



Aqua regia extractable selenium contents of some Scottish topsoils measured by ICP-MS and the relationship with mineral and organic soil components

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3 **Aqua regia extractable selenium contents of some Scottish topsoils measured by**
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5 **ICP-MS and the relationship with mineral and organic soil components**
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10 **RUNNING TITLE:** Selenium in Scottish topsoils
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15 Charles A Shand,^{a,*} Matthias Balsam,^{a,1} Stephen J Hillier,^a Gordon Hudson,^a
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17 Gareth Newman,^a John R Arthur,^b Fergus Nicol^b
18
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22 ^a Macaulay Land Use Research Institute, Craigiebuckler, Aberdeen, AB15 8QH, UK
23

24 ^b Rowett Research Institute of Nutrition and Health, Bucksburn, Aberdeen, AB21 9SB,
25
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31 **Keywords:** aqua regia extraction; inductively coupled plasma - mass spectrometry;
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33 selenium; soil; soil carbon; soil minerals
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38 **Abstract**
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41 **BACKGROUND:** To provide information concerning the geographical distribution of
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43 selenium (Se) in the soils of Scotland, we analysed 47 arable soils selected on the basis
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45 of their parent rock, which were expected to have relatively high, low or unclassified
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47 Se contents. To investigate relationships between the actual minerals in the soils and
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49 the aqua-regia extractable Se content of the soil, soil minerals were quantified by X-ray
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51 diffraction.
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58 * Correspondence to: Charles Shand, Soils Group, Macaulay Land Use Research
59 Institute, Craigiebuckler, Aberdeen, AB15 8QH, UK. E-mail: c.shand@macaulay.ac.uk.
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¹ Present address: Hochschule Fresenius, D-65510 Idstein, Germany.

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3 **RESULTS:** The aqua-regia extractable Se contents of the soils were between 0.19 and
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5 1.46 mg kg⁻¹. No simple correlation between the aqua-regia extractable Se contents of
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7 the soil and the parent rock classification estimated by soil survey was evident. Partial
8
9 least squares analysis revealed that the aqua-regia extractable Se content of the soils
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11 was positively related to loss on ignition (LOI) and negatively related to the K–
12
13 feldspar content with other mineral being less important.
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17 **CONCLUSION:** The Se content of arable topsoils from Scotland is more related to
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19 LOI or carbon content with parent material being less important.
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22 23 24 **INTRODUCTION**

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29 Following the discovery of Se as a factor against liver necrosis in rats ¹ and of the role
30
31 of Se in glutathione peroxidase ² the element is widely recognised as being essential
32
33 for human and animal health. ³ Possible links between Se status and the occurrence of
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35 health disorders in humans have been reviewed. ⁴⁻⁶ Intakes of Se by the UK population
36
37 have declined from a mean of 60 µg Se day⁻¹ in 1974 to 30 - 40 µg Se day⁻¹ in recent
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39 times, primarily due to the replacement of American milling wheat with quantities of
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41 UK sourced grain with lower Se content. ⁷⁻¹¹ Selenium intake by the population is also
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43 relatively low in Scotland ^{12,13} and there is increasing interest in the provision of
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45 information leading to a better understanding of Se supply, especially in situations
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47 where people and animals rely heavily on locally produced foods as a source of
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49 essential elements.
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55 Selenium is a chalcophile element and concentrations of Se in evolved magmatic
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57 rocks, such as granite, are relatively low. During the weathering of rock, Se is
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59 accumulated in fine sediments. ^{14,15} Selenium can also become concentrated in organic
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3 matter and organic-rich sediments. Overall, the Se contents of soils formed from
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5 andesitic, basaltic or argillaceous materials are expected to be richer in Se than soils
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7 formed from granites, sandstones, rhyolites, mica schist or non-volcanic greywacke.¹⁶
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9 The influence of parent material on the Se content of soils has been demonstrated in
10
11 England and Wales.¹⁷ Scottish soils are distinguished from those in England and
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13 elsewhere in that they have geologically diverse parent material and often contain large
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15 amounts of organic C. Yet, relatively little is known^{16,18-20} about the pattern of
16
17 distribution of Se in the Scottish landscape.
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22 Selenium can be measured by inductively coupled plasma – mass spectrometry
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24 (ICP-MS) with an Ar based plasma and the ICP-MS method has advantages over
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26 others with regard to ease of use and multi-element capability. Selenium has six
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28 naturally occurring isotopes; ⁷⁴Se (0.87 %), ⁷⁶Se (9.02 %), ⁷⁷Se (7.58 %), ⁷⁸Se (23.52
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30 %), ⁸⁰Se (49.82 %) and ⁸²Se (9.19 %).²¹ The use of ⁷⁶Se, ⁷⁸Se and ⁸⁰Se suffer
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32 interferences from Ar dimmers e.g. ⁴⁰Ar₂⁺, whereas, the others may suffer from a range
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34 of mixed element ion interferences.^{22,23} Cool plasma conditions reduce Ar₂-based
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36 interference but are not suited for the analysis of Se, which has a large ionisation
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38 potential. Collision / reaction cell methodology using a mixture of H₂ and He has been
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40 developed to simultaneously remove ⁴⁰Ar⁴⁰Ar⁺ and ⁴⁰Ar³⁵Cl⁺ interferences in the
41
42 determination of ⁸⁰Se and ⁷⁵As in chloride-rich matrices and mineral waters.²⁴ Aqua
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44 regia digests of sediments have been analysed by ICP-MS using ⁸²Se: interference
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46 from ⁸²Kr⁺ (Ar contaminant), ³⁴S¹⁶O₃⁺ and ⁶⁶Zn¹⁶O⁺ were found to be insignificant or
47
48 eliminated during blank subtraction. Bromine interference (⁸¹Br¹H⁺) was eliminated
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50 through oxidation of Br⁻ by NOCl, present in aqua regia, to volatile Br₂.²⁵ The use of
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52 H₂ in the reaction cell has advantages over other gases in that H₂ reacts little with Se
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54 and causes minimal scattering. Naturally occurring Ar gas is a mixture of three
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3 isotopes; ^{36}Ar (0.34 %), ^{38}Ar (0.06 %), and ^{40}Ar (99.60 %).²¹ For ICP-MS using an Ar
4 based plasma, measurement of ^{80}Se with interference from $^{40}\text{Ar}_2^+$ is best avoided. The
5
6 use of the less abundant ^{78}Se with interference from $^{38}\text{Ar}^{40}\text{Ar}^+$ is preferred and is
7
8 recommended by the manufacturer of the instrument we used. The use ICP-MS with
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10 H_2 in the reaction cell for the analysis of Se in nitric / perchloric acid digests of soil
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12 using both ^{78}Se and ^{80}Se has been reported¹¹ but no details related to the choice of
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14 isotopes for analytical purposes were presented.
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20 Our aims were: (1) to demonstrate that the analysis of the Se in aqua regia digests of
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22 soils could be satisfactorily achieved by ICP-MS using ^{78}Se with H_2 as the reaction cell
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24 gas under routine, multi-element conditions, and (2), to investigate relationships
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26 between soil Se content of arable soils and other soil components, especially soil
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28 minerals and C.
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35 MATERIAL AND METHODS

