

# London Atlas: Materials and methods I: data acquisition

From Earthwise

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Ferreira, A, Johnson, C C, Appleton, J D, Flight, D M A, Lister, T R, Knights, K V, Ander, L, Scheib, C, Scheib, A, Cave, M, Wragg, J, Fordyce, F and Lawley, R. 2017. London Region Atlas of Topsoil Geochemistry. *British Geological Survey*.

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The London Region Atlas of Topsoil Geochemistry (LRA) covers a rectangular area of 80 x 62 km (4960 km<sup>2</sup>), from British National Grid coordinates X, Y: 490000, 153000 to 570000, 215000. The LRA was produced using the London Region Topsoil Dataset (**LRD**, N=8400), which was created from two BGS geochemical surveys (LOND and SEEN) carried out under the Geochemical Baseline Survey of the Environment (G-BASE<sup>[1]</sup>) project between 2005 and 2009. LOND is an **urban** soil survey based on 6801 sampling sites at a sampling density of 1 per 0.25 km<sup>2</sup>; 6494 (95.5%) of the LOND samples are part of the London Earth<sup>[2]</sup> project as they are located within the GLA. SEEN is a south-east England **rural** soil survey carried out at a sampling density of 1 per 2 km<sup>2</sup>; 1599 (out of the 4089) SEEN sample sites are included in the LRA rectangle area; however, 95% are outwith the GLA limit as these are rural samples ([Figure 2](#)).

Field procedures and laboratory methods were undertaken in a standardised way to ensure consistency and enable quality assessment of the analytical results (Johnson et al., 2005<sup>[3]</sup>). This allowed adequate levelling of geochemical datasets from contiguous areas, sampled and analysed at different times or under different projects. Methods are described in the following sections. Descriptions of the interpolation method (parent material mapping method, Appleton and Adlam, 2012<sup>[4]</sup>) used to generate maps of the soil geochemical properties and of the exploratory data analysis techniques deployed are outlined in the last section.

Throughout this atlas the **LRD** dataset, and **SEEN** and **LOND** subsets are generally represented by the colours **black/white**, **dark green** and **dark red** respectively, while Quaternary, Palaeogene and Cretaceous geological time periods are represented by soft yellow, orange and lime green colours respectively.

## Sampling

Sampling strategies for geochemical mapping using soil samples in rural (regional) and urban areas are described by Johnson et al. (2005)<sup>[3]</sup> and Fordyce et al. (2005)<sup>[5]</sup>, respectively. The only major difference between the two is the sampling density. In rural areas soil samples are collected from alternate British National Grid (BNG) kilometre squares, corresponding to a sampling density of 1

sample/2 km<sup>2</sup> (or 0.5 samples/km<sup>2</sup>); sites are ideally located at least 100 m from roads, buildings, railways, electricity pylons etc., on open unforested, and undisturbed ground whenever possible; the site should be generally representative of the land use within the selected kilometre square. In urban areas, the sample density is 1 sample/0.25 km<sup>2</sup> (or 4 samples/km<sup>2</sup>); samples are collected from open ground (preferably gardens, parks, sports fields, road verges, allotments, open spaces, schoolyards, and waste ground) as close as possible to the centre of each 500 m cell (subdivisions of the BNG 1 km cell) ([Figure 5](#)). The greater density in urban areas allows the capture of more local-scale element concentration variability caused by human activity. The way of defining an urban area for sample collection purposes is described by Johnson and Ander (2008)<sup>[6]</sup>.

Soil sampling was carried out according to the procedures detailed in the G-BASE<sup>[1]</sup> field procedures manual (Johnson, 2005<sup>[7]</sup>). All soil samples were collected and transported in 5"x10" Kraft™ paper bags. Each sample consisted of approximately 250 g of unsieved material and was a composite of five subsamples from auger holes distributed within an area of approximately 20 x 20 m whenever possible. Auger holes were located at the corners and centre of a square ([Figure 6](#)). A 1 m stainless steel Dutch auger with a 15 cm auger flight was used to collect soil samples from a fixed depth.

