THESIS

COMPARISON OF SOIL PROPERTIES AND KENTUCKY BLUEGRASS SHOOTS MINERAL COMPOSITION PRIOR TO AND AFTER10-11 YEARS IRRIGATION WITH RECYCLED WATER

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ABSTRACT

COMPARISON OF SOIL PROPERTIES AND KENTUCKY BLUEGRASS SHOOTS MINERAL COMPOSITION PRIOR TO AND AFTER 10-11 YEARS IRRIGATION WITH RECYCLED WATER

In Colorado, fresh water is one of the most valuable and limited natural resources. Due to population growth, an increase of fresh water withdrawal has been reported by U.S. Geological Survey. Irrigation with recycled water has been utilized as a means to alleviate the stress on potable water supplies and facilitate the reuse of treated wastewater. Recycled water irrigation is taking place at landscape sites such as public parks, golf courses, and school playgrounds. Research information is needed to better understand the long-term effects of recycled water irrigation on urban landscapes. Therefore, the objectives of this research were to: 1) assess changes in soil chemical properties after 5 and 11 years of recycled water irrigation, 2) determine if there is any heavy metal accumulation in soil after 11 years of recycled water irrigation, 3) evaluate Kentucky bluegrass (*Poa pratensis L.*) (KBG) turf quality grown on golf courses irrigated with recycled water, and 4) determine the relationship of turf quality to shoot mineral concentrations and soil chemical properties.

To address Objectives 1 and 2, soil samples were collected and analyzed at the commencement (in 2004) and 11 years after recycled water irrigation on three golf courses, 5 metropolitan parks, 1 school ground, and 1 zoo. Samples were taken at 0-20, 20-40, 40-60, 60-80, and 80-100 cm depths on golf courses and at 0-20 and 20-40 cm depths at other locations. Soil was analyzed for texture, soil pH, soil organic matter, soil salinity [soil electrical conductivity (EC)], exchangeable sodium percentage (ESP), cation exchange capacity (CEC), nitrate-N, chloride (Cl), boron (B), and AB-DTPA extracted phosphorus (P), iron (Fe), manganese (Mn), arsenic(As), chromium (Cr), cadmium (Cd), cobalt (Co), nickel (Ni), lead (Pb), zinc (Zn) and copper (Cu). Averaging over all sites, soil pH was 0.25-0.3 higher in 2015 and 2009 than in 2004. The increase was greater at deeper depths. Soil salinity (EC) was 0.84, 0.88, and 0.98 dS m^{-1}in 2004, 2009 and 2015, respectively. The magnitude of increase in ESP after recycled water irrigation indicated potential sodicity problems. Calcium based product applications reduced ESP at soil surface depths. In contrast, significant increase in ESP was found at deeper soil depths. No increase in soil nitrate-N was observed over 5 and 11 years with recycled water irrigation, therefore, leaching of nitrogen to the groundwater was not a great concern. AB-DTPA extracted As, Co, and Ni decreased after 11 years of recycled water irrigation. Soil Cd, Cr, Cu, Pb, and Zn did not show significant change from 2004 to 2015. Results revealed that there was no sign of heavy metal accumulation.

To address Objectives 3 and 4, research was conducted on eight golf courses, including three courses in Denver after 10 years of recycled water irrigation, three courses in the nearby cities receiving recycled water for more than 10 years, and two courses receiving fresh surface water for irrigation. Results indicated that Na concentration in KBG shoot tissues increased by 4.3-9.9 times, Cl by 1.5-1.3 times, B by 1.3-3.5 times whereas K/Na ratio was reduced by 74-90%. Multiple regression analysis indicated shoot Na accumulation had the highest association to turf quality decline (R^2= 0.65). Soil sodium adsorption ratio (SAR) in 0-20 cm depth was highly associated with KBG shoot Na concentration (R^2= 0.70).

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CHAPTER 1: COMPARISON OF SOIL CHEMICAL PROPERTIES PRIOR TO AND 5-11 YEARS AFTER RECYCLED WATER IRRIGATION

SUMMARY

Increasing demand on fresh water supplies in the arid and semi-arid western US and more stringent wastewater discharge standards have made recycled water a common water source for irrigating golf courses and urban landscapes. This has created the need to study the effects of recycled water irrigation on soil chemical properties. We collected and analyzed soil samples at the commencement (in 2004) and 5 and 11 years after recycled water irrigation on three golf courses, 5 metropolitan parks, 1 school ground, and 1 zoo. Samples were taken at 0-20, 20-40, 40-60, 60-80, and 80-100 cm depths on golf courses and at 0-20 and 20-40 cm depths at other locations. Soil samples were tested for soil texture, soil pH, soil organic matter, soil salinity [soil electrical conductivity (EC)], exchangeable sodium percentage (ESP), Cl and B concentration, and AB-DTPA extracted P, K, Zn, Fe, Mn, and Cu. Nitrate-N was determined using flow-injection Cd reduction analysis. Average soil EC was 0.84, 0.88, and 0.98 dS m^{-1} in 2004, 2009, and 2015, respectively. On average, soil pH was 0.25-0.3 units higher in 2009 and 2015 when compared to 2004. The degree of soil pH increase was greater at deeper than at shallower soil depths. Samples collected in 2004, 2009, and 2015 had an average ESP of 2.65%, 5.35%, and 4.43%, respectively. The increase in ESP suggested that sodicity was of greater concern than salinity when recycled water is used for irrigation. Gypsum application after aerification displaced sodium and reduced ESP at the surface depth (0-20 cm). However, soil ESP increased significantly at deeper soil depths. No increase in soil nitrate-N was observed over 5 and 11 years with recycled water irrigation. Therefore, leaching of nitrogen to the groundwater was not a great concern.

INTRODUCTION

Water is essential for human beings. However, the World Resources Institute (2015) predicted that due to uneven distribution of rainfall, increasing population growth and urbanization, at least 3.5 billion people on earth will face water inseccurity by 2025.

In order to manage finite water sources, western states of the USA have long implemented reuse programs for municipal wastewater. The strategy behind that is to reclaim the increased volume of wastewater due to the population boom, and furthermore to balance the potable water demand.

California began water recycling in 1910, with annual reuse of 826 million cubic meters recorded by California Department of Water Resources in 2013. Sixty percent of the recycled water used for urban and agricultural irrigation, and the rest was for geothermal energy production, groundwater recharge and industrial usage (Ambroselli, 2010). Currently, more than 250 water recycling plants are in operation. Similarly, the Arizona Department of Water Resources reported 320 million cubic meters recycled water reused in 2014 (Arizona Department of Water Resources 2014). Thirty-three million cubic meters of recycled water was used in southern Nevada for golf courses, green belts and median irrigation, cooling water for power plants and dust control (Southern Nevada Water Authority, 2009).

Situated in the front range of Colorado, Denver is geographically classified as a semi-arid climate with average annual precipitation of 391mm (Western Regional Climate Center, 2016). Rainfall throughout the year is concentrated in March to October. Colorado is a fast growing state and population has increased by 65% during the past 25 years (U.S. Census Bureau, 2015). Since anticipating population growth over the next 50 years, recycled water utilization is deemed to be an effective solution to mitigate limited water resources. In Colorado, water conservation through the use of recycled wastewater has been practiced since the 1960’s at several landscape sites. Qian (2006) reported that there were 10 major wastewater treatment facilities in Colorado with an annual treatment capacity of 90 million cubic meters in 2006.

Denver Water is the primary water authority serving 1.1 million customers (Denver Water, 2013). Before 2004 when the new recycled water treatment plant became operational, a large volume of the effluent water processed with secondary treatments in the Metro Wastewater Reclamation District's treatment plant discharged directly into the South Platte River. Even though the majority of suspended solids were removed, high levels of nutrients (N and P) were found in the river basin (Litke, 1996). From 1994 to 1997, Denver Water launched the Integrated Resource Planning study, planned for construction design of the Denver Water Recycling Plant (DWRP) and the Phase One Recycled Water Distribution System. In 2004, DWRP became operational. The effluent from Metro Wastewater Reclamation District's Robert W. Hite treatment facility was transported to DWRP for further treatments including biological aerated filtration, ferric phosphate coagulation and chlorination. The recycled water distribution system began operation in the spring of 2004. Our study area covers parks, school grounds and golf courses in the Phase One Recycled Water Distribution System.

Water reuse for irrigation in urban landscapes is a powerful means of water conservation, water reclamation, and nutrient recycling. Due to their dense plant canopy and active root systems, turfgrass landscapes are increasingly viewed as environmentally desirable disposal sites for recycled water. In fact, dense, well-managed turfgrass areas are among the best bio-filtration systems available for removal of excess nutrients and further reclamation of treated wastewater. While the conservation benefits of wastewater reuse in landscape and turfgrass irrigation are clear, concerns associated with wastewater reuse may include potential salt accumulation in the soil profile and potential contamination of ground water caused by leaching of excess nutrients.

Landscape and golf course soils receiving recycled water irrigation in Tucson, AZ were found to have higher EC. Seven urban landscape sites irrigated with recycled water over 5 or more years had average soil salinity of 3.2 dS m^{-1} at 0-40 cm soil depth. The EC value was 70% higher than nearby soils irrigated with potable water (Schuch et al., 2008). After transitioning to recycled water irrigation for 1.5 to 3.7 years, 3.97 dS m^{-1}mean EC was recorded in golf Course fairways in Las Vegas, NV. Soil salinity was 27% -32% higher than soils irrigated with fresh water (Lockett et al., 2008).

There is limited information available in Colorado concerning effects of irrigation with recycled water on soil salinity, soil exchange sodium percentage (ESP), soil pH, and nitrate and phosphorus leaching potential (Qian and Mecham, 2005). Research is needed to examine the impact of long-term recycled water irrigation on soil chemical properties in cool, arid and semi-arid regions. In this study, we 1) assess changes in soil chemical properties after 5 and 11 years of recycled water irrigation on many landscape facilities by collecting and analyzing soils at the start of using recycled water for irrigation and after 5 and 11 years of recycled water irrigation, 2) determine whether the use of recycled water over time has an effect on the nitrate and phosphorus levels in the soil, and 3) determine the primary effect of one particular management regime (gypsum application following aerification) on soil ESP along the soil profiles.

MATERIALS AND METHODS

Site Description

Our research sites have received recycled water irrigation from the DWRP since 2004. Facilities included in this study were: Swansea Park, Dunham Park, Schaefer Park, Bruce Randolph School, City Park, Washington Park, Park Hill Golf Course, City Park Golf Course, Denver Zoo and the Denver Country Club. In 2004, soil baseline information was collected form these sites. In 2009, five years after the initiation of recycled water for irrigation, we collected and tested soils again from the original sites. In 2015, 11 years after the start of recycled water irrigation of these sites, we sampled those sites again.

Sampling Procedures

From July to September in 2004 (at the commencement of recycled water irrigation), 2009 (5 years after recycled water irrigation), and 2015 (11 years after recycled water irrigation) soil from aforementioned locations were sampled. At each location, 3-6 sites were randomly selected for sampling. At each sample site, three cores were collected using a hand-held boring tool. At parks, Bruce Randolph School, and Denver Zoo, samples were taken at 0-20 and 20-40 cm depths; at golf courses, samples were taken at 0-20, 20-40, 40-60, 60-80, 80-100 cm depths. Three cores at each site and depth were combined. Metal rods were buried at each sampling site in 2004 as a location reference. In 2009 and 2015, soil samples were collected 30 cm away from the 2004 original sampling points. Established turfgrass was grown where soil sampling was conducted. In the parks, school playgrounds, public zoos and golf courses, management practices vary depending on maintenance staff.

Soil Analysis

All soil samples were allowed to air dry, and were then ground and screened to pass through a 10-mesh (2mm) sieve. Soil samples were tested at the Soil, Water, and Plant Testing Laboratory at CSU. Each soil sample was tested for soil organic matter (OM%), soil electrical conductivity (EC), soil texture estimation, soil pH, exchangeable sodium percentage (ESP), sodium adsorption ratio (SAR), soil NO_3-N, soil P, soil B, Cl, Na, Ca, Mg, K, Zn, Fe, Mn, and Cu.

Soil pH and EC were analyzed using a saturated paste extract. Deionized water was added to ground and sieved soil and mixed uniformly until a saturated paste was obtained. The EC value was measured using an electrical conductivity meter. The saturated paste extracts were transferred to auto-sampler tubes and analyzed for Ca, Mg, K and Na concentrations by using an inductively coupled plasma spectrophotometer (ICP-AES).

Ammonium-bicarbonate-DTPA solution was added to soil samples to analyze exchangeable Ca, Mg, K,Na, Fe, Mn, Cu and Zn from ICP-AES. Phosphorus (P) concentration was measured by colorimeter after adding ammonium-bicarbonate-DTPA extractant and ascorbic acid into the soil samples. Nitrate- nitrogen was determined by flow-injection Cd reduction analysis. The Walkley Black test for organic matter uses potassium dichromate ($K_2Cr_2O_7$) as the oxidizer and ferrous sulfate ($FeSO_4.7H_2O$) to titrate dichromate solution. The organic matter (OM %) is calculated by the difference between the total volume of dichromate injected and the titration volume after reaction. B and Cl were determined by the procedure of adding 80ºC hot water filtering, and then analyzing the extract with an ion chromatograph. Soil Na, Ca and Mg concentrations in saturated paste extract were using to determine sodium adsorption ratio (SAR) by the following this equation: $SAR= Na/ [(Ca+Mg)/2]^{1/2}$. Cation Exchange Capacity was measured using the NH_4OA_C method at buffered pH 7. Exchangeable Na concentration was measured by ICP in soil ammonium acetate extracts. Exchangeable sodium percentage was calculated as soil exchangeable Na divided by CEC: ESP= Na/CEC*100%.

Statistical Analysis

Data were subjected to analysis of variance (ANOVA), and significant differences in soil properties prior to, five, and eleven years after recycled water irrigation began were determined by using the general linear model (PROC GLM) procedure using SAS 9.3 (2011). Least significant difference test (LSD) was set at $P \leq 0.05$. PROC Mixed model was used where year, location, depth and their interaction were treated as fixed effects, and the replications (sites) within 10 locations was treated as a random effect.

RESULTS AND DISCUSSION

Water Quality

All locations in this study were irrigated with ditch water, potable water, or well water prior to recycled water irrigation in 2004. The average water quality values of recycled water and potable water provided by Denver Water are presented in Table 1-1.

Soil pH

Soil pH measures the hydrogen ion concentration in soil. Despite the fact that the average pH of recycled water leaving the recycling plant is 7.16 (Table 1-1), on average, soil pH was 0.25-0.3 units higher in 2015 and 2009 when compared to 2004 (Table 1-2). Results from 10 facilities indicated that soil pH increased from 2004 to 2015 for all sites except the Denver Zoo (Table 1-3). The level of pH increase is consistent with previous findings (Qian and Mecham, 2005). Mancino and Pepper (1992) found that irrigation with recycled water for two years increased soil pH by 0.2 units when compared to potable water irrigation. Moreover, the results showed that along the 100 cm soil profile, the degree of soil pH increase was greater at deeper depths than at shallow soil depths at 3 golf courses where soils were sampled to 100cm deep (Fig. 1-1).

The soil pH increase may be partially due to the bicarbonate concentration (92 mg L^{-1}) in recycled water. At many of the facilities, recycled water is stored in irrigation ponds. During the storage, algae activity may increase water pH due the absorption of CO_2. Soil pH measuring 6.1 to 7.0 is considered ideal for most trees and shrubs, although various species will survive in a range from 5.5 to 8.0+. A main implication of increasing soil pH is plant nutrient availability. The availability of certain nutrients in soil solution begins to decrease above pH ~6.5 (Fe, Mn, and Zn), above ~7.0 (P and B), and above 8.5 (Ca^{2+} and Mg^{2+}). Different plants respond differently to high soil pH. Consistent high soil pH often causes Fe and/or Mn deficiencies in sensitive landscape plants, resulting in yellowing of leaves (chlorosis), although the critical pH levels that result in leaf chlorosis are variable among plants.

It is possible to amend soil and water with acidifying products including ammonium sulfate and other sulfur-containing products to prevent significant soil pH increase under recycled water irrigation. However, it is often necessary to re-apply these substances in order to sustain the effect. In addition, it is difficult to prevent soil pH from increasing in the deeper soil profile.

