Forensic soil provenancing in an urban/suburban setting: A sequential multivariate approach

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Abstract
Compositional data from a soil survey over North Canberra, Australian Capital Territory, are used to develop and test an empirical soil provenancing method. Mineralogical data from Fourier transform infrared spectroscopy (FTIR) and magnetic susceptibility (MS), and geochemical data from X-ray fluorescence (XRF; for total major oxides) and inductively coupled plasma-mass spectrometry (ICP-MS; for both total and aqua regia-soluble trace elements) are performed on the survey’s 268 topsoil samples (0–5 cm depth; 1 sample per km²). Principal components (PCs) are calculated after imputation of censored data and centered log-ratio transformation. The sequential provenancing approach is underpinned by (i) the preparation of interpolated raster grids of the soil properties (including PCs); (ii) the explicit quantification and propagation of uncertainty; (iii) the intersection of the soil property rasters with the values of the evidentiary sample (± uncertainty); and (iv) the computation of cumulative provenance rasters (“heat maps”) for the various analytical techniques. The sequential provenancing method is tested on the North Canberra soil survey with three “blind” samples representing simulated evidentiary samples. Performance metrics of precision and accuracy indicate that the FTIR and MS (mineralogy), as well as XRF and total ICP-MS (geochemistry) analytical methods, offer the most precise and accurate provenance predictions. Inclusion of PCs in provenancing adds marginally to the performance. Maximizing the number of analytes/analytical techniques is advantageous in soil provenancing. Despite acknowledged limitations and gaps, it is concluded that the empirical soil provenancing approach can play an important role in forensic and intelligence applications.

Keywords
compositional data analysis, geochemical mapping, geographic information system, interpolation, soil forensics, soil properties, uncertainty

Highlights
- Topsoil mineralogical and chemical properties are determined over a 260-km² area in/around Canberra.
INTRODUCTION

Soils are complex mixtures of minerals, amorphous material, organic matter, water, gasses, organisms, and, in places, man-made particles. The composition of soils is fundamentally controlled by their location through the environmental controls of climate (moisture, temperature), life (plants, organisms), topography (elevation, aspect, slope, relief), substrate (geology, parent material), and time (weathering), among others, as first articulated by Jenny in 1941 [1]. Thus, the natural soil composition varies in a largely predictable and structured, rather than random and chaotic, fashion. Therefore, coherent maps showing the spatial variability of natural soil parameters can be produced provided the density at which they are measured is appropriate relative to the scale of their heterogeneity. Human land use may either confound or complement understanding of the spatial patterns. Once a series of soil property maps are produced, they can serve two important forensic purposes: (i) the evidentiary relevance of observing non-distinguishable questioned and control samples, and (ii) the potential to constrain the spatial provenance of an unknown questioned soil sample.

The use of geological material such as soil in forensic investigations is increasing in police forces around the world, including the Federal Bureau of Investigation, the Royal Canadian Mounted Police, and the Australian Federal Police (e.g., [2–7]). In Australia, successful soil forensic investigations have contributed evidence that has been used in Australian Supreme courts (e.g., [8]). Forensic soil provenancing can be defined as the capability to spatially constrain the likely region of origin of an evidentiary sample of earth-related material [9,10]. Rawlins et al. [9] characterized the prediction of the provenance of a sample of earth-related material as “one of the most difficult and challenging tasks for analytical earth scientists.”

Caritat et al. [11] introduced a predictive soil provenancing method that does not require a specific soil survey to be carried out over an area of interest. More typically, however, forensic soil provenancing is implemented empirically by comparing the spatial multivariate information contained in the evidentiary soil’s geochemistry, mineralogy, bulk properties, etc., to either purposely acquired or pre-existing knowledge (see fig. 1 in [11]). Such knowledge generally is derived from soil geochemical surveys and stored in databases containing this same or similar multivariate information over the region of interest at an appropriate density [12]. Geochemical surveys come in many guises (e.g., [13,14]) and although many already exist at a range of spatial coverages (continental to local), sampling densities (1 sample per 1000’s of km² to 100’s of samples per 1 km²), and sampling media (materials, selections (topsoil, C horizon, sediment,...), forensic applications have specific requirements that may not have been the primary focus of the original surveys [15]. Despite this, these pre-existing surveys and associated databases have their use in forensic applications, as long as their limitations (e.g., sampling density, sampling medium, sample collection method) are understood.

Once a database is selected, a number of statistical and visualization analysis tools can be implemented, including univariate, bivariate, and multivariate statistical analysis, exploratory data analysis, analysis of variance, compositional data analysis, spatial interpolation/geostatistics and smoothing, cluster analysis, supervised or unsupervised classification, and data mining (e.g., [16–26]).

The next step in empirical soil provenancing is the comparison of the evidentiary soil sample’s composition with the selected database. Statistical analysis of differences can be performed using a few or many compositional characteristics (including chemical element abundances, isotopes, mineral abundances), their ratios or other calculated indexes, correlation analysis, and/or factor or principal component analysis (e.g., [27–34]), among others.

Finally, if the evidentiary sample is non-distinguishable with a particular region of origin, a detailed forensic investigation can proceed there. If unsuccessful or inconclusive, more data and better data must be collated (if pre-existing) or collected (if not), which may imply undertaking a more refined geochemical survey at a scale relevant for the case at hand.

In this and a companion paper, we describe and compare different approaches to soil provenancing based on a local (i.e., relatively small area and relatively high sampling density) soil geochemical survey in and around North Canberra, Australian Capital Territory, in inland southeastern Australia. The approaches under consideration are (i) a sequential multivariate approach (this paper), and (ii) a simultaneous multivariate (degree of geochemical similarity) approach (upcoming paper in preparation). A complementary probabilistic (likelihood ratio) approach will be published separately (upcoming paper in preparation). The aims of the present contribution accordingly are to:

• briefly introduce the North Canberra soil geochemical survey
• present the sequential multivariate provenancing approach
• present results for this method
• quantify the performance of this approach
• draw conclusions as to the suitability of the sequential multivariate provenancing approach for forensic and intelligence applications
2 | MATERIALS AND METHODS

2.1 | The North Canberra soil geochemical survey

The North Canberra soil geochemical survey was initiated in 2017 and focused on the northern part of Canberra city and surrounding suburban areas, in the Australian Capital Territory (ACT) (Figure 1). The total area covered by the survey was ~260 km$^2$ sampled at an average density of 1 site/km$^2$ [35]. In addition to the 268 samples in this survey, three “blind” samples (Blind 1, Blind 2, and Blind 3 hereafter) were collected from sites within the survey area (but away from the survey’s grid samples), the geographical coordinates or even approximate locations of which were unknown to the lead researcher until the project had concluded all data analysis and map production.

General background, results, and interpretations of the geochemical mapping of the ACT, including the investigation of the effects of lithology and land use on soil geochemistry, will be presented elsewhere (upcoming paper in preparation). A simple description of the blind sample sites is, however, warranted here as it will have a bearing on the interpretation of the provenance analysis we focus on (see Fig. S1 in Appendix S1). Blind 1 is a Kurosol soil (all soil types from the

![Figure 1](image_url)

Figure 1: Sample locations (crosses) for the North Canberra, Australian Capital Territory (ACT), soil geochemical survey overlain on Australian Soil Classification (ASC) soil orders [36] (A), and high-order lithology types (geology) (B). Study area outlined in solid black line. Principal, main, and secondary roads are shown as thick, thin, and dashed gray lines, respectively. Water bodies and drainage are shown in blue. ACT border is shown as brown dash-dotted line. Geospatial data from ACT Government or Australian Government, unless otherwise indicated.
Australian Soil Classification (ASC) [36]) collected over the Mount Ainslie Volcanics Formation, a Wenlockian (Early Silurian) dacitic ignimbrite with minor ashstone, agglomerate and shale, and porphyry, within the Hawkins Volcanic Suite (all stratigraphic units from the Australian Stratigraphic Units Database https://asud.ga.gov.au/). We note here that Blind 1 was deliberately collected from a local environment not representative of the broader landscape to test the limit of soil provenancing. Blind 2 is Kurosol/Rudosol (Alluvial) soil collected over undifferentiated Quaternary alluvium and fluvial deposits of gravel, sand, silt, and clay along Ginninderra Creek. Blind 3 is a Kurosol soil collected over a thin, folded Acton Shale Member, an Early Ordovician black graptolitic siliceous shale within the broader turbiditic (sandstone, mudstone, shale) Adaminaby Group.

