Improved enrichment factor calculations through principal component analysis: Examples from soils near breccia pipe uranium mines, Arizona, USA☆

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A B S T R A C T

The enrichment factor (EF) is a widely used metric for determining how much the presence of an element in a sampling media has increased relative to average natural abundance because of human activity. Calculation of an EF requires the selection of both a background composition and a reference element, choices that can strongly influence the result of the calculation. Here, it is shown how carefully applied, classical principal component analysis (PCA) examined via biplots can guide the selections of background compositions and reference elements. Elemental data were treated using the centered log ratio (CLR) transformation, and multiple subsets of major and trace elements were examined to gain different perspectives. The methodology was applied to a dataset of elemental soil concentrations from around breccia pipe uranium mines in Arizona, U.S.A., with most samples collected via incremental sampling methodology. Storage of ore at the surface creates the potential for wind dispersal of ore-derived material. Uranium was found to be the best individual tracer of dispersal of ore-derived material to nearby soils, with EF values up to 75. Sulfur, As, Mo, and Cu were also enriched but to lesser degrees. The results demonstrate several practical benefits of a PCA in these situations: (1) the ability to identify one or more elements best suited to distinguish a specific source of enrichment from background composition; (2) understanding how background compositions vary within and between sites; (3) identification of samples containing enriched or anthropogenic materials based upon their integrated, multi-element composition. Calculating the most representative EF values is useful for numerical assessment of enrichment, whether anthropogenic or natural. As shown here, however, the PCA and biplot method provide a visual approach that integrates information from all elements for a given subset of data in a manner that yields geochemical insights beyond the power of the EF.
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1. Introduction

Mining and industrial activity are necessary for a modern society. Geochemical sampling and interpretation help assess the effects of these activities on the surrounding environments (Facchinelli et al., 2001; Thornton, 1996). The tasks have been simplified by modern analytical methods that can rapidly analyze large numbers of samples for a wide spectrum of elements with significant precision and accuracy at relatively low cost. Although producing such datasets has been streamlined, extracting relevant information to address questions of potential anthropogenic impacts on the environment can be less straightforward. Here, techniques from the field of compositional data analysis (CoDa) are used to demonstrate how the resulting information provides important insights into such questions. Specifically, classical principal component analysis (PCA) of centered log ratio transformed data is applied to a large dataset of elemental soil compositions. The resulting geochemical insights can be used to calculate better enrichment factors (EF), a widely employed metric for quantifying environmental effects of anthropogenic activity, and also provide valuable geochemical perspectives of their own.

Enrichment factors are a means of quantifying the enrichment of a potentially contaminant-derived element in an environmental sample relative to a user-defined background composition. The

enrichment factor is calculated

$$EF = \frac{\left[C_x \big/ C_{ref}\right]_{Sample}}{\left[C_x \big/ C_{ref}\right]_{Background}} \qquad (1)$$

where the concentration of the element of interest is C_x, and the concentration of a reference element for the purpose of normalization is C_{ref} (Zoller et al., 1974). The use of a reference element makes the EF superior to other indices such as the pollution index (*PI*) which is just the ratio of the concentration of the element of interest in the sample relative to the background (Chen et al., 2005),

$$PI = [C_x]_{Sample} \big/ [C_x]_{Background} \qquad (2)$$

Other metrics, like the geoaccumulation index (*GI*), include adjustment factors (Müller, 1969) but are also essentially simple ratios

$$GI = log_2 \frac{[C_x]_{sample}}{[C_x]_{background} \times 1.5} \qquad (3)$$

The *GI* is therefore essentially a logarithm of the *PI*. As both metrics are based upon simple ratios of concentrations of a single element, they are vulnerable to distortion by particle size sorting effects, associations of particular trace elements with particular mineral types, and the closed nature of elemental datasets, which contain only relative information because if all components are analyzed they will sum to 100% (Bern, 2009; Reid and Spencer, 2009; Reimann et al., 2008). In contrast, the EF can compensate for the above effects, but selection of an inappropriate reference element can impose distortion of its own and therefore deserves consideration (Reimann and de Caritat, 2005).

Selection of a relevant background composition is also crucial in the calculation of an EF and can be difficult in practice. The geochemical background is "a relative measure to distinguish between natural element… concentrations and anthropogenically-influenced concentrations" (Matschullat et al., 2000). Difficulty arises in the determination of background because of natural variability in elemental concentrations in most media, and the way such variation generally increases with spatial scale (Reimann and Garrett, 2005). Calculation of a local, study-specific background could be a better strategy, but to successfully identify a nearby, geochemically similar, uncontaminated media can be a challenge. Many studies instead use a background derived by other workers from sample media across a much broader area, or use calculated compositions of average shales, or the continental crust (e.g., Çevik et al., 2009; Ghrefat and Yusuf, 2006; Loska et al., 1997; Lu et al., 2009). Such practices can systematically distort EF values because the broader background differs from or may be unrelated to the local background (Reimann and de Caritat, 2000).

Principal component analysis, carefully applied, is a potential tool for addressing the above issues by evaluating samples for calculating a relevant background composition for a specific study, as well as assessing choices among reference elements. The analysis also reveals which elements trace anthropogenic sources and how they relate. In this paper, PCA is applied to centered log ratio transformed elemental data from soils in and around four uranium mine sites, as well as two unmined reference sites, in Arizona, U.S.A. The potential for elevated concentrations of U and other elements in soils around the mines, relative to background, has been one facet of public concern (Wasser, 2016), along with proximity of mining to Grand Canyon National Park (Arnberger and Martin, 2018). The approach described here uses biplots, in which the loadings (eigenvectors) derived from the PCA are plotted together with the scores (sample coordinates with regard to these eigenvectors), to visually evaluate patterns in the data, as well as the performance of the PCA. Several iterations of PCA are performed to illustrate how including and excluding different elements can provide different and important perspectives for tracing anthropogenically affected element enrichment. A fingerprint of uranium ore-derived enrichment of soil is ultimately identified, along with context on variability of major and trace elements in background. The objective is to provide a blueprint for gaining deeper insights into element enrichment in the environment and calculating EFs that provide more accurate measures of that enrichment.

2. Materials and methods

2.1. Study area

Breccia pipe uranium (U) deposits (BPU deposits), located in the Grand Canyon region, have been estimated to contain an undiscovered U endowment of 1.3 million tons of U_3O_8 (Finch et al., 1990), but potential environmental effects of developing the resource are relatively poorly known (Beisner et al., 2017; Hinck et al., 2017; Hinck et al., 2014; Naftz and Walton-Day, 2016; Otton et al., 2010). To allow time for study of these potential effects, the U.S. Department of the Interior enacted a withdrawal of approximately 407,344 ha of Federal lands from future mineral extraction for a 20-year period beginning in 2012 (U.S. Department of the Interior, 2012). Widely spaced U deposits exist roughly 200–400 m below the surface, but mined ore is often stored on the surface for months or years before transport to a processing facility. As a result of the dry, windy climate in the region, ore dust can be transported off-site and expand the geochemical fingerprint of mining to nearby soils (Hinck et al., 2017; Otton et al., 2010). Water can also mobilize ore material, but retention ponds on mine sites exist to catch runoff.

