Sequential element extraction of soils from abandoned farms: an investigation of the partitioning of anthropogenic element inputs from historic land use.

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Enhanced soil element concentrations may serve as indicators not only of modern pollution, but also of former historic and/or pre-historic human activity. However, there is little consensus over the most appropriate means of extraction for identifying chemical signatures of modern and archaeological pollution. This study addressed this question by using a 5-step sequential extraction to examine the partitioning of elements within the soil. Samples were taken from known functional areas (hearth, house, byre, arable, and grazing areas) on a 19th Century abandoned croft (small farm). A hot nitric acid digest and five-stage sequential extraction method were used to examine the partitioning of elements in soil and identify the current elemental distribution of anthropogenic contamination. The results indicate that although a significant proportion of Ca tends to be bound with exchangeable and weak acid soluble fractions, in the hearth and house areas there is also a significant proportion held within the recalcitrant residue. Pb concentrations tend to be associated with organic matter, ammonium oxalate extractable fractions and the residue, whilst Zn generally has a more equitable partitioning between the six soil fractions. The implications of this for extraction methodology are element and soil specific. However, the presence of a significant proportion of anthropogenically significant elements (including Ca, Pb, Zn, Sr, and Ba) within the resistant residue suggests the use of only a weak acid or an exchangeable fraction extraction would result in the loss of information from contamination resulting from former human activity. Hence, a total or pseudo-total extraction method is recommended for this type of study.

Introduction

Contamination of soils by modern agriculture is well documented[1,2]. However, Nineteenth and early Twentieth Century agriculture has also resulted in significantly enhanced trace element and heavy metal soil concentrations in and around formerly inhabited farm steadings[3,4]. These studies have found distinctive patterns of concentration of calcium (Ca), strontium (Sr), barium (Ba), phosphorus (P), zinc (Zn), and lead (Pb) associated with different activity areas (hearth, house, byre, midden, garden, arable fields and grazing areas) indicating significant contamination of such sites by traditional agricultural systems and settlement[4]. The element concentrations are the result of loadings to the soil of materials such as ash and soot, dung, manure, domestic residues, paints and pigments and industrial wastes.

Pollutant element concentrations have been used as indicative analogues for archaeological remains, multi-element soil analysis being used to help locate sites[5,6] and aid interpretation of former space use and activity[7,8,9,10,11,12]. Interpretations in such studies may be complicated by local variations in background patterns associated with geology and soil type. In addition on archaeological sites patterns of element concentration may also be influenced by anthropogenic modifications to soil physical, chemical and biological properties, and by post-abandonment processes of soil formation. Both of these have the potential to create secondary patterns in soil element concentrations.

Extraction methodology is also of fundamental importance to such studies, and is the subject of some debate[13]. The aim is to use an extraction method that isolates the anthropogenic 'pollution' signature, without a significant input from the geological matrix. Some researchers prefer to use strong acid digestions to give pseudototal element concentrations[4], whilst others argue strongly in favour of milder extraction methodologies targeted at the exchangeable, available and weakly acid soluble fractions[13] arguing that the concentrated acid method attacks the geological matrix and this may mask the anthropogenic signature. However, there have been very few studies investigating the partitioning of the anthropogenic signature in archaeological soils. Without such information it is difficult to identify any one suitable method. As multi-element soil analysis becomes more widely used within archaeology, this lack of standardisation within historical and prehistorical pollution studies is problematic.

Sequential extraction methods have been used extensively in modern pollution studies to examine the partitioning of different element concentrations within the soil[14,15,16], and to study the incorporation of anthropogenic pollutants within the soil[17,18,19]. In general, studies have found that anthropogenic metal species are often associated with the more mobile, exchangeable soil fractions[20,21] whilst the fraction retained in the residue is usually explained by the geogenic contribution[22,23]. The incorporation of Pb isotope analyses with sequential extractions has further clarified the situation. For example, a study of Scottish upland soils[19] found that 85% of Pb from atmospheric deposition was bound in the extractable fraction and had been partially mobilised to a depth of 20-30 cm. However, a study of Pb isotopes in roadside soils in Sweden[18] suggested that over time the order for incorporation of anthropogenic Pb in soils is exchangable / carbonates > (hydr) oxides > organic matter >

residual. This clearly has implications for the mobility and retention of lead and other metals in the soil.

