m^{-2})	NH_4-N (mg m^{-2})	DON (mg m^{-2})	PO_4-P (mg m^{-2})
10	DDW	rye	B	0.05	7.44	-2.0	-3.1	-0.3	-1.3	609.0	7.2	60.3	32.0	63.9
10	Tap	Bare	B	0.80	8.25	38.9	-6.4	-0.5	0.0	771.1	2.6	74.7	40.1	6.5
10	Tap	Bare	B	0.53	7.11	48.8	-5.4	-0.5	-0.4	2470.2	39.3	135.5	164.2	32.7
10	Tap	Bare	B	0.77	7.78	44.3	-6.4	-0.7	-0.8	1232.3	9.9	186.8	87.3	72.8
10	Tap	mulch	B	0.59	7.88	49.3	-4.3	-0.5	-1.6	1615.9	10.2	47.5	84.3	13.2
10	Tap	mulch	B	0.93	8.5	40.5	-13.8	-1.0	-0.7	816.0	2.1	68.4	56.7	21.7
10	Tap	mulch	B	0.92	8.56	31.5	-10.5	-1.0	-0.8	882.6	4.1	32.6	51.8	42.9
10	Tap	rye	B	0.78	8.56	42.7	-6.5	-0.6	-0.1	638.0	14.1	61.0	35.6	23.3
10	Tap	rye	B	0.88	8.54	38.4	-12.5	-1.1	-0.2	994.7	8.9	181.7	49.2	42.5
10	Tap	rye	B	0.79	8.5	39.1	-13.0	-1.0	-0.2	1515.6	5.9	151.5	112.6	92.1
10	N	Bare	B	1.02	7.92	30.1	-8.2	-1.5	-0.4	806.9	5.1	92.4	45.6	5.9
10	N	Bare	B	1.16	8.21	17.6	-14.0	-1.2	-0.6	560.4	2.1	46.7	28.7	4.7
10	N	Bare	B	1.12	8.31	20.4	-8.0	-1.2	-0.8	515.1	1.7	108.4	29.9	11.6
10	N	rye	B	1.11	8.13	29.3	-14.5	-1.2	-0.3	571.9	2.1	79.0	51.0	21.8
10	N	rye	B	0.99	8.15	27.3	-13.0	-1.2	-0.3	649.1	2.0	58.6	43.2	32.1
10	N	rye	B	0.99		36.5	-12.3	-1.8	-0.7	501.6	2.3	92.5	38.7	16.6
11	DDW	Bare	A	0.08	7.54	-2.8	-2.9	-0.5	-1.6	403.2	3.0	59.9	26.7	18.6
11	DDW	Bare	A	0.08	7.61	-2.3	-3.7	-0.5	-1.1	668.6	1.9	56.7	36.1	12.9
11	DDW	Bare	A	0.07	7.57	-3.0	-3.0	-0.4	-1.3	422.6	1.7	45.1	24.9	6.2
11	DDW	mulch	A	0.05	6.56	-2.5	-3.3	-0.5	-1.0	720.9	2.7	24.2	45.2	12.0
11	DDW	mulch	A	0.05	7.87	-4.8	-3.9	-0.5	-0.7	680.3	5.4	14.6	38.9	5.4
11	DDW	mulch	A	0.04	7.98	-1.8	-4.3	-0.7	-2.1	786.9	2.8	30.9	50.2	55.2
11	DDW	rye	A	0.03	7.43	-1.7	-2.7	-0.4	-0.7	619.7	2.2	27.9	60.9	20.8
11	DDW	rye	A	0.04	7.61	-1.5	-3.5	-0.5	-0.6	332.7	2.4	63.1	16.9	12.4
11	DDW	rye	A	0.07	7.95	-1.6	-5.3	-0.7	-0.9	591.9	1.6	59.8	33.0	23.0
11	Tap	Bare	A	0.18	8.03	-18.4	-2.8	-0.5	-1.1	851.0	3.2	23.0	52.6	6.0

PV	Water	cover	site	EC (dS m^{-1})	pH	Na (mg g^{-1})	Ca (mg g^{-1})	Mg (mg g^{-1})	K (mg g^{-1})	DOC (mg m^{-2})	NO$_3$-N (mg m^{-2})	NH$_4$-N (mg m^{-2})	DON (mg m^{-2})	PO$_4$-P (mg m^{-2})
11	Tap	Bare	A	0.49	8.07	-30.0	-5.7	-0.8	-3.0	1160.8	3.6	68.3	80.6	29.2
11	Tap	Bare	A	0.41	7.23	-27.8	-5.6	-0.7	-1.3	1256.7	7.7	33.8	71.4	8.6
11	Tap	mulch	A	0.44	7.9	-23.7	-5.7	-0.9	-0.9	1173.1	2.8	79.0	79.9	13.2
11	Tap	mulch	A	0.51	7.75	-31.2	-5.2	-0.8	-1.3	1612.7	11.1	34.6	142.2	8.5
11	Tap	mulch	A	0.20	8.39	-18.0	-3.8	-0.4	-0.7	1683.4	4.6	62.5	123.0	30.0
11	Tap	rye	A	0.18	8.3	-14.3	-2.9	-0.5	-1.0	1064.6	4.5	55.4	65.5	14.7
11	Tap	rye	A	0.34	8.39	-21.2	-3.7	-0.4	-0.8	857.6	2.5	59.4	65.8	24.1
11	Tap	rye	A	0.13	8.46	-10.1	-3.7	-0.5	-0.7	1145.6	2.4	27.5	104.2	7.6
11	N	Bare	A	0.71	7.82	-37.8	-8.0	-0.8	-0.8	820.8	1.9	47.9	60.7	55.5
11	N	Bare	A	0.76	7.67	-33.3	-7.7	-1.1	-0.7	997.5	2.3	76.8	71.6	24.4
11	N	Bare	A	0.53	7.77	-23.5	-6.3	-1.1	-0.7	694.5	3.3	72.7	54.2	5.4
11	N	rye	A	0.47	7.68	-30.2	-5.8	-0.9	-1.1	424.9	2.8	35.8	32.0	15.2
11	N	rye	A	0.38	7.92	-16.7	-6.1	-1.0	-1.0	862.3	2.8	61.1	81.3	23.6
11	N	rye	A	0.69	8	-34.0	-10.3	-1.1	-3.1	683.6	4.3	81.0	25.0	34.7
11	DDW	Bare	B	0.09	7.16	-1.3	-2.6	-0.3	-0.5	416.1	0.9	37.7	31.6	5.3
11	DDW	Bare	B	0.09	7.22	-2.0	-5.4	-0.7	-0.7	894.0	2.2	61.1	76.8	58.5
11	DDW	Bare	B	0.06	7.22	-5.8	-4.7	-0.8	-2.1	750.8	3.5	102.7	46.8	28.0
11	DDW	mulch	B	0.14	7.52	-6.1	-5.4	-0.7	-1.0	546.3	1.5	30.6	36.5	24.6
11	DDW	mulch	B	0.06	7.53	-1.2	-5.1	-0.8	-1.1	663.9	3.1	31.5	45.1	26.8
11	DDW	mulch	B	0.07	7.46	-1.4	-6.2	-0.8	-0.8	913.3	2.1	25.0	80.7	141.6
11	DDW	rye	B	0.09	7.52	-3.8	-6.7	-0.8	-0.6	687.5	2.0	62.7	43.9	49.6
11	DDW	rye	B	0.06	7.66	-3.0	-4.6	-0.6	-0.6	446.8	2.9	62.1	27.7	22.0
11	DDW	rye	B	0.05	7.48	-1.6	-3.7	-0.5	-0.6	652.0	2.0	49.8	43.4	76.3
11	Tap	Bare	B	0.45	7.73	-19.8	-5.2	-0.6	-0.8	968.5	2.5	66.9	67.5	10.7
11	Tap	Bare	B	0.48	8.19	-42.1	-6.9	-0.9	-1.5	2944.6	16.8	113.1	221.2	48.2
11	Tap	Bare	B	0.49	7.98	-28.3	-6.2	-0.8	-1.7	1404.1	4.3	156.6	100.3	102.6

