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The potential for geochemical discrimination of single- and mixed-source soil samples from close proximity urban parkland locations

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This initial study assessed the feasibility of geochemical analysis to discriminate single- and mixed-source soil/sediment samples from close proximity sites, a key attribute for forensic comparison and crime reconstruction. Key techniques including ICP-MS, ICP-AES and XRF were able to discriminate between the sites used in this study. The findings of this experimental study provide empirical evidence that highlights the difficulties associated with interpreting data from the elemental analysis of soil samples from geographically similar locations, and demonstrates the issues associated with samples of mixed provenance. Statistical analysis of mixed-provenance samples in comparison with the single-source control sites revealed no significant difference between the mixed and single source samples illustrating that, in this particular case, the samples could not be excluded from having a similar source in direct contrast to previously published findings. This study underlines the necessity to understand further the degree of complexity that exists for the analysis and interpretation of both single- and mixed-source forensic soil/sediment samples and confirms the need for multiple independent methods to be used in order to begin to draw meaningful conclusions of forensically relevant provenance.

Keywords: forensic geoscience; geochemical analysis; mixed provenance; interpretation

1. Introduction

1.1. Forensic geoscience

Forensic geoscience refers to the assessment of earth materials, be they physical, biological or chemical (see Table 1), in order to be able to indicate a potential provenance and/or establish a relationship between the suspect(s), victim(s) or artefact(s)[1−3]. Where possible, the use of multiple independent methods of analysis is required to ensure meaningful inferences can be made concerning the source of that material and to enable the comparison between samples to be undertaken[3]. Table 1 details the different forms of physical, biological and chemical analyses that may be adopted in forensic geoscience analysis of soil/sediments.

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Table 1. Biological, chemical and physical soil assessment techniques used to assess the provenance of samples, and make comparison between samples of interest.

Assessment	Technique	Reference
Biological	DiatomsBacterial DNA	Peabody[4]MacDonald et al.[5]
	Pollen	Mildenhall et al.[6]
	Mycology	Hawksworth and Wiltshire[7]
	Organic matter	Carvalho et al.[8]
	Plant wax signatures	
Chemical	ICP-MS, ICP-AES, XRF, AAS and SEM-EDX (elemental analysis)	Pye et al.[9]
	FTIR and Loss-on-Ignition (organic analysis)	Cox et al.[10]Salehi et al.[11]
Physical	Binocular microscopy and XRD (mineralogy)	Palenik and Palenik[12]Ruffell and Wiltshire[13]
	Particle size analysis by Laser granulometry	Pye and Croft[14]
	QemSCAN	Pirrie et al.[15]
	Quartz grain surface texture analysis by SEM	Bull and Morgan[16]
	Colour	Sugita and Marumo[17]
	Magnetic susceptibility	Manrong et al.[18]

1.2. Key issues

One of the fundamental issues within forensic geoscience is establishing the balance between the existing knowledge base from its parent disciplines within the geosciences[19−21], the development of a forensically relevant evidence base that provides context to geoforensic samples and an empirical base to enable the accurate interpretation of those samples. To achieve a robust evidence base, a distinctively 'forensic' geoscience philosophical approach is required[3], i.e. taking an exclusionary approach as opposed to identifying a match[22], to ensure that techniques and approaches from the geosciences are applied effectively within the forensic domain. There is, however, also an ongoing need to establish additional understanding as to the particular circumstances of specific forensic investigations in order to inform the collection, analysis and interpretation procedures and practices in particular cases[23] as demonstrated by McKinley and Ruffell[24].

