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

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Abstract. This study extends the application of the portable X-ray fluorescence (PXRF) spectrometry to the examination of elements in semi-arid urban landscapes of the Southern High Plains (SHP) of the United States, 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 in the chemistry of elements between managed (irrigated) and non-managed (non-irrigated) portions of these facilities. Soil samples were collected at 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 a PXRF spectrometer. Findings mostly indicated no significant differences in the concentration of examined elements between the managed and non-managed areas of the facilities. However, strong positive relationships ($R = 0.82 - 0.91$, $p < 0.001$) were observed among elements (e.g., Fe on the one hand and Cr, Mn, Ni, and As on the other; 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 a possible alteration in the chemistry of these elements by anthropogenic influences in the managed areas. Principal component 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 could have anthropogenic influences. Only one possible, likely lithogenic, source of the elements was identified within the non-managed areas. As evidenced by the study, the PXRF spectrometer can be a valuable tool for elemental quantification and rapid investigation of elemental interaction and source apportionment in semi-arid climates.

1 Introduction

Inorganic pollutant contamination of soil and water is an issue of concern worldwide with regard to the environment and human health (Vacca et al., 2012; Roy and McDonald, 2015). Elemental contaminants vary in source, form, level, and fate within landscapes and various land uses, and they 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, the rapid quantification of contaminants using advanced technologies, such as portable X-ray fluorescence (PXRF) spectrometry, is 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). PXRF spectrometry has been a valuable tool in the quantification of contaminants (Clark and Knudsen, 2014; Weindorf et al., 2012a, 2013b; Gardner et al., 2013), the estimation of plant-nutrient elements (Zhu and Weindorf, 2009), the development of pre-

dictive relationships for soil constituents (Weindorf et al., 2009, 2013b), the 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. The rapid quantification of elemental contaminants, a benefit offered by PXRF spectrometry, is important in ensuring faster tracking of contaminants, which will facilitate their containment, thus reducing the risk of entry into the food chain. This work is one such effort to extend the application of this tool to semi-arid regions (e.g., the Southern High Plains (SHP) of the United States), which are typically confronted by challenges of extreme drought, wind erosion, soil salinization, etc. In this region lie economically important 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, and 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 its accumulation in soils. In addition to anthropogenic sources of soil contaminants such as agricultural activities, poor-quality water from the Ogallala Aquifer, which covers almost all the water needs of this area, is also leading to serious environmental challenges (Scanlon et al., 2005).

Lately, growing unrest concerning depleted water quality in the Ogallala Aquifer has also raised concerns regarding the soil quality in irrigated fields and facilities in this region, especially irrigated facilities in urban landscapes such as golf courses because of their unique management practices. Such unique practices include perennial monoculture vegetation, less soil pulverization, and extended irrigation windows. 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 southwestern 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}, the majority of the water needed by 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 that may endanger human health (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 is not readily available.

The first approach to designing a remediation program for a polluted site is a 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 of portable X-ray fluorescence (PXRF) spectrometry and its application to heavy metal detection and quantification in soils can be of immense importance 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 in high-quality in situ PXRF readings; this is a variable with minimal impact in arid regions of west Texas. We hypothesize that differences exist in the level and chemistry of elemental contaminants between managed (irrigated) and non-managed (non-irrigated) zones of golf course facilities in this region, due to limited rainfall and leaching, poor groundwater quality, and the unique management practices of golf courses found in semi-arid climates. As such, the objectives of this study were to apply PXRF spectrometry to the (1) quantification of the differences in the concentration and chemistry (interactions among elements and between elements and soil constituents) of elemental contaminants and (2) examination and source apportionment of these elements among managed and non-managed areas of golf courses in a semi-arid region.

2   Materials and methods

2.1   Study location and site description

This study was conducted in the city of Lubbock, situated in the western part of Texas ($33°34'0''$ N, $101°53'0''$ W; 990 m a.s.l. (USGS, 2014)). Seven golf course facilities, spread throughout Lubbock, each with an average 10–12 ha of irrigated fairways, were selected that met the objectives of this study. The locations of the selected facilities are shown in Fig. 1 and are designated AF, BF, CF, DF, EF, GF, and HF. Each facility has been managed for at least 12 years. Soil types at the study sites included the Amarillo (fine-loamy, mixed, superactive, thermic Aridic Paleustalfs) and Acuff (fine-loamy, mixed, superactive, thermic Aridic Paleustolls) series (Soil Survey Staff, 2014). Managed fairways were generally planted with hybrid Bermuda grass (*Cynodon dactylon* (L.) Pers. × *C. transvaalensis* Burtt-Davy), while non-managed areas of the facilities were composed of either bare soil, poorly managed grass cover, or native vegetation and were generally not irrigated.