PV	Water	cover	site	EC (dS m^{-1})	pH	Na (mg g^{-1})	Ca (mg g^{-1})	Mg (mg g^{-1})	K (mg g^{-1})	DOC (mg m^{-2})	NO$_3$-N (mg m^{-2})	NH$_4$-N (mg m^{-2})	DON (mg m^{-2})	PO$_4$-P (mg m^{-2})
11	Tap	mulch	B	0.36	8.38	-21.8	-4.5	-0.7	-1.7	1679.5	4.1	34.5	95.7	21.3
11	Tap	mulch	B	0.66	8.27	-31.9	-9.0	-1.1	-1.4	1158.9	1.8	27.3	84.1	72.7
11	Tap	rye	B	0.65	8.41	-28.1	-8.2	-1.0	-1.2	1358.5	3.0	91.0	119.8	38.5
11	Tap	rye	B	0.55	8.56	-30.7	-9.1	-1.1	-1.4	1292.3	3.6	113.4	115.7	75.0
11	Tap	rye	B	0.69	8.8	-20.3	-5.5	-0.8	-1.0	916.4	3.0	59.2	74.8	59.8
11	N	Bare	B	0.62	8.13	-24.6	-6.3	-1.0	-1.0	906.0	8.7	75.4	55.9	8.6
11	N	Bare	B	0.79	7.81	-33.5	-11.1	-1.1	-1.1	780.2	1.9	41.8	53.5	9.4
11	N	Bare	B	0.69	7.66	-28.3	-9.7	-0.8	-0.9	635.6	0.0	0.0	85.6	0.0
11	N	rye	B	0.57		-26.8	-9.4	-1.2	-1.0	793.5	2.3	61.9	43.9	41.7
11	N	rye	B	0.58		-28.8	-9.6	-1.1	-1.1	3043.6	2.2	48.6	####	64.8
11	N	rye	B	0.00										
15	DDW	Bare	A	0.06	7.35	-3.4	-1.7	-0.3	-2.0	381.9	3.7	61.1	20.4	19.4
15	DDW	Bare	A	0.06	7.24	-2.0	-3.0	-0.4	-1.5	674.1	1.4	34.5	46.5	9.9
15	DDW	Bare	A	0.05	7.38	-2.0	-2.2	-0.3	-1.6	449.4	2.7	43.7	32.5	6.0
15	DDW	mulch	A	0.05	7.42	-1.8	-2.8	-0.4	-0.9	677.9	1.6	10.9	40.6	7.5
15	DDW	mulch	A	0.05	7.45	-1.8	-2.7	-0.4	-0.7	560.3	1.5	16.7	37.0	4.2
15	DDW	mulch	A	0.03	7	-1.2	-2.7	-0.4	-1.3	508.0	4.2	10.0	38.6	36.5
15	DDW	rye	A	0.03	7.84	-1.9	-2.6	-0.4	-0.4	407.4	1.9	20.9	27.0	17.7
15	DDW	rye	A	0.04	7.46	-1.4	-2.6	-0.4	-0.4	335.7	2.0	57.2	20.8	11.9
15	DDW	rye	A	0.09	7.71	-3.5	-5.6	-0.7	-0.7	543.2	1.9	56.3	27.3	20.3
15	Tap	Bare	A	0.76	8.32	36.7	-4.3	-0.7	-0.7	835.7	5.7	29.3	54.3	8.7
15	Tap	Bare	A	0.79	8.12	35.5	-4.7	-0.7	-3.2	1114.3	5.4	55.7	68.2	21.9
15	Tap	Bare	A	0.77	8.2	33.8	-5.6	-0.9	-1.8	1272.9	12.4	48.1	67.3	6.8
15	Tap	mulch	A	0.82	8.66	37.5	-8.5	-1.3	-0.2	1035.5	3.7	105.0	61.8	13.7
15	Tap	mulch	A	0.82	8.44	33.6	-6.0	-1.0	-0.7	1096.6	15.0	34.9	77.8	7.9
15	Tap	mulch	A	0.67	8.22	42.3	-6.3	-1.1	-0.8	1572.1	5.4	58.3	111.9	16.9

PV	Water	cover	site	EC (dS m^{-1})	pH	Na (mg g^{-1})	Ca (mg g^{-1})	Mg (mg g^{-1})	K (mg g^{-1})	DOC (mg m^{-2})	NO_3-N (mg m^{-2})	NH_4-N (mg m^{-2})	DON (mg m^{-2})	PO_4-P (mg m^{-2})
15	Tap	rye	A	0.75	8.58	27.3	-3.6	-0.6	-0.6	892.1	6.0	46.6	49.1	8.5
15	Tap	rye	A	0.88	8.6	30.4	-6.8	-0.9	-0.7	818.5	3.4	97.5	40.9	17.1
15	Tap	rye	A	0.78	8.84	31.6	-5.7	-0.8	-0.2	1272.7	5.3	40.8	66.1	8.2
15	N	Bare	A	1.12	8.7	29.5	-12.8	-1.3	-0.7	541.7	2.3	127.1	13.3	28.3
15	N	Bare	A	0.96	8.2	25.9	-8.7	-1.3	-0.5	627.7	3.4	59.9	33.4	5.6
15	N	Bare	A	1.05	8.09	27.9	-9.7	-1.7	-0.3	813.4	1.9	96.7	45.8	12.1
15	N	rye	A	1.00	7.82	29.3	-9.5	-1.3	-0.9	493.3	4.1	51.5	23.8	11.1
15	N	rye	A	1.04	7.87	24.5	-7.0	-1.1	-0.5	456.0	2.1	43.8	25.5	13.9
15	N	rye	A	1.09	8.33	29.6	-12.5	-1.1	0.1	578.3	3.1	87.9	26.9	18.2
15	DDW	Bare	B	0.07	7.32	-1.9	-3.3	-0.4	-1.0	502.7	1.9	50.7	41.9	6.3
15	DDW	Bare	B	0.04	7.15	-1.8	-2.4	-0.4	-1.1	510.5	1.8	55.7	35.0	18.2
15	DDW	Bare	B	0.08	7.33	-1.9	-5.6	-0.7	-0.7	768.6	2.1	59.9	67.3	57.8
15	DDW	mulch	B	0.15	7.6	-5.1	-6.1	-0.7	-1.1	503.5	1.7	19.7	34.3	19.2
15	DDW	mulch	B	0.08	7.87	-3.2	-4.7	-0.7	-1.2	578.3	3.6	43.1	43.1	21.6
15	DDW	mulch	B	0.06	7.63	-1.4	-5.6	-0.7	-0.8	692.5	1.5	19.5	59.4	131.7
15	DDW	rye	B	0.08	7.88	-2.1	-5.9	-0.7	-0.9	494.6	1.8	36.8	36.1	39.2
15	DDW	rye	B	0.41	8.05	-3.3	-15.9	-1.4	-0.9	286.5	1.4	66.5	19.8	12.8
15	DDW	rye	B	0.13	7.71	-3.5	-8.4	-1.0	-0.7	463.8	1.6	46.6	34.3	64.0
15	Tap	Bare	B	0.87	8.47	31.0	-6.5	-0.7	-0.3	833.2	2.9	77.3	41.9	6.8
15	Tap	Bare	B	0.77	7.81	31.8	-6.3	-0.8	-0.6	3096.4	23.3	67.2	216.3	33.9
15	Tap	Bare	B	0.80	8.13	35.5	-6.8	-0.9	-0.9	1488.4	4.0	81.5	111.0	86.1
15	Tap	mulch	B	0.69	8.24	37.0	-5.2	-0.8	-1.6	1655.5	5.9	27.4	96.7	15.4
15	Tap	mulch	B	0.99	8.41	32.3	-12.6	-1.1	-0.5	752.7	2.6	59.7	54.6	29.5
15	Tap	mulch	B	0.96	8.52	22.3	-9.0	-0.9	-1.0	873.8	2.8	33.5	59.0	45.1
15	Tap	rye	B	0.90	8.72	30.3	-8.6	-1.0	-0.3	656.8	3.1	90.1	33.6	34.7
15	Tap	rye	B	0.93	8.7	30.3	-12.1	-1.2	-0.4	809.6	2.8	129.4	37.2	47.5

PV	Water	cover	site	EC ($dS\ m^{-1}$)	pH	Na ($mg\ g^{-1}$)	Ca ($mg\ g^{-1}$)	Mg ($mg\ g^{-1}$)	K ($mg\ g^{-1}$)	DOC ($mg\ m^{-2}$)	NO_3-N ($mg\ m^{-2}$)	NH_4-N ($mg\ m^{-2}$)	DON ($mg\ m^{-2}$)	PO_4-P ($mg\ m^{-2}$)
15	Tap	rye	B	0.87	8.71	31.6	-11.1	-1.1	-0.3	1019.0	3.8	93.1	66.1	119.0
15	N	Bare	B	0.99	8.02	26.1	-7.8	-1.4	-0.5	871.1	2.2	80.7	47.3	4.8
15	N	Bare	B	1.19	8.34	20.1	-13.4	-1.1	-0.6	530.5	2.4	128.0	22.0	12.0
15	N	Bare	B	1.20	8.44	17.9	-15.4	-1.1	-0.3	571.3	1.5	49.9	32.2	6.5
15	N	rye	B	1.12	8.3	28.1	-11.7	-1.0	-0.3	390.8	1.7	68.1	23.6	17.9
15	N	rye	B	1.04	8.26	24.2	-10.3	-1.0	-0.3	555.9	1.5	57.5	31.7	29.3
15	N	rye	B	1.06	7.71	24.1	-7.8	-1.1	-0.6	363.3	3.2	95.1	11.8	15.4
16	DDW	Bare	A	0.07	7.66	-9.0	-1.5	-0.3	-1.3	359.1	0.0	44.7	23.6	15.9
16	DDW	Bare	A	0.08	7.62	-4.8	-2.3	-0.3	-1.0	621.6	25.8	34.4	12.4	11.9
16	DDW	Bare	A	0.07	7.63	-4.5	-1.5	-0.2	-1.1	441.0	0.0	35.2	20.4	5.2
16	DDW	mulch	A	0.05	7.6	-3.3	-2.3	-0.3	-1.0	797.6	0.0	41.4	14.1	12.1
16	DDW	mulch	A	0.04	7.65	-2.3	-1.9	-0.2	-0.5	496.6	8.6	14.6	24.5	13.6
16	DDW	mulch	A	0.03	7.1	-2.4	-2.2	-0.3	-1.4	626.8	1.0	15.4	42.1	45.7
16	DDW	rye	A	0.03	7.7	-2.8	-2.2	-0.3	-0.5	464.7	0.0	29.2	25.8	21.5
16	DDW	rye	A	0.03	7.58	-2.4	-1.7	-0.3	-0.4	360.4	6.5	20.0	41.2	9.8
16	DDW	rye	A	0.07	7.54	-2.8	-4.1	-0.5	-0.5	473.1	5.4	34.7	33.3	17.2
16	Tap	Bare	A	0.32	8.08	-17.4	-2.8	-0.4	-0.7	1040.3	8.7	39.4	60.8	10.1
16	Tap	Bare	A	0.63	7.9	-38.2	-3.9	-0.6	-3.2	1233.8	2.6	47.1	87.7	28.4
16	Tap	Bare	A	0.47	8.37	-38.7	-2.6	-0.4	-1.7	1169.3	18.7	50.7	60.5	9.4
16	Tap	mulch	A	0.56	8.34	-44.2	-5.1	-0.7	-0.9	1191.3	19.5	72.4	67.9	17.5
16	Tap	mulch	A	0.49	8.42	-35.2	-3.6	-0.5	-0.9	977.6	7.3	36.7	71.3	17.9
16	Tap	mulch	A	0.30	8.29	-22.2	-2.9	-0.4	-0.8	1737.1	26.7	39.4	111.5	21.8
16	Tap	rye	A	0.18	8.29	-23.2	-2.4	-0.3	-1.1	881.0	2.3	35.7	56.8	12.8
16	Tap	rye	A	0.37	8.67	-23.2	-2.8	-0.3	-0.8	783.6	0.2	63.5	46.7	21.3
16	Tap	rye	A	0.17	8.5	-18.3	-3.0	-0.4	-0.6	1035.8	42.4	39.6	25.3	13.7
16	N	Bare	A	0.80	8.64	-51.4	-7.6	-0.8	-1.1	732.2	1.0	77.1	55.2	47.1