In this paper, the analytical focus is directed to both (i) soil mineralogy via infrared spectroscopy (informing on, e.g., hydrated minerals such as clay minerals, carbonates, and sulfates) and magnetic susceptibility (informing on, e.g., ferrimagnetic minerals such as magnetite or maghemite, and their grain sizes); and (ii) soil geochemistry via major oxides and organic matter concentrations as well as trace element concentrations after two chemical extractions of different strengths. Sample collection, preparation, and analysis methods are detailed in the Appendix S1, as are data analysis, spatial analysis, quality control, and detailed uncertainty analysis procedures.

2.2 | Uncertainty analysis

Uncertainty arises from any attempt to quantify natural phenomena, from sampling through to analysis. In this project, two main types of uncertainty were specifically quantified: measurement uncertainty ($U_m$) and interpolation uncertainty ($U_i$). They were quantified as three standard deviations of field triplicates ($SD_m$) and of residuals ($SD_i$), respectively. Residuals are the differences between the interpolated (modeled) values and the measured values at each sampled site. The combined uncertainty ($U_c$), which applies to the generated property raster surfaces, is calculated using the root sum of squares method (e.g., [37,38]) as follows:

$$U_c = \sqrt{(U_m)^2 + (U_i)^2} = \sqrt{(3 \times SD_m)^2 + (3 \times SD_i)^2}$$

The standard deviations ($SD_m$, $SD_i$) and uncertainties ($U_m$, $U_i$, $U_c$) of each analyte are given in Table S3 in the Appendix S1.

2.3 | Determination of search ranges

For each variable, the Search Range (SR) for a blind (evidentiary) sample was set to the measured value of that variable in that blind sample (Target Value or TV) with a buffer reflecting the sum of the uncertainty in the analytical data ($U_m$) and of the uncertainty in the raster surface ($U_i$), according to:

$$SR = TV \pm (U_m + U_i)$$

This accounts for uncertainty in both the interpolated surface (which is derived from measured values in the database and a smoothing interpolation algorithm), via $U_c$, and the measured value in the blind sample, via $U_m$, as illustrated in Figure 2. The graphic illustrates that the interpolated grid value for a particular soil property needs to fall within the uncertainty envelope ($U_m + U_i$) around that soil property for the evidentiary sample to count as a match and score a 1 in the provenance raster computation (see below and Appendix S1).

2.4 | Raster generation and clipping

Interpolation rasters for each available variable were prepared by inverse distance weighting (IDW), clipped, and analyzed in QGIS as explained in the Spatial Analysis section of the Appendix S1.

2.5 | Provenancing methodology

A sequential multivariate approach to soil provenancing based on an empirical database of soil properties is developed in this
3 | RESULTS AND DISCUSSION

A statistical summary of the data collected during this project can be found in Table 1. Lower limits of detection and proportions of the variance explained for the principal components obtained for the FTIR, XRF, Total, and *aqua regia* (AR) ICP-MS datasets (the latter three after centered log-ratio—CLR—transformation) are given in the Appendix S1 (Tables S1 and S2).

3.1 | Validation

Standard deviations and uncertainties derived for each parameter as described above are given in the Appendix S1 (Table S3). The Target Values and Search Ranges for the Blind 1, Blind 2, and Blind 3 evidentiary samples collected as part of this project are shown in Tables 2, 3, and 4, respectively. The results of soil provenancing investigations using the sequential multivariate approach are discussed below.

The maps of provenance prediction for samples Blind 1, Blind 2, and Blind 3 based on three FTIR principal components and two MS parameters (for a total of five parameters) are shown in Figure 3. Results indicate that for these three blind samples, 3 of (a theoretical maximum of) 5, 2 of 5, and 3 of 5 parameters match the Search Ranges for Blind 1, Blind 2, and Blind 3, respectively. If the three PCs from FTIR are removed from the analysis and only MS data are considered (not shown), the match rates for these three blind samples change to 1 of 2 for all three blind samples.

The soil provenance rasters generated by the present sequential multivariate provenancing method can be interpreted like "heat maps" where raster grid cells with hotter colors are a better match to the evidentiary sample under investigation than cooler colored cells. In Figure 3A, grid cells colored light, medium, and dark red (scores of 3, 4, or 5) indicate a match equivalent or superior to the cell from which simulated evidentiary sample Blind 1 actually comes from (which has score of 3). Provenancing grids computed from the cumulative results from more variables yield smoother, more gradational spatial patterns than those generated from fewer variables, as demonstrated by subsequent figures. In a separate section (Performance Assessment), we will discuss metrics to quantify how good the provenance predictions are.

The maps of provenance prediction for samples Blind 1, Blind 2, and Blind 3 based on 11 compositional XRF parameters are shown in Figure 4. Results indicate that for these three blind samples, 6 of 11, 3 of 11, and 5 of 11 parameters match the Search Ranges for Blind 1, Blind 2, and Blind 3, respectively. If the 8 first PCs are included in the analysis (not shown), the match rates for these three blind samples change to 9 of 27, 20 of 27, and 10 of 27 for Blind 1, Blind 2, and Blind 3, respectively.

The maps of provenance prediction for samples Blind 1, Blind 2, and Blind 3 based on 38 compositional Total ICP-MS parameters are shown in Figure 5. Results indicate that for these three blind samples, 13 of 38, 31 of 38, and 17 of 38 parameters match the Search Ranges for Blind 1, Blind 2, and Blind 3, respectively. If the 8 first PCs are included in the analysis (not shown), the match rates for these three blind samples change to 17 of 46, 39 of 46, and 29 of 46 for Blind 1, Blind 2, and Blind 3, respectively.

The maps of provenance prediction for samples Blind 1, Blind 2, and Blind 3 based on 19 compositional AR ICP-MS parameters are shown in Figure 6. Results indicate that for these three blind samples, 4 of 19, 15 of 19, and 6 of 19 parameters match the Search Ranges for Blind 1, Blind 2, and Blind 3, respectively. If the 8 first PCs are included in the analysis (not shown), the match rates for these three blind samples change to 9 of 27, 20 of 27, and 10 of 27 for Blind 1, Blind 2, and Blind 3, respectively.