2.2. Historical ore data and geochemical background data

To provide geochemical perspective on the potential composition of BPU ore, data were retrieved from the rock portion (https://mrdata.usgs.gov/ngdb/rock/) of the U.S. Geological Survey's (USGS) National Geochemical Database (NGDB). Data were retrieved for rock samples that had latitude-longitude coordinates associated with known BPU mines and prospects and had been submitted by Karen Wenrich, a USGS researcher of such deposits. However, it was not possible to associate data with particular previous studies (e.g., Wenrich, 1985), and some studies from that time period included industry-generated data not stored in the NGDB. The NGDB data were then culled to include only samples containing ≥1000 ppm U, to focus specifically on ore material. Data were further culled to include only samples for which concentrations of all elements of interest were available. The resulting dataset contained elemental concentrations for 96 BPU ore samples from seven locations (Fig. 1): Canyon Mine (CM; n = 7), Hack Canyon Mine (HC, n = 23), Hermit Mine (HM; n = 6), Kanab North Mine (KN; n = 9), Orphan Mine (OM; n = 13), Pigeon Mine (PM; n = 8), and an unnamed prospect (UP; n = 30). Samples from the Canyon Mine and the unnamed prospect were from drill cores, other samples were presumably mined ore. Historical ore data are included in Supplemental Table 1.

To provide geochemical perspective on potential background compositions, two composite backgrounds from the literature are used. The first is calculated from 366 to 717 surface soil samples (Fig. 1), depending upon the element, from a roughly 600-km² region on the Coconino Plateau (Van Gosen, 2016) and about 60 km away from sites sampled for this study (Fig. 1). The Coconino Plateau (CP) soil samples were collected as part of a geochemical
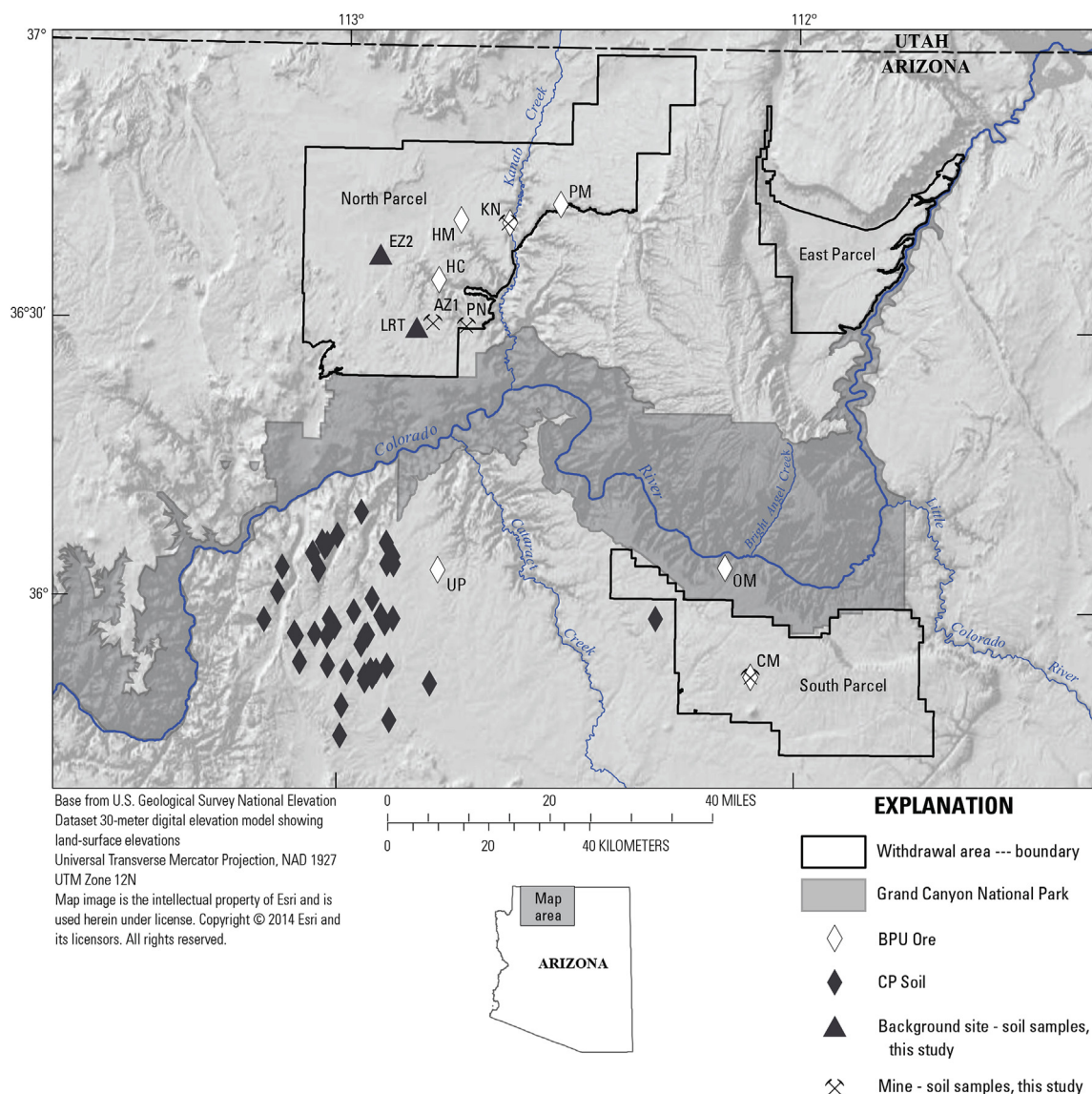
Fig. 1. Map showing locations of mine and background sites sampled as part of this study, breccia pipe uranium (BPU) ore samples from the U.S. Geological Survey National Geochemical Database, and background Coconino Plateau (CP) soil samples from Van Gosen (2016). Labeled site abbreviations are defined in the text.

exploration study (Van Gosen and Wenrich, 1991). The second background is the recommended composition of the upper continental crust (UCC) as calculated by Rudnick and Gao (2003).

2.3. Soil sampling methods

Surface soil samples were collected from six sites for this study (Fig. 1). Four sites were mines. The Canyon Mine (CM) shaft had only been developed to about 60 m-depth at the time of sampling, well above the ore-zone, and neither ore nor waste rock were stored at the surface. At the Pinenut Mine (PN), a large ore pile along with waste rock and overburden rock piles were stored at the surface and ore was being periodically removed from the site. At the Arizona 1 Mine (AZ1), all ore had been removed, but the site had not yet been reclaimed. At the Kanab North Mine (KN), all ore had been removed and the site was being reclaimed. At KN and CM, samples were collected on the mine site itself; at the other sites, samples were collected only outside the perimeter fences. Two potential background sites, where mining activity was absent, were

also sampled. First was the EZ2 pipe, a BPU deposit confirmed by drilling but yet unmined. Importantly, such a BPU deposit will have no recognizable geochemical fingerprint at the surface (Van Gosen and Wenrich, 1991). Second was the Little Robinson Tank (LRT), a livestock watering tank with no known BPU mineralization nearby. Environmental interpretations of these soil data from a mining life-cycle perspective are in progress.