Electrical Conductivity (EC)

Electrical conductivity of the saturated soil paste extract is the most reliable indicator of soil salinity level. In general, EC of soil higher than 4.0 dS m^{-1} is considered saline soil. However, salt sensitive plants may be injured below this value, and salt tolerant plants may tolerate EC levels higher than 4 dS m^{-1}. When data from all facilities were pooled, the average soil salinity was 0.84, 0.88, and 0.98 dS m^{-1} in 2004, 2009, and 2015, respectively (Table 1-2).

All but one sample collected from the 10 sites in 2009 and 2015 had soil salinity less than 4 dS m^{-1}. Five facilities, including Bruce Randolph School, City Park, City Park Golf Course, Denver Country Club, and Denver Zoo showed a trend of increasing soil salinity from 2004 to 2015 (Table 1-4). No clear trend of increasing soil salinity under recycled water irrigation was observed from 2004 to 2015 at Swansea Park, Dunham Park, Schaefer Park, and Park Hill Golf Course (Table 1-4). According to Qian and Mecham (2005), and Skiles and Qian (2013), soil on golf course fairways irrigated with recycled water in another region of Denver also recorded EC increases after 4, 5 and 9 years.

Exchangeable Sodium Percentage (ESP)

ESP is an indicator of sodium hazard for soil (sodicity). An ESP value of 12% or greater indicates a sodic soil with excessive sodium. However, for finely textured soils and heavily traffic areas, an ESP> 6-9 will start to impose sodic effects. Soil with 2:1 clays are much more prone to sodicity effects on soil structural deterioration than 1:1 clays.

All samples collected in 2004, 2009, and 2015 had an average ESP of 2.65%, 5.35%, and 4.43%, respectively (Table 1-2). All facilities showed significant increases in ESP after five years of irrigation with recycled water (Table 1-5). Bruce Randolph Middle School, City Park Golf Course, and Washington Park exhibited linear increases in ESP over time ($P < 0.05$; $R^2 = 0.90$, 0.78 and 0.90, respectively).

At the parks, soils were sampled for 2 depths (0-20 and 20-40 cm); at the golf courses, soil sampling to 100cm allowed for a more comprehensive soil profile examination. The site description and management records were beneficial for evaluating the ESP patterns in each location. Supervisors in the parks utilized little or no pactices to deal with soil sodicity. However, golf courses conducted heavy aerification, gypsum application and soluble Ca injection into the irrigation water.

At the Denver County Club, the increase in ESP from 2004 to 2009 and 2015 at surface 0-20 cm depth was not statistically significant (Fig. 1-3). However, the increase became significant from 20-40cm, 40-60 cm, 60-80 cm, and 80-100 cm. The changes along the soil profile reflect soil types, environmental conditions, and management that are conducive to Na leaching from the surface layer at this golf course. The course was built on alluvial sand deposits developed in association with Cherry Creek. Soils at this golf course are mostly sandy and drain very well, and turf managers have employed aggressive aeration and gypsum addition programs. They generally aerate 1-2 times a year for fairways and apply about 30 lb/1000 sq ft/year gypsum following aerification. Additional gypsum is also injected into irrigation water through a "Diamond K" injection system. Apparently, the aggressive soil aerification and gypsum addition plus the dominant presence of sandy soil effectively prevented a significant increase in soil ESP at the shallow soil depths (0-20 cm). This layer of soil (0-20 cm) is important for turfgrass since most of the turf grass roots are present in this layer. Good permeability and drainage allow for leaching of excessive Na from the root zone by periodic gypsum treatment followed by leaching. Fine textured soils are slow to infiltrate, percolate and difficult to leach. To mitigate some of the negative issues associated with high Na in recycled water, the installation of drainage tiles in predominantly fine-textured soils would aid the drainage effectiveness.

From 2004 to 2015, City Park Golf Course exhibited a linear increase in ESP over time R^2= 0.90 (Fig. 1-3). This golf course has fine textured soil (clay loam to clay). The ability of the soil to retain cations is much higher for fine-textured soils compared to sandy soils. As a result, ESP in fine-textured soil increased slowly at deeper depths; it took longer than five years to exhibit significant ESP increase at the deepest sampling depth (80-100 cm). City Park Golf Course is a public course. Aggressive Ca topdressing programs were not financially feasible, and no gypsum treatment to soil was done over the experiment period. The relatively high levels of Na concentration relative to Ca and Mg in recycled water along with the fine textured soil and the lack of Ca addition resulted in increased soil ESP, especially at the shallow soil depths (Fig. 1-3).

Park Hill Golf Course was previously irrigated with well water with average EC and sodium absorption ratio (SAR) values of 1.17 dS m^{-1} and 2.44%, respectively. The average soil ESP level before recycled water irrigation began was 5.2% (Fig. 1-3). Five and eleven years of irrigation with recycled water did not result in significant changes in soil ESP, with ESP of 5.46 and 4.47 in 2009 and 2015, respectively (Table 1-2). The landscape management program at this golf course includes an aggressive soil aeration program and regular application of acid and Ca products through the irrigation system. The loamy sand and sandy loam soil texture at this golf course may also have helped to prevent the increase of soil ESP from 2004 to 2015. Yet, due to the historic long-term exposure to poor quality well water which had high sodium concentration, high bicarbonate concentration, and high electrical conductivity (EC) for irrigation, salt injury on many conifer trees and some stress in turfgrasses were observed.

Our results indicated that with no or minimal management (aggressive aerification and Ca additions) such as at Bruce Randolph School, City Park Golf Course, and Washington Park, ESP increased linearly over time. With aggressive aerification and Ca addition, the ESP increase became apparent at deeper soil depths although ESP in surface soil could be managed. These results suggest that sodicity (as gauged by soil ESP) is a concern on the reuse sites, since ESP exhibited the most significant changes from 2004 to 2015 on many study sites. Soil and/or water amendments with Ca or sometimes Mg based products may help to displace sodium and reduce ESP and SAR, especially at the surface depth. These treatments may be more effective in sandy soil than in clay soil. Further increases of ESP could potentially cause long-term reductions in soil hydraulic conductivity, especially in deep soil profiles with higher percentage of clay content. More research is needed to develop low cost, pre-irrigation water treatment strategies and specific landscape management techniques to decrease sodicity.

Gypsum application is commonly recommended not only for landscapes irrigated with recycled water but also for agricultural soils in Australia and the Middle East with sodic soils (Naidu and Rengasmy, 1993; Ilyas et al., 1997; Qadir et al., 2005).

Several publications have also stated that soil SAR is correlated with ESP (Qadir and Schubert, 2002; Chi et al., 2011; U.S.Dept. of Agriculture, 1954). In our study the SAR values in every location, year (2004, 2009 and 2015) and depths corresponded with ESP measurements as shown by a simple regression R^2=0.95 (Fig. 1-4).

Cations (exchangeable sodium and potassium)

When all data were pooled, soils in 2009 and 2015 exhibited 66% and 42% higher concentration of exchangeable Na than soils sampled in 2004, respectively (Table 1-2). The high Na concentration reflected Na addition via irrigation with recycled water; the average Na concentration in the recycled water was 120 mg L^{-1} compared to 21 mg L^{-1} in potable water (Table 1-1). Soil Na increased either in 2009, 2015 or both years; Park Hill Golf Course was the only location where Na decreased both in 2009 and 2015. Although no consistent trend was observed across experimental facilities for K, a 10% and 20% higher concentration of AB-DTPA-extractable potassium was observed for 2009 and 2015 soil samples when compared to the 2004 baseline (Table 1-2). The increase in soil K is desirable for turf grasses. The higher K might be a result of the combination of potassium present in recycled water (13mg L^{-1}) and the application of K fertilizers.

Soil Nitrate-Nitrogen and Phosphorus (P)

There are concerns that the nutrients in recycled water can make their way into ground or surface water supplies when recycled water is used for landscape irrigation. Specific concerns are that nitrate will move through the soil profile and cause ground water contamination, and that phosphorus will run off into surface waters. As discussed earlier, the deeper soil sampling procedures at golf courses provided opportunities to examine nitrate and phosphorous movement in the soil profiles. Nitrate–nitrogen concentration decreased with soil depth. ANOVA results indicated mean nitrate concentration at 0-20 cm depth (7.88 mg kg^{-1}) was significantly higher than deeper depths in the range of 1.98 to 3.68 mg kg^{-1} ($P < 0.05$). The evidence suggests that the turf grass root system was very effective in nitrate uptake (Fig. 1-5). Nitrate–N was lowest in 2015 when compared to 2004 and 2009. Nitrate–N dropped below 2 mg kg^{-1} beyond the turfgrass rootzone in 2015, well below the EPA standard for potable water quality (10 mg kg^{-1}). This indicates that nitrate contamination of groundwater should not be a great concern when using recycled water for the irrigation of turf systems. Dense, actively growing, and well-managed turf grass areas are among the best bio-filtration systems available for removal of excess nitrate.

When all data were pooled for analysis, soil P was higher in 2015 than 2009 (Table 1-2). When data from individual locations were analyzed separately, Bruce Randoph School, Schaefer Park, Denver Zoo, and City Park Golf Course (0-20 cm soil depth) had higher soil P under recycled water reuse (Table 1-7), whereas other sites showed no increase in soil P over 11 years with recycled water irrigation (Table 1-7). Phosphorus levels were, in general, lower at depths deeper than 20 cm (Figure 1-6); this is because phosphorus is considered immobile (Bray, 1954). However, movement of phosphorus through the soil structure is possible in sandy soils.

Recycled water contains macro-nutrients [nitrogen (N), phosphorus (P), and potassium (K)] essential for plant growth, which can contribute significantly to a fertilization program. When compared to agricultural sites, a properly managed turf grass site would have less problem with nitrate leaching down into groundwater, or phosphorus running off to surface waters if best management practices are utilized, including fertilizing in several smaller applications instead of one large dosage.

Boron and Chloride

The criteria for B concentration in soils are as follows: sensitive plants (such as some fruit trees) show growth decline as soil B exceeds 0.5-1.0 mg kg^{-1}. Moderately sensitive plants will start to decline when soil boron exceeds 1.0-2.0 mg kg^{-1}. Kentucky bluegrass can tolerate soil B concentration at 2.0-4.0 mg kg^{-1}. The recycled water from Denver Water's recycling system contains about 0.27 mg L^{-1} boron. All soil samples collected from the 10 sites in 2015 had an average soil B concentration of 1.4 mg kg^{-1} and the range of B was from 0.35 to 3.86 mg kg^{-1} (Table 1-2). This average level of soil B concentration was higher compared to what was measured in 2004 (0.67 mg kg^{-1}).

Recycled water typically contains about 50-200 mg L^{-1} chloride. Chloride is a negatively charged ion and cannot be held by the soil CEC sites. Therefore, Cl is highly mobile in soil, and will often move with the wetting front during infiltration and percolation. In addition to contributing to the total soluble salt concentration of irrigation water, Cl may have direct ion effects on plants when absorbed by roots and leaves, especially some trees and shrubs. Despite the fact that recycled water contains higher Cl levels than potable water, no significant increases in soil Cl concentration were observed from 2004 to 2015. In fact, when data from all samples were combined, an average soil Cl level was 17.6 mg kg^{-1} in 2009 which was lower than the Cl level in 2004 (Table 1-2). This is likely due to the great amount of precipitation (217 mm) that occurred during June to July in 2015 (Colorado Climate Center, 2015).

Iron, Manganese, Copper and Zinc

Results of analysis of variance test (ANOVA) on soil Fe, Mn, Cu and Zn concentrations indicated there was no increasing trend. Soil Mn level was lower in 2009 and 2015 than in 2004 for all study locations (Table 1-2). Soil micro-nutrient (Fe^{3+}, Fe^{2+} and Mn^{2+}) availability declined in an Australian sodic soil simultaneously with increasing soil pH (Naidu and Rengasmy, 1993).

CONCLUSIONS

This study of 11 years of recycled water irrigation on Denver landscapes found that soil salinity, pH and ESP increased. Compared to baseline data, soil salinity (EC) increased 17%, pH increased 0.2-0.3 units, ESP increased most significantly after 5 years of recycled water irrigation. Soil nitrate and phosphorus remained mostly in the topsoil. Changes in soil Cl were not observed, but a slight B accumulation was observed in 2015. Cultural practices including aerification and gypsum application, can reduce the sodicity hazard in surface soil (0-20 cm). Salinity should be monitored on a regular basis in soils irrigated with recycled water.

Table 1-1. Average water quality values of recycled water vs. potable water provided by Denver Water.

Water parameter	Recycled water	Potable water
pH	7.16	-
NH_4-N (mg L^{-1})	0.25	-
NO_3-N (mg L^{-1})	11.8	0.1
Total P	0.15	-
Total dissolved solids (mg L^{-1})	-	187
Electrical conductivity (EC) (dS m^{-1})	0.86	0.23
Ca (mg L^{-1})	50	-
Mg (mg L^{-1})	12	-
Na (mg L^{-1})	121	21
Cl (mg L^{-1})	106	29
Bicarbonate (mg L^{-1})	92	-
Sulfate (mg L^{-1})	142	56
Boron (mg L^{-1})	0.27	-
K (mg L^{-1})	13	-
Fe (mg L^{-1})	0.22	-
Sodium adsorption ratio (SAR)	1.7	-

Table 1-2. Mean soil chemical properties from the ten landscape facilities at the initial (baseline) and 5 and11 years after recycled water irrigation (soils were sampled to 1 m at golf courses and 0.4 m at parks).

Soil Parameter	Baseline	5 years after	11 years after
Cation Exchange Capacity (meg/100g)	20.77a	18.51a	14.36b
pH	7.26b	7.55a	7.5a
SOM (%)	2	2	2
Electrical conductivity (EC, dS m^{-1})	0.84b	0.88ab	0.98a
Ca (meq/L)	3	3.1	3.4
Mg (meq/L)	1.34b	0.94c	1.78a
Na (meq/L)	4.35b	5.1b	9.85a
K (meq/L)	0.58c	0.86b	1.08a
Mn (mg kg^{-1})	2.3a	1.4b	1.8b
Cu (mg kg^{-1})	4.4	4	3.6
Zn (mg kg^{-1})	13.9	13	13.5
Fe (mg kg^{-1})	22.8	24.3	27.2
Extractable P (mg kg^{-1})	13.7ab	11.9b	15.5a
NO3-N(mg kg^{-1})	6.2a	6.2a	2.5b
Boron (mg kg^{-1})	0.67b	0.51b	1.4a
Cl (mg kg^{-1})	27.68a	24.6a	17.6b
Exchangable sodium percentage (ESP)	2.65c	5.35a	4.43b
Sodium adsorption ratio (SAR)	2.8c	5.32a	3.64b

The mean followed by a letter “a” is significantly higher than the mean followed by a letter “b” for individual parameters at $P \leq 0.05$.

Table 1-3. Results of soil pH at depth 0-20 cm and 20-40 cm for assessment over three different years (2004, 2009 and 2015) at 10 landscape locations in Denver.

Year	BRS.	City Park	Denver Zoo	Dunham park	Schaefer Park	Swansea Park	Washington Park	Denver Country Club	City Park GC	Park Hill GC
0-20 cm										
2004	7.57b	6.9b	7.7b	6.5b	6.8c	6.7b	6.8b	7.1a	7.1b	7.7a
2009	7.83a	7.2a	7.9a	7.0a	7.3a	7.0a	7.0a	6.8b	7.2a	7.6b
2015	7.93a	7.3a	7.7b	6.8a	6.9b	6.8a	6.9a	7.1a	7.2a	7.3c
20-40 cm										
2004	7.6b	7.1b	7.9b	6.7b	7.1c	6.6b	N.A.	7.3b	7.3b	8.0a
2009	8.0a	7.5a	8.1a	7.1a	7.6a	7.2a	N.A.	7.4a	7.6a	8.0a
2015	7.9a	7.5a	N.A.	7.4a	7.3b	7.3a	N.A.	7.5a	7.5a	7.8b
P value										
Depth 1× 2	0.66^{ns}	0.07^{ns}	0.08^{ns}	0.002	0.0009	0.018	N.A.	<0.0001	0.005	0.0002

*BRS.= Bruce Randolph School; depth1= 0-20cm, depth 2 = 20-40 cm. Within an individual location, each depth with different letters a,b,c are significantly different at $P \leq 0.05$, ns= non-significant.

Table 1-4. Results of soil EC at depth 0-20 cm and 20-40 cm for assessment over three different years (2004, 2009 and 2015) at 10 landscape locations in Denver.