PV	Water	cover	site	EC (dS m^{-1})	pH	Na (mg g^{-1})	Ca (mg g^{-1})	Mg (mg g^{-1})	K (mg g^{-1})	DOC (mg m^{-2})	NO$_3$-N (mg m^{-2})	NH$_4$-N (mg m^{-2})	DON (mg m^{-2})	PO$_4$-P (mg m^{-2})
16	N	Bare	A	0.50	8.25	-26.5	-4.5	-0.6	-0.6	575.9	0.1	37.8	47.5	9.9
16	N	Bare	A	0.71	8.06	-42.3	-6.2	-1.0	-0.7	829.1	0.0	79.7	64.6	16.4
16	N	rye	A	0.58	8.45	-32.4	-6.0	-0.7	-0.9	564.2	0.3	36.9	35.6	11.4
16	N	rye	A	0.44	7.97	-25.9	-4.2	-0.6	-0.7	512.4	0.0	38.9	35.9	14.0
16	N	rye	A	0.73	8.01	-36.4	-6.8	-0.6	-0.5	682.3	0.0	63.8	56.1	26.9
16	DDW	Bare	B	0.08	7.5	-4.1	-2.7	-0.3	-0.8	548.8	7.8	29.3	49.0	9.9
16	DDW	Bare	B	0.04	7.08	-3.2	-2.2	-0.3	-1.0	653.5	0.0	46.4	38.5	23.3
16	DDW	Bare	B	0.08	7.28	-3.0	-4.9	-0.6	-0.5	725.7	0.0	36.3	83.6	58.8
16	DDW	mulch	B	0.13	7.92	-5.2	-4.7	-0.6	-1.0	436.7	0.6	12.9	39.4	22.5
16	DDW	mulch	B	0.06	8.11	-3.7	-3.5	-0.5	-1.3	443.6	0.0	20.3	41.5	19.7
16	DDW	mulch	B	0.06	7.67	-2.3	-4.6	-0.6	-0.6	667.8	3.4	25.8	51.1	132.9
16	DDW	rye	B	0.07	7.85	-3.1	-4.6	-0.5	-0.3	509.3	0.0	34.5	48.0	38.5
16	DDW	rye	B	0.16	7.91	-4.4	-7.9	-0.8	-0.6	410.9	0.0	47.9	35.5	18.1
16	DDW	rye	B	0.15	7.65	-5.0	-6.9	-0.9	-0.6	521.6	3.9	39.2	37.3	51.4
16	Tap	Bare	B	0.45	8.59	-26.7	-3.2	-0.4	-0.6	786.1	0.7	56.7	57.9	9.3
16	Tap	Bare	B	0.68	8.1	-35.1	-3.9	-0.4	-0.9	1329.5	9.0	76.6	88.9	106.0
16	Tap	Bare	B	0.58	8.41	-36.5	-4.6	-0.5	-1.1	2407.2	11.2	24.5	169.0	34.0
16	Tap	mulch	B	0.38	8.11	-23.2	-2.6	-0.4	-1.2	1455.8	1.8	23.9	92.7	18.5
16	Tap	mulch	B	0.67	8.65	-35.7	-7.4	-0.8	-0.8	858.1	44.3	39.6	18.6	46.2
16	Tap	mulch	B	0.59	8.16	-34.6	-5.9	-0.6	-0.9	846.4	0.0	33.7	57.9	61.4
16	Tap	rye	B	0.60	8.64	-33.3	-4.9	-0.6	-0.7	620.1	0.0	61.9	50.3	50.5
16	Tap	rye	B	0.51	8.74	-31.7	-5.9	-0.6	-0.7	923.4	0.0	98.1	60.5	69.9
16	Tap	rye	B	0.63	8.68	-35.0	-6.2	-0.6	-0.7	992.5	0.0	72.6	73.5	163.0
16	N	Bare	B	0.60	7.77	-31.8	-4.4	-0.8	-0.7	892.2	0.0	52.1	66.8	8.8
16	N	Bare	B	0.76	8.02	-32.6	-8.5	-0.8	-0.9	557.1	0.0	79.2	39.8	22.6
16	N	Bare	B	0.83	8.3	-37.5	-9.5	-0.8	-0.7	567.2	0.0	38.2	40.2	10.1

PV	Water	cover	site	EC (dS m^{-1})	pH	Na (mg g^{-1})	Ca (mg g^{-1})	Mg (mg g^{-1})	K (mg g^{-1})	DOC (mg m^{-2})	NO_3-N (mg m^{-2})	NH_4-N (mg m^{-2})	DON (mg m^{-2})	PO_4-P (mg m^{-2})
16	N	rye	B	0.54	8.21	-24.7	-5.7	-0.5	-0.5	452.7	0.0	69.4	41.4	27.4
16	N	rye	B	0.46	8.28	-23.9	-4.4	-0.4	-0.5	487.9	0.0	38.7	43.8	38.5
16	N	rye	B	0.83	7.93	-19.6	-3.9	-0.5	-0.6	397.5	0.0	72.4	32.3	26.0

APPENDIX B

Appendix B Chemistry of municipal tap water used for irrigation at 33 cities across Texas: sodium and calcium concentrations, sodium adsorption ration (SAR), electrical conductivity (EC), the SAR divided by the EC (SAR/EC), pH, alkalinity (Alk), and percentage of sodium charge (% Na).

City	Na (mg L^{-1})	Ca (mg L^{-1})	SAR	EC (dS m^{-1})	SAR/EC	pH	Alk (mg L^{-1})	% Na (mmol(+) L^{-1})
Abilene	86.0	44.6	2.83	0.82	3.44	8.11	113.3	45.5
Austin	37.0	17.3	1.80	0.29	6.20	8.92	54.6	55.5
Bastrop	43.0	73.1	1.03	0.70	1.47	8.44	222.8	26.7
Beaumont	39.0	10.6	2.96	0.25	11.65	7.72	41.2	66.8
Bryan	189.0	1.0	30.00	0.93	32.26	9.08	369.0	88.4
Bryan	189.0	1.0	30.00	0.93	32.26	9.08	369.0	88.4
College Station	232.0	1.0	38.50	0.93	41.40	9.10	393.5	100.0
College Station	232.0	2.0	40.50	0.93	43.55	9.10	395.5	108.5
El Paso	110.0	5.0	3.70	0.67	5.52	7.78	102.0	71.4
El Paso	124.0	5.0	5.00	0.62	8.06	7.96	114.0	87.0
Falfurruias	149.0	41.8	5.97	1.23	4.84	7.71	189.7	52.6
Fort Stockton	86.0	26.7	3.10	0.57	5.44	7.88	124.8	65.6
Fredericksburg	43.0	67.1	1.03	0.81	1.27	7.54	236.2	23.1
Giddings	222.0	0.8	54.90	0.74	74.09	8.98	475.0	100.0
Giddings	257.0	0.9	69.00	0.82	84.15	8.87	475.0	110.0
Grand Prairie	47.0	25.3	2.28	0.34	6.77	7.12	62.0	60.6
Houston	43.0	34.3	1.88	0.44	4.30	8.29	98.7	42.8
Houston	43.0	34.3	1.91	0.44	4.37	8.29	98.7	42.8
Junction	31.0	11.7	1.90	0.18	10.56	7.88	102.0	74.9
Midland	313.0	121.4	4.82	2.43	1.98	7.24	74.3	56.0
Navasota	220.0	28.1	10.46	1.07	9.75	8.71	600.0	89.1
Round Rock	25.0	37.6	0.93	0.38	2.46	8.38	144.4	28.6
San Antonio	11.5	89.8	0.35	0.48	0.73	8.52	190.0	10.5
San Antonio	11.5	78.3	0.35	0.48	0.73	8.52	190.0	10.5
San Marcos	14.0	89.0	0.38	0.51	0.74	8.65	60.0	11.9
Snook	147.0	0.5	37.23	0.63	58.72	8.67	223.7	100.8
Somerville	136.0	1.2	32.75	0.58	56.96	8.57	212.0	102.8
Somerville	136.0	1.0	32.75	0.58	56.96	8.57	212.0	102.8
Sweetwater	35.0	70.6	0.96	0.76	1.27	7.57	125.9	20.0
Temple	31.0	49.5	0.99	0.44	2.23	8.27	143.7	30.4
Victoria	27.0	34.9	1.00	0.43	2.36	7.68	110.1	27.6

APPENDIX C

Appendix C Chemistry of 10:1 soil extract of 33 urban Texas soils: pH, electrical conductivity (EC), phosphate-P (PO_4-P), dissolved organic carbon (DOC), total dissolved nitrogen (TDN), nitrate-N (NO_3-N), ammonium-N (NH_4-N), and dissolved organic nitrogen (DON).

