

**Elemental chemistry
in semi-arid
landscapes by PXRF**

T. K. Udeigwe et al.

This discussion paper is/has been under review for the journal Solid Earth (SE).
Please refer to the corresponding final paper in SE if available.

Elemental quantification, chemistry, and source apportionment in golf course facilities in semi-arid urban landscape using portable x-ray fluorescence spectrometer

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Received: 10 November 2014 – Accepted: 16 November 2014 – Published: 6 January 2015

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

This study extends the application of the portable x-ray fluorescence (PXRF) spectrometry to examination of elements in semi-arid urban landscapes of the Southern High Plains (SHP) of the United States (US), focusing on golf courses. The complex environmental challenges of this region and the unique management practices at golf course facilities could lead to differences in concentration and chemistry of elements between managed (irrigated) and non-managed (non-irrigated) portions of these facilities. Soil samples were collected at the depths of 0–10, 10–20, and 20–30 cm from managed and non-managed areas of seven different facilities in the city of Lubbock, Texas, and analyzed for a suite of soil properties. Total elemental quantification was conducted using PXRF. Findings mostly indicated no significant differences in concentration of examined elements between the managed and non-managed areas of the facilities. However, strong positive relationships ($R^2 = 0.82$ – 0.91 , $p < 0.001$) were observed among elements (e.g. Fe and each of Cr, Mn, Ni, and As; Cu and Zn; As and Cr) and between these elements and soil constituents or properties such as clay, calcium carbonate, organic matter, and pH. The strengths of these relationships were mostly higher in the non-managed areas, suggesting possible alteration in the chemistry of these elements by anthropogenic influences. Principal component analyses (PCA) and correlation analyses within the managed areas suggested that As, Cr, Fe, Mn, and Ni could be of lithogenic origin, while Cu, Pb, and Zn were attributed to anthropogenic influences. Only one possible source of element, likely lithogenic, was identified within non-managed areas. As evidenced from the study, the PXRF can be a valuable tool for elemental quantification, and rapid investigation of elemental interaction and source apportionment in semi-arid climates.

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1 Introduction

Elemental contaminants vary in source, form, level, and fate within landscapes and various land uses, and are generally impacted by geological formations, climatic conditions, and anthropogenic influences (Kabata-Pendias, 2010). It is therefore important to conduct site-specific evaluations in any environmental quality assessment and remediation effort. In an attempt to overcome the lag time associated with conventional wet chemistry analyses, rapid quantification of contaminants using advanced technologies such as the portable x-ray fluorescence (PXRF) are gaining importance in the fields of soil and environmental sciences (Weindorf et al., 2012a; McWhirt et al., 2012; Gardner et al., 2013; Hu et al., 2014). The PXRF has been a valuable tool in the quantification of contaminants (Clark and Knudsen, 2014; Weindorf et al., 2012a, 2013b; Gardner et al., 2013), estimation of plant-nutrient elements (Zhu and Weindorf, 2009), development of predictive relationships for soil constituents (Weindorf et al., 2009, 2013b), identification of soil diagnostic features (Weindorf et al., 2012b), and soil reaction (pH) (Sharma et al., 2014). The exploration of its applications is continually growing in scope and in different environmental and climatic settings. This work is one such effort to extend the application of this tool in semi-arid regions (e.g., the Southern High Plains (SHP) of the United States), which are often confronted by challenges of extreme drought, wind erosion, soil salinization, etc. In this region lies important economic cities such as Lubbock which produces close to 25 % of US cotton (USDA-NASS, 2014), and Midland, currently known for intense oil exploration activities. Lubbock's climatic and environmental challenges are typical of those of the SHP and other semi-arid areas of the world (e.g., Spain, parts of northern Africa, Australia); generally characterized by high pH (mostly > 7.5) soils, and low precipitation (< 470 mm yr⁻¹) which limits soil contaminant leaching, thereby increasing the likelihood of their accumulation in soils. In addition to anthropogenic sources of soil contaminants such as agricultural activities, poor quality water from

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Ogallala aquifer, which supplies almost all the water needs of this area, is also causing serious environmental challenges (Scanlon et al., 2005).