Year	BRS.	City park	Denver Zoo	Dunham park	Schaefer Park	Swansea Park	Washington Park	Denver Country Club	City Park GC	Park Hill GC
0-20 cm										
2004	1.2b	0.7b	0.5b	0.6b	0.8b	0.8a	0.7c	1.2b	1.1a	0.9b
2009	0.8b	0.9a	1.0a	1.0a	1.0a	1.0a	1.0a	1.1b	1.2a	1.3a
2015	1.9a	1.2a	1.0a	0.8b	0.9a	0.9a	0.8b	1.6a	1.1a	0.9b
20-40 cm										
2004	1.2b	0.6b	0.6b	0.5c	0.9b	0.8a	N.A.	0.9c	0.8b	0.7b
009	0.5c	1.0a	0.8a	0.9a	1.1a	0.8a	N.A.	1.2b	1.1a	0.8a
2015	2.4a	1.2a	N.A.	0.6b	0.6c	0.6b	N.A.	1.4a	1.2a	0.6b
P value										
Depth 1× 2	0.83 ^{ns}	0.51 ^{ns}	0.87 ^{ns}	0.44 ^{ns}	0.89 ^{ns}	0.81 ^{ns}	N.A.	0.03	0.03	0.03

*BRS.= Bruce Randolph School; depth1= 0-20cm, depth 2 = 20-40 cm. Within an individual location, each depth with different letters a,b,c are significantly different at $P \leq 0.05$, ns= non-significant. All units in two depths are dS m^{-1}.

Table 1-5. Results of soil ESP at depth 0-20 cm and 20-40 cm for assessment over three different years (2004, 2009 and 2015) at 10 landscape locations in Denver.

				0-20 cm						
Year	BRS.	City Park	Denver Zoo	Dunham park	Schaefer Park	Swansea Park	Washington Park	Denver Country Club	City Park GC	Park Hill GC
2004	2.93c	2.60b	1.23b	3.53b	2.57b	3.13b	2.16c	3.24 b	2.23b	3.30b
2009	3.97b	4.55a	3.60a	6.40a	6.07a	6.20a	3.87b	4.13a	6.16a	4.13a
2015	5.73a	2.92b	2.07b	2.30b	2.67b	2.60b	5.85a	3.28b	6.13a	2.20b
				20-40 cm						
2004	1.8c	2.03b	1.53b	2.60b	1.73b	2.63b	N.A.	2.80b	1.57b	4.30b
2009	4.83b	5.08a	5.07a	9.40a	6.83a	9.53a	N.A.	4.83a	6.25a	5.27a
2015	6.73a	4.18a	N.A.	4.37b	4.70b	4.60b	N.A.	5.05a	6.30a	3.50b
				P value						
Depth 1× 2	0.63^{ns}	0.23^{ns}	0.16^{ns}	0.007	0.20^{ns}	0.001	N.A.	0.05	0.006	0.007

*BRS.= Bruce Randolph School; depth1= 0-20cm, depth 2 = 20-40 cm. Within an individual location, each depth with different letters a,b,c are significantly different at $P \leq 0.05$, ns= non-significant.

Table 1-6. Results of soil NO_3 at depth 0-20 cm and 20-40 cm for assessment over three different years (2004, 2009 and 2015) at 10 landscape locations in Denver.

Year	BRS.	City Park	Denver Zoo	Dunham park	Schaefer Park	Swansea Park	Washington Park	Denver Country Club	City Park GC	Park Hill GC
0-20 cm										
2004	1.7b	7.7a	3.3b	8.8a	13.0a	10.0a	6.9a	20.6a	12.9a	15b
2009	13.7a	9.5a	7.3a	2.4b	4.3b	5.63b	6.5a	15.2b	7.8b	30.9a
2015	3.3b	3.2b	8.1a	2.2b	3.5b	2.83c	5.1a	5.6c	5.0c	3.7c
20-40 cm										
2004	1.3b	3.2b	1.4b	2.3a	4.3a	2.9a	N.A.	9.5a	3.0a	4.0b
2009	11.6a	7.8a	5.8a	2.1a	1.9b	1.5b	N.A.	4.9b	2.8a	6.3a
2015	1.7b	2.0c	N.A.	1.7a	1.7b	1.7b	N.A.	3.1c	2.8a	1.5c
P value										
Depth 1× 2	0.55 ^{ns}	0.14 ^{ns}	0.53 ^{ns}	0.27 ^{ns}	0.056 ^{ns}	0.067 ^{ns}	N.A.	0.001	0.0078	0.001

*BRS.= Bruce Randolph School; depth1= 0-20cm, depth 2 = 20-40 cm. Within an individual location, each depth with different letters a,b,c are significantly different at $P \leq 0.05$, ns= non-significant. All units in two depths are mg kg^{-1}.

Table 1-7. Results of soil P (AB-DTPA extracted) at soil depth 0-20 cm and 20-40 cm for assessment over three different years (2004, 2009 and 2015) at 10 landscape locations in Denver.

				0-20 cm						
Year	BRS.	City Park	Denver Zoo	Dunham park	Schaefer Park	Swansea Park	Washington Park	Denver Country Club	City Park GC	Park Hill GC
2004	50.9b	6.5b	15.6c	18.7a	23.9b	15.2a	22.9a	20.6a	14.5b	17.0a
2009	26.2c	6.2b	16.8b	21.4a	34.9a	19.7a	14.6b	18.4b	15.6b	13.9b
2015	74.2a	15.9a	32.5a	17.6a	35.2a	17.6a	14.6b	19.0b	29.4a	15.5b
				20-40 cm						
2004	9.7c	3.4a	28.6a	12.0a	11.6b	9.9b	N.A.	9.7a	6.7b	15.2a
2009	12.8b	3.5a	15.4b	15.7a	17.0a	14.8a	N.A.	7.9b	6.9b	9.1b
2015	17.9a	6.3a	N.A.	15.6a	20.7a	15.3a	N.A.	10.1a	9.6a	11.8b
				P value						
Depth 1× 2	0.02	0.23 ^{ns}	0.04	0.007	0.03	. 0.001	N.A.	0.05	0.006	0.007

*BRS.= Bruce Randolph School; depth1= 0-20cm, depth 2 = 20-40 cm. Within an individual location, each depth with different letters a,b,c are significantly different at $P \leq 0.05$, ns= non-significant. All units in two depths are mg kg^{-1}.

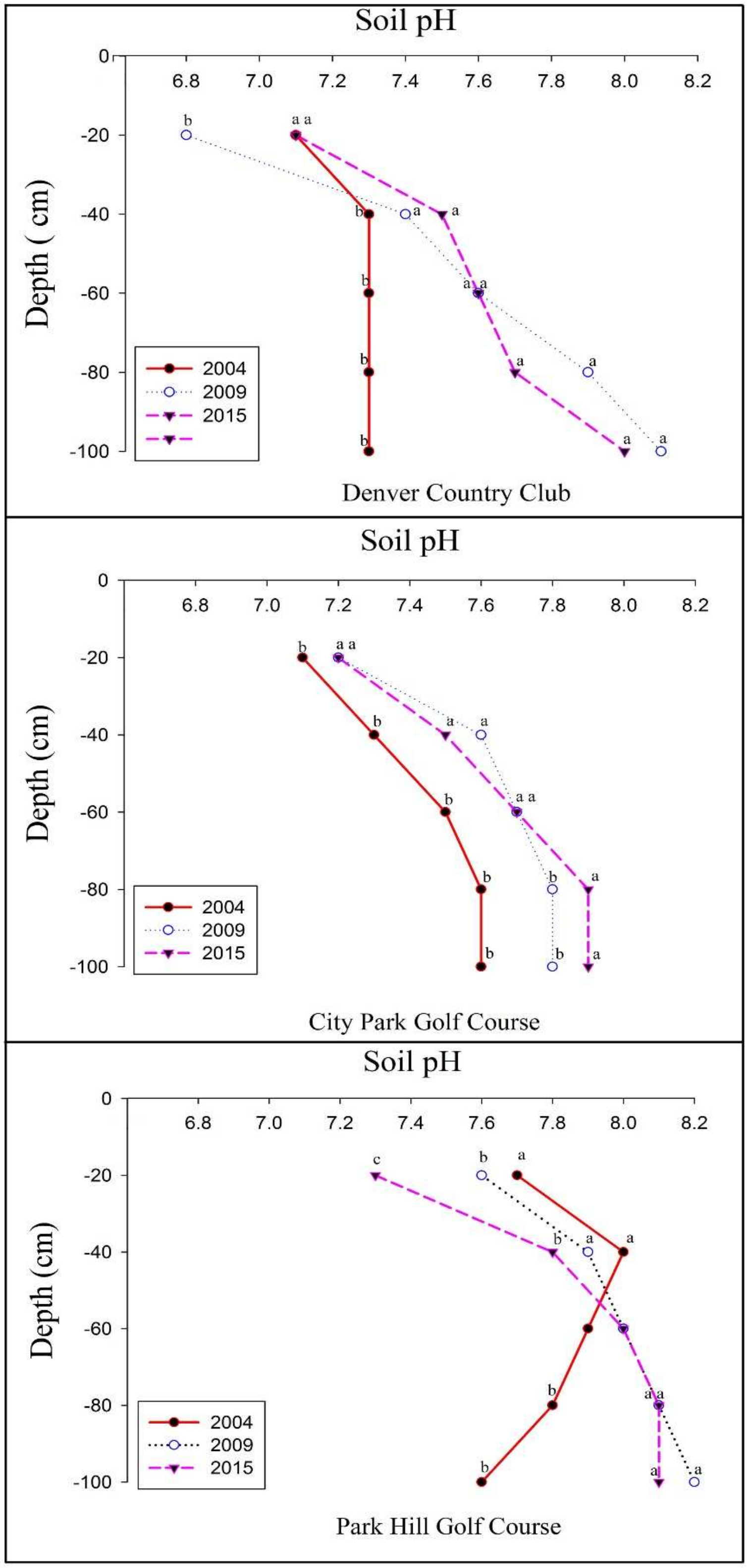

Figure 1-1. Soil pH of 2004, 2009 and 2015 at Denver Country Club, City Park Golf Course and Park Hill Golf Course. Letters indicate significant difference ($P \leq 0.05$) among years at each depth, no letters shown indicate not statistically significant.

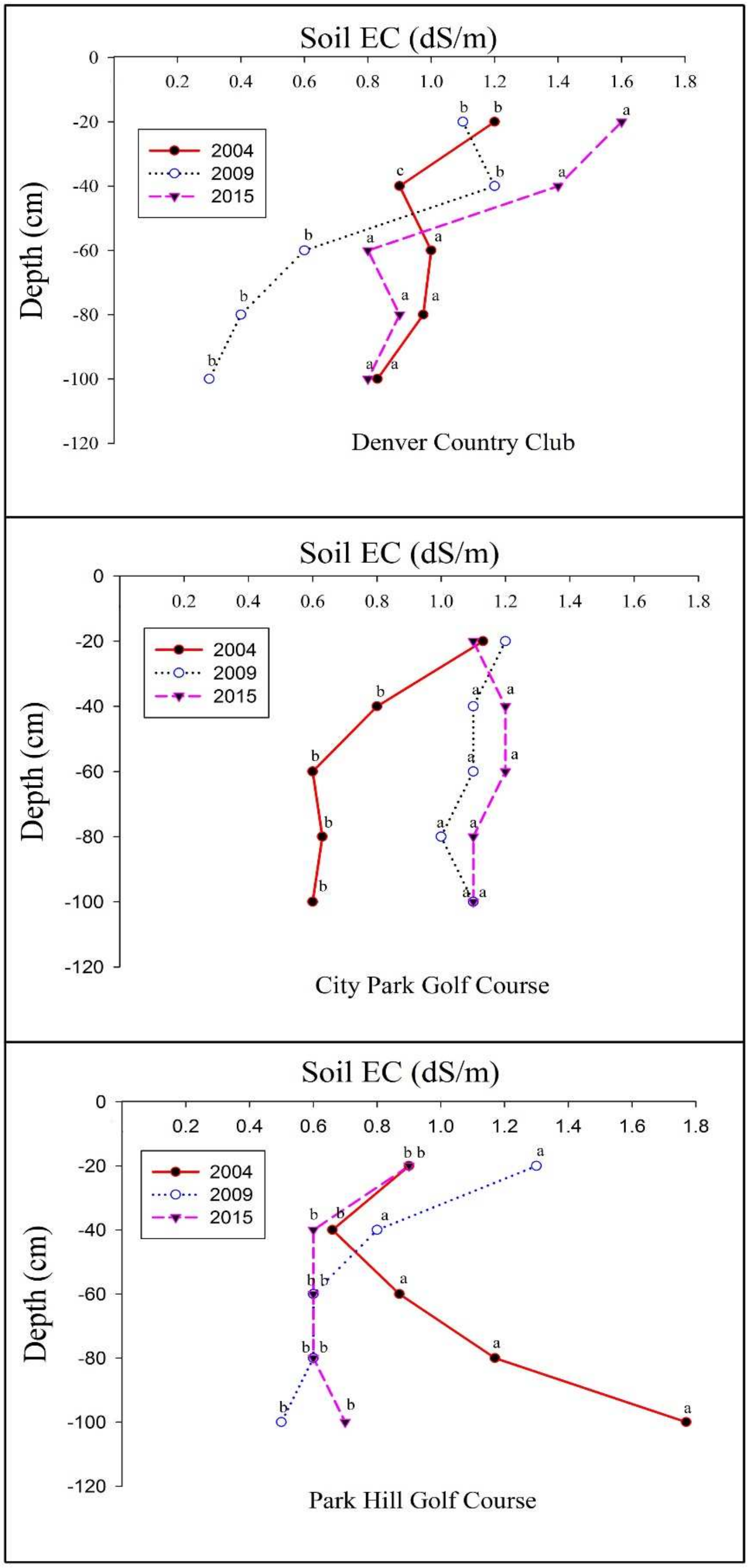

Figure 1-2. Soil EC of 2004, 2009 and 2015 at Denver Country Club, City Park Golf Course and Park Hill Golf Course. Letters indicate significant difference ($P \leq 0.05$) among years at each depth, no letters shown indicate not statistically significant.

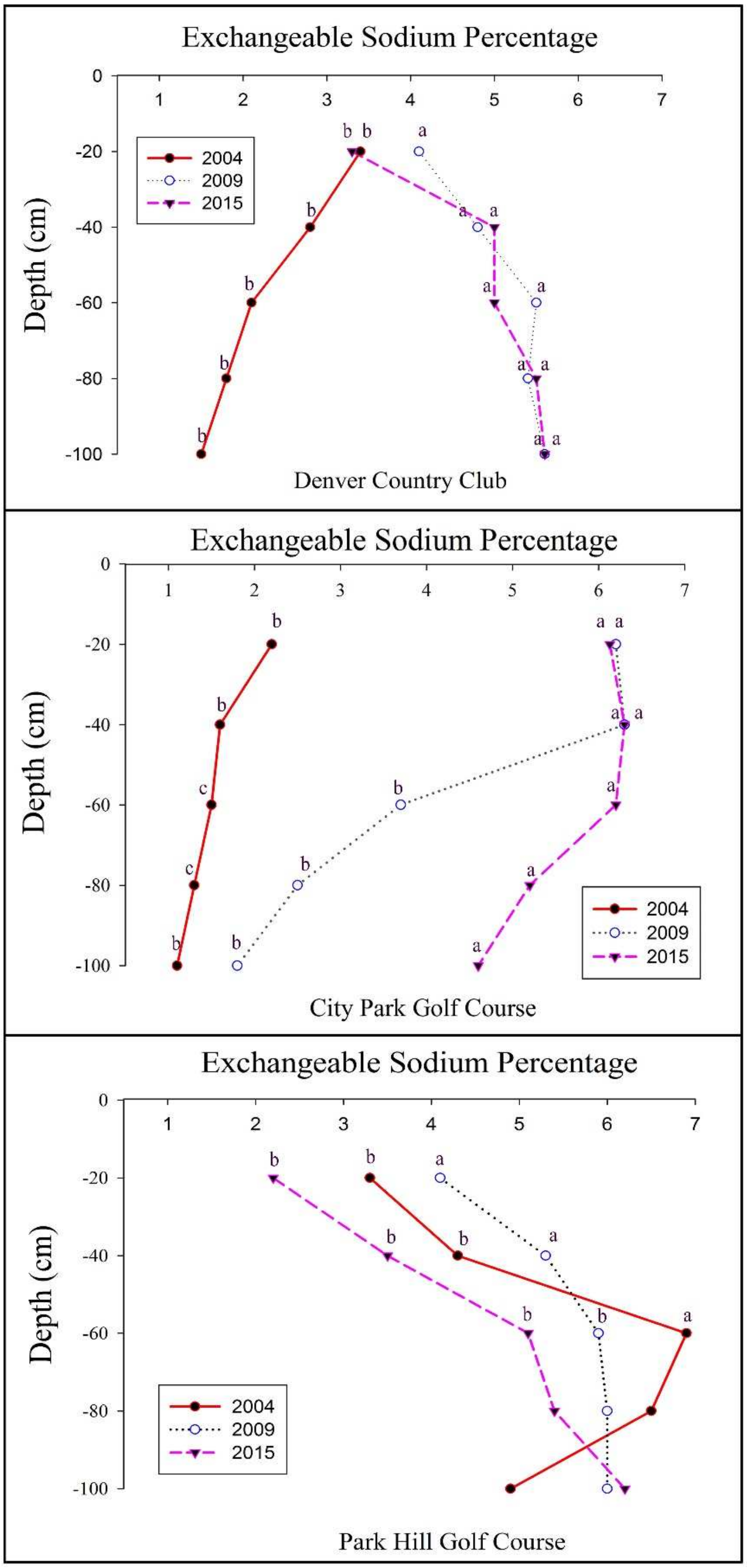

Figure 1-3. Soil ESP of 2004, 2009 and 2015 at Denver Country Club, City Park Golf Course and Park Hill Golf Course. Letters indicate significant difference (*P* ≤ 0.05) among years at each depth, no letters shown indicate not statistically significant.

