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Naturally elevated metal contents of soils in northeastern North Dakota, USA, with a focus on cadmium

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Abstract

Purpose—Association of element concentrations for the escarpment soils of northeastern North Dakota formed from different geologic parent materials was determined based on geochemical data. These soils overlie the Cretaceous Pierre Formation, and parent materials consist of shale rich glacial till, residual shale, and colluvial materials.

Materials and methods—Samples were analyzed for cadmium and other trace elements using nitric acid digestion followed by optical emission spectroscopy. Morphologic and laboratory analysis of soil cores indicate high clay content, indicative of the influence of shale residuum on the parent materials of the escarpment soils.

Results and discussion—An average, cadmium concentration of 0.24 ± 0.22 mg/kg was determined for 136 samples from eight (approx. 2.4 m deep) cores. The concentration of molybdenum had a range between 0.00 and 7.99 mg/kg. Zinc levels determined in the samples had a wide range between 18.76 and 128.02 mg/kg. Principal component analysis revealed that elevated trace element concentrations for the shale-rich portion of the soils in northeastern North Dakota are linked to a variety of factors including organic matter content, pH, elevation, and electrical conductivity.

Conclusions—Results of this study suggest that erosion and transport of Cretaceous shales downslope on the escarpment have resulted in enriched trace element concentrations in the soils.

Keywords

Cadmium; Elevated; Natural; North Dakota; Soil

1 Introduction

Soils in the Red River Valley of North Dakota, Minnesota, and Canada are widely recognized as some of the most fertile in the world. However, studies in Canada and North Dakota have revealed some soils containing naturally elevated concentrations of certain metals, including cadmium (Cd) (Holmgren et al. 1993; Garrett 1994; Li et al. 1994; Eberl and Smith 2009). Of the trace elements considered here, cadmium is of specific interest because of its toxic and carcinogenic health effects at low concentrations (Satarug et al. 2010). Kippler et al. (2012) have reported that children who had been exposed to low concentrations of Cd in the womb have statistically lower IQ scores. While no reports exist of excessive Cd in agricultural products from the study region, there is the potential for certain regional food crops, such as confectionary sunflowers and durum wheat, to bioaccumulate Cd (Comis 1995).

Interaction of several factors and processes has resulted in high levels of Cd in certain soils of northeastern North Dakota (Hopkins et al. 1999). These factors include glacial and geomorphic history, sub-surface lithology and its weathering history, and the overall geochemical regime. In this region, shale-bearing sediments were deposited during Wisconsinan time by multiple glacial advances from a north–northwesterly direction. In specific areas, these sediments overlie bedrock that is also shale, typically the Cretaceous Pierre Formation (Bluemle 2000). The presence of shale as bedrock and as fragments in glacial material on which soils were formed is an important factor influencing soil chemistry in the region (cf. Erickson and Barnes 2005).

Availability of major and trace elements can be limited or enhanced by various processes in the soil profile including weathering intensity, sorption (cation/anion exchange), specific adsorption of anions by ligands, co-precipitation, organometallic complex formation, and pedogenic processes such as leaching, salinization, calcification, and eluviation/illuviation (Alloway 1990). Research based on the analysis of physico-chemical and mineralogical properties can provide significant information for geochemical assessment of the processes that trace elements undergo in soils as they form from parent materials through various pedogenic stages (Brantley and Lebedeva 2011). Such research can document potential trace element availability to the food chain (Page et al. 1987). Keeping these perspectives in mind, this geochemical survey was undertaken to improve understanding of metal-enriched soils and their spatial variability in a region of northeastern North Dakota. This contribution provides a base for comparison with other areas that contain naturally high levels of metals in soils and bedrock.

Trace element surveys of soils have been conducted at both national and international scales, and some of these sites were located in northeastern North Dakota. An early geochemical survey for the conterminous US (Shacklette and Boerngen 1984) provided background concentrations of trace elements in soils free from anthropogenic interferences. Smith et al. (2005) presented the results of his survey revealing 0.5 mg/kg Cd in both A and O horizons and 0.4 mg/kg in C horizon soils of northeastern North Dakota. The United States Geological Survey (USGS) conducted a nationwide geochemical survey in the conterminous US reporting Cd concentration from 0.3 to 0.5 mg/kg in A horizons and 0.2 to 0.5 mg/kg in