City	pH	EC (dS m^{-1})	PO_4-P (mg g^{-1})	DOC (mg g^{-1})	TDN (mg g^{-1})	NO_3-N (mg g^{-1})	NH_4-N (mg g^{-1})	DON (mg g^{-1})
Abilene	8.23	0.12	3.27	155.4	30.3	15.9	4.6	9.7
Austin	8.32	0.15	3.28	187.5	55.8	40.8	3.1	11.8
Bastrop	8.85	0.09	1.28	68.4	11.5	2.5	0.0	9.0
Beaumont	7.47	0.06	3.55	231.1	32.9	9.8	6.6	16.6
Bryan	9.47	0.34	6.67	548.5	50.5	5.5	9.0	36.0
Bryan	9.13	0.17	7.41	658.7	84.2	9.0	6.0	69.2
College Station	9.54	0.27	6.97	558.6	66.3	11.5	11.0	43.8
College Station	8.92	0.27	10.51	744.8	77.7	12.0	5.0	60.7
El Paso	8.77	0.07	2.41	83.0	7.2	1.8	1.3	4.1
El Paso	8.40	0.13	7.51	233.9	34.4	14.1	7.5	12.8
Falfurruias	8.17	0.12	8.86	132.6	27.5	18.9	3.5	5.2
Fort Stockton	8.15	0.25	7.08	313.6	58.8	29.9	5.6	23.3
Fredericksburg	8.24	0.12	9.86	195.5	39.9	20.8	5.4	13.7
Giddings	10.05	0.27	10.33	337.2	49.8	6.5	6.9	36.3
Giddings	10.04	0.47	18.58	1180.5	129.8	7.8	8.4	113.6
Grand Prairie	8.26	0.16	1.71	132.6	33.7	32.0	0.9	0.8
Houston	8.28	0.14	0.60	91.3	23.7	18.2	1.2	4.4
Houston	7.89	0.20	7.62	203.7	52.1	27.5	1.2	10.5
Junction	8.22	0.17	10.86	234.0	41.7	-	-	-
Midland	7.70	0.31	6.85	124.9	20.6	12.3	5.4	2.9
Navasota	8.64	0.20	16.89	322.5	61.0	8.5	11.9	40.6
Round Rock	8.35	0.14	0.89	117.2	20.5	8.4	1.2	10.9
San Antonio	8.16	0.17	2.65	146.7	39.7	15.0	-	24.7
San Antonio	8.19	0.16	3.53	125.8	41.2	20.0	-	21.2
San Marcos	8.45	0.16	1.41	163.2	32.6	16.2	5.1	11.2
Snook	7.86	0.11	14.10	285.8	56.6	19.0	12.3	25.3
Somerville	9.03	0.15		307.1	48.8	4.4	7.1	37.3
Somerville	8.10	0.15	17.81	294.3	40.1	-	7.2	32.9
Sweetwater	8.15	0.15	7.76	169.7	37.8	16.1	5.2	16.5
Temple	8.71	0.15	0.47	105.1	13.8	2.4	0.0	11.4
Victoria	8.07	0.14	9.63	185.0	48.8	32.3	3.9	12.6
Waco	7.92	0.27	2.31	211.4	50.6	33.5	3.4	13.7
Weslaco	8.82	0.10	7.70	128.9	20.2	6.6	2.6	11.0

APPENDIX D

Appendix D: Soil properties of 33 urban soils from Texas: percent sand, total soil nitrogen (N_S), total soil carbon (C_S), and calcium carbonate equivalents.

City	Sand (%)	N_S (%)	C_S (%)	$CaCO_3$
Abilene	44.8	0.18	2.3	38
Austin	57.1	0.23	4.2	13
Bastrop	57.6	0.04	3.7	14
Beaumont	58.1	0.15	1.9	21
Bryan	50.5	0.09	1.62	3.25
Bryan	56.7	0.16	1.13	32
College Station	47.8	0.11	1.45	9
College Station	59.4	0.18	2.335	20
El Paso	71.5	0.04	0.9	4
El Paso	85.7	0.12	1.5	8
Falfurruias	78.7	0.08	0.96	11
Fort Stockton	27.1	0.32	7.88	2
Fredericksburg	66.6	0.19	2.57	28
Giddings	88.7	0.12	1.52	3
Giddings	65.0	0.16	2.44	8
Grand Prairie	38.7	0.23	3.64	4
Houston	33.1	0.13	1.66	2
Houston	55.7	0.29	4.64	33
Junction	39.3	0.23	6.17	4
Midland	72.0	0.16	1.54	2
Navasota	65.8	0.2	2.03	2
Round Rock	32.6	0.15	4.99	2.25
San Antonio	16.2	0.21	3.9	2.25
San Antonio	20.1	0.19	7.515	2
San Marcos	50.5	0.22	4.95	2
Snook	73.7	0.18	1.93	2
Somerville	52.7	0.09	1.52	4
Somerville	59.1	0.34	3.50	2
Sweetwater	60.1	0.16	2.19	2
Temple	32.4	0.09	5.87	2
Victoria	66.2	0.24	5.69	2
Waco	41.6	0.3	4.88	2
Weslaco	59.1	0.09	1.61	2

APPENDIX E

Appendix E – Data from leaching of vegetation with salt solutions (Chapter III): salt type, vegetation (veg.) sodium adsorption ratio (SAR), initial (EC_i) and final (EC_f) electrical conductivity, pH, dissolved organic carbon (DOC), total dissolved nitrogen (TDN), nitrate-N (NO_3-N), ammonium-N (NH_4-N), and dissolved organic nitrogen (DON).

Salt	SAR	EC_i (d Sm^{-1})	Veg	EC_f (dS m^{-1})	pH	DOC (mg g^{-1})	TDN (mg g^{-1})	NO_3-N (µg g^{-1})	NH_4-N (µg g^{-1})	DON (mg g^{-1})
NaCl	2	0.1	august	2.00	5.63	24.2	6.52	4.28	1106	5.41
NaCl	2	0.1	august	2.16	5.62	13.0	2.40	2.25	864	1.53
NaCl	2	0.1	august	1.95	5.64	10.5	1.92	1.61	756	1.16
NaCl	2	0.3	august	2.35	5.52	12.2	2.66	5.45	1010	1.64
NaCl	2	0.3	august	2.34	5.53	11.3	2.16	3.42	862	1.30
NaCl	2	0.3	august	2.46	5.6	11.1	2.15	3.33	1006	1.14
NaCl	2	0.7	august	2.48	5.5	11.2	2.02	1.94	570	1.44
NaCl	2	0.7	august	2.76	5.56	13.2	2.27	1.44	614	1.65
NaCl	2	0.7	august	2.63	5.55	13.6	2.29	1.09	689	1.60
NaCl	2	1	august	4.13	5.65	13.4	1.77	0.00	330	1.44
NaCl	2	1	august	3.94	5.73	19.4	2.63	0.00	468	2.16
NaCl	2	1	august	4.03	5.61	17.5	2.43	0.00	556	1.88
NaCl	2	2	august	4.67	5.66	16.3	2.32	0.00	445	1.88
NaCl	2	2	august	4.54	5.52	15.6	2.18	0.00	320	1.86
NaCl	2	2	august	4.66	5.31	14.5	2.03	0.00	480	1.55
NaCl	2	3	august	5.38	5.55	16.5	2.47	0.00	339	2.13
NaCl	2	3	august	5.33	5.59	16.4	2.52	0.00	338	2.18
NaCl	2	3	august	5.42	5.42	15.2	2.27	0.00	313	1.96
NaCl	10	0.1	august	3.90	5.61	25.2	3.56	0.00	1052	2.51
NaCl	10	0.1	august	3.87	5.71	25.2	3.69	0.00	1219	2.48
NaCl	10	0.1	august	3.91	5.68	28.2	3.80	0.00	1040	2.76
NaCl	10	0.3	august	4.03	4.9	27.2	3.91	0.00	1125	2.79
NaCl	10	0.3	august	4.11	4.96	27.1	3.90	0.00	1184	2.72
NaCl	10	0.3	august	3.59	5.01	23.3	3.24	0.00	1034	2.20
NaCl	10	0.7	august	4.21	5.2	22.7	3.39	0.00	1025	2.37
NaCl	10	0.7	august	4.08	5.42	23.8	3.30	0.00	966	2.34
NaCl	10	0.7	august	4.25	5.35	23.0	3.01	0.00	990	2.02
NaCl	10	1	august	4.84	5.03	26.4	4.24	0.00	557	3.68
NaCl	10	1	august	4.92	5.04	27.0	3.96	0.00	461	3.50
NaCl	10	1	august	4.83	5.01	26.4	3.82	0.00	457	3.36
NaCl	10	2	august	5.04	4.97	23.6	3.67	0.00	592	3.08
NaCl	10	2	august	5.64	5.26	23.8	3.48	0.00	509	2.98
NaCl	10	2	august	5.87	5.23	20.9	3.24	0.00	524	2.71
NaCl	10	3	august	5.94	5.52	21.5	3.76	0.00	936	2.82
NaCl	10	3	august	5.80	5.42	19.4	2.98	0.00	630	2.35
NaCl	10	3	august	5.68	5.34	20.2	3.15	0.00	680	2.47
NaCl	30	0.1	august	3.41	4.82	34.3	4.88	0.00	872	4.01
NaCl	30	0.1	august	3.38	4.95	32.6	4.53	0.00	790	3.74
NaCl	30	0.1	august	3.24	5.27	39.2	5.57	0.00	1093	4.48
NaCl	30	0.3	august	3.74	5.41	35.3	5.61	31.76	1451	4.13
NaCl	30	0.3	august	3.81	5.36	34.8	4.94	0.00	671	4.27
NaCl	30	0.3	august	3.84	5.27	34.3	4.90	0.00	798	4.10
NaCl	30	0.7	august	4.82	5.11	32.4	4.74	69.25	485	4.19
NaCl	30	0.7	august	4.64	5.18	34.6	4.73	0.00	719	4.01
NaCl	30	0.7	august	3.74	5.14	29.9	4.02	0.00	582	3.44
NaCl	30	1	august	4.01	4.46	37.4	5.07	3.83	54.94	5.01
NaCl	30	1	august	4.42	5.18	33.9	4.56	2.41	72.53	4.49