The maps of provenance prediction for samples Blind 1, Blind 2, and Blind 3 based on the 97 combined FTIR, MS, XRF, Tot, and AR ICP-MS parameters (including PCs) are shown in Figure 7. Results indicate that for these three blind samples, 39 of 97, 67 of 97, and 39 of 97 parameters match the Search Ranges for Blind 1, Blind 2, and Blind 3, respectively. If the 27 PCs are removed from the analysis (not shown), the match rates for these three blind samples change to 26 of 70, 51 of 70, and 31 of 70 for Blind 1, Blind 2, and Blind 3, respectively.
| Variable | Min | Med | Ave | Max | SD |
|----------|-----|-----|-----|-----|----|
| As_Tot | 0.83 | 3.55 | 4.77 | 107 | 0.46 |
| Ba_Tot | 1.39 | 3.10 | 4.90 | 107 | 0.46 |
| Bi_Tot | 0.30 | 0.40 | 0.40 | 107 | 0.46 |
| Ce_Tot | 1.69 | 3.58 | 4.77 | 107 | 0.46 |
| Cr_Tot | 2.93 | 4.81 | 5.09 | 107 | 0.46 |
| Dy_Tot | 2.12 | 4.14 | 4.95 | 107 | 0.46 |
| Eu_Tot | 0.90 | 2.79 | 4.35 | 107 | 0.46 |
| Ga_Tot | 0.11 | 0.56 | 0.85 | 107 | 0.46 |
| Gd_Tot | 0.22 | 0.71 | 1.44 | 107 | 0.46 |
| Ge_Tot | 0.11 | 0.46 | 0.71 | 107 | 0.46 |
| Hf_Tot | 0.02 | 0.29 | 0.63 | 107 | 0.46 |
| Ho_Tot | 0.11 | 0.22 | 0.43 | 107 | 0.46 |
| La_Tot | 1.67 | 2.63 | 3.12 | 107 | 0.46 |
| Lu_Tot | 0.22 | 0.29 | 0.31 | 107 | 0.46 |
| Nb_Tot | 0.02 | 0.03 | 0.06 | 107 | 0.46 |
| Ni_Tot | <2.40 | 8.61 | 68.1 | 107 | 0.46 |
| Pb_Tot | 6.71 | 19.1 | 23.7 | 107 | 0.46 |
| Pr_Tot | 4.15 | 7.66 | 7.92 | 107 | 0.46 |
| Rb_Tot | 33.7 | 83.0 | 86.0 | 107 | 0.46 |
| Sc_Tot | 4.42 | 9.72 | 9.88 | 107 | 0.46 |
| Sn_Tot | 1.65 | 3.06 | 3.71 | 107 | 0.46 |
| Sr_Tot | 21.6 | 51.4 | 54.3 | 107 | 0.46 |
| Ta_Tot | 0.85 | 1.26 | 1.28 | 107 | 0.46 |
| Tb_Tot | 0.48 | 0.84 | 0.86 | 107 | 0.46 |
| Th_Tot | 8.36 | 13.3 | 13.7 | 107 | 0.46 |
| Ti_O2 | 0.65 | 2.12 | 2.22 | 107 | 0.46 |
| TiO2_XRF | 0.63 | 2.12 | 2.22 | 107 | 0.46 |
| TiO2_Le | 1.11 | 2.79 | 2.80 | 107 | 0.46 |
| TIO2_XRF | 0.65 | 2.12 | 2.22 | 107 | 0.46 |
| TIO2_Le | 1.11 | 2.79 | 2.80 | 107 | 0.46 |
| V2O5 | 0.31 | 0.73 | 1.74 | 107 | 0.46 |
| V2O5_XRF | 0.31 | 0.73 | 1.74 | 107 | 0.46 |
| V2O5_Le | 1.11 | 2.79 | 2.80 | 107 | 0.46 |
| Zn_Tot | 0.02 | 0.03 | 0.06 | 107 | 0.46 |

(Continues)
| Variable | Min   | Med  | Ave  | Max   | SD   | Variable | Min   | Med  | Ave  | Max   | SD   |
|----------|-------|------|------|-------|------|----------|-------|------|------|-------|------|
| Eu_AR    | 0.13  | 0.57 | 0.60 | 2.57  | 0.30 | U_Tot    | 2.18  | 3.12 | 3.23 | 6.97  | 0.58 |
| Fe_AR    | 4742  | 13081| 14269| 130186| 8813 | V_Tot    | 22.5  | 60.9 | 62.4 | 209   | 17.4 |
| La_AR    | 5.10  | 18.0 | 18.6 | 58.5  | 7.15 | W_Tot    | 1.69  | 2.53 | 2.78 | 10.7  | 0.95 |
| Mn_AR    | 17.0  | 432  | 463  | 2984  | 320  | Y_Tot    | 16.8  | 28.3 | 28.9 | 82.4  | 6.3  |
| Nd_AR    | 4.02  | 17.1 | 17.4 | 61.7  | 7.34 | Yb_Tot   | 2.06  | 3.29 | 3.36 | 11.1  | 0.72 |
| Ni_AR    | 1.86  | 8.32 | 9.11 | 28.8  | 4.49 | Zn_Tot   | 12.9  | 44.6 | 50.8 | 315   | 31.3 |
| Pb_AR    | 3.71  | 15.3 | 20.4 | 394   | 27.0 | Zr_Tot   | 175   | 564  | 579  | 1621  | 174  |
| Rb_AR    | 4.35  | 11.5 | 13.0 | 33.3  | 5.34 | PC1_Tot  | -10.567| -0.216 | 0.035 | 23.291 | 4.385 |
| Sr_AR    | 1.84  | 12.7 | 13.9 | 40.0  | 6.69 | PC2_Tot  | -14.872| 0.065  | 0.143 | 9.352  | 3.750 |
| Th_AR    | 0.52  | 1.92 | 2.19 | 16.1  | 1.38 | PC3_Tot  | -10.272| -0.047 | -0.506 | 4.520  | 2.468 |
| Tm_AR    | 0.01  | 0.09 | 0.10 | 0.49  | 0.06 | PC4_Tot  | -6.613 | 0.151  | 0.122 | 12.971 | 2.365 |
| Zn_AR    | <15.0 | 43.7 | 51.0 | 369   | 35.1 | PC5_Tot  | -4.082 | 0.114  | 0.195 | 7.237  | 1.811 |
| PC1_AR   | -10.009 | -0.242 | -0.138 | 7.409 | 2.338 | PC6_Tot  | -6.451 | -0.066 | 0.013 | 6.767  | 1.866 |
| PC2_AR   | -6.681 | 0.343 | 0.016 | 3.211 | 1.719 | PC7_Tot  | -4.621 | -0.154 | -0.259 | 4.564  | 1.563 |
| PC3_AR   | -6.217 | 0.046 | 0.000 | 3.458 | 1.366 | PC8_Tot  | -6.424 | 0.140  | 0.140 | 4.334  | 1.462 |
| PC4_AR   | -3.845 | -0.052 | -0.082 | 3.493 | 1.227 |
| PC5_AR   | -4.227 | 0.094 | 0.036 | 3.675 | 1.128 |
| PC6_AR   | -3.077 | 0.122 | 0.033 | 2.708 | 1.029 |
| PC7_AR   | -2.799 | -0.012 | 0.000 | 2.828 | 0.873 |
| PC8_AR   | -3.315 | 0.095 | 0.029 | 2.463 | 0.799 |

Methods are as follows: Fourier transform infrared (_FTIR), mass-specific (Xlf) and frequency-dependent in percent (Xfd_pc) magnetic susceptibility, X-ray fluorescence (_XRF), and aqua regia (_AR) and total (_Tot) inductively coupled plasma-mass spectrometry. Units are as follows: All PCs: dimensionless; Xlf: 10−6 m³/kg; Xfd_pc: %; XRF: wt%; AR and Tot: mg/kg (ppm). See text for details.
### TABLE 2  Target Values (TV) and Search Ranges (SR) for unknown sample Blind 1 for all variables

