EFFECT OF SODIUM EXPOSURE ON DISSOLVED ORGANIC CARBON AND ITS BIODEGRADABILITY IN URBAN SOILS

A Thesis

by

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

MASTER OF SCIENCE

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August 2016

Major Subject: Water Management and Hydrological Science

ABSTRACT

As climate change progresses, carbon sequestration is becoming an increasingly important strategy for long term carbon storage in soil. Adding to and preserving this carbon storage is crucial for the development of future management strategies that maintain this natural process. This study examines the effects of sodium in urban soils on water extractable dissolved organic carbon (DOC) and organic nitrogen (DON) and biodegradable DOC (BDOC) from 1) de-icing salts, 2) irrigation water, and 3) deposition of oceanic aerosols. Evaluation of the effects of time of soil exposure to sodium from the different sources was a major objective of this study. Urban soil samples were collected from Chicago, IL (n=36), Galveston, TX (n=36), and Bryan-College Station, TX (n=36). Soil samples were extracted with a 1:10 soil/deionized water ratio and DOC, DON, BDOC, EC, pH, alkalinity, and soil chemistry (Ca, Mg, K, Na, Fe, Zn, Mn, B, S, Cu) was measured.

Univariate analysis of variance determined that sodium source had a significant effect on all major dependent variables tested, which included %BDOC ($p < 0.001$), DOC ($p = 0.03$), DON ($p < 0.001$), and specific UV absorbance ($SUVA_{254}$) ($p < 0.001$). Soil exposure time to sodium had a significant effect on water extractable DOC ($p < 0.001$) and DON ($p < 0.001$) but not on %BDOC ($p = 0.13$) or $SUVA_{254}$ ($p = 0.25$). %BDOC and $SUVA_{254}$ did not exhibit a significant relationship; however, when %BDOC and $SUVA_{254}$ were analyzed by city a significant relationship existed for all three cities. There was a significant positive relationship between DOC concentration and $SUVA_{254}$ across all three cities ($p < 0.001$, $r^2 = 0.33$).

The implications of this study can help predict water extractable DOC and DON and %BDOC loss resulting from increased soil sodium accretion from deicing salts, irrigation, and atmospheric deposition. Increased accretion of soil sodium could have large scale implications on carbon storage and potentially offer an explanation for the increased DOC concentrations observed in urban streams.

ACKNOWLEDGEMENTS

I would like to thank my committee members, Dr. R. Karthikeyan, Dr. Jacqueline Aitkenhead-Peterson, Dr. Saqib Mukhtar, and Dr. Kevin Wagner for their help, guidance and support throughout the course of this research. I have learned so much during my time at Texas A&M University and I really appreciate all that my committee has done for me.

I would also like to thank my department and Texas Water Resources Institute for supporting me during my time at Texas A&M. Thanks also goes out to Dr. Saqib Mukhtar for providing me funds for my research.

Without all of this help, my experience at Texas A&M University would not have been possible and I would not have been able to achieve as much as I have today.

NOMENCLATURE

BCS	Bryan/College Station
BDOC	Biodegradable Dissolved Organic Carbon
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DON	Dissolved Organic Nitrogen
EC	Electric Conductivity
ESP	Exchangeable Sodium Percentage
SAR	Sodium Adsorption Ratio
$SUVA_{254}$	Specific UV Absorbance at the wavelength 254nm
TDN	Total Dissolved Nitrogen

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1. INTRODUCTION AND LITERATURE REVIEW

Sources, Transport, and Fates of DOC

Dissolved organic carbon (DOC) is a continuum of molecules of variable Dalton weights that fit through the pores of a 0.45 µm filter (Thurman 1985). Its highest concentration is found in organic soil horizons (Aitkenhead-Peterson et al. 2003) and its primary sources include throughfall from the vegetation canopy, decomposition of vegetation overlaying the soil, and rhizo-deposited exudates released by roots (Aitkenhead-Peterson & Kalbitz 2005; Aitkenhead-Peterson et al. 2003). The terrestrial DOC pool comprises labile and recalcitrant fractions of carbon. The labile and semi-labile fractions are called biodegradable dissolved organic carbon (BDOC) (Yano et al. 1998). BDOC consists of simple carbon compounds that are low in molecular weight and are usually consumed by microbes within a short time period (Servais et al. 1989; Yano et al. 1998). Glucose is the simplest molecule that heterotrophic bacteria consume readily; therefore it is typically utilized as an indicator of viable microbes when used as an inoculant (Cioce & Aitkenhead-Peterson 2015; McDowell et al. 2006). Due to the rapid uptake of BDOC, it is generally not a major contributor to DOC concentrations in surface water compared to the more recalcitrant, aromatic compounds of DOC (McLaughlin & Kaplan 2013; Mei et al. 2012) and is usually removed as it passes through the watershed soils (Fellman et al. 2009; Mei et al. 2012).

The three major fates of terrestrially derived DOC include: 1) adsorption to soil in the mineral horizon, where it often complexes with iron and aluminum oxides to form spososols (McDowell & Wood 1984), 2) mineralization to CO_2-C by heterotrophic microbes (Aitkenhead-Peterson & Kalbitz 2005; Marschner & Kalbitz 2003; McDowell et al. 2006) and 3) transportation from terrestrial to aquatic ecosystems in runoff from rain or irrigation events. For the first fate of DOC, the degree of DOC adsorption to soil mineral surfaces is proportional to the aluminum and iron oxide contents (Kahle et al. 2004; Palmer et al. 2013) as well as the pH (Tavakkoli et al. 2015) and clay content of the soil (Nelson et al. 1993). Adsorption to soil minerals does not preclude DOC from being degraded by soil microorganisms (Kalbitz et al. 2003a) or from being released during certain environmental soil conditions. An example of an environmentally-stimulated DOC release includes DOC being released resulting from a decline of Ca^{2+} in soil water, which causes a reduction of cation bridging, and in turn, a reduction of adsorption to soil minerals (Kerr & Eimers 2012). In addition, sodium has also been shown to affect DOC release through irrigation water application. A study showed that reactive soil pools of DOC (DOC_{RSP}) irrigated with sodic water (sodium adsorption ratio > 35) had higher DOC release when compared to remnant soils of wetland forests, forests, and range land uses which are exposed to rainfall only (Aitkenhead-Peterson & Cioce 2013). The second fate of DOC is mineralization to CO_2-C by heterotrophic microbes. The biodegradable or labile DOC (BDOC) is the proportion that is usually mineralized. The proportion of BDOC (%BDOC) in a bulk DOC sample obtained from a terrestrial ecosystem varies. Currently, the literature states that %BDOC in throughfall ranges from 19 to 75% (McDowell et al. 2006; Qualls & Haines 1992; Yano et al. 2000), 25% and 53% for water extracted urban grasses and remnant forest leaf litter, respectively, (Cioce & Aitkenhead-Peterson 2015), and 56% for water extracted spruce needle litter (McDowell et al. 2006). In soil solution collected from the organic layer under a hardwood forest and a spruce forest with zero tension lysimeters, BDOC was approximately 30% and 20% biodegradable, respectively (McDowell et al. 2006). Water extractable agricultural soil was 44% biodegradable (McDowell et al. 2006) while root exudate derived from Norway spruce varied in its biodegradability from 30 to 69% depending on N fertilization (Aitkenhead-Peterson & Kalbitz 2005). In urban soils under turfgrass and landscaping shrubs in south-central Texas, %BDOC ranged from 2 to 70% and tended to be affected by sodium inputs from irrigation water (Cioce & Aitkenhead-Peterson 2015). As illustrated, %BDOC in terrestrial ecosystems can be extremely variable. The final fate of DOC is transport to surface water by runoff where it is termed allochthonous DOC (Aitkenhead-Peterson et al. 2003). Once terrestrial or allochthonous DOC is transported into aquatic systems, surface water %BDOC can range from 6% in urban streams to 10% in rural streams (Cioce 2012). Exceptionally high values of %BDOC in surface waters, specifically lentic waters, may be due to the mixture of allochthonous and autochthonous DOC.

Increases in Aquatic DOC

Over the past three decades, increased dissolved organic carbon (DOC) concentrations were reported in many streams in North America and the UK (Evans et al. 2005; Filella & Rodríguez-Murillo 2014; Monteith et al. 2007). There are several conflicting explanations as to why the color and concentration of aquatic DOC are increasing. The most frequently mentioned hypotheses in the literature states that the increased release of DOC from terrestrial to aquatic ecosystems is due to a) the reduction in oceanic salt deposition and atmospheric sulfur as acid deposition; b) climate change in terms of temperature, distribution of precipitation, and increased atmospheric CO_2; and c) changes in land management (Clark et al. 2010). Currently, a general consensus has not yet been determined as many studies have conflicting results.

Atmospheric deposition can influence DOC solubility by changing the ionic strength and pH of the soil solution. Sulfur deposition impacts soils by increasing acidity and ionic strength which decreases DOC solubility (Kalbitz et al. 2000). Declining trends in sulfur deposition has been observed since 1988 and is thought by many scientists to be responsible for increasing instream DOC concentrations by reducing soil acidity which allowed the pH to rise and DOC solubility to increase (Evans et al. 2006; Monteith et al. 2007; Vet et al. 2014). On the other hand, decreased sea salt deposition is also thought to influence increased DOC release from soils. Sea salt deposition occurs in soils through a cation exchange process where marine cations, such as sodium and magnesium, displace acidic cations, such as aluminum and hydrogen on soil particle exchange sites. The aluminum and hydrogen in soil solution makes the soil water acidic and decreases DOC solubility. Therefore, a decreased input of sea salt has been postulated as the cause for increased DOC release to surface waters. The effects of wet sea salt deposition typically occurs within 500 km of the coast while dry deposition can occur over much greater distances (Vet et al. 2014). Sea salt deposition varies by meteorological factors, such as the North Atlantic Oscillation, however, declines in deposition have been postulated to increased DOC release in soils (Clark et al. 2011; Evans et al. 2001; Monteith et al. 2007).

As climate change progresses, increasing DOC concentrations in urban rivers can have large scale implications on carbon sequestration in soils. Recently, carbon isotope analysis revealed that 3-9% of the DOC concentrations in rivers is aged carbon originating from terrestrial carbon sinks that were disturbed and mobilized by human influence (Butman et al. 2015). Additionally, the age of the riverine carbon increased by the degree of population density and urbanization (Butman et al. 2015). Although that study is not the first to link increased DOC concentrations with urbanization, (Aitkenhead-Peterson et al. 2009; Westerhoff & Anning 2000), it is the first to show that urbanization may effect a soils' capacity to store older and typically more stabilized C.

Land use change will continue to increase with population growth as agricultural and native landscapes are converted to urban land use. By 2030, urban land cover is projected to increase by 1.2 million km^2 globally (Seto et al. 2012) and by 75% in the United States by 2051 (Lawler et al. 2014). This expansion is expected to have a large impact on future DOC release from soils from urban centers, as shown in Butman et al. (2015). Until recently, wastewater effluent was thought to be the major contributor of observed DOC increases in urban streams (Sickman et al. 2007; Westerhoff & Anning 2000). However other studies have shown that the impact of wastewater effluent on instream DOC concentrations is minimal. For example, an urban stream in Illinois showed slight DOC increases (23%) from wastewater effluent contribution (Kalscheur et al. 2012) while urban streams in Texas showed no differences in DOC concentrations between urban streams with and without wastewater effluent outfalls (Aitkenhead-Peterson et al. 2009; Kalscheur et al. 2012). In the Dallas/ Fort Worth area, wastewater effluent was shown to contribute only 35% of the total DOC loading in streams, with the remaining 65% derived from non-point sources (Aitkenhead-Peterson & Steele 2016). Since most lotic surface water DOC is derived from allochthonous sources, such as the organic soil horizon (Aitkenhead-Peterson et al. 2003), recent attention has turned to the role watershed soil plays as the source for increased DOC input and the potential mechanisms that may be causing the increased allochthonous DOC release.

The Role of Sodium in DOC Release

Increased salinization of surface waters has been observed over the last few decades and attributed to deicing salts, wastewater effluent, saltwater intrusion and groundwater irrigation (Duan & Kaushal 2015). Highest concentrations of salts have been reported to occur in urban watersheds (Kaushal et al. 2005). This increase in salts, specifically sodium, has been attributed to a disruption of the biogeochemical cycles of carbon and nitrogen (Aitkenhead-Peterson & Cioce 2013; Cioce & Aitkenhead-Peterson 2015; Compton & Church 2011; Green et al. 2008; Green et al. 2009; Lancaster et al. 2016; Steele & Aitkenhead-Peterson 2013). Disruptions in the bioreactive cycles of phosphorus and sulfer have also been attributed to increased salinization (Compton & Church 2011; Nielsen et al. 2003). The mobilization of these bioreactive compounds due to sodium may be through a direct influence, such as an ion exchange mechanism, where sodium replaces H^+ on exchange sites which increases soil pH over time. Green et al. (2009) showed the complete removal of H+ ions (0%) and large increase of Na+ ions

(85%) on soil exchange sites in soils exposed to road salt drainage compared to soils not exposed to road salts (Na^+ 1% and H^+ 98%). As a consequence of increased pH there is an increase in the solubility of humic acids (Stevenson et al. 1996). Indirect effects such as release of monovalent and divalent cations such as NH_4^+, K^+, Ca^{2+} and Mg^{2+} with a high Na^+ input (Eimers et al. 2015; Shainberg & Letey 1984) would necessitate an equivalent release of anionic compounds such as DOC, DON, SO_4^{2-}, or PO_4^{3-} to maintain electroneutrality of soil solution.

Findlay and Kelly (2011) examined the emerging indirect and long term road salt effects on ecosystems. While their paper was concerned mainly about the toxic effect of Cl^- to soil ecosystem function, they acknowledged the effect that sodium may also have on bioreactive cycles. Astebol et al. (1996) and McBean and Al-Nassari (1987) determined that road salt deposition could be found up to 10 m from the road with higher concentrations in soil closer to roads. One of the only studies directly linking road salt use to DOC and soil organic matter was the work by Green et al. (2008) and Green et al. (2009). Green et al. (2008) examined the land adjacent to the A6 (a relatively rural road in northern England) with land use dominated by cattle and sheep grazing on grasses overlying an acidic spodosol (pH 3.78) with varying depths of organic matter. Control soils, soils exposed to drainage from road salts and soils exposed to road salt spray were examined. They reported that DOC concentrations were significantly lower in soils exposed to road salt drainage and pH significantly increased relative to control soils. Only 33% of the variance in DOC concentration was explained by pH and NaCl content of the soil suggesting that other factors may be responsible as well. The second study by

Green et al. (2009) was conducted at the same site, but soil solution samplers were used. Control site DOC ranged from 5 to 32 mg L^{-1} for the October to July sampling period and sodium concentrations ranged from 2 to 5 mg L^{-1} for the same period. Soil solution sodium concentrations reached a high of 5,800 mg L^{-1} closest to the road and declined with distance from the road. DOC concentrations showed a seasonal pattern for all distances from the road (8 to 60 mg L^{-1}) but concentrations appeared to be much lower at the sites 2 m and 4 m from the road during the winter months (8 to 20 mg L^{-1}) compared to sites 16 m from the road (35 to 60 mg L^{-1}). Green and co-authors also ran laboratory simulation experiments with NaCl additions to soil and unfortunately most of their statistical analyses and discussion was on the simulation experiments and not the field experiments conducted. The simulation studies were not however without merit as they were able to examine the effect of NaCl on soil not previously exposed to road salts. Based on these simulation studies by Green et al. (2008) and Green et al. (2009), the effect of road salts on DOC concentration is that newly exposed soils will have the greatest DOC release due to soil dis-aggregation while previously exposed soils that have already had some degree of dis-aggregation will release less DOC.

Multiple studies by Aitkenhead-Peterson and colleagues have investigated the effect of Na^+ derived from irrigation water on DOC and DON release (Aitkenhead-Peterson & Cioce 2013; Cioce & Aitkenhead-Peterson 2015; Pannkuk et al. 2011; Steele & Aitkenhead-Peterson 2012; Steele & Aitkenhead-Peterson 2013) and its effect on the relative abundance of soil microbial communities (Holgate et al. 2011).

In cities with municipal water high in sodium and used for irrigation, DOC solubility was shown to increase significantly in Texas soils (Steele & Aitkenhead-Peterson 2012). Other studies have shown a strong proportional relationship between DOC concentrations and sodium absorption ratios (SAR) within urban streams (Aitkenhead-Peterson et al. 2009; Steele & Aitkenhead-Peterson 2013) and soils (Aitkenhead-Peterson & Cioce 2013; Steele & Aitkenhead-Peterson 2012). There also may be a combined role of bicarbonate (HCO_3) and SAR on DOC release as irrigation water. $NaCO_3$ and $CaCO_3$ showed no significant difference on DOC release, yet a significant relationship between DOC and bicarbonates was observed (Pannkuk et al. 2011). In a study examining NaCl and $NaHCO_3$ with differing EC and SAR values, it was found that the type of sodium in the form of NaCl and $NaHCO_3$ showed some difference in the mass of DOC and DON leached from urban landscape vegetation in Texas (Steele & Aitkenhead-Peterson 2013). Mass of DOC leached increased as salinity (EC) increased with $NaHCO_3$ solutions, however at low salinity, the mass of DOC lost was higher in the NaCl solutions compared to the $NaHCO_3$ solutions (Steele & Aitkenhead-Peterson 2013). Although not all municipal water supplies are high in sodium, the eventual move to alternative sources of irrigation water in urban landscapes will increase as water resources continue to diminish. The sources of this alternative water will most likely be brackish water or treated effluent that is high in dissolved salts (Martinez & Clark 2012). As a result, it is highly likely that sodium loading will increase in urban watersheds.

Fewer studies have investigated the role of sodium in sea salt deposition on DOC release from soils. Salt additions closely resembling coastal salt spray in Oregon showed reduced DOC release from soils with increasing salt concentrations (Compton & Church 2011). Additionally, sodium from coastal seawater has been shown to influence ionic strength in forested soils and cause a decrease in DOC release as seawater concentrations increased (Moldan et al. 2012).

The Role of Sodium and BDOC in Urban Soils

To date, the role of sodium on biodegradable dissolved organic carbon (BDOC) in urban soils is not well understood and only one study has been completed (Cioce & Aitkenhead-Peterson 2015). It is known that DOC biodegradability decreases with soil depth (Boyer & Groffman 1996) and is controlled by DOC molecular structure and size, soil nutrient availability, microbial communities, and soil solution in the soil, as well as temperature and precipitation patterns (Marschner & Kalbitz 2003). However, the mechanisms in which different sodium sources (NaCl and $NaHCO_3$) might mobilize DOC and effect its biodegradation in soils is lacking. A recent laboratory experiment found that high concentrations of sodium fluoride (1105 - 6631 mg kg^{-1} NaF; 605 - 3631 mg kg^{-1} Na) actually increased the degradation of glucose and until inhibition occurred at concentrations higher than 8841 mg kg^{-1} NaF (Ropelewska et al. 2016). The findings from the study by Ropelewska et al. (2016) supported the only urban BDOC study completed, which showed samples containing water extractable soil sodium concentrations above 500 mg kg^{-1} had less than 10% BDOC in the soil (Cioce & Aitkenhead-Peterson 2015). This indicates that the high water extractable soil sodium concentrations may have stimulated microbial communities to degrade and/or mineralize BDOC in soils before the soil samples were obtained. These two studies imply that sodium fertilization within a certain threshold may be stimulating microbial activity in soils and could be influencing terrestrial soil carbon sinks. If BDOC is mineralized or broken down by sodium-stimulated microbial degradation, more organic carbon pools could be accessed and utilized by microbes. As a result, the proportion of refractory DOC available for runoff would increase and microbial degradation of the refractory DOC would decrease due to the increased availability of BDOC.

Determining DOC and BDOC from Optics

Specific UV absorbance (SUVA) could prove to be a powerful technique for determining the amount of DOC available to leach into streams. Previous work determined that SUVA at 254 nm and 280 nm can be used to determine the percent of aromatic DOC fractions as well as estimating DOC concentrations and molecular weight (Chin et al. 1994; Simonsson et al. 2005; Traina et al. 1990). Larger SUVA values indicate a higher percentage of aromatic DOC compounds while smaller SUVA values indicate larger amounts of biodegradable DOC compounds that are simple molecules and low in molecular weight as well as decreased amounts of lignin-derived compounds that are high in molecular weight (Kalbitz et al. 2003b). Since some aromatic compounds of DOC are semi-labile, aromaticity would not be the best predictor for determining the potential amount of water extractable BDOC. Rather, a relationship between SUVA and %BDOC may be more applicable as the remaining percent would be refractory DOC potentially able to runoff into streams.

SUVA at 254nm and 280nm have been used to determine the %BDOC in soil solutions for forests, wetlands, and grasslands with conflicting results (Fellman et al. 2009; Sun et al. 2012). $SUVA_{280}$ was a significant predictor of %BDOC across land uses when soil samples from China and Canada were combined, however when analyzed separately there was no significant relationship (Sun et al. 2012). This was likely due to the small range of $SUVA_{280}$ (Canada: 0.15-0.17 and China: 0.09-0.10) and %BDOC (Canada: 42-52% and China: 37 – 44%) within each continent. Conflicting results were also observed in temperate soils in Alaska when wetland soils showed a significant relationship between %BDOC and $SUVA_{254}$ while forest soils did not (Fellman et al. 2009). This may be indicative of anaerobic vs aerobic decomposition of terrestrial C compounds. However, $SUVA_{280}$ has been successfully used to identify significant positive relationships with %DOC aromaticity (Kalbitz et al. 2003a; Kalbitz et al. 2003b) as well as inverse relationships with %DOC mineralization (Marschner & Kalbitz 2003) and %BDOC (McDowell et al. 2006). $SUVA_{254}$ has been successfully used for determining significant positive relationships between %DOC aromaticity by ^{13}C-NMR (R^2=0.97) and $SUVA_{254}$ (Weishaar et al. 2003), changes in DOC aromaticity and changes in acidity (Clark et al. 2011), direct positive relationships between $SUVA_{254}$ and molecular weight and humic-like fluorescence and a direct negative relationship with fulvic-like fluorescence (Nguyen & Hur 2011). Furthermore, $SUVA_{254}$ has been used to identify a significant relationship between aromatic compound enrichment during biodegradation and %BDOC, revealing that aromatic compounds are relatively stable and accumulate as DOC biodegradation increases (Kalbitz et al. 2003b). If significant relationships between %BDOC and $SUVA_{254}$ are found, further work could apply this predictive tool at a watershed scale and use it to estimate future trends in terrestrial DOC available for runoff.

Study Objectives

The objectives of this study were to:

- Examine if sodium from different sources effect %BDOC
- Determine if time of exposure to sodium from 1) deicing salts, 2) irrigation water, or 3) deposition of sea salts effect %BDOC in urban soils
- Investigate if %BDOC in urban soils can be predicted using optics such as $SUVA_{254}$

This study will expand on previous knowledge of BDOC in urban soils and assess the roles of sodium from three different sources on %BDOC. It has been shown that sodium derived from high $NaHCO_3$ irrigation water impacts %BDOC in urban and rural soils in Texas (Cioce & Aitkenhead-Peterson 2015); however, it is unknown if the impact of sodium on %BDOC is consistent across different cities and sodium sources. This study will determine the effect of sodium on %BDOC, $SUVA_{254}$ and water extractable soil DOC and DON across three cities (Chicago, IL; Galveston, TX; Bryan/College Station, TX) and determine whether the sodium source (road salts, sea salt deposition, or irrigation water) influences a response. This information will be valuable for determining whether sodium influences BDOC and is related to DOC availability for runoff.

The hypotheses for this study are:

1. $H1_0$: There will be no significant relationship between %BDOC, DOC, DON and SUVA254 when soils are exposed to differing sodium sources.

   $H1_1$: %BDOC and water extractable DOC, DON and SUVA254 will significantly differ when soils are exposed to differing sodium.

2. $H2_0$: There is no significant difference in %BDOC, DOC, DON or $SUVA_{254}$ whether soil is exposed to a sodium source for 0-5, 6-10, 11-20, 21-30. or >30 years irrespective of the specific sodium source.

   $H2_1$: %BDOC, DOC, DON and $SUVA_{254}$ will alter dependent upon the exposure time of soil to

   $H3_0$: %BDOC, DOC and DON cannot be modeled across cities using $SUVA_{254}$

   $H3_1$: %BDOC, DOC and DON can be modeled across cities using $SUVA_{254}$

2. MATERIALS AND METHODS

Experimental Design

This experiment examines the effects of time of exposure to three sources of sodium: 1) deicing salts, 2) oceanic deposits and 3) irrigation water on %BDOC, DOC, and DON. Time of exposure is assumed to be the time since the site was developed and new soil or turfgrass sod was installed on the property. Age ranges selected were new development 0-5 years, 6-10 years, 11-20 years, 21-30 years and >30 years. Cities were selected based on their exposure to the selected sodium sources: Chicago, IL for deicing salts, Galveston, TX for oceanic deposition and Bryan/College Station, TX for irrigation water. Thus the independent factors for this study are 1) sodium source and 2) length of time of exposure to sodium and the dependent factors are %BDOC, DOC, and DON.

Site Descriptions

Chicago is the largest city examined and has the highest population density, while Galveston is the smallest city examined and has the lowest population density (Table 1). Chicago experiences yearly snow precipitation and below freezing temperatures necessitating the use of deicing salts while the lack of snow in Galveston and Bryan/College Station negates their use of deicing salts (Table 1). Galveston is a barrier island in the Gulf of Mexico and is subject to high sodium inputs from sea salt deposition. Bryan/College Station was selected because prior research suggested that irrigation with sodic groundwater effected DOC and DON adsorption in soils (Aitkenhead-Peterson & Cioce 2013), %BDOC (Cioce & Aitkenhead-Peterson 2015), relative abundance and community composition of soil microbes (Holgate et al. 2011), general leaching of DOC and DON (Holgate et al. 2011; Pannkuk et al. 2011), and runoff to surface waters (Aitkenhead-Peterson & Steele 2016; Aitkenhead-Peterson et al. 2009). Irrigation with municipal water is likely to be a greater issue in Bryan/College Station than in Chicago or Galveston due to its higher sodium concentration (Table 2). Soil groups differ among the three cities with sandy soil being dominant in Galveston and College Station and clayey soils being dominant in Chicago (Table 3).