Salt	SAR	EC_i (d Sm^{-1})	Veg	EC_f (dS m^{-1})	pH	DOC (mg g^{-1})	TDN (mg g^{-1})	NO_3-N (µg g^{-1})	NH_4-N (µg g^{-1})	DON (mg g^{-1})
NaCl	30	1	august	2.33	5.24	33.8	4.53	2.31	51.82	4.48
NaCl	30	2	august	5.27	5.04	35.7	4.74	2.78	50.81	4.68
NaCl	30	2	august	5.12	5.19	31.0	4.06	1.66	52.09	4.01
NaCl	30	2	august	4.58	5.06	33.3	4.28	1.69	48.42	4.23
NaCl	30	3	august	5.98	5.05	27.6	3.36	0.00	76.72	3.28
NaCl	30	3	august	6.34	5.11	24.9	3.35	0.00	54.90	3.29
NaCl	30	3	august	5.50	5.24	28.5	3.68	0.00	45.72	3.63
NaCl	2	0.1	mulch	0.17	6.34	1.3	0.04	0.00	1.27	0.04
NaCl	2	0.1	mulch	0.15	6.45	0.9	0.03	0.00	0.11	0.03
NaCl	2	0.1	mulch	0.16	6.39	1.4	0.04	0.00	0.09	0.04
NaCl	2	0.3	mulch	0.35	6.11	1.2	0.05	0.00	14.34	0.04
NaCl	2	0.3	mulch	0.34	6.08	1.3	0.03	0.00	0.81	0.03
NaCl	2	0.3	mulch	0.36	6.19	1.3	0.03	0.00	0.00	0.03
NaCl	2	0.7	mulch	0.75	5.7	1.3	0.08	0.00	27.15	0.05
NaCl	2	0.7	mulch	0.75	5.83	1.3	0.03	0.00	2.67	0.03
NaCl	2	0.7	mulch	0.74	5.53		0.05	0.00	2.21	0.04
NaCl	2	1	mulch	1.08	5.43	1.6	0.11	0.00	14.85	0.09
NaCl	2	1	mulch	1.09	5.23	1.3	0.03	0.00	0.00	0.03
NaCl	2	1	mulch	1.09	5.28	1.2	0.03	0.00	0.00	0.03
NaCl	2	2	mulch	1.84	5.19	1.2	0.07	0.00	10.71	0.06
NaCl	2	2	mulch	1.84	5.15	0.9	0.02	0.00	0.00	0.02
NaCl	2	2	mulch	1.90	5.25	1.0	0.02	0.00	0.00	0.02
NaCl	2	3	mulch	2.67	5.01	1.6	0.10	0.00	8.43	0.09
NaCl	2	3	mulch	2.68	5.1	1.1	0.01	0.00	0.00	0.01
NaCl	2	3	mulch	2.68	5.07	1.0	0.01	0.00	0.00	0.01
NaCl	10	0.1	mulch	0.23	6.24	2.2	0.14	0.00	53.48	0.08
NaCl	10	0.1	mulch	0.17	6.3	1.2	0.03	0.00	6.64	0.02
NaCl	10	0.1	mulch	0.16	6.32	1.1	0.01	0.00	1.45	0.01
NaCl	10	0.3	mulch	0.39	5.89	1.7	0.10	0.00	39.55	0.06
NaCl	10	0.3	mulch	0.39	5.91	1.3	0.04	0.00	8.00	0.04
NaCl	10	0.3	mulch	0.38	5.89	1.0	0.03	0.00	3.95	0.02
NaCl	10	0.7	mulch	0.84	5.74	1.3	0.05	0.00	15.74	0.03
NaCl	10	0.7	mulch	0.81	5.76	1.8	0.09	0.00	32.94	0.05
NaCl	10	0.7	mulch	0.81	5.87	1.0	0.02	0.00	4.77	0.02
NaCl	10	1	mulch	1.11	5.6	1.8	0.08	0.00	26.48	0.06
NaCl	10	1	mulch	1.12	5.55	1.5	0.02	0.00	3.16	0.01
NaCl	10	1	mulch	1.12	5.64	1.1	0.02	0.00	1.98	0.02
NaCl	10	2	mulch	2.14	5.34	1.1	0.02	0.00	66.03	-0.04
NaCl	10	2	mulch	1.95	5.46	1.9	0.15	0.00	12.41	0.13
NaCl	10	2	mulch	1.93	5.35	1.2	0.02	0.00	3.88	0.01
NaCl	10	3	mulch	3.02	5.32	1.5	0.12	0.00	60.60	0.06
NaCl	10	3	mulch	2.81	5.05	0.9	0.01	0.00	1.76	0.01
NaCl	10	3	mulch	2.78	5.04	1.5	0.10	0.00	3.00	0.09
NaCl	30	0.1	mulch	0.29	6.09	1.8	0.14	0.00	42.36	0.09
NaCl	30	0.1	mulch	0.20	6.1	1.3	0.02	0.00	0.00	0.02
NaCl	30	0.1	mulch	0.19	6	1.4	0.02	0.00	0.00	0.02
NaCl	30	0.3	mulch	0.47	5.95	1.9	0.12	0.00	37.86	0.08
NaCl	30	0.3	mulch	0.41	6.06	1.8	0.04	0.00	2.98	0.04
NaCl	30	0.3	mulch	0.42	5.92	1.7	0.03	0.00	0.00	0.03
NaCl	30	0.7	mulch	0.87	5.77	2.7	0.17	0.00	56.95	0.11
NaCl	30	0.7	mulch	0.81	5.71	1.4	0.05	0.00	12.10	0.04
NaCl	30	0.7	mulch	0.81	5.77	1.4	0.03	0.00	0.00	0.03
NaCl	30	1	mulch	1.07	5.86	2.2	0.15	1.29	6.41	0.14

Salt	SAR	EC_i (d Sm^{-1})	Veg	EC_f (dS m^{-1})	pH	DOC (mg g^{-1})	TDN (mg g^{-1})	NO_3-N (μg g^{-1})	NH_4-N (μg g^{-1})	DON (mg g^{-1})
NaCl	30	1	mulch	1.06	5.82	1.2	0.04	1.01	0.91	0.03
NaCl	30	1	mulch	1.10	5.8	1.5	0.03	1.20	0.67	0.03
NaCl	30	2	mulch	1.91	5.52	2.3	0.15	1.08	6.52	0.15
NaCl	30	2	mulch	1.86	5.56	1.2	0.03	0.92	1.28	0.03
NaCl	30	2	mulch	0.00		1.5	0.03	0.86	0.61	0.03
NaCl	30	3	mulch	2.78	5.64	2.2	0.18		8.05	0.17
NaCl	30	3	mulch	2.73	5.56	-	-	-	-	-
NaCl	30	3	mulch	2.74	5.59	1.3	0.06	-	-	0.06
NaCl	2	0.1	Oak	0.39	5.14	10.8	0.30	0.00	3.22	0.30
NaCl	2	0.1	Oak	0.42	5.12	12.4	0.28	0.00	4.14	0.28
NaCl	2	0.3	Oak	0.60	5.16	13.7	0.36	0.00	10.91	0.35
NaCl	2	0.3	Oak	0.53	5.22	10.5	0.28	0.00	19.72	0.26
NaCl	2	0.3	Oak	0.54	5.14	8.9	0.28	0.00	45.57	0.24
NaCl	2	0.7	Oak	0.86	5.14	8.7	0.34	0.00	15.46	0.32
NaCl	2	0.7	Oak	0.84	5.1	7.0	0.20	0.00	1.47	0.20
NaCl	2	0.7	Oak	0.85	4.99	7.2	0.21	0.00	2.10	0.21
NaCl	2	1	Oak	1.29	4.7	10.5	0.34	0.00	0.00	0.34
NaCl	2	1	Oak	1.28	4.72	12.1	0.40	0.00	0.00	0.40
NaCl	2	1	Oak	1.28	4.7	11.5	0.32	0.00	0.00	0.32
NaCl	2	2	Oak	1.99	4.78	11.6	0.43	0.00	50.53	0.38
NaCl	2	2	Oak	1.99	4.72	11.7	0.37	0.00	49.18	0.32
NaCl	2	2	Oak	2.01	4.79	11.7	0.32	0.00	0.00	0.32
NaCl	2	3	Oak	2.86	4.59	10.8	0.15	0.00	23.20	0.13
NaCl	2	3	Oak	2.82	4.63	10.9	0.31	0.00	0.96	0.31
NaCl	2	3	Oak	2.86	4.6	12.1	0.25	0.00	48.93	0.21
NaCl	10	0.1	Oak	0.41	4.96	12.7	0.30	0.00	1.99	0.30
NaCl	10	0.1	Oak	0.46	4.96	15.0	0.32	0.00	2.18	0.32
NaCl	10	0.1	Oak	0.39	5.01	12.8	0.25	0.00	1.61	0.25
NaCl	10	0.3	Oak	0.64	5.21	13.5	0.24	0.00	1.39	0.24
NaCl	10	0.3	Oak	0.63	5.13	15.0	0.30	0.00	2.42	0.30
NaCl	10	0.3	Oak	0.64	5.08	13.2	0.25	0.00	1.38	0.25
NaCl	10	0.7	Oak	0.98	4.73	9.4	0.16	0.00	0.06	0.16
NaCl	10	0.7	Oak	0.98	4.87	12.9	0.27	0.00	0.12	0.27
NaCl	10	0.7	Oak	1.05	4.72	11.9	0.24	0.00	0.71	0.24
NaCl	10	1	Oak	1.63	4.04	15.1	0.37	0.00	50.70	0.32
NaCl	10	1	Oak	1.41	4.51	17.2	0.34	0.00	35.12	0.31
NaCl	10	1	Oak	1.44	4.3	17.3	0.30	0.00	38.7	0.26
NaCl	10	2	Oak	2.08	4.36	12.3	0.33	0.00	131	0.20
NaCl	10	2	Oak	2.07	4.65	15.9	0.50	0.00	135	0.37
NaCl	10	2	Oak	2.15	4.6	15.8	0.44	0.00	129	0.31
NaCl	10	3	Oak	2.34	4.41	13.4	0.43	0.00	144	0.28
NaCl	10	3	Oak	3.00	4.65	15.0	0.35	0.00	58.24	0.29
NaCl	10	3	Oak	3.05	4.18	14.4	0.30	0.00	51.51	0.25
NaCl	30	0.1	Oak	0.57	4.24	16.2	0.57	0.00	131	0.44
NaCl	30	0.1	Oak	0.62	4.23	24.0	0.43	0.00	0.00	0.43
NaCl	30	0.1	Oak	0.57	4.34	15.6	0.41	0.00	48.12	0.37
NaCl	30	0.3	Oak	0.78	4.41	17.3	0.41	-	-	0.41
NaCl	30	0.3	Oak	0.76	4.56	17.7	0.44	-	-	0.44
NaCl	30	0.3	Oak	0.77	4.53	17.3	0.45	0.00	54.51	0.40
NaCl	30	0.7	Oak	1.12	4.73	18.1	0.41	0.00	47.18	0.36
NaCl	30	0.7	Oak	1.18	4.66	18.0	0.52	0.00	23.96	0.50
NaCl	30	0.7	Oak	1.17	4.46	16.4	0.50	0.00	142	0.36
NaCl	30	0.7	Oak	1.17	4.46	16.4	0.50	0.00	142	0.36

