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The discrimination of geoforensic trace material from close proximity locations by organic profiling using HPLC and plant wax marker analysis by GC

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ABSTRACT

There is a need to develop a wider empirical research base to expand the scope for utilising the organic fraction of soil in forensic geoscience, and to demonstrate the capability of the analytical techniques used in forensic geoscience to discriminate samples at close proximity locations. The determination of wax markers from soil samples by GC analysis has been used extensively in court and is known to be effective in discriminating samples from different land use types. A new HPLC method for the analysis of the organic fraction of forensic sediment samples has also been shown recently to add value in conjunction with existing inorganic techniques for the discrimination of samples derived from close proximity locations.

This study compares the ability of these two organic techniques to discriminate samples derived from close proximity locations and finds the GC technique to provide good discrimination at this scale, providing quantification of known compounds, whilst the HPLC technique offered a shorter and simpler sample preparation method and provided very good discrimination between groups of samples of different provenance in most cases. The use of both data sets together gave further improved accuracy rates in some cases, suggesting that a combined organic approach can provide added benefits in certain case scenarios and crime reconstruction contexts.

1. Introduction

Earth materials such as soils and sediments can be useful in crime reconstruction since their composition is a reflection of the underlying geology of their source location, the history of climatic and physical geographical processes occurring at that location, and the cumulative action of organisms living on and in the soil or sediment [1–5]. These factors result in a wide array of soil types which vary across different geographical scales, and which can be highly specific to a particular location, such as a crime scene [6–8]. Since earth materials can be readily transferred to items of forensic interest such as clothing, footwear, tools and vehicles, analysis of the components of samples taken from such items and samples taken from a crime scene can allow investigators to compare and exclude geographical areas, or compare and potentially exclude questioned items of suspect evidence from an investigation. For instance, analysis of soil adhering to an item of clothing or tool belonging to a suspect may be used for intelligence purposes to help narrow down the search area for a missing person or item, or be used in an evidentiary context to exclude an alibi location as the source of the material [9–12] or to compare samples derived from two items of interest.

The majority of the reported physical and chemical analyses performed on geoforensic evidence target the elemental composition and/or the minerals in the soil or the size and morphology of the mineral grains [13,7,4,14] in addition to determining the bulk characteristics such as colour or pH [15,16] and, with the exception of palynology [14] and the use of organic wax markers in the UK [12,17,5], there are few well established forensic techniques to study the organic fraction of soils [15,18,19]. If the organic component is not considered, there is a risk that variations in the soil composition between known and questioned samples, resulting from vegetation or micro-organisms, may not be

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detected, leading to false-positive or false-negative interpretations of the evidence [17]. Inorganic analysis generally identifies differences between locations of forensic interest, often due to different underlying geology. Since bedrock composition tends to be consistent over relatively large geographical areas (kilometre scale variations), the ability of physical and inorganic techniques can be spatially constrained [20]. There is therefore a need to consider techniques which are able to compare and exclude samples on the basis of the composition of the organic fraction of the soil and to develop an empirical evidence base to ascertain the limits of applicability of these techniques, for instance in the degree of variation in vegetation, or the spatial separation required to observe distinct, accurate differences between locations [5,17,20–23].

There are many analytical techniques used in soil science to characterise the organic composition of soils for agricultural or environmental protection purposes, or in earth sciences research. For forensic purposes however it is problematic that many of these analyses require large quantities of sample or require complex sample preparation, to the extent that they cannot provide the appropriate levels of accuracy and precision required for forensic work, nor can they be considered practical for implementation in a large scale forensic context [4,17]. There are, however, two chromatographic approaches which have been demonstrated to offer valuable data from the analysis of the composition of targeted component groups within the organic fraction of soil; the determination of wax markers by Gas Chromatography (GC) [5,12,17,21,24,25] and (currently) untargeted profiling of soil components by High Performance Liquid Chromatography (HPLC) [20,23,26–29]. Both approaches produce profiles which are known to vary across small andforensically relevant spatial scales [20,23] and for sites with different management and land uses [5,12,17,21,24–29].