Table 1. Physical demographics of the three cities examined during this study.

City	Sodium Source	Year Settled	Area (km^2)	Population	Density (# km^{-2})	Snow (mm)	Rain (mm)	Temp (°C)	Prior Land Use
Chicago, IL	Deicing salts	1780	606	2,695,598	4,447	945	843	9.8†	Savannah/ Woodland
Bryan/College Station, TX	Irrigation water	1866	115	228,660	926	0	1020	20.7‡	Post Oak Savannah
Galveston, TX	Sea salt	1816	539	47,243	479	0	1114	21.8‡	Saltgrass Marsh

Climate (Koopen-Geiger): †Dfa ‡Cfa

Table 2. Sources of municipal water and associated sodium concentrations for each city examined

City	Year	Source		Na$^+$ (mg L^{-1})
Chicago, IL	2014	Surface	Lake Michigan	9.53 – 10.0
Galveston, TX	2015	Surface	Brazos River	46.9 – 62.8
College Station, TX	2011	Ground	Carrizo Wilcox/ Sparta Aquifer	193
Bryan, TX	2011	Ground	Simsboro Aquifer	230

Source: City water quality reports

Table 3. Soil groups and soil attributes for cities sampled in this study.

City	Soil Group	Sample Size (%)	Clay (%)	Sand (%)	Silt (%)	OM (%)	Ksat (mm/hr)	BD (g/cm^3)	CEC (cmol charge kg^{-1} soil)
Galveston	Entisol	74.3	5±0	94±0	1±0	1±0	331±0	1.6±0	3±0
	Beach	25.7	2±0	98±0	1±0	0±0	508±0	1.5±0	3±0
BCS	Alfisol	97.1	11±2	68±7	21±6	1+0	44±53	1.5±0.1	5±1
	Vertisol	2.9	50±0	22±0	28±0	2±0	0.8+0	1.8±0	50±0
Chicago	Urban-Orthent	69	36±0	8±0	56±0	3±0	3±0	1.9±0	19±0
	Urban-Alfic-Udarent	25	44±0	8±0	48±0	1±0	1±0	2±0	23±0
	Urban-Psamment	6	25±0	35±0	40±0	2±0	10±0	1.8±0	18±0

OM = organic matter, Ksat = saturated hydraulic conductivity, BD = soil bulk density, CEC = cation exchange capacity

Sample Collection and Processing

Sampling locations in each city were selected from realtor websites based on the age of the house and the presence of in-ground irrigation systems in BCS. In each city, seven single family homes were selected based on their fit into each of the five pre-determined time of sodium exposure categories (0-5yr, 6-10yr, 11-20 yr, 21-30 yr, >30 yr) for a total of 35 sampling locations in each city and 105 total locations for the experiment. A benefit of using this method of selection was that it ensured that in-ground irrigation systems were installed at the BCS sites (Figure 1). For the older Chicago sites (Figure 2), if imagery data existed, the address was checked using the historic function in Google Earth to ensure it was indeed built on the date displayed on the realtor website and there was not a rebuild on a previous home site. Figure 3 displays the sampling location sites for Galveston, TX.

At each sampling site, three soil cores (2 cm diameter, 15 cm depth) were obtained and composited for analysis. Samples were air dried, sieved (2 mm), and weighed. 25 g of each soil sample was added to 250 mL of ultra-pure water (reverse osmosis water fed through a Beckman water purification system which filtered, UV sterilized and filtered water through a 0.2 μm filter) for a 1:10 soil:water ratio. The solutions were placed on a shaker at 400 rpm for 4 hours and then centrifuged for 5 min at 19,000 g-force. The extracted solutions were then filtered to remove any floating organic material with a Whatman GF/F (nominal pore size 0.7 μm) filter and DOC concentrations were quantified within 24 h of extraction. Extracts were then diluted to 10 mg L^{-1} DOC prior to running the biodegradability procedure.

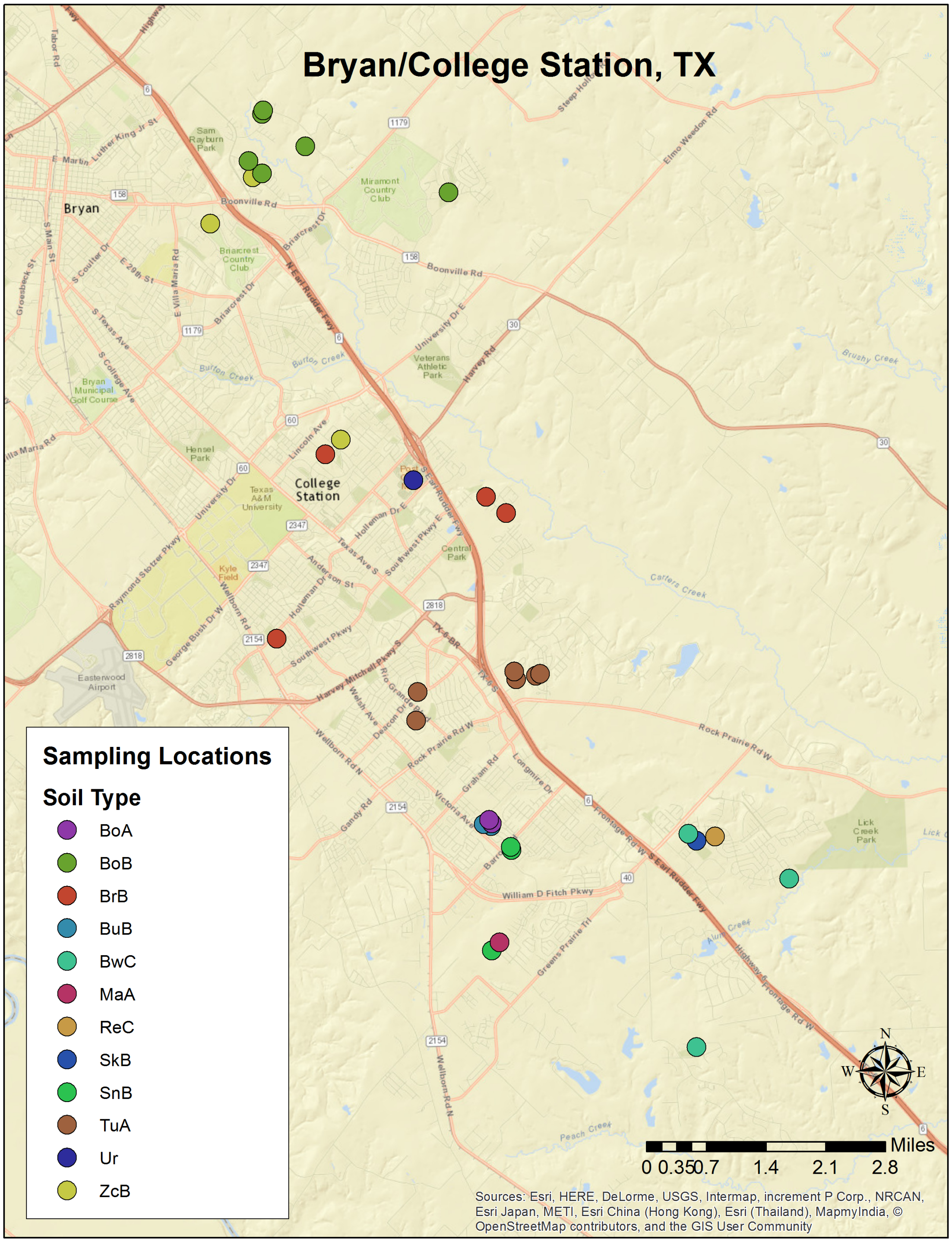

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Figure 1. Relative sampling locations and soil series of sample sites in BCS, TX.

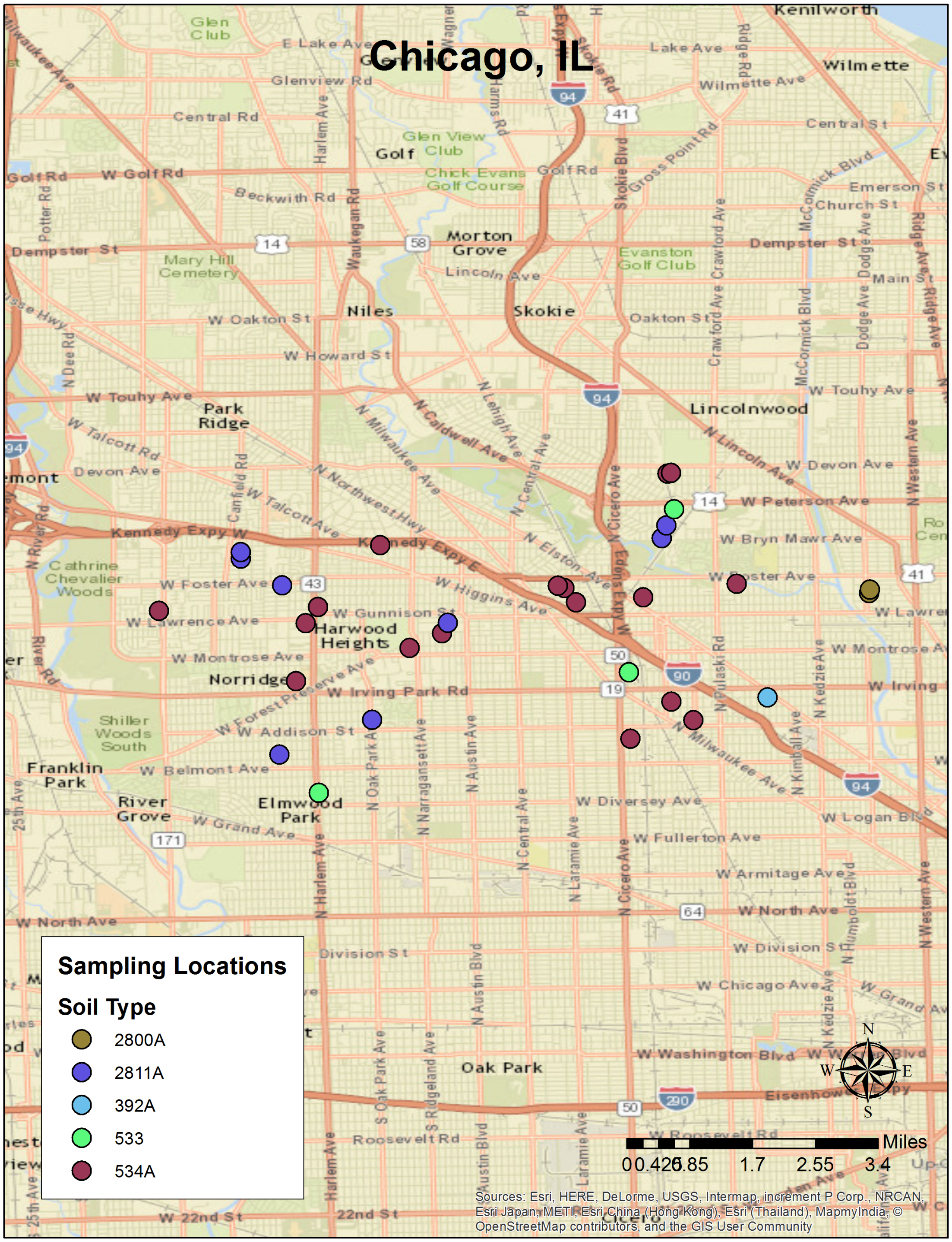

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Figure 2. Relative sampling locations and soil series of sample sites in Chicago, IL.

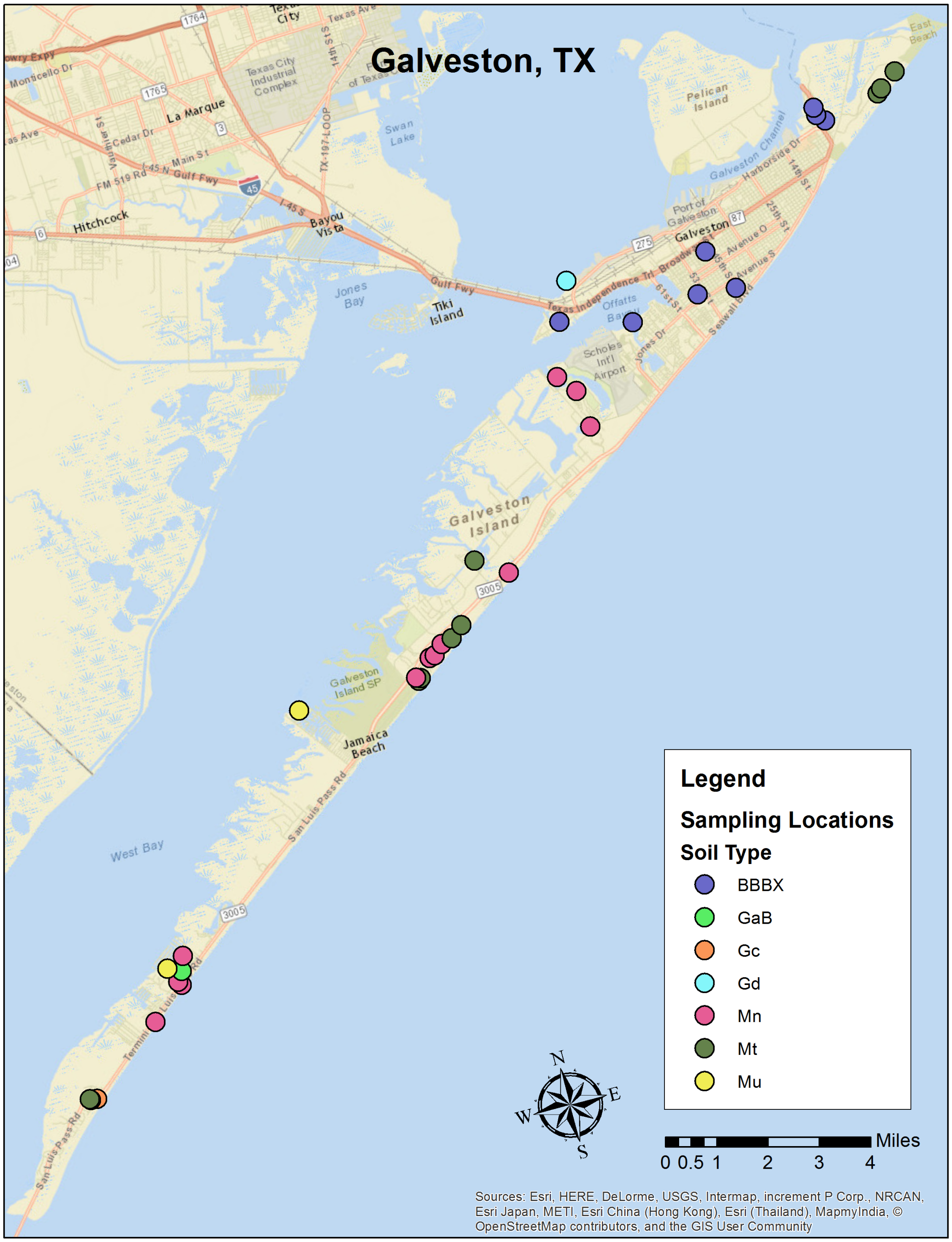

Figure 3. Relative sampling locations and soil series of sample sites in Galveston, TX.

DOC Biodegradation Method

The BDOC method used in Cioce and Aitkenhead-Peterson (2015) was modified for this study. 50 mL of the diluted extracts (10 mg/L DOC) were combined in an Erlenmeyer flask with 7.14 mL of freshly treated, but un-disinfected effluent (collected from treatment effluent prior to UV disinfection), and 1.43 mL nutrient solution. Effluent was obtained from the Carter's Creek Wastewater Treatment Plant, College Station, TX in 1.9 L containers. The effluent was used as a bacterial inoculant source for DOC biodegradation. The nutrient solution (1.43 mL) was modified from McDowell et al. (2006) and comprised of 0.3085 mM (0.0165 g) NH_4Cl, 1.21 mM (0.1647 g) KH_2PO_4, 0.62 mM (0.0527 g) $NaNO_3$, 0.0113 mM (0.0016 g) Na_2SO_4, and 0.0198 mM (0.0022 g) $CaCl_2$ to create ideal nutrient conditions for DOC biodegradation by microbes. Three small pieces (1 cm^2) of ashed glass fiber filter paper was added to each incubation flask to stabilize microbes. The contribution of DOC from the filter paper to the incubation solution was assumed to be negligible as it was non-detectable in prior work (Cioce & Aitkenhead-Peterson 2015).

The samples were covered with parafilm to prevent evaporation with small holes poked into the parafilm to allow release of CO_2. The samples were incubated at 25 ºC for 7 days and then analyzed for DOC. Input DOC (μg) derived from soil extracts (50 mL) and effluent (7.14 mL) were calculated while the final DOC (μg) was calculated as combined soil extract and effluent (57.14 mL). Two controls were used: 1) A blank including double deionized water (50 mL), 7.14 mL untreated effluent, and 1.43 mL nutrient solution to assess microbial DOC uptake of the effluent and 2) a 10 mg/L glucose solution (50 mL) with 7.14 mL untreated effluent, and 1.43 mL nutrient solution to monitor the inoculants' validity as a source for the biodegradation of DOC through glucose uptake. All controls and samples were run in triplicates.

Chemical Analysis

Electrical conductivity (EC) and pH were recorded for all unfiltered soil extracts. Filtered extracts were analyzed for dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) using high temperature Pt-catalyzed combustion with a Shimadzu TOC-VCSH and Shimadzu total measuring unit TNM-1 (Shimadzu Corp. Houston, TX, USA). Dissolved organic carbon was measured as non-purgeable carbon which entails acidifying the sample (250 µL 2 M HCl) and sparging for 4 min with C-free air.

Ammonium-N was analyzed using the phenate hypochlorite method with sodium nitroprusside enhancement (USEPA method 350.1), nitrate-N was analyzed using Cd-Cu reduction (USEPA method 353.3), and orthophosphate-P was analyzed using the ascorbic acid-molybdate blue method. All colorimetric analyses were performed using a Westco Scientific Smartchem Discrete Analyzer (Westco Scientific Instruments Inc. Brookfield, CT, USA). Calcium (Ca), magnesium (Mg), potassium (K) and sodium (Na) in the extracts were used for the estimation of sodium adsorption ratio (SAR) and exchangeable sodium percentage (ESP). Other elements (Fe, Zn, Mn, B, S, Cu) in the extracts were also quantified using inductively coupled plasma mass spectrometry (ICP) (Spectro Genesis: Spectro, Germany) using the method described in (Franson 1989). Dissolved organic nitrogen was estimated by deducting inorganic-N (NH_4-N + NO_3-N) from TDN. $SUVA_{254}$ was quantified on a Shimadzu 280 spectrophotometer (Shimadzu Corp. Houston, TX, USA) at wavelength of 254 nm.

Statistical Analysis

Tests of normality and equal variance were run on the data to assess the need for transformation prior to statistical analysis. Analyzed DOC and Zn data was transformed using the reciprocal square root to meet the assumptions of normality and equal variances. Analyzed DON data met the assumption of equal variances but failed to meet the assumption of normality for all data transformations. The Kruskal - Wallis nonparametric test then was used. $SUVA_{254}$ and EC data were log transformed for analysis. All other extract data was analyzed using the nonparametric Kruskal - Wallis test and the post hoc test used was pairwise comparisons. Untransformed data was reported in the thesis.

A univariate analysis of variance was performed with 1) sodium source and 2) length of exposure to sodium (soil age) as independent variables and water extractable dissolved organic matter (DOM) fractions (DOC and DON, %BDOC and $SUVA_{254}$) as dependent variables. The data was pooled and the univariate analysis of variance was rerun if any independent variable was not significant. A post hoc Tukey test was performed to determine the significant differences among groups.

The following equations were used to calculate ESP and SAR:

$$ESP = \frac{Na^{+}}{Na^{+} + K^{+} + Mg^{2+} + Ca^{2+}} * 100$$

$$SAR = \frac{Na^{+}}{\sqrt{\frac{1}{2}Mg^{2+} + Ca^{2+}}}$$

Regression analysis was performed on %BDOC and various independent variables to assess their relationship and determine if a significant trend existed.

A backward stepwise regression analysis was performed using all extraction data, soil age, and source to determine the best independent variables for predicting %BDOC, DOC, and DON. Those independent variables selected were used in a partial least squares (PLS) regression analysis with a full cross validation using an Orthogonal Scores algorithm (Martens & Naes 1989). The full cross validation removes one sample at a time and refits the model using the new equation to predict the removed sample. The full cross validation method is often preferred over a test set validation when the sample size is limited such as this study (Martens & Dardenne 1998). In this experiment, the best model was chosen based on a high R^2 and low root mean square error (RMSE).

The modeling step was not to produce a predictive model per se, but to identify the independent variables that had the largest significant effect on %BDOC, DOC and DON in order to identify and interpret potential mechanisms in their production. Statistical analysis was performed using SPSS v22 and the cross validation was performed using Unscrambler v9.8 (Camo Software Inc., Woodbridge, NJ, USA).

3. RESULTS AND DISCUSSION

This study examined the theory that sodium exposure to watershed soils would increase DOC solubility of humic acids, leading to a smaller fraction of labile DOC and larger fraction of refractory DOC available for transport in soil solution. To test this hypothesis, urban soils from three U.S. cities were examined based on their source of sodium and length of exposure time to the sodium source. An assumption was made that newly constructed homes had new top soil and/or sod that had not been previously exposed to the sodium source. The study concentrated on the labile fraction (%BDOC) and refractory fraction ($SUVA_{254}$) of water extractable DOC and also on water extractable DON. Univariate analysis of variance determined that sodium source had a significant effect on all major dependent variables tested, which included %BDOC ($p < .001$), DOC ($p = .03$), DON ($p < .001$), and $SUVA_{254}$ ($p < .001$) and soil exposure time had a significant effect on water extractable DOC ($p < .001$) and DON ($p < .001$) but not on %BDOC ($p = 0.13$) or $SUVA_{254}$ ($p = 0.25$).

Sodic soils are classified as having an EC< 4 dSm^{-1}, pH > 8.5, SAR > 13, and ESP > 15 while saline soils have an EC > 4, pH < 8.5, SAR < 13, and ESP < 15. In this experiment, BCS soils exposed to irrigation water have sodic characteristics whereas Galveston soils exposed to sea salt deposition have saline characteristics. Chicago soils have sodic characteristics except that the pH (at an average of 7.5) is less than the required pH of 8.5 to classify it as a sodic soil (Table 4). All extract data is shown in Table 4.

Table 4. Mean values for data. Numbers in parenthesis are standard deviation. Significant differences within age and source are indicated with a lowercase letter ($p < .05$).

	Source			Age				
	Deicing	Irrigation	Sea Salt	0 to 5	6 to 10	11 to 20	21 to 30	> 30
Number of Samples	33	34	35	20	21	20	18	23
pH	^{a}7.5 (0.2)	^{b}8.7 (0.8)	^{a}7.8 (0.57)	7.7 (0.7)	8.0 (0.7)	8.1 (0.8)	8.3 (0.8)	7.9 (0.8)
EC (uScm)	^{a}149 (36)	^{a}169 (97)	^{b}94 (36)	123 (36)	148 (97)	127 (79)	152 (79)	136 (70)
Na (µg/g soil)	^{a}180 (133)	^{a}333 (287)	^{b}34 (36)	106 (83)	155 (201)	206 (280)	260 (252)	186 (226)
SAR	^{a}35 (27)	^{a}49 (32)	^{b}7 (8)	20 (15)	24 (27)	33 (34)	43 (37)	33 (32)
ESP (%)	^{a}35 (17)	^{a}45 (18)	^{b}13 (9)	29 (17)	27 (21)	31 (20)	36 (22)	31 (22)
Ca (µg/g soil)	^{ab}124 (45)	^{a}171 (108)	^{b}115 (39)	132 (44)	163 (115)	137 (84)	131 (42)	122 (61)
Mg (µg/g soil)	^{a}54 (25)	^{a}85 (84)	^{b}25 (9)	35 (12)	56 (72)	56 (46)	75 (71)	55 (56)
K (µg/g soil)	^{a}83 (46)	^{ab}80 (66)	^{b}88 (228)	54 (24)	60 (39)	79 (69)	96 (64)	127 (278)
Fe (µg/g soil)	^{a}150 (177)	^{b}652 (1013)	^{c}54 (24)	71 (40)	270 (745)	281 (451)	597 (1068)	241 (470)
Zn (µg/g soil)	^{ab}1.2 (0.8)	^{a}1.9 (1.7)	^{b}0.87 (0.30)	^{a}0.8 (0.24)	^{a}1.0 (1.0)	^{ab}1.3 (0.7)	^{b}1.9 (1.8)	^{b}1.6 (1.2)
Cu (µg/g soil)	^{a}0.31 (0.22)	^{b}0.51 (0.32)	^{a}0.29 (0.11)	0.29 (0.14)	0.29 (0.17)	0.40 (0.24)	0.48 (0.27)	0.41(0.34)
Mn (µg/g soil)	^{ab}0.46 (0.51)	^{a}1.12 (1.44)	^{b}0.18 (0.11)	^{a}0.19 (0.13)	^{ab}0.54 (1.0)	^{ab}0.56 (0.61)	^{b}1.06 (1.36)	^{ab}0.62(1.12)
HCO$_3$ (µg/g soil)	^{a}384 (187)	^{b}591 (292)	^{c}108 (129)	359 (239)	392 (318)	350 (293)	413 (292)	292 (316)
S (µg/g soil)	^{a}16 (5)	^{b}46 (83)	^{c}10 (5)	24 (29)	41 (103)	17 (11)	23 (25)	14 (9)
B (µg/g soil)	^{a}0.54 (0.60)	^{a}0.91 (1.21)	^{b}0.03 (0.10)	0.13 (0.17)	0.41 (0.98)	0.46 (0.62)	0.97 (1.24)	0.52 (0.79)
NH$_4$ – N (µg/g soil)	^{a}9.0 (4.0)	^{b}2.7 (2.0)	^{b}2.9 (2.2)	3.2 (2.8)	4.6 (3.6)	4.8 (5.2)	4.9 (3.8)	6.3 (4.2)
SUVA254 (Lmg^{-1}m^{-1})	^{a}5.8 (3.3)	^{b}11.0 (4.7)	^{b}9.3 (5.9)	8.5 (5.6)	9.5 (5.4)	7.0 (4.4)	7.7 (5.1)	13.2 (7.6)

The Influence of Sodium Source on Soil Chemistry

It was assumed that sodium entered the soil in the form of NaCl for soils exposed to sea salt deposition and deicing salts in Galveston and Chicago, respectively. While sodium from soils collected in BCS were assumed to enter the soils in the form of $NaHCO_3$. The concentrations of Na within the soils were significantly different among the sodium sources ($p < 0.001$). Figure 4 shows that soils exposed to sea salt deposition in Galveston had significantly lower Na concentrations (34 ± 6 µg/g) than soils exposed to deicing salts (180 ± 23 µ/g) and irrigation water (333 ± 49 µg/g). Due to this difference in Na concentration, it is expected that DOC, %BDOC, and DON in soils exposed to sea salt deposition will not be influenced in the same way as soils exposed to higher Na concentrations.