Salt	SAR	EC$_i$ (d Sm^{-1})	Veg	EC$_f$ (dS m^{-1})	pH	DOC (mg g^{-1})	TDN (mg g^{-1})	NO$_3$-N (µg g^{-1})	NH$_4$-N (µg g^{-1})	DON (mg g^{-1})
NaCl	30	1	Oak	1.46	4.45	18.6	0.44	1.34	7.95	0.43
NaCl	30	1	Oak	1.43	4.64	19.6	0.46	1.19	8.59	0.45
NaCl	30	1	Oak	1.40	4.57	17.4	0.35	1.38	2.65	0.35
NaCl	30	2	Oak	2.14	4.62	15.9	0.25	1.07	2.88	0.24
NaCl	30	2	Oak	2.15	4.64	18.2	0.38	1.42	0.48	0.38
NaCl	30	2	Oak	2.15	4.43	19.7	0.41	1.15	10.17	0.40
NaCl	30	3	Oak	3.05	4.36	7.1	0.20	0.00	8.32	0.19
NaCl	30	3	Oak	2.98	4.46	20.3	0.57	0.00	7.20	0.56
NaCl	30	3	Oak	2.95	4.52	20.6	0.49	0.00	11.31	0.47
NaCl	2	0.1	Ripar	0.75	5.68	11.7	1.19	0.00	415	0.78
NaCl	2	0.1	Ripar	0.85	5.82	10.6	1.04	0.00	335	0.70
NaCl	2	0.1	Ripar	0.85	5.75	11.3	0.99	0.00	302	0.69
NaCl	2	0.3	Ripar	0.81	5.87	11.0	0.79	0.00	148	0.64
NaCl	2	0.3	Ripar	0.79	5.91	9.4	0.82	0.00	268	0.55
NaCl	2	0.3	Ripar	0.89	5.84	9.9	0.94	0.00	280	0.66
NaCl	2	0.7	Ripar	1.13	5.74	8.7	0.72	0.80	241	0.48
NaCl	2	0.7	Ripar	1.19	5.72	9.8	0.83	0.00	281	0.55
NaCl	2	0.7	Ripar	1.48	5.69	12.5	1.17	0.00	318	0.85
NaCl	2	1	Ripar	1.51	5.78	10.5	0.88	0.00	120	0.75
NaCl	2	1	Ripar	1.56	5.84	10.1	0.92	0.00	159	0.77
NaCl	2	1	Ripar	1.52	5.75	11.0	1.04	0.00	176	0.86
NaCl	2	2	Ripar	2.18	5.74	12.1	0.83	0.00	45.62	0.78
NaCl	2	2	Ripar	2.22	5.56	14.0	1.03	0.00	94.68	0.93
NaCl	2	2	Ripar	2.12	5.7	10.1	0.78	0.00	92.22	0.68
NaCl	2	3	Ripar	3.05	5.44	10.5	0.94	0.00	188	0.75
NaCl	2	3	Ripar	3.07	5.59	12.4	0.95	0.00	141	0.81
NaCl	2	3	Ripar	3.07	5.65	13.3	0.87	0.00	56.32	0.81
NaCl	10	0.1	Ripar	0.70	5.77	10.3	0.77	0.00	35.96	0.73
NaCl	10	0.1	Ripar	0.67	5.96	8.1	0.70	0.00	109	0.59
NaCl	10	0.1	Ripar	0.67	5.96	8.8	0.75	0.00	85.99	0.66
NaCl	10	0.3	Ripar	0.93	5.89	-	-	-	-	-
NaCl	10	0.3	Ripar	0.92	8.82	10.3	0.92	0.00	37.85	0.88
NaCl	10	0.3	Ripar	0.75	5.66	10.0	0.72	0.00	168	0.55
NaCl	10	0.7	Ripar	1.36	5.58	10.4	0.71	0.00	56.14	0.66
NaCl	10	0.7	Ripar	1.28	5.54	10.7	0.81	0.00	78.8	0.74
NaCl	10	0.7	Ripar	1.24	5.69	8.8	0.75	0.00	110	0.64
NaCl	10	1	Ripar	1.79	5.46	11.5	0.96	0.00	358	0.61
NaCl	10	1	Ripar	1.79	5.6	11.1	1.06	0.00	295	0.77
NaCl	10	1	Ripar	1.77	5.46	14.3	0.95	0.00	255	0.69
NaCl	10	2	Ripar	2.48	5.78	9.5	0.88	0.00	291	0.59
NaCl	10	2	Ripar	2.46	5.77	10.4	0.94	0.00	285	0.66
NaCl	10	2	Ripar	2.51	5.4	12.2	0.78	0.00	246	0.53
NaCl	10	3	Ripar	3.22	4.99	12.8	0.69	0.00	182	0.50
NaCl	10	3	Ripar	3.31	5.45	11.1	0.97	0.00	238	0.73
NaCl	10	3	Ripar	3.22	5.3	11.4	0.85	0.00	270	0.58
NaCl	30	0.1	Ripar	0.87	5.05	15.9	0.95	0.00	0.00	0.95
NaCl	30	0.1	Ripar	0.76	5.02	13.6	0.88	0.00	0.00	0.88
NaCl	30	0.1	Ripar	0.71	4.95	13.1	0.90	0.00	7.30	0.89
NaCl	30	0.3	Ripar	1.11	5.06	16.5	1.12	0.00	278	0.84
NaCl	30	0.3	Ripar	1.22	4.99	18.3	1.15	0.00	215	0.93
NaCl	30	0.3	Ripar	0.99	5.19	15.4	0.94	-	-	0.94
NaCl	30	0.7	Ripar	1.38	5.14	16.3	1.07	0.00	198	0.87
NaCl	30	0.7	Ripar	1.46	5.22	13.3	0.90	0.00	231	0.66