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42 The information concerning the relative Se contents of different rock types¹⁶ discussed
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44 in the introduction, was used to identify areas of soils (Fig. 1) with associations (i.e.
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46 parent material) expected to have relatively “high” or “low” Se status, the remainder
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48 being “unclassified” because there was insufficient information. To test the validity of
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50 the hypothesis that soils formed from these different parent materials would indeed
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52 have different Se contents, we selected 47 soils from an archive of 981 air-dried, 2-mm
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54 sieved topsoils, which had been taken across Scotland on a 10-km grid basis as part of
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56 a national inventory.²⁶ Our selection of samples was based firstly on a restriction to
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58 soils which had been ploughed (224 samples), and secondly, to soils from associations
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3 with extensive coverage (Table 1) within which we selected examples of soils
4 representing the major soil groups (alluvial soils, brown earths, podzols and gleys).
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6 The particle size distribution of the soil was determined by a hydrometer method after
7 dispersion in 0.02 M sodium hydroxide. Loss on ignition (LOI) was determined by
8 recording the weight loss after heating the soil at 900 °C for 2 h. Soil pH was measured
9 in 0.01 M CaCl₂ using a 1:3 (mass to volume) soil to solution ratio. For the
10 determination of Se and C contents, the soil was ground in an agate ball mill to a
11 particle size < 150 µm. The total C content of the soil was determined by combustion
12 in a Hewlett-Packard CHN analyzer.
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27 **Mineralogical composition of soils**

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29 To provide information about the mineralogical composition of the soils they were
30 quantitatively analysed by X-ray diffraction using an X'Pert Pro diffractometer
31 (PANalytical, Almelo, The Netherlands) with an X'Celerator position sensitive
32 detector. Randomly orientated samples of the soil for X-ray analysis were prepared by
33 spray-drying.²⁷ Analysis of the diffractograms was performed by a full-pattern fitting
34 reference intensity ratio method.²⁸
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46 **Aqua regia extraction of soils**

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48 The soil extraction with aqua regia was based on the British standard reflux method,
49 ISO 11466.²⁹ Each determination used 2 g of the finely-ground soil and high purity
50 “Aristar” grade hydrochloric and nitric acids from VWR International Ltd, Poole, UK.
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52 A small amount of gold (III) chloride was added to each of the aqua regia digests to
53 preserve them³⁰ for future Hg analysis (not reported here).
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ICP-MS analysis of soil extracts

We used an Agilent 7500ce instrument with an octopole reaction cell employing H₂, micro flow nebuliser and integrated autosampler to measure ⁷⁸Se⁺. Instrument performance was optimised using a solution containing 10 µg l⁻¹ each of Li, Y, Tl and Ce. Maximum sensitivity was achieved by monitoring ⁷Li, ⁸⁹Y and ²⁰⁷Tl signals and minimum oxide formation by monitoring the ¹⁴⁰Ce:¹⁶O¹⁴⁰Ce ratio. For calibration we used a 1g Se l⁻¹ solution diluted to provide a range of working standards containing up to 1 mg Se l⁻¹ in a matrix of 2.5 M hydrochloric acid and 1.4 M nitric acid. To minimise damage to the Ni skimmer cones, sample extracts and standard solutions were diluted by a factor of ten before entering the plasma. To correct for instrument instabilities a solution of 500 µg Ge l⁻¹ was aspirated and the signal from ⁷²Ge monitored.

Quality control

To provide a check on the quality of the ICP-MS data for Se we analysed the aqua regia extracts by an independent method. An aliquot of the aqua regia digest containing up to 0.1 µg Se was placed in a reflux tube, perchloric acid was added, and the mixture heated to remove nitric acid. The solution remaining was treated with hydrochloric acid to reduce Se(VI) to Se(IV) and the Se concentration of the extract determined fluorimetrically.³¹

To provide a check on the accuracy of the methods we used reference soils NCS DC 73387 and NCS DC 73389 from the Laboratory of the Government Chemist (LGC), Promochem, Teddington, UK. Additionally, we measured aqua regia extractable Se in a soil sample (C3a) also provided by LGC as part of their contaminated land proficiency testing scheme. Soil with certified aqua regia extractable Se content was

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3 not available. The performance of the fluorimetric method was also assessed by
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5 analysis of IAEA-A-13 dried blood. The NCS reference soils and the dried blood were
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7 analysed in triplicate, whereas, reference soil C3a was analysed six-times.
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10 11 12 13 **Statistical analysis**

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15 Statistical analysis was performed using Minitab 15. Unless otherwise noted, error
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17 terms presented are standard deviations. Partial least squares (PLS) analysis provides a
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19 non-mechanistic approach to investigate mathematical relationships between soil
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21 properties. The technique has most often been applied to spectroscopic data but has
22
23 been used for prediction of soil properties from non-spectroscopic data and is
24
25 particularly useful for analysis of data sets with collinear information and where there
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27 is a large number of variables.³²
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34 **RESULTS**

35 36 37 38 **Selenium content of inventory soils**

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40 The Scottish soils (n = 47) were found to have Se contents ranging from 0.19 to 1.46
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42 mg kg⁻¹ measured by ICP-MS (Table 2). The mean value and median values were
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44 0.630 and 0.577 mg Se kg⁻¹, respectively. There was considerable variation between
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46 replicate values for soils with Se values near to the detection limit. A comparison of
47
48 the ICP-MS results of analysis with those from fluorimetry is presented in Fig. 2.
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50 Statistical analysis of the data by the paired t-test led to the acceptance of the
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52 hypothesis that the mean difference between the results of the ICP-MS and those by
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54 fluorimetry was significantly different from zero (at $p = 0.05$) and that the ICP-MS
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56 method, overall, gave slightly greater values. There were no significant differences (p
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3 = 0.05) between the mean values of Se in the parent material derived categories of high
4 (0.630 mg Se kg⁻¹), low (0.604 mg Se kg⁻¹) and the unclassified (0.658 mg Se kg⁻¹)
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= 0.05) between the mean values of Se in the parent material derived categories of high (0.630 mg Se kg⁻¹), low (0.604 mg Se kg⁻¹) and the unclassified (0.658 mg Se kg⁻¹) soils. Similarly, there was no significant difference ($p = 0.05$) between Se concentration in soil divided into major soil groups; the average concentration of Se in alluvial soils was 0.603 (n = 5), brown earths 0.619 (n = 21), gleys 0.551 (n = 9) and podzols 0.720 (n = 12) mg kg⁻¹. A more general significant link between the Se content of the soils and their C content ($R^2 = 0.578$) or LOI, ($R^2 = 0.700$) was apparent from a plot of soil C content or LOI against Se concentration in the soil (Fig. 3), both relationships being statistically significant ($p = < 0.001$).