2.2   Soil sampling and handling

Fairways that are consistently irrigated were designated "managed areas", whereas non-irrigated and non-managed adjacent areas of similar soil types were designated "non-managed areas". At each facility, a well-managed fairway and an adjacent poorly managed fairway were identified, and
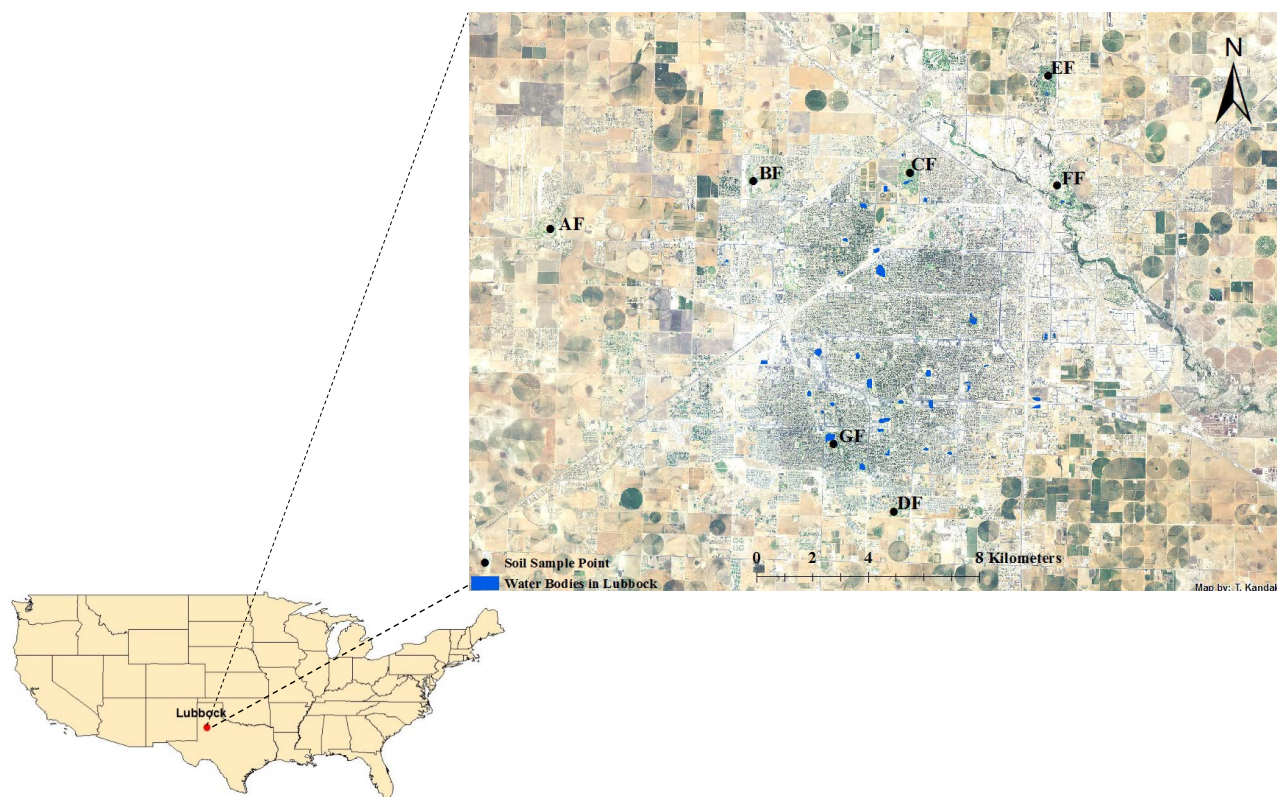
Figure 1. Map showing the seven golf facilities examined in Lubbock, Texas, USA. The facilities are designated AF, BF, CF, DF, EF, FF, and GF.

soil samples were collected using a core sampler. In 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) was determined by the modified Walkley and Black method (using sodium dichromate and read on a Gilford unit) (Nelson et al., 1996), and calcium carbonate percentage ($CaCO_3$) was determined 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 spectrometry