Physical techniques, such as those listed in Table 1, have been well documented in the published geoforensic literature, and studies have highlighted their ability to identify mixed-source samples (often of anthropogenic origin)[21]. Certain biological parameters in Table 1, e.g. pollen[6] and fungi[7] are also an effective means of discriminating samples. However, such techniques are often time consuming and dependent upon the knowledge and experience of the analyst conducting the assessment[25]. Chemical assessment is desirable due to its ability to automate analysis, its relative speed, its applicability to trace geoforensic materials and its capacity for quantitative and qualitative results for both major and trace elements[26]. However, questions regarding the effectiveness of these methods when applied to mixed provenance samples (which often comprise pre-, syn- and post-forensic event materials) have arisen due to samples requiring homogenisation prior to analysis, which complicates the interpretation of such samples[27]. Additionally, the comparison of elemental profiles for mixed provenance samples to sites of interest (single source) can be problematic due to potential variances in the elemental abundances, which can be complicated further if the samples used for comparison are not representative of where the suspect, victim or item has

been[28]. It should also be noted that in previous studies[9,29−30], the applicability of elemental techniques, listed in Table 1, on soil/sediment samples within spatially discrete locations has been neglected. This limits their use within forensic investigation[31] as the extent has not been established to which samples derived from locations of the same or similar parent material can be distinguished from one another based upon their geochemical composition[32]. These issues need to be addressed in order to provide a more robust evidence base for the analysis and interpretation of geoforensic samples.

This study therefore set out to establish an empirical evidence base to determine the degree to which samples from close proximity sites, in a forensically relevant situation can be discriminated, and to assess the capacity of elemental chemical techniques to discriminate between samples of single source (such as the crime scene) and samples of mixed source (such as items of footwear).

2. Method

Four sample sites were chosen and sampled from within a park area in West London, UK, each with the same geology but differing in land-use (see Figure 1). This forensically relevant area was selected as crimes often occur in secluded areas within urban environments, such as parks, due to the lack of natural surveillance[33]. The parkland was located near to public transport and local businesses and therefore also offered a location that could feasibly be frequented during the course of the daily routine of an
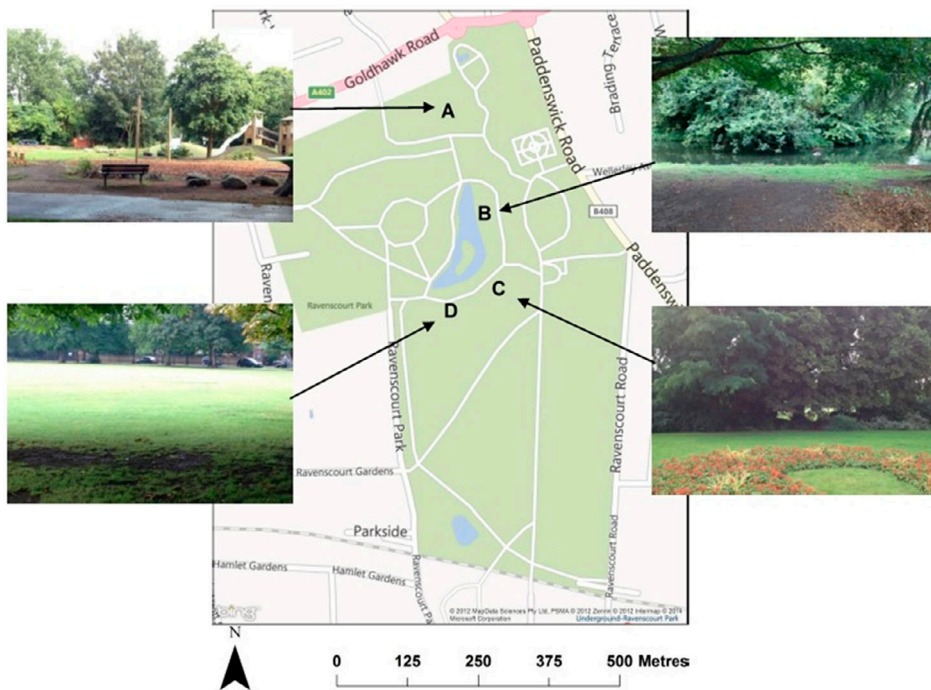

Figure 1.   Park area used in study. Site A – a children's play area with a high content of wood chippings, Site B – next to a pond area, Site C – amongst trees and bushes, Site D – in a grassy area. (Sample location marked on map of England)

Table 2. Single and mixed source samples (each with equal proportions of control site material, i.e. 1:1, 1:1:1 and 1:1:1:1 ratios) collected for this study.