Validation of analytical methodology to determine Se

The aqua regia extractable Se contents of certified reference soils were found to be 1.21 ± 0.25 mg kg⁻¹ for NCS DC 73387 (certified total 1.34 ± 0.17 mg kg⁻¹) and 0.16 ± 0.08 mg kg⁻¹ for NCS DC 73389 (certified total 0.10 ± 0.01 mg kg⁻¹). The value found for the aqua regia extractable Se content of the proficiency testing “Contest” soil was 1.49 ± 0.02 mg kg⁻¹ (assigned value 1.49 mg Se kg⁻¹). The Se content of the IAEA dried blood determined by fluorimetry gave a value of 0.22 ± 0.009 mg kg⁻¹ (certified value 0.24 ± 0.009 mg kg⁻¹). The Se content of the aqua regia digests of the certified soils determined by fluorimetry were 1.34 ± 0.12 mg kg⁻¹ for NCS DC 73387 and 0.08 ± 0.00 mg kg⁻¹ for NCS DC 73389. The limit of detection for Se analysis by ICP-MS estimated as 3 × standard deviation of ten intraset blank readings was 1.4 µg Se l⁻¹, which is equivalent to the concentration of a digest derived from a soil containing 0.07 mg Se kg⁻¹.

Mineralogical composition determined by XRD

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3 The minerals present in the soils included quartz with lesser amounts of K-feldspar,
4 plagioclase and amphibole; for simplicity the minerals have been grouped together into
5 classes (Table 2). The amount of clay-sized material in the soils measured by classical
6 sedimentation methods presented in Table 1 was generally less than the amount of
7 phyllosilicates measured by X-ray diffraction. This difference has been observed in
8 many other samples analysed in the same way in our laboratory and is indicative of the
9 presence of aggregates in the chemically dispersed samples.
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22 **Correlations between Se and other soil components**

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24 Partial least squares analysis of the data with the Se content of the soils determined by
25 ICP-MS as the response variate and the mineralogical phases shown in Table 2 and the
26 percentage LOI or C as the predictors indicated that the aqua regia extractable Se
27 content of the soils was best explained (optimal with regard to cross validation) by a 3-
28 component model which had an R^2 value of 0.79 and a predicted R^2 value of 0.71 by
29 cross validation. The PLS response plot indicated that the model fitted the data well
30 and that there was no extreme leverage. The PLS coefficient plot (Fig. 4a) showed that
31 the most important components were LOI (standardised regression coefficient 0.68)
32 and K-feldspar (standardised regression coefficient - 0.26) with data for other mineral
33 phases being less important and varying in sign. The loading plot (Fig. 4b) indicated
34 that the influences of LOI and K-feldspar on Se content of the soil were relatively
35 important and opposite in direction within component 1 of the model, which contains
36 terms related to all the predictors.
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55 We were unable measure S in the aqua regia digests because of isobaric
56 interferences but found significant ($p < 0.05$), linear correlations with other elements
57 including As ($r = 0.426$), Cd ($r = 0.623$), Cr ($r = 0.347$), Cu ($r = 0.348$), Fe ($r = 0.348$),
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3 P ($r = 0.453$) and Pb ($r = 0.449$).
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6 The map (Fig. 5) shows the predicted distribution of aqua regia extractable Se in
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8 arable soils based on the relationship, aqua regia extractable soil S concentration (mg
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10 kg^{-1}) = $0.0381 \times \text{percent LOI} + 0.1655$ (Fig. 3b). The data for LOI was from the
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12 National Soils Inventory of Scotland, 10–km grid positions and was restricted to
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14 mineral soils (C content < 25 %).
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20 DISCUSSION

21 Aqua regia extraction

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27 The range of values we obtained for the Se contents of the arable soils from Scotland
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29 (0.19 to 1.46; median 0.58 mg kg^{-1}) is consistent with the range of previously reported
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31 values (0.11 to 1.59; median 0.69 mg kg^{-1}).^{16,18,20} Lesser values, ranging from 0.02 to
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33 0.36 mg Se kg^{-1} have been reported¹⁹ for a group of ten Scottish soils analysed by
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35 molecular fluorescence but Se may have been lost during preliminary ashing of the soil.
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37 In comparison, soils from 34 farms in Wales and the Midlands of England were
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39 reported³³ to contain 0.2 to 1.8 mg Se kg^{-1} , median 0.6 mg Se kg^{-1} . Analysis of soil
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41 and stream sediments from England and Wales by the British Geological Survey have
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43 shown that the total Se ranged between 0.1 and 4 mg Se kg^{-1} and that > 95 % of them
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45 contained < 1 mg Se kg^{-1} .¹⁰
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51 The data for the analysis of the standard reference or test materials agreed well with
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53 the given values providing confidence in the accuracy of the data. The considerable
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55 variation in Se concentration values measured by ICP-MS especially those for soils
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57 containing < 0.4 mg Se kg^{-1} is a reflection of closeness of values to the limit of the
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59 method. The use of ⁷⁸Se (23.52 % natural abundance) was recommended by the
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3 instrument manufacturer for the analysis of Se and we used their standard operating
4 conditions. Optimising the tune conditions for this mass alone and adjustment of H₂
5 pressure may provide improvement. The nitric and hydrochloric acids used to prepare
6 the aqua regia were of a high-purity, analytical grade but it is possible that further
7 purification of the acids may result in a lower quantification limit for Se in soils.
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15 A study involving sequential extraction of Se from four Scottish soils using 0.25 M
16 potassium chloride (soluble fraction), 0.1 M potassium dihydrogen phosphate (ligand-
17 exchangeable), 4 M hydrochloric acid (acid extractable), potassium chlorate /
18 hydrochloric acid (oxidisable fraction) and hydrofluoric acid (residual fraction) has
19 shown that most of the Se (62 %) was associated with the residual hydrofluoric acid
20 soluble fraction.³⁴ It can be assumed that aqua regia will extract Se associated with the
21 soluble, ligand exchangeable and oxidisable fractions but the extent to which aqua
22 regia extracts Se from the residual fraction is unknown. Near quantitative recovery of
23 Se from reference soils RTC-CRM 023-050 (117 mg Se kg⁻¹) and RTC-CRM 025-050
24 (518 mg Se kg⁻¹) by aqua regia extraction has been reported.³⁵ However, these soils are
25 from contaminated sites and the bulk of the Se may be present in easily accessible
26 forms. The recovery of Se from certified reference materials [sediment 2704 (1.16 mg
27 Se kg⁻¹), sandy soil 2709 (1.56 mg Se kg⁻¹), and contaminated soil 2711 (1.54 mg Se
28 kg⁻¹)] by open beaker aqua regia digestion was 112 ± 24, 96 ± 8.0 and 85 ± 3.5 %,
29 respectively.³⁶ Variable recoveries of other aqua regia extractable elements from soils
30 in Scotland are reported but refluxing is generally more effective than open digestion.³⁷
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32 We have no information about the proportion of the total Se dissolved by aqua regia
33 from Scottish soils, which tend to be relatively rich in organic matter. Boiling aqua
34 regia effectively decomposes soil organic matter but dissolves only some mineral
35 phases including iron oxides and iron-rich and trioctahedral phyllosilicates, which may
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3 be linked with Se. Although the total amount of an element in soil can be a poor
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5 indicator of its bioavailability to plants, there are conflicting reports regarding the
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7 suitability of different extractants for the determination of plant available Se in soil.¹⁴
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10 11 12 **Relationships between Se and other soil components**