C horizons (Smith et al. 2014). Holmgren et al. (1993) carried out a nationwide sampling of soils and crops to determine Cd, Pb, Ni, Cu, and Zn levels. Results of this survey also showed elevated levels of Cd in the region of northeastern North Dakota, with a mean of 0.36 mg/kg. Garrett (1994) reported that the mean Cd concentration of 1273 soils from the prairie provinces of Canada and adjoining areas in Montana, North Dakota, and Minnesota was 0.28 mg/kg, and he suggested an environmental baseline of 0.3 mg/kg. Investigations by White et al. (1997) showed high Zn (>55 mg/kg) levels in soils of the northern USA. We might expect high levels of Zn in escarpment soils due to its similar geochemical behavior as Cd. Hopkins et al. 1999 found threefold higher total Zn levels on the Pembina Escarpment, relative to till soils west of the Escarpment (75 mg/kg; $n=50$). Regional surveys by Hopkins et al. (1999) showed Cd levels ten to 20 times higher than the baseline (0.3 mg/kg) total Cd established by Garret in the topsoils on the Pembina Escarpment in northeastern North Dakota. Franzen et al. (2006) showed Cd concentrations in North Dakota soils varying from 0.01 to 0.31 mg/kg. A survey of wetland soils across North Dakota and northern Minnesota shows that they contain an average of 0.38 mg/kg (Jacob et al. 2013). The North American Soil Geochemical Landscapes Project (Smith et al. 2009, 2013, 2014; Klassen 2009; Woodruff et al. 2009) has released data collected as part of a nationwide geochemical sampling of soils.

The dispersion of metals from shale into the environment is well documented and is particularly relevant to this study. Burau et al. (1973) investigated agricultural soils developed from or near Monterey shale in California and reported a mean level of 1.24 mg/kg Cd, while Lund et al. (1981) showed that soils developed from shale residuum in that area contained Cd ranging from 0.6 to 33 mg/kg, with a mean level of 7.5 mg/kg. Kim and Thornton (1993) showed elevated concentrations of trace elements (6.3 mg/kg Cd, 136 mg/kg Mo, 8.6 mg/kg Se) in Ordovician black shales in Korea. Lee et al. (1998a, b) reported high concentrations of trace elements in soils formed from the Okchon Group black shales and slates in Korea. Soils containing naturally high trace metal contents derived from shales are found in other regions including China (Fang et al. 2002) and Luxembourg (Horckmans et al. 2005). However, Tuttle et al. (2009) show decreases in Cd, Co, Cu, Mn, Ni, S, and Zn in material weathered from shales in Kentucky, USA.

2 Study area and methods

Cavalier County lies in the northeastern part of North Dakota (48°40'9" N, 98°49'56" W) and is within the physiographic division of the Drift Prairie. The elevation for the county ranges between 493.8 m in the western part and less than 365.8 m in the northeastern part, covering 3911 sq. km (Arndt 1975; Simmons and Moos 1990). The majority of Cavalier County is covered by glacial till, but the eastern part is a dissected upland, the Pembina Escarpment, which exposes Cretaceous shales ranging in age from the Carlile to the Pierre Formations of Late Cretaceous age (Gill and Cobban 1965).

The Pembina Escarpment (Fig. 1) is a 70–100-m-high east-facing escarpment extending from near the town of Park River, ND, USA, about 160 km (100 miles) to the north near the town of Treherne in southern Manitoba. It marks the northwestern edge of the Red River Valley. Average annual mean temperature and precipitation of Cavalier County over the 30-

year period of 1971–2000 were 2.2 °C and 45 cm, respectively (NDAWN 2010; NCDC 2010).

Bluemle (2000) linked the development of the Pembina Escarpment to the development of the Red River Valley itself. Erosion of soft shale and sandstone that covered Canadian Shield basement formed an east-facing escarpment which was steepened by glacial ice (Bluemle 2000). The Pembina Escarpment continues to the north, where it is referred to as the Manitoba Escarpment in southern Manitoba (Smith et al. 1973).

2.1 Field and laboratory methods

Samples were taken in June 2008 on a former agricultural field currently in grass in North Dakota State Wildlife Management Area (NDSWMA). Soil samples were collected at 76-m distances to effectively sample the entire elevation range of the field. Cores of approximately 2.4 m in depth and 5.5 cm in diameter were taken using a percussive soil probe from eight locations (Table 1). One site was cored to 3.7 m.

Cores were refrigerated until each was thawed and sawn open; morphology and lithology were described in detail (Jyoti 2010; Fig. 2). All horizons including topsoils, argillic, eluvial, shale, and bedrock were documented. Sub-samples were taken at 15-cm intervals for chemical analysis. Logs depicting the lithology, soil properties, and element concentrations for all cores were created using LogPlot 7 V.7.3.62.87 and Rockworks 6 by RockWare Incorporated software.