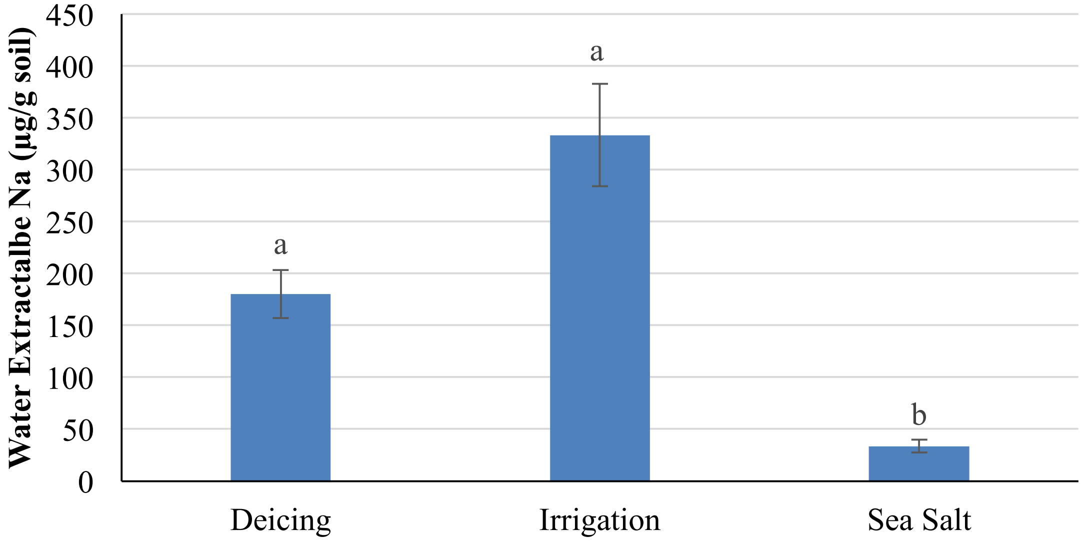

Figure 4. Mean water extractable Na concentrations in urban soils exposed to different sodium sources. Different lower case letters indicate a significant difference at $p < 0.05$. Error bars are standard error.

%BDOC

BDOC is that fraction of labile (easily mineralized C) carbon found in soil solution, throughfall or water extracts (McDowell et al. 2006). The range of %BDOC values in the current study (0-56%) is similar to the only other study completed on urban soils (19-46%) (Cioce & Aitkenhead-Peterson 2015). To date, no studies have examined the influence of different sodium sources on BDOC in urban soils. The mean %BDOC in soils was significantly different among sources (Figure 5). Urban soils exposed to sea salt had the highest %BDOC (46 ± 6%), urban soils irrigated with sodic water had the second highest %BDOC (29 ± 3%), and urban soils exposed to deicing salts (18 ± 2%) experienced the lowest %BDOC. The null hypothesis ($H1_0$) that sodium source does not affect %BDOC in soils was rejected ($p < 0.001$).

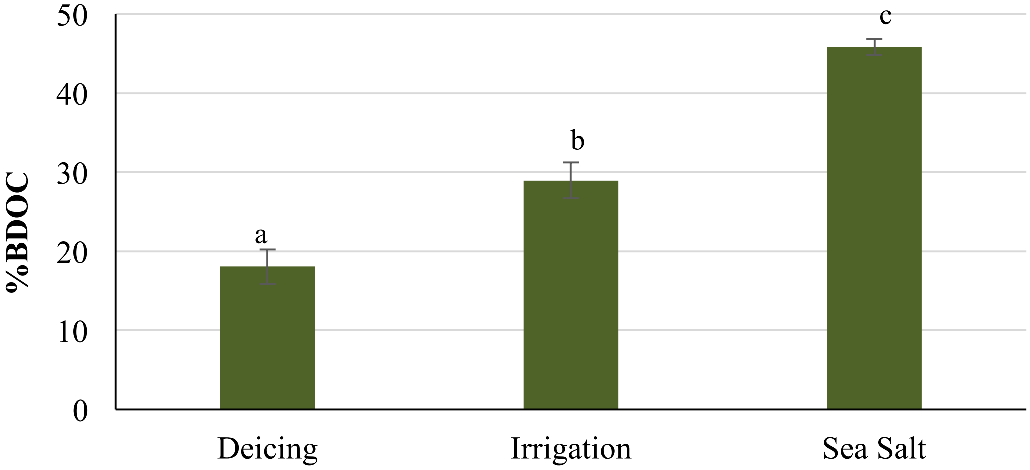

Figure 5. Mean %BDOC in urban soils exposed to deicing salts, sodic irrigation water and sea salt deposition. Differences in lower case letters indicate significant differences at $p < 0.05$. Error bars are standard error.

The soils exposed to sea salt deposition have the highest %BDOC and the lowest Na concentrations. Although there was no significant difference in the mean Na concentrations between soils exposed to deicing salts and irrigation water, there was a significant difference in %BDOC. This suggests a potential influence from the form that Na enters the soil (NaCl or $NaHCO_3$) on %BDOC. This relationship is demonstrated when observing that %BDOC in soils exposed to sodium in the form of NaCl decrease in %BDOC at a faster rate than soils exposed to $NaHCO_3$ (Figure 6). Although it is expected that the effect is due to sodium the fact that soil textures are different among the sites cannot be ignored.

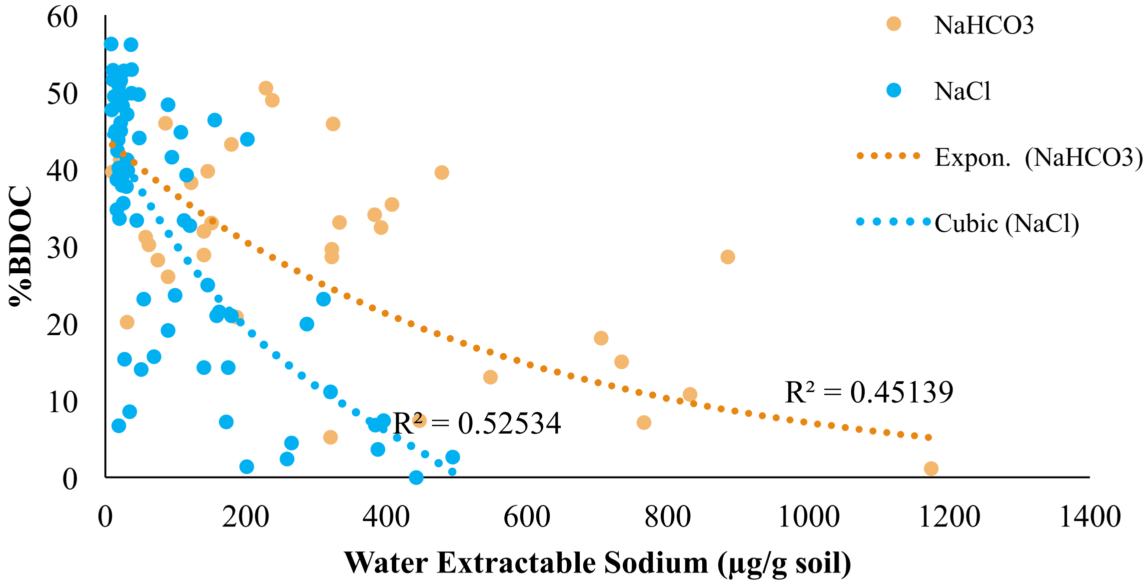

Figure 6. Relationship between %BDOC and water extractable sodium for NaCl and $NaHCO_3$ ($p < 0.001$).

DOC

DOC solubility in soils has been shown to have a direct relationship with S.A.R and Na concentrations (Steele & Aitkenhead-Peterson 2012) as well as bicarbonate concentrations (Pannkuk et al. 2011) within soils. However, the influence Na source on DOC release in soils has not been compared. DOC release was significantly different among sodium sources, ($p = 0.03$; Figure 7) The mean DOC concentration was significantly higher in soils exposed to irrigation water (388 ± 53 μg/g soil) compared to those exposed to sea salt deposition (235 ± 21 μg/g soil), while soils exposed to deicing salts (275 ± 31 μg/g soil) did not significantly differ from irrigation or sea salt deposition sources.

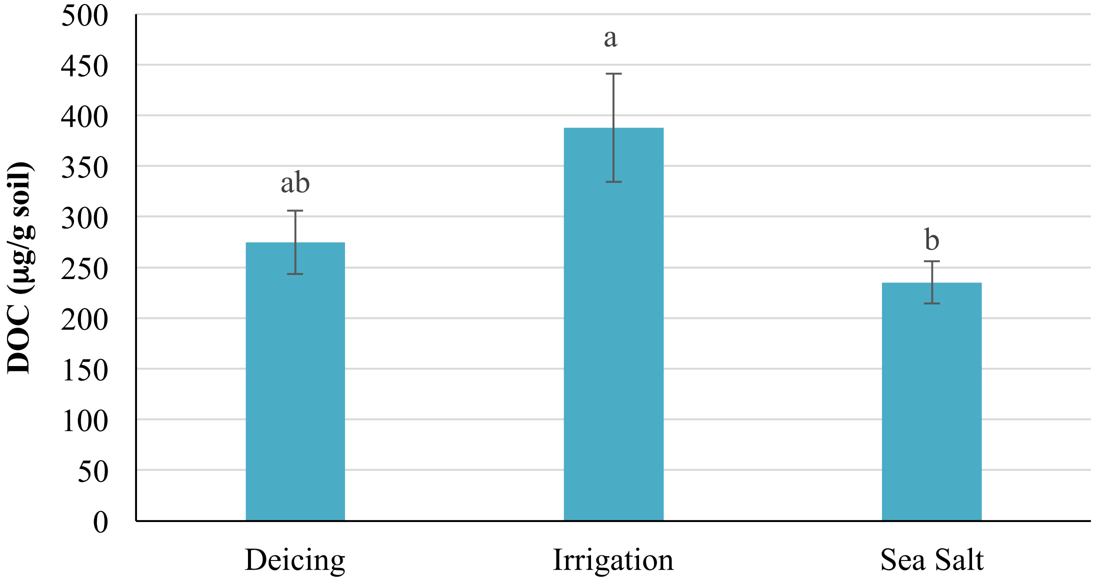

Figure 7. Water extractable DOC concentrations in urban soils exposed to different sodium sources. Different lower case letters indicate a significant difference at $p < 0.05$. Error bars are standard error.

The significant difference in DOC release between sea salt and irrigation sources can be explained by the significantly large difference in Na concentrations in the soils (Figure 4). Due to the large amount of Na exposure in soils exposed to irrigation water, DOC release is expected to be higher than soils exposed to less Na, as seen in sea salt deposition. There is an obvious direct relationship between DOC release and Na concentrations between all sources (Figure 8) however, the lack of significance difference in DOC release between deicing and sea salt deposition suggests another parameter may be influencing DOC release besides just Na. High alkalinity can also increase DOC release in soils (Tavakkoli et al. 2015) which may be influencing the higher DOC release observed in soils exposed to irrigation water (Figure 9). Since Na enters the soil in the form of $NaHCO_3$, the bicarbonate ion increases soil pH and as a result, increases DOC solubility. Since Na enters the soils as NaCl for deicing salts and sea salt deposition, DOC solubility is dependent on Na concentrations which does not influence pH as strongly as HCO_3 (Tavakkoli et al. 2015).

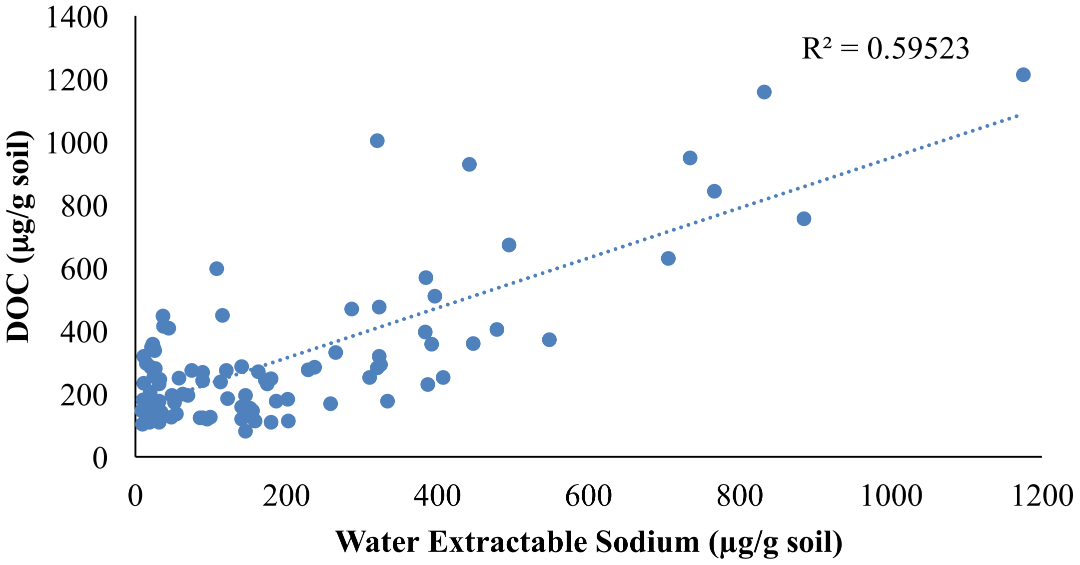

Figure 8. The relationship between DOC and water extractable sodium ($p < 0.001$).

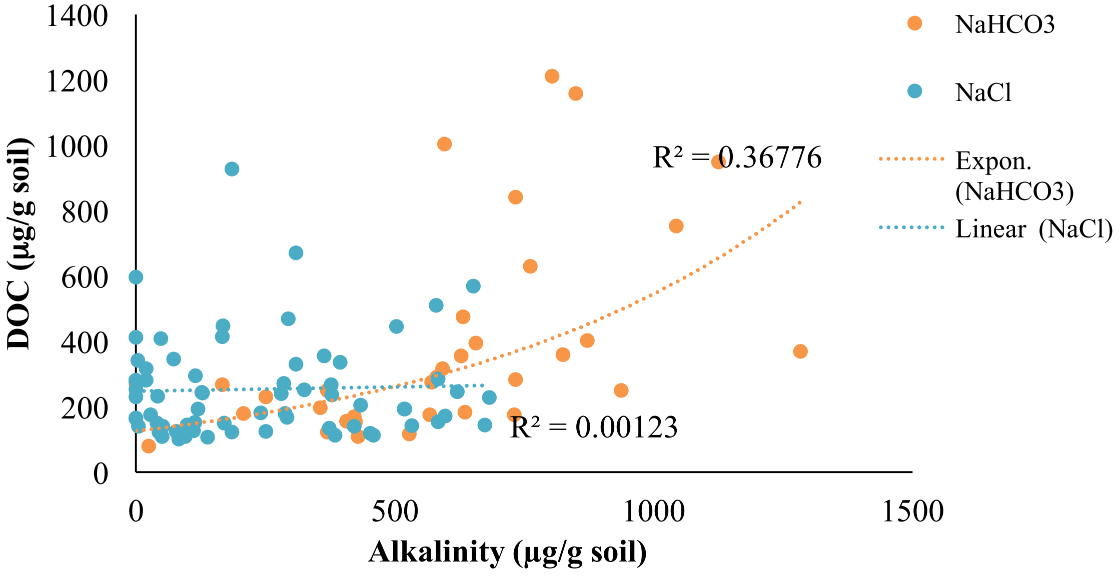

Figure 9. Relationship between DOC and alkalinity in soils for NaCl ($p = 0.78$) and NaHCO3 ($p = 0.001$).

DON

DON and DOC are usually highly correlated because DON is a subset of DOC in that it is a C compound with amino groups (NH_3) attached. Microbes and soil enzymes cleave NH_3 off the molecule and the amino group becomes NH_4^+. Therefore, factors influencing DON solubility are similar to DOC. Mean water extractable DON concentrations in urban soils were significantly different among sodium sources ($p < 0.001$; Figure 10). Urban soils exposed to deicing salts had significantly lower DON concentrations (17 ± 3 μg/g soil) compared to soils exposed to irrigation water (33 ± 5 μg/g soil) and sea salt deposition (23 ± 2 μg/g soil). Soils exposed to deicing salts also experienced significantly higher mean $NH_4 – N$ concentrations (9 μg/g soil) than soils exposed to irrigation water (2.7 μg/g soil) and sea salt deposition (2.9 μg/g soil), suggesting microbes may have been inhibited to uptake $NH_4 – N$.

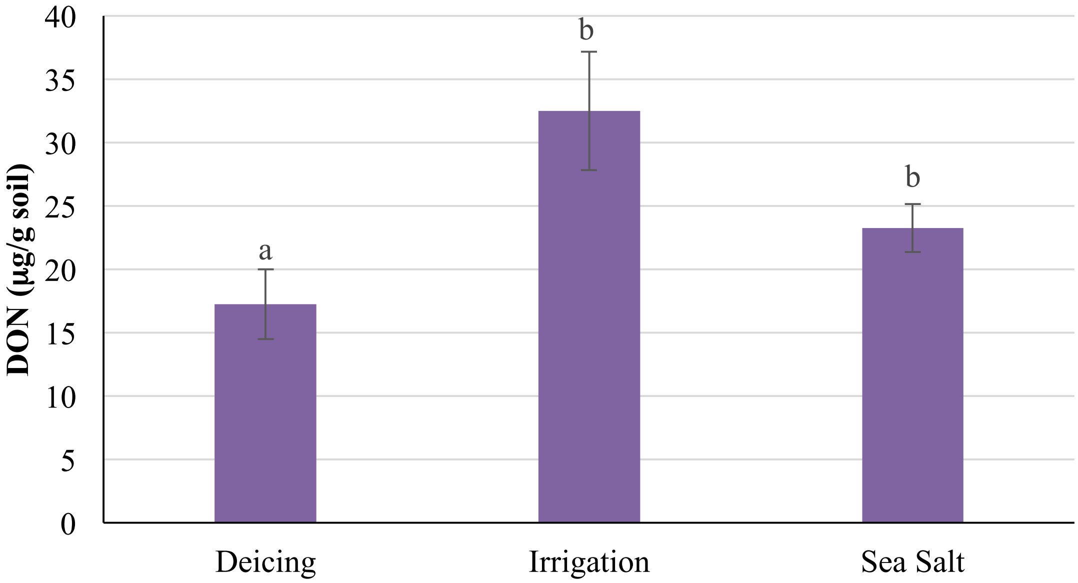

Figure 10. Water extractable DON concentrations in urban soils exposed to different sodium sources. Different lower case letters indicate a significant difference at $p < 0.05$. Error bars are standard error.

SUVA$_{254}$

Large SUVA$_{254}$ values indicate a higher percentage of aromatic, recalcitrant DOC compounds while smaller SUVA values indicate a larger proportion of BDOC compounds that are simple molecules that are low in molecular weight (Kalbitz et al. 2003b). It has previously been shown that %BDOC has an inverse relationship with SUVA$_{280}$ values and as %BDOC decreases, SUVA$_{280}$ values increased along with structural aromatic DOC molecules (Kalbitz et al. 2003a). In this study, mean SUVA$_{254}$ values in soils exposed to deicing salts were significantly lower than soils exposed to irrigation water and sea salt deposition ($p < 0.001$; Figure 11), regardless of exposure time.

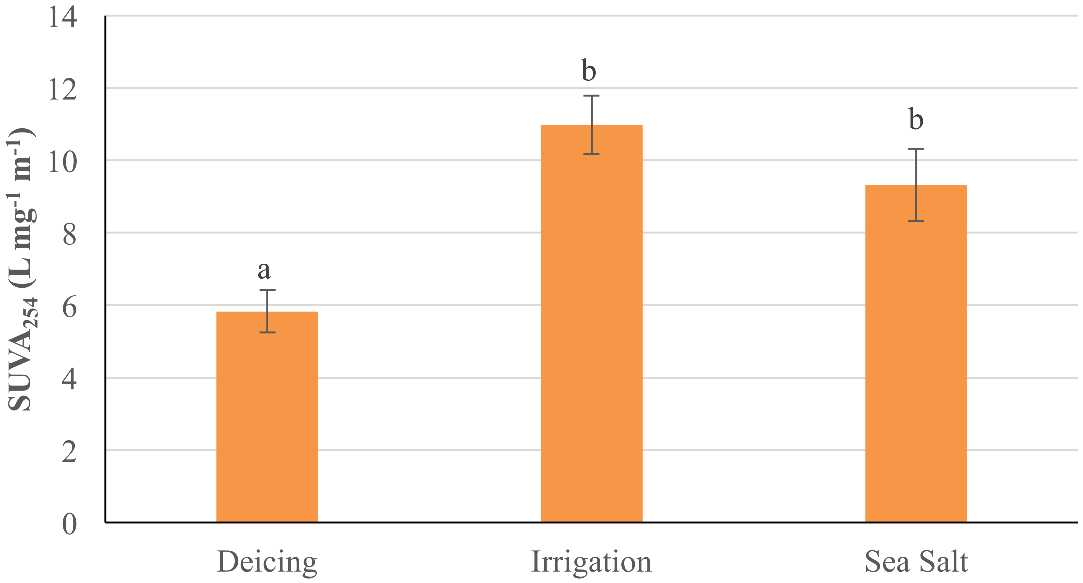

Figure 11. Mean water extractable SUVA$_{254}$ values in urban soils exposed to different sodium sources. Different lower case letters indicate a significant difference at $p < 0.05$. Error bars are standard error.

It would be expected that soils exposed to sea salt deposition would have the lowest SUVA values due to its high %BDOC and low DOC release. However, this was not observed in this study. The high SUVA$_{254}$ values observed in soils exposed to irrigation water are likely due to the combination of high sodium and alkalinity in the soils (Figure 9) stimulating the highest DOC release. As a result, soils exposed to irrigation water would have a larger amount of highly reflective aromatic DOC compounds and high mean SUVA$_{254}$ values compared to soils exposed to deicing salts. As stated above, %BDOC is a measurement of the amount of labile DOC compounds where a low %BDOC is known to have a high aromatic DOC concentration. The high SUVA$_{254}$ values observed in urban soils exposed to sea salt are likely indicative of a higher fraction of aromatic C compounds, some of which may have been derived from the numerous oil spills that have occurred in the Gulf of Mexico over the last three decades. Evidence of this is also shown in Figure 12, where soils exposed to irrigation water and deicing salts demonstrate an inverse relationship between %BDOC and DOC. Soils in Galveston do not demonstrate this relationship suggesting an input of highly aromatic DOC compounds, which explains the high DOC release without sodium exposure as well as the high %BDOC and $SUVA_{254}$ values

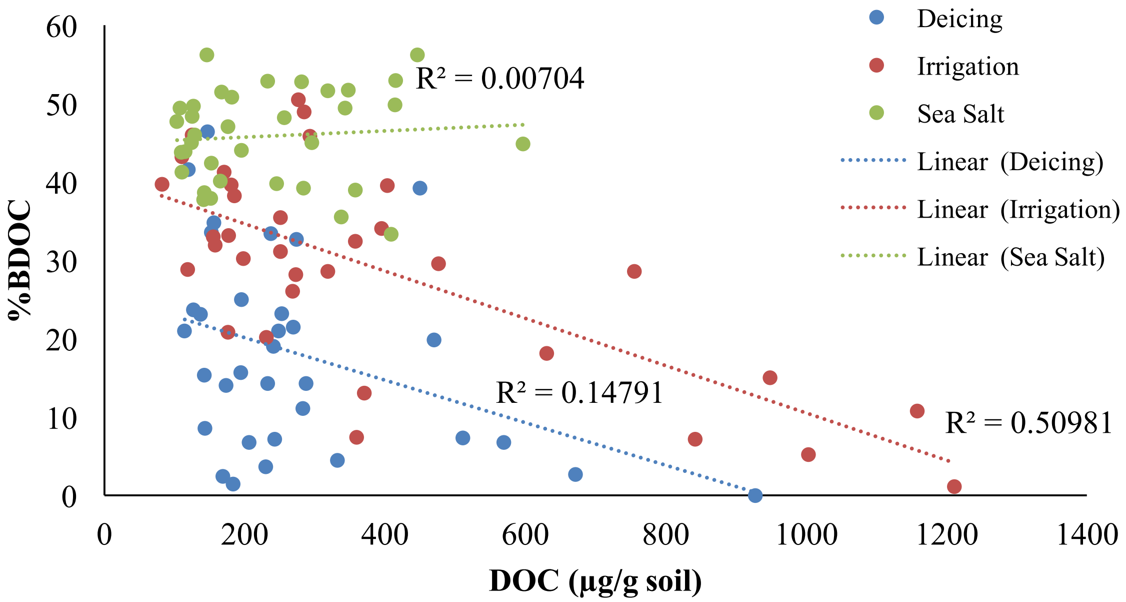

Figure 12. Demonstrating the inverse relationship between %BDOC and DOC across BCS ($p < 0.001$), Chicago ($p = 0.03$), and Galveston ($p = 0.63$).