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15 No simple correlation between the aqua regia extractable Se contents of the soil and
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17 the parent material as assessed by traditional soil survey in the field²⁶ was evident.
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19 This could be explained by a lack of contrast in the nature of the parent materials, or a
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21 lack of resolution in the classification themselves. Positive relationships between the
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23 amounts of Se and soil organic matter have been reported.^{38,39} For the soils studied by
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25 us, the C content of the soil was a more important factor in determining the aqua regia
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27 extractable Se content of soil than the parent rock type as assessed by soil surveyors in
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29 the field. There is also the possibility of inputs of Se from the atmosphere, fertilisers or
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31 organic matter, or by loss or gain of soil forming minerals by physical effect such as
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33 outwashing.⁴⁰ A comparatively high concentration of Se in Norwegian coastal areas
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35 was found to be associated with atmospheric inputs and a high content of soil organic
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37 matter.⁴¹ Other studies have also shown that Se in soils is can be associated with
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39 organic matter although the mechanism of interaction and the chemical species present
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41 in the complex is unclear because of the presence of mixed organic matter and mineral
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43 phases.⁴²
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51 The C content of soils from the National Inventory of Scotland (10-km grid) follows
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53 a bimodal distribution reflecting the composition of mineral soils (mean 5.5 % C for
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55 219 samples) and organic soils (mean 43.6 % C for 414 samples).⁴³ In the Scottish
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57 context, soils with a C content < 25% are considered to be mineral soils, whereas, soils
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59 with a C content of > 25% are considered to be organic soils. The soils studied here in
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3 relation to Se content fall into the mineral soil category and the Se content of organic
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5 soils such as peat or of soils with peaty surface horizons is not part of the study.
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8 The improved linear correlation between the Se content and LOI of the soils ($R^2 =$
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10 0.847) compared to Se content and percentage C content of the soils ($R^2 = 0.578$) may
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12 be explained by the inclusion of the weight loss due to structural dehydroxylation in
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14 the LOI measurement. For soil minerals, structural dehydroxylation on heating is
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16 largely a phenomenon associated with phyllosilicates, which on heating first loose
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18 interlayer water and then water from structural hydroxyl groups as the temperature is
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20 increased. Clay minerals are important for the fixation of Se⁴⁴ and the improved
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22 correlation may in part also reflect this phenomenon. However, the value of correlation
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24 coefficient between Se content and soil C or LOI (Fig 3) is dependent on the variation
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26 associated with the measurement of C or LOI. The values for C and LOI taken from
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28 the database of the Soil Survey of Scotland were single values and the associated error
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30 terms were not available.
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36 The apparent link between Se and K-feldspar content of the soil is more difficult to
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38 explain. Nonetheless, feldspars are a major component of granite and other evolved
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40 igneous rocks. The negative link between Se and feldspar content could reflect the fact
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42 that rock with large K-feldspar contents are not of sedimentary origin and therefore
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44 less likely to contain S bearing minerals and associated Se components. Although we
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46 could not measure S in the aqua regia digests we did observe significant ($p < 0.05$),
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48 positive correlations with other elements such as Cu that are associated with S.¹⁴
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53 For arable topsoils in Scotland it is possible to construct crude maps of Se
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55 distribution from soil carbon contents or LOI alone with mineralogical information
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57 adding improvements. At present this refinement is not possible because a complete set
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59 of quantitative mineralogical data for the arable soil of Scotland is not available.
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Table 1. Properties of the soils. Apart from the predicted Se status, the data is from the National Soils Inventory of Scotland