Core sub-samples were analyzed for multi-elements including Al, As, B, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, Ti, Tl, V, and Zn. The procedure used was modified from EPA Method 3051 by Kingston (1997). Digestion of each 500-mg aliquot of soil (<2 mm) was carried out using concentrated nitric acid in a CEM MARS XPRESS Microwave digester using Xpress Vessels (55 mL PFA venting). Samples were analyzed with a Spectro Genesis Inductively Coupled Plasma Optical Emission Spectroscopy with cross flow nebulizer, using Ar gas. Smart Analyzer Vision V. 3.013.0752 software was used for the interpretation. The instrument was calibrated using multi-element and individual standards. The results were recorded as mean concentrations of three measurements of elements from the same sample in g/L. Values for respective elements were then calculated in mg/kg. Standards used for multi-element analyses were Natural Matrix Certified Reference Materials (CRM026-050, CRM022-020, CRM028-050, and CRM200) and Montana Soil Standard 2711. Method error was calculated after running a standard (CRM026-050) for 21 times with an error of 6 %.

Soil organic matter content (OM) was determined on all samples using loss on ignition as outlined by Storer (1984) and Combs and Nathan (1998). Details are presented in Jyoti (2010). Method error was calculated after running 20 check standards and was found to be 0.25 %. Ten grams of soil were used to determine pH and electrical conductivity (EC). (1:1 soil/water ratio) using the methods of Watson and Brown (1998) and Whitney (1998), respectively.

Principal component analysis (PCA) was performed using Matlab (V. R2010a) software on data matrices for shale horizons described during core descriptions consisting of elements and soil characteristics for samples from cores taken on transect 4. The data were normalized with zero mean, and variance was set to unity. Principal components having eigenvalue > 1 were retained according to Kaiser's rule. Varimax rotation was applied to PCs, and the resulting PC loadings having value 0.6 or greater which are considered stronger were retained for data interpretation (Nowak 1998; Garcia et al. 2004; Cheng et al. 2009).

3 Results and discussion

3.1 Core description and characteristics

Based on morphological description (Table 2), the typical master soil horizons present in the cores were dark topsoils (A horizons), formed by the degradation and accumulation of OM. The A horizons were commonly underlain by a thin eluvial horizon (E), which is light-colored due to leaching and loss of dark-colored organic pigments and ferric oxyhydroxides. Below the E, argillic horizons (B_t) with accumulated clay were common. Rarely, a B horizon with carbonate accumulation (B_k) was encountered. Regolith consisted of either shale colluvium (C) or residual shale (R).

Figure 2 shows the cross section A–A' for eight cores taken in the field. The dark thick solid line over the top of all cores marks the surface of the field (see legend for color codes, symbols, and corresponding lithologies present in these eight cores). It can be seen from Fig. 2 that the argillic horizon is expressed as a thick lithologic horizon in all the cores. The soil profiles contained many argillic horizons, several thin but morphologically distinct E horizons, and numerous mineralogic accumulations including several small spherical shale units. Presence of charcoal in the soils might be due to existence of forests on the hill slope before they were cleared for agriculture.

Table 2 shows organic matter (% OM), pH, and EC measured on the soil core samples. Organic matter content was significantly higher for samples taken downslope in comparison to those from upslope. Sub-surface samples, on the other hand, show a different trend with upslope samples containing slightly higher OM than the downslope samples. Reduced OM in upslope samples could reflect the erosion of topsoil by wind and water and thus its accumulation near the base. The maximum OM present in the A horizon of core samples was 15.04 % for core 1 (downslope), and the minimum was 7.92 % in core 10 (upslope) near the forested area. Soil samples ranged from being extremely acidic (pH=3.6) to slightly alkaline (pH=7.4) and clearly reflect the presence of relatively unweathered shale (and its component sulfides). The EC of the samples ranged between 0.31 and 3.3 dS/m.

3.2 Multi-element analysis

Table A.1 (Electronic supplementary material) shows the results of element analysis for core samples. To avoid overestimation of the average for Cd, all nondetects (values below detection limit) were set to zero. Using this method, the arithmetic average Cd concentration for eight cores was found to be 0.24 ± 0.22 mg/kg ($n=136$). However, setting all nondetects to zero also likely provides a low estimate of the mean and an unrealistically high variance.

Zinc levels were high for all samples (19–128 mg/kg), although similar concentrations were found by White et al. (1997) (>55 mg/kg). Other elements such as Cu (avg. 33 ± 13), Cr (25 ± 7) and Ni (33 ± 17) mg/kg also tend to predominate the trace elements in the soils in this region.