The Influence of Time of Sodium Exposure on Soil Chemistry

To test whether exposure time to sodium influenced %BDOC, DOC, DON, and SUVA, it was assumed that house age equaled soil exposure time to sodium and new soil was laid once the house build was complete. As soil exposure time increased it was thought that Na would increase and accumulate in soils. Although there was no significant difference among Na concentrations and soil exposure time across all cities ($p = 0.23$), Na concentrations show an increase over time until soil age reached < 30 years and a decline began (Figure 13).

When analyzed by sodium source, the decline in soil Na after 30 years was present for deicing salts and irrigation water (Figure 14). The decline in sodium for irrigation water exposure may be due to the fact that in-ground irrigation systems were not installed on properties over 30 years ago. Similarly, Chicago may have mixed deicing salts with sand until 30 years when a switch occurred to NaCl. With the potential influence of these factors, the results still demonstrate that time of sodium exposure can be seen between 0 and 30 years before changes occur in soils exposed over 30 years.

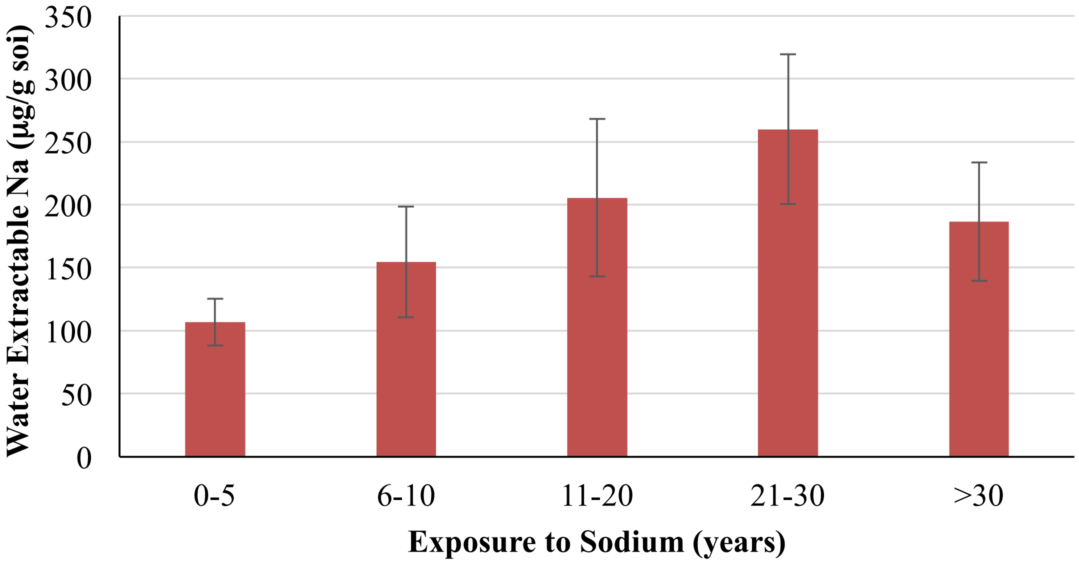

Figure 13. Mean water extractable Na concentrations over exposure time (p = 0.23). Error bars are standard error.

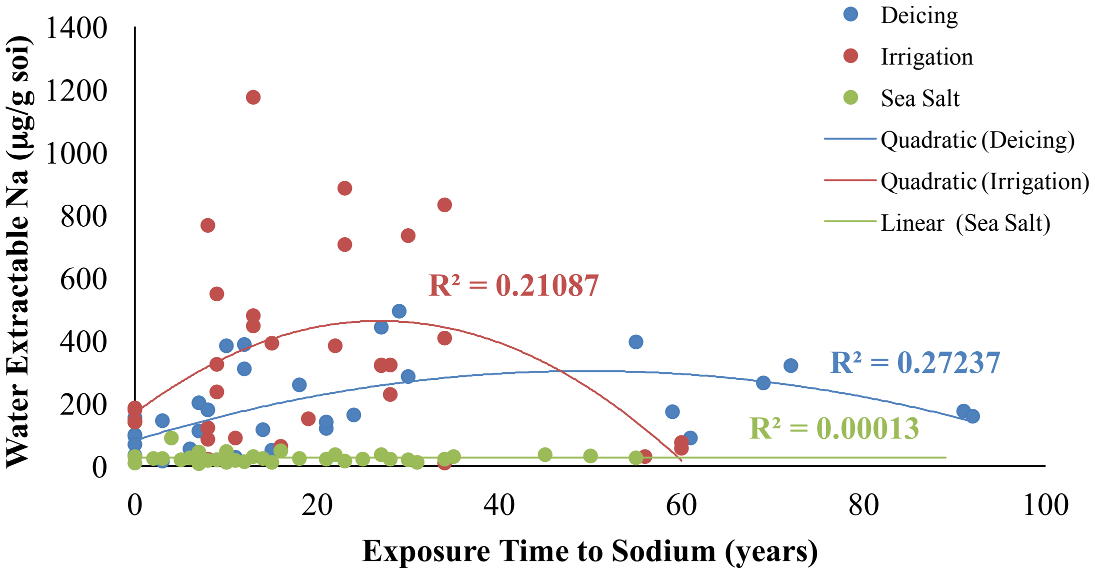

Figure 14. Water extractable Na concentrations by sodium source over exposure time for deicing salts (p = 0.01), irrigation water (p = 0.03), and sea salt deposition (p = 0.95).

%BDOC

To date, no study has examined the relationship of %BDOC over time of Na exposure. As Na concentrations increase with soil exposure time, it would be expected that %BDOC would decrease (Figure 6) due to increased solubility of DOC compounds (Figure 8). However, %BDOC was not significantly different among soil age groups ($p = 0.13$; Figure 15) and when analyzed by sodium source, no significant difference among exposure times were present (Figure 16). On the other hand, %BDOC does demonstrate a non-significant decrease as exposure time to sodium increases for deicing salts and irrigation water, likely due to the accumulation of sodium over time. The null hypothesis ($H2_0$) that soil age has no significant effect on %BDOC was accepted

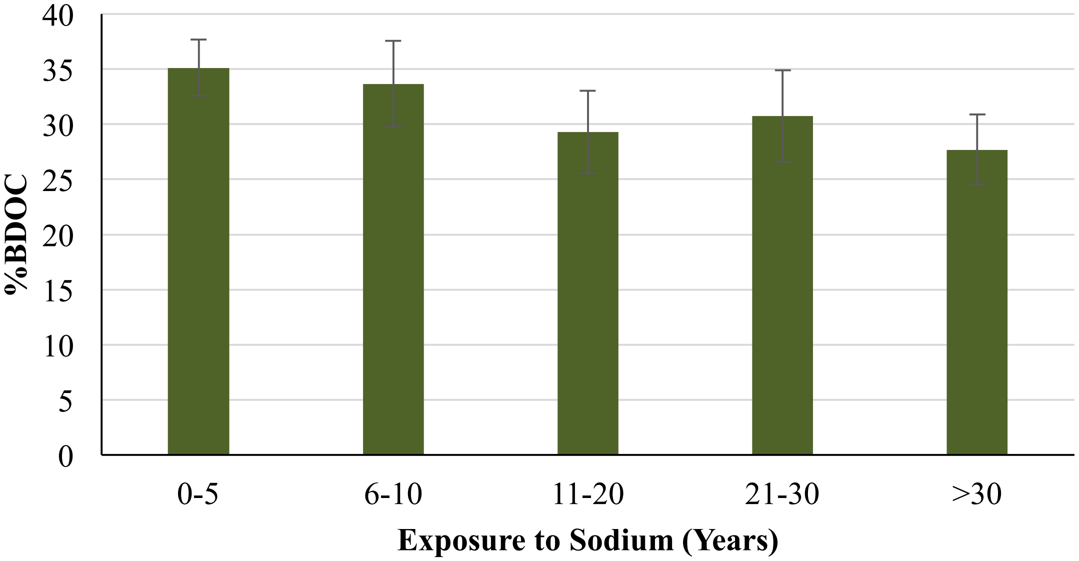

Figure 15. Mean %BDOC in urban soils exposed to sodium over time ($p = 0.134$). Error bars are standard error.

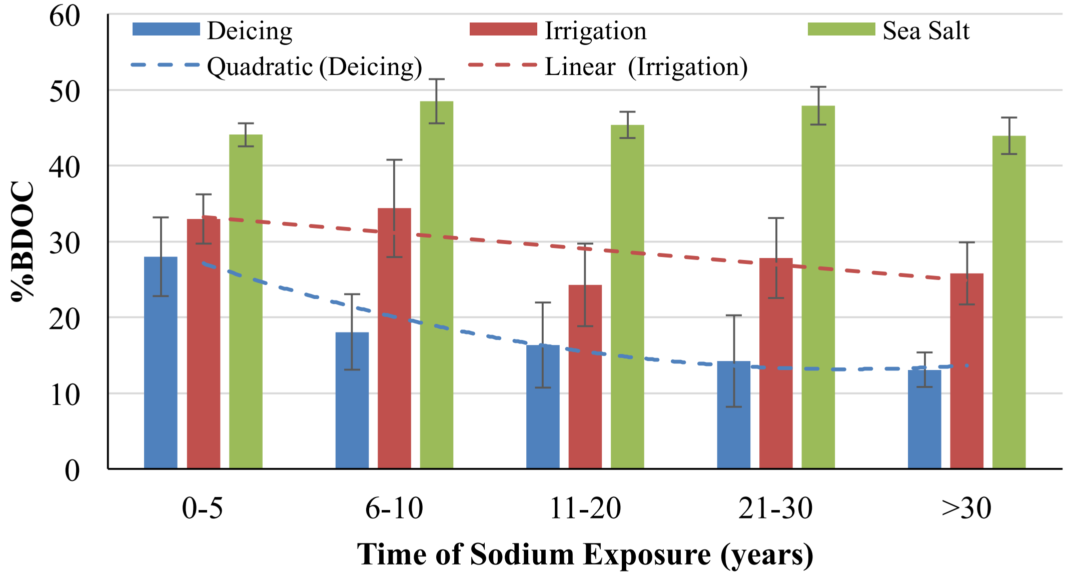

Figure 16. %BDOC by sodium source over time of sodium exposure. There was a significant quadratic trend for deicing salts ($p = 0.03$; $r^2 = 0.20$) while the trends for irrigation and sea salt sources were not significant ($p = 0.40$; $r^2 = 0.02$ and $p = 0.57$; $r^2 = 0.01$, respectively)

DOC

Studies by Green et al. (2008) and Green et al. (2009) found that newly exposed soils to sodium have the largest DOC release compared to previously exposed soils. They state it is because newly exposed soils experience dispersion and allow a greater release of soluble DOC, while previously exposed soils already had most of their soluble DOC flushed. In this study DOC was significantly different among sodium exposure times ($p < 0.001$), however, these results do not agree with the “Once it has gone, it’s gone” hypothesis by Green et al. (2008). Rather, soils exposed to sodium for the shortest time (0 to 5 years) had significantly lower DOC release (156 ± 14 µg/g soil) compared to the remaining soil age groups whose means ranged from 261 ± 38 μg/g soil to 428 ± 63 μg/g soil and did not significantly differ from one another (Figure 17).

Significant increases of DOC among exposure time were present in soils exposed to deicing salts and irrigation water among age groups (Figure 18). These differences are likely influenced by increasing sodium concentrations over time (Figure 14) especially because all soils, regardless of sodium source, had similar DOC concentrations at exposure time 0 to 5 (Figure 18). Soils exposed to sea salt deposition show a slight increasing trend in DOC release over time. This increase in DOC solubility may be a result of a natural accumulation of DOC that microbes cannot degrade or an accumulation of highly recalcitrant DOC from oil spills in the Gulf of Mexico.

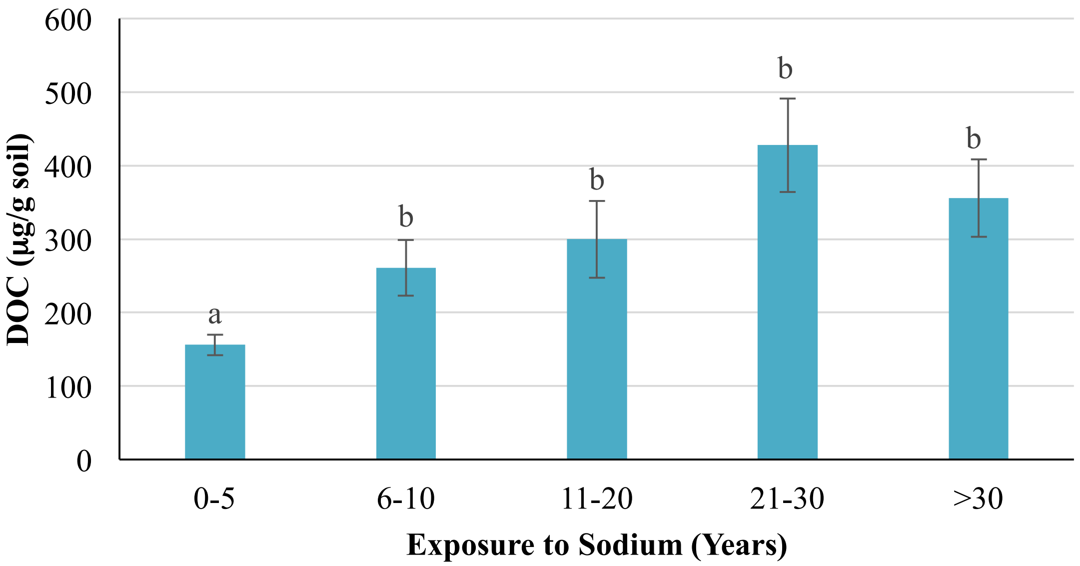

Figure 17. Mean water extractable DOC concentrations in urban soils grouped by time of exposure to a sodium source. Different lower case letters indicate a significant difference at $p < 0.05$. Error bars are standard error.

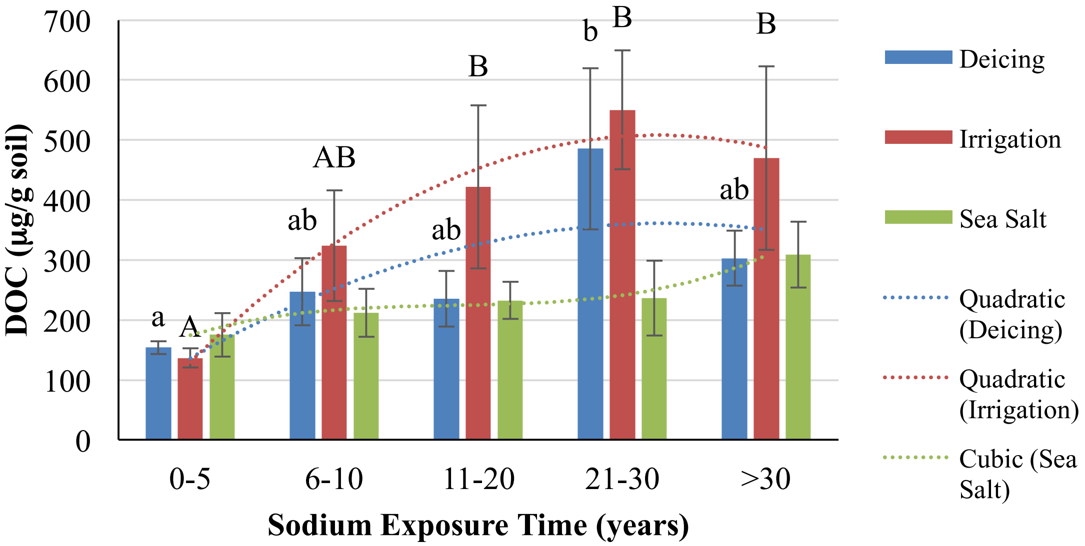

Figure 18. DOC concentrations by sodium source over exposure time to sodium. Lowercase letters denote significant differences for deicing salts ($p = 0.001$) and uppercase letters denote significant differences for irrigation ($p = 0.001$) while sea salt exposure had no significant differences ($p = 0.32$) using univariate analysis. Regression analysis determined significant quadratic trends for deicing salts ($p = 0.001$, $r^2 = 0.40$) and irrigation ($p = 0.002$; $r^2 = 0.36$) and a cubic trend for sea salt ($p = 0.004$; $r^2 = 0.35$).

DON

DOC and DON are structurally similar with the exception that DON contains one or more amino acid(s) (NH_3) as a functional group and when cleaved, simple low molecular weight DON becomes DOC. As a result, factors influencing DOC release are similar to DON release and they are highly correlated. To date, one study has examined DON concentrations over time. Results from the study by Aitkenhead-Peterson and Cioce (2013) showed that DON release increased with time since soil disturbance until 35 years where a decline is present in their data. However, since the decline in DON was so dramatic as time increased, they attributed the decline to soils reaching an equilibrium that was previously present before soils were disturbed.

The results in this study show DON concentrations significantly increased over time of sodium exposure ($p < .001$; Figure 19). Soils with smallest exposure time had the lowest mean DON concentration (12 ± 2 μg/g soil) and DON concentrations significantly increased with length of exposure time (6-10 yr: 21 ± 3 μg/g soil, 11-20 yr: 25 ± 5 μg/g soil) until it peaked at 21-30 yrs (38 ± 5 μg/g soil) before beginning to decrease for soils > 30 yrs (28 ± 5 μg/g soil). These results agree with those found by Aitkenhead-Peterson and Cioce (2013) which showed increased DOC and DON release in soils until time was greater than 34 years when a sharp decrease in solubility was observed. However, this decrease may be a result of decreased sodium exposure from irrigation systems not being installed over 30 years ago or from previous decreased use of deicing salts. These results mirror DOC (Figure 18) as well as the trends observed for sodium (Figure 14), demonstrating that DON solubility increases with sodium exposure, regardless of sodium source.

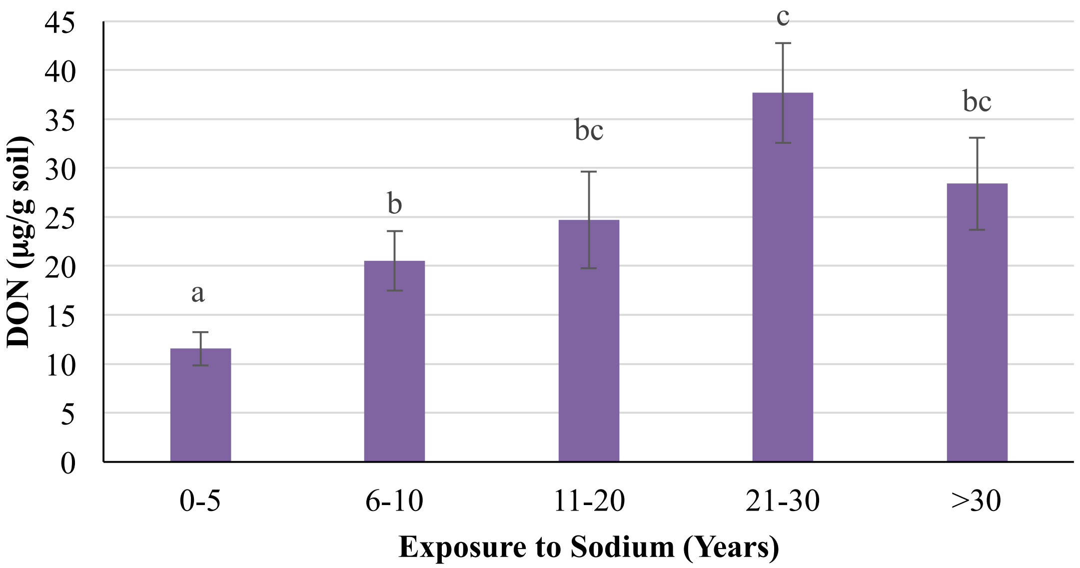

Figure 19. Mean water extractable DON concentrations in urban soils grouped by time of exposure to a sodium source. Different lower case letters indicate a significant difference at $p < 0.05$. Error bars are standard error.

SUVA$_{254}$

It would be expected for SUVA$_{254}$ values to increase over time of sodium exposure due to the increased release of DOC for sodium. In this study, time of exposure to sodium had no significant effect on mean SUVA$_{254}$ values ($p = 0.25$; Figure 20) across all cities. When analyzed by individual cities, there was no significant differences in SUVA$_{254}$ values over time. This is likely due to the lack of significant differences in %BDOC over exposure time within individual sources (Figure 16). Since SUVA can be used to determine %BDOC (inverse relationship) and DOC (direct relationship) (Kalbitz et al. 2003b), the lack of significant decreasing trends observed for %BDOC could have created enough variability that differences could not be detected in $SUVA_{254}$ values over time, even though DOC had significant differences over time.

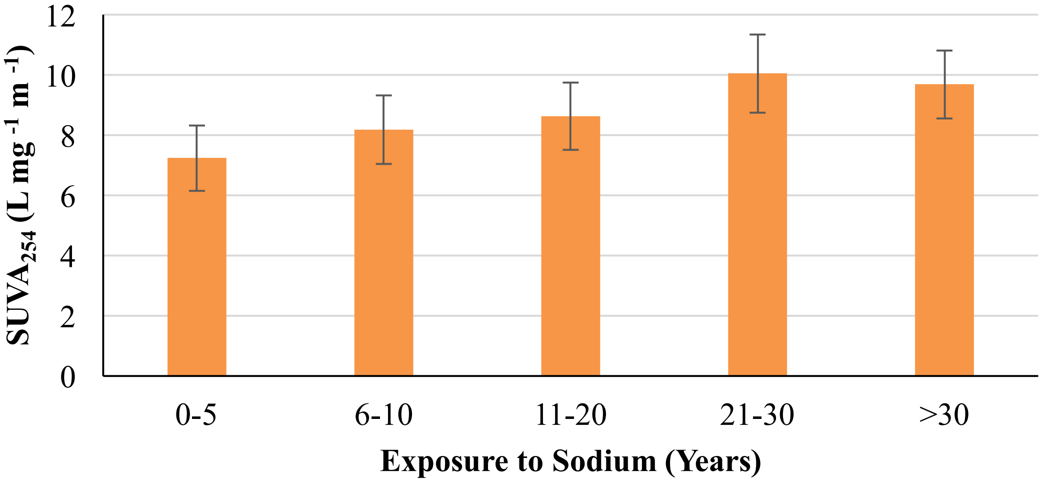

Figure 20. Mean $SUVA_{254}$ values grouped by soil age. Error bars are mean standard errors.

Predicting %BDOC and DOC from Optics

SUVA is a measure of the amount of aromatic compounds within soils (Traina et al. 1990). Since aromatic compounds are recalcitrant to degradation, it is also a measure of %BDOC by determining the amount of labile compounds within the solution from the amount of recalcitrant fractions (Weishaar et al. 2003). SUVA has successfully been used to predict BDOC (Fellman et al. 2009; Kalbitz et al. 2003a) and DOC concentrations (Sun et al. 2012) in soils.

In this experiment, linear regression analysis was preformed to determine if DOC and %BDOC could be predicted. A significant positive relationship was found between $SUVA_{254}$ and DOC concentrations within soils across all cities ($p < 0.001$, $r^2 = 0.33$, adj. $r^2 = 0.33$; Figure 21). This relationship was improved by examining it by sodium source. Significant positive relationships were present in Chicago soils ($p < 0.001$, $r^2 = 0.36$), BCS soils ($p < 0.001$, $r^2 = 0.48$), and Galveston soils ($p < 0.001$, $r^2 = 0.40$) (Figure 22). As DOC concentrations increased, the amount of aromatic/refractory compounds also increased. This relationship is similar to results obtained in previous studies that successfully related DOC concentrations to SUVA values (Nguyen & Hur 2011; Simonsson et al. 2005).

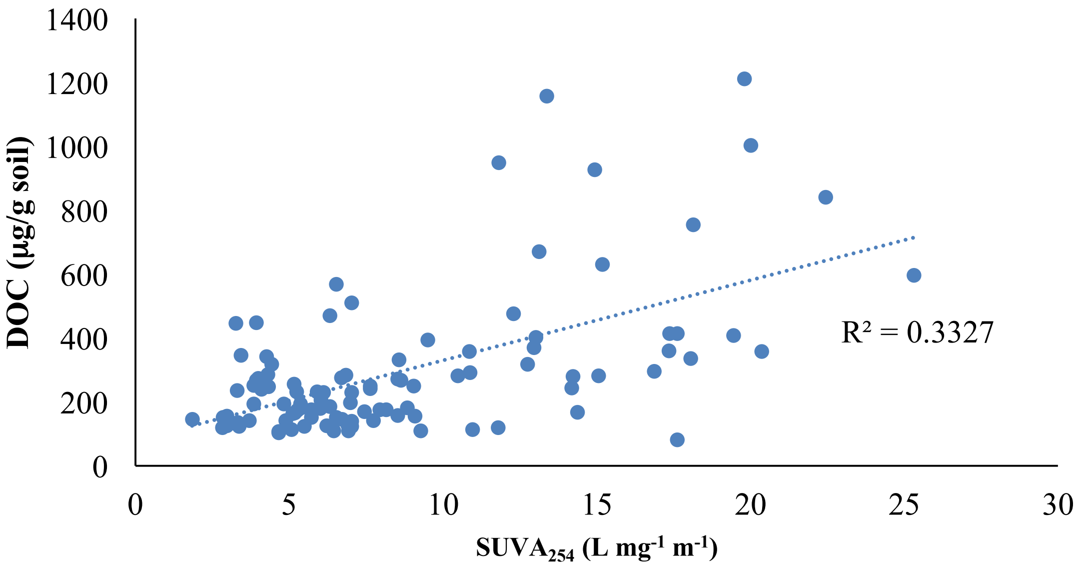

Figure 21. Relationship between DOC and $SUVA_{254}$ across all cities ($p < 0.001$).