| Soil association, parent material, and land area of Scotland | Predicted Se status ^a | Soil No. | Major soil group | Sand-Silt-Clay (%) ^b | Carbon (%) | pH (CaCl ₂) |
|----------------------------------------------------------------------------------------------------------------------------------|----------------------------------|----------|------------------|---------------------------------|------------|-------------------------|
| Darleith, drifts derived from basaltic rocks, 3.53 % ^c | H | 1 | Brown earth | 55-28-10 | 4.94 | 5.31 |
| | | 2 | Gley | 40-36-24 | 2.3 | 5.57 |
| | | 3 | Podzol | 56-27-17 | 10.5 | 4.22 |
| Ettrick, drifts derived from lower Paleozoic greywackes and shales, 9.26 % | H | 4 | Brown earth | 55-30-8 | 6.17 | 5.6 |
| | | 5 | Brown earth | 52-41-7 | 5.99 | 5.31 |
| | | 6 | Brown earth | 70-27-3 | 3.54 | 6.28 |
| | | 7 | Gley | 50-37-13 | 1.72 | 5.55 |
| Foudland, drifts derived from slates, phyllites and other weakly metamorphosed argillaceous rocks, 3.25 % | H | 8 | Brown earth | 54-38-8 | 4.42 | 4.44 |
| | | 9 | Podzol | 62-24-14 | 4.18 | 5.37 |
| | | 10 | Podzol | 60-24-16 | 6.88 | 5.11 |
| Sourhope, drifts derived from Old Red Sandstone intermediate lavas, 1.71 % | H | 11 | Brown earth | NA | 15.5 | 5.12 |
| | | 12 | Brown earth | 65-24-6 | 3.67 | 5.33 |
| | | 13 | Brown earth | 49-31-20 | 3.55 | 5.35 |
| | | 14 | Brown earth | 59-35-6 | 3.99 | 4.88 |
| | | 15 | Gley | 65-20-12 | 1.64 | 6.51 |
| | | 16 | Podzol | 88-11-2 | 10.5 | 3.9 |
| Balrownie, drifts derived from sandstones of Lower Old Red Sandstone age, often water-modified, 1.83 % | L | 17 | Brown earth | 70-26-4 | 3.66 | 4.94 |
| | | 18 | Brown earth | NA | 16.9 | 3.73 |
| | | 19 | Brown earth | 70-23-7 | 2.69 | 5.42 |
| | | 20 | Brown earth | 72-17-11 | 2.92 | 5.19 |
| | | 21 | Gley | 70-16-13 | 3.25 | 5.27 |
| Countesswells, drifts derived from granites and granitic rocks, 5.75 % ^c | L | 22 | Podzol | 77-12-11 | 2.72 | 5.29 |
| | | 23 | Podzol | 73-13-14 | 4.06 | 5.34 |
| Corby, fluio-glacial and raised beach sands and gravels derived from acid rocks, 3.08 % ^c | L | 24 | Gley | 86-9-5 | 11.3 | 4.34 |
| | | 25 | Podzol | 36-56-8 | 3.26 | 5.18 |
| | | 26 | Podzol | 88-8-4 | 5.6 | 3.9 |
| Strichen, drifts derived from arenaceous schists and strongly metamorphosed argillaceous schists of the Dalradian Series, 7.98 % | L | 27 | Brown earth | 72-24-4 | 1.15 | 5.51 |
| | | 28 | Brown earth | 71-21-8 | 3.41 | 4.2 |
| | | 29 | Gley | 73-13-13 | 3.85 | 5.11 |
| | | 30 | Podzol | 62-24-15 | 6.16 | 5.65 |
| | | 31 | Podzol | 91-6-3 | 9.56 | 4.1 |
| | | 32 | Podzol | 87-9-4 | 9.32 | 3.6 |
| Alluvial, recent riverine and lacustrine alluvial deposits, 1.63 % | UC | 33 | Alluvial | 87-9-4 | 2.34 | 5.06 |
| | | 34 | Alluvial | 79-16-4 | 2.83 | 5.43 |
| | | 35 | Alluvial | 51-37-12 | 1.65 | 5.76 |
| | | 36 | Alluvial | 64-30-3 | 1.73 | 6.49 |
| | | 37 | Alluvial | 44-35-9 | 12.1 | 5.35 |
| Deecastle, drifts derived from Dalradian limestones and calc-silicate rocks, 0.19 % | UC | 38 | Brown earth | 59-34-7 | 6.02 | 3.95 |
| | | 39 | Podzol | 74-19-7 | 6.42 | 3.94 |
| Hindsward, drifts derived from Carboniferous sediments and basic igneous rocks, 0.24 % | UC | 40 | Brown earth | 63-20-17 | 2.24 | 5.73 |
| | | 41 | Gley | 57-21-23 | 5.1 | 3.93 |
| Kilmarnock, drifts derived from igneous and sedimentary rocks of Carboniferous age, 0.40 % | UC | 42 | Brown earth | 57-30-7 | 4.65 | 5.33 |
| | | | | | | |
| Peterhead, drifts derived from Old Red Sandstone sediments with igneous metamorphic rocks and conglomerate cobbles, 0.18 % | UC | 43 | Brown earth | 61-20-14 | 4.68 | 4.99 |
| | | | | | | |
| Rowanhill, drifts derived from Carboniferous sandstones, shales and limestones, 3.04 % ^c | UC | 44 | Brown earth | 75-20-5 | 3.58 | 6.17 |
| | | 45 | Gley | NA | 10.8 | 4.51 |
| Tarves, drifts derived from intermediate rocks or mixed acid and basic rocks, both metamorphic and igneous, 2.07 % | UC | 46 | Brown earth | 63-20-12 | 4.27 | 4.71 |
| | | 47 | Gley | 64-21-15 | 3.12 | 5.8 |

^a H = high, L = low, UC = unclassified.

^b Sand 2000 - 20, silt 20 - 2, clay < 2 μm.

^c Includes some other soils with similar parent material.

NA = Not available.

Table 2. Average Se content of soils determined by ICP-MS and the mineralogical composition of soil