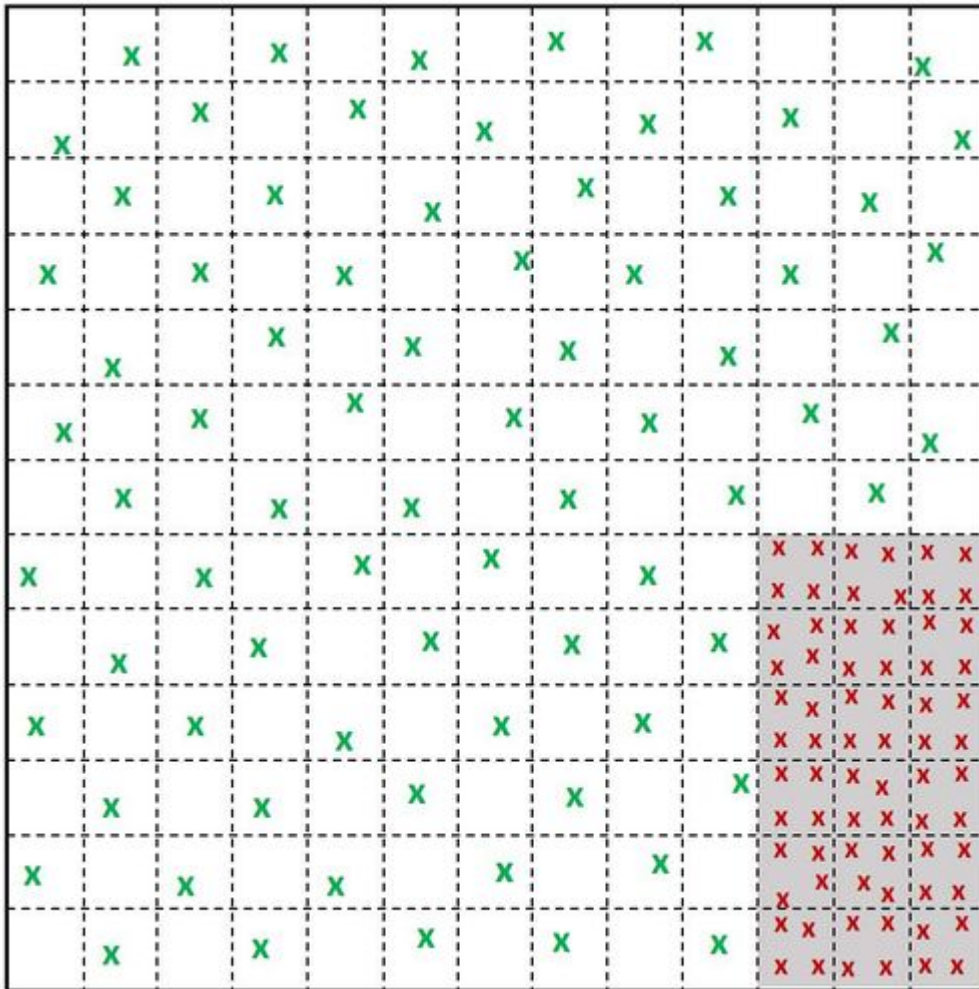
Topsoil samples (sample type code 'A') were collected to a depth of 20 cm, after removal of surface vegetation, surface litter and root zone. The bottom depth of the sample was recorded on the field card and the depth of any rootlet zone and surface litter was also noted. The deep soil sample (sample type code 'S') was targeted to collect to a depth of 35-50 cm (in rural areas this had the objective of sampling below any ploughed horizon), the actual sampling depth was recorded on the field card. Over terrains where only thin soils were developed e.g. over chalk, then a topsoil sample was collected from the normal surface depth, i.e. 5 to 20 cm and the S sample from as deep as possible down to bedrock. In such instances there may be little difference in the sampling depths between the A and S samples.

An extra surface sample (0-2 cm) was collected in the London Earth<sup>[2]</sup> GLA area, designated as sample type code 'X'. The X samples often demanded material from additional auger holes within the 20 m square in order to reach the required sample weight of ca. 250 g. If a root layer was present this was collected as part of the surface sample (Knights and Scheib, 2010<sup>[8]</sup>).