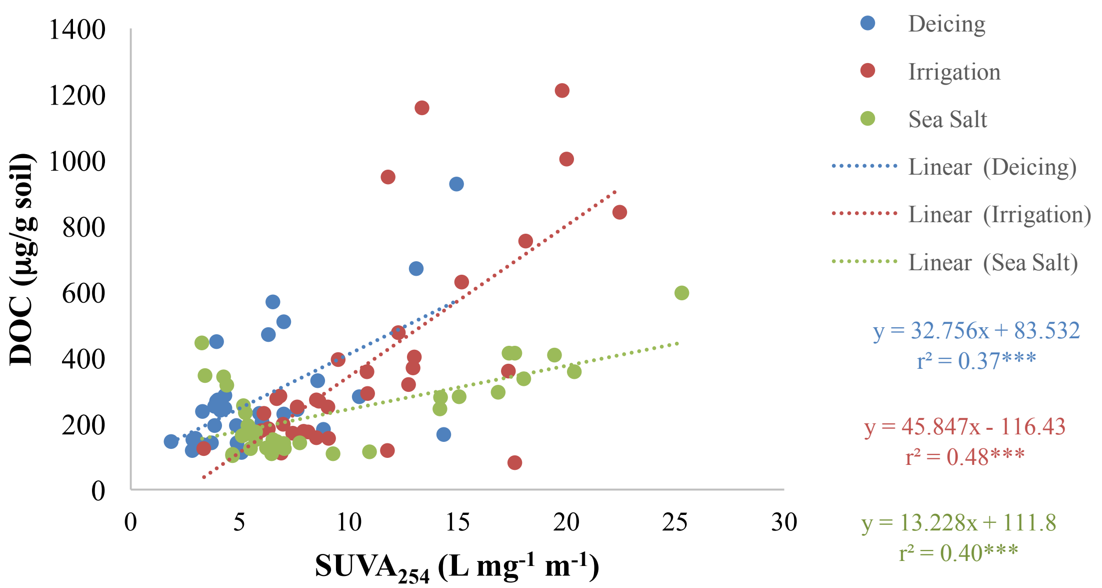

Figure 22. Relationship between DOC and SUVA$_{254}$ grouped by sodium source. *** $p < 0.001$

Usually as refractory DOC concentrations increase, the amount of labile compounds decreases and a negative relationship between BDOC and SUVA can be observed (Marschner & Kalbitz 2003). In this study, %BDOC and SUVA$_{254}$ did not have a significant relationship ($p = 0.08$, $r^2 = 0.03$) (Figure 23) and %BDOC could not be predicted across all cities. However, when analyzed by sodium source there was a significant relationship between %BDOC and SUVA$_{254}$ in soils exposed to deicing salts ($p < 0.001$, $r^2 = 0.58$), irrigation water ($p < 0.001$, $r^2 = 0.46$), and sea salt deposition ($p = 0.03$, $r^2 = 0.14$) (Figure 24). The lack of significance in overall data is likely due to the weaker, negative relationship observed in soils exposed to sea salts compared to the strong negative relationships observed in soils exposed to deicing salts and irrigation water (Figure 24). This difference in relationships caused greater variance around the regression line which increased residual error and prevented a significant trend to be detected over all cities.

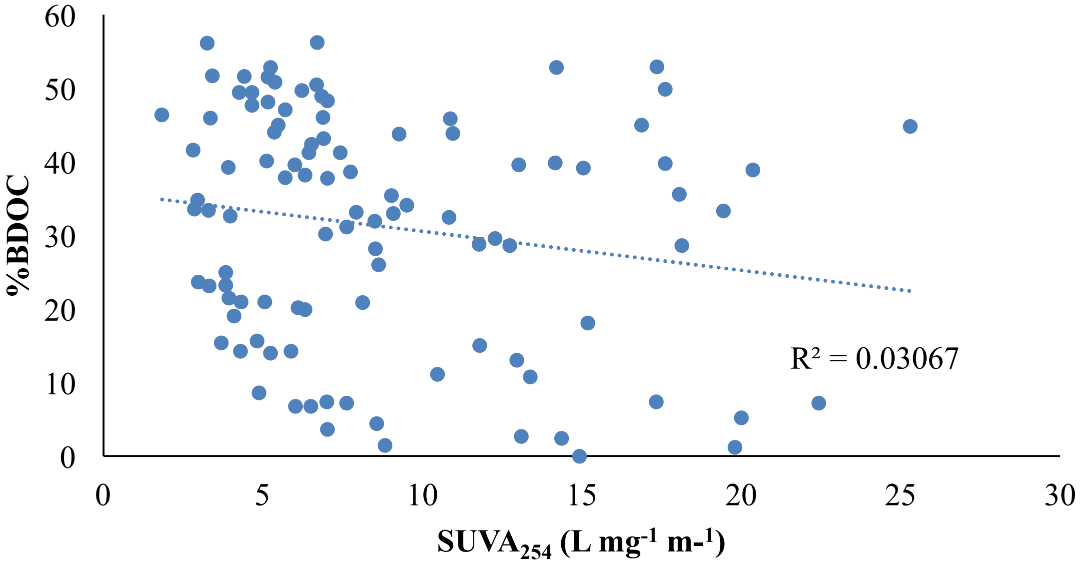

Figure 23. The relationship between %BDOC and $SUVA_{254}$ across all cities (n=102) (p = 0.08)

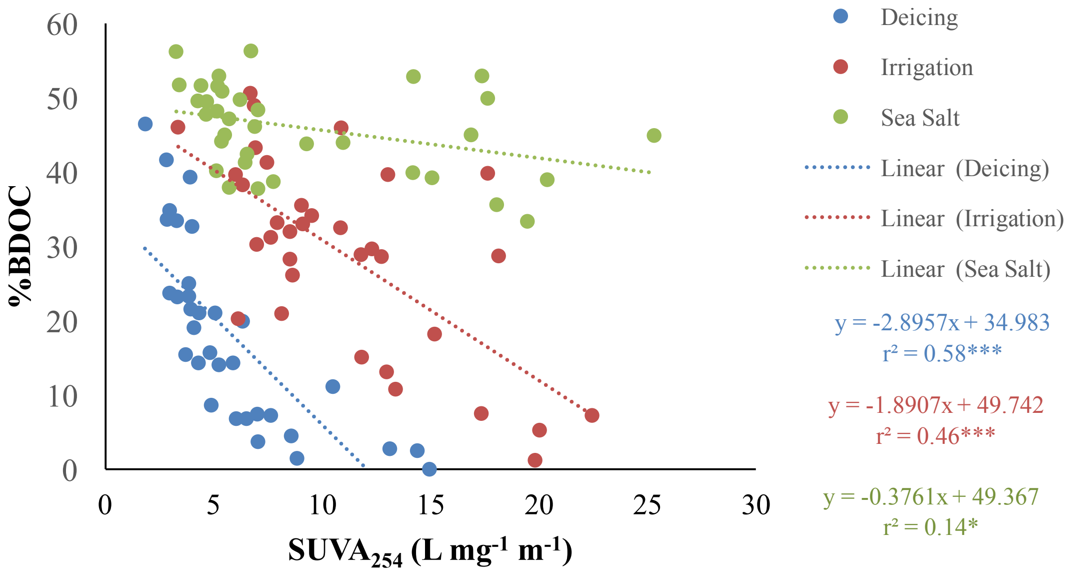

Figure 24. Relationship between %BDOC and SUVA$_{254}$ grouped by city. * $p < 0.5$ and *** $p < 0.001$

Models of %BDOC, DOC, and DON

Backward, stepwise multiple linear regression analysis identified several independent variables that were significant predictors for %BDOC, DOC, and DON across all cities and within cities. These independent variables selected were used in a partial least squares (PLS) regression analysis with a full cross validation using an Orthogonal Scores algorithm (Martens & Naes 1989). The full cross validation removes one sample at a time and refits the model using the new equation to predict the removed sample. The full cross validation method is often preferred over a test set validation when the sample size is limited such as this study (Martens & Dardenne 1998). In this experiment, the best model was chosen based on a high R^2 and low root mean square error (RMSE).

Modeling is often done to predict a dependent variable when an analysis of that variable is complex. This certainly describes %BDOC and DON where analysis of these parameters are time consuming and costly. DON is derived as the difference between total dissolved N (TDN) and inorganic N (NO_3-N + NH_4-N). Confidence in the value of DON can only be achieved if the sample is run for all N analyses within 18 hours of collection due to likely transformation between N species. In the case of %BDOC, the recommended method is 7-day incubation (McDowell et al. 2006).

It is always prudent to check individual correlations between the dependent and independent variables particularly when running multiple linear regression analysis because there may be mediational or confounding effects among the independent variables selected. Differences in the direction (negative or positive) reflected in the equation coefficients and correlation analysis is quite common.

An objective of this study was to isolate independent variables that may be involved in release mechanisms for DOC and DON in urban soils and to recognize the variables that may have an effect on the presence of BDOC in soils.

%BDOC

While %BDOC has been quantified in multiple undisturbed and agricultural soils (Boyer & Groffman 1996; Fellman et al. 2009; McDowell et al. 2006; Yano et al. 2000) fewer studies have quantified %BDOC in urban soils (Cioce & Aitkenhead-Peterson 2015) and to date %BDOC in urban soils has not been modeled using soil chemistry. Four models were created and compared in this study for %BDOC to examine the significant measured variables that relied on the concentration of %BDOC across all cities and within individual cities. This study also determined the relationship between %BDOC and the selected significant variables and the potential mechanisms influencing one another (Table 5).

Table 5. Summary of %BDOC model statistics and predictors

	n	Slope	Offset	RMSE	R^2	p	Independent Variables
All Cities	102	0.631	11.522	9.578	0.63	< 0.001	City, NO_3-N, DON, DOC, Na
Chicago	33	0.657	6.191	7.276	0.66	<0.001	$SUVA_{254}$, HCO_3, Mn
BCS	34	0.662	9.781	7.508	0.66	<0.001	EC, Ca, Na, Mn
Galveston	35	0.578	19.375	3.821	0.58	ns	pH, EC, DOC, Mg, K, Zn, Mn

<u>All-Cities %BDOC Model</u>

The selected independent variables for the All-City %BDOC Model were city, NO_3-N, DON, DOC and Na ($R^2 = 0.63$, $p < 0.001$;Table 5). All independent variables selected for this model were significant ($p < 0.01$; Table 6) suggesting a change in that independent variable would elicit a response in %BDOC. The cross validation for this %BDOC model showed that the relationship between predicted and observed %BDOC was relatively weak but nonetheless significant (Figure 25A). Under- and over-predictions generally occurred within ± 20% of the real values except for one sample which was under-predicted by 38% (Figure 25A). The cross validation trend line intercepts zero because of the expectations of a 1:1 relationship between observed and predicted values.

%BDOC was significantly and negatively correlated with all the independent variables selected except city which was significantly which displayed a significant positive correlation: city (R = 0.27; $p < 0.01$), NO_3-N (R = -0.51; $p < 0.001$), DON (R = -0.25; p = 0.01), DOC (R = -0.42; $p < 0.001$) and Na (R = -0.54; $p < 0.001$).

All-Cities %BDOC = 35.242 + 3.948*City – 0.366*NO_3-N + 0.95*DON – 0.037*Na – 0.083*DOC

Table 6. All-Cities %BDOC Model coefficient statistics.

MODEL				CORRELATION	
Predictors	Unstandardized Coefficients	Standardized Coefficients	Model P value	Correlation Coefficients (R)	Correlation P value
(Constant)	35.242		< 0.001		
City	3.948	0.203	0.013	0.27	0.005
NO_3-N	- 0.366	- 0.207	0.007	- 0.51	< 0.001
DON	0.950	1.203	< 0.001	- 0.25	0.011
Na	- 0.037	- 0.513	< 0.001	- 0.54	< 0.001
DOC	- 0.083	- 1.184	< 0.001	- 0.42	< 0.001

Model ANOVA Table

	Sum of Squares	df	Mean Square	F value	p
Regression	16,007	5	3,201	33	< 0.001
Residual	9,357	96	97		
Total	25,364	101			

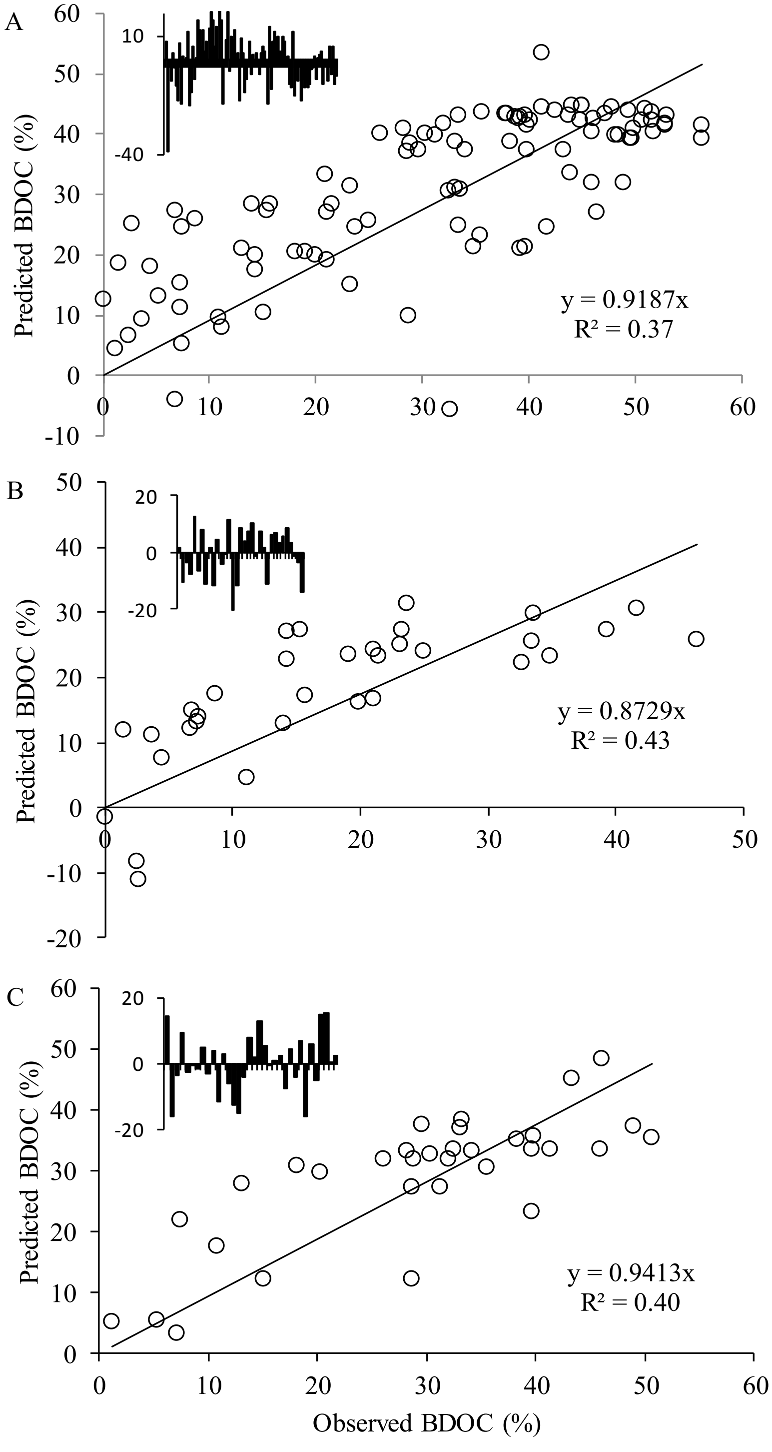

Figure 25. Cross validations of %BDOC Models for A) all cities, B) Chicago, and C) BCS. Inset figures display differences for each sample between observed and predicted values.

Chicago %BDOC Model

Percent BDOC in the urban soils in the city of Chicago was modeled relatively well ($R^2 = 0.66$; $p < 0.001$; Tables 5 and 7). Cross-validation of the Chicago BDOC model yielded a weak but significant relationship between predicted and observed BDOC concentrations (Figure 25B) and under- and over-estimates of BDOC were generally ±14% (Figure 25B).

All independent variables selected for the Chicago DOC were significant ($p < 0.05$) with the exception of HCO_3 ($p = 0.09$) suggesting that any change in them would stimulate a change in %BDOC (Table 7). Pearson bivariate correlation analysis showed that all independent variables selected during the backward stepwise regression analysis had significant and negative correlations with %BDOC with the exception of HCO_3 which had a positive correlation with %BDOC and was non-significant: $SUVA_{254}$ ($R = -0.76$; $p < 0.001$), Mn ($R = -0.60$; $p < 0.001$) and HCO_3 ($R = 0.10$; $p > 0.05$).

Chicago %BDOC $= 46.386 – 0.013*HCO_3 + 13.151*Mn – 5.004*SUVA_{254}$

Table 7. Chicago %BDOC Model coefficient statistics.

MODEL				CORRELATION	
Predictors	Unstandardized Coefficients	Standardized Coefficients	Model P value	Correlation Coefficients (R)	Correlation P value
(Constant)	46.386		< 0.001		
HCO_3	- 0.013	- 0.199	0.096	0.10	0.096
Mn	13.151	0.535	0.047	- 0.60	< 0.001
$SUVA_{254}$	- 5.004	- 1.312	< 0.001	- 0.76	< 0.001

Model ANOVA Table

	Sum of Squares	df	Mean Square	F value	p
Regression	3,352	3	1,117	19	< 0.001
Residual	1,747	29	60		
Total	5,099	32			

BCS %BDOC Model

The resultant model for BCS %BDOC was relatively strong and significant ($R^2 = 0.66$; $p < 0.001$; Table 5 and 8). Although the full cross validation yielded a poor relationship between predicted and observed %BDOC, it was still significant (Figure 25C). All under- and over-predictions were less than ± 16%. All independent variables selected during regression analysis were significant ($p < 0.05$) indicating that any change their concentration would stimulate a change in %BDOC (Table 8). When predictors were analyzed for significant correlations, %BDOC was negatively correlated with all the independent variables selected for the BCS %BDOC model but only Na and Mn had a significant correlation: EC ($R = -0.30$; $p > 0.05$), Ca ($R = -0.26$; $p > 0.05$), Na ($R = -0.60$; $p < 0.001$) and Mn ($R = 0.64$; $p < 0.001$).

BCS %BDOC = $\%BDOC = 32.984 + 0.189*EC - 0.094*Ca - 0.047*Na - 3.745*Mn$

Table 8. BCS %BDOC Model coefficient statistics.

MODEL				CORRELATION	
Predictors	Unstandardized Coefficients	Standardized Coefficients	Model P value	Correlation Coefficients (R)	Correlation P value
(Constant)	32.984		< 0.001		
EC	0.189	1.401	< 0.001	- 0.30	0.087
Ca	- 0.094	- 0.779	0.001	- 0.26	0.143
Na	- 0.047	- 1.033	0.001	- 0.60	< 0.001
Mn	- 3.745	- 0.412	0.045	- 0.64	< 0.001

Model ANOVA Table

	Sum of Squares	df	Mean Square	F value	p
Regression	3,756	4	939	14	< 0.001
Residual	1,917	29	66		
Total	5,673	33			

Galveston %BDOC Model

The Galveston model for %BDOC was the poorest ($R^2 = 0.58$; Table 5). A full cross validation for this model was not possible and likely due to the small range of %BDOC values for this site. All independent variables selected for the Galveston model were significant ($p < 0.05$) except DOC ($p = 0.07$) (Table 9). Percent BDOC did not have a strong or significant correlation with any of the independent variables the backward stepwise multiple linear regression analysis selected when analyzed separately using a Pearson bivariate correlation analysis.

Galveston %BDOC = 6.096*pH + 0.076*EC + 0.045*DOC - 0.515*Mg - 0.023*K - 11.198*Zn + 30.019*Mn – 0.362

Table 9. Galveston %BDOC Model coefficient statistics.

MODEL				CORRELATION	
Predictors	Unstandardized Coefficients	Standardized Coefficients	Model P value	Correlation Coefficients (R)	Correlation P value
(Constant)	- 0.362		0.985		
pH	6.096	0.586	0.008	0.22	0.194
EC	0.045	0.943	< 0.001	- 0.07	0.702
DOC	0.076	0.463	0.077	0.08	0.632
Mg	- 0.515	- 0.766	0.002	- 0.12	0.475
K	- 0.023	- 0.888	0.002	- 0.03	0.871
Zn	- 11.085	- 0.552	0.002	- 0.32	0.058
Mg	30.019	0.570	0.007	0.17	0.319

Model ANOVA Table

	Sum of Squares	df	Mean Square	F value	p
Regression	705	7	101	33	0.001
Residual	503	27	19		
Total	1,208	34			

Similarities and Dissimilarities in %BDOC Predictors Across Urban Ecosystems

Slightly improved models were achieved for predicting %BDOC in urban soils when examined by individual cities compared to grouping cities together. The variables selected in the All-Cities Model were city, NO_3-N, DON, Na, and DOC. These selected variables are supported in the literature to be dependent on the presence of %BDOC. It is well known that nitrification (the production of NO_3-N) is dependent on the presence of labile DOC, which is used as a substrate along with NH_4; However, NYSERDA (2015) was able to show that microbial immobilization (or uptake) of NO_3-N increased with increasing %BDOC. The All City Model demonstrated this mechanism through the relationship showing if %BDOC increased, the concentration of NO_3-N decreased. The model also showed that increases in Na concentrations caused %BDOC to decrease. This relationship was noted by Cioce and Aitkenhead-Peterson (2015) in a similar study of urban soils where they reported that soil Na concentrations > 518 µg g soil^{-1} had significantly lower %BDOC when compared to soil Na concentrations < 390 µg g soil^{-1}. Several of the soils in the current study had soil sodium concentrations > 518 µg g soil^{-1} and while there was a general tendency for high Na soils to have lower %BDOC, other factors may be responsible for depressing %BDOC. The negative but significant correlation between %BDOC and DOC suggests that as DOC concentrations increase then more of their composition is in the form of recalcitrant DOC.

City (or source of Na) was selected during backward regression analysis as an important independent variable. While the source of sodium might be important and was in fact the reason for the experiment, other differences among the cities examined must be considered. There were climatic (temperature and precipitation) differences among the cities and furthermore soil texture was also very different. For example, in Chicago 69% of the soils were a silty clay loam and 25% were silty clay, in BCS the dominant soil was a sandy loam and in Galveston the soils were classified as sandy soils. Individual site factors such as annual temperature, precipitation and soil characteristics need to be included in any future models across cities to understand how these factors might affect %BDOC.

Different independent variables incorporated into the individual city models are likely to be site specific and reflect conditions occurring in the soil of that city but not elsewhere. The only similar independent variable for describing %BDOC in urban soils in Chicago and BCS was Mn and the correlation between the two was significant and negative in both cities. The concentrations of Mn ranged between 0.02 and 2.29 μg g soil^{-1} in Chicago and between 0.01 and 4.97 μg g soil^{-1} in BCS. Manganese is known to strongly interact with DOC and form Mn-DOC complexes (Lovley 1991; Stone & Morgan 1984; Sunda & Kieber 1994); thus, it would be expected that a Mn-DOC complex would be refractory and increases in DOC would lead to decreased %BDOC within a sample. It should be noted that Galveston had the lowest soil Mn concentrations (0.01 to 0.49 μg g soil^{-1}) and higher %BDOC concentrations relative to Chicago and BCS.

The significant negative correlation between %BDOC and $SUVA_{254}$ in Chicago soils makes sense as $SUVA_{254}$ is a measure of aromaticity of the sample. Aromatic compounds are typically not biodegradable it is expected that increased aromaticity would result in lower %BDOC values. For BCS soils the significant negative correlation between %BDOC and Na supports prior work by Cioce and Aitkenhead-Peterson (2015) on soils collected at different sites during the summer months.

DOC

To date, it is poorly understood as to which soil characteristics stimulate DOC mobilization (Emsens et al. 2016). Few studies have examined the drivers for producing water extractable DOC *in situ* and whether the extraction method recovers different DOC concentrations than one would see in soil leachate. Some studies have examined the effect of shaking time and extraction solution on the recovery of DOC from soils (Jones and Willett 2005; Carillo-Gonzalez et al. 2013). Carrillo-Gonzalez et al. (2013) reported that DOC concentrations after extraction of a soil with ultra-pure water were not significantly different from DOC concentrations in soil leachate. It was also determined that the extract solution used can impact the strong relationship between DOC and DON in undisturbed and rotational crop agricultural soils (Carillo-Gonzalez et al. 2013). The study by (Carrillo-Gonzalez et al. 2013) highlighted the impact of cations present in the soil solution and their potential to alter DOC or DON release differently. The major objective for modeling water extractable DOC in this study was to identify those independent variables that were potentially responsible for initiating DOC release during water extraction, rather than merely producing a model using predictors that are already known to have high association to DOC. Therefore, prior to running the linear regression analysis using backward selection, independent variables known to have a strong relationship with DOC were removed from the dataset. These variables included DON, which is thought to be a subset of DOC or a DOC molecule with an amino group attached, and $SUVA_{254}$, which has been used to quantify DOC (Sun et al. 2012).

Four models were created and compared for DOC to identify the possible mechanisms involved in its release from the soil (Table 10).

Table 10. Summary of DOC model statistics and predictors.

	n	Slope	Offset	RMSE	R^2	p	Independent Variables
All Cities	102	0.759	74.22	112.412	0.75	0.001	Exposure Time, NO_3-N, NH_4-N, HCO_3, Ca, Na, K, S, Fe, Cu
Chicago	33	0.903	26.524	54.783	0.90	0.001	pH, EC, NH_4-N, Fe, Zn, Mn
BCS	34	0.925	28.996	83.635	0.93	0.001	Exposure Time, Ca, B, S, Fe, Cu, SAR
Galveston	35	0.873	29.855	43.403	0.87	0.001	Ca, B, Fe, Zn

All-Cities DOC Model

The All-Cities DOC Model was relatively strong and significant ($R^2 = 0.75$; $p < 0.001$; Table 10). All of the independent variables selected for predicting DOC concentrations across all cities were significant ($p < 0.05$) except HCO_3 ($p = 0.08$) suggesting that as their concentrations changed, so would DOC (Table 11). The full cross validation of the model produced a moderately strong relationship between predicted and observed DOC concentrations (Figure 26A) with under- and over-predictions within ± 340 µg g $soil^{-1}$. Correlation analysis revealed that all selected variables had a positive correlation with DOC and for most, this correlation was significant: Soil Age) ($R = 0.32$; $p = 0.001$), NH_4-N ($R = 0.33$; $p = 0.001$), HCO_3 ($R = 0.41$; $p < 0.001$), Ca ($R = 0.40$), K ($R = 0.38$; $p < 0.001$), Fe ($R = 0.77$; $p < 0.001$), Cu ($R = 0.67$; $p < 0.001$) and Na ($R = 0.77$; $p < 0.001$). NO_3-N ($R = 0.15$; $p > 0.05$) and S ($R = 0.06$; $p > 0.05$) had positive but weak and non-significant correlations with DON (data not shown).