| Soil No. ^a | Se (mg kg ⁻¹) | Quartz (%) | K-feldspar (%) | Plagioclase (%) | Amphibole (%) | Fe-oxides ^b (%) | Other minerals ^c (%) | Phyllosilicates ^d (%) |
|-----------------------|---------------------------|------------|----------------|-----------------|---------------|----------------------------|---------------------------------|----------------------------------|
| 1 | 0.77 ± 0.03 | 22 | 8.3 | 4.6 | 0.7 | 5.6 | 2.2 | 35 |
| 2 | 0.51 ± 0.13 | 27 | 10.5 | 11.8 | 1.1 | 4.2 | 1.5 | 30 |
| 3 | 1.06 ± 0.10 | 3 | 4.1 | 9.4 | 1.5 | 8.0 | 11.9 | 28 |
| 4 | 0.80 ± 0.08 | 49 | 0.9 | 2.7 | 1.1 | 1.0 | 1.2 | 34 |
| 5 | 0.77 ± 0.05 | 41 | 1.1 | 9.0 | 1.0 | 1.3 | 1.9 | 29 |
| 6 | 0.73 ± 0.05 | 45 | 9.0 | 5.5 | 0.8 | 2.1 | 1.1 | 26 |
| 7 | 0.29 ± 0.06 | 49 | 4.6 | 8.8 | 0.8 | 1.6 | 1.2 | 27 |
| 8 | 0.75 ± 0.11 | 35 | 2.8 | 12.0 | 0.7 | 2.9 | 1.7 | 35 |
| 9 | 0.58 ± 0.07 | 49 | 5.8 | 10.2 | 1.5 | 1.4 | 1.5 | 19 |
| 10 | 0.71 ± 0.10 | 28 | 4.7 | 8.3 | 5.1 | 3.6 | 2.6 | 27 |
| 11 | 0.96 ± 0.04 | 14 | 9.1 | 20.1 | 2.5 | 3.5 | 2.2 | 20 |
| 12 | 0.36 ± 0.18 | 45 | 9.6 | 10.8 | 1.9 | 2.2 | 1.0 | 15 |
| 13 | 0.20 ± 0.14 | 12 | 7.7 | 26.7 | 1.5 | 2.7 | 2.9 | 31 |
| 14 | 0.42 ± 0.10 | 38 | 4.3 | 14.7 | 0.8 | 2.3 | 1.4 | 23 |
| 15 | 0.27 ± 0.04 | 46 | 19.8 | 4.9 | 1.1 | 0.8 | 0.8 | 14 |
| 16 | 0.90 ± 0.17 | 34 | 7.4 | 17.6 | 4.9 | 1.5 | 3.4 | 14 |
| 17 | 0.64 ± 0.07 | 42 | 5.4 | 19.5 | 1.1 | 0.8 | 1.4 | 16 |
| 18 | 1.25 ± 0.03 | 38 | 3.1 | 14.6 | 1.6 | 2.1 | 1.1 | 15 |
| 19 | 0.38 ± 0.05 | 45 | 5.9 | 17.5 | 1.1 | 1.1 | 1.8 | 18 |
| 20 | 0.33 ± 0.12 | 48 | 7.1 | 14.9 | 1.6 | 1.0 | 2.2 | 13 |
| 21 | 0.27 ± 0.02 | 60 | 7.5 | 5.5 | 1.2 | 0.8 | 0.6 | 15 |
| 22 | 0.42 ± 0.13 | 36 | 14.6 | 25.8 | 2.8 | 1.2 | 1.3 | 11 |
| 23 | 0.52 ± 0.14 | 33 | 10.3 | 24.9 | 2.4 | 1.0 | 1.5 | 16 |
| 24 | 0.48 ± 0.14 | 37 | 11.8 | 22.4 | 1.5 | 0.1 | 0.9 | 8 |
| 25 | 0.49 ± 0.12 | 51 | 7.0 | 9.2 | 2.8 | 1.0 | 1.3 | 15 |
| 26 | 0.59 ± 0.02 | 41 | 7.2 | 17.2 | 6.7 | 1.5 | 1.6 | 15 |
| 27 | 0.21 ± 0.10 | 47 | 7.6 | 10.7 | 1.3 | 1.0 | 0.5 | 26 |
| 28 | 0.81 ± 0.05 | 39 | 2.3 | 15.5 | 2.9 | 2.8 | 2.9 | 28 |
| 29 | 0.54 ± 0.11 | 51 | 8.5 | 13.2 | 2.9 | 1.8 | 3.4 | 11 |
| 30 | 0.98 ± 0.12 | 45 | 4.2 | 5.0 | 1.0 | 3.0 | 1.2 | 25 |
| 31 | 0.70 ± 0.06 | 37 | 3.0 | 15.8 | 4.4 | 1.3 | 3.3 | 19 |
| 32 | 1.06 ± 0.09 | 25 | 2.5 | 17.2 | 8.7 | 5.8 | 3.1 | 20 |
| 33 | 0.19 ± 0.16 | 61 | 13.0 | 12.4 | 0.7 | 0.5 | 0.7 | 6 |
| 34 | 0.47 ± 0.04 | 33 | 2.7 | 20.1 | 1.1 | 2.8 | 2.7 | 26 |
| 35 | 0.37 ± 0.05 | 39 | 8.3 | 14.5 | 1.4 | 1.2 | 1.6 | 22 |
| 36 | 0.54 ± 0.07 | 46 | 4.1 | 13.1 | 0.6 | 1.5 | 1.4 | 21 |
| 37 | 1.46 ± 0.09 | 30 | 3.4 | 7.8 | 0.4 | 1.5 | 0.7 | 27 |
| 38 | 0.92 ± 0.24 | 33 | 2.8 | 10.8 | 6.2 | 1.6 | 1.8 | 31 |
| 39 | 0.64 ± 0.01 | 31 | 3.0 | 15.1 | 3.9 | 2.3 | 3.3 | 27 |
| 40 | 0.40 ± 0.06 | 47 | 7.2 | 9.8 | 1.1 | 2.2 | 2.1 | 18 |
| 41 | 1.08 ± 0.09 | 34 | 2.6 | 5.8 | 0.4 | 0.5 | 1.0 | 33 |
| 42 | 0.62 ± 0.07 | 42 | 6.3 | 7.5 | 1.5 | 4.1 | 2.0 | 20 |
| 43 | 0.47 ± 0.09 | 44 | 8.2 | 11.9 | 1.1 | 1.8 | 1.4 | 19 |
| 44 | 0.67 ± 0.02 | 56 | 4.6 | 6.3 | 1.0 | 2.8 | 2.4 | 14 |
| 45 | 1.28 ± 0.02 | 46 | 3.0 | 4.7 | 0.4 | 2.3 | 0.6 | 16 |
| 46 | 0.54 ± 0.08 | 33 | 9.6 | 18.9 | 2.7 | 3.7 | 3.4 | 19 |
| 47 | 0.24 ± 0.17 | 42 | 5.1 | 12.5 | 1.6 | 2.4 | 1.2 | 25 |

^a See Table 1.

^b Sum of goethite, hematite and magnetite.

^c Sum of pyroxene, garnet, anatase and ilmenite.

^d Sum of chlorite, saponite / trioctahedral smectite, muscovite, illite, illite / smectite, biotite, vermiculite, hydrobiotite, kaolinite, halloysite and Fe-smectite.