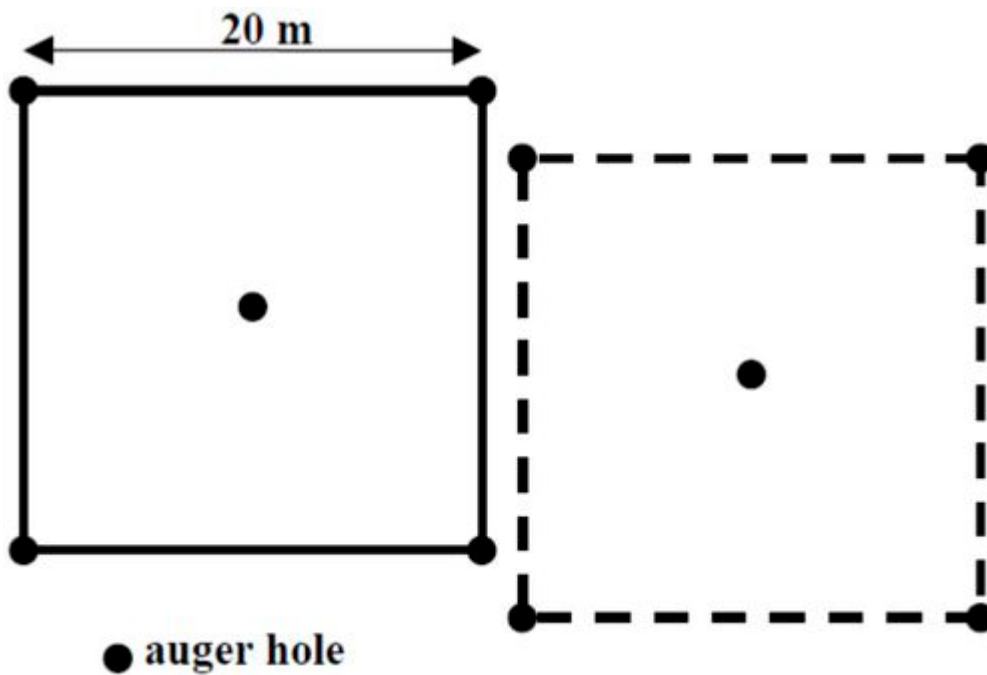
Field duplicate samples were collected at a rate of 1 duplicate per 100 sampling sites in rural surveys. This rate was doubled (2 per 100 sampling sites) in urban surveys following the higher sampling density implemented in these areas. For quality control purposes, the field duplicates were collected with exactly the same procedure as a regular sample, but in an adjacent auger square ([Figure 6](#)).

At each sampling site, information about date of sampling, local details (location, geology, visible contamination, land use, etc.) and observations of the sample, such as soil colour, depth, clast lithology and apparent abundance, and textural classification, were recorded on a field card.

The geochemical results for the topsoil samples type 'A' (5-20 cm depth) only are presented in this atlas.



**Figure 5** The G-BASE strategy for urban (red X) and rural (green X) soil sampling sites. The grid represents 1 km squares and the urban region is shaded (adapted from Johnson, 2005<sup>[7]</sup>). ([P929861](#)).



**Figure 6** Plan of composite auger holes for collecting a soil sample (dashed square represents adjacent duplicate sample) (from Johnson, 2005<sup>[7]</sup>). ([P929862](#)).

## Sample preparation and analysis

Soil samples were prepared and analysed at the BGS laboratories in Keyworth. All samples were dried and sieved but only the topsoils were routinely analysed by XRFs. After air-drying at <35°C (to prevent volatilisation of Se and Hg), each sample was sieved through a nylon sieve to give the <2 mm fraction. The sample was then homogenised, coned and quartered before a 50 g subsample was pulverised in an agate planetary ball mill to create a homogeneous sample (95% under 53 mm), from which a portion (12 g) was taken to prepare a pressed powder pellet for XRFs analysis.