All-City DOC = 20.282*Exposure time – 3.228*NO_3-N + 11.386*NH_4-N – 0.085*HCO_3 + 0.878*Ca + 0.167*K – 1.067*S + 0.129*Fe + 152.672*Cu + 0.354*Na – 3.123

Table 11. All-Cities DOC Model coefficient statistics.

MODEL				CORRELATION	
Predictors	Unstandardized Coefficients	Standardized Coefficients	Model P value	Correlation Coefficients (R)	Correlation P value
(Constant)	- 3.123		0.922		
Exposure Time	20.282	0.144	0.002	0.315	0.001
NO_3-N	- 3.228	- 0.128	0.010	0.152	0.127
NH_4-N	11.386	0.204	< 0.001	0.335	0.001
HCO_3	- 0.085	- 0.110	0.084	0.409	< 0.001
Ca	0.878	0.291	< 0.001	0.396	< 0.001
K	0.167	0.104	0.021	0.376	< 0.001
S	- 1.067	- 0.235	< 0.001	0.059	0.556
Fe	0.129	0.368	< 0.001	0.769	< 0.001
Cu	152.672	0.170	0.006	0.665	< 0.001
Na	0.354	0.344	< 0.001	0.772	< 0.001

Model ANOVA Table

	Sum of Squares	df	Mean Square	F value	p
Regression	4,391,413	10	439,141	52	< 0.001
Residual	764,106	91	8,397		
Total	5,155,519	101			

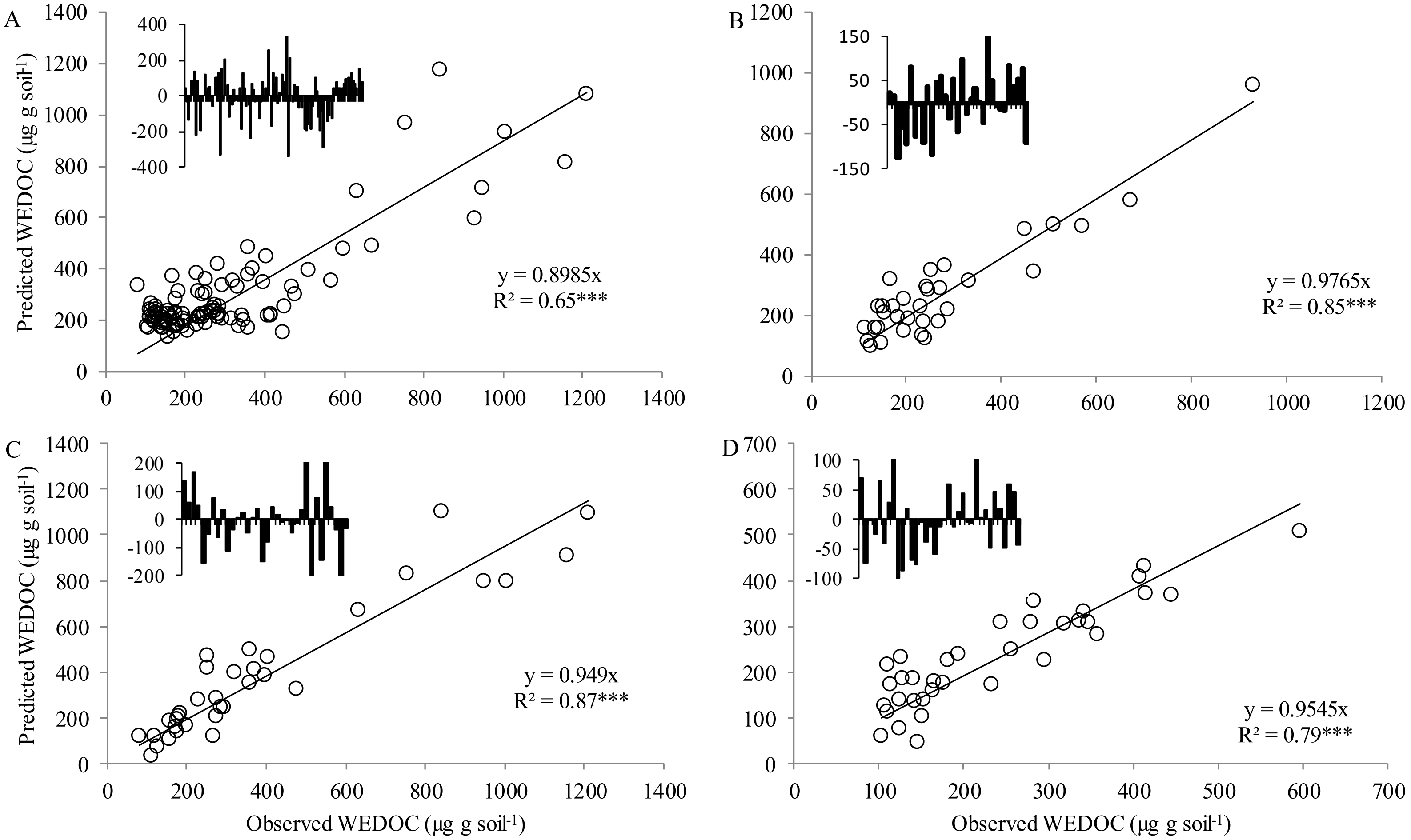

Figure 26. Cross validations of DOC models for A) All cities, B) Chicago, C) BCS and D) Galveston. Inset figures display difference for each sample between observed and predicted values. * denotes significance at $p < 0.0001$**

Chicago DOC Model

Release of DOC in the urban soils in the city of Chicago was modeled relatively well ($R^2 = 0.90$; $p < 0.001$; Table 10 and 12). Cross-validation of the Chicago DOC Model yielded a strong and significant relationship between predicted and observed DOC concentrations and under and over-estimates of DOC were within ± 150 µg g $soil^{-1}$ with many of the under- and over-estimates occurring at lower DOC concentrations (Figure 26B). All independent variables selected for the Chicago DOC Model were significant ($p < 0.05$; Table 12) suggesting that any change in them would stimulate a change in DOC release. Correlation analysis showed that all independent variables selected during the backward stepwise regression analysis had significant and positive correlations with DOC; pH ($R = 0.57$; $p < 0.001$), EC ($R = 0.49$; $p = 0.004$), NH_4-N ($R = 0.62$; $p < 0.001$) Fe ($R = 0.83$; $p < 0.001$) Zn ($R = 0.68$; $p < 0.001$) and Mn ($R = 0.64$; $p < 0.001$).

Chicago DOC = 101.034*pH + 0.994*EC+15.888*NH_4-N + 1.204*Fe – 76.862*Zn – 131.344*Mn – 799.542

Table 12. Chicago DOC Model coefficient statistics.

	MODEL			CORRELATION	
Predictors	Unstandardized Coefficients	Standardized Coefficients	Model P value	Correlation Coefficients (R)	Correlation P value
(Constant)	- 799.542		0.029		
pH	101.034	0.148	0.040	0.573	< 0.001
EC	0.994	0.198	0.004	0.493	0.004
NH_4-N	15.888	0.353	< 0.001	0.624	< 0.001
Fe	1.204	1.191	< 0.001	0.825	< 0.001
Zn	- 76.862	- 0.331	0.012	0.680	< 0.001
Mn	- 131.344	- 0.377	0.023	0.644	< 0.001

Model ANOVA Table

	Sum of Squares	df	Mean Square	F value	p
Regression	942,032	6	157,005	48	< 0.001
Residual	84,635	26	3,255		
Total	1,026,667	32			

<u>BCS DOC Model</u>

Release of DOC in the urban soils in the twin cities of Bryan and College Station was modeled well ($R^2 = 0.93$; $p < 0.001$; Table 10 and 13) Cross-validation of the BCS DOC Model yielded a strong and significant relationship between predicted and observed DOC concentrations with under and over-estimates of DOC of ± 200 µg g soil^{-1} (Figure 26C). All independent variables selected for the BCS DOC Model were significant ($p < 0.05$) suggesting that any change in them would stimulate a change in DOC release (Table 13). Correlation analysis showed the independent variables selected during the backward stepwise regression analysis had positive correlations with DOC; Age ($R = 0.35$; $p < 0.05$), Ca ($R = 0.43$; $p = 0.01$), B ($R = 0.88$; $p < 0.001$), Fe ($R = 0.84$;

$p < 0.001$), Cu ($R = 0.73$; $p < 0.001$) and SAR ($R = 0.71$; $p < 0.001$) with the exception of S which had a weak, non-significant negative relationship ($R = -0.06$; $p > 0.05$).

BCS DOC = 39.927*Exposure Time + 1.078*Ca – 125.275*B – 1.067*S + 0.262*Fe + 246.704*Cu + 3.133*SAR

Table 13. BCS DOC Model coefficient statistics.

MODEL				CORRELATION	
Predictors	Unstandardized Coefficients	Standardized Coefficients	Model P value	Correlation Coefficients (R)	Correlation P value
(Constant)	- 155.232		0.001		
Exposure Time	32.927	0.160	0.004	0.355	0.039
Ca	1.078	0.376	< 0.001	0.430	0.011
B	- 125.275	- 0.485	0.041	0.876	< 0.001
S	- 1.067	- 0.284	0.002	- 0.063	0.724
Fe	0.262	0.854	< 0.001	0.843	< 0.001
Cu	246.704	0.253	0.002	0.727	< 0.001
SAR	3.133	0.327	< 0.001	0.714	< 0.001

Model ANOVA Table

	Sum of Squares	df	Mean Square	F value	p
Regression	3,020,414	7	431,488	70	< 0.001
Residual	159,569	26	6,137		
Total	3,179,983	33			

Galveston DOC Model

Release of DOC in the urban soils on the island of Galveston was modeled relatively well ($R^2 = 0.87$; $p < 0.001$; Table 10 and 14). Cross-validation of the Galveston DOC Model yielded a strong and significant relationship between predicted and observed DOC concentrations, with under and over-estimates of DOC within ± 108 µg g $soil^{-1}$ (Figure 26D). All independent variables selected for the BCS DOC model were significant ($p < 0.05$) suggesting that any change in them would stimulate a change in DOC release (Table 14). The Galveston DOC Model had the fewest independent variables to predict DOC compared to the other DOC models. Correlation analysis showed that all independent variables selected during the backward stepwise regression analysis had positive correlations with DOC; Ca ($R = 0.71$; $p < 0.001$), B ($R = 0.43$; $p = 0.01$) and Zn ($R = 0.54$; $p = 0.001$) with the exception of Fe which had a weak, non-significant negative relationship ($R = -0.06$; $p > 0.05$).

Galveston DOC = 2.481*Ca + 471.254*B – 1.834*Fe + 101.039*Zn – 59.764

Table 14. Galveston DOC Model coefficient statistics.

	MODEL			CORRELATION	
Predictors	Unstandardized Coefficients	Standardized Coefficients	Model P value	Correlation Coefficients (R)	Correlation P value
(Constant)	- 59.764		0.075		
Ca	2.481	0.781	< 0.001	0.710	< 0.001
B	471.254	0.391	< 0.001	0.426	0.011
Fe	- 1.834	- 0.355	< 0.001	- 0.055	0.752
Zn	101.039	0.243	0.002	0.545	< 0.001

Model ANOVA Table

	Sum of Squares	df	Mean Square	F value	p
Regression	453,356	4	113,339	52	< 0.001
Residual	65,934	30	2,198		
Total	519,290	34			

Similarities and Dissimilarities in Predictors for DOC Across Urban Ecosystems

Models for predicting water extractable DOC were best at the individual city scale rather than compositing all cities into one model. This was likely due to individual environmental conditions and land management within each city. The only commonly observed independent variables that occurred in individual city models for DOC were Fe in all cities but only significant in Chicago and BCS, Zn in Chicago and Galveston and Ca and B in BCS and Galveston.

It is known that the binding of Fe with functional groups of DOC molecules creates metal chelates within soil. Due to the polyvalent nature of Fe, it can compete for binding sites on DOC fractions that are also involved in soil sorption (Kaiser & Zech 1997). It has been shown that the degree of metal dissolution from soils depends on the concentration of DOC present; as levels of DOC increased, the amount of Fe dissolution from soils also increased, most likely caused by higher affinity of Fe for DOC functional groups than the soils (Pohlman & McColl 1988). Furthermore, a study by Emsens et al. (2016) demonstrated that Fe-rich soils, subjected to rewetting, stimulated much higher DOC, NH_4, Fe, and dissolved inorganic carbon (DIC) release from soils into solution than Fe-poor soils, of which they attributed to the presence of Fe. They suggested that the mechanism may be once the soils were rewetted, the reduction of Fe caused the release of complexed DOC into solution. This further demonstrates the importance of the quantity of Fe present in soils and its influence on DOC mobilization. As Fe increases within the soils, high affinity binding sites on DOC molecules become taken and competition for lower affinity binding sites begin, which could include those involved in cation-bridging with soil and as a result, DOC release occurs (Guggenberger & Zech 1993).

Soil Fe content in the current study ranged from 0.25 to 4091 μg g soil^{-1}. Although the expectations that the Fe and DOC link are due to metal complexation, the causative effect of the reduction of Fe on DOC release posited by Emsens et al. (2016) is compelling. Although BCS and Chicago soils are not considered highly organic, peaty soils (Table 3), rewetting of the samples after air drying and shaking for 4 hours may have prompted a disproportionate amount of DOC to be released from the higher Fe soils in this study.

A link between DOC mobilization and Zn has been reported in some studies (Antoniadis et al. 2007; Gungor & Bekbolet 2010; Rekasi & Filep 2015). However, the effect that Zn has on DOC release is highly variable. A study completed by Rekasi and Filep (2015) analyzed the metal mobility in forest and arable soils and the potential influence of clay, DOC concentrations, pH and CEC. Although arable soils had higher metal concentrations of Zn, Cu, Cr, and Ni, the mobility of these metals was higher in forest soils, likely due to the higher DOC content while the higher clay content in arable soils was likely impacting mobility (Rekasi & Filep 2015). Gungor and Bekbolet (2010) also experienced a similar result in their study where the additions of Zn had little effect on DOC releases of humic acids from soils, instead changes in pH stimulated DOC release. These studies demonstrate that Zn concentrations in soils play little causative role in DOC release and environmental factors, such as clay content and pH may have a larger impact.

In the current study, Zn concentrations ranged from 0.31 to 3.96 µg g soil^{-1} in Chicago soils and from 0.35 to 1.84 µg g soil^{-1} in Galveston soils; although BCS soils had a similar range and a significantly higher mean concentration than Galveston, Zn had no predictive effect in BCS. These results may be due to the difference in soil types between each city where sandy soils in Galveston showed a moderate positive correlation between DOC and Zn and while the clayey loam soils in Chicago had a stronger, positive DOC correlation with Zn.

Boron has a close relationship with calcium and DOM in soils likely because Ca reduces the availability of B through the formation of to a calcium metaborate complex (Sillanpaa 1972). Increased DOC concentrations in soils stimulate the release of B adsorbed to soils to form DOM-B complexes (Communar & Keren 2008). Furthermore, Communar and Keren (2008) showed that in a sandy loam soil more B was adsorbed than in a loamy sand soil, regardless, both soils did exhibit a B release from soils as DOC increased.

Both B and Ca had positive effects on DOC mobilization in BCS in Galveston in the current study and this may be due to their Ca:B ratio or to the individual analytes effects on DOC mobilization. No studies have examined the effect of the soil Ca:B ratio on DOC mobilization but it was observed that an increased Ca:B stimulated DOC release in Galveston and decreased Ca:B stimulated DOC in BCS (data not shown) and these conflicting results suggest that B and Ca should be considered separately as mobilizers of DOC. While little if anything is known about B and DOC mobilization, more is known about the link between DOC and Ca (e.g. Whittinghill & Hobbie 2012;

Kerr and Eimers 2012). Whittinghill & Hobbie (2012) reported that high soil Ca inhibited microbial respiration in soil with a pH of 6.5 and 4.5 but increased microbial respiration in circum-neutral pH soils with a concomitant inhibition on the release of DOC. Kerr and Eimers (2012) found that as Ca concentrations increased, DOC adsorption to soil particles increased. The data in the current study do not support these studies because increased soil Ca promoted increased DOC mobility.

City specific controls on DOC release varied with SAR and Cu being dominant, positive predictors of DOC and soil age (soil exposure time to sodium) a moderate and positive predictor for DOC mobilization. Sodium adsorption ratio (SAR) had a significant and positive effect on DOC mobilization in BCS and Na has been shown in prior studies to increase DOC release in soils (Aitkenhead-Peterson and Cioce 2013; Steele & Aitkenhead-Peterson), particularly newly exposed soils (Green et al. 2008, 2009) and senescent vegetation (Steele & Aitkenhead-Peterson 2013). The mechanism behind increases in DOC with increases in Na is unclear but current theory suggests that as Na^+ increases in soil, H^+ is removed from soil exchange sites which leads to an increase in soil pH and the increased soil pH is responsible for solubilization of humic acids resulting in an increase in DOC concentration. An alternative theory is indirect effects such as release of monovalent and divalent cations such as NH_4^+, K^+, Ca^{2+} and Mg^{2+} with a high Na^+ input (Eimers et al. 2015; Shainberg & Letey 1984) would necessitate an equivalent release of anionic compounds such as DOC, DON, SO_4^{2-}, or PO_4^{3-} to maintain electroneutrality of soil solution.

Dissolved copper plays a role of micronutrient and toxicant depending on its concentration to microorganisms in surface waters (Brand et al. 1986; Manahan & Smith 1973; Peers et al. 2005) and can be assumed to play a similar role in soil. Lockwood et al. (2015) suggested that alkalization of a soil increases DOC release and with it any complexed Cu.

As soils age, their organic carbon (OC) content tends to increase due to inputs from precipitation, throughfall, decomposition of plants and animals and root exudate (Aitkenhead-Peterson et al. 2003). Depending on the type of C input, much of this organic carbon may be mineralized resulting in a relatively stable, generally recalcitrant, organic carbon pool, over time. In BCS as soil age increased so did DOC release up to 30 years.

In Chicago, the correlation between DOC and pH is likely due to the solubilization of humic acids as pH increases (Stevenson et al. 1996); although the pH range for Chicago soils was small (6.9 to 7.9). The correlation between DOC and NH_4-N may be due to maintenance of electroneutrality as described earlier but without evidence of losses of K, Mg and Ca this is unlikely. Yang et al. (2006) in a study examining DOC leachate in a meadow marsh soil found a strong relationship between DOC and NH_4-N and suggested that nitrogen mineralization potential may be a main factor affecting DOC production. The incidence of more clayey soils in Chicago would support this theory. Emsens et al. (2016) demonstrated that rewetting soils can stimulate increased DOC, Fe, NH_4-N, and TIC release over time. Furthermore, they concluded that the increasing NH_4-N levels in soil cores could be a result of iron-mediated anerobic degradation of

DON within the soil that released produced NH_4-N and NO_3-N. Results in the current study demonstrate a similar process. Dissolved organic carbon also had a significant and relatively strong correlation Mn in the Chicago soils and as described earlier may be due to its relationship through complexation rather than metals having a causative effect on DOC release.

DON

Fewer studies have been conducted on DON compared to DOC. Yet DON is a significant pool of soluble N in many ecosystems (Wherley et al. 2015) and its low molecular weight fraction is an important source of N for direct uptake by some plants (Jones et al. 2004). Jones et al. (2004) posited that there are two pools of DON in soil: 1) low molecular weight (LMW) free amino acids and proteins that are turned over relatively rapidly by soil microorganisms and 2) high molecular weight (HMW) compounds rich in humic substances that represent the observed losses of DON to surface waters. Kusliene et al. (2015) suggested that DON was derived from soil microbial lysis in a study of legume based (white clover) grassland soils. While the current study does not seek to describe DON fractions, use of the linear regression analyses using backward selection may provide some insight into its release in urban soils. Four models were created and compared for DON to identify the possible mechanisms involved in its release from the soil (Table 15)

Table 15. Summary of all DON model statistics and predictors.

	n	Slope	Offset	RMSE	R^2	p	Independent Variables
All Cities	102	0.781	5.331	9.338	0.78	< 0.001	Soil Age, pH, EC, NO_3-N, HCO_3, Ca, S, Fe, Cu
Chicago	33	0.839	2.764	6.204	0.84	< 0.001	EC, NH_4-N, Ca, Fe, Zn, Mn
BCS	34	0.944	1.824	6.368	0.95	< 0.001	pH, EC, NH_4-N, HCO_3, Ca, Mg, Cu, Mn, SAR
Galveston	35	0.852	3.438	4.239	0.85	< 0.001	Soil Age, HCO_3, Ca, K, B, S, Fe, Zn

All-Cities DON Model

Dissolved organic nitrogen release from soils across three urban ecosystems was modeled relatively well ($R^2 = 0.78$; $p < 0.001$; Table 15 and 16). All of the independent variables selected for predicting DON concentrations across all cities were significant ($p < 0.05$; Table 16). Cross-validation of the All-Cities DOC Model yielded a relatively strong and significant relationship between predicted and observed DOC concentrations (Figure 27A). Correlation analysis showed that all independent variables selected for modeling DON had a positive correlation with DON and all but two of the correlations were significant: Soil Age ($R = 0.30$; $p < 0.01$), pH ($R = 0.55$; $p < 0.001$), EC ($R =0.57$; $p < 0.001$), HCO_3 ($R = 0.32$; $p = 0.001$), Ca ($R = 0.38$; $p < 0.001$), Fe ($R = 0.71$; $p < 0.001$). Cu ($R = 0.66$; $p < 0.001$), NO_3-N ($R = 0.05$; $p > 0.05$) and S ($R = 0.05$; $p > 0.05$).

All-City DON = 2.181*Exposure Time + 4.666*pH + 0.153*EC – 0.364*NO_3-N – 0.021*HCO_3 + 0.055*Ca – 0.16*S+ 0.012*Fe + 13.499*Cu

Table 16. All-Cities DON Model coefficient statistics.

	MODEL			CORRELATION	
Predictors	Unstandardized Coefficients	Standardized Coefficients	Model P value	Correlation Coefficients (R)	Correlation P value
(Constant)	- 39.553		0.005		
Exposure Time	2.181	0.174	0.001	0.302	0.002
pH	4.666	0.181	0.008	0.551	< 0.001
EC	0.153	0.538	< 0.001	0.568	< 0.001
NO_3-N	- 0.364	- 0.163	0.006	0.050	0.618
HCO_3	- 0.021	- 0.303	< 0.001	0.323	0.001
Ca	0.055	0.203	0.016	0.379	< 0.001
S	- 0.160	- 0.397	< 0.001	0.049	0.628
Fe	0.012	0.382	< 0.001	0.708	< 0.001
Cu	13.499	0.170	0.010	0.659	< 0.001

Model ANOVA Table

	Sum of Squares	df	Mean Square	F value	p
Regression	32,232	9	3,581	39	< 0.001
Residual	8,447	92	92		
Total	40,679	101			

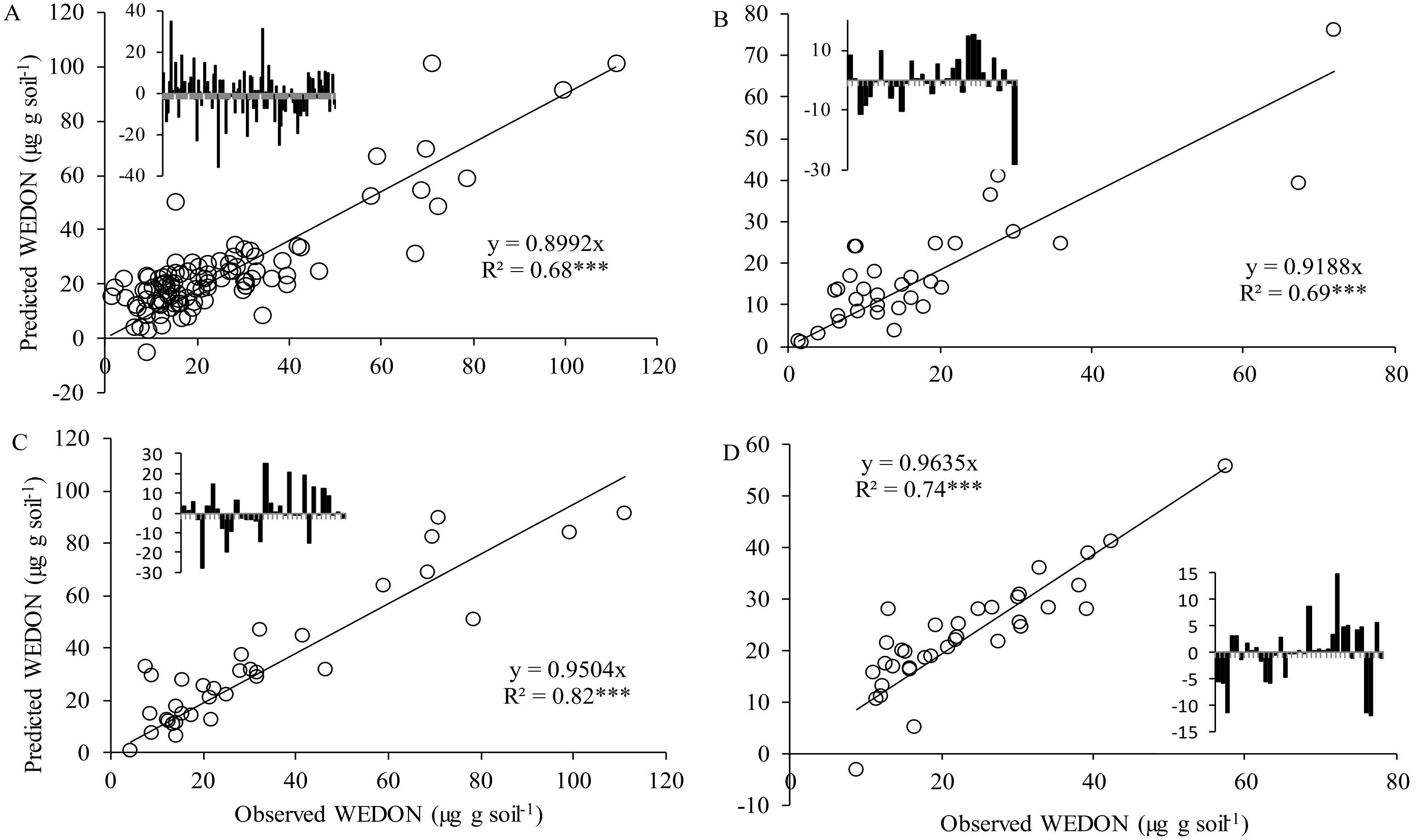

Figure 27. Cross Validation of DON Models for A) All cities, B) Chicago, C) BCS and D) Galveston. Inset figures display difference for each sample between observed and predicted values. * Denotes significance at p < 0.0001.**

Chicago DON Model

Release of DON in the urban soils in the city of Chicago was modeled relatively well ($R^2 = 0.84$; $p < 0.001$; Table 15 and 17). Cross-validation of the Chicago DOC model yielded a relatively strong and significant relationship between predicted and observed DOC concentrations and under- and over-estimates of DON ranging from -28 to 15 µg g soil^{-1} (Figure 27B). All independent variables selected for the Chicago DON model were significant ($p < 0.05$) suggesting that any change in them would stimulate a change in DON release (Table 17). Correlation analysis showed that all independent variables selected during the backward stepwise regression analyses had significant positive correlations with DON; EC ($R = 0.44$; $p < 0.05$), NH_4-N ($R = 0.53$; $p < 0.01$), Fe ($R = 0.79$; $p < 0.001$) Zn ($R = 0.60$; $p < 0.001$) and Mn ($R = 0.62$; $p < 0.001$) with the exception of Ca which was negatively correlated with DON ($R = -0.31$; $p > 0.05$) and non-significant.