The aim of this paper is to investigate the partitioning of anthropogenic element loadings within the soils of an abandoned farm with a known history of use. This study will inform extraction methodology for future multi-element soil analyses in archaeology and modern pollution studies.

Methods

Study site

The study site was the abandoned croft of Grumby, Sutherland, Northeast Scotland (OS grid reference, NC 7126 0971). The stone built steading was abandoned in 1940, since which time the land has been used as rough grazing and has received no lime or fertiliser. The croft was originally built and run as a sheep farm by the Sutherland Estate in 1815, but was converted to a croft in 1893 with 8 acres of arable and 92 acres of unimproved land. The geology is gneiss and granite and the soils are mapped by the Soil Survey of Scotland[24] as free-draining humic iron podzols and blanket peats.

The croft steading consists of a linear arrangement of house, byre and barns, with further outbuildings, enclosures and a stackyard to the rear. To the front are a small garden area, the remains of the midden (dung heap) and the arable fields. The steading is stone built with a dry clay mortar, but lime had been used in patches particularly around the hearth; the remains of an iron grate were also found in the hearth area. The arable fields have been in cultivation since at least the mid 18th Century[25]. The dominant crops were oats and barley, and the arable fields were manured with material from the midden. The midden would contain dung from the byre mixed with bedding (straw, turf or bracken), domestic waste and ash from the hearth, and periodically the thatch from the roof[26].

Test pits 0.7 m x 0.7 m were opened in areas of known former function based on standing remains and the memories of older locals who remember the croft when it was inhabited. Samples were taken from the hearth, house floor, house overburden (the soil from material accumulated over the house floor and consisting of the collapsed turf roof construction debris and animal dung), the byre, midden, garden, arable field, and grazing. Five replicate samples were taken from each context at a depth of 5-15 cm, except for the floor layer, which was buried to a depth of 20 cm.

Laboratory analysis

Soils were oven-dried (80°C) and sieved to < 2 mm. Five grams of soil was digested in 5 ml ARISTAR conc. nitric acid at 120°C for 1 hour. The digest was filtered through Whatman no. 2 filter paper and made to 100 ml volume with deionised water to give a 5% nitric acid matrix. A second 5 g sub-sample of soils from the hearth house floor, house overburden, byre, arable and grazing soils was used for the five-step sequential extraction procedure outlined in Table 1. Thirty samples were fractionated in this way, including five samples each from the hearth, house floor, house overburden, byre, arable fields and grazing.

Many sequential extraction procedures have been used to investigate the fractionation of metal concentrations in soils. Probably the 3-step original and revised BCR[27, 28, 29] and 5-step Tessier[30] extraction protocols are the most well known, however, even these standard protocols are routinely 'modified' to suit specific research conditions. Likewise in this study neither protocol was ideally suited to the variable soil conditions. The exchangeable, reducible and oxidisable fractions of the BCR protocol don't provide an acid soluble step. This was felt to be important because of the high pH of the hearth samples (pH 7.1) and the occasional presence of lime mortar in soils from the hearth and house. The Tessier scheme[30] includes an acid soluble step (Acetic Acid, pH 5), however the oxidising step in both the BCR and Tessier schemes employ hydrogen peroxide, which is also capable of dissolving oxides of manganese,[31] and poorly crystalline minerals at low pH[32].

The methods used in this study are based most closely on the protocols of Shuman[31,33]. Extractants were chosen to differentiate between operationally defined exchangeable, acid soluble, oxidisable (specifically organic matter[31,34]), and reducible fractions. For the reducible fraction a two-stage ammonium oxalate[36] extraction was used in preference to hydroxylamine hydrochloride[30,35] because of the potential to differentiate between amorphous and more crystalline forms of Fe, Mn and Al oxides[33,36,37]. The formation of stable oxalate salts has been reported to reduce the recovery of Ca and Pb in ammonium oxalate extractions compared to hydroxylamine hydrochloride[38]. However, in this study the percentage recovery of Ca and Pb by the sequential extraction compares favourably with that of zinc, which should be less affected by the precipitation of salts[38] (see table 3). A weak acid extraction step (1M sodium acetate, pH5) was included because of the high pH (pH 7.1) of samples from the hearth, which contained quantities of lime mortar that had washed out from the masonry of the chimney.