Samples were analysed for total element concentration by XRFs in the BGS laboratories<sup>[9]</sup> in Keyworth. Analysis is accredited to ISO 17025 and to the Environment Agency's Monitoring Certification Scheme (MCERTS) standard for soils. Several different XRFs instruments were used, namely a PANalytical Axios advanced and a Philips MagiX PRO wavelength dispersive XRF spectrometer (WD-XRFs); and a PANalytical Epsilon-5 polarised energy dispersive XRF spectrometer (ED(P)XRFs), to determine 53 chemical elements. Forty-four of these elements are listed together with their lower limit of detection (LLD<sup>[10]</sup>) and the number of samples below LLD in [Table 3](#). The remaining nine elements ([Table 4](#)) were excluded as six of them (Cl, In, S, Te, Hg and Ta) showed more than 90% of the results below the LLD in at least one of the **LRD** subsets (**SEEN**, **LOND**) and five of them (Sm, Tl, Yb, Hg and Ta) showed a very small between-site variability (less than 35%), due to high within-sample and/or within-site variability mostly as a result of data close to the LLD ([Table 5](#)). Of the 44 elements shown in the London Region Atlas of Topsoil Geochemistry, the 10 most abundant elements ([Al<sub>2</sub>O<sub>3</sub>](#), [CaO](#), [Fe<sub>2</sub>O<sub>3</sub>](#), [K<sub>2</sub>O](#), [MgO](#), [MnO](#), [Na<sub>2</sub>O](#), [P<sub>2</sub>O<sub>5</sub>](#), [SiO<sub>2</sub>](#), [TiO<sub>2</sub>](#)) are expressed in terms of weight percent oxide (wt%) as concentration units, while the remaining 34 ([Ag](#), [As](#), [Ba](#), [Bi](#), [Br](#), [Cd](#), [Ce](#), [Co](#), [Cr](#), [Cs](#), [Cu](#), [Ga](#), [Ge](#), [Hf](#), [I](#), [La](#), [Mo](#), [Nb](#), [Nd](#), [Ni](#), [Pb](#), [Rb](#), [Sb](#), [Sc](#), [Se](#), [Sn](#), [Sr](#), [Th](#), [U](#), [V](#), [W](#), [Y](#), [Zn](#) and [Zr](#)) are shown in mg/kg (equivalent to the non-SI old notation ppm - parts per million).

Two extra parameters, loss on ignition (**LOI**) and **pH** were also determined on the topsoil samples from the **LOND** subset (except one for **LOI**) and about two thirds (1128 out of 1599) of the **SEEN** subset, resulting in a total of 7928 (for **LOI**) and 7929 (for **pH**) measurements. The loss on ignition, a proxy for the soil's organic matter content (but can be affected by the loss of structural water in clay soils (Rowell, 1994<sup>[11]</sup>), was determined on 2 g of <2 mm size material by weighing the sample before and after heating in a furnace at 450°C for 24 hrs. The soil **pH** was determined with a pH electrode after mixing 10 g of <2 mm size material in 25 ml of 0.01 M CaCl<sub>2</sub>.2H<sub>2</sub>O and shaking until a slurry was formed.

Table 3 List of elements determined by XRFs reported in the London Region Atlas of Topsoil Geochemistry. The lower limit of detection (LLD), the number of samples below the LLD (n<LLD) and the n<LLD in percent (%<LLD) are shown for the London Region Dataset (LRD), and the two subsets (**SEEN** and **LOND**). Number of samples (N) is as follow: LRD = 8400, **SEEN** = 1599 and **LOND** = 6801.