Topsoil (0–30 cm) samples ($n=16$) of the Pembina Escarpment had elevated concentrations for the elements As (4–17), Co (9–19), Cr (19–30), Cu (19–38), Ni (21–68), and Zn (73–128) mg/kg. The arithmetic mean value of Cd in topsoils was analyzed as 0.4 ± 0.4 mg/kg, with a highest Cd concentration of 1.04 mg/kg found in core 1 at a depth interval of 0–15 cm. While our mean Cd concentration in the topsoils is higher than the geometric mean Cd concentration (0.302 mg/kg) reported by Holmgren et al. (1993) for surface soils in Northern Great Plains and the mean value of 0.18 mg/kg in surface soils reported by Franzen et al. (2006) for depressions in North Dakota soils, the large standard deviation does not allow for a statistical difference.

Average concentrations for various elements in the shale horizon ($n=74$) were As (12.6 ± 7.4), Co (10.5 ± 2.6), Cr (25.7 ± 7.6), Cu (35.9 ± 16.0), Ni (29.7 ± 18.8), and Zn (76.0 ± 17.6) mg/kg. Mean Cd concentration for shale horizon samples was 0.22 mg/kg. This Cd concentration is approximately equal to the baseline value of 0.3 ppm reported by Garrett (1994) for the Northern Prairies region and the median value of 0.3 mg/kg reported by Page et al. (1987) for agricultural soils from across the entire USA. However, if we compare mean Cd concentration in topsoils with shale horizons, topsoils have a higher content which could be attributed to its ability to bind with organic matter present in the A horizon (topsoils).

To assess the elements associated with Cd in the field area, we examined the metal contents of the shale horizons for eight cores (a subset of the data analyzed for multielements). Element cross plots show strong differences in upslope vs. down-slope samples that extend beyond OM to concentration variation of metals. Plots of Ni, Cr, Cu, Co, pH, and others show that the shale horizon in upslope cores 8, 9, and 10 form a distinct group from that in the downslope cores (Fig. 3).

3.3 Role of soil morphology and chemical properties in metal retention

The parent materials for Pembina Escarpment soils are Cretaceous shale and glacial till which itself contains remobilized shale material. The escarpment soils of the backslope and shoulder landscape settings are shallow soils having a shale horizon high in the profile, at a depth averaging 70 cm. These soils are thus heavily enriched with clay. A soil surface in this region would be net negatively charged due to charge imbalance caused by isomorphous substitution of Al^{3+} for Si^{+4} in the tetrahedral layers and/or Mg^{2+} , Fe^{2+} for Al^{3+} in the octahedral layers of aluminosilicate clays. This creates a perfect adsorption site for metals onto negatively charged clay surfaces, leading to increased metal concentrations in the soil.

Key observations of the cores point to the process of slopewash as having been significant in the formation of these soils from shale parent material. Soils of the footslope landscape enriched in organic matter in the A horizon support the process of water and wind movement in these soils (Table 2). Highly oxidized zones in the soil profile occur due to leaching and translocation of minerals from upper to lower horizons due to vertical and lateral water flow.

Presence of charcoal lenses and thick roots indicate high organic matter content in these soils, which supports the fact that these soils have their origin from organic-rich shale and that these parent materials were modified by pre-existing forests in this area. Volcanic ash layers found in the lower soil horizons indicate the occurrence of bentonitic layers in Pierre Formation shale of this region.

The colluvial/alluvial nature of soils is also morphologically supported by the occurrence of stratifications in shale. Shale fragments (1–2 cm) in B and C horizons indicate residual shale. Occurrence of thick E horizons over B_t horizons (Fig. 2) for some cores might be due to enhanced eluviation (gain in E horizon thickness) and degradation of the B_t which could have occurred due to vertical and lateral water movement down the slope. Iron and Mn concretions due to redox conditions occurring in the E horizon above degraded B_t support this fact. The dominant secondary minerals observed in this study, e.g., ferric-oxyhydroxides, sulfur-bearing minerals like jarosite, clay minerals, and gypsum, are consistent with fine-textured shale and shale regolith as the parent material for these escarpment soils. It has been well documented (Jenne 1968) that Fe and Mn oxides are the main soil surface controlling the mobility of metals in soils. Correlation results for Cd, Ni, and Zn indicate its significance to OM, Mn, and Fe hydroxides and clay content having abundant cation exchange sites. Cadmium is more mobile in soils with such chemical properties (Schultz et al. 1980; Adriano 1986; Alloway 1990). Adsorption on clay minerals and precipitation with sulfides and carbonates increase the Zn and Cd concentration in mineralized zones, i.e., B horizons (Alloway 1990).