Single source samples		Mixed source samples		
March	May	For both March and May		
A (n=5)	A (n=5)	AB	BD	BCD
B (n=5)	B (n=5)	AC	CD	ACD
C (n=5)	C (n=5)	AD	ABC	ABCD
D (n=5)	D (n=5)	BC	ABD	

offender[31]. Such locations often present problems to geoforensic analysis in forensic investigations as there can be reasonable alternative explanations for a suspect to have been in the vicinity of the crime. It is therefore important to be able to assess the degree to which it is possible to identify whether a geoforensic sample collected from a suspect can be excluded not only from the crime scene but also from locations within the local vicinity.

Two sample collections were carried out, the first in March and the second in May (61 days between collections), in order to make comparisons between samples from the same location. The two collection times enabled an assessment of the degree of temporal variation that may occur in forensic samples given that there is often a time lapse between the occurrence of a crime event and subsequent sample collection. Five control samples, one central and four 1 m away at 90° angles, were taken at 2 cm depth from each location at each time of sampling to account for within-site spatial variation (overall n=40) and 11 artificial mixed provenance samples (overall n=22) were created (Table 2), each weighing ca. 30 g[9]. Whilst this amount of material would not generally be available in an investigation from exhibits, location samples are often collected in larger quantities. The larger quantity of material was collected in this experimental study to allow multiple forms of analyses to be carried out. More realistic forensic soil/sediment transfer quantities will be explored in subsequent studies.

Samples were then freeze-dried and sub-samples of 4 g were taken for bulk elemental analysis by X-ray Fluorescence (XRF) Spectroscopy[34], which provides a non-destructive bulk analysis with simple sample preparation, Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) for major, minor and some trace elements and is cheaper than Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS)[35], and ICP-MS for minor and trace elements, some of which the ICP-AES cannot assess. Organic materials, i.e. plant matter, were removed from the sub-samples before manually homogenising using an agate pestle and mortar and then powdered samples were analysed by XRF (Spectro X-Lab 2000) using a helium carrier gas. A further sub-sample (0.1 g) of this powder was then taken and subjected to a HF/HNO$_3$ digestion at 70°C. This involved three HNO$_3$/HF fluxes (4 ml and 2 ml respectively) followed by two additions of HNO$_3$ (2 ml) with the first being evaporated off to near dryness then after the final addition, made up to 100 ml with deionised water to give a 2% solution. These samples were then analysed by ICP-AES (Varian 720 with axial configuration) and ICP-MS (Bruker M90) coupled with an SPS3 Autosampler. All samples were run against SSP certified reference material (MBH Analytical Ltd, registration number 034/04) and control blanks run during the analysis according to the standard procedures.

The results were analysed using multivariate statistics. Both Canonical Discriminant Function Analysis (CDFA) and Principal Component Analysis (PCA) are regularly used

to analyse forensic sediment samples in forensic investigations. CDFA (via SPSS v21) was applied to assess the degree of difference between and within sample sites and PCA[36–37] (via Canoco v4.5) to compare single-source samples to mixed-source samples.

3. Results

Five single-source samples from each site (20 samples for each collection time) and a further 11 samples composed of artificial mixtures of materials from these sites (to cover all possible mixture permutations as outlined in Table 2) were analysed using ICP-MS, ICP-AES and XRF. Forty-seven common and 15 rare earth elements were analysed in total by these techniques (49 by XRF, 27 by ICP-MS and 13 by ICP-AES).

3.1. *Spatial assessment*

Results derived from the single source site samples were analysed by CDFA of all the elemental data obtained from each technique. One-hundred percent of the samples were correctly classified by location for XRF and ICP-AES. For ICP-MS, 100% of the samples were correctly classified for the May results and 95% for March. The statistical outputs for the CDFA are presented in Figure 2, which shows it was possible to discriminate between the four single-source sites of close geographical proximity at the 99% significance level with the results from each technique for both the March and May samples ($p = < 0.01$).