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3 **1 Figure captions**
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8 **Fig. 1.** Map of Scotland showing areas predicted to have soils with relatively high, low
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10 or unclassified Se contents, and the soil sampling locations.
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13 **Fig. 2.** Comparison of values for the aqua regia extractable Se concentrations of soils
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15 measured by ICP-MS and fluorimetry.
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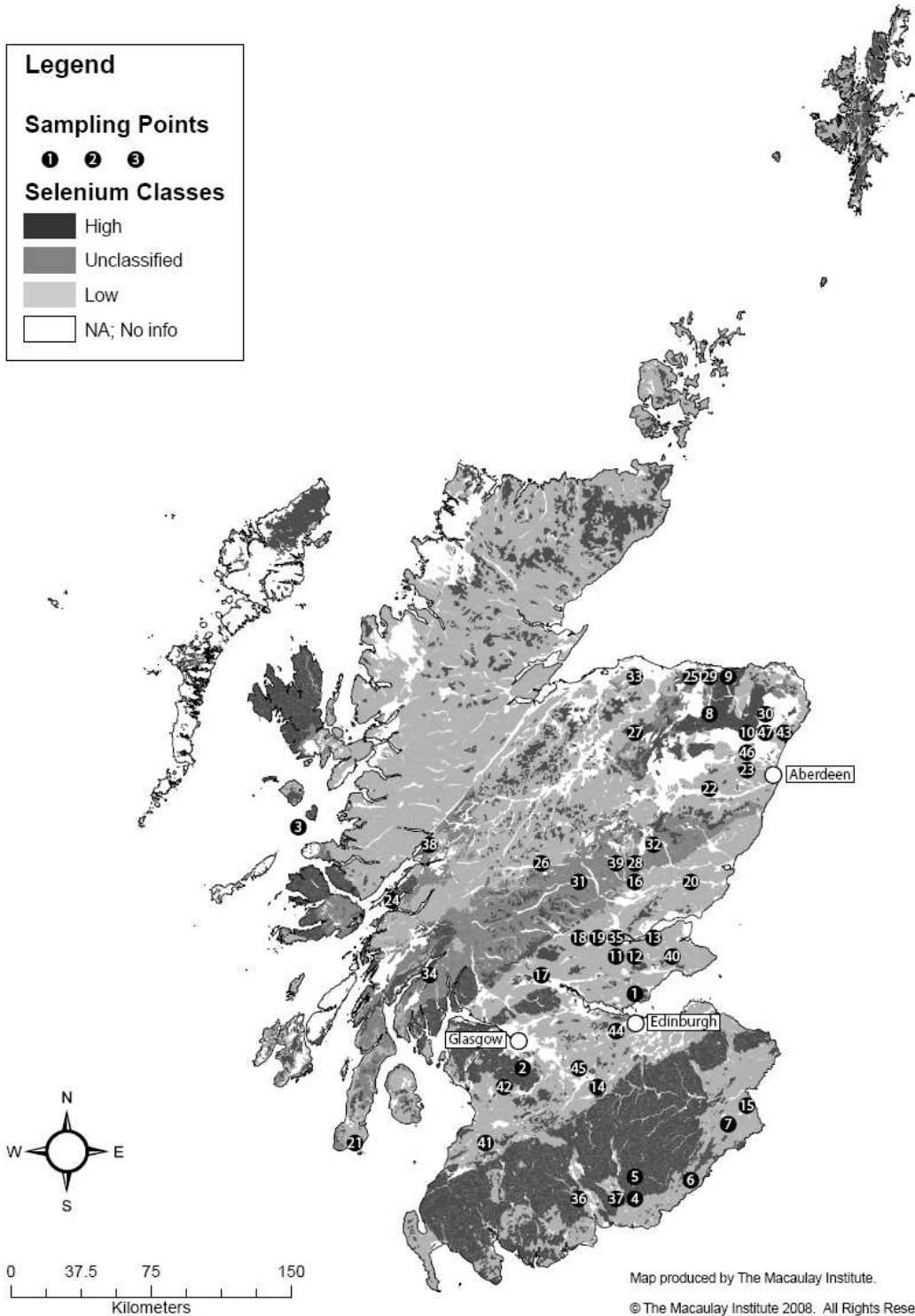
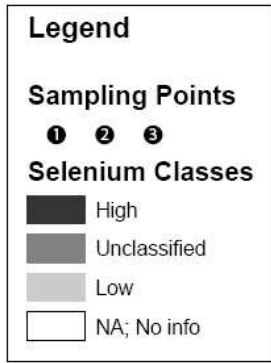
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18 **Fig. 3.** Relationship between the aqua regia extractable Se concentrations of the soils
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20 measured by ICP-MS and (a) the C contents of the soils, and (b) the LOI of the
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22 soils.