Two sampling methodologies were used to collect soils. The first was the incremental sampling methodology (ISM) described in detail by Naftz and Walton-Day (2016) and based upon methodology from the Interstate Technology & Regulatory Council (ITRC, 2012). Briefly, multiple polygons called decision units (DU) were established for areas around a given mine site ranging in size from 4880 to 63,000 m^2. Two rings of DUs surrounded each site, and the maximum distance from the fenced edge (currently or formerly) of any mine site that samples were collected was 220 m. Interior ring polygons were generally within 100 m of the mine sites. Additional DUs were set up along haul roads leading to mine sites (e.g., Naftz and Walton-Day, 2016). Within each DU, the latitude and longitude

of 48–123 primary sampling locations were determined prior to sampling. At each of these sampling points, the top 5 cm of soil was collected using a Multi-Incremental Sampling Tool (ITRC, 2012) and composited in a bucket. Triplicate samples were collected using two fixed distances and compass angles from each of the primary sampling locations. Triplicate samples were analyzed separately and all were used in subsequent data analysis. Intensive compositing and triplicate sampling both address and assess variability issues without adding unduly to the analytical burden. Samples from each DU (>1 kg) were sieved to <2 mm using plastic screens in the field and maintained under USGS chain-of-custody procedures (Murphy et al., 1997) until and throughout analysis.

Additional soil samples were collected at mine sites AZ1, CM, and PN at topographic locations of likely dust accumulation. Soil from the top 5 cm was integrated from approximately 30 locations over 10 m^2 to produce what are referred to here as "point" samples. The total numbers and types of samples were 54 DU and 13 point samples for AZ1, 81 DU and 16 point samples for CM, 51 DU samples for KN, and 51 DU and 13 point samples for PN. At KN, 39 DU samples were from outside and 12 were from inside the perimeter fence. A total number 27 DU samples each were collected from the background sites EZ2 and LRT.

2.4. Analytical methods

Soil samples were ground to <100 μm by using a mill with ceramic plates. Analyses of the solid phase composition of bulk soil samples were conducted by SGS Mineral Services (Lakefield, Ontario, Canada). Total concentrations of major and trace elements were measured by decomposing powdered samples using a mixture of HCl, HNO$_3$, HClO$_4$ and HF and analyzing the resulting solution using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively-coupled plasma mass-spectrometry (ICP-MS) (Lamothe et al., 2002). Carbonate C was measured by coulometric titration (Brown et al., 2002). Total C was determined separately by combustion and detection on LECO instrumentation (Saint Joseph, Michigan) (Brown and Curry, 2002). Organic C was calculated by difference between total and carbonate C. Blind reference standards constituted 10% of submissions. Data were deemed acceptable if recovery of each element was ±15% at five times the lower limit of determination and the calculated relative standard deviation (RSD) of laboratory duplicate samples was no greater than 15%. All data collected as part of this study are available via a USGS Science Base data release (https://doi.org/10.5066/P9KTLXL8).

2.5. Statistical methods

Principal component analysis (PCA) was used to discern patterns in bulk elemental data in surface soils collected for this study. Prior to PCA, concentration data were subjected to a centered log ratio (CLR) transformation,

$$clr\,(C_{Al}) = log_{10}\left(\frac{C_{Al}}{\sqrt[n]{C_1 C_2 ... C_n}}\right) \tag{4}$$

in which the log ratio was taken of concentrations of individual elements after dividing by the geometric mean of a particular subset of all element concentration for that sample (Aitchison, 1986; Reimann et al., 2008). Here C_{Al} represents the concentration of Al and $C_1 C_2 ... C_n$ represent all the elements in the subset. All concentrations must share the same units. Such transforms are integral to CoDa and are becoming accepted as prerequisites for the analysis of compositional data (Aitchison, 1986; Buccianti, 2013).

Results from CLR are less subjective than those from additive log ratio transformation, which requires choice of a normalizing element, and less abstract than those from the isometric log ratio transform (Buccianti and Grunsky, 2014; Egozcue et al., 2003; Reimann et al., 2008). When used correctly, the CLR transformation can address spurious statistical relationships between elements in soil that arise from variable dilution by a predominant matrix phase like quartz, or in this case, carbonate (Bern, 2009). However, it is important to note that CLR transformation cannot be identified directly with the original elements but rather interpreted in terms of dominance of the elements with regard to all components included in a given subcomposition. Classical PCA was completed using singular value decomposition via the "prcomp" function in the "stats" library of R (v 3.5.1; R Core Team, 2017). Loadings (eigenvectors) are returned in the component "rotation" by "prcomp". Data were centered using "prcomp" but not scaled as a form of scaling had already been accomplished by the log ratio portion of the CLR transformation.

Several iterations of PCA were conducted using different subsets or subcompositions of elemental data as identified in the Results and Discussion section. In each case, the CLR was performed using only the subset of elements identified, thus yielding a different geometric mean in the denominator of the CLR transformation in each case (Eq. (4)). Reduction of the number of elements in the subcomposition can be done objectively (Hron et al., 2013). Here it is done subjectively using geochemical knowledge to gain specific perspectives. Results of the PCA iterations are presented as biplots in which the "prcomp" rotations (eigenvectors) are plotted as lines or rays and the scores (sample coordinates with regard to eigenvectors) of individual samples are plotted as points (Gabriel, 1971).

3. Results and Discussion

3.1. PCA of enriched elements

Ore from BPU deposits is enriched in many elements relative to sedimentary rock that hosts the deposits (Wenrich, 1985). Perspective on which elements are most likely to be enriched relative to soils near mine sites was obtained by calculating the ratio of the median concentration in BPU ore to either the UCC or background soils of the Coconino Plateau (Table 1). Such ratios are equivalent to the PI (Eq. (2)) and provide a rough estimate of potential contrast against background. Enriched elements are, in descending order, U, S, As, Mo, Cu, Se, Cd, Pb, Co, Ni, and Zn.

One approach to evaluate the effect of anthropogenic activity on the environment is to perform PCA exclusively on elements considered enriched in the material introduced into the environment by the activity (e.g., Lu et al., 2010). The first PCA of soil data presented here uses the 11 enriched elements identified above except Se because Se concentrations in many samples were below the reporting limit of 0.2 ppm. One sample each was below the reporting limit for S (100 ppm) and Cd (0.1 ppm) and concentrations were imputed by setting them to two thirds the reporting limit (Martín-Fernández et al., 2003). The DU and "point" samples are not differentiated in the PCA biplots for ease of interpretation but their EFs are compared at the end of the Discussion.

It should be noted that the clarity of patterns discerned in all the biplots presented is partly due to the incremental sampling methodology used for the DU samples and the less formal compositing of the point samples. Such strategies substantially reduce both between-sample variance and skewness of trace element distributions compared to grab sampling (e.g., Clausen et al., 2018). Environmental heterogeneity is a major obstacle to distinguishing environmental patterns, but compositing is an effective strategy for addressing it.