Soil properties such as OM and pH are thus some of the key properties controlling the chemical composition of soil. Soil chemical properties are largely dependent on the colloids found in soil, e.g., organic matter and clay minerals, and thus the chemical interactions are more determined by the surface properties of these colloids (Miller and Gardiner 2000).

Organic matter accumulation takes place in the surface layers of the upper soil horizon (A). Organic matter retains the trace elements in the soil as it forms organometallic complexes with metals. Increased OM content in the surface layer (A horizon) compared to the subsurface layer (B and C horizons) correlates very well to the elevated Cd concentrations for surface samples (Table A.1, Electronic supplementary material). High Cd levels related to humus content in soils were found in Swedish topsoils (Andersson 1977; Adriano 1986). Closer to the study area, Schultz et al. (1980) suggest the association of Mo, Se, As, and likely Cd and uranium (U) with marine OM, signifying trace element enrichment of the Pierre shale. The strength of organometallic complex depends on the competitive ability of the metal binding surface site and the soluble organic ligand (McLean and Bledsoe 1992). Thus, metals that form stable complexes with OM have a tendency to be more mobile in soils. Khan et al. (1982) reported that the mobility of metals in the soils they studied were in the order of Cu>Ni> Pb>Ag>Cd. Strong complex formation between Cu and Ni with soluble OM leads to the increased mobility of these metals in the studied soils. Haas and Horowitz (1986) stated that the presence of an adsorbed layer of OM over a clay layer increases Cd adsorption in soils.

The pH of the soil also affects the mobility of elements within the soil profile. Acidic pH generally increases element mobility (Alloway 1990; Miller and Gardiner 2000). Most of the Pembina escarpment soil samples have low pH values (avg. 5.2) due to their genesis from acidic shale parent material. Schultz et al. (1980) reported that weathering, prominently of pyrite minerals, caused otherwise alkaline unweathered shale near the surface to result in acidic soils. They reported a mean pH for the Pierre shale of 6.6, but varying between two groups having pH ranges between 2–5 and 7–9. These values can be compared to those of Franzen et al. (2006) who reported a pH range of 5.3 to 8.5 for soils found in the state of North Dakota. Soil pH plays a significant role in adsorption of cations by controlling pH-dependent H^+ sites in organic matter, clays, and oxyhydroxides. Exchange of H^+ ions at these sites with the cations of elements in the soil can have a marked effect in increasing element concentration (Alloway et al. 1985; Alloway 1990; Miller and Gardiner 2000). This is attributed to the preferred adsorption of hydrolyzed metal species over free metal ions which increase with higher pH (McBride 1977; McLean and Bledsoe 1992). However, in a study reported by Harter (1983), the metal retention capacity of the soil, specifically cations, increases significantly when the pH is >7 ; on the other hand, sorption of oxyanions such as As and Cr decreases with increasing pH (Neal et al. 1987), which is in accordance with our negative correlation of pH with these two abovementioned elements. In an interesting study by Cavallaro and McBride (1980), Cu adsorbed strongly compared to Cd with respect to changing pH, supporting the selective retention of hydrolyzed Cu at pH 6 over hydrolyzed Cd until pH 8. The negative correlation of pH with Cd for shale samples in our study follows this expected behavior as soils in our case are acidic; however, Cu showed an opposite correlation in our case.

3.4 Principal component analysis and its implications on soil landscape chemistry

Principal component analysis was carried out on the shale horizons for eight cores to reduce the large dataset and to see significant patterns among Cd and other elements. Principal component analysis would show which metals and soil characteristics and which shale samples are similar to each other, i.e., provide comparable information as well as the ones that are unique. An assumption was made during the analysis that metals and soil characteristics express critical information about shale samples in terms of their location in the field. The correlation matrix is presented in Table 3. Values in bold indicate significance at $p < 0.05$. Arsenic showed a significant correlation with Cu and a moderate correlation with Be and Cr and was negatively correlated with pH, Ni, and Mo. Aluminum and Be belong to the same group in the periodic table and share a common chemistry. Both are correlated with OM, Zn, and Cr. Calcium correlated negatively with As, Be, Cr, and Cu. Correlations of Cr with Al, As, and Be were found to be positive and significant, whereas with Ca and Co, they were negative but significant. Nickel showed negative significant correlations with Be, As, Cr, and Cu. Strong correlation with pH favors increased Ni levels in soils having an alkaline pH (Alloway 1990). Highly significant negative correlation (-0.90) was obtained for Cu with pH. Copper showed a very significant correlation (0.89) with Cr. Chromium and Cu have a tendency to be associated with insoluble hydroxides and oxides which in our case of soils are Fe and Mn. These elements can also be found associated with clay minerals. The smectite group mineral, montmorillonite, has been reported to adsorb high amounts of Cr in the form of Cr^{2+} , while Cu also behaves in a similar fashion (Griffin et al. 1977).