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24
25 **Fig. 4.** Partial least squares analyses with aqua regia extractable Se concentrations of
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27 the soil as the response and various mineral and LOI as predictors: (a) standard
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29 coefficient plot; and (b) loading plot.
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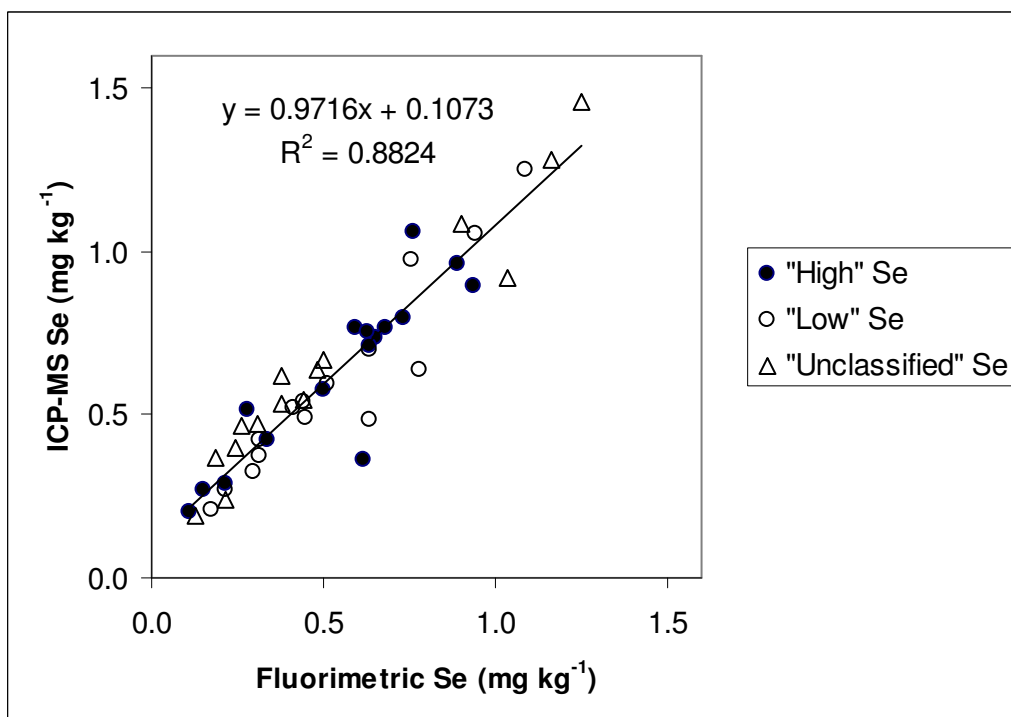
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32 **Fig. 5.** Map of Scotland showing the predicted values of aqua regia extractable Se in
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34 arable soils at the National Soils Inventory of Scotland, 10-km grid positions.
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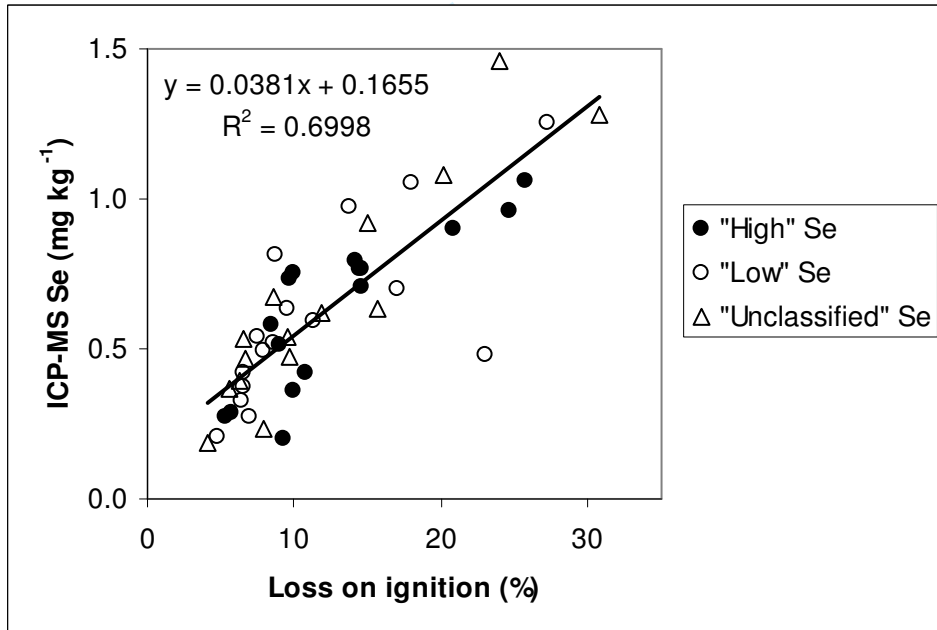
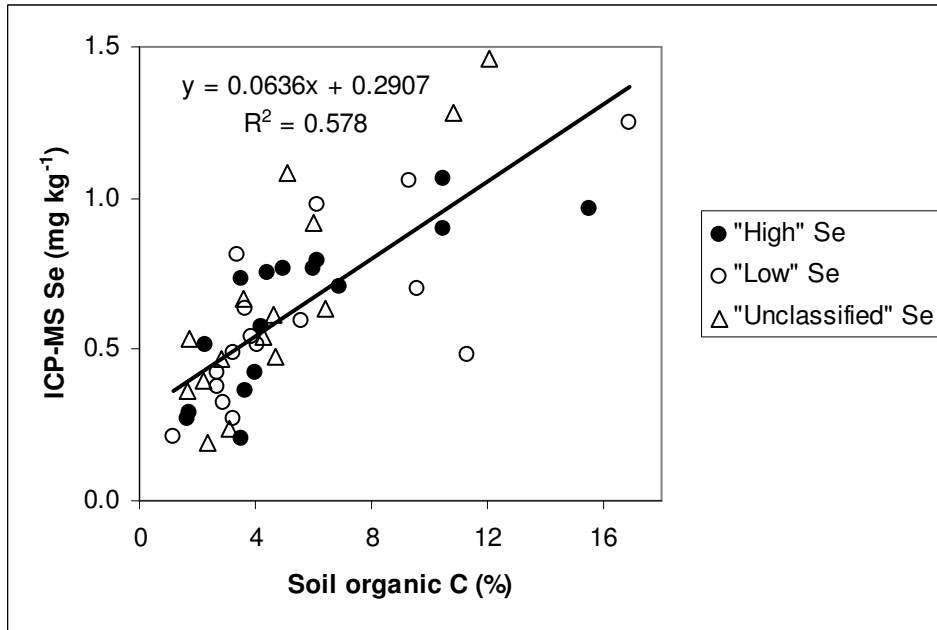
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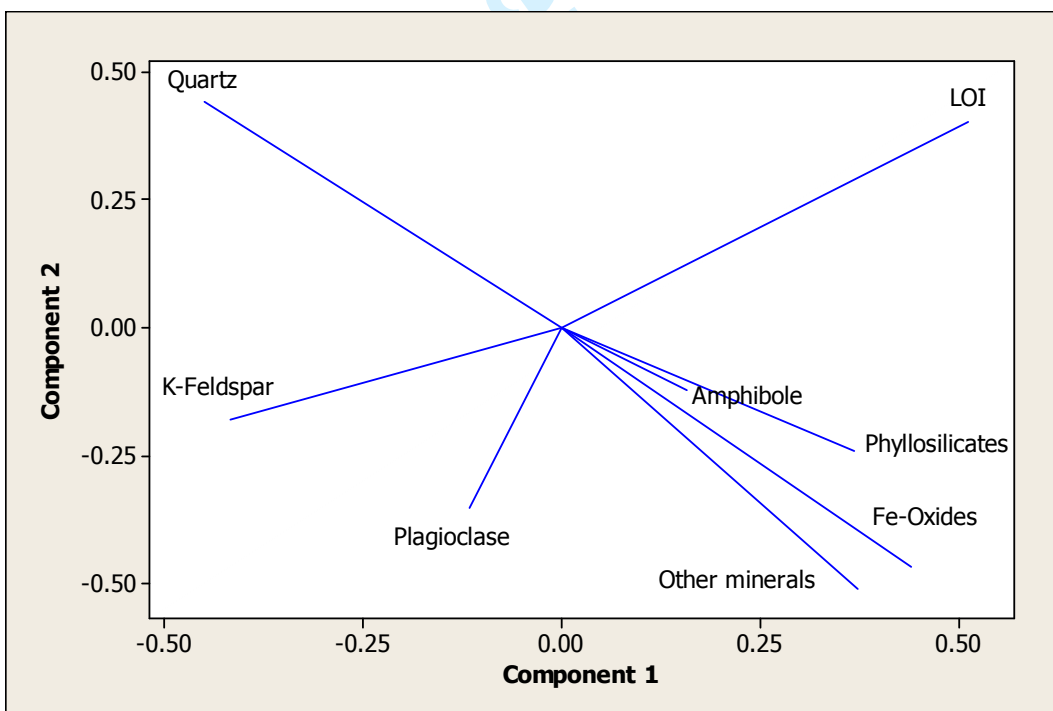
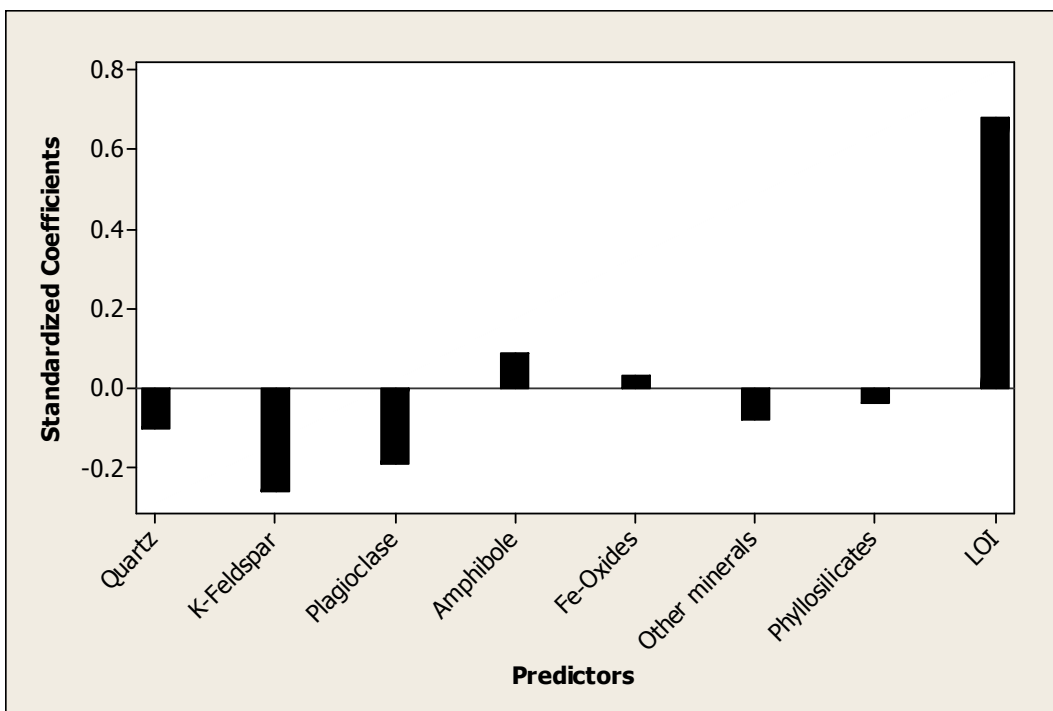


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