Table 1

Summary statistics for geochemical data considered in the paper and described in the text. BPU ore compositions from the National Geochemical Database (NGDB), average UCC from Rudnick and Gao (2003), CP soils from Van Gosen (2016), and mine area and background soils from this study. For reference, and a measure of potential enrichment in BPU ore, ratios of median concentrations in ore versus UCC and CP soil are provided. Data not available indicated by "-".

	n	Al (wt. %)	Ca (wt. %)	Fe (wt. %)	K (wt. %)	Mg (wt. %)	Na (wt. %)	P (wt. %)	Ti (wt. %)	S (ppm)	As (ppm)	Ba (ppm)	Cd (ppm)	Co (ppm)
Breccia Pipe Uranium (BPU) Ore	96	1.7 0.2–8.4	2.6 0.04–15	2.5 0.01–35	0.7 0.03–3.3	0.24 0.01–7	—	0.04 0.005–0.71	0.08 0.01–0.36	29,000 100–354,000	1500 29–43,000	180 16–5700	4.5 2–560	215 7–26000
Upper Continental Crust (UCC)		8.2	2.6	3.9	2.3	1.5	2.4	0.065	0.38	62	4.8	628	0.09	17.3
Background soil of the Coconino Plateau (CP)	366–717	4.9	2	2.3	1.6	0.97	0.47	0.1	0.26	—	<10	430	<0.5	10
Mine Area and Background Soils (AZ1, CM EZ2, KN, LRT, PN)	307	4.1 1.5–6.3	5.2 0.3–15	1.9 0.7–2.9	1.8 0.8–3.5	1.4 0.3–3.7	0.3 0.07–0.6	0.08 0.04–0.22	0.21 0.07–0.4	300 <100–5100	10 4–58	428 207–612	0.2 <0.1–1.5	8.1 3.8–82
Ratio: Ore/UCC		0.2	1.0	0.6	0.3	0.2	—	0.6	0.2	468	313	0.3	50	12
Ratio: Ore/CP soil		0.3	1.3	1.1	0.4	0.2	—	0.4	0.3	—	-	0.4	—	22

|	n	Cr (ppm)	Cu (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	Pb (ppm)	Sb (ppm)	Se (ppm)	Sr (ppm)	Th (ppm)	U (ppm)	V (ppm)	Zn (ppm)
Breccia Pipe Uranium (BPU) Ore	96	37.5 2–350	2400 23–270,000	67 8–860	125 4–12,000	530 6–62,000	605 30–22,000	—	4.9 0.1–1900	100 17–1900	8 4–480	6150 900–700,000	46 4–39,000	360 7–59,000
Upper Continental Crust (UCC)		92	28	1000	1.1	47	17	0.4	0.09	320	10.5	2.7	97	67
Background soil of the Coconino Plateau (CP)	366–717	64	22	510	<2	25	13	<0.25	<1	140	10.1	3.5	52	57
Mine Area and Background Soils (AZ1, CM EZ2, KN, LRT, PN)	307	33 11–60	20 10–129	565 212–1160	1.2 0.5–8.8	17 6.8–201	15.4 7.2–43	0.7 0.3–1.2	0.2 <0.2–3.4	113 72–273	7.7 3.1–10	2.1 1.2–119	43 18–71	49 23–1113
Ratio: Ore/UCC		0.4	86	0.1	114	11	36	—	54	0.3	0.8	2278	0.5	5.4
Ratio: Ore/CP soil		0.6	109	0.1	-	21	47	—	—	0.7	0.8	1757	0.9	6.3
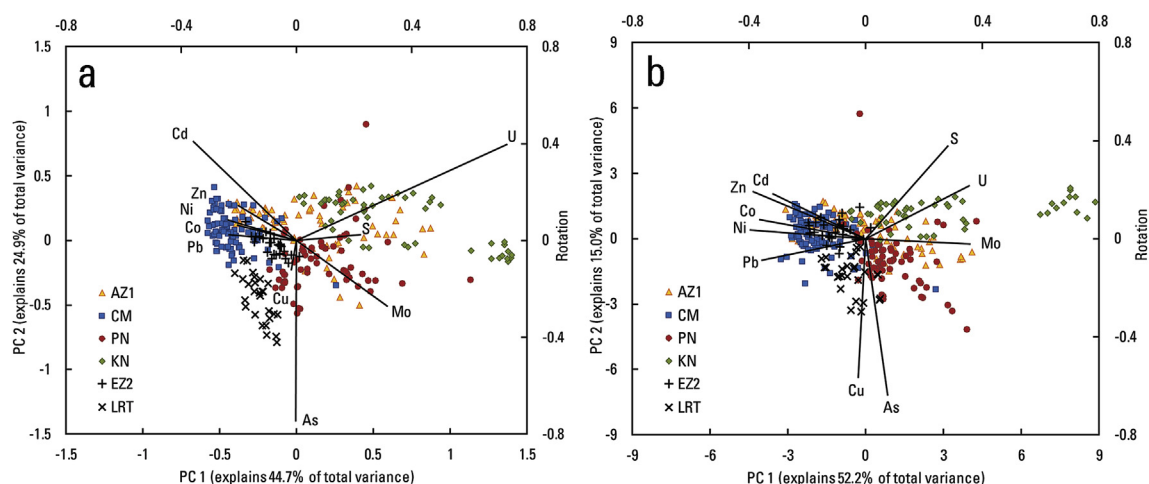
Fig. 2. Biplots of the first two principal components (PC1 and PC2) from a PCA using soil data for 10 elements substantially enriched in BPU ore relative to expected background. The proportion of explained variance is indicated for each component. Scores for samples are plotted versus the bottom and left axes, and rotations (eigenvectors) for variables (elements) are plotted on the top and right axes. The PCA in (a) is identical to that in (b) except that in (b) two samples are omitted for which a concentration of Cd and S, respectively, had been imputed to be two thirds the reporting limit.

Several patterns can be discerned in the first biplot (Fig. 2a). Three of the four elements expected to be most enriched in ore relative to background (U, S, and Mo) do not align, but their individual rays plot generally opposite many of the rest of the elements. Many of the mine site samples (AZ1, PN, KN) fall between the U and Mo rays and in the direction of the S ray. Such positioning of expectedly enriched samples indicates these three elements to be the strongest components of a fingerprint for BPU ore material in the soils. Positioning of background samples (EZ2, LRT) and a mine early in its lifecycle (CM) away from the enrichment trend reinforce the interpretation. Opposite the enrichment trend, Cd, Co, Ni, Pb, and Zn cluster more tightly together with moderate influence, except for Cd, and form their own trend. Even though these five elements are expected to be enriched in BPU ore material, restriction of the subcomposition to only potentially enriched elements and their lesser enrichment relative to U, S, and Mo cause them to occupy the trend that would be associated with less enrichment or resembling background. A third trend, defined primarily by As, might identify differences in the enrichment fingerprint between sites, possibly driven by differences in ore composition between deposits. Separation of trends between the AZ1 and KN versus PN samples might reflect such differences in the fingerprint of the ore material. Discerning such differences might be the best use of a PCA restricted to a subcomposition of enriched elements. In this case, however, positioning of background site (LRT) samples along the As trend suggests that variations in As might simply reflect site to site background differences in As.