| Variable   | TV  | SR From | SR To  | Variable   | TV  | SR From | SR To  |
|------------|-----|---------|--------|------------|-----|---------|--------|
| PC1_FTIR  | 2.034 | 0.124 | 3.943  | As_Tot    | 1.78 | 0.62 | 2.94 |
| PC2_FTIR  | 0.013 | -0.099 | 0.125  | Ba_Tot    | 373  | 296 | 450 |
| PC3_FTIR  | -0.106 | -0.355 | 0.143  | Bi_Tot    | 0.12 | -0.20 | 0.44 |
| Xf         | 0.35  | -0.25 | 0.95   | Ce_Tot    | 46.5 | 36.5 | 56.5 |
| Xfd_pc     | 9.74  | 8.53 | 11.0   | Co_Tot    | 6.52 | 4.41 | 8.64 |
| SiO2_XRF   | 76.0  | 73.9 | 78.2   | Cr_Tot    | 36.4 | 25.9 | 47.0 |
| TiO2_XRF   | 1.00  | 0.94 | 1.05   | Cs_Tot    | 1.83 | 0.84 | 2.83 |
| Al2O3_XRF  | 8.34  | 7.42 | 9.26   | Cu_Tot    | 15.4 | -17.0 | 47.8 |
| Xf          | 2.19  | 1.31 | 3.08   | Dy_Tot    | 4.00 | 3.25 | 4.74 |
| MfO_XRF    | 0.04  | 0.02 | 0.06   | Er_Tot    | 2.67 | 2.27 | 3.06 |
| MgO_XRF    | 0.83  | 0.66 | 1.01   | Eu_Tot    | 0.73 | 0.56 | 0.89 |
| CaO_XRF    | 0.15  | -0.02 | 0.33   | Ga_Tot    | 8.97 | 6.79 | 11.1 |
| Na2O_XRF   | 1.05  | 0.95 | 1.14   | Gd_Tot    | 3.53 | 2.84 | 4.21 |
| TiO2_XRF   | 1.92  | 1.69 | 2.14   | Ge_Tot    | 1.21 | 0.93 | 1.50 |
| P2O5_XRF   | 0.09  | 0.07 | 0.10   | Hf_Tot    | 15.3 | 13.3 | 17.2 |
| LOI_XRF    | 8.11  | 6.59 | 9.62   | Ho_Tot    | 0.85 | 0.71 | 0.98 |
| PC1_XRF    | -0.403 | -1.313 | 0.507  | La_Tot    | 24.2 | 17.5 | 30.8 |
| PC2_XRF    | 2.153  | 0.871 | 2.155  | Lu_Tot    | 0.47 | 0.40 | 0.53 |
| PC3_XRF    | 0.474  | -0.223 | 1.171  | Nb_Tot    | 15.9 | 14.3 | 17.4 |
| PC4_XRF    | -1.566 | -2.423 | -0.710  | Nd_Tot    | 18.9 | 14.4 | 23.4 |
| PC5_XRF    | 0.620  | 0.111 | 1.128  | Ni_Tot    | 12.4 | 5.83 | 19.0 |
| PC6_XRF    | -1.087 | -1.824 | -0.349  | Pb_Tot    | 14.1 | -0.67 | 28.9 |
| PC7_XRF    | -0.544 | -0.996 | -0.092  | Pr_Tot    | 5.19 | 3.97 | 6.41 |
| PC8_XRF    | -1.334 | -1.726 | -0.942  | Rb_Tot    | 81.5 | 62.9 | 100 |
| Ba_AR      | 40.2  | 22.2 | 58.2   | Sc_Tot    | 12.7 | 11.0 | 14.3 |
| Be_AR      | 0.37  | 0.19 | 0.54   | Sm_Tot    | 3.56 | 2.53 | 4.58 |
| Ce_AR      | 21.5  | 11.9 | 31.1   | Sn_Tot    | 1.97 | 1.37 | 2.58 |
| Co_AR      | 5.48  | 1.84 | 9.12   | Sr_Tot    | 53.9 | 45.5 | 62.3 |
| Cs_AR      | 0.44  | 0.23 | 0.64   | Ta_Tot    | 1.37 | 1.22 | 1.51 |
| Dy_AR      | 0.93  | 0.26 | 1.60   | Tb_Tot    | 0.61 | 0.42 | 0.79 |
| Er_AR      | 0.42  | 0.10 | 0.74   | Th_Tot    | 10.7 | 8.67 | 12.7 |
| Eu_AR      | 0.33  | 0.09 | 0.57   | U_Tot     | 2.95 | 2.60 | 3.30 |
| Fe_AR      | 10672 | 5581 | 15764  | V_Tot     | 61.5 | 45.2 | 77.8 |
| La_AR      | 11.6  | 7.70 | 15.5   | W_Tot     | 3.27 | 2.97 | 3.57 |
| Mn_AR      | 237   | 16.7 | 457    | Y_Tot     | 22.9 | 18.7 | 27.0 |
| Nd_AR      | 8.77  | 3.30 | 14.2   | Yb_Tot    | 2.88 | 2.45 | 3.31 |
| Ni_AR      | 3.80  | 1.35 | 6.25   | Zn_Tot    | 45.0 | 32.8 | 57.2 |
| Pb_AR      | 9.45  | -5.32 | 24.2   | Zr_Tot    | 613  | 519 | 707 |
| Rb_AR      | 12.2  | 9.41 | 15.0   | PC1_Tot   | -0.052 | -4.558 | 4.455 |
| Sr_AR      | 5.89  | 0.32 | 11.5   | PC2_Tot   | 4.131 | 1.479 | 6.783 |
| Th_AR      | 1.97  | 1.37 | 2.56   | PC3_Tot   | -4.094 | -7.734 | -0.455 |
| Tm_AR      | 0.05  | 0.02 | 0.08   | PC4_Tot   | -1.648 | -3.217 | -0.078 |
| Zn_AR      | 28.9  | 2.34 | 55.5   | PC5_Tot   | 0.783 | -1.693 | 3.259 |
| PC1_AR     | 0.653 | -1.282 | 2.588  | PC6_Tot   | -0.178 | -1.463 | 1.106 |
| PC2_AR     | -0.674 | -1.273 | -0.075  | PC7_Tot   | 1.527 | 0.796 | 2.259 |

(Continues)
3.2 | Performance assessment

The performance statistics of the sequential method of provenancing soil samples are summarized in Table 5. Two performance indicators are calculated. First “precision” (Prc) is defined as the ratio of cells in a grid that have scores equivalent to, or lower than, the score of the cell containing the Blind (evidentiary) sample over the total number of cells. If Prc is 99%, only 1% of cells are identified as provenance matches, a highly precise result. Thus for instance, Blind 1 for FTIR + MS (5 variables) has a score of 3; there are 3634 cells of the total 4638 cells of the FTIR + MS grid that has a score of 3 or less (0, 1, or 2), giving Prc = 3634/4638 or 78.4%. Second “accuracy” (Acc) is defined as the ratio of the score for the cell containing the Blind (evidentiary) sample in a particular provenancing grid over the (actual) maximum score obtained at any cell within the grid. If Acc is 100%, all variables making up the provenance grid correctly identify the cell containing the evidentiary sample as a match, a highly accurate result. Thus for instance, Blind 1 for the FTIR + MS grid (maximum recorded score of 5) has a score of 3, giving Acc = 3/5 or 60%.

Each Blind sample behaves slightly differently in terms of provenancing performance (Table 5). The most precise and accurate results for Blind 1 were obtained for the XRF with PCs method (Prc = 93.6%; Acc = 66.7%). The next highest Prc came from XRF without PCs (86.6%), while the next highest Acc was obtained for both XRF without PCs and FTIR + MS with PCs (60%).

For Blind 2, the most precise results came from FTIR + MS without PCs (Prc = 99.8%), while the most accurate results were obtained for Total ICP-MS with PCs (Acc = 86.7%). The next highest Prc came from Total ICP-MS with PCs (94%), while the next highest Acc was obtained for ALL variables with PCs (84.8%).

The most precise and accurate results for Blind 3 were obtained for FTIR + MS with PCs (Prc = 92.2%; Acc = 60%). The next highest Prc came from XRF without PCs (88.7%), while the next highest Acc was obtained for ALL variables with PCs (52.7%) then Total ICP-MS with PCs (51.2%).

Considering average rather than maximum (or next highest) precision and accuracy, provenancing performance improved from Blind 1 (50.1% and 45.4%), to Blind 3 (70.6% and 46.6%), to Blind 2 (86.2% and 66.1%). The authors believe that the poorer results for Blind 1 are due to the fact that this sample was collected in a non-representative location for that grid cell (see above).

In terms of the best-suited analytical method for deterministic provenancing across all Blind samples, FTIR + MS without PCs has the highest precision of any method (Prc = 99.8% for Blind 2), followed by Total ICP-MS with PCs (94.0% for Blind 2), while Total ICP-MS with PCs has the highest accuracy of any method (Acc = 86.7% for Blind 3), followed by ALL variables with PCs (84.8% for Blind 2) then AR ICP-MS without PCs (83.3% for Blind 2).

Across all three Blind samples, FTIR + MS with PCs has the highest average precision (80.7%), closely followed by XRF without PCs (80.0%) then XRF with PCs (76.9%); ALL methods with PCs have the highest average accuracy (61.3%), followed by Total ICP-MS with PCs (59.1%) then ALL methods without PCs (56.2%).

Inclusion of principal components (PCs) in the provenancing workflow provides a marginal advantage in terms of provenancing performance (Table 5). For all Blind samples confounded, both average Prc and Acc are higher with PCs (70.3% and 54.5%) than without (67.6% and 50.9%). From those figures, one can also observe that of the two performance metrics, Prc (ranges from 28.4% to 94.0% with PCs, and from 25.6% to 99.8% without PCs) tends to have higher values than Acc (ranges from 33.3% to 86.7% with PCs, and from 21.1% to 83.3% without PCs).