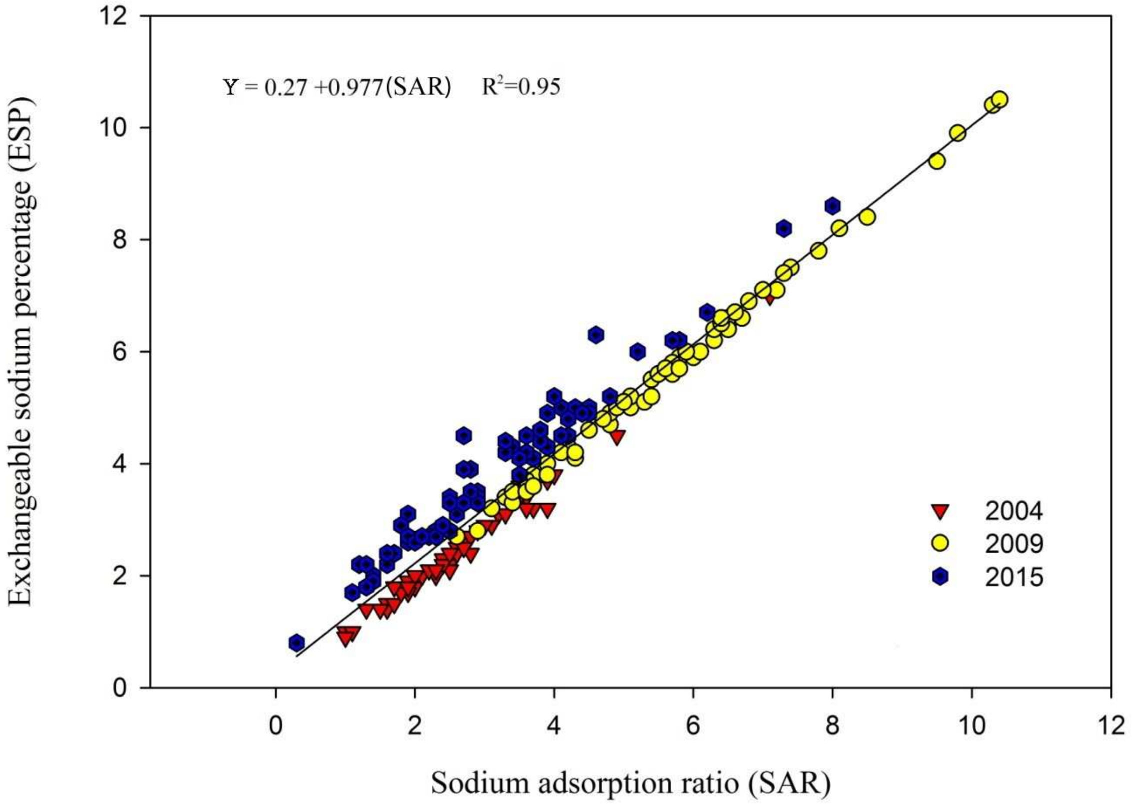

Figure 1-4. Simple regression analysis of SAR and ESP, data combined from 2004, 2009 and 2015 soil sampling results.

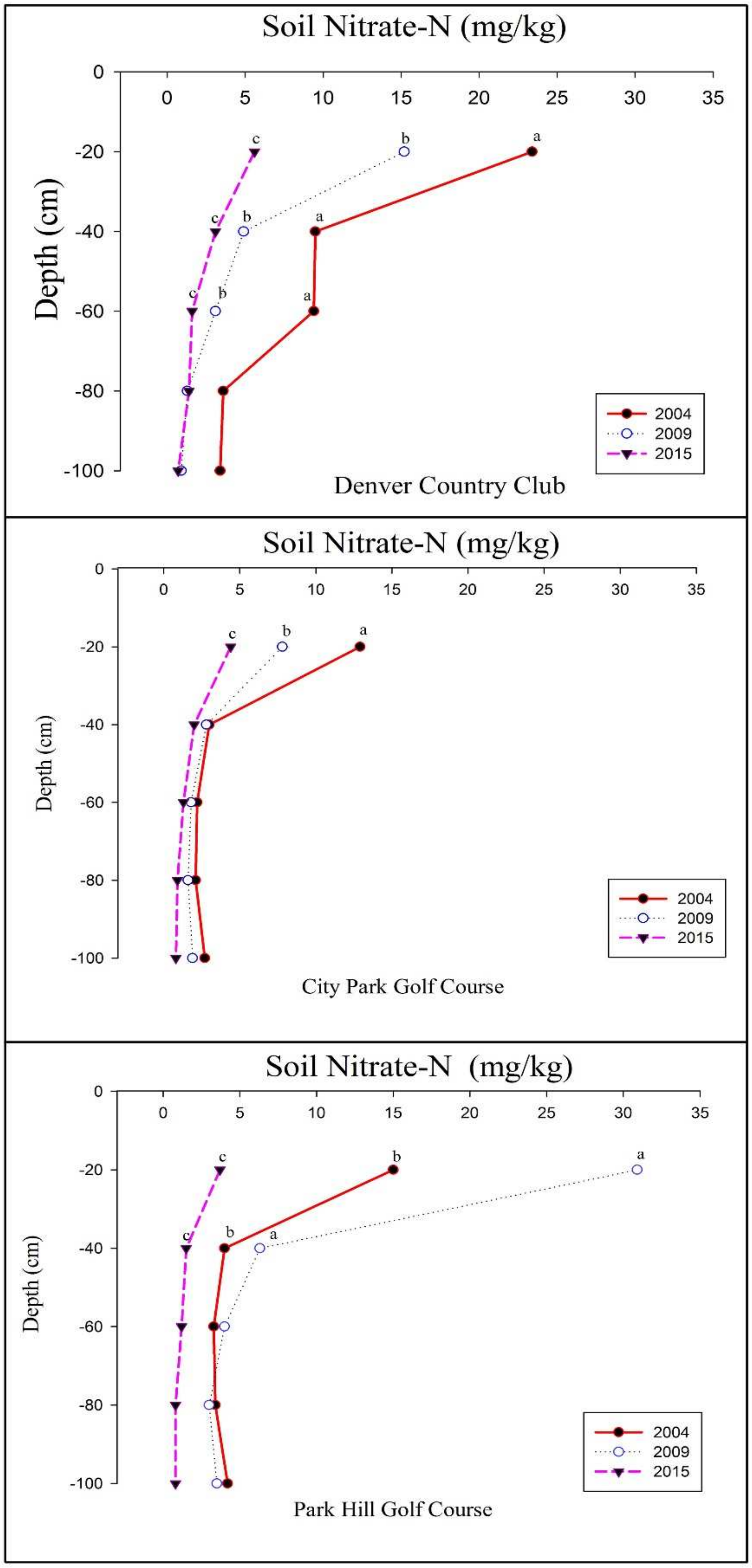

Figure 1-5. Soil nitrate levels of 2004, 2009 and 2015 at Denver Country Club, City Park Golf Course and Park Hill Golf Course. Letters indicate significant difference (*P* ≤ 0.05) among years at each depth, no letters shown indicate not statistically significant.

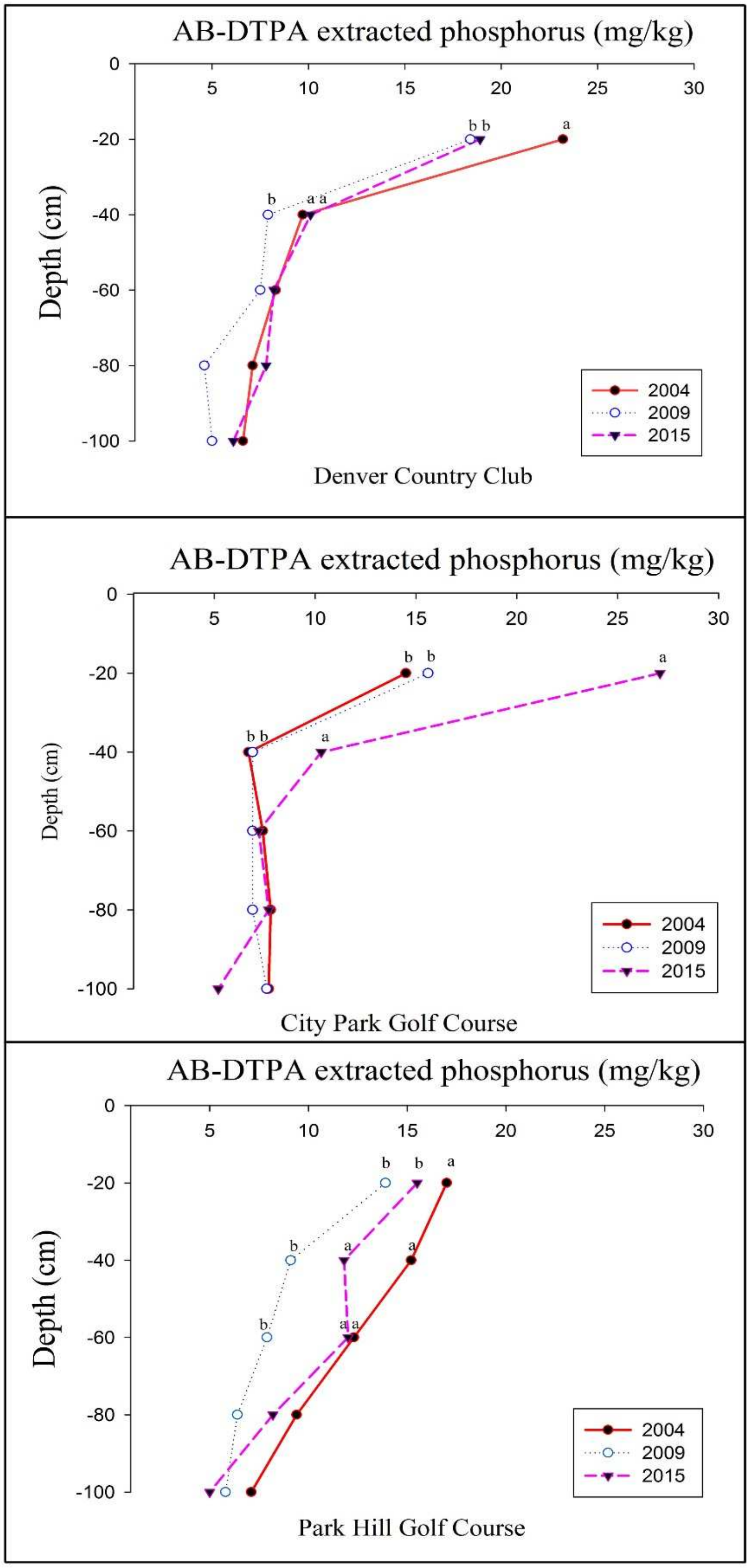

Figure 1-6. Soil extractable Phosphorus of 2004, 2009 and 2015 at Denver Country Club, City Park Golf Course and Park Hill Golf Course. Letters indicate significant difference ($P \leq 0.05$) among years at each depth, no letters shown indicate not statistically significant.

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CHAPTER 2: SOIL HEAVY METAL CONCENTRATIONS BEFORE AND 11 YEARS FOLLOWING CONVERSION TO RECYCLED WATER IRRIGATION

SUMMARY

The potential for heavy metal accumulation in soils receiving recycled water irrigation has been a concern in recent years. To determine if there is any heavy metal accumulation in soil after 11 years of recycled water irrigation, we tested the heavy metal concentration of archived soil samples collected in 2004 (prior to the commencement of recycled water irrigation) and 2015 (11 years after recycled water irrigation) from five parks in Denver, CO. Heavy metals, including arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn) were extracted from soil samples using the ammonium bicarbonate-diethylene triamine pentaacetic acid (AB-DTPA extractant) and measured by ICP. Results indicated that soil As and Co concentrations decreased by 50 to 83% and 66 to 83% from 2004 to 2015, respectively. Soil Ni decreased from 2004 to 2015 at Dunham Park, City Park, and Washington Park, but the Ni reduction was not significant at Schaefer Park and Swansea Park. At all parks, soil Cd, Cr, Cu, Pb, and Zn did not show significant change from 2004 to 2015.

INTRODUCTION

Recycled water can be utilized as a water resource for decorative fountains, groundwater recharge, cooling towers, car washing and fire protection. In many states of America, a substantial quantity of recycled water is distributed to farmlands and cities for irrigation purposes (Parsons et al., 2010; Lewis and Wright, 2011).

Heavy metal contamination in soils has been reported around the world (Wuana and Okieimen, 2011). Lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu) and nickel (Ni) are metals commonly found in excessive amounts at polluted sites. Sources of heavy metals usually are from mining activities, industrial waste, and land application of industrial or domestic sludge. For instance, communities built nearby mine tailings and dumps in Aspen, CO had high levels of Pb, Cd and Zn in home garden soils (Boon, 1985).

Heavy metal accumulation is rarely a problem in agricultural soils with regular cropping systems including sowing, cultivation, fertilization, chemical application and harvesting. Nevertheless, Barbarick and Workman (1987) observed high Zn and Pb concentration in wheat when the plants were grown on soils where sewage sludge was applied as a soil amendment. In Florida, Hanlon et al. (1996) found that ammonium bicarbonate-DTPA extracted Zn and Ni were higher in calcareous soil receiving sewage sludge application when compared to the control. In Turkey, heavy metal concentration (Mn, Zn, Cu, Ni, Pb and Cd) in red cabbage and cauliflower increased when the vegetables were grown on calcareous Aridisol irrigated with treated municipal wastewater (Kiziloglu et al., 2008). In Greece, broccoli and brussels sprouts grown under recycled water irrigation had increased heavy metal accumulation in plant tissues (Kalavrouziotis et al., 2010).

Recycled water has been primarily used for landscape irrigation in Colorado. However, recently there is interest in planting community gardens on sites where recycled water has been used for irrigation. Recycled water irrigation has many positive effects such as saving fresh water and fertilizer, increasing crop yield, and reducing pollutant discharge to watersheds. In the meantime, there are concerns regarding pollutants (such as heavy metals, disinfection byproducts, and pharmaceuticals) building up in soil. If heavy metals accumulate in soil to critical levels, there is a risk for increased plant uptake of these elements and safety concerns for vegetable and food crops. Leafy portions of plants generally take up the highest concentrations of heavy metals followed by roots (Kalavrouziotis et al., 2010; Khan et al., 2008). It is unknown whether there has been any heavy metal accumulation after 11 years of irrigation with Denver Water's recycled water.

To determine if there was any heavy metal accumulation in soil after over 11 years of water reuse practices in Denver, this study was conducted to test the heavy metal concentration of archived soil samples collected in 2004 and from soils sampled in 2015 from five parks. All five parks started to use recycled water for irrigation in August 2004.

MATERIALS AND METHODS

Site Description and Soil Sampling

Ten locations which were switched to Denver Water's recycled water irrigation in 2004 were described in Chapter 1. Selected facilities in this study were: Swansea Park, Dunham Park, Schaefer Park, City Park and Washington Park.