The length of the Cd ray in Fig. 2a and its general alignment with the trend of lesser enrichment or resembling background deserves attention. As shown in subsequent biplots, elements along a non-enrichment trend are commonly more balanced. Prominence of Cd is suggestive of an issue with the underlying data. The PCA was repeated, omitting the two samples for which concentrations below the detection limit for Cd and S had to be imputed. The result is a biplot (Fig. 2b) in which all the rays are more evenly balanced, revealing that the two imputed values had distorted the rotations (eigenvectors) of the previous PCA, though relative positioning of the samples was less affected. Distinctions between the composition of the most enriched samples from AZ1, PN, and KN are slightly more apparent, supporting the idea that site to site differences in the ore-derived material can be discerned.

Omitting data from an analysis to achieve desired results can be a violation of scientific ethics. In this case, two samples were

omitted due to reporting limit issues. An alternative strategy would be to keep the two samples and instead omit the elements Cd and S from the analysis. Omitting Cd would have minimal effect but omitting S might reduce the ability to see site to site differences. Thus, options must be carefully weighed, and judgments honestly reported.

3.2. PCA of 39 analytes

In some situations, PCA of all available elements for which the vast majority of data fall within reporting limits is considered to provide the most powerful explanatory perspective (Tolosana-Delgado and McKinley, 2016). The second PCA presented here incorporates data on 39 analytes: Al, Ca, Fe, K, Mg, Na, S, Ti, As, Ba, Be, Bi, Ce, Co, Cr, Cu, Ga, La, Li, Mn, Mo, Nb, Ni, P, Pb, Rb, Sb, Sc, Sn, Sr, Th, Tl, U, V, W, Y, Zn, along with carbonate C and organic C. Cadmium is excluded, and the one sample below the reporting limit for S is excluded.

The biplot resulting from the PCA (Fig. 3) shows the rotations of the analytes divided into three major geochemical trends. A carbonate trend is indicated by Ca, Mg and carbonate C and likely reflects either calcite and dolomite inherited by soil from the Kaibab Formation (Richard et al., 2000) or pedogenic carbonate. A second trend includes all of the elements thought to be enriched in BPU ore, which here fall together because non-enriched elements provide contrast. In this context, the enriched composition samples can start to be distinguished from the background composition samples. A divide between the rays for Tl, Zn, and Pb (along with unlabeled Co and Ni), versus U, Mo, S, As, and Cu can be distinguished. Zinc, Co, Ni, and Pb plotted opposite the enrichment trend of the previous PCAs (Fig. 2a and b), and Tl was not thought to be substantially enriched in BPU ore (Table 1). The pattern here suggests that they are lesser markers of ore-related enrichment and may have other influences on their distribution. Zinc, Co, Ni, Pb, and Tl can be excluded from a subsequent PCA focused to more specifically trace enrichment. The remaining elements form a third, broad trend marked by Al, Fe, Mn, and organic C. Such elements are likely not associated with ore and instead are derived from clays in sedimentary rock, organic matter, and regional dust inputs. Most elements on the trend have low weighting and thus their variability may contribute mostly noise to the PCA. Such noise can be reduced while retaining that trend by narrowing the selection of elements in a subsequent PCA.
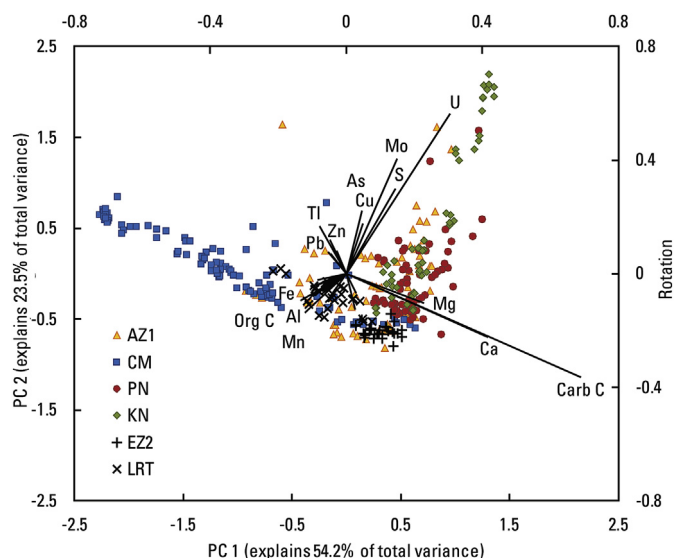
Fig. 3. Biplot of the first two principal components (PC1 and PC2) from a PCA using soil data for 39 analytes. The proportion of explained variance is indicated for each component. Scores for samples are plotted versus the bottom and left axes, and rotations (eigenvectors) for variables (analytes) are plotted on the top and right axes. For clarity, not all 39 elements are labeled. Carbonate C abbreviated as Carb C and organic carbon as Org C.

Sample data points in Fig. 3 show boundary effects, that is, roughly linear edges of the distribution beyond which few or no points plot. Such boundary effects are considered undesirable in some cases as they constrain potentially observable patterns and can be addressed through CLR transformation combined with robust PCA (Tolosana-Delgado and McKinley, 2016). Robust PCA is a modification of classical PCA that reduces or eliminates the influence of multivariate outliers. However, for the purposes of tracing enrichment, the influence of such extreme compositions is desired to shape the output and expose a geochemical trend that reflects the fingerprint of enrichment. Thus, classical PCA, as applied here, is preferable.

The boundary orthogonal and opposite to the trend defined by the enriched elements is useful to a study of dispersion of elements related to anthropogenic activity. Points arrayed along and near that boundary are likely to represent samples having background concentrations of the enriched elements. The boundary orthogonal to and defined by samples weighted towards Ca, Mg, and carbonate C may reflect upper levels of carbonate mineral inheritance from the Kaibab Formation.

3.3. PCA of 13 selected elements

The above evaluations of the previous PCAs allow refinement of the list of elements to be included for a PCA that offers perhaps the best insights into element enrichment and background. To represent enrichment from BPU ore, U, Mo, S, As, and Cu are included, chosen based upon their common alignment and strong weighting in the previous PCA (Fig. 3). To represent carbonate minerals, Ca and Mg are included. Based upon the previous PCA, any of about a dozen different elements might be chosen to represent the non-carbonate portion of background (i.e., clays, organic matter, and regional dust). Here, the major elements Al, Fe, K, Mn, Na, and Ti are chosen because major elements normally have higher precision in their analysis, relative to measured concentration, than trace elements. Less noise is therefore contributed to the resulting PCA. Carbonate C and organic C are excluded as they require specialized

analyses and this PCA illustrates analysis of elements solely from digest and ICP-MS/AES analysis.