Soil samples were scanned using a DP-6000 Delta Premium PXRF spectrometer (Olympus, Waltham, MA, USA) per USEPA Method 6200 (USEPA, 2007). The PXRF instrument is equipped with a Rh X-ray tube, which is operated at 10–40 kV with an integrated silicon drift detector (165 eV). The instrument was operated in Soil Mode. This mode consists of three X-ray beams operating sequentially, each set to scan for 30 s for a total scan time of 90 s. The beams ensure full coverage of elemental detection, with each beam or combination of beams detecting different groups of elements. The 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 the PXRF unit repositioned between scans such that an average value was reported. The elements measured include As (manufacturer's suggested limit of detection: < 5 ppm), Ca (< 50 ppm), Cu (< 10 ppm), Cl (< 200 ppm), Cr (< 10 ppm), Fe (< 10 ppm), K (< 50 ppm), Mn (< 10 ppm), Ni (< 10 ppm), Pb (< 5 ppm), S (< 200 ppm), and Zn (5 ppm). Relative percentage differences between two replicates were generally less than 10. Elemental concentration data and the limit of detection (LOD) (3 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 given above. 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. Principal 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 soil pH, OM, EC, and selected nutrient elements in managed and non-managed areas of each investigated facility. Soil pH was generally > 7.9 with a 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 percentage of $CaCO_3$ 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. Soil EC ($p < 0.05$ 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 spectrometry, although mostly non-significantly different, tended to be higher in the non-managed areas, in four out of seven and five 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. The majority of the observed differences between managed and non-managed areas were not significant. Copper and Zn were higher in the managed areas of five facilities (AF, CF, DF, FF, and GF), while As, Cr, and Pb were higher in the managed areas of four of the facilities (AF, DF, FF, and GF) (Table 2). Nickel and Mn were higher in the managed areas of three of the facilities (AF, CF, and GF); the same was the case for Fe for AF, DF, and GF (Table 2). Although not significant, the findings suggest a degree of association among the metals. These associations show evidence of the interac-

tions of these elementals with other soil constituents, such as clay, $CaCO_3$, and 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 extensively 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 with the non-managed areas at each 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

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), extending these findings to different environmental and climatic settings can be misleading due to soil heterogeneity. Such interactions can vary with environmental and climatic variables as well as with the presence and proportion of other soil constituents. As a result, the site-specific evaluation of these interactions is often an invaluable resource for the source allocation of pollutant and remediation purposes. The summary of the correlations 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 ($R = 0.91$, $p < 0.001$), Mn ($R = 0.89$, $p < 0.001$), Ni ($R = 0.82$, $p < 0.001$), and As ($R = 0.86$, $p < 0.001$), as well as between Cu and Zn ($R = 0.82$, $p < 0.0001$) and between As and Cr ($R = 0.87$, $p < 0.001$). The weakest relationships were between Ni and Zn ($R = 0.34$, $p < 0.028$) and between Ni and Pb ($R = 0.40$, $p < 0.009$). One striking finding here is that, when the managed and non-managed sites were analyzed separately and compared, the strengths of these relationships were generally greater in the non-managed areas (Table 4). The most notable differences were between Cr and Zn (R of 0.88 vs. 0.35), Cr and Pb (R of 0.83 vs. 0.36), Pb and Mn (R of 0.78 vs. 0.46), Pb and Ni (R of 0.61 vs. 0.17), and Pb and As (R 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 have been documented in different landscapes, land uses, and environ-

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

Golf facility	Management	pH	OM	CaCO$_3$	EC	S	Cl	K	Ca	Clay
				%	µs cm^{-1}			mg kg^{-1}		%
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; CaCO$_3$ – 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, $\alpha = 0.05$).

Table 2. Summary of heavy metals and As quantified using the PXRF spectrometer in the managed and non-managed areas of the golf course facilities in Lubbock, Texas, 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, $\alpha = 0.05$).

mental media (Tkalin et al., 1996; Li et al., 2000; Facchinelli, 2001; Dragovic et al., 2008; Eze 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

Table 3. Correlation matrix of the elements in all soil samples (managed and non-managed) from the golf course facilities examined in Lubbock, Texas, 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.

Table 4. Correlation matrix of the elements in soils for managed (bold) and non-managed sites of the golf course facilities examined in Lubbock, Texas, 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.

summarized for all data points (managed and non-managed) in Table 5. Of interest, with the exception of Zn, clay significantly ($R > 0.86$, $p < 0.001$) controls the distribution of these elements, an interaction that has been documented previously (Bradl, 2004; Sparks, 2003). This association is partly attributed to the abundance of negatively charged sites and high surface area created by clay minerals and, thus, high adsorption capacity for metals (Sparks, 2003; Sposito, 2008). Among other soil constituents, significant positive correlations were also observed between OM on the one hand and Cu, Pb, Mn, and Zn on the other ($R = 0.40 - 0.70$, $p < 0.01$) as well as between $CaCO_3$ on the one hand and Ni and As on the other ($R > 0.41 - 0.42$, $p < 0.01$) (Table 5). Soil OM contains functional groups such as enol, phenol, and carboxyl, which in their deprotonated forms have a high 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 and OM–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 ($R = -0.31$ to -0.62, $p < 0.01$), an indication that metal retention in 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 by 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 resulting in the negative relationships observed between these elements and pH. Interestingly, when the managed and non-managed sites were analyzed separately, it was observed that the strengths of these relationships (i.e., elements on the one hand vs. OM, $CaCO_3$, and clay on the other) were notably higher in the non-managed areas compared to the managed areas (Table 6). The major contrast here was the relationship between the percentage of $CaCO_3$ and the elements, which was highly significant ($R = 0.51 - 0.75$, $p < 0.01$) for all the elements in the non-managed area but almost nonexistent in the managed area. These strong relationships could be an indication that these elements are naturally bound to carbonates in the semi-arid 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 a re-

Table 5. Correlation 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, Texas, USA ($n = 42$).