After each step the residue was washed with 20 ml of deionised water and centrifuged (10 minutes, 3500 rpm). The supernatant was filtered and added to the extract. For steps 1 to 3, the extraction was repeated twice. Multiple extractions have been found to give better recovery than single extractions for exchangeable[39, 40] and oxidisable[33] fractions, hence the inclusion of a second extraction in this protocol. Two extractions were found necessary in step 2 to maintain the end pH at pH 5. Each extract was diluted to minimise problems of matrix interference in the subsequent analysis. Procedural blanks, replicates and external standards were also prepared in the same matrices.

Multi-element soil concentrations were determined using a Perkin Elmer Optima 3300RL ICP-AE spectrometer. A sub-set of 40 samples from the nitric acid extraction were also analysed using ICP-MS (Surrey Research Instrument with a 2% nitric acid matrix). Although there were small absolute differences in values (65% of samples differed by <10%) the results showed strong linear correlation (R^2 values of 0.830-0.999) for all except the Rare Earth Elements (Nd R^2 0.235; Eu R^2 0.523; Sm R^2 0.704). The poor correlation for Nd appears to be due to interference on the ICP-AES at high Ca concentrations (>10 g kg^{-1}), and hence this data was discarded. Subsequent analyses

were carried out using ICP-AES. Three measurements were made for each sample; Laboratory Reference Material KC11 was used to monitor accuracy for the nitric acid analytical methods (RSDs 1.45% - 7.87%) and an in-house 10 mg kg^{-1} standard solution (RSDs 0.43% - 1.78%). Replicate samples from the sequential extraction gave average RSD's of 6.85% Pb, 6.65% Zn, and 4.60% Ca. The analytical lower limits of detection were 0.01mg kg^{-1} Pb and Zn, and 0.1 mg kg^{-1} Ca.

Loss-on-ignition (405°C, overnight[41]), soil pH (1:5 v/v, 0.125M CaCl$_2$), particle size distribution (Perkin Elmer LS 230, Coulter Counter), and cation exchange capacity[42,43] were also determined to characterise background soil conditions for each functional area.

Results and discussion

Mean element concentrations in the nitric acid extraction are shown in Table 2. Univariate analysis of variance for the log transformed soil concentrations of each of the elements shown in Table 2 produces a significant between context effect (p <0.01). The pattern of enhancement is element specific. For each element the lowest concentrations are in the unamended grazed soils. The results of the fractioneation of Ca, Zn, and Pb are presented in detail here. These three elements were found to have the most consistently, and independently, elevated concentrations on the historical rural settlement sites[4]. The concentrations of other significant anthropogenic elements (including Ba, Sr, Cu, P) correlated strongly with either Ca, Zn or Pb[4].

The highest Ca concentrations are found in the hearths (73.2 g kg^{-1}), and then the house and house floor (12.3 g kg^{-1}), and byre (7.99 g kg^{-1}). The midden, garden, and arable fields each have very similar Ca concentrations (2 - 2.54 g kg^{-1}). Likewise, the highest Pb concentrations are found in the hearth (142 mg kg^{-1}) and house overburden (117 mg kg^{-1}). However, there is no significant enhancement of Pb relative to the grazed soils in the arable, garden, midden or byre soils. Greatly enhanced concentrations of Zn are present in the house floor and overburden relative to the grazed soils (535 mg kg^{-1}, 359 mg kg^{-1}, and 14.0 mg kg^{-1} Zn respectively). The hearth, byre, and midden show moderate enhancement (7 - 8 x value for grazed soil) and the garden and arable slight enhancement (3.5 - 5 x value for grazed soil) of Zn.

The results of the sequential extraction for Ca, Zn and Pb are shown in Figure 1. For Ca the exchangeable fraction is dominant (80% - 90% of total Ca from sequential extraction) in all but the hearth soils, where the weak acid soluble fraction accounts for the highest proportion of Ca (78%). The ammonium oxalate extractable fractions account for a maximum of 12% Ca in the arable field soils. However, there is also a significant difference (p < .01) between the total extracted by the 5-stage sequential extraction and that extracted by the hot concentrated nitric acid digest (Table 3) for all contexts except the house floor. This indicates that the proportion of Ca (13-69% of the total) bound within the residue is significant.