Salt	SAR	EC_i (d Sm^{-1})	Veg	EC_f (dS m^{-1})	pH	DOC (mg g^{-1})	TDN (mg g^{-1})	NO_3-N (µg g^{-1})	NH_4-N (µg g^{-1})	DON (mg g^{-1})
NaCl	30	0.7	Ripar	1.57	5.56	12.4	0.95	0.00	186	0.77
NaCl	30	1	Ripar	1.83	5.57	14.2	0.94	1.27	0.35	0.94
NaCl	30	1	Ripar	1.77	5.51	15.2	1.11	1.70	10.71	1.10
NaCl	30	1	Ripar	1.77	5.23	16.2	1.08	1.40	16.97	1.06
NaCl	30	2	Ripar	2.71	5.45	20.5	1.13	1.71	0.56	1.13
NaCl	30	2	Ripar	2.45	5.65	12.8	1.05	1.39	11.06	1.04
NaCl	30	2	Ripar	2.40	5.4	13.9	0.97	1.56	12.22	0.96
NaCl	30	3	Ripar	3.20	5.76	15.1	0.67		18.27	0.65
NaCl	30	3	Ripar	3.18	5.62	23.4	0.71		25.87	0.68
NaCl	30	3	Ripar	3.22	5.48	16.9	0.55		17.20	0.53
NaCl	2	0.1	rye	5.97	5.52	48.5	11.87	2178	1213	8.48
NaCl	2	0.1	rye	5.19	5.57	51.5	12.76	1018	3365	8.38
NaCl	2	0.1	rye	5.05	5.62	41.1	11.08	501	5300	5.27
NaCl	2	0.3	rye	4.89	5.58	44.7	10.60	1048	1801	7.76
NaCl	2	0.3	rye	5.13	5.47	59.0	14.56	1351	1901	11.31
NaCl	2	0.3	rye	5.07	5.61	55.8	14.46	1543	1927	10.98
NaCl	2	0.7	rye	4.69	5.57	51.9	13.46	2174	2337	8.94
NaCl	2	0.7	rye	4.83	5.52	59.5	15.80	2262	1994	11.54
NaCl	2	0.7	rye	5.07	5.53	55.4	15.27	2434	1819	11.01
NaCl	2	1	rye	5.07	5.45	55.0	13.48	1572	2105	9.80
NaCl	2	1	rye	5.80	5.56	56.2	13.69	1653	2627	9.41
NaCl	2	1	rye	6.18	5.64	55.8	11.82	2133	2235	7.45
NaCl	2	2	rye	5.50	5.66	48.3	7.53	531	1893	5.11
NaCl	2	2	rye	6.06	5.53	55.0	10.80	454	2443	7.90
NaCl	2	2	rye	6.84	5.51	55.0	12.66	698	3311	8.65
NaCl	2	3	rye	7.89	5.44	50.5	12.32	972	1321	10.03
NaCl	2	3	rye	6.15	5.3	59.4	14.97	1479	1345	12.15
NaCl	2	3	rye	6.47	5.52	55.8	12.83	1267	1374	10.18
NaCl	10	0.1	rye	4.84	5.35	50.4	11.19	0.00	5855	5.33
NaCl	10	0.1	rye	3.76	5.49	55.1	13.04	243	6136	6.66
NaCl	10	0.1	rye	4.53	5.48	54.8	13.44	4.84	6587	6.85
NaCl	10	0.3	rye	6.00	5.46	49.7	12.28	1043	5665	5.57
NaCl	10	0.3	rye	5.05	5.47	57.3	14.39	1159	7073	6.15
NaCl	10	0.3	rye	5.19	5.42	55.2	13.73	382	6683	6.66
NaCl	10	0.7	rye	4.99	5.23	50.1	12.02	992	5315	5.71
NaCl	10	0.7	rye	5.54	5.22	53.7	13.23	1055	6389	5.79
NaCl	10	0.7	rye	6.28	5.34	57.9	15.29	1688	6615	6.99
NaCl	10	1	rye	6.72	5.25	52.3	13.65	0.00	181	13.47
NaCl	10	1	rye	6.32	5.5	54.0	14.61	0.00	171	14.44
NaCl	10	1	rye	6.48	5.13	50.0	12.37	0.00	176	12.19
NaCl	10	2	rye	7.12	4.83	56.0	11.99	0.00	158	11.83
NaCl	10	2	rye	6.80	5.14	55.0	12.91	0.00	166	12.74
NaCl	10	2	rye	7.06	5.04	60.3	14.52	0.00	188	14.33
NaCl	10	3	rye	7.96	5.02	51.8	11.32	0.00	116	11.21
NaCl	10	3	rye	8.18	5.04	55.1	13.12	0.00	145	12.97
NaCl	10	3	rye	8.07	5.36	50.9	11.93	0.00	249	11.68
NaCl	30	0.1	rye	5.41	4.73	73.5	15.74	801	1715	13.22
NaCl	30	0.1	rye	5.79	4.67	68.2	13.89	277	2152	11.46
NaCl	30	0.1	rye	4.89	4.71	73.8	14.87	283	2064	12.53
NaCl	30	0.3	rye	5.72	4.84	60.9	11.18	174	2133	8.87
NaCl	30	0.3	rye	3.74	4.74	78.1	14.80	380	1649	12.77
NaCl	30	0.3	rye	4.90	4.81	68.2	14.36	546	1860	11.95
NaCl	30	0.7	rye	4.83	5.36	63.4	14.04	823	2735	10.48

Salt	SAR	EC_i (d Sm^{-1})	Veg	EC_f (dS m^{-1})	pH	DOC (mg g^{-1})	TDN (mg g^{-1})	NO_3-N (µg g^{-1})	NH_4-N (µg g^{-1})	DON (mg g^{-1})
NaCl	30	0.7	rye	5.45	4.8	71.1	12.84	441	1930	10.46
NaCl	30	0.7	rye	5.87	4.84	78.1	16.54	1414	1891	13.24
NaCl	30	1	rye	4.87	5.12	64.2	13.30	64.29	1141	12.09
NaCl	30	1	rye	4.88	4.68	71.0	12.41	37.81	158	12.22
NaCl	30	1	rye	4.30	5.31	70.1	13.25	46.05	287	12.92
NaCl	30	2	rye	4.72	5.21	67.7	12.79	75.20	241	12.47
NaCl	30	2	rye	4.97	4.94	73.8	13.09	47.15	166	12.87
NaCl	30	2	rye	6.32	4.57	63.1	9.73	11.87	85	9.63
NaCl	30	3	rye	6.59	5.03	46.5	0.57	90.34	139	0.34
NaCl	30	3	rye	5.97	5.33	35.1	12.89	48.69	174	12.66
NaCl	30	3	rye	7.46	5.27	43.0	8.30	64.38	156	8.08
NaHCO3	30	1	august	3.91	4.93	23.6	3.52	0.00	600	2.92
NaHCO3	30	1	august	4.11	5	19.4	2.94	0.00	583	2.35
NaHCO3	30	1	august	5.13	5.49	17.9	2.72	0.00	747	1.98
NaHCO3	30	3	august	3.66	5.84	18.1	2.90	0.00	645	2.26
NaHCO3	30	3	august	3.59	5.5	12.8	2.28	0.00	1106	1.17
NaHCO3	30	3	august	4.10	6.89	18.0	2.80	0.00	684	2.12
NaHCO3	30	7	august	4.03	6.14	17.9	3.30	0.00	1327	1.97
NaHCO3	30	7	august	4.43	6.21	16.3	2.86	0.00	1334	1.53
NaHCO3	30	7	august	4.04	6	15.8	2.82	0.00	761	2.05
NaHCO3	30	1	august	3.54	6.6	27.6	3.25	0.00	62.75	3.19
NaHCO3	30	1	august	3.87	6.6	23.6	2.75	0.00	42.42	2.71
NaHCO3	30	1	august	3.90	6.6	2.0	0.07	0.00	8.19	0.06
NaHCO3	30	2	august	4.71	6.8	20.6	2.86	0.00	62.75	3.19
NaHCO3	30	2	august	4.44	6.88	21.2	3.13	0.00	42.42	2.71
NaHCO3	30	2	august	4.33	6.86	21.2	3.37	0.00	-	-
NaHCO3	30	3	august	4.63	7.1	27.7	3.14	0.00	68.76	3.07
NaHCO3	30	3	august	5.02	7.1	28.9	3.45	0.00	50.48	3.40
NaHCO3	30	3	august	4.97	7.12	-	-	-	-	-
NaHCO3	30	1	mulch	0.13	6.64	4.4	0.30	0.00	83.75	0.22
NaHCO3	30	1	mulch	0.14	6.65	1.4	0.04	0.00	5.09	0.04
NaHCO3	30	1	mulch	0.15	6.59	1.3	0.03	0.00	1.86	0.03
NaHCO3	30	3	mulch	0.33	6.92	1.6	0.06	0.00	12.46	0.05
NaHCO3	30	3	mulch	0.32	6.88	1.5	0.03	0.00	2.41	0.03
NaHCO3	30	3	mulch	0.32	5.87	1.6	0.03	0.00	0.80	0.03
NaHCO3	30	7	mulch	0.75	7.13	2.2	0.19	0.00	59.84	0.13
NaHCO3	30	7	mulch	0.68	7.2	1.6	0.05	0.00	5.79	0.04
NaHCO3	30	7	mulch	0.71	7.28	1.4	0.02	0.00	2.88	0.01
NaHCO3	30	1	mulch	0.90	7.41	1.6	0.03	0.00	1.60	0.03
NaHCO3	30	1	mulch	0.86	7.38	1.4	0.02	0.00	0.00	0.02
NaHCO3	30	1	mulch	0.88	7.38	1.5	0.03	0.00	0.00	0.03
NaHCO3	30	2	mulch	1.82	7.54	1.8	0.10	0.00	1.60	0.03
NaHCO3	30	2	mulch	1.79	7.6	1.5	0.04	0.00	0.00	0.02
NaHCO3	30	2	mulch	1.78	7.6	1.3	0.03	0.00	0.00	0.03
NaHCO3	30	3	mulch	2.31	7.67	1.7	0.09	0.00	8.49	0.08
NaHCO3	30	3	mulch	2.34	7.68	2.5	0.10	0.00	1.71	0.09
NaHCO3	30	3	mulch	2.35	7.69	2.4	0.04	0.00	0.00	0.04
NaHCO3	30	0.1	Oak	0.65	4.79	3.7	0.14	0.00	80.80	0.06
NaHCO3	30	0.1	Oak	0.48	4.78	8.7	0.21	0.00	73.51	0.13
NaHCO3	30	0.1	Oak	0.61	4.66	12.0	0.22	0.00	90.77	0.13
NaHCO3	30	0.3	Oak	0.58	5.29	8.2	0.22	0.00	87.35	0.13
NaHCO3	30	0.3	Oak	0.63	5.18	11.4	0.20	0.00	50.96	0.15
NaHCO3	30	0.3	Oak	0.66	5.19	11.1	0.25	0.00	115	0.13