The performance of individual analytes, such as specific major oxides or trace elements, can be deduced from the sequential multivariate approach presented here. The following analytes were successful at matching all three Blind samples’ Search Ranges and can thus be put forward as the most effective soil provenancing indicators in the present study: Ba, Cu, Ge, Nb, Pb, Ta, and V by total ICP-MS; Pb and Zn by aqua regia ICP-MS; and two PCs for each of these analytical methods. However, seeing that analytical methods such as XRF or ICP-MS are commonly available as packages of analytes rather than oxide-by-oxide or element-by-element analyses, realistically, comprehensive Analyte packages are probably the most practical and cost-effective requests to submit to institutional or commercial laboratories.

3.3 | Sensitivity analysis

The sequential multivariate soil provenancing method developed here suggests a number of steps to take for identifying regions within
| Variable   | TV From | TV To  | Variable   | TV From | TV To  |
|------------|---------|--------|------------|---------|--------|
| PC1_FTIR  | -1.481  | 0.429  | As_Tot     | 4.72    | 5.88   |
| PC2_FTIR  | -0.556  | -0.444 | Ba_Tot     | 306     | 383    |
| PC3_FTIR  | -0.220  | 0.029  | Bi_Tot     | 0.36    | 0.68   |
| Xlf        | 0.24    | 0.83   | Ce_Tot     | 306     | 383    |
| Xfd_pc     | 2.04    | 3.25   | Co_Tot     | 8.15    | 10.3   |
| SiO2_XRF   | -0.556  | -0.444 | Cr_Tot     | 55.9    | 66.5   |
| TiO2_XRF   | 0.80    | 0.85   | Cs_Tot     | 3.86    | 4.86   |
| Al2O3_XRF  | 3.50    | 4.39   | Dy_Tot     | 5.03    | 5.77   |
| MnO_XRF    | 0.05    | 0.07   | Er_Tot     | 3.02    | 3.41   |
| MgO_XRF    | 0.96    | 1.14   | Eu_Tot     | 1.01    | 1.18   |
| CaO_XRF    | 0.84    | 1.01   | Ga_Tot     | 13.0    | 15.2   |
| Na2O_XRF   | 0.68    | 0.77   | Gd_Tot     | 5.08    | 5.77   |
| K2O_XRF    | 1.79    | 2.01   | Ge_Tot     | 1.58    | 1.86   |
| CaO_AR     | 0.10    | 0.11   | Hf_Tot     | 10.8    | 12.7   |
| LOI_XRF    | 10.6    | 12.1   | Ho_Tot     | 1.01    | 1.15   |
| PC1_XRF    | -2.884  | -1.974 | La_Tot     | 32.3    | 38.9   |
| PC2_XRF    | -0.392  | -0.609 | Nd_Tot     | 28.7    | 33.2   |
| PC3_XRF    | -0.998  | -0.301 | Nb_Tot     | 12.7    | 14.3   |
| PC4_XRF    | 0.247   | 1.04   | Ni_Tot     | 19.3    | 25.9   |
| PC5_XRF    | 0.873   | 1.382  | Pb_Tot     | 25.0    | 30.4   |
| PC6_XRF    | 0.497   | 1.234  | Pr_Tot     | 7.72    | 8.93   |
| PC7_XRF    | 1.633   | 2.085  | Rb_Tot     | 98.8    | 117    |
| PC8_XRF    | -0.860  | -0.468 | Sc_Tot     | 11.4    | 13.0   |
| Be_AR      | 0.67    | 0.85   | Sm_Tot     | 5.50    | 6.52   |
| Ce_AR      | 37.8    | 47.4   | Sn_Tot     | 2.93    | 3.54   |
| Co_AR      | 7.90    | 11.5   | Sr_Tot     | 72.3    | 80.7   |
| Cs_AR      | 0.56    | 0.76   | Ta_Tot     | 1.08    | 1.22   |
| Dy_AR      | 2.17    | 2.84   | Tb_Tot     | 0.81    | 0.99   |
| Er_AR      | 1.07    | 1.39   | Th_Tot     | 13.1    | 15.1   |
| Eu_AR      | 0.74    | 0.98   | U_Tot      | 2.79    | 3.14   |
| Fe_AR      | 16685   | 21777  | V_Tot      | 70.1    | 86.4   |
| La_AR      | 18.0    | 21.9   | W_Tot      | 2.09    | 2.39   |
| Mn_AR      | 315     | 535    | Y_Tot      | 26.7    | 30.9   |
| Nd_AR      | 18.7    | 24.1   | Yb_Tot     | 3.00    | 3.42   |
| Ni_AR      | 13.2    | 15.6   | Zn_Tot     | 72.4    | 84.6   |
| Pb_AR      | 21.0    | 35.8   | Zr_Tot     | 421     | 515    |
| Rb_AR      | 10.4    | 13.2   | PC1_Tot    | -3.842  | 0.664  |
| Sr_AR      | 35.5    | 41.1   | PC2_Tot    | -0.444  | 1.208  |
| Th_AR      | 2.10    | 2.70   | PC3_Tot    | -0.945  | 2.695  |
| Tm_AR      | 0.13    | 0.17   | PC4_Tot    | 0.456   | 2.025  |
| Zn_AR      | 73.27   | 99.87  | PC5_Tot    | -0.165  | 2.311  |
| PC1_AR     | 0.082   | 2.017  | PC6_Tot    | 0.986   | 2.270  |
| PC2_AR     | 0.955   | 1.554  | PC7_Tot    | 0.900   | 1.632  |

(Continues)
The sensitivity analysis (Table 6) reveals that performance metrics can vary by up to ±40% relative to the reference scenario for Blinds 1, 2, and 3 combined and that Prc tends to deteriorate (−41% to +17%; i.e., negative bias) when parameters are changed, whereas Acc tends to improve (−20% to +39%; i.e., positive bias). Median changes in Prc relative to the base scenario are −10% and −7% with and without PCs, respectively. Median changes in Acc relative to the base scenario are +12% and +8% with and without PCs, respectively. The dependency of provenancing performance on parameter choices is relatively significant: performance across all three Blind samples and five scenarios averages 61.5% and 64.4% for Prc when PCs are and are not included, respectively. Therefore, we recommend that values of 60% be used for both Prc and Acc as minimum thresholds for accepting a provenance prediction. On this basis, Table 5 clearly shows that provenancing of Blind 1 largely failed (4 out of 20 performance metrics ≥60%), most likely because of the uncharacteristic choice of location of this blind sample as discussed above, whereas provenancing of Blind 3 (10 out of 20) and especially Blind 2 (16 out of 20) was (more) successful.

3.4 | Limitations and future research

The present study focussed specifically on data analysis workflows for the provenancing of soil trace evidence. It did not address the (acknowledged) issues of (i) sample size available for analysis in a geochemical survey situation vs a crime scene forensic casework; (ii) soil transfer and persistence from the crime scene to the point where soil is sampled for forensic assessment; (iii) the potential for a questioned soil sample from an urban/suburban environment being impacted by human activity (e.g., transported soil for landscaping or engineering purpose); and (iv) the choice of interpolation method to predict the values of a soil property between survey grid points. The latter point has been the focus of investigations in the past (e.g., [39–42]), though perhaps not specifically with a forensic application in mind. Other limitations to this provenancing approach, such as contamination, are common to all forensic traces, for example, fingerprinting, biological tissues, fibers, and not specific to soil provenancing; they are of course an important concern and need to be managed by appropriate protocols.

Future research could thus include expanding the present investigation to include (i) micro-analysis techniques, and (ii) quantitative mineralogical and geochemical assessment of soil transfer and persistence (e.g., as footsteps are taken with dirty boots, a car is driven with muddied tires, or a shovel is subjected to drying and shaking to simulate transport in a vehicle).

Despite the acknowledged limitations to the empirical soil provenancing approach developed herein and the recognition that additional research is recommended, it is concluded that empirical soil provenancing based on soil mineralogical and geochemical surveys can play an important role in forensic and intelligence applications.