Lately, growing unrest concerning depleted water quality in the Ogallala aquifer has also stirred concerns over the soil quality in irrigated fields and facilities in this region; especially irrigated facilities on urban landscapes such as golf courses because of their unique management practices. Such unique practices include perennial monoculture vegetation, less soil pulverization, extended irrigation windows, etc. Golf courses are one of the major users of irrigation water per unit area in this region. A typical 18-hole golf facility in the southwest US region could use an average of 1200 mm of water annually (USGA, 2012) compared to 600 mm for fully irrigated cotton in the same region (Snowden et al., 2013). With a rainfall total of approximately 470 mm yr^{-1} , most of the water needed for golf courses comes from groundwater sources. Thus, contaminants carried in the water will be more evident in areas more frequently irrigated (Udeigwe et al., 2013). In addition to contamination from irrigation sources, contaminants in agrochemicals such as fertilizers which carry traces of heavy metals of human health concern (Nziguheba and Smolders, 2008), will also be more evident under managed (irrigated and fertilized) conditions. Unfortunately, information on the extent of contamination, chemistry, and interactions of such contaminants in urban landscape facilities in semi-arid climates are not readily available.

The first approach to designing a remediation program for a polluted site is proper quantification of the pollutant level and identification of the possible sources. Usually, extensive soil sampling and laborious digestion techniques are required to quantify heavy metal concentration in soils. However, the advent and application of portable x-ray fluorescence (PXRF) spectrometry for heavy metal detection and quantification in soils can be a valuable tool for probing environmental contamination in different landscapes and land uses in semi-arid climates. In fact, several studies (e.g., Ge et al., 1997; Laiho and Perämäki, 2005) have noted that moisture is one factor that must be considered as a possible interference for high quality in situ PXRF readings; a variable with minimal impact in arid regions of West Texas. We hypothesize that differences

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“non-managed areas”. At each facility, a well-managed fairway and an adjacent poorly-managed fairway were identified and soil samples collected using a core sampler. At each area, 3–4 core samples (30 cm deep by 6 cm wide; diameter) were randomly collected and then separated into three depths of 0–10, 10–20, and 20–30 cm, which were then combined for each depth to obtain a representative sample. Soil samples were then air dried, ground, and passed through a 2 mm sieve. All sampling was conducted in June and July of 2013. All sampling sites were georeferenced using a global positioning system receiver (GPSmap 60CSx, Garmin, Olathe, KS, USA).

2.3 Soil characterization

Soil samples were analyzed for electrical conductivity (EC) and pH in 1 : 2 solid (soil) to water suspension (Rhoades et al., 1996); organic matter (OM) by the modified Walkley and Black method (using sodium dichromate and read on Gilford unit) (Nelson et al., 1996); and calcium carbonate percentage (CaCO₃) using the tensimeter method (a modification of the pressure calcimeter approach) (Loeppert and Suarez, 1996; Soil Survey Staff, 1996). Particle size distribution was determined using the hydrometer method (Gee et al., 1986).

2.4 Elemental quantification: PXRF

Soil samples were scanned using a DP-6000 Delta Premium PXRF (Olympus, Waltham, MA, USA) per US EPA Method 6200 (USEPA, 2007). The PXRF is equipped with a Rh-X-ray tube which is operated at 10–40 kV with integrated silicon drift detector (165 eV). It was operated in *Soil Mode* to measure the following elements: As, Ca, Cu, Cl, Cr, Fe, K, Mn, Ni, Pb, S, and Zn. This mode consists of three beams operating sequentially, each set to scan for 30 s for a total scan time of 90 s per sample. Calibration of the instrument was conducted before sample analysis using a 316 alloy clip tightly fitted over the aperture. Each soil sample was scanned in triplicate with PXRF unit repositioned between scans such that an average value was reported.

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Elemental concentration data and limit of detection (LOD) (three times the standard error) for each element were obtained and compiled.

2.5 Statistical analyses

Mean values for each location (managed or non-managed) were obtained by using the averages of the three depths. All statistical analyses were performed using the Statistical Analysis Software (SAS 9.3, SAS Institute, Cary, NC). Mean differences were examined using PROC GLM. Single and multiple linear regression analyses to establish the relationships among elements and between elements and soil constituents were performed using the PROC REG procedure. Principle component analysis (PCA), used in evaluating potential sources of heavy metals and other trace elements of interest, was performed using PROC FACTOR.