Before switching to recycled water irrigation, 36 soil baseline samples from the listed five parks were collected. Samples were taken at 0-20 cm at Washington Park. Soils were sampled to 0-20 cm and 20-40 cm depths at the four parks. Three cores at each site and depth were combined. A metal rod was buried at each sampling site in 2004 as a location reference. Soil samples collected in 2004 were air dried, ground, screened to pass through a 10-mesh (2mm) sieve, and stored in zip-lock bags. In 2015, after 11 years of recycled water irrigation, soil samples were collected 30 cm away from the 2004 original sampling points.

Heavy Metal Analysis

Heavy metals, including arsenic (As), chromium (Cr), cadmium (Cd), cobalt (Co), nickel (Ni), copper (Cu), lead (Pb), and zinc (Zn) from soil samples were extracted using the ammonium bicarbonate-diethylene triamine pentaacetic acid (AB-DTPA extractant. Heavy metal concentrations at baseline point in 2004 were compared to samples collected in 2015.

Samples were air-dried at room temperature and pulverized with porcelain mortar and pestle. Ten g of soil sample were then passed through a 10-mesh (2mm) sieve. Ammonium-bicarbonate-DTPA was used for metal element extraction. The AB-DTPA soil testing method (Soltanpour and Schwab, 1977), modified by Soltanpour and Workman (1979) was developed for extraction of exchangeable heavy metals. The extracted solution was measured for heavy metal concentration using ICP-AES method (inductively coupled plasma optical emission spectroscopy).

Statistical Analysis

Data on heavy metal concentrations were subjected to analysis of variance (ANOVA) and evaluate elements differences at two soil depths between 2004 and 2015 by SAS PROC GLM (SAS 9.3 2011). Least significant difference (LSD) was set at $P \leq 0.05$.

RESULTS AND DISCUSSION

Heavy Metal Concentration

The average As concentration in the baseline soil from five parks ranged from 0.29 to 0.42 mg kg^{-1}. Arsenic decreased to 0.19 to 0.28 mg kg^{-1} after eleven years of irrigation with recycled water (Fig. 2-1). Likewise, the average Co concentration from five parks was 0.05 mg kg^{-1} with a range of 0.03 to 0.08 mg kg^{-1} in 2004. Soil Co was reduced to 0.01 mg kg^{-1} after eleven years of irrigating with recycled water (Fig. 2-3). There are similar trends among the five parks regarding the changes in As and Co from 2004 to 2015. At all five parks, soil As and Co were similar between two sampling depths (0-20 and 20-40 cm) (Fig. 2-1 and Fig. 2-3). Soil As and Co decreased by 50 to 83% and 66 to 83% from 2004 to 2015, respectively. Most of the soil samples had a lower As concentration than EPA determined soil screen guidance for residential contamination clean up level. Co concentration is considered to be only trace amount.

All archived samples collected from the 5 parks in 2004 had an average Cd, Cr, Cu, Ni, Pb and Zn concentration of 0.60, 0.05, 7.07, 0.66, 11.62 and 27.25 mg kg^{-1}, respectively (Fig. 2-2, 2-4, 2-5, 2-6, 2-7 and 2-8). Eleven years after irrigating with recycled water, the average soil Cd, Cr, Cu, Ni, Pb and Zn concentration were 0.46, 0.04, 4.75, 0.43, 11.38 and 25.73mg kg^{-1}, respectively. Based on ANOVA procedure analyzing metal concentration at two depths before and 11 years after receiving recycled water irrigation, at all parks, soil Cr, Cd, Cu, Pb and Zn did not show significant change from 2004 to 2015.

Soil Ni decreased from 2004 to 2015 at City Park, Dunham Park and Washington Park, but the Ni reduction was not significant from ANOVA results at Schaefer Park and Swansea Park (Fig. 2-6).

Our results demonstrated that soil heavy metal accumulation was not a concern on parks irrigated with Denver Water's recycled water. This is likely a result of very low heavy metal concentration in the recycled water. The influent at Denver Water's wastewater treatment plan was likely from residential wastewater. Secondly, soil pH may have played a role in the extractable heavy metal concentration. Soil pH ranged from 6.4 to 7.6 in five parks with the average of 6.8 in baseline 2004 year (see Chapter 1). After 11 years of recycled water irrigation, the pH value increased by 0.3 up to 7.1. Kabata-Pendias (2011) stated that whenever soil pH increases over 5, the ion mobility of Cd^{2+}, Co^{2+}, Cu^{2+}, Cr^{3+} , Mn^{2+}, Mo^{5+}, Ni^{2+}, Pb^{2+}, Hg^{2+} and

Zn^{2+} can be impeded in soil solution. The reduction in AB-DTPA extracted As, Co and Ni may attribute to plant uptake and the increase in soil pH.

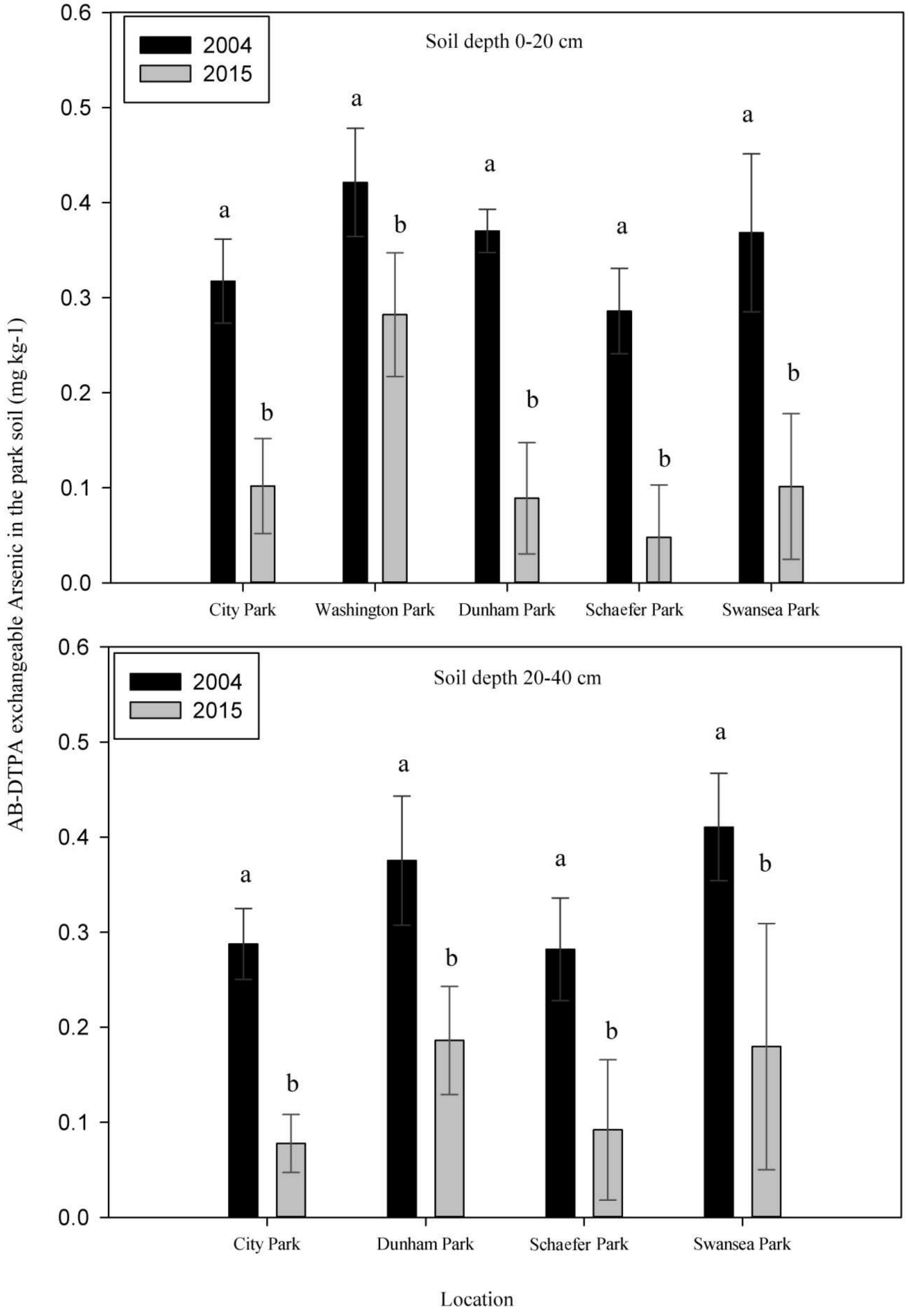

Figure 2-1. Soil Arsenic (As) prior to recycled water irrigation in 2004 and 11 years after. Means with different letters represent significant differences between two years ($P \leq 0.05$).

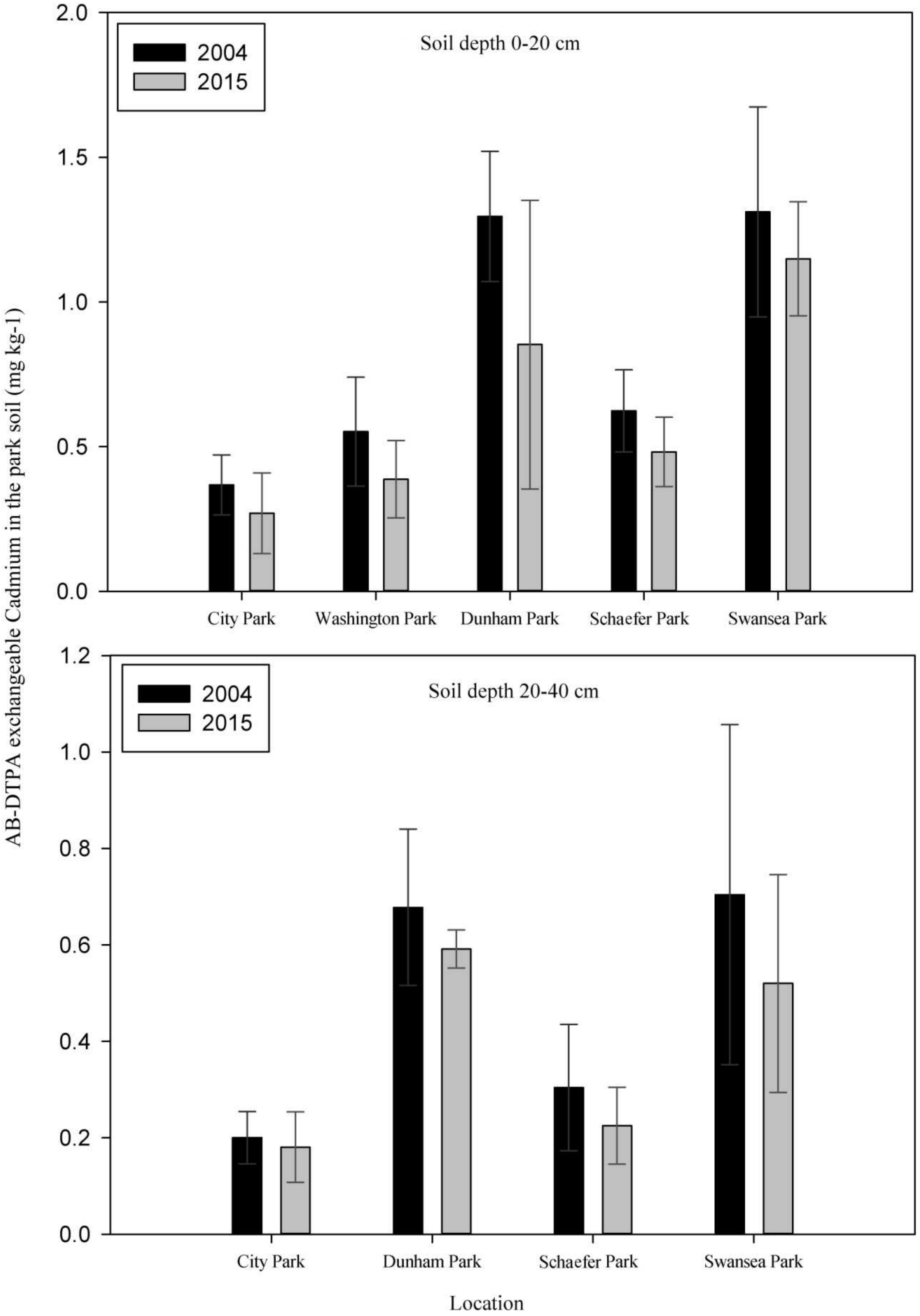

Figure 2-2. Soil Cadmium (Cd) prior to recycled water irrigation in 2004 and 11 years after. Means with different letters represent significant differences between two years ($P \leq 0.05$), no letters shown indicate not statistically significant.

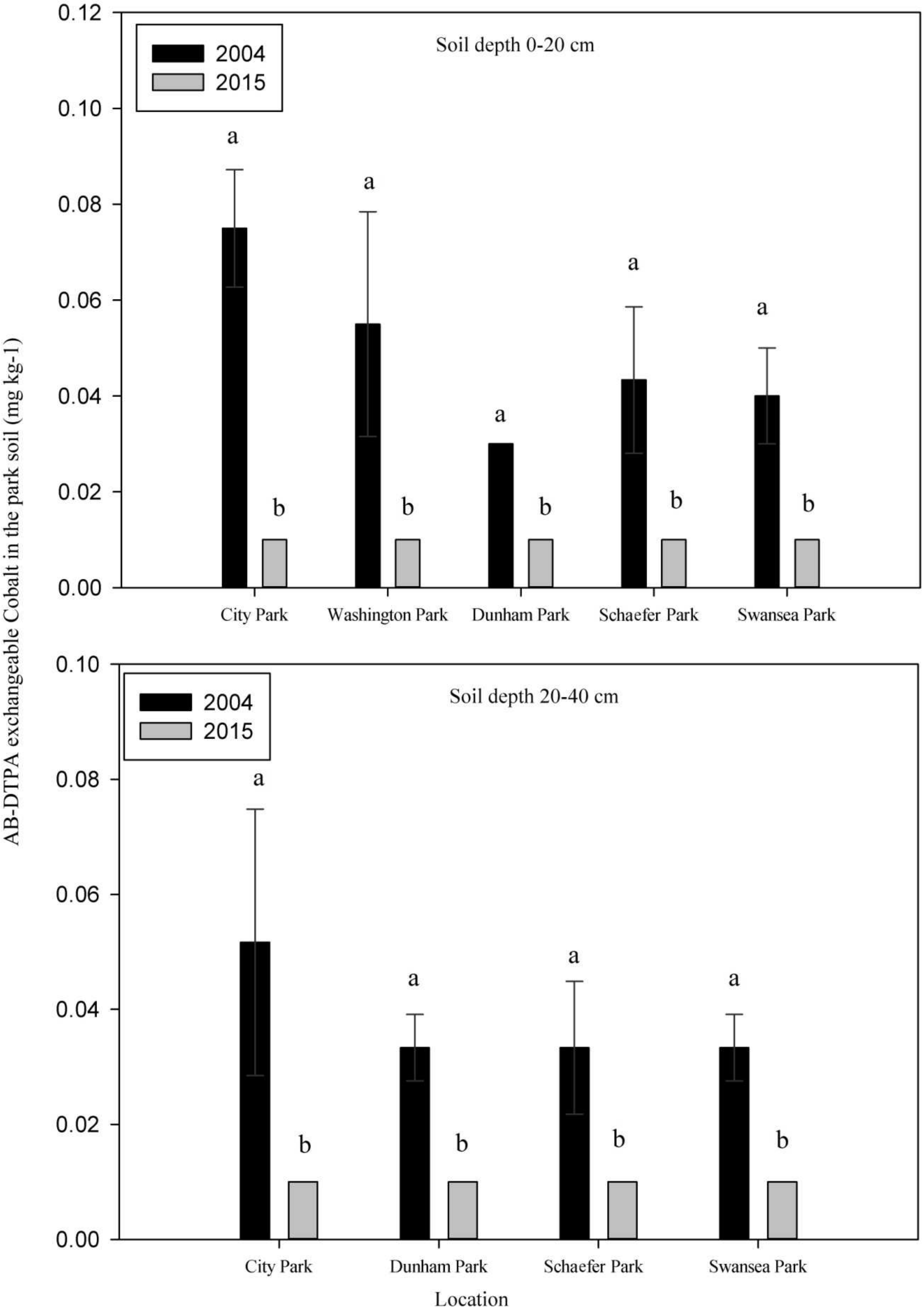

Figure 2-3. Soil Cobalt (Co) prior to recycled water irrigation in 2004 and 11 years after. Means with different letters represent significant differences between two years ($P \leq 0.05$).