4 | SUMMARY AND CONCLUSIONS

A sequential multivariate method of soil provenancing was applied to a high-density (1 sample per km²) soil geochemical survey around North Canberra, southeastern Australia. In this survey, 268 air-dried topsoil samples (0–5 cm) were analyzed for mineralogical and geochemical properties (Fourier transform infrared (FTIR) spectroscopy, magnetic susceptibility (MS), and geochemical composition by X-ray fluorescence (XRF) for total major oxides, and inductively coupled plasma-mass spectrometry (ICP-MS) for total trace elements as well as for aqua regia-soluble trace elements).
| Variable     | TV   | SR From | SR To  | Variable     | TV   | SR From | SR To  |
|--------------|------|---------|--------|--------------|------|---------|--------|
| PC1_FTIR     | 2.656| 0.746   | 4.656  | As_Tot      | 3.45 | 2.29    | 4.61   |
| PC2_FTIR     | 0.644| 0.532   | 0.756  | Ba_Tot      | 248  | 171     | 326    |
| PC3_FTIR     | 0.135| -0.115  | 0.384  | Bi_Tot      | 0.22 | -0.10   | 0.54   |
| Xif          | 0.37 | -0.23   | 0.97   | Ce_Tot      | 48.0 | 38.0    | 58.0   |
| Xfd_pc       | 10.2 | 9.02    | 11.4   | Co_Tot      | 2.38 | 0.26    | 4.49   |
| SiO2_XRF     | 83.4 | 81.3    | 85.6   | Cr_Tot      | 44.2 | 33.7    | 54.8   |
| TiO2_XRF     | 0.90 | 0.85    | 0.95   | Cs_Tot      | 2.00 | 1.00    | 2.99   |
| Al2O3_XRF    | 4.89 | 3.97    | 5.81   | Cu_Tot      | 17.9 | -14.5   | 50.3   |
| Fe2O3_XRF    | 1.63 | 0.74    | 2.51   | Dy_Tot      | 4.10 | 3.35    | 4.84   |
| MnO_XRF      | 0.03 | 0.00    | 0.05   | Er_Tot      | 2.78 | 2.39    | 3.18   |
| MgO_XRF      | 0.21 | 0.03    | 0.38   | Eu_Tot      | 0.55 | 0.39    | 0.72   |
| CaO_XRF      | 0.17 | -0.01   | 0.34   | Ga_Tot      | 6.13 | 3.95    | 8.31   |
| Na2O_XRF     | 0.22 | 0.12    | 0.31   | Gd_Tot      | 3.54 | 2.85    | 4.23   |
| K2O_XRF      | 0.84 | 0.62    | 1.07   | Ge_Tot      | 1.37 | 1.08    | 1.66   |
| P2O5_XRF     | 0.09 | 0.07    | 0.10   | Hf_Tot      | 20.0 | 18.0    | 21.9   |
| LOI_XRF      | 7.43 | 5.92    | 8.94   | Ho_Tot      | 0.87 | 0.74    | 1.01   |
| PC1_XRF      | 3.842| 2.932   | 4.752  | La_Tot      | 24.3 | 17.7    | 31.0   |
| PC2_XRF      | -1.175| -1.817 | -0.534 | Lu_Tot      | 0.51 | 0.45    | 0.58   |
| PC3_XRF      | -1.633| -2.330 | -0.936 | Nb_Tot      | 14.6 | 13.1    | 16.2   |
| PC4_XRF      | -1.417| -2.273 | -0.560 | Nd_Tot      | 19.5 | 15.0    | 24.0   |
| PC5_XRF      | 1.414 | 0.905  | 1.922  | Ni_Tot      | 10.4 | 3.83    | 17.0   |
| PC6_XRF      | 0.527 | -0.211 | 1.264  | Pb_Tot      | 12.6 | -2.21   | 27.4   |
| PC7_XRF      | 0.905 | 0.453  | 1.357  | Pr_Tot      | 5.40 | 4.19    | 6.62   |
| PC8_XRF      | 0.594 | 0.202  | 0.987  | Rb_Tot      | 46.7 | 28.2    | 65.3   |
| Ba_AR        | 52.4 | 34.4    | 70.4   | Sc_Tot      | 6.28 | 4.62    | 7.93   |
| Be_AR        | 0.27 | 0.09    | 0.45   | Sm_Tot      | 3.62 | 2.60    | 4.64   |
| Ce_AR        | 12.4 | 2.80    | 22.0   | Sn_Tot      | 2.07 | 1.47    | 2.68   |
| Co_AR        | 1.64 | -2.00   | 5.28   | Sr_Tot      | 34.0 | 25.6    | 42.4   |
| Cs_AR        | 0.48 | 0.28    | 0.69   | Ta_Tot      | 1.20 | 1.06    | 1.35   |
| Dy_AR        | 0.36 | -0.31   | 1.04   | Tb_Tot      | 0.60 | 0.41    | 0.78   |
| Er_AR        | 0.15 | -0.17   | 0.47   | Th_Tot      | 11.3 | 9.34    | 13.3   |
| Eu_AR        | 0.16 | -0.08   | 0.40   | U_Tot       | 3.06 | 2.71    | 3.41   |
| Fe_AR        | 10923| 5832   | 16015  | V_Tot       | 65.9 | 49.5    | 82.2   |
| La_AR        | 5.98 | 2.06    | 9.89   | W_Tot       | 2.06 | 1.76    | 2.36   |
| Mn_AR        | 179  | -41.3   | 399    | Y_Tot       | 24.3 | 20.1    | 28.5   |
| Nd_AR        | 5.00 | -0.47   | 10.5   | Yb_Tot      | 3.17 | 2.74    | 3.59   |
| Ni_AR        | 4.74 | 2.30    | 7.19   | Zn_Tot      | 17.6 | 5.37    | 29.8   |
| Pb_AR        | 10.6 | -4.15   | 25.4   | Zr_Tot      | 807  | 713     | 900    |
| Rb_AR        | 8.31 | 5.53    | 11.1   | PC1_Tot     | 4.123| -0.383  | 8.629  |
| Sr_AR        | 15.1 | 9.54    | 20.7   | PC2_Tot     | 5.258| 2.606   | 7.910  |
| Th_AR        | 0.98 | 0.38    | 1.58   | PC3_Tot     | -1.376| -5.015  | 2.263  |
| Tm_AR        | 0.02 | -0.01   | 0.05   | PC4_Tot     | 0.694| -0.875  | 2.263  |
| Zn_AR        | 21.9 | -4.67   | 48.5   | PC5_Tot     | -3.347| -5.823  | -0.870 |
| PC1_AR       | 6.347| 4.412   | 8.282  | PC6_Tot     | 1.585| 0.301   | 2.869  |
| PC2_AR       | -2.496| -3.095 | -1.897 | PC7_Tot     | -1.328| -2.059  | -0.596 |

(Continues)
Quality control measures, including the analysis of several sample triplicates, internal project standards, and certified reference materials, were applied. Appropriate compositional data and multivariate statistical analyses were carried out, including imputation of censored values, centered log-ratio transformation, and calculation of principal components (PCs). Uncertainty was explicitly quantified and propagated through all computations. Three blind samples, whose locations were unknown to the principal investigator, were collected by an Australian Federal Police forensic scientist to simulate forensic soil evidence to be provenanced by the method. These Blind samples were analyzed by the same techniques and their Target Values (TVs) and Search Ranges (SRs) determined, where SR = TV ± total uncertainty.

The multivariate sequential provenancing method consists of preparing an interpolated soil property raster for each reported mineralogical/geochemical variable. This was done here using the common inverse distance weighting (power of 3) interpolation method using a grid cell size of 250 x 250 m. Interpolation uncertainty was determined for every soil property raster. For any measured variable, each grid cell receives a score of 1 if it satisfies the Search Range for any of these parameters, and 0 if not. Maximum theoretical score = 5. Geospatial data from ACT Government or Australian Government, unless otherwise indicated.

Methods are as follows: Fourier transform infrared (FTIR), mass-specific (Xlf) and frequency-dependent in percent (Xfd_pc) magnetic susceptibility, X-ray fluorescence (XRF), and aqua regia (AR) and total (Tot) inductively coupled plasma-mass spectrometry. Units are as follows: All PCs: dimensionless; Xlf: $10^{-6}$ m$^3$/kg; Xfd_pc: %; XRF: wt%; AR and Tot: mg/kg (ppm). See text for details.
**Figure 4** Provenance prediction maps for unknown samples Blind 1 (A), Blind 2 (B), and Blind 3 (C) based on XRF parameters (overview on top, detail below). Each raster cell gets a score of 1 if it satisfies the Search Range for any of these parameters, and 0 if not. Maximum theoretical score = 11. Geospatial data from ACT Government or Australian Government, unless otherwise indicated.