3 Results and discussions

3.1 Fundamental soil chemical properties

Table 1 summarizes the pH, OM, EC, and selected nutrient elements in managed and non-managed areas of each investigated facility. Soil pH was generally > 7.9 with small to no difference between managed and non-managed areas, suggesting that pH was not strongly influenced by management practices. Differences in soil OM and percent CaCO_3 were noted between the two areas, despite not being significant. The higher soil OM observed in the managed areas could be attributed to higher biomass induced by management practices. Electrical conductivity ($p < 0.05$ in five facilities), S ($p < 0.05$ in two facilities) and Cl ($p < 0.05$ in five facilities) were consistently higher in the managed areas of facilities examined; indicating the influence of irrigation water quality and fertilization. Total K and Ca quantified by PXRf, although mostly non-significantly different, tended to be higher in the non-managed areas, in four out of seven and five

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out of seven facilities, for K and Ca, respectively. One notable finding is that PXRF-measured Ca predicted over 92 % ($p < 0.001$) of the variability associated with CaCO_3 . This finding supports those of Zhu and Weindorf (2009) and suggests that this tool can be used to approximate calcite in semi-arid soils.

3.2 Heavy metals and As

Findings on heavy metals and As in the managed and non-managed areas of each facility are summarized in Table 2. Majority of the observed differences between managed and non-managed areas were not significant. Copper (range = 7.90–25.6 mg kg^{-1} ; mean = 14.2 mg kg^{-1} ; $n = 42$) and Zn (16.7–139; 48.0; $n = 42$) were higher in the managed areas of five facilities (AF, CF, DF, FF, and GF), while As (3.50–14.0; 6.08; 42), Cr (10.0–59.0; 28.3; 42), and Pb (6.30–61.2; 17.2; 42) were higher in managed areas of four of the facilities (AF, DF, FF, and GF). Nickel (12.0–54.0; 31.8; 42) and Mn (83.0–470; 229; 42) were higher in the managed areas of three of the facilities (AF, CF, and GF); the same with Fe (6148–26 093; 12 841; 42) for AF, DF, and GF. Although not significant, the findings suggest a degree of association among the metals. These associations show evidence of the interactions of these elementals with other soil constituents such as clay, CaCO_3 , OM, and will be further examined in Sect. 3.3. Among facilities, the managed areas of GF, were higher in all the elements examined ($p < 0.05$ for Cr, Mn, and Fe). The higher concentration of these elements in the managed areas of the GF facility could be attributed to the mean clay content (46 %) at this site, which was the highest among all the managed sites. As will be discussed later (Sect. 3.3), clay exhibited a significant positive interaction with all the examined elements; a finding that has been considerably documented (Sparks, 2003; Sposito, 2008; Eze et al., 2010).

The distribution of each element between managed and non-managed areas was further examined within the depths of 0–10, 10–20, and 20–30 cm. Thus, all the managed areas were grouped and compared against the non-managed areas at each

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depth for each of the elements. However, there was no consistent and substantial difference between managed and non-managed areas within depths (data not shown).

3.3 Chemistry of elements: interactions among elements and between elements and soil constituents elements

5 Although interactions among elements and between elements and soil constituents have been widely documented (Yu et al., 2001; Biasioli et al., 2006; Micó et al., 2006; Jørgensen and Jensen, 2009; Eze et al., 2010), extrapolation of these findings in different environmental settings can be difficult due to soil heterogeneity. Such interactions can vary with environmental and climatic variables as well as the presence
10 of other soil constituents. As a result, site specific evaluation of these interactions is often an invaluable resource for source allocation of pollutant and remediation purposes. The summary of the relationships among the examined elements when all data points ($n = 42$) from managed and non-managed areas were considered is presented in Table 3. The strongest relationships were between Fe and Cr ($R^2 = 0.91$, $p < 0.001$), Mn ($R^2 = 0.89$, $p < 0.001$), Ni ($R^2 = 0.82$, $p < 0.001$), and As ($R^2 = 0.86$, $p < 0.001$), as well as between Cu and Zn ($R^2 = 0.82$, $p < 0.0001$), and As and Cr ($R^2 = 0.87$, $p < 0.001$). The weakest relationships were between Ni and Zn ($R^2 = 0.34$, $p < 0.028$), and Ni and Pb ($R^2 = 0.40$, $p < 0.009$). One striking finding here is that, when the managed and non-managed sites were analyzed separately and compared,
20 the strengths of these relationships were generally higher in the non-managed areas (Table 4). Most notable differences were between Cr and Zn (R^2 of 0.88 vs. 0.35), Cr and Pb (R^2 of 0.83 vs. 0.36), Pb and Mn (R^2 of 0.78 vs. 0.46), Pb and Ni (R^2 of 0.61 vs. 0.17), and Pb and As (R^2 of 0.80 vs. 0.24). These differences can be attributed to the influence of anthropogenic sources in the managed areas which possibly altered the natural background relationships among these elements. Interactions among metals
25 have been documented in different landscapes, land uses, and environmental media (Tkalin et al., 1996; Li et al., 2000; Facchinelli, 2001; Dragović et al., 2008; Eze