The results for Pb, in contrast to those for Ca, show that the proportion bound in the exchangeable (maximum 11% of Pb in byre) and weak acid soluble (with the exception of the hearth) fractions are generally low. It is the oxidisable and ammonium oxalate reducible fractions that account for the greatest proportion of Pb and in particular the crystalline Fe-oxides (maximum 44% Pb in arable soils). In the hearth, where the input of lime mortar has resulted in free carbonate in the soil (pH 7.1), weak acid soluble is also an important fraction (24% sequential total Pb). The difference between the total Pb content extracted using the sequential extraction and the nitric acid is variable. Only for the hearth samples was significantly (p <.05) more Pb (76% of the total Pb) extracted by the concentrated nitric acid extraction. In the grazing soils the nitric acid extraction apparently recovered 61% less Pb than the cumulative sequential procedure.

The partitioning of Zn shows a more equitable division between all five extractable fractions. The lowest proportions occur within the acid soluble and, with the exception of the house overburden, the oxidisable fractions. The exchangeable fraction accounts for between 9% and 59% of the sequential total Zn in the hearth and grazing respectively. Whilst the ammonium oxalate A (amorphous Fe, Mn-oxide) fraction accounts for between 11% and 46% (grazing and byre respectively), and the Fe-oxide crystalline fraction between 9% and 32% (house floor and hearth respectively). For Zn the concentrated nitric acid method recovered significantly (p <.05) higher concentrations (11-57% of total Zn) than the total sequential extraction in all contexts except the house floor and grazing.

Relative recovery by concentrated nitric acid extraction compared to that by the sequential procedure, therefore, is specific to element and functional area with relatively poor recovery of Pb, Cu, titanium (Ti), and vanadium (V), particularly from the grazing soils (Table 3). This context has the highest organic matter content (as determined by loss-on-ignition) whilst the oxidisable fraction was substantial for Cu, Pb, and Ti concentrations. Hence, it appears that the nitric acid digestion is less efficient at extracting metals from the oxidisable fraction than the sodium hypochlorite. It also suggests that poor recovery of Pb and Ca in the two ammonium oxalate stages through the formation of oxalate salts is not a significant problem.

The results of a Kruskal-Wallis test with functional area as a grouping variable are shown in Table 4. Kruskal-Wallis is a non-parametric equivalent of a one way ANOVA that compares the medians of two or more samples to determine if they have come from two different populations. Table 4 shows the concentrated nitric acid digestion and the sodium hypochlorite oxidisable extraction step identified significant differences in element concentrations between the seven functional areas for each element analysed. The magnesium nitrate exchangeable fraction fails to detect concentration differences between functional areas for chromium (Cr) and Pb. The sodium acetate, weakly acid soluble, fraction failed to detect differences in Ti, though the Ti in the soils may be a geological background signal rather than an anthropogenic loading[4]. The ammonium oxalate extractable (Fe and Mn oxide) fractions failed to differentiate between context for Sr and potassium (K).

As in previous soil fractionation studies[18,44,45] most Pb is bound with the organic matter and Fe and Mn oxide fractions

(Ammonium Oxalate A and B), whilst the weak acid soluble fraction was also significant in the hearth where lime mortar provided a source of free carbonate. For Ca the exchangeable and weakly acid soluble fractions are most important. However, for Pb, Ca and Zn a significant amount of each is also retained within the more resistant residual and/or geological matrix, only extractable using concentrated acid digestions. The manner of adsorption of different elements within the soil is important to their long term retention and redistribution through the profile. This is important in modern pollution studies where the dispersal of pollutants is of concern[46,47] but is also a critical issue in archaeological and historical studies of former human activity where the time scale involved can be in the order of millenia. Elements preferentially bound to exchangeable sites, such as Ca, in these acid soils, will be particularly susceptible to exchange with protons in the soil solution and progressive leaching. Elements such as Pb, which are specifically adsorbed to Fe, Al, and Mn oxides, will tend to be less easily leached; though as Ca and other base cations are leached from the soil, more exchange sites will be available to Pb ions. Therefore, the potential for development over time of post-depositional, pedogenic patterns is high.