Element Symbol Units	Data	LLD	n<LLD	%<LLD	Element Symbol Units	Data	LLD	n<LLD	%<LLD	Element Symbol Units	Data	LLD	n<LLD	%<LLD
Aluminium oxide <a href="#">Al<sub>2</sub>O<sub>3</sub></a> %	LRD SEEN LOND	0.2 0.2 0.2	0 0 0	0.0 0.0 0.0	Cadmium <a href="#">Cd</a> mg/kg	LRD SEEN LOND	0.5 0.5 0.5	2317 787 1530	27.6 49.2 22.5	Lead <a href="#">Pb</a> mg/kg	LRD SEEN LOND	1.3 1.3 1.3	0 0 0	0.0 0.0 0.0
Calcium oxide <a href="#">CaO</a> %	LRD SEEN LOND	0.05 0.05 0.05	14 14 0	0.2 0.9 0.0	Cerium <a href="#">Ce</a> mg/kg	LRD SEEN LOND	1 1 1	0 0 0	0.0 0.0 0.0	Rubidium <a href="#">Rb</a> mg/kg	LRD SEEN LOND	1 1 1	0 0 0	0.0 0.0 0.0
Iron (III) oxide <a href="#">Fe<sub>2</sub>O<sub>3</sub></a> %	LRD SEEN LOND	0.01 0.01 0.01	0 0 0	0.0 0.0 0.0	Cobalt <a href="#">Co</a> mg/kg	LRD SEEN LOND	1.5 1.5 1.5	27 19 8	0.3 1.2 0.1	Antimony <a href="#">Sb</a> mg/kg	LRD SEEN LOND	0.5 0.5 0.5	84 68 16	1.0 4.3 0.2
Potassium oxide <a href="#">K<sub>2</sub>O</a> %	LRD SEEN LOND	0.01 0.01 0.01	0 0 0	0.0 0.0 0.0	Chromium <a href="#">Cr</a> mg/kg	LRD SEEN LOND	3 3 3	0 0 0	0.0 0.0 0.0	Scandium <a href="#">Sc</a> mg/kg	LRD SEEN LOND	3 3 3	374 198 176	4.5 12.4 2.6
Magnesium oxide <a href="#">MgO</a> %	LRD SEEN LOND	0.3 0.3 0.3	376 83 293	4.5 5.2 4.3	Caesium <a href="#">Cs</a> mg/kg	LRD SEEN LOND	1 1 1	0 0 0	0.0 0.0 0.0	Selenium <a href="#">Se</a> mg/kg	LRD SEEN LOND	0.2 0.2 0.2	140 51 89	1.7 3.2 1.3
Element Symbol Units	Data	LLD	n<LLD	%<LLD	Element Symbol Units	Data	LLD	n<LLD	%<LLD	Element Symbol Units	Data	LLD	n<LLD	%<LLD
Manganese oxide <a href="#">MnO</a> %	LRD SEEN LOND	0.005 0.005 0.005	20 12 8	0.2 0.8 0.1	Copper <a href="#">Cu</a> mg/kg	LRD SEEN LOND	1.3 1.3 1.3	0 0 0	0.0 0.0 0.0	Tin <a href="#">Sn</a> mg/kg	LRD SEEN LOND	0.5 0.5 0.5	0 0 0	0.0 0.0 0.0
Sodium oxide <a href="#">Na<sub>2</sub>O</a> %	LRD SEEN LOND	0.3 0.3 0.3	447 167 280	5.3 10.4 4.1	Gallium <a href="#">Ga</a> mg/kg	LRD SEEN LOND	1 1 1	0 0 0	0.0 0.0 0.0	Strontium <a href="#">Sr</a> mg/kg	LRD SEEN LOND	1 1 1	0 0 0	0.0 0.0 0.0
Phosphorous pentoxide <a href="#">P<sub>2</sub>O<sub>5</sub></a> %	LRD SEEN LOND	0.05 0.05 0.05	16 15 1	0.2 0.9 0.0	Germanium <a href="#">Ge</a> mg/kg	LRD SEEN LOND	0.5 0.5 0.5	384 109 275	4.6 6.8 4.0	Thorium <a href="#">Th</a> mg/kg	LRD SEEN LOND	0.7 0.7 0.7	3 1 2	0.0 0.1 0.0