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et al., 2010), although the strengths of these interactions often vary. Such variability necessitates the need for site-specific investigations as presented in this study.

The interactions between the examined elements and the soil constituents such as carbonates, OM, clay, and pH are summarized for all data points (managed and non-managed) in Table 5. Of interest, with the exception of Zn, clay significantly ($p < 0.001$, $R^2 > 0.86$) controls the distribution of these elements in semi-arid landscapes; an interaction that has been previously documented (Bradl, 2004; Sparks, 2003). This association is partly attributed to the abundance of negatively charged sites created by clay minerals, high surface area, and thus, high adsorption capacity for metals (Sparks, 2003; Sposito, 2008). Among other soil constituents, significant positive correlations were also observed between OM and each of Cu, Pb, Mn, and Zn ($R^2 = 0.40$ – 0.70 , $p < 0.01$) as well as between CaCO_3 and each of Ni and As ($R^2 > 0.41$ – 0.42 , $p < 0.01$). Soil OM contains functional groups such as enol, phenol, and carboxyl, that in their deprotonated forms have high a affinity for metal ions (Sparks, 2003; Sposito, 2008). Also humic substances form a strong complex with clay which will enhance its interaction with metal ions (Evangelou, 1998), explaining some of the strong OM-clay-metal interactions observed (Table 6). One notable finding was that all the elements, with the exception of Ni, showed a significant negative relationship with pH ($R^2 = 0.31$ – 0.62 , $p = 0.004$ – < 0.001), an indication that metal retention onto these soils decreases with pH (within the pH range of 7.7–8.8) (Table 5). Metal adsorption generally increases within a narrow pH range (adsorption edge) where sorption is maximized (Sposito, 2008). As evidenced from this study, the pH range of 7.7–8.8 observed for these soils could be outside the adsorption edge for the examined elements. Thus, the negative relationships observed between these elements and pH. Of interest, when the managed and non-managed sites were analyzed separately, it was observed that the strengths of these relationships (i.e., elements vs. each of OM, CaCO_3 , and clay) were notably higher in the non-managed areas compared to the managed areas (Table 6). The major contrast here was the relationship between % CaCO_3 and the elements which was highly significant ($R^2 = 0.51$ – 0.75 , $p = 0.01$ – 0.001) for all the

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elements in the non-managed area but almost none existed in the managed area. These strong relationships could be an indication that these elements are naturally bound to carbonates in calcareous (average of 2.94 %) soils of the SHP; a situation not evident in the managed areas because of potential anthropogenic influences which can alter these natural background relationships.

Information on these interactions within urban landscapes in this region has not been widely documented and as such, reference materials on this subject area are scarce. As will be shown later (Sect. 3.4), these relationships find usefulness in pollutant source allocation (Facchinelli, 2001; Yu et al., 2001; Jørgensen and Jensen, 2009; Eze et al., 2010) and environmental remediation purposes (García-Sánchez et al., 1999; Hartley and Lepp, 2008; Kabata-Pendias, 2010). For instance, the strong affinity of Fe for As as evidenced from the findings here, is often characterized as an inner-sphere complexation (Sparks, 2003; Sposito, 2008). This suggests that Fe-containing materials can be used to immobilize As in these soils. The same can also be said for the other heavy metals such as Cr and Ni, which also exhibited strong interaction with Fe. Typically, heavy metal fractionation identifies different pools of metals such as easily exchangeable, Fe/Mn oxide-bound fraction, carbonate-bound fraction, and OM-bound fraction (Sposito et al., 1982; Tack and Verloo, 1995; McLaren and Clucas, 2001). Thus, the strong relationship observed between Fe/Mn and the heavy metals, Cr and Ni, could suggest that a significant portion of these metals are in the Fe and Mn oxide-bound fraction at the examined sites. Likewise, the stronger relationships between the examined elements (heavy metals and As) and CaCO_3 in the non-managed areas suggest that a significant pool of these elements are bound to carbonates. In summary, the examination of the chemistry and interactions among elements and between elements and soil constituents indicated that the nature and strengths of the relationships vary within managed and non-managed areas of the golf course facilities examined. This can be attributed to management practices such as irrigation, fertilization, addition of other soil amendments and agrochemicals, and surface soil modifications, which constitute anthropogenic influences that can temporally alter the

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natural background relationships among these elements, and thus, their chemistry and interactions.