Salt	SAR	EC_i (d Sm^{-1})	Veg	EC_f (dS m^{-1})	pH	DOC (mg g^{-1})	TDN (mg g^{-1})	NO_3-N (µg g^{-1})	NH_4-N (µg g^{-1})	DON (mg g^{-1})
NaHCO3	30	0.7	Oak	0.86	5.85	12.3	0.24	0.00	70.88	0.17
NaHCO3	30	0.7	Oak	0.89	5.81	11.1	0.28	0.00	106	0.17
NaHCO3	30	0.7	Oak	0.96	6.32	11.6	0.24	0.00	61.12	0.18
NaHCO3	30	1	Oak	0.94	6.37	18.0	0.46	0.00	8.65	0.45
NaHCO3	30	1	Oak	0.96	6.55	20.7	0.58	0.00	7.35	0.58
NaHCO3	30	1	Oak	0.91	6.73	19.3	0.38	0.00	11.07	0.37
NaHCO3	30	2	Oak	1.75	6.87	20.8	0.39	0.00	0.00	0.39
NaHCO3	30	2	Oak	1.72	6.93	14.9	0.30	0.00	0.00	0.30
NaHCO3	30	2	Oak	1.68	6.97	13.0	0.27	0.00	0.00	0.27
NaHCO3	30	3	Oak	2.31	7.07	23.2	0.52	0.00	8.70	0.51
NaHCO3	30	3	Oak	2.36	7.1	22.8	0.47	0.00	7.66	0.46
NaHCO3	30	3	Oak	2.23	7.06	20.9	0.44	0.00	11.7	0.43
NaHCO3	30	0.1	Ripar	1.02	5.76	8.2	0.48	0.00	131	0.35
NaHCO3	30	0.1	Ripar	0.97	5.65	7.1	0.45	0.00	303	0.14
NaHCO3	30	0.1	Ripar	0.80	5.51	7.4	0.43	0.00	99	0.33
NaHCO3	30	0.3	Ripar	1.20	5.93	7.5	0.55	0.00	352	0.20
NaHCO3	30	0.3	Ripar	1.18	5.91	8.7	0.71	0.00	383	0.32
NaHCO3	30	0.3	Ripar	1.11	5.95	7.1	0.55	0.00	376	0.18
NaHCO3	30	0.7	Ripar	1.45	6.28	6.7	0.48	0.00	292	0.18
NaHCO3	30	0.7	Ripar	1.41	6.28	7.9	0.64	0.00	344	0.30
NaHCO3	30	0.7	Ripar	1.28	6.08	9.8	0.76	0.00	408	0.35
NaHCO3	30	1	Ripar	1.19	6.7	12.6	0.74	0.00	19.06	0.72
NaHCO3	30	1	Ripar	1.44	6.67	18.4	0.75	0.00	25.72	0.72
NaHCO3	30	1	Ripar	1.42	6.68	22.3	0.82	0.00	17.13	0.80
NaHCO3	30	2	Ripar	1.90	6.94	7.4	0.63	0.00	0.00	0.63
NaHCO3	30	2	Ripar	1.82	6.98	10.1	0.76	0.00	0.00	0.76
NaHCO3	30	2	Ripar	1.98	6.96	9.6	0.81	0.00	0.00	0.81
NaHCO3	30	3	Ripar	2.70	6.98	13.5	0.83	0.00	19.18	0.81
NaHCO3	30	3	Ripar	2.62	7.07	25.4	0.96	0.00	26.89	0.93
NaHCO3	30	3	Ripar	2.68	7.08	20.4	0.80	0.00	17.86	0.78
NaHCO3	30	0.1	rye	4.56	4.91	45.6	9.94	0.00	1699	8.24
NaHCO3	30	0.1	rye	5.50	4.84	53.8	11.27	0.00	1455	9.81
NaHCO3	30	0.1	rye	4.26	4.94	57.6	10.76	0.00	1485	9.28
NaHCO3	30	0.3	rye	3.89	5.17	43.7	7.93	0.00	1720	6.21
NaHCO3	30	0.3	rye	3.74	5.16	44.4	8.99	0.00	1845	7.15
NaHCO3	30	0.3	rye	3.90	5.4	46.3	9.67	0.00	2074	7.60
NaHCO3	30	0.7	rye	4.32	5.61	39.6	8.73	0.00	2466	6.26
NaHCO3	30	0.7	rye	4.05	5.62	43.5	9.28	0.00	2618	6.66
NaHCO3	30	0.7	rye	-	-	-	-	-	-	-
NaHCO3	30	1	rye	2.29	6.65	35.6	6.50	0.00	2589	4.01
NaHCO3	30	1	rye	-	-	-	-	-	-	-
NaHCO3	30	1	rye	-	-	-	-	-	-	-
NaHCO3	30	2	rye	3.09	6.93	42.3	8.58	0.00	2698	6.50
NaHCO3	30	2	rye	-	-	-	-	-	-	-
NaHCO3	30	2	rye	-	-	-	-	-	-	-
NaHCO3	30	3	rye	3.39	7.36	34.8	7.91	0.00	2890	5.89
NaHCO3	30	3	rye	-	-	-	-	-	-	-
NaHCO3	30	3	rye	-	-	-	-	-	-	-

APPENDIX F

Appendix F Concentration of sodium and chloride, electrical conductivity (EC), pH, and discharge of Trinity River at five gauges, beech street, Grand Prairie, Lewisville, Below Dallas, and Rosser.

Date	site	Discharge (m^3 sec)	pH	EC (dS m^{-1})	Na (mg L^{-1})	Cl (mg L^{-1})
5/29/2009	B	2.4	8.33	0.27	13.1	13.5
7/8/2009	B	3.3	8.05	0.39	24.6	26.2
8/16/2009	B	0.8	8.24	0.43	18.4	27.0
10/23/2009	B	29.7	8.02	0.40	14.9	15.8
11/24/2009	B	9.1	8.2	0.31	17.7	18.7
1/18/2010	B	3.2	8.22	0.54	29.1	30.9
2/8/2010	B	52.7	8.12	0.50	20.5	27.1
3/15/2010	B	30.3	8.25	0.70	22.4	33.5
4/16/2010	B	1.5	7.73	0.52	25.7	27.2
5/28/2010	B	24.9	8.03	0.39	20.9	41.8
5/29/2009	D	59.5	7.97	0.47	39.2	35.5
7/8/2009	D	27.5	7.99	0.75	74.7	70.4
8/16/2009	D	16.5	8.06	1.15	85.9	88.4
10/23/2009	D	475.7	7.86	0.37	18.1	15.6
11/24/2009	D	160.0	8.17	0.32	30.7	26.6
1/18/2010	D	38.2	7.97	0.72	62.3	62.3
2/8/2010	D	248.6	8.05	0.41	23.8	27.5
3/15/2010	D	232.5	8.16	0.62	40.8	38.4
4/16/2010	D	32.0	7.73	0.88	45.5	58.0
5/28/2010	D	85.0	7.86	0.49	40.4	57.0
5/29/2009	C	11.8	8.02	0.49	38.7	38.1
7/8/2009	C	9.0	8.1	0.64	55.6	55.9
8/16/2009	C	4.1	8.17	0.12	99.4	105.0
10/23/2009	C	275.5	8	0.31	14.9	12.6
11/24/2009	C	22.1	8.12	0.37	38.3	35.8
1/18/2010	C	13.3	8.03	0.76	63.6	68.2
2/8/2010	C	75.0	8.02	0.60	35.4	41.9
3/15/2010	C	36.5	8.21	0.79	37.8	50.4
4/16/2010	C	9.5	7.74	0.85	85.7	122.5
5/28/2010	C	44.2	7.81	0.44	49.5	74.2
5/29/2009	A	30.3	7.63	0.33	26.6	21.1
7/8/2009	A	13.1	7.99	0.37	28.4	23.2
8/16/2009	A	15.5	7.76	0.49	38.7	25.7

Date	site	Discharge (m^3 sec)	pH	EC (dS m^{-1})	Na (mg L^{-1})	Cl (mg L^{-1})
10/23/2009	A	22.1	7.78	0.41	34.2	22.1
11/24/2009	A	93.4	8.1	0.22	22.5	16.7
1/18/2010	A	5.6	7.99	0.36	27.4	22.0
2/8/2010	A	104.8	8.08	0.26	27.5	22.1
3/15/2010	A	101.7	8.18	0.44	19.0	17.8
4/16/2010	A	6.1	7.87	0.36	32.5	47.0
5/28/2010	A	4.0	7.71	0.37	27.8	30.2
5/29/2009	E	90.9	8.05	0.45	35.0	33.6
7/8/2009	E	25.3	8.11	0.77	76.4	76.4
8/16/2009	E	18.3	8.39	1.14	85.9	81.1
10/23/2009	E	532.4	7.91	0.38	30.6	21.1
11/24/2009	E	229.6	8.17	0.33	30.1	27.9
1/18/2010	E	48.4	8.04	0.67	53.2	55.3
2/8/2010	E	339.8	8.13	0.48	17.7	22.3
3/15/2010	E	257.7	8.12	0.65	28.5	37.0
4/16/2010	E	34.3	7.81	0.78	69.3	78.8
5/28/2010	E	77.3	7.91	0.49	41.1	57.7

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