Molybdenum correlated significantly with Al, Be, and Cd. Zinc metal showed correlations with Al, Be, Co, Cr, and Cu. Cadmium correlated positively with Be and Mo but negatively with Co and Ni. Soil pH and electrical conductivity were found to have negative correlations with most of the elements. The majority of the elements showed significant correlations with organic matter content.

Trace elements Co, Ni, Zn, Cd, Cr, Cu, Mo, and As have been reported to have their association with organic matter and sulfur (pyrite) in Pierre shales (Schultz et al. 1980). Cobalt, Ni, and Zn show great correlation with clay minerals (Schultz et al. 1980), which is also evident in this study area as shown by the strong correlations in Table 3.

Table 4 represents the determined varimax-rotated PC loadings and their eigenvalues with percent of variance contributed in each PC along with Kaiser normalization. Components with eigenvalues more than 1 have been varimax-rotated. Four components were sufficient to explain 80 % of the variance for correlation matrix. The largest component loading measures the degree of association between the variables, and the PC loading (either positive or negative) gives meaning to the dimension; positive loading indicates that the contribution of the variables increase with increasing loading in dimension, and the negative loading suggests a decrease (Lawrence and Upchurch 1982).

The PCA results (Table 4) show that PC1 corresponds to 44 % of data variation with an eigenvalue of 6.21. The eigenvalue of PC2 and PC3 is 1.77 and 1.71, respectively, which accounts for 57 and 69 % of cumulative variance. PC4 has the lowest eigenvalue of 1.57. Shale horizons exhibit strong loadings for As, Be, Cr, Cu, Mo, Ni, pH, and OM for PC1. Strong correlations were also observed among these elements in the correlation matrix in Table 3, indicating the association of these metals with organic matter. A moderate positive correlation was observed between pH and Ni in Table 3, which is reflected in PC1. PC2 has correlation with Cd and EC only, whereas Co and Zn are correlated in PC3. Aluminum and Ca correlate in PC4, explaining 80 % cumulative variation.

Varimax-rotated PC scores for PC1 and PC2 are shown in Fig. 4. Here, strong differences become apparent between up-slope versus downslope shale horizon samples. The shale horizon samples for core 7 (encircled samples 38 to 43; cluster 3), which was located near the shoulder slope, plot relatively close to zero in a region separated from the other samples. The downslope shale horizon samples taken from cores 1, 4, 5, and 6 (samples 1 to 37; cluster 1) plot in a distinct region on the left of Fig. 4 compared to the upslope samples taken from cores 8, 9, and 10 (samples 44 to 74; cluster 2), which plot on the right. Samples from stations 15, 18, 53, and 56 indicate an exceptionally different element geochemistry from their relative tight clusters. In summary, it is evident from Fig. 4 that a majority of downslope shale horizon samples show relatively close statistical association among themselves in terms of PC1. The difference in values for PC2 may reflect the effect of slopewash and weathering, resulting in the accumulation of OM and weathered shale sediments at lower landscape positions leading to metal-enriched soils. Upslope shale samples also show close statistical associations with each other in terms of both PCs 1 and 2.

The first two varimax-rotated PC loadings for shale horizons are plotted in Fig. 5. The loading plot shows grouping and relationship between different variables. Principal component 1 divides the data into two major groupings, i.e., Cu, As, Cr, Mo, OM, and Be, with strong positive loadings and pH and Ni as strong negative loadings. The correlation between Cu, Cr, As, and Mo in relation to the data is unambiguous and significant. Chromium carries similar information as Cu, while As behaves similarly as Be and Mo and has a low loading on PC 2 (close to 0). Therefore, it can be concluded that these metals have no significant information on the attained classification of the shale samples. Such a grouping pattern in the fourth quadrant signifies their strength of relationship with organic matter as OM has strong affinity for trace elements to form organometallic complexes (Aoyama 1982). These results reinforce the conclusion that these organometallic complexes form a significant group and play a major role in separating downslope from upslope shale horizon samples. Nickel and pH behave similarly for PC1; however, for PC2, their behavior is opposite as pH tends to be extremely low (close to 0) but cannot be ignored, especially because pH influences the mobility of metals in soils. Cadmium correlates negatively with PC2, while EC exhibits a positive correlation which is expected as EC is an important soil property affected by soil texture, cation/anion exchange capacity, soil organic matter, and other subsoil characteristics. Close association between Ni and Co in the second quadrant indicates that these transition elements have a strong affinity for mutual substitution (Mitchell 1974).