The graphical output for the CDFA (Figure 2) illustrates that for the single-source samples, the variation within each site is less than the between-sites variability and that there is a clear distinction between each of the four sites. Whilst within-site variation appears to be minimal, there are two clear outliers within the ICP-MS data for the March collection, for sites A and D (Figure 2b). For site A there appears to be elevated levels of Mo and Sn and lower levels of Cu, Zr and U in the ICP-MS data and lower levels of Ca, Mg, P and Zn in the ICP-AES data. For site D, sample 2 has elevated levels of W, at over double the concentration, of the other four samples taken from this site in the ICP-MS data.

3.2. *Temporal assessment*

ANOVA assessment of the elemental data indicated that there was generally no significant difference in elemental composition between the collection periods at the 95% significance level (*p*-values ranging from 0.053–1 > 0.05). There were, however, some exceptions presented in Table 3. The *p* values for these elements were found to be in the range of 0–0.037 for XRF, 0–0.042 for ICP-MS and 0.004–0.047 for ICP-AES.

3.3. *Single-source versus mixed-source samples*

Table 4 presents the results of a paired t-test applied to assess the degree of difference that could be identified between the mixed-source samples and the single-source-site samples (each of which contributed to the mixed-source samples). In general, a significant difference could not be identified between the single-source and mixed-source samples at the 95% significance level. This represents a significant finding given the assertion in the published literature that suggests that elemental analysis will identify a
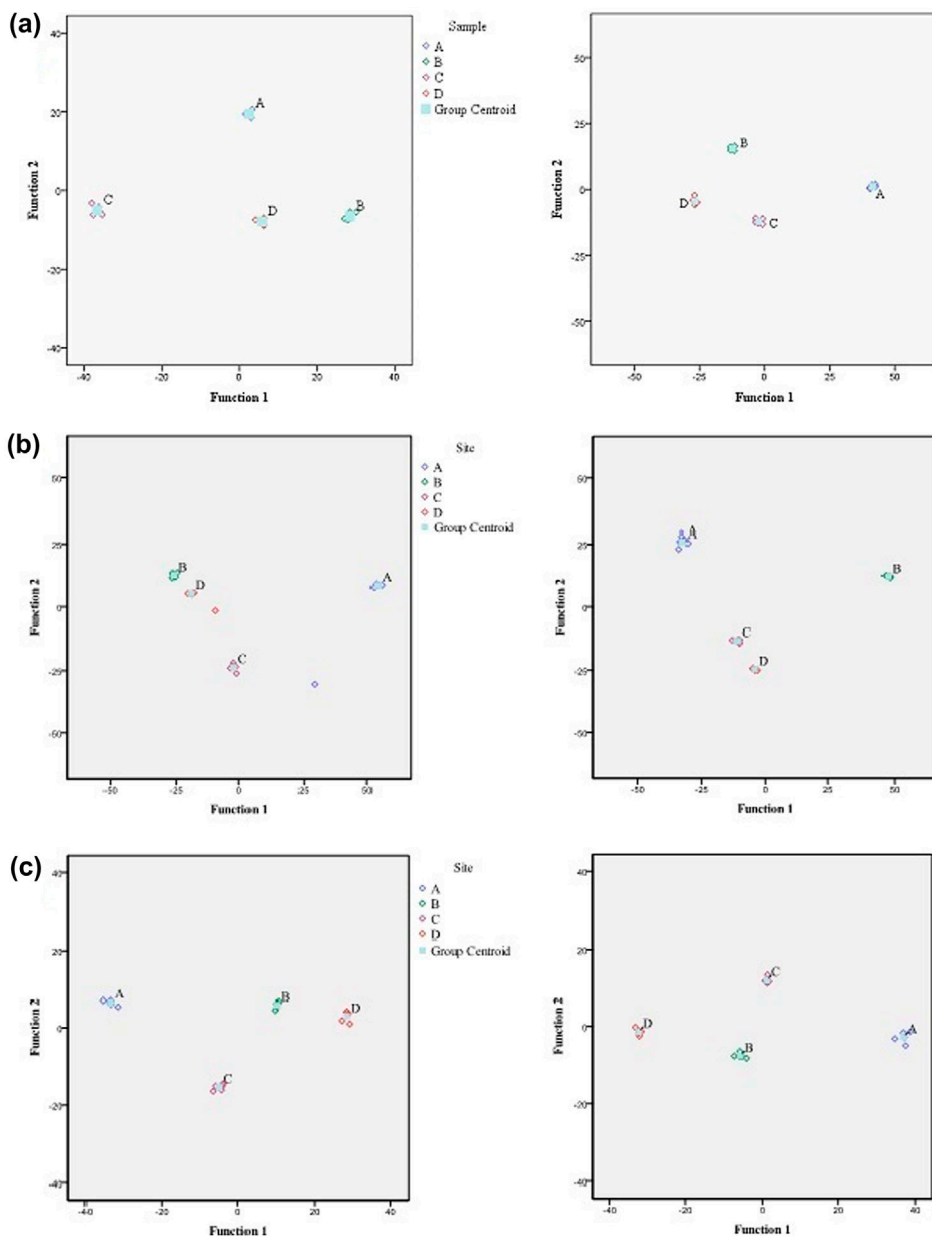
Figure 2.　CDFA Results of Elemental Analysis of single source samples from each location via a) XRF b) ICP-MS and c) ICP-AES for March (left) and May (right) collections