3.4 Source apportionment

With the findings obtained from the PXRF quantification of the heavy metals and As, an attempt was made to define the sources of these contaminants at the examined facilities. Pollutant source apportionment was conducted individually within managed (irrigated) and non-managed (non-irrigated) areas, as well as both areas combined, with the aid of principal component analysis (PCA) and the correlation matrix discussed under Sect. 3.3. The PCA is a tool commonly used in geochemical applications to define pollutant sources, mostly natural vs. anthropogenic sources (Facchinelli, 2001; Micó et al., 2006; Eze et al., 2010).

The PCA loading plots of elements examined at the seven golf facilities are presented in in Fig. 2. The critical eigenvalue of 1 was used for each analysis. For the managed site, only the first two components with an eigenvalue > 1 were retained. The elements were grouped into a two-component model that accounted for 88 % of the variation. For the managed (irrigated) areas ($n = 21$), it was evident that As, Cr, Fe, Mn, and Ni were associated with the F1 component, while Cu, Pb, and Zn were associated with the F2 component. These associations indicated two different possible pollutant sources. The strong positive relationships ($R^2 = 0.76-0.94$, $p < 0.001$) observed between Fe and the rest of the F1 elements within the managed site (Table 4), an association often used to distinguish natural levels of trace elements from anthropogenic ones (Facchinelli, 2001; Micó et al., 2006; Eze et al., 2010), suggest that the F1 component (As, Cr, Fe, Mn, and Ni) could be of lithogenic origin. This implies that the concentrations of the elements are probably controlled by soil parent materials. Thus, the F2 component (Cu, Pb, and Zn) possibly has an anthropogenic influence (e.g. fertilization). A major highlight of the finding was that for the non-managed sites ($n = 21$), using the eigenvalue of 1, only one factor that explained 83 % of the variation was extracted. This finding suggests that the examined elements within the non-managed sites could be of one source, possibly,

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lithogenic. This is a significant finding that supports the hypothesis that management practices can be a potential source of pollutant inputs at these facilities. Furthermore, PCA analysis of the elemental composition of soils from the combined sites (managed and non-managed) extracted two components, F1 (As, Cr, Fe, Mn, and Ni) and F2 (Cu, Pb, and Zn) that explained 85%, a finding similar to that of the managed site, suggesting that overall, background contaminant levels within the entire study area have anthropogenic influences. The total elemental concentration values suggested that the concentration of the commonly cited heavy metals (Cr, Cu, Ni, and Pb) in the soils at these facilities were within the maximum permissible concentration (MPC) in soils set by the United State Environmental Protection Agency (USEPA) and European Commission (Kabata-Pendias, 2010; Selinus et al., 2013).

4 Conclusions

The quantification and identification of possible sources of environmental contaminants are often the first conscious steps taken toward any environmental protection effort. This work extends the application of the PXRf to rapid probing of contaminants in the semi-arid soils of the SHP, US, an area confronted by complex environmental challenges. It was hypothesized that limited rainfall and leaching, poor groundwater quality, and unique management practices can affect the concentration, chemistry, and sources of contaminants in urban landscape facilities such as golf courses in the semi-arid climate. Although the investigation of heavy metals (Cr, Pb, Ni, Cu, Mn, Fe, and Zn) and As revealed little differences between the managed and non-managed areas of these facilities, however, findings show possible associations among elements. Strong relationships and interactions were observed among the elements examined and between elements and soil constituents such as % clay, CaCO₃, OM, and pH. Of interest, the strengths of these relationships were mostly higher in the non-managed area, an indication of the alteration of the chemistry of these elements by anthropogenic influences. Evidence gathered from PCA and correlation analyses

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within the managed area suggested that As, Cr, Fe, Mn, and Ni could be of lithogenic origin, while Cu, Pb, and Zn could possibly have anthropogenic influences. Within the non-managed sites, only one source of contaminant, possibly lithogenic, was identified. Most of the heavy metals examined within the facilities were within the MPC set by the USEPA and EU. The findings helps to understand the interactions of soil contaminants in the urban landscape in this semi-arid region, which is currently an area of environmental research focus, and provides a background information for future studies and remediation programs. Findings could also be extended to other semi-arid and arid regions of the world.