The three geochemical trends described above emerge again but are more distinct with the reduced number of elements (Fig. 4). The relative arrangement of points is similar but perhaps tighter, and the two boundary effects emerge again. The mine sites AZ1, KN, and PN have points arrayed along the enrichment trend that point back to the boundary effect zone that generally suggests background. In the context of the study and methods described here, there are two criteria for identification and selection of a good background. First, the samples are from an area that can be assumed to be free of enrichment from the source being investigated. In this study, EZ2 and LRT meet this criterion because no mining activities had occurred there prior to sampling. For studies in which geographically separate potential background sites were not sampled, samples collected farther from the source and arrayed along the boundary effect orthogonal to the enrichment trend would be suitable. However, it might be a challenge to objectively draw a line between the background and enriched samples. The second criterion is overlap or adjacency in the biplot between the samples representing background and those in the area being investigated for enrichment. Such association indicates geochemical similarity prior to the addition of the enriching source.

Points from the unmined background site EZ2 cluster at the intersection of the enrichment trend and background boundary and suggest that EZ2 is a good background composition for use in calculating EFs for sites AZ1, KN, and PN. As some AZ1 points overlap with EZ2 points, the case is strongest there. Lack of overlap of KN or PN with EZ2 suggests either that the background concentrations of the BPU-enriched elements are slightly higher at those sites, or that the fingerprint of enrichment is detectable in every sample collected through the combination of high quality data and PCA as described.

The CM points are arrayed roughly parallel to the Ca and Mg trend, and orthogonal to the boundary it defines. The distribution reflects more variation and lesser dominance of these carbonate-associated elements at CM relative to all elements in the sub-composition. It also suggests that LRT is a better representation of background for CM than EZ2, as LRT points cluster near the middle
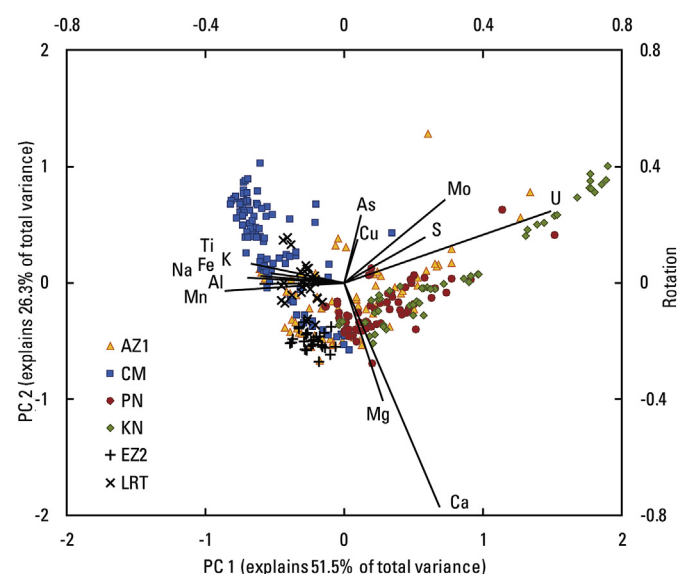

Fig. 4. Biplot of the first two principal components (PC1 and PC2) from a PCA using soil data for 13 selected elements. The proportion of explained variance is indicated for each component. Scores for samples are plotted versus the bottom and left axes, and rotations (eigenvectors) for elements are plotted on the top and right axes.

of the CM distribution along the background boundary area. Neither geology (Richard et al., 2000) nor soil series (Soil Survey Staff, 2018) appear to explain the differences between backgrounds among the different sites. Possibly such differences reflect the localized variation in the composition and degree of accumulation of regional dust (Reheis, 2006).

A biplot of another PCA that includes samples representing the enriching material, in this case the 96 historical samples of BPU ore, is included as Supplementary Fig. 1. The goal was to further cement the link between the pattern of enrichment in soils and the enriching material. The biplot achieves this, as BPU ore samples are arrayed far out along the enrichment trend. Unfortunately, the ore samples are scattered broadly across the plot, reflecting substantial but not unexpected heterogeneity. Additionally, the soil samples are compressed into a small area of the plot, making it difficult to discern the environmental patterns apparent in previous biplots. Such results illustrate the potentially limited usefulness of PCAs that include samples of enriching material with exceptionally high trace-element concentrations.

3.4. PCA to evaluate other background compositions

A final PCA biplot is used to illustrate UCC and CP soils as being imperfect background compositions. Some studies use the UCC composition to represent background if nothing more appropriate is available. The median CP soils composition represents a better scenario in which data on soils from the same region have been generated by a previous study (Fig. 1). Ten of the elements from the 13-element PCA (Fig. 4) are used, including Al, Ca, Fe, K Mg, Mn, Na, Ti, Cu, and U. Median concentrations of As, Mo, and S were below reporting limits or not measured for CP soils (Table 1), thus they are excluded. The PCA was conducted without the UCC or CP soils data, then those data were scaled and rotated for addition to the biplot. The result in Fig. 5 shows similar overall patterns to those in Figs. 3 and 4. The new perspective is on the two potential background compositions. The UCC point falls far beyond one of the boundary effect zones defined by the dataset as a whole. The CP soil point falls where it reflects lower carbonate-related Ca and Mg dominance in the subcomposition and greater dominance of aluminosilicate-related elements (Table 1). CP soil would be a poor representation of background for all of the mine sites except CM, and it can be noted that unlike the other sites, CM and CP soil share geography in terms of locations south of the Grand Canyon (Fig. 1). For CP soil to be such an imperfect background is surprising, given regional proximity and similarity of soil parent materials but illustrates the hazard of blindly accepting a background composition based solely on geographical similarity. Although comparing concentrations of individual background or potentially enriched elements among sample populations can reveal such problems (Table 1), the PCA provides a multivariate perspective that makes holistic comparisons between sample populations faster and easier.

3.5. Background compositions, reference elements, and calculation of EFs

Using the perspective from the PCAs, more representative EFs can now be calculated. Fig. 4 suggests that site EZ2 is a reasonable geochemical background relative to the AZ1, KN, and PN sites. For the CM site, LRT is a reasonable background. Calculation of EF values requires selection of a reference element. Aluminum, Fe, and Ti are common choices among the major elements (Reimann and de Caritat, 2000) based upon natural association with trace elements in background and relatively low mobility in the weathering environment. Fig. 4 reveals general similarity of distribution between Al, Fe, and Ti in the overall dataset. Thus, bias or distortion of
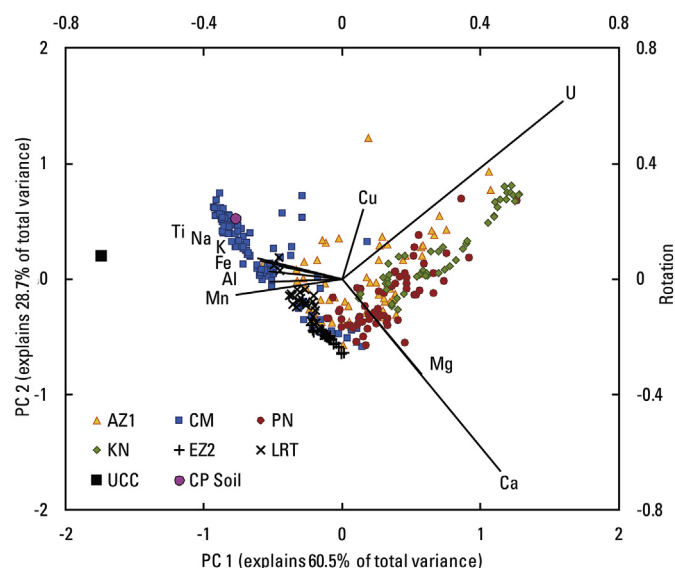

Fig. 5. Biplot of the first two principal components (PC1 and PC2) from a PCA using soil data for 10 selected elements. The proportion of explained variance is indicated for each component. Scores for samples are plotted versus the bottom and left axes, and rotations (eigenvectors) for variables (elements) are plotted on the top and right axes. The composition of potential background compositions Upper Continental Crust (UCC) and Coconino Plateau soils (CP) were not part of the PCA but were scaled, rotated, and plotted for comparison purposes.