difference between mixed-source and single-source samples (and therefore not be able to identify false negative conclusions)[3,38]. Some exceptions to this finding were identified for the ICP-AES and ICP-MS results and are highlighted in Table 4. These findings illustrate that interpreting data of this nature is highly complex and further investigation is still necessary to establish the degree to which this complexity can be understood and utilised to make forensic comparisons between soil/sediment samples.

Table 3. Elements found to be significantly different between the four sites at different collection periods.

Method	Site A	Site B	Site C	Site D
XRF	Co (p=0.029)	Ca, Hg, Pb, Si, Sr and Ti (p=0.003–0.046)	Ba, Br, Ca, Ce, Cu, Hg, Mg, Mn, P, Pb, S, Si, Sr, Th, Ti and Zn (p=0.002–0.040)	Br, Cd, Cl, K, S and Zn (p=0.006–0.046)
ICP-MS	Cu, Lu, Sr, Tm and U (p=0.000–0.042)	rare earth elements, U, V, W and Zr (p=0.000–0.012)	Cu (p=0.006) and Mo (p=0.008)	Cu (p=0.21), Nb (p=0.22) and V (p=0.11)
ICP-AES	Al, Ca, P and Zn (p=0.000–0.047)	Be, Fe, Ni and Ti (p=0.004–0.038)	Al, Be Ca and P (p=0.010–0.046)	Al, Be, Ca, Sc and Zn (p= 0.004–0.022)

PCA was then applied to the data in order to further assess any relationships that may be present between the single-site and the mixed-site samples. Table 5 presents the percentage contribution to the variance between samples for each of the axes from the graphs shown in Figures 3 and 4. Figure 3 illustrates that sites A–D can be distinguished from one another, as was shown with CDFA, but it can also be seen that the mixtures cluster between the sites. It is also seen again that site A has an outlier in the ICP-MS data on the March samples and it is evident from performing PCA that this is also the case for ICP-AES data. Figure 4 indicates the elements that are most significant for each site and hence distinguish them from the other sites. For instance, Cl and Mn appear to be significant at site A; Na and Hg at site B; Zn, S, Cu, Ca and Br at site C and Mo, Pb and Mg at site D in March based on XRF.

4. Discussion

Table 6 summarises the main findings of the elemental analysis of the samples. All techniques used in this study had a similar capacity to discriminate between samples. Based on the CDFA and PCA statistical assessments of the data (Figures 2–4), XRF consistently provides a clear distinction between the four sites compared with ICP-MS and ICP-AES, where there were some outliers. With regards to comparing single-source with mixed-source samples, XRF and ICP-AES appear to potentially be more able to infer a relationship between the mixed-source sample and the single source that has contributed to it based on the PCA statistical assessment (Figures 3 and 4), but this is clearly a highly complex issue and further research is needed to establish the reproducibility of this finding at other sites and scenarios.