Chicago DON = $7.193 + 0.089 \cdot EC + 1.075 \cdot NH_4\text{-}N - 0.089 \cdot Ca + 0.139 \cdot Fe - 13.022 \cdot Zn - 15.97 \cdot Mn$

Table 17. Chicago DON Model coefficient statistics.

	MODEL			CORRELATION	
Predictors	Unstandardized Coefficients	Standardized Coefficients	Model P value	Correlation Coefficients (R)	Correlation P value
(Constant)	7.193		0.375		
EC	0.089	0.201	0.035	0.435	0.011
NH4	1.075	0.272	0.008	0.527	0.002
Ca	- 0.089	- 0.254	0.021	- 0.314	0.075
Fe	0.139	1.565	< 0.001	0.790	< 0.001
Zn	- 13.022	- 0.638	0.002	0.605	< 0.001
Mn	- 15.970	- 0.521	0.030	0.617	< 0.001

Model ANOVA Table

	Sum of Squares	df	Mean Square	F value	p
Regression	6,659	6	1,110	23	< 0.001
Residual	1,270	26	49		
Total	7,930	32			

BCS DON Model

In the urban soils in the twin cities of Bryan and College Station, release of DON was modeled extremely well ($R^2 = 0.95$; $p < 0.001$; Table 15 and 18). Cross-validation of the BCS DON Model yielded a strong and significant relationship between predicted and observed DOC concentrations with under and over-estimates of DON within ± 30 µg g soil^{-}(Figure 27C). All independent variables selected for the BCS DON Model were significant ($p < 0.05$; Table 18) suggesting that any change in them would stimulate a change in DON release. Cross validation showed that all independent variables selected during the backward stepwise regression analysis had a significant and positive correlation with DON; pH ($R = 0.71$; $p < 0.001$), EC ($R = 0.65$; $p < 0.001$). NH$_4$-N ($R = 0.77$; $p < 0.001$), HCO$_3$ ($R = 0.52$; $p = 0.001$), Ca ($R = 0.42$; $p < 0.05$), Mg ($R = 0.81$; p

< 0.001), Cu ($R = 0.78$; $p < 0.001$), Mn ($R = 0.86$; $p < 0.001$) and SAR ($R = 0.76$; $p < 0.001$).

BCS DON $= 8.66*\text{pH} - 0.22*\text{EC} + 4.246*\text{NH}_4\text{-N} - 0.017*\text{HCO}_3 + 0.175*\text{Ca} - 0.114*\text{Mg} + 24.103*\text{Cu} + 9.947*\text{Mn} + 0.524*\text{SAR}$

Table 18. BCS DON Model coefficient statistics.

	MODEL			CORRELATION	
Predictors	Unstandardized Coefficients	Standardized Coefficients	Model P value	Correlation Coefficients (R)	Correlation P value
(Constant)	- 76.961		0.004		
pH	8.660	0.252	0.010	0.710	
EC	- 0.220	- 0.782	0.001	0.647	< 0.001
NH4	4.246	0.308	< 0.001	0.765	< 0.001
Alk	- 0.017	- 0.180	0.026	0.524	< 0.001
Ca	0.175	0.697	< 0.001	0.419	0.001
Mg	- 0.114	- 0.351	0.014	0.809	0.014
Cu	24.103	0.281	< 0.001	0.779	< 0.001
Mn	9.947	0.526	0.001	0.858	< 0.001
SAR	0.524	0.622	< 0.001	0.757	< 0.001

Model ANOVA Table

	Sum of Squares	df	Mean Square	F value	p
Regression	23,651	9	2,628	70	< 0.001
Residual	899	24	37		
Total	24,550	33			

Galveston DON Model

Release of DON in the urban soils in the island of Galveston was modeled relatively well ($R^2 = 0.85$; $p < 0.001$; Table 15 and 19). Cross-validation of the

Galveston DON Model yielded a relatively strong and significant relationship between predicted and observed DON concentrations with under and over-estimates of DON within ± 15 µg g $soil^{-1}$ (Figure 27D). All independent variables selected for the Galveston DON model were significant ($p < 0.05$; Table 19) with the exception of time soil was exposed to sodium ($p = 0.08$) suggesting that any change in them would stimulate a change in DOC release. Correlation analysis showed that all independent variables selected during the backward stepwise regression analysis had significant positive correlations with DON; soil age ($R = 0.41$; $p < 0.05$), Ca ($R = 0.70$; $p < 0.001$), K ($R = 0.58$; $p < 0.001$), B ($R = 0.42$; $p < 0.05$), S ($R = 0.46$; $p < 0.01$), Zn ($R = 0.54$; $p = 0.001$) with the exception of HCO_3 which was non-significant ($R = 0.10$; $p > 0.05$) and Fe which had a negative correlation with DON and was non-significant ($R = -0.11$; $p > 0.05$).

Galveston DON = -0.821*Exposure Time + 0.014*HCO_3 + 0.254*Ca + 0.012*K + 32.354*B – 0.519*S – 0.0187*Fe + 9.522*Zn – 1.221

Table 19. Galveston DON Model coefficient statistics.

MODEL				CORRELATION	
Predictors	Unstandardized Coefficients	Standardized Coefficients	Model P value	Correlation Coefficients (R)	Correlation P value
(Constant)	- 1.221		0.590		
Exposure Time	- 0.821	- 0.111	0.079	0.415	0.013
HCO_3	0.014	0.162	0.007	0.096	0.581
Ca	0.254	0.885	< 0.001	0.702	< 0.001
K	0.012	0.252	0.023	0.579	< 0.001
B	32.354	0.297	0.009	0.423	0.011
S	- 0.519	- 0.225	0.007	0.461	0.005
Fe	- 0.187	- 0.400	< 0.001	- 0.112	0.522
Zn	9.522	0.253	< 0.001	0.535	0.001

Model ANOVA Table

	Sum of Squares	df	Mean Square	F value	p
Regression	3,990	8	499	49	< 0.001
Residual	264	26	10		
Total	4,253	34			

Similarities and Dissimilarities in Predictors for DON Across Urban Ecosystems

It is known that DON is highly correlated to DOC due to the structural complex of DON which is a DOC molecule with amino functional groups (NH_3). Once these functional groups are cleaved by microorganisms, the DON molecule becomes a DOC molecule. Therefore, factors influencing DOC release in soils are similar to those influencing DON release and they are highly correlated (Figure 28). The purpose of developing models for DON was to determine the most significant predictors influencing DON release and whether they differ from the factors in DOC release.

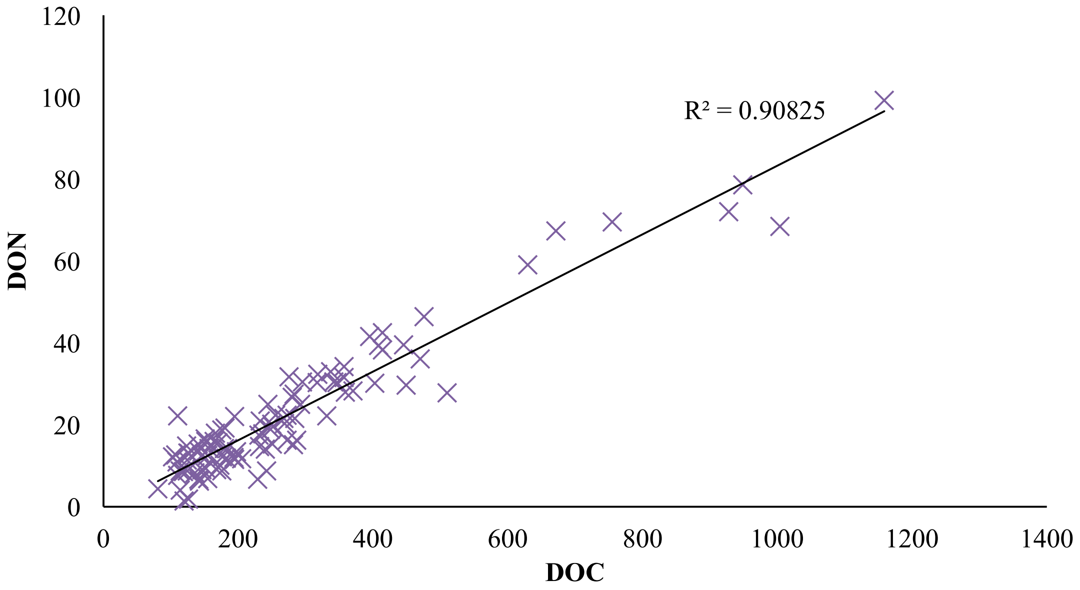

Figure 28. The strong relationship between DOC and DON ($p < 0.001$) demonstrating that factors that influence DOC release in soils are similar to those for DON release.

When comparing the predictors of the All- Cities DON and DOC Models, the predictors that were most influential on DON, in order of importance, were EC, S, and Fe (Table 16) while the most influential predictors in DOC model were Fe, Na, and Ca (Table 11). Correlation analysis for DON revealed that Fe had the strongest relationship ($R = 0.71$) with EC ($R = 0.57$) and S ($R = 0.05$) following. Fe also had the strongest relationship with DOC ($R = 0.77$) with Na ($R = 0.77$) and Ca ($R = 0.40$) following. This strong relationship with Fe is likely due to its polyvalent nature and its high affinity for functional groups. DOC and Fe have a strong proportional relationship and the concentration of Fe in solution has been shown to be dependent on the concentration of solubilized DOC, most likely because the affinity for DOC functional groups is higher than the soil (Pohlman & McColl 1988). If there are large amounts of Fe in the soil, the affinity for binding sites on DOC molecules become taken by Fe and competition for those sites may include those involved in binding with soil, causing DOC to be released (Guggenberger & Zech 1993). Although there was a strong relationship of DON and with Fe, the fact that Fe was not as significant of a predictor for DON suggests that other factors have a larger effect on its concentration, such as EC.

EC is a measure of the salt concentration in a solution. It has been shown that small increases in EC from greatly decreases microbial mineralization of N (Adviento-Borbe et al. 2006; Rietz & Haynes 2003). The strong positive relationship between EC and DON demonstrates that increases in EC stimulated increases in DON concentrations. The All-Cities DON Model also showed that a change in EC caused the largest change in DON, reflecting that DON concentrations are most dependent on EC concentrations. This strong relationship is likely due to the effects of EC on microbial communities and increased osmotic stress from increasing EC reduced the amount of DON mineralized, explaining the increasing concentrations of DON with EC. Furthermore, EC was not a selected predictor in the DOC model, showing DON concentrations most likely due to controls on microbial communities.

Conditions favorable of S mineralization are similar to those that lead to N mineralization in soils (Williams 1967). Both DON and DOC had positive, weak relationships with S that were not significant. In the DON model, changes in S had the second largest effect on DON, as shown in the standardized coefficients of Table 16. The weak relationship between DON and S along with the large significant effect S has on DON, suggests small increases in S, perhaps from lack of mineralization from microbes, is related to large increases in DON, which could also be from lack of mineralization.

The selected predictors in the All-Cities DON Model with the largest impact on DON (EC, S, Fe) compared to the All-Cities DOC Model (Fe, Na, Ca) suggest that both metals and sodicity had an effect on DON and DOC concentrations. However, the predictors for DON suggest DON concentrations are influenced by metals and sodicity (EC) and potentially microbial activity. Whereas the DOC predictors suggest metals and sodicity have the largest impact on DOC concentrations. Comparing individual city DON models with DOC models also reflect this.

The Chicago and Galveston DOC and DON models have similar predictors that had the greatest effect on their concentrations. The most influential parameters for the Chicago model for DON were Fe, Zn, and Mn (Table 17) and for the Galveston model they were Ca, Fe, and B (Table 19). These parameters reflect strong influence of metal complexes on DON solubility. The most influential parameters for the Chicago DOC Model were Fe, Mn, and Zn (Table 12) and for the Galveston model they were Ca, B, and Fe (Table 14). These DOC models also show strong influences of metals on DOC. The BCS models show that DON is more influenced by sodicity effects since the most influential predictors were EC, Ca, and SAR. The BCS DOC Model showed that Fe, B, and Ca had the largest effect on DOC, suggesting metals and sodic effects.

Results from this study show that DON solubility is related to metal concentrations in the soil, which was shown to be similar for DOC. The All-Cities DON Models also showed a strong influence of sodicity on DON solubility whereas the All-

Cities DOC Model showed a strong influence of metals on DOC solubility. This difference may be due to microbial stress from increasing sodicity in soils, preventing DON mineralization.

4. CONCLUSIONS

Carbon sequestration in soil is important as climate change progresses and atmospheric CO_2 concentrations continue to rise. However, increasing DOC concentrations in surface waters demonstrates a loss of this terrestrial carbon storage. This study sought to determine what might be affecting %BDOC, DOC and DON in urban soils. While it was apparent from this study that sodium exposure increases the release of water extractable DOC and DON in soils, while decreasing the availability of BDOC within soils there is a question of cause and effect. Soils exposed to sodium in the form of $NaHCO_3$ (from irrigation water) showed greater DOC and DON release than soils exposed to NaCl (from deicing salts and sea salt deposition). $SUVA_{254}$ values were significantly different among sodium sources suggesting that sodium type may play a role in the amount of aromatic DOC release. Furthermore, soils exposed to high sodium concentrations had increased release of water extractable DOC and DON over time of sodium exposure until soils were exposed for 30 years; after a 30 year exposure to sodium a decline in DOC and DON concentrations were observed. This decline is likely due to the lack of irrigation installations and decreased use of deicing salts pre the mid 1980s. DOC was successfully predicted by $SUVA_{254}$ while %BDOC was not. This was likely due to large %BDOC values observed in soils exposed to sea salt deposition with high aromatic DOC release. It may be that the different soil characteristics in each of the cities examined have a greater affect on the variables examined and this should be considered in future cross-city research. These results could be used to help develop future management strategies that minimize carbon loss in soils and help determine a threshold of sodium exposure for DOC, DON, and %BDOC release in soils.

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APPENDIX

Table 20. Physical and Chemical soil attributes for the soils collected in Chicago, IL.

Lat	Long	Series	Name	Group	Clay	Sand	Silt	OM	Ksat	BD	CEC
					%				mm/hr	g/cm^3	cmol charge /kg soil
41.9736	-87.7593	534A	Urban-Orthent	Entisol	44.0	8.0	48.0	1.3	1.0	1.98	23.4
41.9732	-87.7580	534A	Urban-Orthent	Entisol	44.0	8.0	48.0	1.3	1.0	1.98	23.4
41.9704	-87.7557	534A	Urban-Orthent	Entisol	44.0	8.0	48.0	1.3	1.0	1.98	23.4
41.9714	-87.7425	534A	Urban-Orthent	Entisol	44.0	8.0	48.0	1.3	1.0	1.98	23.4
41.9740	-87.7242	534A	Urban-Orthent	Entisol	44.0	8.0	48.0	1.3	1.0	1.98	23.4
41.9830	-87.7389	2811A	Urban-Alfic-Udarent	Entisol	36.0	8.0	56.0	2.5	3.3	1.85	19.4
41.9855	-87.7380	2811A	Urban-Alfic-Udarent	Entisol	36.0	8.0	56.0	2.5	3.3	1.85	19.4
41.9887	-87.7364	533	Urban-Orthent	Entisol	44.0	8.0	48.0	1.3	1.0	1.98	23.4
41.9956	-87.7377	534A	Urban-Orthent	Entisol	44.0	8.0	48.0	1.3	1.0	1.98	23.4
41.9958	-87.7370	534A	Urban-Orthent	Entisol	44.0	8.0	48.0	1.3	1.0	1.98	23.4
41.9729	-87.6980	2800A	Urban-Psamment	Entisol	25.0	35.0	40.0	2.0	10.2	1.78	18.3
41.9722	-87.6982	2800A	Urban-Psamment	Entisol	25.0	35.0	40.0	2.0	10.2	1.78	18.3
41.9518	-87.7181	392A	Urban-Orthent	Entisol	44.0	8.0	48.0	1.3	1.0	1.98	23.4
41.9509	-87.7370	534A	Urban-Orthent	Entisol	44.0	8.0	48.0	1.3	1.0	1.98	23.4
41.9473	-87.7327	534A	Urban-Orthent	Entisol	44.0	8.0	48.0	1.3	1.0	1.98	23.4
41.9436	-87.7450	534A	Urban-Orthent	Entisol	44.0	8.0	48.0	1.3	1.0	1.98	23.4
41.9566	-87.7454	533	Urban-Orthent	Entisol	44.0	8.0	48.0	1.3	1.0	1.98	23.4
41.9664	-87.7809	2811A	Urban-Alfic-Udarent	Entisol	36.0	8.0	56.0	2.5	3.3	1.85	19.4
41.9643	-87.7820	534A	Urban-Orthent	Entisol	44.0	8.0	48.0	1.3	1.0	1.98	23.4

41.9615	-87.7883	534A	Urban-Orthent	Entisol	44.0	8.0	48.0	1.3	1.0	1.98	23.4
41.9474	-87.7957	2811A	Urban-Alfic-Udarent	Entisol	36.0	8.0	56.0	2.5	3.3	1.85	19.4
41.9331	-87.8062	533	Urban-Orthent	Entisol	44.0	8.0	48.0	1.3	1.0	1.98	23.4
41.9405	-87.8139	2811A	Urban-Alfic-Udarent	Entisol	36.0	8.0	56.0	2.5	3.3	1.85	19.4
41.9550	-87.8107	534A	Urban-Orthent	Entisol	44.0	8.0	48.0	1.3	1.0	1.98	23.4
41.9663	-87.8087	534A	Urban-Orthent	Entisol	44.0	8.0	48.0	1.3	1.0	1.98	23.4
41.9695	-87.8063	534A	Urban-Orthent	Entisol	44.0	8.0	48.0	1.3	1.0	1.98	23.4
41.9737	-87.8134	2811A	Urban-Alfic-Udarent	Entisol	36.0	8.0	56.0	2.5	3.3	1.85	19.4
41.9687	-87.8376	534A	Urban-Orthent	Entisol	44.0	8.0	48.0	1.3	1.0	1.98	23.4
41.9790	-87.8215	2811A	Urban-Alfic-Udarent	Entisol	36.0	8.0	56.0	2.5	3.3	1.85	19.4
41.9803	-87.8215	2811A	Urban-Alfic-Udarent	Entisol	36.0	8.0	56.0	2.5	3.3	1.85	19.4
41.9816	-87.7942	534A	Urban-Orthent	Entisol	44.0	8.0	48.0	1.3	1.0	1.98	23.4
41.9478	-87.8702	534A	Urban-Orthent	Entisol	44.0	8.0	48.0	1.3	1.0	1.98	23.4

Table 21. Physical and Chemical soil attributes for the soils collected in Galveston, TX.

Lat	Long	Series Code	Soil Series	Group	Clay	Sand	Silt	OM	Ksat	BD	CEC
					%				mm/hr	g/cm^3	cmol charge /kg soil
29.2833	-94.8698	BBBX	Beaches	NA	1.5	97.9	0.6	0.0	507.6	1.5	3
29.2937	-94.8639	Gd	Galveston	Entisol	5.0	94.4	0.6	0.3	331.2	1.67	2.5
29.2902	-94.8182	BBBX	Beaches	NA	1.5	97.9	0.6	0.0	507.6	1.5	3
29.3200	-94.7713	BBBX	Beaches	NA	1.5	97.9	0.6	0.0	507.6	1.5	3
29.3178	-94.7712	BBBX	Beaches	NA	1.5	97.9	0.6	0.0	507.6	1.5	3
29.3156	-94.7690	BBBX	Beaches	NA	1.5	97.9	0.6	0.0	507.6	1.5	3
29.3231	-94.7429	Mt	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3
29.3196	-94.7487	Mt	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3
29.3185	-94.7503	Mt	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3
29.2778	-94.8123	BBBX	Beaches	NA	1.5	97.9	0.6	0.0	507.6	1.5	3
29.2792	-94.8247	BBBX	Beaches	NA	1.5	97.9	0.6	0.0	507.6	1.5	3
29.2771	-94.8473	BBBX	Beaches	NA	1.5	97.9	0.6	0.0	507.6	1.5	3
29.2685	-94.8758	Mn	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3
29.2631	-94.8712	Mn	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3
29.2524	-94.8701	Mn	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3
29.2259	-94.9185	Mt	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3
29.2197	-94.9090	Mn	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3
29.2095	-94.9286	Mt	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3
29.2067	-94.9328	Mt	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3
29.2059	-94.9365	Mn	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3
29.2035	-94.9396	Mn	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3
29.2032	-94.9415	Mn	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3
29.1985	-94.9461	Mn	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3

29.1979	-94.9469	Mt	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3
29.1990	-94.9474	Mn	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3
29.1998	-94.9865	Mu	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3
29.1431	-95.0453	Mn	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3
29.1409	-95.0514	Mu	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3
29.1391	-95.0472	GaB	Galveston	Entisol	5.0	94.4	0.6	0.3	331.2	1.67	2.5
29.1353	-95.0485	Mn	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3
29.1275	-95.0600	BBBX	Beaches	NA	1.5	97.9	0.6	0.0	507.6	1.5	3
29.1115	-95.0852	Gc	Galveston	Entisol	5.0	94.4	0.6	0.3	331.2	1.67	2.5
29.1120	-95.0874	Mt	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3
29.1117	-95.0872	Mt	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3
29.1364	-95.0492	Mn	Mustang	Entisol	5.0	94.4	0.6	0.6	331.2	1.57	3

Table 22. Physical and Chemical soil attributes for the soils collected in Bryan/College Station, TX.

Lat	Long	Series	Name	Group	Clay	Sand	Silt	OM	Ksat	BD	CEC
						%			mm/hr	g/cm^3	cmol charge /kg soil
30.5975	-96.3303	BrB	Boonville	Alfisol	10.0	68.5	21.5	0.8	32.4	1.49	6
30.5878	-96.3028	TuA	Tabor	Alfisol	14.0	69.6	16.4	0.8	32.4	1.63	3.5
30.5830	-96.3033	TuA	Tabor	Alfisol	14.0	69.6	16.4	0.8	32.4	1.63	3.5
30.5658	-96.2894	BoA	Boonville	Alfisol	10.0	68.5	21.5	0.8	32.4	1.49	6
30.5651	-96.2905	BuB	Burleson	Vertisol	50.0	22.1	27.9	2.0	0.8	1.78	50
30.5652	-96.2888	BoA	Boonville	Alfisol	10.0	68.5	21.5	0.8	32.4	1.49	6
30.5647	-96.2890	BoA	Boonville	Alfisol	10.0	68.5	21.5	0.8	32.4	1.49	6
30.5605	-96.2851	SnB	Singleton	Alfisol	12.5	70.9	16.6	0.8	32.4	1.62	6
30.5611	-96.2853	SnB	Singleton	Alfisol	12.5	70.9	16.6	0.8	32.4	1.62	6
30.5449	-96.2879	MaA	Mabank	Alfisol	17.5	43.0	39.5	1.5	32.4	1.65	7.5
30.5436	-96.2894	MaA	Mabank	Alfisol	17.5	43.0	39.5	1.5	32.4	1.65	7.5
30.5263	-96.2497	BwC	Burlewash	Alfisol	10.0	65.0	25.0	1.3	32.4	1.55	4.3
30.5546	-96.2306	BwC	Burlewash	Alfisol	10.0	65.0	25.0	1.3	32.4	1.55	4.3
30.5620	-96.2450	ReC	Rehburg	Alfisol	7.0	83.5	9.5	0.8	331.2	1.52	3.5
30.5614	-96.2487	SkB	Shiro	Alfisol	8.5	82.2	9.3	0.8	100.8	1.52	4.5
30.5626	-96.2502	BwC	Burlewash	Alfisol	10.0	65.0	25.0	1.3	32.4	1.55	4.3
30.5896	-96.2834	TuA	Tabor	Alfisol	14.0	69.6	16.4	0.8	32.4	1.63	3.5
30.5909	-96.2837	TuA	Tabor	Alfisol	14.0	69.6	16.4	0.8	32.4	1.63	3.5
30.5905	-96.2787	TuA	Tabor	Alfisol	14.0	69.6	16.4	0.8	32.4	1.63	3.5
30.5901	-96.2795	TuA	Tabor	Alfisol	14.0	69.6	16.4	0.8	32.4	1.63	3.5
30.6179	-96.2846	BrB	Boonville	Alfisol	10.0	68.5	21.5	0.8	32.4	1.49	6
30.6208	-96.2885	BrB	Boonville	Alfisol	10.0	68.5	21.5	0.8	32.4	1.49	6
30.6239	-96.3026	Ur-BrB	Urban	Alfisol	10.0	68.5	21.5	0.8	32.4	1.49	6

30.6310	-96.3167	ZcB	Zack	Alfisol	11.0	67.7	21.3	0.7	32.4	1.29	7.5
30.6286	-96.3198	BrB	Boonville	Alfisol	10.0	68.5	21.5	0.8	32.4	1.49	6
30.6684	-96.3415	ZcB	Zack	Alfisol	11.0	67.7	21.3	0.7	32.4	1.29	7.5
30.6767	-96.3310	BoB	Boonville	Alfisol	10.0	68.5	21.5	0.8	32.4	1.49	6
30.6788	-96.3336	BoB	Boonville	Alfisol	10.0	68.5	21.5	0.8	32.4	1.49	6
30.6761	-96.3329	ZcD	Zack	Alfisol	11.0	67.7	21.3	0.7	32.4	1.29	7.5
30.6874	-96.3305	BoB	Boonville	Alfisol	10.0	68.5	21.5	0.8	32.4	1.49	6
30.6868	-96.3308	BoB	Boonville	Alfisol	10.0	68.5	21.5	0.8	32.4	1.49	6
30.6811	-96.3224	BoB	Boonville	Alfisol	10.0	68.5	21.5	0.8	32.4	1.49	6
30.6811	-96.3224	BoB	Boonville	Alfisol	10.0	68.5	21.5	0.8	32.4	1.49	6
30.6727	-96.2944	BoB	Boonville	Alfisol	10.0	68.5	21.5	0.8	32.4	1.49	6

Table 23. Raw data for water extractable metals.