Therefore, it appears that PC1 explains about half of the variation in the data, separating shale horizon samples with the metals forming a close association with OM from those with metals that are absorbed to the soil surface by either precipitation or substitution under the effect of favoring pH conditions. Furthermore, based on the PCA loadings and Figs. 3, 4, and 5, it can be inferred that landscape location has definitely contributed to the natural metal enrichment of these soils.

Spatial variations of Cd, Cu, and Zn due to landscape positions and OM have been reported in other soils from North Dakota (Franzen et al. 2006). Elevated Cd observed in both surface and subsurface samples from upslope locations suggests an association with clay that is a result of translocation within the soil profile and or natural enrichment due to the shallow shale horizons in these cores. A sudden increase in concentration of Ni, Zn, Co, Cu, and Mo noticed in the majority of cores below 45 cm in depth indicates their association with fine-grain fractions at these depths (Cornelis et al. 1993; Horckmans et al. 2005). Also, the mobility of these elements within the soil profile and then an increase in pH with depth causing their precipitation can lead to soil enrichment (Horckmans et al. 2005). Weathering of the Pembina Escarpment during the early glacial periods causing loss of Cd^{2+} and SO_4^{2-} associated with pyrite in shales and then genesis of soils from these modified parent materials could be responsible for the incorporation of Cd in the escarpment soils. Therefore, differences in surface and subsurface metal concentrations suggest an impact of landscape position in the natural enrichment of Pembina Escarpment soils.

4 Conclusions

Results of soil chemistry and principal component analysis of multi-elements in shale horizon samples from Pembina Escarpment soils suggest that weathering and slopewash resulting in the accumulation of OM and weathered shale sediments at lower landscape positions might have resulted in naturally high distribution of metals in soils of the Pembina Escarpment. Based on the results from the current study, questions can be raised about the specific transport mechanisms of metals as a result of soil formation and the existence of zones with anomalously high Cd. Soils near the forested areas can be critical in terms of trace element concentrations in the field. Also, regions that mark the base of the escarpment can contain high levels of metals due to transport and accumulation of material from upslope landscape settings. Thus, it can be summarized that regions towards the base of the escarpment falling within the same elevation range can be assumed to have high trace element concentrations. These results can provide a guide for future geochemical surveys in the region.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1. Location of the Pembina Escarpment in northeastern North Dakota. *Rectangle* shows field sampling location on the escarpment. Geology map source: North Dakota State Agencies, the ND GIS Hub

Fig. 2. Dominant morphologic and lithologic components observed in eight cores taken along a transect in the field

Fig. 3. Biplots of Ni, Cr, Cu, Co, pH and others show the shale horizon in upslope cores 8, 9, and 10 form a distinct group from that in the downslope cores

Fig. 5. Varimax principal component loadings PC1 vs. PC2 for shale horizon samples. *Horizontal axis* represents values for PC 1, whereas PC 2 values are shown on the *vertical axis*

Table 1

Identification of eight cores taken along a transect in the field in Cavalier County, ND

Core no.	Core ID	Elevation (m)
1	1500 N, 0 W	376.1
4	1500 N, 250 W	381.6
5	1500 N, 500 W	383.4
6	1500 N, 750 W	387.1
7	1500 N, 1000 W	389.2
8	1500 N, 1250 W	392.3
9	1500 N, 1500 W	396.5
10	1500 N, 1750 W	399.0

Table 2

Soil characteristics for eight core samples (see core description for horizon distinctions)

Sample ID	Depth (cm)	% OM	pH	EC (dS/m)	Station nos. for shale (C) horizon subsamples
Core 1					
A	0–24	15.04	6.2	0.39	
B _t	24–120	3.83	5.1	0.43	
BC	120–168	3.04	6.0	0.46	
C	168–235	3.30	6.6	0.60	1–5
Core 4					
A	0–11	9.22	6.2	0.50	
E	11–24	2.89	5.8	0.57	
B _t	24–112	2.39	4.5	1.07	
BC	112–147	2.44	4.6	1.49	
C	147–233	1.9	5.3	1.83	6–11
Core 5					
A	0–20	11.63	6.5	1.91	
E	20–28	4.01	6.9	1.33	
B _t	28–80	3.22	4.8	1.80	
C	80–239	2.70	5.5	3.30	12–21
Core 6					
A	0–19	10.34	6.2	1.01	
E	19–26	5.12	5.7	1.10	
B _t	26–83	3.43	5.0	1.52	
BC	83–120	2.27	6.4	1.83	
C	120–357	2.05	6.4	1.70	22–37
Core 7					
A	0–15	9.24	6.4	0.47	
B _t	17–144	3.54	7.0	0.85	
C	144–238	1.96	7.4	0.93	38–43
Core 8					
A	0–14	7.79	5.1	0.33	