4.1. Spatial assessment

It has previously been asserted that elemental variation would be much lower over smaller distances and that it could therefore be problematic to discriminate between samples situated close together based on their elemental composition[2,32]. Overall, XRF, ICP-MS and ICP-AES identified a clear distinction between sites A–D, similar findings have been found by Morrisson et al.[33] through other independent forms of analysis, which highlights the benefit of adopting multiple techniques to provide reliable and

Table 4. Paired T-test statistics for elemental analysis (highlighted cells indicate a significant difference was identified at the 95% significance level between samples collected at different times).

Comparison pair	XRF significance		ICP-MS significance		ICP-AES significance	
	March	May	March	May	March	May
A - AB	0.182	0.506	0.363	0.022	0.372	0.119
AC	0.063	0.415	0.733	0.011	0.333	0.076
AD	0.160	0.551	0.875	0.019	0.376	0.102
ABC	0.151	0.455	0.355	0.018	0.397	0.089
ABD	0.154	0.521	0.276	0.018	0.398	0.105
ACD	0.138	0.442	0.808	0.022	0.436	0.088
ABCD	0.155	0.476	0.363	0.017	0.381	0.098
B - AB	0.046	0.312	0.444	0.160	0.142	0.099
BC	0.263	0.314	0.023	0.610	0.513	0.765
BD	0.278	0.326	0.126	0.028	0.103	0.033
ABC	0.312	0.296	0.277	0.049	0.166	0.664
ABD	0.568	0.317	0.198	0.042	0.105	0.040
BCD	0.298	0.309	0.102	0.115	0.151	0.092
ABCD	0.229	0.302	0.371	0.018	0.161	0.071
C - AC	0.217	0.302	0.090	0.030	0.276	0.155
BC	0.339	0.354	0.053	0.047	0.450	0.996
CD	0.311	0.340	0.052	0.030	0.704	0.744
ABC	0.313	0.342	0.023	0.105	0.724	0.478
ACD	0.288	0.316	0.940	0.066	0.858	0.829
BCD	0.313	0.347	0.033	0.043	0.565	0.632
ABCD	0.349	0.335	0.018	0.023	0.668	0.419
D - AD	0.057	0.329	0.199	0.579	0.094	0.689
BD	0.770	0.327	0.370	0.856	0.156	0.400
CD	0.238	0.304	0.009	0.290	0.615	0.413
ABD	0.402	0.317	0.187	0.185	0.167	0.179
ACD	0.280	0.288	0.321	0.082	0.437	0.335
BCD	0.341	0.308	0.200	0.063	0.118	0.340
ABCD	0.093	0.301	0.145	0.583	0.104	0.087

Table 5. The percentage of variation determined by PCA on the elemental data.

Method	Collection	Axis 1 (horizontal)	Axis 2 (vertical)	Total variance (%)
XRF	March	39.9 %	16.1 %	56.0 %
	May	41.3 %	13.5 %	54.8 %
ICP-MS	March	82.6 %	6.3 %	88.9 %
	May	84.7 %	6.9 %	91.6 %
ICP-AES	March	69.7 %	17.9 %	87.8 %
	May	71.0 %	18.5 %	89.5 %