Author contributions. T. K. Udeigwe, and J. Young, initiated the study. T. Kandakji assisted in field and laboratory activities. M. A. Mahmoud and H. M. Stietiya suggested ideas and assisted in various aspect of the project as needed. D. C. Weindorf assisted with portable x-ray fluorescence (PXRF) spectrometer and manuscript proofreading.

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Table 1. Summary of selected soil chemical and physical properties, and nutrient elements at the managed and non-managed areas of the golf course facilities examined in Lubbock, TX, USA*.

Golf facility	Management	pH	CaCO ₃		EC	S	Cl	K	Ca	Clay
			%							
AF	M	8.2a	1.5a	1.1a	445a	1804a	145a	11 729a	9654a	21a
	N	8.1a	0.7a	0.2b	199b	1287a	133a	11 275a	5098a	21a
BF	M	8.3b	1.0a	8.8a	1561a	2542a	677a	14 700a	52 738a	30a
	N	8.4a	0.5a	4.5a	417b	1467b	78.0b	15 915a	33 205a	37a
CF	M	8.2b	1.2a	1.9a	1187a	1997a	582a	14 172b	10 137a	29a
	N	8.5a	0.5a	1.2a	219b	1273b	0.0b	15 800a	10 233a	29a
DF	M	8.6a	0.8a	0.5a	426a	1354a	265a	10 502a	5409a	20a
	N	8.6a	0.3a	0.7a	221b	1179a	154b	9310a	10 796a	17a
EF	M	8.2a	1.1a	4.6a	815a	2046a	342a	11 990b	28 090a	23b
	N	7.9a	1.3a	6.4a	699a	1910a	73.7b	18 594a	36 222a	46a
FF	M	8.0a	1.3a	0.7a	991a	2015a	521a	13 119a	13 335a	22a
	N	8.1b	0.9a	1.6a	605a	1507a	337a	14 501a	16 051a	27a
GF	M	8.1a	1.5a	4.2a	810a	1874a	293a	20 820a	32 476a	46a
	N	8.3a	0.7a	4.7a	409b	1318a	95.7b	15 808b	32 575a	36b

* M, managed area; N, non-managed area; CaCO₃, calcium carbonate equivalent; EC, soil electrical conductivity. Mean values in a column within a golf course with the same letter are not statistically different (Fisher's LSD, $\alpha = 0.05$).

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Table 2. Summary of heavy metals and As quantified at the managed and non-managed areas of the golf course facilities in Lubbock, TX, USA*.

Golf facility	Management	As	Cr	Pb	Ni	Cu	Zn	Mn	Fe
		mg kg ⁻¹							
AF	M	4.9a	22.7a	13.7a	26.3a	11.5a	36.6a	205a	10 638a
	N	4.07a	19.3a	10.8a	25.0a	8.70a	24.8a	157a	8985a
BF	M	6.80a	25.3a	12.5a	31.0a	11.4b	39.3a	175b	11 428b
	N	7.90a	33.3a	13.2a	37.0a	15.2a	40.7a	217a	15 493a
CF	M	5.70b	29.7a	13.4b	34.7a	16.1a	74.0a	279a	12 917b
	N	7.00a	34.3a	17.2a	32.7a	14.1a	41.2a	271a	14 463a
DF	M	4.47a	16.7a	8.67a	19.3a	9.37a	26.5a	126a	9322a
	N	4.10a	15.3a	7.93a	26.0a	8.77a	19.3a	154a	7356a
EF	M	4.70a	22.0b	20.1b	30.7b	11.2b	55.5a	184b	9297b
	N	9.83a	48.0a	43.6a	45.7a	21.1a	83.0a	346a	20 963a
FF	M	4.70a	28.0a	26.3a	25.0a	20.6a	74.0a	202a	10 676a
	N	4.67a	23.3b	14.3a	28.0a	12.2a	37.7a	225a	11 280a
GF	M	10.47a	48.3a	21.3a	45.7a	22.3a	76.7a	425a	22 734a
	N	5.77a	29.7b	15.6a	38.0a	15.6a	42.7a	239b	14 226b

* M, managed area; N, non-managed area.