In order to identify suitable methods for optimal extraction of the anthropogenic element loadings it is necessary to consider whether the element concentrations in the residue are geologically or anthropogenically derived. Figure 1 clearly shows that compared to the un-amended grazing soils the concentrations of Ca, Pb and Zn in the residue are significantly higher. This difference persists even when the concentrations are converted to mineral matter mass to adjust for the dilution effects of organic matter content. For anthropogenic element loadings of the sort found in the hearth, house and byre, therefore, a significant portion is held within the more resistant soil matrix fractions. It may be that these are occurring in association with finely divided inclusions of archaeological pottery, bone, metal work, charcoal etc. in the soil. More work is needed to clarify the exact origin of these loadings.

In general, environmental studies of anthropogenic effects are concerned with the bioavailability of pollutants, however, spatial studies of historical and prehistoric pollutants seek to maximise recovery of the anthropogenic signal, and information would be lost if a weak acid or exchangeable extraction was employed as has previously been suggested for archaeological studies[10,13].

The choice of extraction method, therefore, is important in identifying patterns of element enhancement due to former anthropogenic activity, but this influence is also element and soil specific. To optimise recovery it is important that consideration is first given to:

1. The elements of interest; which element concentration patterns are likely to provide most anthropogenic information?
2. Where these signatures are likely to bound within the soil; this will be affected by the element, the background soil and environmental conditions, the nature of the loadings and time elapsed since the deposition of the anthropogenic loading.

This supposes a knowledge of elemental patterns across the site, obtained from a preliminary study. On the basis of these results,

where a sequential approach is not feasible because of limitations on laboratory and instrumental time, a concentrated acid pseudo-total method would be most appropriate. The switch to a fraction-specific extraction method can then be made if compelling evidence is presented in the preliminary results.

Acknowledgements

References

1 R. A. During and S. Gath, *J Plant Nutr Soil Sci -Z Pflanzenernahr Bodenkd*, 2002, **165**, 544-556.
2 F. A. Nicholson, S. R. Smith, B. J. Alloway, C. Carlton-Smith and B. J. Chambers, *Sci Total Environ*, 2003, **311**, 205-219.
3 J. A. Entwistle, P. W. Abrahams and R. A. Dodgshon, *J Archaeol Sci*, 2000, **27**, 287-303.
4 C. A. Wilson, D. A. Davidson and M. S. Cresser, *Holocene*, 2005, 1 **15**, 1094-1099.
5 J. L. Bintliff, B. Davies, C. Gaffney, A. Snodgrass and A. Waters, in *Geoprospection in the Archaeological Landscape,* ed. P. Spoerry, Oxbow Monographs, Oxford, 1992, vol. 17, pp. 9-24.
6 M. A. Aston, M. H. Martin and A. W. Jackson, *Chemosphere*, 1998 **37**, 465-477.
7 W. D. Middleton and T. D. Price, *J Archaeol Sci*, 1996, **23**, 673-687.
8 J. J. Parnell, R. E. Terry and Z. Nelson, *J Archaeol Sci*, 2002, **29**, 379-404.
9 K. A. Sullivan and L. Kealhofer, *J Archaeol Sci*, 2004, **31**, 1659-1673.
10 E. C. Wells, *Archaeometry*, 2004, **46**, 67-84.
11 K. J. Knudson, L. Frink, B. W. Hoffman, T. D. Price, *J Archaeol Sci*, 2004, **31**, pp. 453-456.
12 M. A. Griffith, *Geoderma*, 1981, **25**, 27-34.
13 W. D. Middleton, *Archaeometry*, 2004, **46**, 47-65.
14 L. M. Shuman, *Soil Sci*, 1985, **140**, 11-22.
15 M. K. Zhang and Z. X. Ke, *Pedosphere*, 2004, **14**, 177-185.
16 B. D. Lee, B. J. Carter, N. T. Basta and B. Weaver, *Soil Sci Soc Am J*, 1997, **61**, 218-223.
17 Y. B. Ma and N. C. Uren, *Aust J Soil Res*, 1997, **35**, 727-738.
18 M. Backstrom, S. Karlsson and B Allard, *Environ Monit Assess*, 2004, **90**, pp.135-160.
19 J. R. Bacon and I. J. Hewitt, *Geochim Cosmochim Acta*, 2005, **69**, 19-33.
20 Karczewska, A., *Appl Geochem*, 1996, **11**, 35-42.
21 M. Pueyo, J. Sastre, E. Hernandez, M. Vidal, J. F. Lopéz-Sánchez, and G. Rauret, *J Environ Qual*, 2003, **32**, 2054-2066.
22 A. D. Karathanasis, and J. R. V. Pils, *Soil Sediment Contam*, 2005, **14**, 293-308.
23 M. K. Anderson, K. Raulund-Rasmussen, H. C. B. Hansen, and B. W. Strobel, *Eur J Soil Sci*, 2002, **53**, 491-502.
24 Soil Survey of Scotland, *Sheet 103, Golspie*, 1:63,360,
25 W. Roy, *Military Survey of Scotland, 1747-1755*, sheet 36/2.
26 J. MacKay, personal communication.
27 Ph. Quevauviller, *Trends Anal Chem*, 1998, **17**, 289-298.
28 A. M. Ure, Ph. Quevauviller, H. Muntau, B. Griepink. *Int J Environ Anal Chem*, 1993, **51**, 135-151.
29 G. Rauret, J. F. López-Sánchez, A. Sahuquillo, E. Barahona, M. Lachica, A. M. Ure, C. M. Davidson, A. Gomez, D. Lück, J. Bacon, M. Yli-Halla, H. Muntau, Ph. Quevauviller, *J Environ Monit*, 2000, **2**, 228-233.
30 A. Tessier, P. G. C. Cambell and M. Bisson, *Anal Chem*, 1979, **51**, 844-851.
31 L. M. Shuman, *Soil Sci Soc Am J*, 1983, **47**, 656-660.
32 R. Mikkuta, M. Kleber, K. Kaiser, and R. Jahn, *Soil Sci Soc Am J*, 2005, **69**, 120-135.
33 L. M. Shuman, *Soil Sci*, 1985, **140**, pp. 11-22.
34 C. Gleyzes, S. Tellier, M. Astruc, *Trends Anal Chem*, 2002, **21**, 451-467.