The profiles of wax markers in soil have been found to reflect the composition of the compounds found in the leaves, stems and roots of the plants grown in them, and these profiles are known to remain stable over time, providing a historical record of the vegetation present at a site [17]. A database of wax marker profiles has been developed for a range of forensically relevant land use and vegetation types in the UK, and the wax marker profiles of numerous plant species are now well understood, and as such, this type of analysis is an excellent intelligence and evidential tool [21]. In addition, since the wax marker profiles can include unusual compounds, it has been demonstrated that it is possible to profile soil from a specific location at a scale relevant for evidentiary purposes [24].

HPLC has only rarely been reported in the literature as a geoforensic analysis tool, however it has long been known that soil gives rise to highly complex chromatograms that can be highly individual to specific locations [26–29]. More recent work has developed a method to improve the practicality and cost of the HPLC analysis of geoforensic samples and has shown this technique to add value when used in conjunction with more established techniques, giving highly accurate results in a forensic scenario where Quartz Grain Surface Texture Analysis, a technique that has been used successfully in many cases, was unable to provide full discrimination between locations [20], and further studies have identified that this analytical technique can offer a choice of markers for comparing known and questioned samples [23].

The importance of using a combination of independent forms of analysis for geoforensic analysis of samples has been outlined in the published literature [12], and it is therefore of significant value to incorporate the complementary analysis of the organic with the analyses of the inorganic fractions. This study aims to demonstrate the variability of GC and HPLC profiles over a forensically relevant, close-proximity spatial scale in order to evaluate the relative and complementary benefits of both HPLC and GC profiling techniques for assisting crime reconstruction.

2. Methodology

2.1. Site description

Three sites in the UK were selected for this study as outlined by McCulloch et al. [23]. All three sites were parklands in urban areas and comprised different areas where a person could legitimately come into contact with earth materials, but also contained spaces and thoroughfares that lacked natural surveillance, which could provide opportunities for crimes to be committed. These sites were Brockwell Park in London, UK, Lochend Park in Edinburgh, UK, Craigiebuckler Estate in Aberdeen, UK. In addition one additional site was chosen in the USA; Central Park in New York City in a similar manner to previous studies [20,23] to ensure comparability of the results. All the chosen sites were well-established municipal parkland, and maintained for public recreational use. At each site, four forensically relevant locations were chosen for sampling that represented potential alibi sites and potential crime scene sites (McCulloch et al. [23]). The positioning of these locations at close-proximity to one another was chosen in order to demonstrate the forensic relevance of this study compared to many previously published works, where the locations of interest had been situated several miles apart, at areas of different underlying geology and of markedly different land uses [26–28]. Large distances and significant differences in land use between sample locations may not be applicable to many crime scenarios, for instance in urban environments with similar land use, or environments where the underlying geology is less variable [22,17,20,23].

Although there were broad qualitative similarities in the land-use for each location chosen within a site, there were no additional pre-selection criteria, such as controlling the variation and species of surrounding vegetation for each type of location. This approach was, again, considered more forensically relevant since offenders are more likely to consider situational factors such as visibility, accessibility and frequency of public usage, rather than the specific vegetation planting, when selecting a location to undertake criminal activities [30–32].

The mock crime-scene at each site was characterised by having exposed soil adjacent to a fresh water pond, with resident waterfowl and miscellaneous wild vegetation, with bamboo growing immediately adjacent to the sample points in London and Aberdeen. This was chosen to represent a potentially viable site for the concealment of a murder weapon. These locations (Fig. 1) had limited pedestrian access and would therefore be unlikely to be entered as part of normal leisure activities and therefore lacked natural surveillance.

Soil from a natural path through woodland (Fig. 2) was sampled at each site, to represent a secluded route to and from the mock crime-scene. The sample location was an area of bare earth with dense tree cover and leaf litter, immediately adjacent to a residential area and used by local residents as a thoroughfare to and from the park.

The mock alibi location was a flat area of managed grassland (Fig. 3), that was well-maintained by the land owner. It was chosen to represent an alibi site where soil has been transferred as a result of sports and recreation activities. In Edinburgh and London, these areas were in use as football pitches at the time of sampling, while the primary users of these locations in New York and Aberdeen were used by dog-walkers.

The final location at each site was a sloping area of unmanaged grassland (Fig. 4), with wild vegetation, mixed grasses and wild flowers. These sites were chosen to represent an additional alibi

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