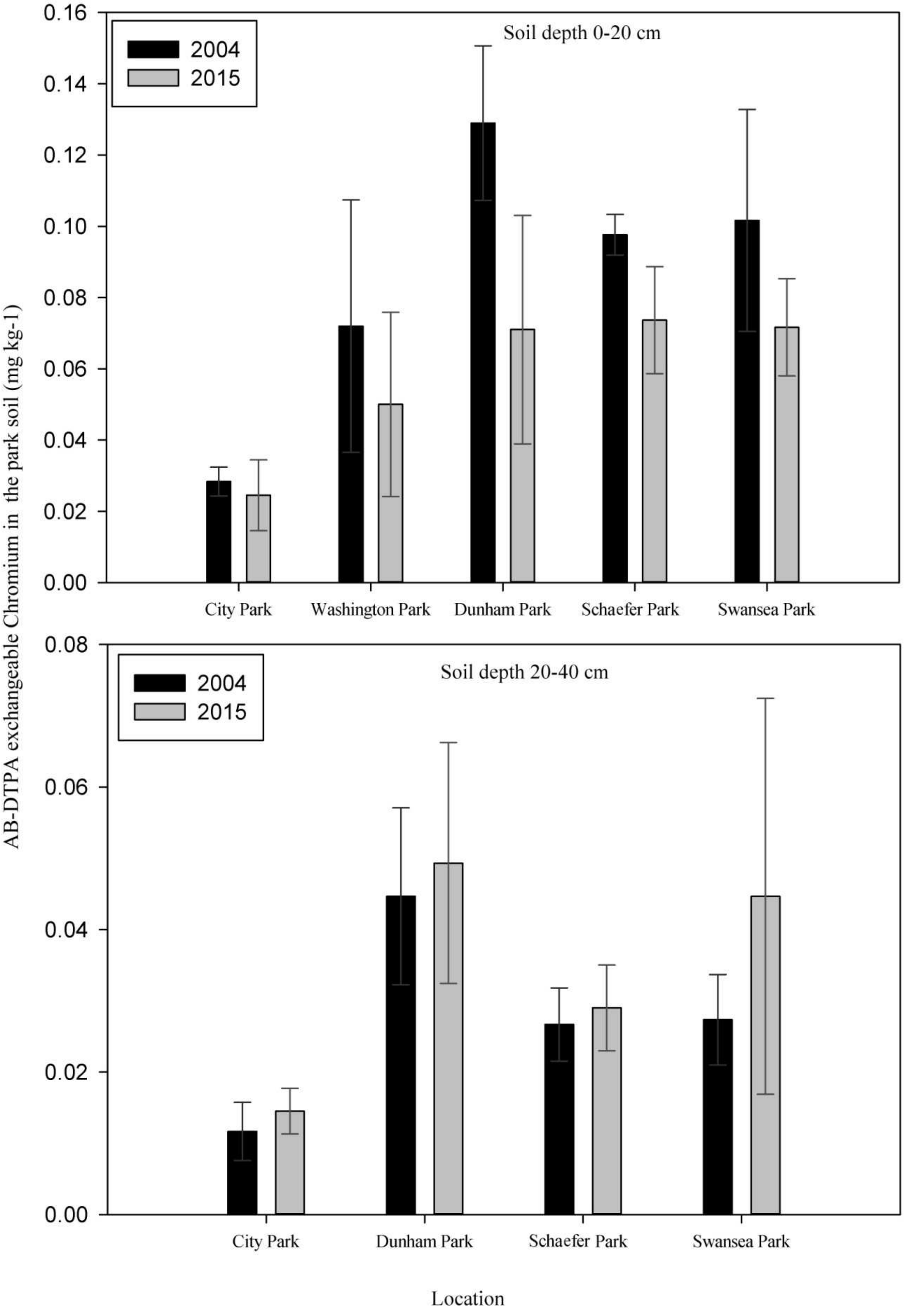

Figure 2-4. Soil Chromium (Cr) prior to recycled water irrigation in 2004 and 11 years after. Means with different letters represent significant differences between two years ($P \leq 0.05$), no letters shown indicate not statistically significant.

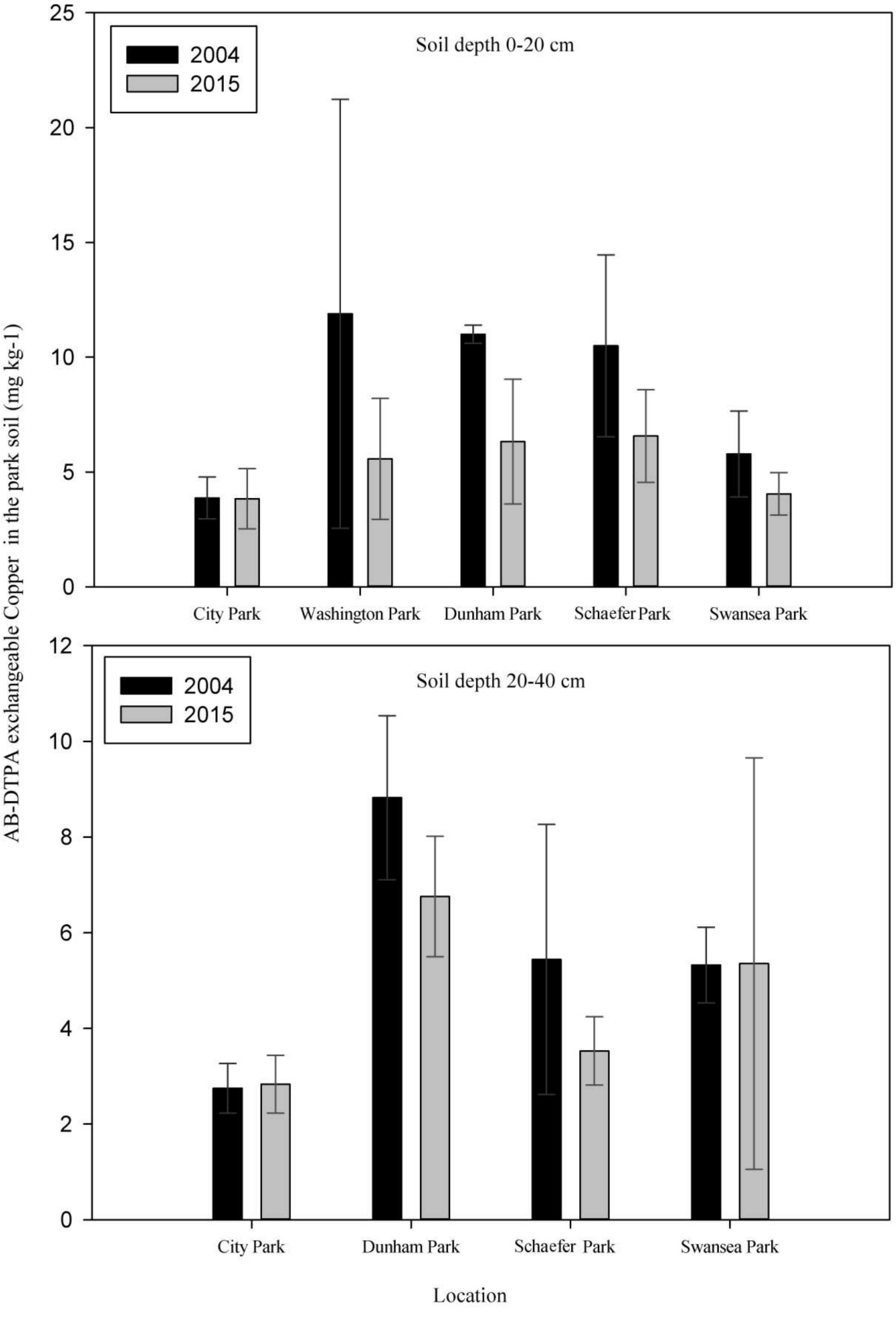

Figure 2-5. Soil Copper (Cu) prior to recycled water irrigation in 2004 and 11 years after. Means with different letters represent significant differences between two years ($P \leq 0.05$), no letters shown indicate not statistically significant.

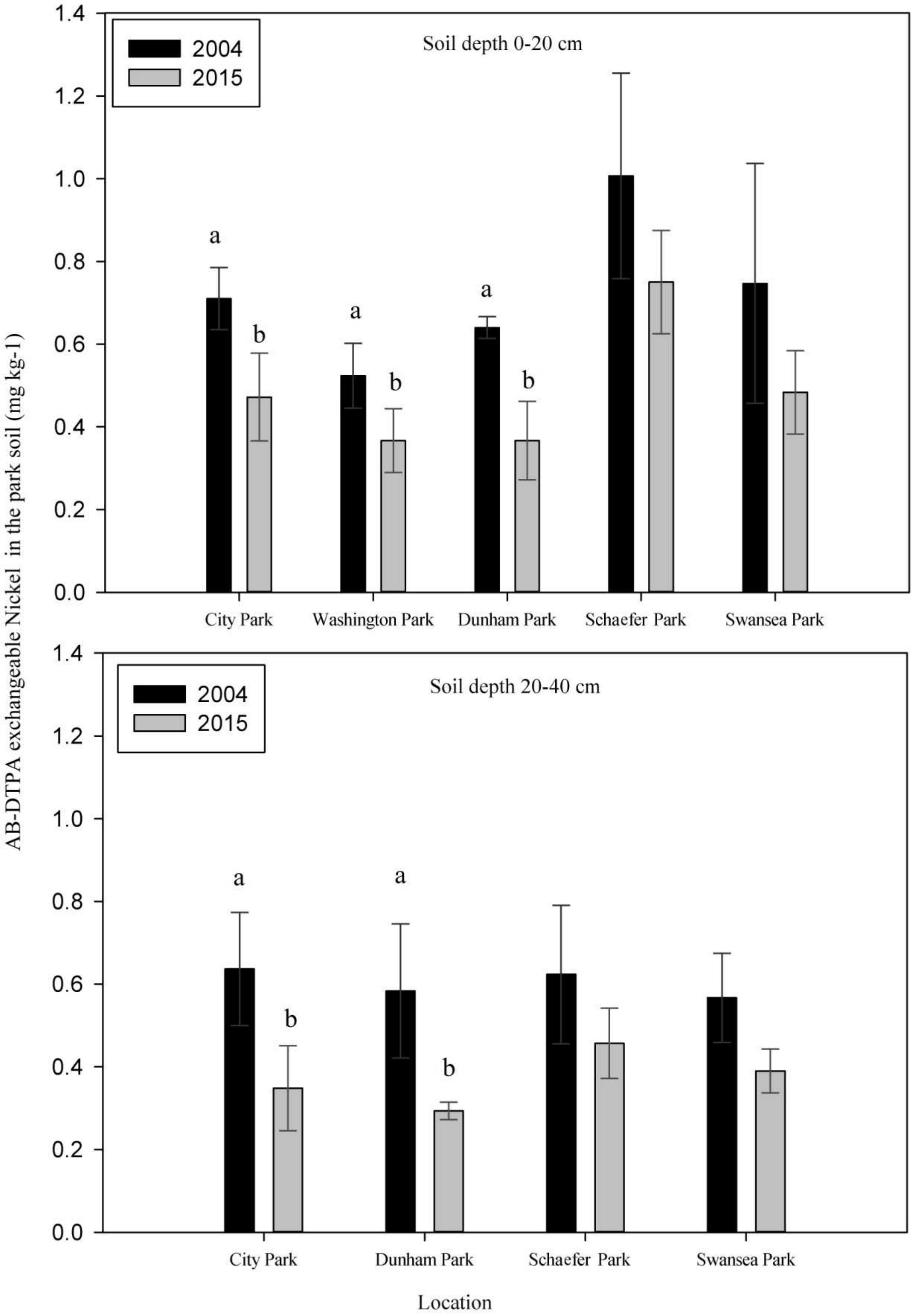

Figure 2-6. Soil Nickel (Ni) prior to recycled water irrigation in 2004 and 11 years after. Means with different letters represent significant differences between two years ($P \leq 0.05$), no letters shown indicate not statistically significant.

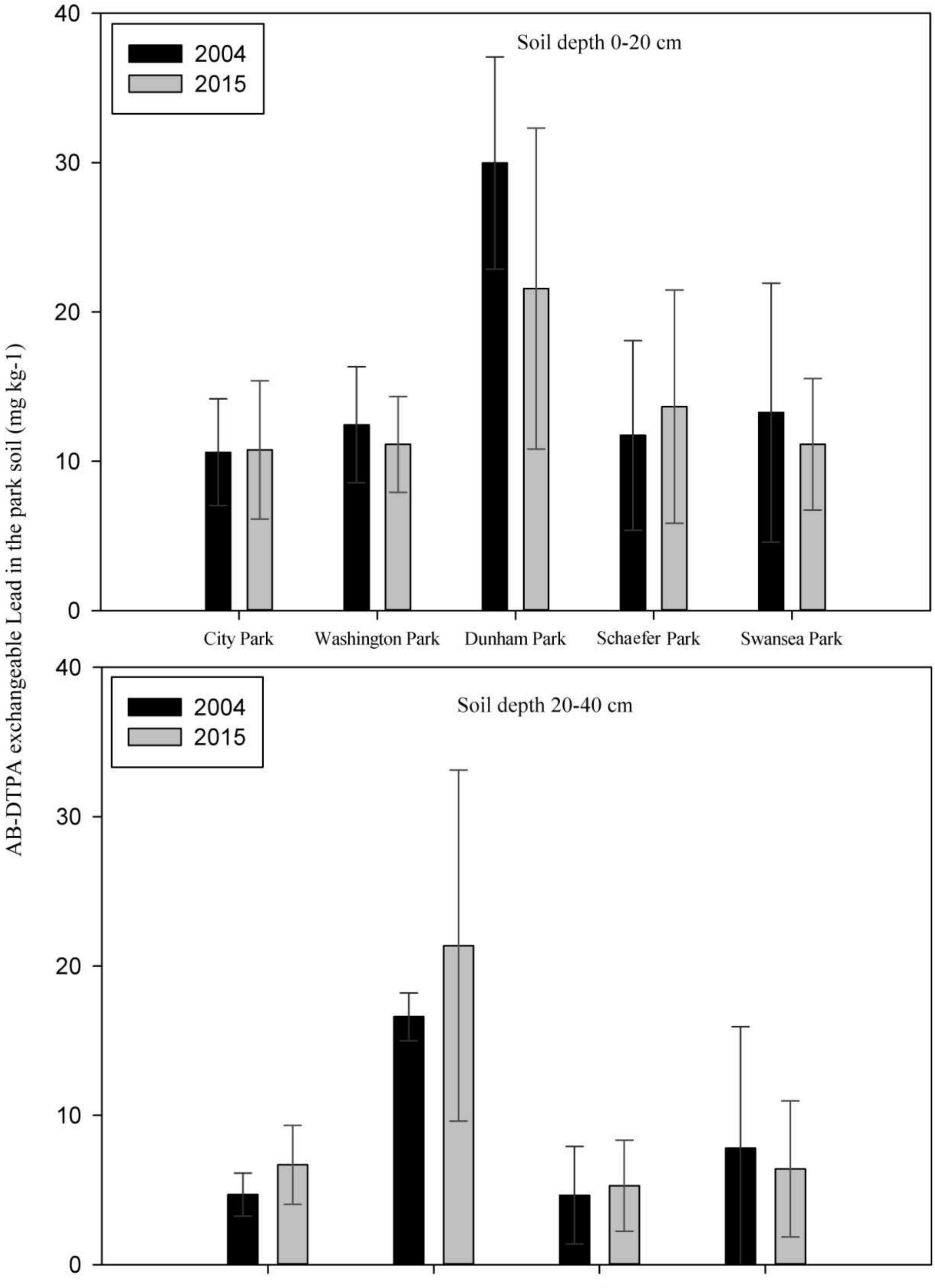

Figure 2-7. Soil Lead (Pb) prior to recycled water irrigation in 2004 and 11 years after. Means with different letters represent significant differences between two years ($P \leq 0.05$), no letters shown indicate not statistically significant.