	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	−0.08	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.

sult, reference materials on this subject area are scarce. As will be shown later (Sect. 3.4), these relationships are useful in pollutant source allocation (Facchinelli, 2001; Yu et al., 2001; Jørgensen and Jensen, 2009; Eze et al., 2010) and for 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 by 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- or 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, the addition of other soil amendments and agrochemicals, and surface soil modifications, which constitute anthropogenic influences that can temporally alter the natural background relationships among these elements and, thus, their chemistry.
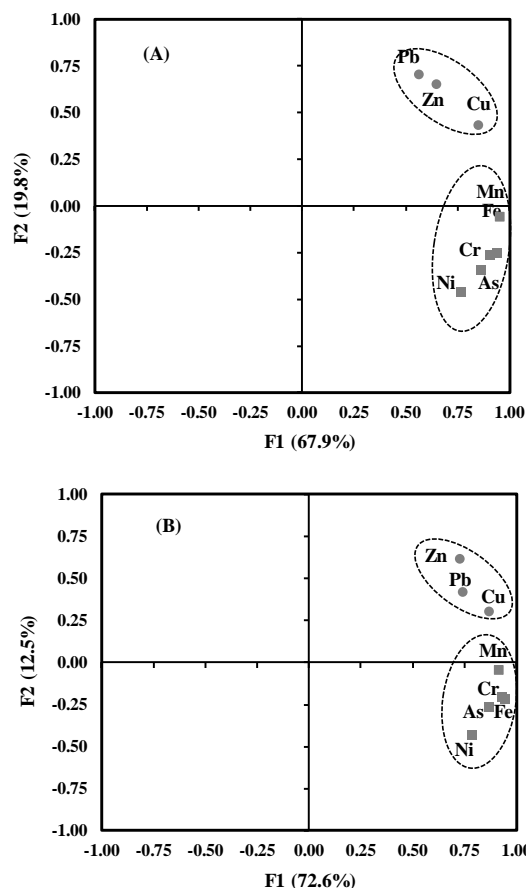

Figure 2. Principal component analysis loading plots of elements in soils of the golf course facilities in Lubbock, Texas, USA, for **(a)** managed site only and **(b)** managed and non-managed sites combined. Only two factors were extracted and interpreted.

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 in both areas combined, with the aid of PCA and the correlation matrix discussed in 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 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,

Table 6. Correlation coefficients of the relationships between elements and other soil constituents at managed and non-managed sites of the golf course facilities in Lubbock, Texas, USA ($n = 21$).

	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.

while Cu, Pb, and Zn were associated with the F2 component. These associations indicated two different possible pollutant sources. The strong positive relationships ($R = 0.76$–0.94, $p < 0.001$) observed between Fe and the rest of the F1 elements at 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) is possibly due to an anthropogenic influence (e.g., fertilization). A finding of major significance was that for the non-managed sites ($n = 21$), using the eigenvalue of 1, only one factor explaining 83 % of the variation was extracted. This finding suggests that the examined elements at the non-managed sites could be due to one source, which is possibly 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 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 are affected by anthropogenic influences. The total elemental concentration values suggested that the concentrations 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 the European Commission (Kabata-Pendias, 2010; Selinus et al., 2013).

4 Conclusions

The identification and quantification of possible sources of environmental contaminants are often the first conscious steps taken toward any environmental protection effort. This work extends the application of PXRF spectrometry to the rapid probing of potential elemental contaminants in the semi-arid soils of the SHP, USA, 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 a semi-arid climate. Although the investigation of heavy metals (Cr, Pb, Ni, Cu, Mn, Fe, and Zn) and As revealed few differences between the managed and non-managed areas of these facilities, findings do, however, show possible associations among elements. Strong relationships and interactions were observed among the elements examined and between elements and soil constituents such as clay, CaCO$_3$, and OM contents, as well as pH. Interestingly, 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 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. At the non-managed sites, only one source of contaminant, possibly lithogenic, was identified. Most of the heavy metals examined at the facilities were within the MPC set by the USEPA and European Commission. The findings help 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 they provide background information for future studies and remediation programs. Findings could also be extended to other semi-arid and arid regions of the world.

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