**Figure 5** Provenance prediction maps for unknown samples Blind 1 (A), Blind 2 (B), and Blind 3 (C) based on Total ICP-MS parameters (overview on top, detail below). Each raster cell gets a score of 1 if it satisfies the Search Range for any of these parameters, and 0 if not. Maximum theoretical score = 38. Color ramps are in quantile classes. Geospatial data from ACT Government or Australian Government, unless otherwise indicated.
FIGURE 6 Provenance prediction maps for unknown samples Blind 1 (A), Blind 2 (B), and Blind 3 (C) based on AR ICP-MS parameters (overview on top, detail below). Each raster cell gets a score of 1 if it satisfies the Search Range for any of these parameters, and 0 if not. Maximum theoretical score = 19. Color ramps are in quantile classes. Geospatial data from ACT Government or Australian Government, unless otherwise indicated.

FIGURE 7 Provenance prediction maps for unknown samples Blind 1 (A), Blind 2 (B), and Blind 3 (C) based on All FTIR, MS, XRF, Tot, and AR parameters and their PCs (overview on top, detail below). Each raster cell gets a score of 1 if it satisfies the Search Range for any of these parameters, and 0 if not. Maximum theoretical score = 97. Color ramps are in quantile classes. Geospatial data from ACT Government or Australian Government, unless otherwise indicated.
The three blind samples showed a range of performance against the various analytical methods, with Blind 1 performing on average the worst and Blind 2 the best. This indicates that an evidentiary sample may not always be representative of a sample taken for geochemical mapping purposes. Thus, natural soil heterogeneity is potentially a challenge requiring further research in forensic provenancing.

The most precise analytical methods for soil provenancing identified in this study are FTIR + MS with PCs (average precision 80.7%), closely followed by XRF without PCs (80.0%) then XRF with PCs (76.9%). The most accurate analytical methods are ALL methods with PCs (average accuracy 61.3%), followed by Total ICP-MS with PCs (76.9%). The most accurate analytical methods are ALL methods with PCs (average accuracy 61.3%), followed by Total ICP-MS with PCs (76.9%) then ALL methods without PCs (56.2%). We conclude that (i) empirical soil provenancing should prioritize FTIR, MS, and XRF

### TABLE 5 Provenancing performance statistics for the sequential multivariate method for unknown samples Blind 1, Blind 2, and Blind 3 for all analytical methods, with and without principal components (PCs) included

| Method  | With PCs | Without PCs |
|---------|----------|-------------|
|         | Prc (%)  | Acc (%)     | Prc (%)  | Acc (%)     |
| FTIR + MS |          |             |          |             |
| Blind 1  | 78.4     | 60.0        | 51.9     | 50.0        |
| Blind 2  | 71.5     | 40.0        | 99.8     | 50.0        |
| Blind 3  | 92.2     | 60.0        | 62.7     | 50.0        |
| XRF     |          |             |          |             |
| Blind 1  | 93.6     | 66.7        | 86.6     | 60.0        |
| Blind 2  | 73.0     | 42.9        | 64.8     | 33.3        |
| Blind 3  | 64.1     | 33.3        | 88.7     | 50.0        |
| AR      |          |             |          |             |
| Blind 1  | 35.9     | 34.6        | 25.6     | 21.1        |
| Blind 2  | 92.3     | 80.0        | 92.1     | 83.3        |
| Blind 3  | 66.8     | 38.5        | 63.3     | 31.6        |
| Tot     |          |             |          |             |
| Blind 1  | 28.4     | 39.5        | 30.1     | 36.1        |
| Blind 2  | 94.0     | 86.7        | 91.0     | 81.6        |
| Blind 3  | 65.0     | 51.2        | 66.5     | 48.6        |
| ALL     |          |             |          |             |
| Blind 1  | 40.4     | 46.4        | 30.6     | 40.0        |
| Blind 2  | 93.1     | 84.8        | 90.3     | 78.5        |
| Blind 3  | 65.7     | 52.7        | 70.7     | 50.0        |

Methods are as follows: Fourier transform infrared (FTIR), magnetic susceptibility (MS), X-ray fluorescence (XRF), and aqua regia (AR) and total (Tot) inductively coupled plasma-mass spectrometry; ALL represents all the above methods combined. Precision (Prc) is defined as the ratio of cells in a grid that have scores equivalent to, or lower than, the score of the cell containing the Blind (evidentiary) sample over the total number of cells. Accuracy (Acc) is defined as the ratio of the score for the cell containing the Blind (evidentiary) sample over the (actual) maximum score obtained at any cell within the grid. Prc and Acc reported in %. See text for details.

The reference scenario (Sc 0) is the base case developed herein (IDW power 3; grid origin 679750,6090750; cell size 500 m x 250 m; and uncertainty multiplier 3). Variations modifying one of these parameters at a time are Sc 1 (IDW power 2), Sc 2 (grid origin 679625,6090625), Sc 3 (cell size 500 m x 500 m), and Sc 4 (uncertainty multiplier 6). Precision (Prc) and accuracy (Acc) reported in %. See text for details.
as comprehensive an analytical suite as possible is advantageous as shown by the performance of the ALL methods category; and (iv) inclusion of PCs in the provenancing workflow provides a marginal advantage in terms of provenancing performance compared to not considering PCs. In a companion paper, we will investigate a simultaneous, rather than sequential, empirical soil provenancing method.