EF values from selection of one versus another would be expected to be small.

Using samples from KN for illustration purposes, Fig. 6 compares EF values for U. Values calculated using Al, Fe, and Ti are compared, as well as using EZ2, UCC, and CP soil as background compositions. Values of the PI (Eq. (2)) using the three different backgrounds are also compared. The EF values are greater using UCC as a background
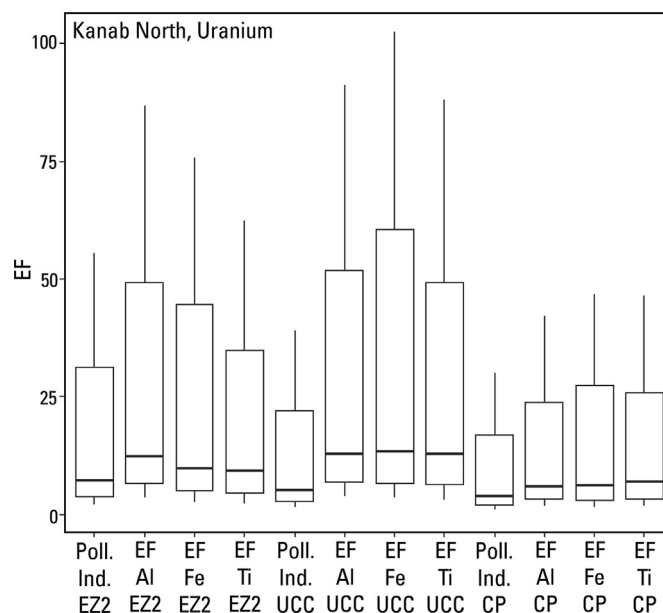

Fig. 6. Box and whiskers plot comparing enrichment factor (EF) values for U in soils collected at the Kanab North (KN) site calculated using different reference elements (Al, Fe, and Ti) and different background compositions (EZ2 soils, upper continental crust (UCC), Coconino Plateau (CP) soils). For reference, the pollution index calculated using each background is also shown.

and lower using CP soil, compared to using EZ2, illustrating how the selection of a background composition influences EF values. Differences are more pronounced at greater EF values. Selection of the most appropriate background will provide the most accurate picture of enrichment wheras other choices of background may skew results upward or downward. Values of the PI are substantially lower than EF values regardless of which background is used. This pattern arises because the PI does not account for the lower concentrations of the alumino-silicate-associated, non-carbonate-related elements at KN compared to EZ2, UCC, or CP soils. The inability to compensate for differences in background within individual samples of enriched media is a disadvantage of the PI as well as the GI (Eq. (3)).

Although EZ2 provides a good background composition for KN and the EF is a good metric, differences are apparent depending upon whether Al, Fe, or Ti is selected as the reference element. Unfortunately, it is difficult to recommend methodology or criteria that would suggest one as better than the others. Examination of third principal components and PCAs of only background site data (analyses not shown) failed to find associations that provide substantial insight. Thus, selection of a reference element remains difficult to optimize in the calculation of EF values.

Fortunately, choices between different backgrounds and reference elements, or even between enrichment metrics, affect absolute values but have limited influence on their enrichment order within a set of samples. The idea is explored using the data from all four mine sites. One comparison is EF values of U using Fe as a reference element to Al as a reference element, with both EF values using site EZ2 as the background (Fig. 7a). Using Fe yields values that average only 84% as large as those using Al and there is scatter in the differences between the two, particularly at higher values. Thus, both absolute values and the order of values within the set of samples are affected. When comparing the EF values of U using Fe as a reference element versus the PI, with both using site EZ2 as the background, again both absolute values and order are affected

(Fig. 7b). In contrast, examples using different backgrounds, such as LRT or CP soil versus EZ2, show how background controls absolute values but has no influence on the order of values within a set of samples (Fig. 7c). Understanding these differences is important because they illustrate how decisions on how enrichment is calculated influence the outcome of the calculations. Sizeable differences in EF values can arise from using inappropriate backgrounds, as illustrated by comparing EF values using EZ2 versus CP soil, both with Fe as the reference element (Fig. 7d). The biplot in Fig. 5 shows that CP soil is an inappropriate background for all sites, though the case is least clear for CM.

The comparisons above illustrate that the order of enrichment within any sample set can be known with high confidence, but the absolute degree of enrichment will always be less certain. Background selection is likely to be more influential than reference element selection. Picking the best available background, by using techniques like the PCAs presented here, will yield the most representative EFs. Ultimately, however, it must be remembered that EF values should only be compared relatively and within a given area (Reimann and de Caritat, 2005).

3.6. Patterns in enrichment factors at study sites

Although the focus of the present paper is on methods to recognize and determine enrichment of elements mobilized by anthropogenic activity, certain patterns of enrichment at the study sites emerge from the exercise. One is that U, S, As, Mo, and Cu are the best tracers of BPU ore material presence in soils for these study sites, as seen both in PCA biplots (Figs. 3 and 4) and in calculated EF values (Table 2). Among these, U is far the best tracer. Another pattern is that ore-related enrichment is detectable at all the mine sites, though the degree of enrichment substantially differs (Table 2). At most sites, the greatest enrichment was found in the "point" samples, collected at discrete locations where dust accumulation might be expected, rather than the DU samples that
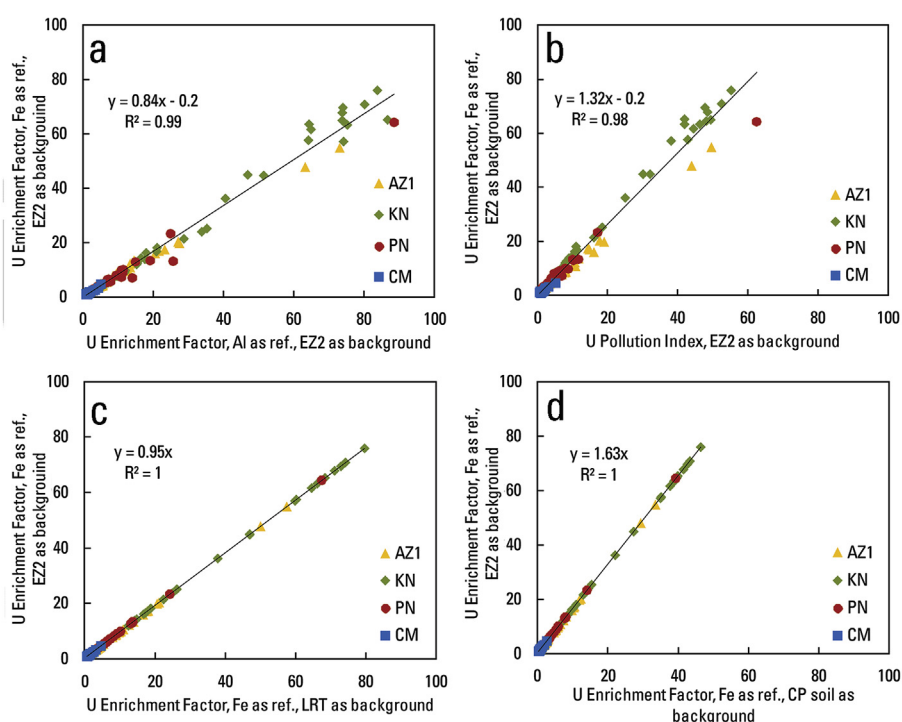