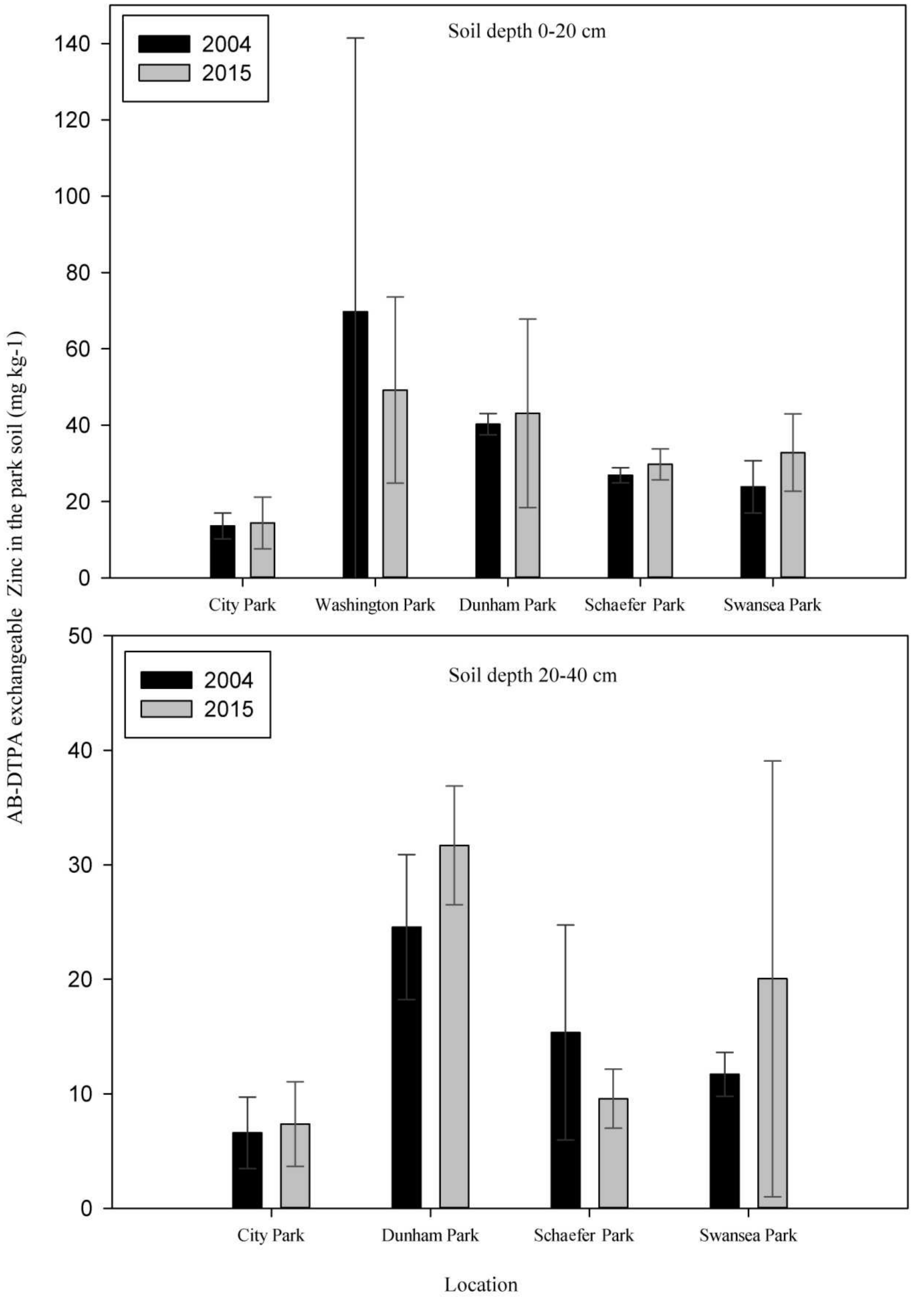

Figure 2-8. Soil Zinc (Zn) prior to recycled water irrigation in 2004 and 11 years after. Means with different letters represent significant differences between two years ($P \leq 0.05$), no letters shown indicate not statistically significant.

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CHAPTER 3: MINERAL COMPOSITION OF KENTUCLY BLUEGRASS UNDER RECYCLED WATER IRRIGATION IN DENVER GOLF COURSES

SUMMARY

Golf courses in the western United States are increasingly being irrigated with recycled water. Kentucky bluegrass (*Poa pratensis L.*) (KBG) is the most widely used turfgrass species in Colorado. Research was conducted on eight golf courses, including three courses in Denver after 10 years of recycled water irrigation, three courses in the nearby cities receiving recycled water for more than 10 years, and two courses receiving surface water for irrigation. Soil pH, EC, organic matter, Ca, Mg, K, Na, B, and SAR of soil saturated paste were determined. Kentucky bluegrass shoots were sampled from 25 roughs and analyzed for mineral concentration including Na, Ca, Mg, K, Cl, B, S, P, Mn, Fe, Zn, Cu and Mo. Recycled water irrigation increased clipping Na by 4.3-9.9 times, Cl by 1.5 - 1.3 times, B by 1.3 - 3.5 times, whereas tissue K/Na ratio was reduced by 74- 90%. Multiple regression analysis was conducted to identify the relationships between mineral concentration in clippings and turf quality. There was a negative linear relationship between turf quality and sodium concentration in the clippings (R^2= 0.65). Soil SAR in 0-20 cm depth was highly associated with KBG shoot Na as documented by a logarithmic regression of R^2=0.70.

INTRODUCTION

Water scarcity and expanding population are the impetuses for the authorities to search for alternative strategies to improve water conservation. In general, water deficiency is well known in western states such as California, Nevada, Arizona, Utah, Colorado and New Mexico

(National Drought Mitigation Center, 2016). Moreover, Denver, as it is situated in the semi-arid geographic location often has to deal with drought in the summer seasons. From April through October, more than 50% of the city's potable water is used for outdoor landscape irrigation purposes.

The total area of golf courses in the U.S. was 608,732 hectares in 2007. It is estimated that during 2003-2005, 80 percent of maintained turfgrass on 18-hole golf courses had been irrigated annually with 285 million cubic meters of water (GCSAA, 2009). Residential turfgrass is another turfgrass sector using water resources. According to conservative estimates from the EPA 1997 census, the 7.16 million hectares of home lawn in the whole nation consumed 4,369 million cubic meters of water (Watson et al., 2004). Dated back to 1910 in California, recycled water irrigation was already adopted for agricultural irrigation. Recycled water can significantly reduce fresh water and fertilizer requirements of turfgrass. However, salinity issues related to recycled water irrigation have imposed challenges with this water conservation practice. Qian and Mecham (2005) examined the water quality of recycled water and found recycled water had higher level of soluble salts, when compared to fresh water. Sodium was accumulated in soils from golf courses under recycled water irrigation. Therefore, it is possible to induce salinity stress to turfgrass if toxic ions (Na and Cl) accumulate in leaf and shoot tissues.

A series of papers have investigated salinity tolerance of C3 and C4 turfgrass species under controlled environments. Marcum and Murdoch (1990) found that shoot Na^+ and Cl^- concentrations in C4 turfgrass increased relative to the increment of salinity treatments. Bermudagrass 'Tifway' (*Cynodon dactylon*), centipedegrass (*Eremochloa ophiuroides*), zoysiagrass (*Zoysia japonica and Zoysia matrella*), seashore paspalum (*Paspalum vaginatum*) and St. Augustinegrass (*Stenotaphrum secundatum*) salinity tolerance was strongly associated with Na^+ and Cl^- exclusion in the shoot; salt tolerance also highly depended on lower ion concentrations retained in the shoot tissue (Gorham et al., 1985; Marcum and Murdoch, 1990). A yield reduction of 50% was used as the parameter determining plant vigor status under stress. Evidence showed that seashore paspalum, *Zoysia matrella* and St. Agustinegrass were more tolerant to salinity stress (Marcum and Murdoch, 1994).

Kentucky bluegrass (*Poa pratensis L.*) is the most commonly used cool-season turfgrass species in Colorado and other regions with latitudes above the transition zone in North America. Alshammary et al. (2004) examined salinity tolerance of Kentucky bluegrass, tall fescue (Festuca arundinacea), alkaligrass (*Puccinellia distans.*) and saltgrass (Distichlis spicata) in a greenhouse experiment. Kentucky bluegrass was the most sensitive to salinity treatment among these four species, based on criteria of turf quality, shoot and root dry weight, and root to shoot ratio. ‘Challenger’ Kentucky bluegrass suffered 50% shoot growth reduction at 4.9 dS m^{-1} salinity level. In other research, two Kentucky bluegrass cultivars, ‘ Limousine’ and ‘Kenblue’ were chosen by Qian et al.(2001) to test leaf water content, osmotic potential and shoot mineral concentration under saline treatments ranging from 2.2 to14.2 dS m^{-1}. Cultivar ‘Limousine’ had less shoot Na^+ and Cl^- accumulation and a higher shoot K/Na ratio. Shoot growth reduction of 25% for ‘Limousine’ was observed at EC 4.7 dS m^{-1}.

Many of the studies intending to uncover turf salinity tolerance were conducted in controlled environments and received different levels of salt treatments (Suplick-Ploense et al., 2002 ; Qian et al., 2001 and 2004 ; Alshammary et al., 2004).

The objectives of this research were to evaluate 1) turf quality of KBG and 2) determine the relationship between turf quality and shoot mineral concentrations and soil chemical properties for KBG grown on golf courses irrigated with recycled water from different water treatment authorities for different periods.

MATERIALS AND METHODS

Site Description

In the City and County of Denver, Denver Water serves as the wastewater treatment authority to roughly around 1.1 million people (Kenney et al., 2004). With the $78 million facility completed in 2004, the capacity of 170,343 cubic meters of effluent per day was able to be treated in the Denver Water Recycling Plant. With similar practices in Aurora, Thornton and Westminster, Big Dry Creek wastewater treatment facilities in Westminster, the City and County of Broomfield’s water treatment facility and Sand Creek reuse facility in Aurora operate with the secondary or tertiary treatment processes and deliver recycled water for irrigation of golf courses, parks and greenways. Although their treatment capacities are on a smaller scale than Denver Water, reuse of treated municipal wastewater for golf courses and parks dated back to 1964 from Sand Creek water reuse facility.

The experiment was undertaken on three courses within the City and County of Denver that switched to recycled water irrigation from Denver Water in 2004. Additionally, three golf courses from Thornton, Broomfield and Aurora that observed turfgrass decline after recycled water irrigation for more than 10 years were also included in the study. Recycled water in these counties was separately treated in Big Dry Creek, Sand Creek and the City and County of Broomfield’s wastewater treatment facilities. The reuse program was initiated in these courses more than 10 years ago, and superintendents expressed concern about the elevated EC and SAR levels based on periodic soil testing over the years. We refer to golf courses in this group as pioneer recycled water irrigation group. Other than these courses, two courses irrigated with surface water in the Rocky Mountain region were selected as controls. All of the eight courses have 18 holes and had Kentucky bluegrass on roughs.

Climate Conditions

In Denver, average monthly rainfall ranges between 4.75 cm and 6.5 cm. May to August are the months that typically precipitation have exceeding 5 cm. The reference evapotranspiration in northern Colorado ranges from 95.25 to 120.65 cm during the growing season (Clifford and Doesken, 2009).

Plant Materials

The experimental design was classified as a completely randomized design. In the City and County of Denver, three to four random holes from each golf course were chosen as replications, turf samples were collected from eleven holes in 2014 (10 years after the start of recycled water irrigation). For the pioneer recycled water irrigation group, turf samples were collected from three golf courses, and three holes were selected for sample collection from each course; the total number of holes included for sample collection in this group was nine. Control samples were collected from golf courses irrigated with surface water (in five holes from two different golf courses that had been established at least 15 years prior in the Rocky Mountain Region). We collected turf shoot samples on the roughs less than 4.5m away from the fairways corresponding to the subjected holes. Turfgrass was mowed at the range between 40 to 50 mm, clipping samples were gathered after mowing. Three clipping samples from three random sites of each hole were combined. All samples were sealed in zip-lock plastic bags and placed in a cooler for transportation to the lab.

Turf Quality

Concurrent with clipping sample collection, turf quality was rated based on color, density and uniformity, with a rating of 1 representing brown, thin, dead turf. A rating of 6 was considered minimum acceptable turf and 9 was considered the best quality with appearance of dense, uniform turf with an emerald green color (Morris and Shearman, 2010).

Analysis of Shoot Mineral Concentration

Turf shoots were rinsed with deionized water and dried in an oven at 70°C for 24 hours. Afterwards, the materials were ground in a Thomas Wiley Mill to pass through a screen with 425-µm openings. Approximately 1 g of screened and dried sample was weighed and ashed for 7 h at 500° C. Ash was dissolved in 10 ml of 1N HCl and diluted with deionized water. Solution aliquots were analyzed on inductively-coupled plasma atomic emission spectrophotometry (ICP-AES) (Model 975 plasma Atomcomp, Thermo Jarrell Ash Corp., Franklin, MA02038). Chloride concentration was analyzed using the Cl- selective electrode (Thermo Electron Co. Orion 9617BNWP).

Soil Analysis

The details for soil sampling and analyses were described in Chapter 1. Soil sampling was conducted in 2014 for pH, EC, organic matter, Ca, Mg, K, Na, B, Cl, P levels and Sodium Adsorption Ratio (SAR).

Statistical Analysis

Shoot mineral concentrations including Na, Ca, Mg, K, Cl, B, S, P, Mn, Fe, Zn, Cu and Mo were subjected to statistical analysis procedures to investigate the relationships between individual mineral ions and turf quality.

Turf quality and mineral concentrations in the KBG shoots were tested by analysis of variance (ANOVA). Comparison of the three different irrigation water groups was accomplished by the least significance difference method. The Pearson correlation test was performed by PROC CORR to obtain Pearson statistic coefficients of individual minerals and its correspondence to turf quality. Stepwise regression was conducted to determine if any of the minerals accumulated in shoot tissues were related to the decline of turf quality. Stepwise multiple regression (PROC REG) used turf quality as a response variable and 13 mineral concentrations plus K/Na ratio as predictor variables. Significance was chosen at the probability level of 0.05 (SAS 9.3, 2011). Shoot Na concentration and soil chemical properties were compared between two groups (10 year recycled water irrigation vs. pioneer recycled water irrigation groups) by PROC T-TEST (SAS 9.3, 2011).

RESULTS AND DISCUSSION

Recycled water irrigation affected turf quality. Compared to the control courses, 10 year recycled water irrigation (City and County of Denver golf courses) had 5% lower turf quality ratings. Turf quality from surface water control had an average of 8.2. Quality ratings were 7.8 for the City and County of Denver group and 7.1 for the pioneer group. Evaluation of turf quality from courses in the pioneer recycled water irrigation group in Thornton, Aurora and Westminster all represented lower turf quality scores when compared to the control sites (Table 3-1). There was a linear relationship ($R^2=0.65$, $P \leq 0.05$) between turf quality and Na concentration in the clippings (Table 3-3).

Recycled water irrigation increased clipping Na by 4.3 times in the City and County of Denver group and 9.9 times in the pioneer recycled water irrigation group. B concentration increased by 1.3 – 3.5 times and Cl increased 1.5- 1.3 times in the City and County of Denver group and the pioneer recycled water irrigation group (Table 3-1).

Specific Ion Concentration in Kentucky Bluegrass Shoots under Recycled Water Irrigation

Sodium accumulation in the shoots was found in all recycled water irrigated courses (Table 3-1). In the City and County of Denver group, Denver Country Club hole no. 4 recorded the highest Na^+ concentration (2,281mg kg^{-1}) in shoot tissue. For the rest of the turf samples, Na^+ concentration in KBG shoots ranged from 921 to 1698 mg kg^{-1}. Mean Na^+ in this group was 1427 mg kg^{-1}. In contrast, in the pioneer recycled water irrigation courses, there were four roughs with Na^+ concentration over 4,000 mg kg^{-1}. Three of the four were from the Thorncreek Golf Club. The clipping mean Na^+ at Thorncreek Golf Club was 4,122 mg kg^{-1}. One rough sample in the Heritage Golf Course recorded shoot Na^+ exceeding 4,000 mg kg^{-1}, while the other five roughs clipping Na^+ ranged from 1,889 to 3,516 mg kg^{-1}. The overall mean from the pioneer group (3,256 mg kg^{-1}) was 2.28 times higher than the mean from the City and County of Denver group (1,427 mg kg^{-1}). Kentucky bluegrass shoot samples from surface water irrigated sites contained a mean Na^+ concentration of 329 mg kg^{-1}.

Potassium (K) stood out as the highest nutrient mineral in shoot tissue, ranging from 11,780 to 26,804 mg kg^{-1} in all samples. Mean potassium concentration was 22,642mg kg^{-1} in KBG samples of the City and County of Denver group (Table 3-1). The lowest K concentration in this group was found in Denver Country Club hole no.2 with a reading of 17,167mg kg^{-1}. This sample contained 24.2 % less K^+ than average, whereas Na^+ concentration was 13.5 % above the average. In the pioneer group, mean K^+ was 17,372 mg kg^{-1}, 16% lower when compared to the surface water irrigation group (20,637 mg kg^{-1}). Although KBG shoot K^+ varied between holes from recycled water irrigated courses, the lowest three readings all appeared in the Thorncreek

Golf Club. On average, the Thorncreek Golf Club exhibited a mean shoot K^+ of 11,863 mg kg^{-1}, which was 32% lower than the average of pioneer group (17,372mg kg^{-1}). Interestingly, the three highest shoot Na^+ concentrations were found at the Thorncreek Golf Club.