NAWA			Age	Na	Ca	Mg	Na	K	B	S	Fe	Zn	Cu	Mn
									mg/kg					
S06887	Chicago	6	6 to 10	Deicing1	106	28	54	43	0	7	38	0	0	0
S06888	Chicago	21	21 to 30	Deicing1	141	38	120	82	0	17	28	1	0	0
S06889	Chicago	30	> 30	Deicing1	66	60	286	68	1	14	186	2	0	0
S06890	Chicago	7	6 to 10	Deicing1	149	31	112	59	0	25	16	0	0	0
S06891	Chicago	91	> 30	Deicing1	55	44	174	64	0	12	148	2	0	1
S06892	Chicago	72	> 30	Deicing1	58	64	320	96	1	13	239	3	0	1
S06893	Chicago	10	6 to 10	Deicing1	142	62	384	11	1	20	219	1	1	1
S06894	Chicago	0	0 to 5	Deicing1	171	36	95	56	0	11	110	1	1	1
S06895	Chicago	24	21 to 30	Deicing1	106	43	162	89	0	17	61	1	0	0
S06896	Chicago	14	11 to 20	Deicing1	104	40	115	52	1	14	137	1	0	0
S06897	Chicago	61	> 30	Deicing1	102	46	89	102	0	10	20	1	1	0
S06899	Chicago	92	> 30	Deicing1	183	49	158	76	0	15	19	1	0	0
S06900	Chicago	3	0 to 5	Deicing1	120	43	145	66	0	17	105	1	0	0
S06901	Chicago	11	11 to 20	Deicing1	176	42	27	79	0	11	105	1	0	0
S06902	Chicago	0	0 to 5	Deicing1	146	43	155	46	0	24	45	0	0	0
S06903	Chicago	3	0 to 5	Deicing1	213	53	16	47	0	19	28	1	0	0
S06904	Chicago	21	21 to 30	Deicing1	150	56	140	115	1	20	103	1	0	0
S06905	Chicago	12	11 to 20	Deicing1	89	49	310	118	0	14	129	1	0	0
S06906	Chicago	0	0 to 5	Deicing1	172	37	99	57	0	15	29	1	0	0
S06907	Chicago	7	6 to 10	Deicing1	74	60	201	82	1	12	229	1	0	1
S06908	Chicago	27	21 to 30	Deicing1	135	175	442	253	3	20	964	4	1	2
S06909	Chicago	12	11 to 20	Deicing1	90	43	387	183	1	30	190	2	1	1
S06910	Chicago	0	0 to 5	Deicing1	153	54	69	61	0	14	73	1	0	0
S06911	Chicago	18	11 to 20	Deicing1	86	71	258	133	1	11	326	2	0	2
S06912	Chicago	59	> 30	Deicing1	57	52	172	73	1	12	173	2	0	0
S06913	Chicago	55	> 30	Deicing1	93	79	396	128	1	18	320	2	0	1
S06914	Chicago	69	> 30	Deicing1	69	56	265	80	1	14	196	1	0	1
S06915	Chicago	9	6 to 10	Deicing1	155	47	19	48	0	11	49	1	0	0
S06916	Chicago	0	0 to 5	Deicing1	166	51	34	99	0	20	54	0	0	0
S06917	Chicago	8	6 to 10	Deicing1	118	47	179	53	0	11	126	1	0	1

S06918	Chicago	15	11 to 20	Deicing1	179	49	51	45	0	12	45	0	0	0
S06919	Chicago	10	6 to 10	Deicing1	200	41	20	48	0	16	39	1	0	0
S06920	Chicago	29	21 to 30	Deicing1	82	89	494	133	1	19	419	2	0	1
S06956	BCS	13	11 to 20	Irrigation	183	158	447	78	1	36	962	3	0	1
S06957	BCS	13	11 to 20	Irrigation	155	116	478	72	1	29	711	2	0	1
S06958	BCS	60	> 30	Irrigation	177	31	57	24	0	11	123	1	0	0
S06959	BCS	56	> 30	Irrigation	148	31	31	24	0	10	67	2	0	0
S06960	BCS	30	> 30	Irrigation	237	251	734	159	3	32	1501	4	2	3
S06961	BCS	0	0 to 5	Irrigation	103	28	140	36	0	11	96	1	0	0
S06962	BCS	28	21 to 30	Irrigation	109	56	322	52	1	12	451	2	1	1
S06963	BCS	60	> 30	Irrigation	44	24	74	33	0	9	107	2	1	0
S06964	BCS	8	6 to 10	Irrigation	173	23	122	39	0	18	54	1	1	0
S06965	BCS	13	11 to 20	Irrigation	454	185	1175	318	2	44	1900	3	1	2
S06966	BCS	9	6 to 10	Irrigation	146	49	237	76	0	20	159	1	0	0
S06967	BCS	0	0 to 5	Irrigation	138	28	140	36	0	26	20	1	0	0
S06968	BCS	34	> 30	Irrigation	104	17	10	47	0	6	47	1	0	0
S06969	BCS	9	6 to 10	Irrigation	130	75	324	57	0	51	337	1	0	1
S06970	BCS	28	21 to 30	Irrigation	90	29	228	60	0	15	144	1	0	1
S06971	BCS	0	0 to 5	Irrigation	109	41	145	122	0	20	177	1	0	0
S06972	BCS	27	21 to 30	Irrigation	93	20	322	55	0	19	96	0	0	0
S06973	BCS	0	0 to 5	Irrigation	179	32	179	51	0	131	58	1	0	0
S06974	BCS	23	21 to 30	Irrigation	176	156	705	135	2	52	1328	5	1	3
S06975	BCS	0	0 to 5	Irrigation	168	31	333	27	0	75	91	1	0	0
S06976	BCS	22	21 to 30	Irrigation	102	62	383	55	1	22	309	1	1	1
S06977	BCS	15	11 to 20	Irrigation	110	79	392	62	1	26	381	2	1	1
S06978	BCS	8	6 to 10	Irrigation	608	53	85	55	0	486	0	0	0	0
S06979	BCS	8	6 to 10	Irrigation	166	29	21	71	0	17	91	1	0	0
S06980	BCS	19	11 to 20	Irrigation	108	32	151	57	0	29	113	1	0	0
S06981	BCS	8	6 to 10	Irrigation	312	352	766	213	4	49	3478	5	1	4
S06982	BCS	34	> 30	Irrigation	280	201	832	90	3	38	1894	6	1	5
S06983	BCS	23	21 to 30	Irrigation	207	217	885	195	3	113	2414	5	1	5
S06984	BCS	11	11 to 20	Irrigation	73	33	89	45	0	9	130	1	0	0
S06985	BCS	34	> 30	Irrigation	136	40	407	32	1	31	171	1	0	0
S06986	BCS	9	6 to 10	Irrigation	149	123	548	68	1	34	491	2	0	2

S06987	BCS	0	0 to 5	Irrigation	127	33	186	32	0	23	103	1	0	0
S06988	BCS	27	21 to 30	Irrigation	207	236	320	202	3	39	4091	6	0	3
S06989	BCS	16	11 to 20	Irrigation	119	29	62	46	0	8	85	1	0	0
S06990	Galveston	30	> 30	Seasalt	112	23	20	62	0	9	46	2	0	0
S06991	Galveston	3	0 to 5	Seasalt	145	33	23	55	0	12	75	1	0	0
S06992	Galveston	7	6 to 10	Seasalt	138	31	44	57	0	13	33	1	0	0
S06993	Galveston	55	> 30	Seasalt	152	34	25	89	0	13	52	1	0	0
S06994	Galveston	50	> 30	Seasalt	145	32	32	62	0	11	66	1	0	0
S06995	Galveston	45	> 30	Seasalt	185	30	37	117	0	15	42	1	0	0
S06996	Galveston	6	6 to 10	Seasalt	147	23	26	62	0	12	54	1	0	0
S06997	Galveston	0	0 to 5	Seasalt	105	24	31	47	0	3	50	1	0	0
S06998	Galveston	7	6 to 10	Seasalt	41	3	8	10	0	3	6	0	0	0
S06999	Galveston	89	> 30	Seasalt	121	26	107	1394	1	19	20	1	0	0
S07000	Galveston	27	21 to 30	Seasalt	169	32	37	57	0	14	48	1	0	0
S07001	Galveston	12	11 to 20	Seasalt	148	36	14	59	0	9	90	1	0	0
S07002	Galveston	22	21 to 30	Seasalt	181	37	36	69	0	16	74	1	0	0
S07003	Galveston	2	0 to 5	Seasalt	152	30	24	70	0	14	84	1	0	0
S07004	Galveston	34	> 30	Seasalt	122	24	21	49	0	9	40	1	0	0
S07005	Galveston	15	11 to 20	Seasalt	156	24	11	47	0	8	59	1	0	0
S07006	Galveston	10	6 to 10	Seasalt	127	28	11	55	0	7	85	1	0	0
S07007	Galveston	18	11 to 20	Seasalt	158	31	24	56	0	11	54	1	0	0
S07008	Galveston	13	11 to 20	Seasalt	111	34	31	50	0	10	66	1	0	0
S07009	Galveston	25	21 to 30	Seasalt	112	28	22	49	0	8	61	1	0	0
S07010	Galveston	11	11 to 20	Seasalt	91	22	17	28	0	7	60	1	1	0
S07011	Galveston	28	21 to 30	Seasalt	99	24	22	26	0	8	44	1	0	0
S07012	Galveston	16	11 to 20	Seasalt	117	28	48	29	0	15	48	1	0	0
S07013	Galveston	5	0 to 5	Seasalt	80	18	19	37	0	6	33	1	0	0
S07014	Galveston	23	21 to 30	Seasalt	112	28	16	41	0	8	85	1	0	0
S07015	Galveston	10	6 to 10	Seasalt	128	26	47	47	0	19	49	0	0	0
S07016	Galveston	8	6 to 10	Seasalt	95	23	18	46	0	6	72	1	0	0
S07017	Galveston	21	21 to 30	Seasalt	79	16	22	66	0	5	36	1	0	0
S07018	Galveston	4	0 to 5	Seasalt	79	30	89	54	0	12	67	1	0	0
S07019	Galveston	35	> 30	Seasalt	111	25	30	43	0	6	65	1	0	0
S07020	Galveston	31	> 30	Seasalt	58	7	12	15	0	3	13	1	0	0

S07021	Galveston	14	11 to 20	Seasalt	36	9	23	14	0	6	29	1	0	0
S07022	Galveston	0	0 to 5	Seasalt	69	43	202	54	0	19	118	1	0	0
S07023	Galveston	9	6 to 10	Seasalt	115	24	19	52	0	20	45	1	0	0
S07024	Galveston	0	0 to 5	Seasalt	38	6	9	17	0	3	12	1	0	0

Table 24. Raw data for water extractable nutrients.

		pH	EC	NO3-N	NH4-N	PO4-P	DOC	DON	Alk 2	SAR	ESP	SUVA254	BDOC
			µS/cm				µg g soil						%
Chicago	1	7.70	135	7.07	3.85	1.18	136.00	8.31	372.40	11.18	23.04	3.32	23.19
Chicago	3	7.27	199	56.39	12.03	5.22	273.00	16.18	285.44	21.54	29.84	3.98	32.69
Chicago	4	7.85	120	10.70	13.98	8.44	469.70	36.04	294.32	64.91	58.26	6.32	19.92
Chicago	1	7.39	127	19.75	7.67	4.40	236.70	17.83	378.30	19.86	31.23	3.30	33.41
Chicago	5	7.41	114	27.37	7.60	6.83	231.90	14.71	0.00	44.22	49.15	5.89	14.33
Chicago	5	7.75	229	27.67	11.90	7.41	282.40	15.12	0.00	74.69	56.37	10.49	11.14
Chicago	1	7.57	229	14.27	14.12	8.17	569.00	26.64	650.73	65.81	68.66	6.52	6.84
Chicago	0	7.24	122	3.50	4.10	4.37	119.50	1.30	452.40	15.66	26.46	2.82	41.64
Chicago	3	7.61	140	5.09	5.89	5.54	268.80	20.21	376.93	32.37	37.81	3.94	21.52
Chicago	2	7.68	100	9.69	21.50	6.59	449.20	29.70	167.32	23.32	36.48	3.92	39.28
Chicago	5	7.56	101	24.24	10.40	5.45	240.30	14.06	279.70	17.93	23.69	4.10	19.08
Chicago	5	7.22	143	23.19	7.92	4.05	113.70	3.99	457.80	24.93	33.45	5.07	21.04
Chicago	0	7.53	142	7.98	8.05	4.81	194.70	11.46	517.30	27.55	37.70	3.84	25.03
Chicago	2	7.10	108	15.62	5.10	4.92	141.70	6.67	420.68	4.37	8.01	3.69	15.39
Chicago	0	7.03	154	4.99	1.91	1.01	146.10	9.00	673.96	27.14	40.45	1.84	46.41
Chicago	0	7.33	172	27.43	7.95	10.16	155.40	6.82	583.54	2.35	5.17	2.96	34.83
Chicago	3	7.43	186	15.62	6.26	49.18	286.60	16.22	582.98	23.71	28.23	4.30	14.29
Chicago	2	7.60	167	26.05	12.71	9.61	252.20	19.44	325.14	65.34	50.47	3.84	23.23
Chicago	0	7.26	134	6.10	5.10	3.60	126.10	1.80	250.82	16.33	27.09	2.98	23.71
Chicago	1	7.91	107	27.92	4.13	5.29	182.70	11.85	240.30	43.94	46.03	8.83	1.48
Chicago	3	7.88	197	9.90	13.06	10.80	927.70	72.04	184.55	65.37	40.83	14.94	0.00
Chicago	2	7.00	166	9.38	10.64	13.39	229.30	6.67	682.58	82.50	48.41	7.03	3.70
Chicago	0	7.48	141	10.44	4.63	3.39	194.20	11.94	519.04	11.63	20.62	4.83	15.72
Chicago	2	7.35	139	51.41	5.11	6.03	168.10	9.09	291.50	52.16	43.24	14.38	2.48
Chicago	5	7.60	110	16.42	12.12	12.57	242.40	8.77	127.96	41.98	46.07	7.63	7.24

Chicago	5	7.76	170	8.12	12.11	9.10	510.30	27.77	579.21	76.62	53.77	7.02	7.41
Chicago	5	7.37	162	14.93	9.99	11.57	331.50	22.19	309.00	59.98	53.99	8.57	4.49
Chicago	1	7.25	135	16.32	8.32	3.40	205.30	11.75	433.17	3.22	7.29	6.02	6.77
Chicago	0	6.90	138	18.25	8.83	5.34	142.40	6.22	532.72	5.56	9.09	4.88	8.61
Chicago	1	7.62	131	8.24	10.65	4.89	247.60	18.81	619.81	33.96	45.11	4.32	21.03
Chicago	2	7.12	165	11.95	7.00	13.97	173.00	10.05	596.71	8.11	16.48	5.25	14.06
Chicago	1	7.47	128	10.18	9.30	2.21	151.80	9.32	170.39	3.06	6.72	2.85	33.64
Chicago	3	7.69	220	21.03	11.72	12.28	671.10	67.36	308.61	97.30	58.90	13.11	2.72
BCS	2	9.11	163	9.63	2.10	2.92	359.40	27.94	824.46	61.48	54.33	17.34	7.45
BCS	2	9.27	170	6.23	1.90	3.17	402.81	30.20	871.08	73.13	59.98	13.02	39.60
BCS	5	8.44	78	10.30	2.24	1.72	250.33	20.04	369.02	9.36	21.23	7.62	31.19
BCS	4	7.60	60	10.47	2.34	3.69	230.52	17.50	249.96	5.51	14.27	6.11	20.22
BCS	4	9.63	250	13.70	4.30	9.39	948.62	78.63	1124.35	85.45	54.62	11.80	15.08
BCS	0	8.31	83	2.65	1.56	2.10	157.04	14.25	406.64	29.35	45.78	8.52	31.94
BCS	3	9.32	122	7.24	2.52	5.15	318.22	32.37	591.41	61.85	60.18	12.74	28.63
BCS	5	8.12	45	6.60	1.94	13.76	272.72	22.25	0.00	22.21	40.85	8.52	28.23
BCS	1	8.36	130	5.20	0.75	0.57	184.73	14.22	634.64	20.49	34.73	6.32	38.27
BCS	2	9.69	402	13.50	8.06	11.01	1211.42	111.04	803.81	113.41	53.18	19.81	1.19
BCS	1	8.54	165	7.20	2.38	10.01	283.96	21.60	732.82	41.06	45.63	6.84	48.96
BCS	0	8.47	102	5.30	0.76	1.12	118.60	8.49	527.80	25.85	41.65	8.63	28.88
BCS	4	8.34	60	6.10	1.73	3.04	179.91	14.12	207.00	2.15	5.27	6.00	39.65
BCS	1	8.62	164	5.60	2.02	4.33	292.68	24.96	580.29	56.17	56.45	10.88	45.90
BCS	3	8.75	130	8.50	2.86	5.64	275.80	31.76	570.30	50.48	53.80	6.69	50.56
BCS	0	6.68	111	4.20	0.73	1.50	81.23	4.36	24.80	28.78	30.90	17.62	39.77
BCS	3	8.90	155	7.41	2.29	3.45	475.73	46.40	631.30	72.13	63.49	12.29	29.63
BCS	0	6.73	198	2.78	6.94	0.39	110.04	7.62	428.50	29.19	40.80	6.91	43.25
BCS	3	9.60	301	12.11	3.47	7.00	629.89	58.99	761.70	98.43	60.23	15.19	18.15
BCS	0	8.69	196	1.10	0.60	0.50	176.36	12.21	730.04	55.96	61.47	7.93	33.17

BCS	3	9.48	169	6.22	2.84	3.79	394.76	41.55	655.72	74.45	64.02	9.51	34.12
BCS	2	9.23	170	6.24	1.41	4.31	357.37	31.52	627.99	71.64	61.72	10.84	32.46
BCS	1	7.30	394	3.61	1.35	0.32	124.26	8.77	369.52	7.72	11.54	3.36	46.01
BCS	1	8.37	97	7.06	2.62	5.15	170.55	15.59	421.10	3.56	6.96	7.43	41.28
BCS	2	8.50	117	5.01	1.00	3.53	154.84	12.47	423.32	30.72	42.06	9.09	33.03
BCS	1	9.67	280	13.87	6.55	7.12	841.86	70.74	733.37	76.74	48.29	22.44	7.21
BCS	4	9.80	352	12.61	4.91	8.00	1158.20	99.20	848.74	95.32	62.30	13.38	10.80
BCS	3	9.69	333	14.15	4.87	6.10	754.57	69.52	1042.87	110.46	58.54	18.14	28.65
BCS	2	8.31	57	6.55	2.08	3.14	268.06	21.48	166.51	21.19	36.09	8.63	26.07
BCS	4	9.10	167	4.37	0.91	4.23	250.48	15.30	936.93	73.84	67.71	9.03	35.46
BCS	1	9.43	220	6.58	2.41	4.69	370.34	28.30	1283.04	84.17	63.83	12.96	13.10
BCS	0	8.50	125	3.70	0.75	0.68	175.85	8.78	566.97	35.23	50.46	8.14	20.90
BCS	3	8.71	96	18.32	7.03	6.11	1003.42	68.42	595.20	39.28	33.03	20.01	5.26
BCS	2	8.29	76	3.77	1.62	1.27	197.75	13.42	355.65	12.18	23.91	6.98	30.27
Galveston	4	7.10	106	6.50	6.22	3.60	282.90	27.48	19.80	4.09	8.50	15.06	39.24
Galveston	0	7.05	112	7.20	2.38	1.20	357.40	34.22	362.80	4.11	8.83	20.36	38.98
Galveston	1	7.03	143	5.80	6.31	9.90	408.60	39.29	48.00	8.07	15.85	19.45	33.37
Galveston	4	6.88	155	5.50	4.63	4.10	337.00	32.87	394.50	4.37	7.65	18.05	35.61
Galveston	4	7.38	130	10.20	9.51	4.20	244.60	24.89	127.00	5.73	11.40	14.18	39.86
Galveston	4	6.92	178	11.00	4.66	4.30	414.50	42.44	167.00	5.96	8.96	17.36	52.95
Galveston	1	7.37	128	6.50	3.99	5.80	280.20	26.71	0.00	4.71	9.57	14.22	52.84
Galveston	0	8.00	106	4.10	3.70	4.70	109.90	22.20	94.30	6.45	14.25	6.45	41.31
Galveston	1	7.77	85	2.20	3.26	1.80	145.20	12.34	98.40	2.81	12.83	6.71	56.27
Galveston	5	9.50	177	4.40	9.53	13.30	596.50	57.47	0.00	21.01	4.12	25.30	44.85
Galveston	3	7.01	130	6.60	3.82	10.70	413.90	38.28	0.00	6.19	12.41	17.61	49.89
Galveston	2	7.10	114	6.40	4.39	2.50	295.10	30.51	114.00	2.47	5.34	16.87	45.02
Galveston	3	8.23	103	6.04	3.24	4.09	445.77	39.43	503.30	5.80	10.89	3.26	56.21
Galveston	0	8.20	77	5.63	1.83	4.11	255.67	22.25	0.00	4.23	8.24	5.15	48.20

Galveston	4	7.63	60	4.41	2.82	9.03	346.71	30.27	72.20	4.13	9.40	3.42	51.72
Galveston	2	8.06	68	6.73	1.97	4.80	317.78	30.22	19.20	1.93	4.59	4.42	51.65
Galveston	1	8.22	61	3.87	3.50	5.33	232.52	20.85	41.00	2.11	4.78	5.24	52.89
Galveston	2	7.57	77	8.15	2.50	3.74	342.26	30.39	3.50	4.15	8.78	4.25	49.50
Galveston	2	8.44	101	4.83	2.42	1.83	176.02	18.67	27.40	6.21	13.43	5.71	47.12
Galveston	3	8.11	59	3.23	1.76	2.13	127.92	12.88	110.50	4.45	10.10	6.90	46.06
Galveston	2	7.56	62	2.78	1.58	1.18	152.01	15.93	113.80	3.82	10.93	6.52	42.43
Galveston	3	8.26	71	4.32	1.27	1.83	166.23	17.93	0.00	4.74	13.32	5.17	51.53
Galveston	2	8.33	93	3.95	1.72	4.69	194.72	21.99	119.90	9.52	22.42	5.37	44.10
Galveston	0	8.13	60	4.33	1.87	5.27	164.25	15.91	0.00	4.58	11.79	5.11	40.19
Galveston	3	8.26	63	2.75	1.73	2.25	141.63	13.60	51.10	3.24	8.07	7.74	38.70
Galveston	1	8.04	103	10.58	1.56	0.81	126.01	13.10	77.88	9.00	18.63	6.22	49.72
Galveston	1	7.57	62	1.65	0.42	1.17	109.47	10.96	49.88	3.96	9.41	9.27	43.81
Galveston	3	7.62	56	3.53	1.00	2.65	123.87	14.86	185.10	5.36	10.40	5.49	45.02
Galveston	0	8.45	97	0.78	0.60	1.63	124.34	11.42	44.40	20.73	33.51	7.04	48.38
Galveston	4	7.53	76	4.18	1.46	5.60	140.59	15.33	4.80	6.13	14.08	7.03	37.77
Galveston	4	8.28	78	4.98	1.42	1.94	107.26	12.65	137.60	3.49	13.08	4.66	49.46
Galveston	2	8.31	21	5.57	0.80	1.42	151.14	16.53	40.90	8.20	27.73	5.71	37.92
Galveston	0	8.30	129	1.17	0.66	1.56	114.10	8.74	384.50	47.58	53.62	10.96	43.94
Galveston	1	8.17	86	3.73	1.89	2.42	180.72	19.21	287.80	3.83	8.62	5.39	50.87
Galveston	0	7.55	56	3.08	0.80	1.55	102.92	12.08	82.90	3.20	12.13	4.66	47.76