Mean values in a column within a golf course with the same letter are not statistically different (Fisher's LSD, $\alpha = 0.05$).

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Table 3. Correlation matrix of the elements in all soil samples (managed and non-managed) from the golf course facilities examined in Lubbock, TX, USA ($n = 42$).

	Cr	Mn	Fe	Ni	Cu	Zn	As	Pb
Cr								
Mn	0.85 ^c							
Fe	0.91 ^c	0.89 ^c						
Ni	0.77 ^c	0.68 ^c	0.82 ^c					
Cu	0.72 ^c	0.75 ^c	0.78 ^c	0.60 ^c				
Zn	0.50 ^c	0.65 ^c	0.56 ^c	0.34 ^a	0.82 ^c			
As	0.87 ^c	0.77 ^c	0.86 ^c	0.71 ^c	0.60 ^c	0.48 ^b		
Pb	0.65 ^c	0.59 ^c	0.57 ^c	0.40 ^b	0.66 ^c	0.68 ^c	0.58 ^c	

^a Significant at 0.05 probability level; ^b significant at 0.01 probability level;
^c significant at 0.001 probability level.

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Table 4. Correlation matrix of the elements in soils for managed (bold) and non-managed sites of the golf course facilities examined in Lubbock, TX, USA ($n = 21$).

		Managed							
		Cr	Mn	Fe	Ni	Cu	Zn	As	Pb
Non-Managed	Cr		0.86^c	0.92^c	0.79^c	0.69^c	0.35	0.83^c	0.36
	Mn	0.87 ^c		0.94^c	0.73^c	0.76^c	0.61^b	0.81^c	0.46^a
	Fe	0.90 ^c	0.84 ^c		0.76^c	0.69^c	0.44^a	0.93^c	0.33
	Ni	0.76 ^c	0.63 ^b	0.90 ^c		0.44	0.20	0.76^c	0.17
	Cu	0.82 ^c	0.74 ^b	0.95 ^c	0.94 ^c		0.81^c	0.57^b	0.75^c
	Zn	0.88 ^c	0.84 ^c	0.92 ^c	0.81 ^c	0.89 ^c		0.36	0.69^c
	As	0.90 ^c	0.74 ^c	0.80 ^c	0.66 ^b	0.67 ^c	0.78 ^c		0.24
Pb	0.83 ^c	0.78 ^c	0.75 ^c	0.61 ^b	0.70 ^c	0.92 ^c	0.80 ^c		

^a Significant at 0.05 probability level; ^b significant at 0.01 probability level; ^c significant at 0.001 probability level.

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Table 5. Correlations coefficients of the relationships between elements and other soil constituents for all soil samples (managed and non-managed) from the golf course facilities examined in Lubbock, TX, USA ($n = 42$). Values in bold indicate inverse relationship.

	OM	CaCO ₃	Clay	pH
Cr	0.24	0.37	0.86 ^c	0.43^b
Mn	0.40 ^b	0.18	0.75 ^c	0.50^c
Fe	0.25	0.32 ^a	0.91 ^c	0.38^b
Ni	0.09	0.42 ^b	0.88 ^c	0.15
Cu	0.43 ^b	0.20	0.65 ^c	0.50^c
Zn	0.70 ^c	0.21	0.39 ^a	0.61^c
As	0.30	0.41 ^b	0.79 ^c	0.31^a
Pb	0.49 ^c	0.29	0.46 ^b	0.63^c

^a Significant at 0.05 probability level; ^b significant at 0.01 probability level; ^c significant at 0.001 probability level.

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Table 6. Correlations coefficients of the relationships between elements and other soil constituents within managed and non-managed sites of the golf course facilities in Lubbock, TX, USA ($n = 21$). Values in bold indicate inverse relationship.