Fig. 7. Scatterplots comparing U enrichment in mine area soils using different reference elements, background compositions, and enrichment metrics (enrichment factor, pollution index).

Table 2
Summary statistics for enrichment factors (EFs) calculated for selected elements in soils sampled in this study. Iron is used as the reference element and EZ2 as the background composition for all sites except CM. For CM, LRT is used as the background composition. Sample counts include triplicate collections as three separate samples for DU categories. KN Outside and KN Inside refer to outside and inside the mine site perimeter, respectively.

		U	S	As	Mo	Cu	Pb	Co	Ni	Zn
AZ1 DU	median	2.0	1.6	1.3	1.1	1.2	1.4	0.9	1.1	1.3
N = 54	range	1.0–13.4	0.6–3.0	0.9–7.2	0.6–8.4	0.8–2.6	1.2–2.0	0.7–1.0	1.0–1.5	1.1–1.7
AZ1 Point	median	16.4	3.2	3.0	2.5	2.7	1.9	1.0	1.4	1.7
N = 13	range	2.2–54.8	1.2–7.2	0.9–9.0	0.8–7.3	1.0–8.2	1.2–3.9	0.7–2.0	0.8–2.5	1.1–4.4
CM DU	median	1.0	1.2	0.4	1.1	1.0	1.1	1.1	1.1	1.0
N = 81	range	0.8–4.7	0.4–3.6	0.2–1.7	0.7–2.7	0.7–4.0	0.8–2.5	0.8–2.4	0.9–1.4	0.8–1.3
CM Point	median	1.1	0.9	0.4	1.1	0.9	1.0	1.1	1.2	1.3
N = 16	range	0.9–1.2	0.7–1.3	0.3–0.6	0.8–1.4	0.6–0.9	0.8–1.3	0.9–1.2	0.8–1.4	1.0–1.4
KN Outside	median	8.2	2.1	1.9	1.4	1.3	1.5	0.8	1.0	1.4
N = 39	range	2.6–65.2	1.1–7.7	0.8–5.7	0.8–8.1	0.8–3.0	1.1–4.6	0.6–2.4	0.7–2.3	1.0–3.7
KN Inside	median	63.9	27.0	8.0	35.5	3.8	2.4	2.0	2.2	3.0
N = 12	range	36.1–75.8	15.6–40.6	6.2–10.8	15.3–61.0	3.2–6.7	2.0–5.1	1.4–2.5	1.7–2.5	2.1–3.5
PN DU	median	2.5	2.0	3.0	2.0	1.9	1.5	0.9	1.2	1.3
N = 51	range	1.2–9.9	1.1–13.2	1.7–7.2	1.1–5.1	1.5–3.8	1.1–3.3	0.7–2.0	1.1–2.6	1.0–3.9
PN Point	median	7.9	2.2	3.2	2.2	3.5	1.5	1.0	1.3	1.3
n = 13	range	1.6–64.2	0.3–26.1	1.3–6.5	1.5–10.1	1.7–7.4	1.1–2.1	0.7–8.4	1.1–12.6	0.7–26.5

integrated larger areas. The exception was CM, where ore had not yet been brought to the surface. At CM, enrichment was just detectable in DU samples (Table 2). By themselves, EF values of 4.7 for U or 4.0 for Cu might be considered natural variability. The multivariate context of a PCA biplot helps to establish such enrichment as originating from BPU ore.

High EF values at AZ1, KN, and PN reflect dispersal of BPU ore-derived elements to surrounding soils. Several considerations provide context for that conclusion. First is that all samples were collected within 220 m of the fenced (currently or formerly) perimeter of the mine site, and most less than 100 m. Exceptions are of 1–3 sets of triplicate samples collected along haul roads at each site. Thus, areas in which ore-derived material was detected are generally close to the mine site. Second, except for samples from within the KN mine site, values close to 1 and thus approximating background were found within each sample set for individual mine sites. Therefore, enrichment of ore-derived elements is not universally detected in soils surrounding these mine sites. Finally, detectability of BPU ore-derived elements is separate from the issue of establishing environmental risk or toxicity effects from presence of those elements at particular levels (Hinck et al., 2013).

4. Conclusions

As demonstrated here, carefully applied, classical PCAs in combination with biplots are powerful tools for studying potential anthropogenic enrichment in multi-element environmental datasets. The methodology draws upon advances from CoDa and involves examining patterns using multiple subsets of CLR-transformed data and including both major and trace elements. Such examination can help understand the fingerprint of anthropogenic enrichment and identify one or more elements that trace it best. Examining multiple subsets of elements and samples can help identify and exclude problematic data, such as data which are imputed due to reporting limits. Progressively narrowing the subsets to reduce noise and clarify patterns is an important aspect of the approach, but different PCAs can provide distinct and valuable perspectives. A single PCA using a particular subset of samples and elements is unlikely to tell the full story of any particular dataset. Boundary effects, an emergent property of PCA of elemental data, appear quite useful for identifying background compositions and understanding how background varies within and between sites. With the list of elements refined, and background composition understood, samples containing enriched or anthropogenic materials can be identified in biplots based upon their integrated, multi-element composition. Datasets based upon incremental sampling methodology or other compositing techniques should be particularly amenable to analysis.

Using PCA biplots for context, EF values can be calculated with thoughtful choices as to the background and reference element used. However, such choices remain subjective. Thus, it should be remembered that relative order of enrichment is less sensitive to such choices, but absolute magnitudes of EF values are quite sensitive and particularly to background. Additionally, although the EF is a good numerical metric for assessing enrichment, the PCA biplot may be superior as it integrates multiple enriched and non-enriched elements and does so visually.

Substantial enrichment of U, S, As, Mo, and Cu was detected in soils in and around BPU mine sites. The similarity of the elemental fingerprint indicates it is derived from BPU ore. Using unmined background sites in the region for comparison, U was enriched by factors up to 75, and the other elements were enriched to lesser degrees. Detection of enrichment indicates that ore-derived elements are dispersed in and around mine sites but determining environmental risk or toxicological effects is a separate issue.

Declarations of interest

None.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2019.01.122.

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