robust evidence. Being able to discriminate between geographically similar sites is extremely valuable to forensic investigations as offenders have a tendency to commit criminal acts within relatively discrete areas and often within close proximity to where they are resident and/or go about their daily activities[39], or indeed have alibi sites close to the location of the crime event. The ability to distinguish between such areas could provide valuable intelligence and/or evidence to an investigation. This is dependent on
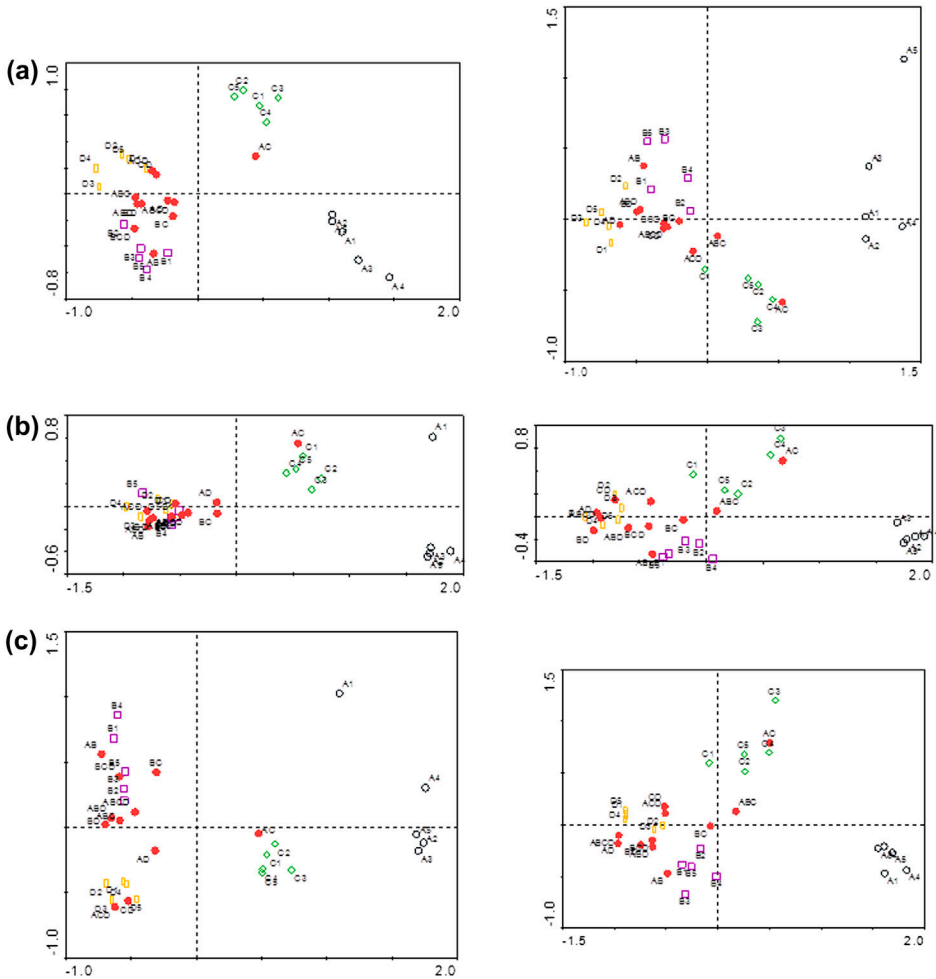
Figure 3.   PCA graphs illustrating relationship between sites A – D and the mixed source samples composed of material derived from these sites via a) XRF, b) ICP-MS and c) ICP-AES in March (left) and May (right). (Site A - black outlined circle, Site B - purple square, Site C - green diamond, site D - yellow rectangle, mixed sites - red filled circle).

small-scale spatial variability within the area being investigated[9]. This study represents just one parkland location and it will therefore be important to assess whether the findings identified here are similar in other locations, and the degree to which these different factors impact the discrimination ability of these elemental analysis techniques.

4.2.   *Temporal Assessment*

Statistical assessment of the two collections were carried out in order to address the time lapse that takes place between the occurrence of a crime and the sample collection. A paired t-test performed on the elemental data found no significant difference at

Figure 4.   PCA graphs illustrating the significant elements found for single source and mixed source samples via a) XRF, b) ICP-MS and c) ICP-AES in March (left) and May (right). (Site A - black outlined circle, Site B - purple square, Site C - green diamond, site D - yellow rectangle, mixed sites - red filled circle).

Table 6.   Summary of main findings.

Variation factor	ICP-MS	ICP-AES	XRF
Within sites	N	N	N
Between sites	Y	Y	Y
Between collections	N	N	N
Between single and mixed source	N	N	N

the 95% significance level between the samples collected at the two different times of year. However, CDFA indicated that the elements contributing to the distinct variation between the sites vary. For instance, for ICP-MS elements Cu, Tm, Sr, Er, Dy, Lu and Zr are the significant contributory variables to function 1 in March and Ti Sr and V in May. This could be the result of changes in the environment, such as anthropogenic contributions from animal or human activity, plant life or – as found by Pye et al.[9] – spatial soil variability, i.e. how inhomogeneous the sites are themselves.