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REFERENCES

1. Jenny H. Factors of soil formation – A system of quantitative pedology. New York, NY: McGraw Hill Book Co.; 1941.
2. Zala K. Dirty science: Soil forensics digs into new techniques. Science. 2007;318:386–7. https://doi.org/10.1126/science.318.5849.386.
3. Dalpe C, Blanchard C, Chartrand M, St-Jean G, Wojtyk J. Trace element analysis of Canadian surface soil and associated quartz by LA-ICP-MS: Preliminary development of a geo-location database for forensic investigations. 2020. https://scisoc.confex.com/crops/2010/am/webprogram/Paper63392.html. Accessed 24 Feb 2021.
4. Woods B, Lennard C, Kirkbride KP, Robertson J. Soil examination for a forensic trace evidence laboratory – Part 1: spectroscopic techniques. Forensic Sci Int. 2014;245:187–94. https://doi.org/10.1016/j.forsciint.2014.08.009.
5. Woods B, Lennard C, Kirkbride KP, Robertson J. Soil examination for a forensic trace evidence laboratory – Part 2: elemental analysis. Forensic Sci Int. 2014;245:195–201. https://doi.org/10.1016/j.forsciint.2014.10.018.
6. Maggio RMD, Donnelly LJ, Naimi KSA, Barone PM, Salvador FADS, Dawson L, et al. Global developments in forensic geology. Episodes. 2017;40:120–31. https://doi.org/10.18814/epiugs/2017/v40i2/017014.
7. Webb JB, Bottrell M, Stern LA, Sagarin I. Geology of the FBI lab and the challenge to the admissibility of forensic geology in US court. Episodes. 2017;40:118–9. https://doi.org/10.18814/epiugs/2017/v40i2/017013.
8. Fitzpatrick R, Raven M, Self P. The role of pedology and mineralogy in providing evidence for 5 crime investigations involving a wide range of earth materials. Episodes. 2017;40:148–56. https://doi.org/10.18814/epiugs/2017/v40i2/017017.
9. Rawlings BS, Kemp SJ, Hodgkinson EH, Riding JB, Vane CH, Poulton C, et al. Potential and pitfalls in establishing the provenance of earth-related samples in forensic investigations. J Forensic Sci. 2006;51:832–45. https://doi.org/10.1111/j.1556-4029.2006.00152.x.
10. Ritz K, Dawson L, Miller D, editors. Criminal and environmental forensics. S Dordrecht, Netherlands: Springer Science + Business Media B.V.; 2009.
11. de Caritat P, Simpson T, Woods B. Predictive soil provenancing (PSP): an innovative forensic soil provenance analysis tool. J Forensic Sci. 2019;64:1359–69. https://doi.org/10.1111/1556-4029.14060.
12. Lark RM, Rawlings BS. Can we predict the provenance of a soil sample for forensic purposes by reference to a spatial database? Eur J Soil Sci. 2008;59:1000–6. https://doi.org/10.1111/j.1365-2389.2008.01064.x.
13. Darnley AG, Björklund A, Belviken B, Gustavsson N, Koval PV, Plant JA, et al. A global geochemical database for environmental and resource management. Recommendations for international geochemical mapping, Final Report of IGCP Project 259. Ottawa, Canada: UNESCO Publishing; 1995.
14. Garrett RG, Reimann C, Smith DB, Xie X. From geochemical prospecting to international geochemical mapping: a historical overview. Geoch Expl Environ Anal. 2008;8:205–17. https://doi.org/10.1111/j.1467-7873.08-174.
15. McKinley J. The application of geographic information system (GIS) in forensics geoscience. Episodes. 2017;40:166–71. https://doi.org/10.18814/epiugs/2017/v40i2/017019.
16. Kürzl H. Exploratory data analysis: recent advances for the interpretation of geochemical data. J Geochem Expl. 1988;30:309–22. https://doi.org/10.1016/0375-6742(88)90066-0.
17. Johnson CC. Within site and between site nested analysis of variance (ANOVA) for geochemical surveys using MS EXCEL. British Geol Survey. 2009; IR/02/043. http://nora.nerc.ac.uk/8364/. Accessed 24 Feb 2021.
18. Temp M, Filzmoser P, Reimann C. Cluster analysis applied to regional geochemical data: problems and possibilities. Applied Geoch. 2008;23:2198–213. https://doi.org/10.1016/j.apgeochem.2008.03.004.
19. Campbell GP, Curran JM, Miskelly GM, Coulson S, Yaxley GM, Grunsky EC, et al. Compositional data analysis for elemental data in forensic science. Forensic Sci Int. 2009;188:81–90. https://doi.org/10.1016/j.forsciint.2009.03.018.
20. Grunsky EC. The interpretation of geochemical survey data. Geoch Expl Environ Anal. 2010;10:27–74. https://doi.org/10.1111/j.1467-7873/09-210.
21. de Caritat P, Grunsky EC. Defining element associations and inferring geological processes from total element concentrations in Australian catchment outlet sediments: multivariate analysis of continental-scale geochemical data. Applied Geoch. 2013;33:104–26. https://doi.org/10.1016/j.apgeochem.2013.02.005.
22. Allkenhead MJ, Coull MC, Dawson LA. Predicting sample source location from soil analysis using neural networks. Env Forensics. 2014;15:281–92. https://doi.org/10.1080/15275922.2014.930764.
23. Bonetti J, Quarino L. Comparative forensic soil analysis of New Jersey State Parks using a combination of simple techniques with multivariate statistics. J Forensic Sci. 2014;59:627–36. https://doi.org/10.1111/1556-4029.12375.

24. Cracknell MJ, Reading AM, de Caritat P. Multiple influences on regolith characteristics from continental-scale geophysical and mineralogical remote sensing data using self-organizing maps. Remote Sens Environ. 2015;165:86–99. https://doi.org/10.1016/j.rse.2015.04.029.

25. Harris JR, Grunsky EC. Predictive lithological mapping of Canada’s north using random forest classification applied to geophysical and geochemical data. Comp Geosci. 2015;80:9–25. https://doi.org/10.1016/j.cageo.2015.03.013.

26. Zuo R, Carranza EJM, Wang J. Spatial analysis and visualization of exploration geochemical data. Earth-Sci Rev. 2016;158:9–18. https://doi.org/10.1016/j.earsrev.2016.04.006.

27. Kment P, Mihaljevič M, Ettler V, Šebek O, Strnad L, Rohlová L. Differentiation of Czech wines using multielement composition – a comparison with vineyard soil. Food Chem. 2005;91:157–65. https://doi.org/10.1016/j.foodchem.2004.06.010.

28. Feng J-L, Hu Z-G, Ju J-T, Zhu L-P. Variations in trace element (including rare earth element) concentrations with grain sizes in loess and their implications for tracing the provenance of eolian deposits. Quat Int. 2011;236:116–26. https://doi.org/10.1016/j.quaint.2010.04.024.

29. Feng J-L, Zhu L-P, Zhen X-L, Hu Z-G. Grain size effect on Sr and Nd isotopic compositions in eolian dust: implications for tracing dust provenance and Nd model age. Geoch J. 2009;43:123–31. https://doi.org/10.2343/geochemj.1.0007.

30. Pye K, Blott SJ. Development of a searchable major and trace element database for use in forensic soil comparisons. Sci Justice. 2009;49:170–81. https://doi.org/10.1016/j.scijus.2009.02.007.

31. Frei R, Frei KM. The geographic distribution of Sr isotopes from surface waters and soil extracts over the island of Bornholm (Denmark) – A base for provenance studies in archeology and agriculture. Applied Geoch. 2013;38:147–60. https://doi.org/10.1016/j.apgeochem.2010.12.006.

32. Woods B, Lennard C, Kirkbride KP, Robertson J. Soil examination for a forensic trace evidence laboratory – Part 3: a proposed protocol for the effective triage and management of soil examinations. Forensic Sci Int. 2016;262:46–55. https://doi.org/10.1016/j.forsciint.2016.02.034.

33. de Caritat P, Mann A. An improved method for assessing the degree of geochemical similarity (DOGS2) between samples from multielement geochemical datasets. Geoch Expl Env Anal. 2019;19:58–73. https://doi.org/10.1144/geochem2018-021.

34. Hoogewerff JA, Reimann C, Ueckermann H, Frei R, Frei KM, van Aswegen T, et al. Bioavailable $^{87}$Sr/$^{86}$Sr in European soils: a baseline for provenancing studies. Sci Tot Env. 2019;672:1033–44. https://doi.org/10.1016/j.scitotenv.2019.03.387.

35. Nichols C. The mapping of Canberra urban geochemistry within a forensic context [Honours thesis]. Canberra, Australia: National Centre for Forensic Studies, University of Canberra; 2018.

36. Isbell RF, NCST (National Committee on Soil and Terrain). The Australian soil classification, 2nd edn. Melbourne, Australia: CSIRO Publishing; 2016.

37. Ellison S, Wegscheider W, Williams A. Measurement uncertainty. Anal Chem. 1997;69(19):607A–613A. https://doi.org/10.1021/ac971793j.

38. Taylor JA. Uncertainty Analysis. ES 223: Rigid Body Dynamics- Fall 2004. Jonesboro, AR: Arkansas State University. Online Lecture Notes; 2005. http://myweb.astate.edu/sharan/PMC/LectureNotes/2006/Paper%20on%20Uncertainty%20Analysis.pdf. Accessed 24 Feb 2021.

39. Lam NSN. Spatial interpolation methods: a review. Amer Cartographer. 1983;10:129–49. https://doi.org/10.1559/15230483783914958.

40. Mitas L, Mitasova H. Spatial interpolation. In: Longley PA, Goodchild MF, Maguire DJ, Rhind DW, editors. Geographical information systems (GIS): Principles, techniques, management and applications. New York, NY: John Wiley; 1999. p. 481–92.

41. Karydas CG, Gitas IZ, Koutsogiannaki E, Lydakis-Simatiris N, Silleos GN. Evaluation of spatial interpolation techniques for mapping agricultural soil properties in Crete. EARSel eProceed. 2009;8:26–39.

42. Zandi S, Ghobakhlou A, Sallis P. Evaluation of spatial interpolation techniques for mapping soil pH. In: Chan F, Marinova D, Anderssen RS, editors. Proceedings of the 19th International Congress on Modelling and Simulation (MODSIM2011); 2011 Dec 12-16; Perth, Australia. Canberra, Australia: Modeling and Simulation Society of Australia and New Zealand; 2011. p. 1153–9. Accessed 2021 February 24.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

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