35 N. Belzile, P. Lecomte and A. Tessier, *Environ Sci Technol*, 1989, **23**, 1015-1020.
36 L. M. Shuman, *Soil Sci. Soc. Am. J.*, 1982, **46**, 1099-1102.
37 T. T. Chao and L. Zhou, *Soil Sci Soc Am J*, 1983, **47**, 225-232.
38 C. A. Davidson, A. S. Hursthouse, D. M. Tognarelli, A. M. Ure, and G. J. Urquhart, *Anal Chimica Acta*, 2004, **508**, 193-199.
39 S. K. Dhillon, and K. S. Dhillon, *Aust J Soil Res*, 2004, **42**, 247-257.
40 J. Shiowatana, N. Tantidanai, S. Nookabkaew, and D. Nacapricha, *J Environ Qual*, 2001, **30**, 1195-1205.
41   D. F.Ball, *J Soil Sci*, **15**, 84-92.
42 G. P. Gillman and E.A. Sumpter. *Aust J Soil Res*, 1986, **24**, 61-66.
43 G. W. Thomas, in *Methods of Soil Analysis, Part 2 Chemical and Microbiological Properties,* ed. A. L. Page, R. H. Miller and D. R. Keeney, American Society of Agronomy, Wisconsin, 1982, 2nd edn. pp. 159-165.
44 J. R. Bacon, I. J. Hewitt and P. Cooper, *J Environ Monit*, 2004, **9**, 766-773.
45 V. Ettler, A. Vanek, M. Mihaljevick, and P. Bezdicka, *Chemosphere*, **58**, 1449-1459.
46 M. K. Zkang, Z. L. He, D. V. Calvert and P. J. Stoffella, *Soil Sci*, 2004, **169**, pp. 528-540.
47 J. Y. Kim, K. W. Kim, J. Ahn, I. Ko, and C. H. Lee, 2005, *Environ Geochem Hlth*, **27**, 193-203.
48 L. M. Shuman, *Soil Sci*, 1979, **127**, 10-17.
49 A. M. Ure, *Sci Total Environ*, 1996, **178**, 3-10.

Figure 1: Absolute and relative partitioning of Ca, Zn, and Pb within soils from different functional areas