	Managed				Non-Managed			
	OM	CaCO ₃	Clay	pH	OM	CaCO ₃	Clay	pH
Cr	0.15	0.17	0.88 ^c	0.45^a	0.53 ^a	0.69 ^c	0.86 ^c	0.44^b
Mn	0.41	0.02	0.79 ^c	0.53^b	0.49 ^a	0.51 ^a	0.74 ^c	0.48^a
Fe	0.28	0.11	0.88 ^c	0.39	0.37	0.70 ^c	0.95 ^c	0.39
Ni	0.13	0.28	0.83 ^c	0.10	0.18	0.74 ^c	0.93 ^c	0.26
Cu	0.47 ^a	0.06	0.50 ^a	0.63^b	0.30	0.72 ^c	0.94 ^c	0.31
Zn	0.69 ^c	0.02	0.23	0.65^b	0.65 ^b	0.75 ^c	0.85 ^c	0.58^b
As	0.24	0.22	0.85 ^c	0.32	0.53 ^a	0.72 ^c	0.75 ^c	0.33
Pb	0.48 ^a	0.08	0.14	0.70^c	0.79 ^c	0.69 ^c	0.66 ^b	0.64^b

^a Significant at 0.05 probability level; ^b significant at 0.01 probability level; ^c significant at 0.001 probability level.

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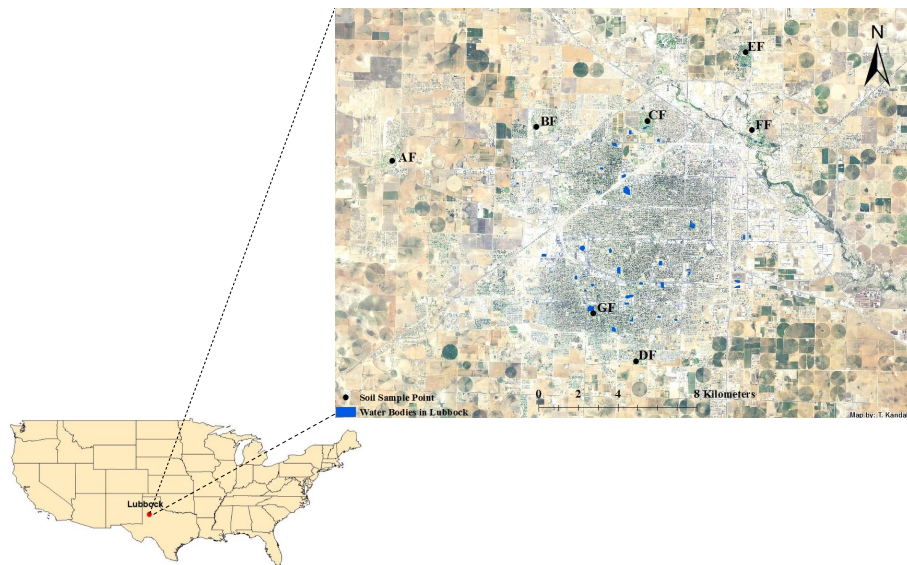


Figure 1. Map showing the seven golf facilities examined in Lubbock, TX, USA. The facilities are designated as AF, BF, CF, DF, EF, FF, and GF.

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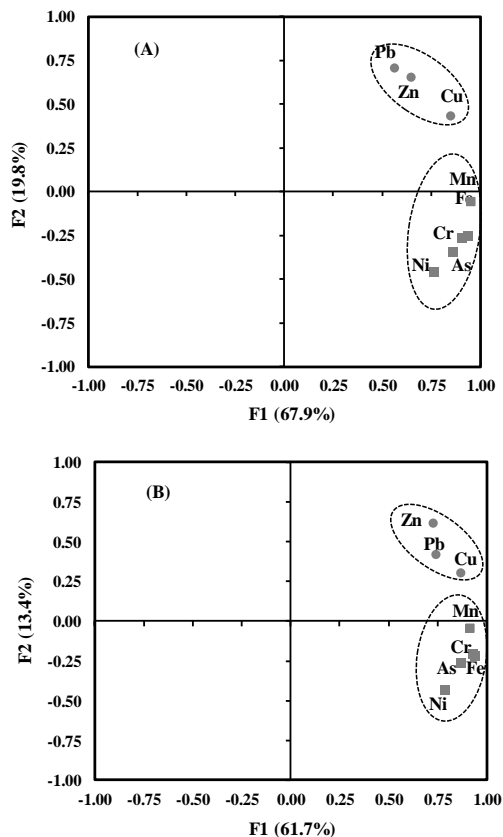


Figure 2. Principle component analysis loading plots of elements in soils of the golf course facilities in Lubbock, TX, USA for (a) managed site only and (b) managed and non-managed sites combined. Only two factors were extracted and interpreted.

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