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Sample ID	Depth (cm)	% OM	pH	EC (dS/m)	Station nos. for shale (C) horizon subsamples
B _t	14–88	5.40	4.4	0.69	
C _r	88–238	4.42	3.6	1.53	44–53
Core 9					
A	0–9	8.40	4.9	0.37	
B _t	9–67	6.30	4.0	0.36	
C _r	67–239	3.90	3.8	0.59	54–64
Core 10					
A	0–14	7.92	5.1	0.33	
B _t	14–75	5.20	4.0	0.32	
BC	75–90	3.99	3.7	0.31	
C _r	90–236	3.70	3.9	0.45	65–74

Table 3

Correlation table for analytes, OM, pH, and EC in the shale horizons of eight cores

	Al	As	Be	Ca	Co	Cr	Cu	Mo	Ni	Zn	Cd	OM	pH	EC
Al	1.00													
As	0.06	1.00												
Be	<i>0.44</i>	<i>0.69</i>	1.00											
Ca	0.22	-0.32	-0.25	1.00										
Co	0.20	-0.31	-0.16	<i>0.34</i>	1.00									
Cr	<i>0.43</i>	<i>0.73</i>	<i>0.79</i>	-0.34	-0.38	1.00								
Cu	0.19	<i>0.81</i>	<i>0.75</i>	-0.46	-0.43	<i>0.89</i>	1.00							
Mo	<i>0.22</i>	-0.72	<i>0.75</i>	0.03	<i>0.41</i>	<i>0.72</i>	-0.72	1.00						
Ni	-0.06	-0.61	-0.57	<i>0.49</i>	<i>0.78</i>	-0.69	-0.73	-0.61	1.00					
Zn	<i>0.29</i>	0.14	<i>0.33</i>	-0.14	<i>0.33</i>	<i>0.22</i>	<i>0.28</i>	0.02	-0.28	1.00				
Cd	-0.09	0.12	<i>0.27</i>	-0.21	-0.13	0.03	0.12	<i>0.06</i>	-0.35	-0.12	1.00			
OM	<i>0.32</i>	<i>0.56</i>	<i>0.64</i>	-0.10	-0.49	<i>0.63</i>	<i>0.65</i>	<i>0.78</i>	-0.66	0.09	<i>0.21</i>	1.00		
pH	-0.13	-0.78	-0.64	<i>0.48</i>	<i>0.41</i>	-0.76	-0.90	<i>0.63</i>	<i>0.70</i>	-0.14	-0.02	-0.53	1.00	
EC	0.14	-0.20	-0.27	<i>0.37</i>	<i>0.42</i>	-0.30	-0.35	-0.25	<i>0.48</i>	-0.11	-0.34	-0.31	0.18	1.00

Values in italic are significant at p 0.05

Table 4Varimax rotated PC loadings for shale horizons ($n=74$)

	PC1	PC2	PC3	PC4
Al	0.3545	0.0734	-0.407	<i>-0.6168</i>
As	<i>0.842</i>	-0.0219	-0.0212	0.1658
Be	<i>0.8267</i>	-0.2571	-0.277	-0.1558
Ca	-0.313	0.2338	0.0867	<i>-0.8064</i>
Co	-0.434	0.3105	<i>-0.6936</i>	-0.2299
Cr	<i>0.9254</i>	-0.0652	-0.0972	0.0168
Cu	<i>0.9276</i>	-0.1152	-0.0898	0.2294
Mo	<i>0.8478</i>	-0.1117	0.191	-0.259
Ni	<i>-0.7449</i>	0.3784	-0.3692	-0.2132
Zn	0.1696	-0.1616	<i>-0.8575</i>	0.0666
Cd	-0.0107	<i>-0.8535</i>	-0.1059	0.0091
OM	<i>0.7481</i>	-0.3381	0.1714	-0.3055
pH	<i>-0.8825</i>	-0.0952	-0.0004	-0.3223
EC	-0.2227	<i>0.7058</i>	-0.1078	-0.2578
Eigenvalue	6.21	1.77	1.71	1.57
% variation	44.37	12.66	12.21	11.20
% cumulative variation	44.37	57.03	69.24	80.45

Values in italic indicate strong loading, i.e., > 0.6