Chloride concentration in the City and County of Denver group ranged from 5,205 to 12,938 mg kg^{-1} with an overall mean 7,545 mg kg^{-1}. In the pioneer group, the concentration ranged between 3,950 to 10,670 mg kg^{-1} and overall mean was 6,734 mg kg^{-1}. In contrast to the surface water irrigated KBG clippings, the Cl concentration increased by 1.5 and 1.3 times respectively, with City and County of Denver and pioneer recycled water irrigation groups (Table 3-1).

Boron in the shoot tissue was increased in the holes irrigated with recycled water in the pioneer group. From surface water irrigation controls, the average B concentration in KBG shoots was 5.9 mg kg^{-1}. In the City and County of Denver group, B concentration (with a mean of 7.7 mg kg^{-1}) was 30% higher. In the pioneer group, B concentration (with a mean of 20.8 mg kg^{-1}) was 3.5 times higher than control (Table 3-1). Butler and Hodges (1967) reported tissue B levels of 6 and 9 mg kg^{-1} in two Kentucky bluegrass species. Jones (1980) suggested that the ideal B concentration range in cool and warm season turfgrass tissue is between 10 to 60 mg kg^{-1}. Turner (1980) found that turfgrass under 10 mg kg^{-1} B in soils did not suffer deficiency symptoms.

Sulfur concentration in KBG shoots was in the range of 827 to 5,947 mg kg^{-1}. In the three groups, the average S concentration was 1,285mg kg^{-1} for the City and County of Denver group, 4,517 mg kg^{-1} in pioneer group and 1,996 mg kg^{-1} for the surface water group. Sulfur concentration was higher in the pioneer group than others. Different management programs may affect sulfur variation in shoot tissues.

Shoot Na, along with Ca and B accumulated under recycled water irrigation. Regarding for Pearson correlation results, shoot Na concentration negatively associated with K and K/Na ratio (Table 3-2). Magnesium was negatively correlated with S, P, Mn, Mo and Zn. Potassium was positively correlated with P and Cu. Boron had moderate correlation with S and Mn. Finally, Fe correlated with Zn; all correlation mentioned above achieved a significance level higher or equal to $P \leq 0.01$.

Turf Quality and the Relationship with shoot Na^+ and K/Na Ratio

From Table 3-2, three elements (Na, B, S) and K/Na ratio showed higher correlation with turf quality. Sodium posed negative effect ($r = -0.81$, $P \leq 0.001$) to turf quality with the highest significance level, followed by B ($r = -0.71$, $P \leq 0.001$), S ($r = -0.66$, $P \leq 0.001$) and K/Na ratio ($r = 0.65$, $P \leq 0.001$). Stepwise regression results showed that, among all elements, the only mineral with significant P-value was Na (Table 3-3). Turf quality ratings from courses in the pioneer recyled water irrigation group represented the lowest scores.

K/Na ratio differed significantly among the three different irrigation regiments (Table 3-1). The highest K/Na ratio was observed in the surface water irrigation group (64.3). The mean K/Na dropped to 16.6 and 6.3 for the City and County of Denver group and the pioneer group. Drop for the K/Na ratio accompanied with turf quality declined (Table 3-2). This finding was in agreement with previous published research (Qian et al., 2001; Wang et al., 2013). The same findings have also been highlighted in other papers on both cool season and warm season turfgrasses (Krishnan and Brown, 2009; Marcum et al., 1998)

Results from this study showed that as Na accumulated in the Kentucky bluegrass exceeding 4,000 mg kg^{-1}, turf quality decreased. Carrow (2001) explained two physiological functions regarding how Na influences turfgrass growth: the first is causing ion toxicity to plant tissue and the other is causing an ion imbalance. Kentucky bluegrass in the pioneer group averaged a Na level over 3,000 mg kg^{-1} in the shoots and displayed lower turf quality. In a greenhouse study (Wang et al., 2013), ‘ Brilliant’ Kentucky bluegrass had shoot Na of 4,289 mg kg^{-1} when treated with saline irrigation water at 3dS m^{-1} and mowed at 50 mm height. This level of shoot Na concentration was represented for samples collected at the Thorncreek Golf Club.

Soil Chemical Property Link to KBG Shoot Na Accumulation and Turf Quality

Apparently, shoot Na concentration influenced turf quality with R^2 as high as 0.65 (Fig. 3-1). The surface soil SAR showed a logarithm nonlinear relationship to shoot Na (R^2 =0.70, $P \leq 0.001$) (Fig. 3-2). T-Test results confirmed that soil SAR in the pioneer group was higher than city and county of Denver group (Table 3-4). Kentucky bluegrass with lower turf quality (courses in the pioneer group) had higher shoot Na concentration, and higher SAR in the topsoil (0-20cm).

CONCLUSIONS

Kentucky bluegrass shoot Na concentration was higher in the pioneer recycled water irrigation group than in the City and County of Denver group. Based on stepwise regression analyses, Na accumulation in KBG shoots was the major factor leading to negative influences on turf quality. Additionally, soil SAR, EC, Ca and B were higher in the pioneer group ($P \leq 0.05$). A lower turf quality was associated with higher Na concentration in the shoots, and higher SAR in the top soil (0-20 cm) under recycled water irrigation.

Table 3-1. Mean separation of turf quality and clipping mineral concentration of Kentucky bluegrass grown on golf course roughs under different years of recycled water irrigation.

	Surface Water	City and County of Denver (10 years)	Thornton, Westminster and Aurora (10-21 years)
Turf quality	8.2a	7.8a	7.1b
Na	329c	1427b	3256a
Ca	3856b	3426b	5159a
Mg	1874b	2725a	1800b
K	20637a	22642a	17372b
Cl	5027b	7545a	6734a
B	5.9b	7.7b	20.8a
P	4513	3864	4517
K/Na	64.3a	16.6b	6.3c
S	1996b	1285c	4517a
Fe	282a	105b	271a
Zn	35.99a	25.29b	36.31a
Cu	5.28	5.4	4.42
Mn	51.77b	33.45b	104.64a
Mo	2.84	2.24	3.1

Means within a row followed by the same letter are not significantly different based on LSD (0.05).
Units are mg kg^{-1} except for turf quality and K/Na ratio.

Table 3-2. Pearson correlation coefficients among 13 minerals, K/Na ratio and turf quality in Kentucky bluegrass shoots.

	Na	Ca	Mg	K	Cl	B	S	P	Fe	Mn	Zn	Cu	Mo	K/Na
Na														
Ca	0.55^{**}													
Mg	-0.04	-0.07												
K	-0.56^{**}	-0.43^{*}	-0.1											
Cl	0.2	-0.05	0.47^{*}	-0.11										
B	0.76^{***}	0.66^{***}	-0.37	-0.37	-0.17									
S	0.71^{***}	0.56^{**}	-0.59^{**}	-0.42^{*}	-0.10	0.70^{***}								
P	-0.23	0.04	-0.58^{**}	0.63^{**}	-0.13	0.05	0.22							
Fe	0.22	0.31	-0.36	-0.10	-0.08	0.11	0.46^{*}	0.34						
Mn	0.46^{*}	0.11	-0.66^{***}	-0.16	-0.31	0.56^{**}	0.76^{***}	0.14	0.25					
Zn	0.04	0.32	-0.58^{**}	0.37	-0.15	0.22	0.46^{*}	0.88	0.57^{**}	0.20				
Cu	-0.39	-0.27	0.004	0.70^{***}	0.05	-0.35	-0.33	0.50^{*}	0.06	-0.24	0.30			
Mo	-0.1	-0.02	-0.45^{*}	0.21	-0.41^{*}	0.11	0.30	0.42^{*}	-0.19	0.50^{*}	0.46^{*}	0.07		
K/Na	$- 0.75^{**}$	-0.02	-0.15	0.23	-0.31	-0.49^{*}	-0.35	0.22	0.26	-0.21	0.30	0.25	0.14	1
TQ	-0.81^{***}	-0.36	0.15	0.51^{*}	-0.06	-0.71^{***}	-0.66^{**}	0.11	-0.20	-0.44^{*}	0.04	0.46^{*}	0.14	0.65^{***}

TQ= Turf quality, * Significant at $P \le 0.05$; ** Significant at $P \le 0.01$;
*** Significant at $P \le 0.001$

Table 3-3. Stepwise regression analysis of variables of leaf tissue mineral concentrations attributing to Kentucky bluegrass turf quality.

Variables[+]	Coefficient	Partial R^2	P value
Na	-0.00031	0.65	<0.001
Overall		0.65	

[+] Included all variables to meet 0.05 significance level to enter the final model; all the variables except Na were not significant at $p \leq 0.05$

Table 3-4. Comparison of Turf quality, sodium concentration in Kentucky bluegrass shoots and soil chemical properties between two groups of golf courses under different regiments of recycled water irrigation.

	City and County of Denver (10 years)	Thornton, Westminster and Aurora (10-21 years)	T-Test *P* value
Turf Quality	7.8	7.1	0.0013
Na in shoot (mg kg-^{1})	1427	3256.4	0.0005
Na in soil (meq/L)	5.4	28.1	0.06
Soil EC (dS m^{-1})	1.2	7.6	0.0217
Soil SAR (0-20cm)	3.5	9.4	0.0051
Ca (meq/L)	4.9	16.1	0.03
Mg (meq/L)	2.5	14.1	0.03
K (meq/L)	1.52	1.75	0.63
B (mg kg-^{1})	0.021	0.486	0.0002
P (mg kg-^{1})	20.1	9.7	0.015
Cl (mg kg-^{1})	4.51	2.94	0.033

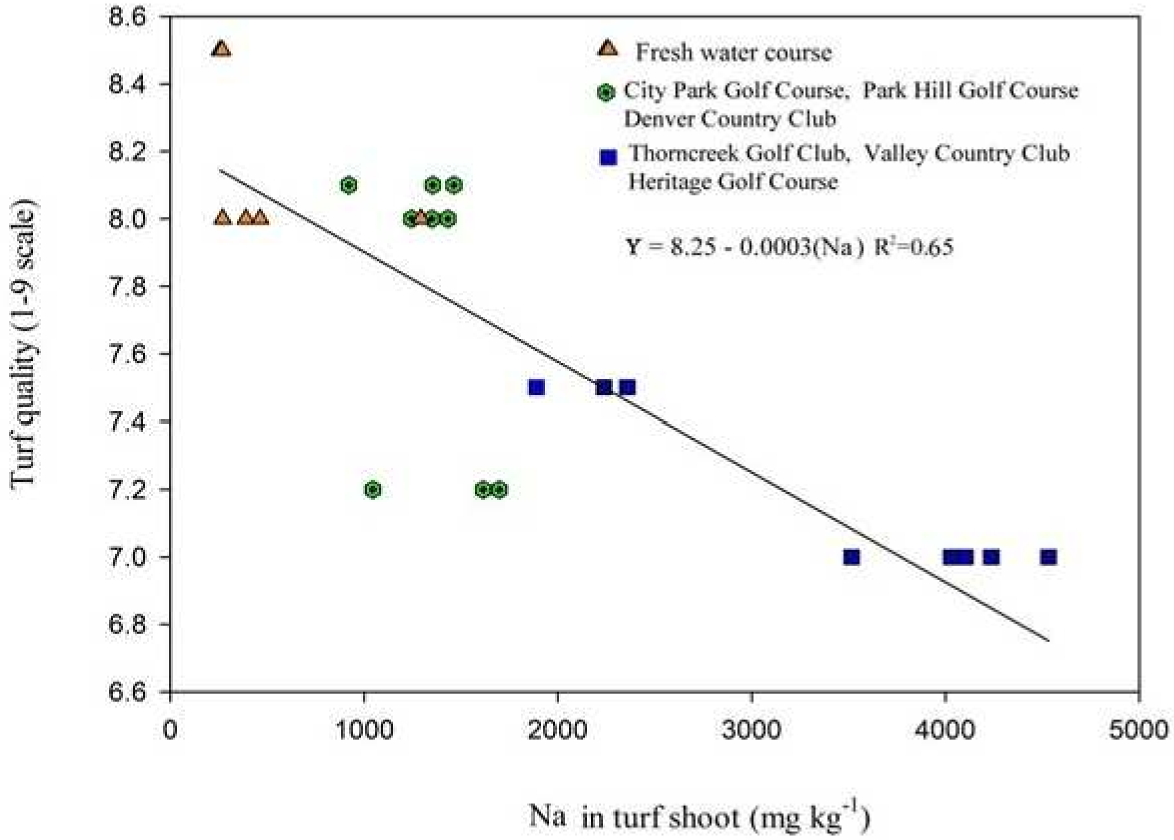

Figure 3-1. Regression analysis of shoot Na concentration to turf quality under three irrigation groups.

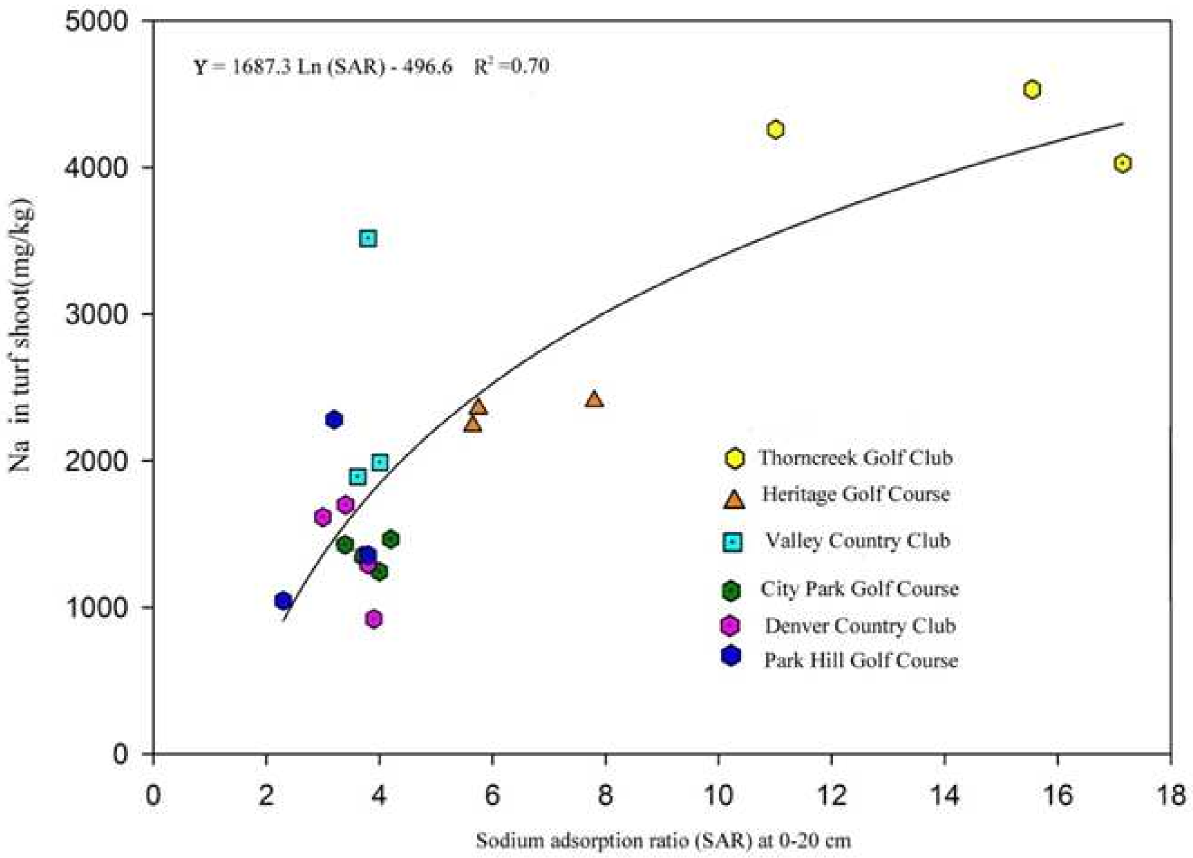

Figure 3-2. Logarithmic regression analysis of soil SAR (0-20cm) to corresponding turf shoot Na concentration under different recycled water irrigation groups.

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