4.3 Single source versus mixed source

Interpreting data of this nature is a highly complex process and this study highlights the degree of complexity that can be encountered in forensic analysis of samples. Paired t-tests performed on the elemental data indicated that a significant difference between a mixed-source sample and a contributory single-source sample could not be identified at the 95% significance level. This is a significant result that needs further investigation to assess the degree to which this trend is identified in other similar mixed- and single-source sample comparisons given the current theories articulated in the published literature[3].

PCA was applied to the elemental data in order to assess the extent to which the techniques could discriminate the sample sites from each other, and how the mixed-source samples related to these sites, in order to identify the potential these techniques have for applications to real forensic case samples. From Figure 3, a clear distinction can be seen between the sites, in particular for sites A and C, with these samples isolated from the rest of the results. Sites B and D are more closely related to one another but are still discriminated at the 95% significance level. The samples comprising mixtures of sediment from different sources are generally located between the samples from sites B and D with the exception of mixture AC. This sample falls between sites A and C but appears to be associated closer to site C despite being comprised of equal amounts of material from both sites. Although there is a slight variation in the elements responsible for this distinction, as demonstrated in Figure 4, it was consistently found that the mixed-source samples are not statistically significantly distinctive from the single-source samples. This indicates that it may be possible to exclude samples from a particular provenance using geochemical techniques. However, as acknowledged throughout this study, these results are preliminary and further analysis is required to assess the applicability of this approach to other locations and samples. Of course, careful interpretation in conjunction with the results from other forms of independent analysis will be crucial to these interpretations.

5. Conclusion

In this study, the effectiveness of XRF, ICP-AES and ICP-MS in distinguishing between control (single-source) and mixed-provenance samples, all derived from a discrete known park location, was investigated. It has been shown that major and trace elemental analysis, via XRF, ICP-AES and ICP-MS, is able to distinguish between close proximity sites with precision. This finding offers an empirical evidence base for the validity of using these forms of analyses for single-source samples from close proximity locations. This is a significant finding given the common requirement to exclude an alibi site that is located close to the crime scene. It is also potentially advantageous to forensic investigations as these methods of analysis are rapid and require a minimal

amount of sample to be able to provide a reliable analytical result and can be used in combination with other independent analyses such as those discussed by Guedes et al.[40] and Macdonald et al.[41].

The significant complexity that exists for the analysis of mixed provenance samples has also been demonstrated. Careful interpretation of the results produced from these methods is necessary to avoid false positive or negative conclusions. To that end, these techniques should be used with care, where sample size allows, and certainly in conjunction with other techniques to provide a meaningful insight into the potential provenance of a sample. Particular caution should be taken when interpreting data obtained from mixed provenance samples so as not to falsely include or exclude a site of interest. The experimental approach utilised here with known mixed-source samples offers a promising insight into the analysis of mixed-source samples, with initial results indicating that mixed-source samples are not always excluded from the single-source location that contributed to the mixed sample. However, it also indicates that further research is needed to more fully understand the nature of such mixtures and to assess the degree to which the trends identified here are reproducible in different regions that have different land use and/or different underlying geology. This will allow for the best approaches for sample collection, analysis and interpretation to be established, so that these techniques may play a valuable role in the comparison of samples within a forensic investigation. Mixed-source samples of pertinence to forensic investigations are common, and these findings pave the way to identifying the best approach to comparing samples from footwear and vehicles with samples taken from known locations. However, a fuller understanding and an empirical evidence base is still needed to enable reproducible and robust interpretations to be made from such sample comparisons in order to aid crime reconstructions.

In summary

1. Major and trace elemental analysis can be reliably used to discriminate between close-proximity urban sites successfully.
2. Without a priori knowledge, interpretation of geochemical signatures for mixed-provenance sites is incredibly complex and needs to be approached with caution.
3. Further assessment in other regions is required to determine if the same observations can be made in order to provide a robust foundation on which to base evidence interpretation.

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