Silica <a href="#">SiO<sub>2</sub></a> %	LRD SEEN LOND	0.1 0.1 0.1	0 0 0	0.0 0.0 0.0	Hafnium <a href="#">Hf</a> mg/kg	LRD SEEN LOND	1 1 1	0 0 0	0.0 0.0 0.0	Uranium <a href="#">U</a> mg/kg	LRD SEEN LOND	0.5 0.5 0.5	43 1 42	0.5 0.1 0.6
Titanium dioxide <a href="#">TiO<sub>2</sub></a> %	LRD SEEN LOND	0.01 0.01 0.01	0 0 0	0.0 0.0 0.0	Iodine <a href="#">I</a> mg/kg	LRD SEEN LOND	0.5 0.5 0.5	15 3 12	0.2 0.2 0.2	Vanadium <a href="#">V</a> mg/kg	LRD SEEN LOND	3 3 3	0 0 0	0.0 0.0 0.0
Element Symbol Units	Data	LLD	n<LLD	%<LLD	Element Symbol Units	Data	LLD	n<LLD	%<LLD	Element Symbol Units	Data	LLD	n<LLD	%<LLD
Silver <a href="#">Ag</a> mg/kg	LRD SEEN LOND	0.5 0.5 0.5	1232 175 1057	14.7 10.9 15.5	Lanthanum <a href="#">La</a> mg/kg	LRD SEEN LOND	1 1 1	0 0 0	0.0 0.0 0.0	Tungsten <a href="#">W</a> mg/kg	LRD SEEN LOND	0.6 0.6 0.6	219 81 138	2.6 5.1 2.0
Arsenic <a href="#">As</a> mg/kg	LRD SEEN LOND	2.4 2.4 2.4	9 5 4	0.1 0.3 0.1	Molybdenum <a href="#">Mo</a> mg/kg	LRD SEEN LOND	0.2 0.2 0.2	18 11 7	0.2 0.7 0.1	Yttrium <a href="#">Y</a> mg/kg	LRD SEEN LOND	1 1 1	0 0 0	0.0 0.0 0.0
Barium <a href="#">Ba</a> mg/kg	LRD SEEN LOND	1 1 1	0 0 0	0.0 0.0 0.0	Niobium <a href="#">Nb</a> mg/kg	LRD SEEN LOND	1 1 1	0 0 0	0.0 0.0 0.0	Zinc <a href="#">Zn</a> mg/kg	LRD SEEN LOND	1.3 1.3 1.3	3 1 2	0.0 0.1 0.0
Bismuth <a href="#">Bi</a> mg/kg	LRD SEEN LOND	0.3 0.3 0.3	4490 918 3572	53.5 57.4 52.5	Neodymium <a href="#">Nd</a> mg/kg	LRD SEEN LOND	4 4 4	19 14 5	0.2 0.9 0.1	Zirconium <a href="#">Zr</a> mg/kg	LRD SEEN LOND	1 1 1	0 0 0	0.0 0.0 0.0
Bromine <a href="#">Br</a> mg/kg	LRD SEEN LOND	0.8 0.8 0.8	0 0 0	0.0 0.0 0.0	Nickel <a href="#">Ni</a> mg/kg	LRD SEEN LOND	1.3 1.3 1.3	3 3 0	0.0 0.2 0.0	.				

Table 4 List of elements determined by XRFs not reported in the London Region Atlas of Topsoil Geochemistry. The lower limit of detection (LLD), the number of samples below the LLD (n<LLD) and the n<LLD in percent (%<LLD) are shown for the London Region Dataset (LRD), and the two



subsets (**SEEN** and **LOND**). Number of samples (N) is as follow: LRD = 8400, **SEEN** = 1599 and **LOND** = 6801.

Element Symbol Units	Data	LLD	n<LLD	%<LLD	Element Symbol Units	Data	LLD	n<LLD	%<LLD	Element Symbol Units	Data	LLD	n<LLD	%<LLD
<b>Chlorine</b>	<b>LRD</b>	200	8378	99.7	<b>Tellurium</b>	<b>LRD</b>	0.5	8347	99.4	<b>Samarium</b>	<b>LRD</b>	3.0	3217	38.3
<b>Cl</b>	<b>SEEN</b>	200	1596	99.8	<b>Te</b>	<b>SEEN</b>	0.5	1583	99.0	<b>Sm</b>	<b>SEEN</b>	3.0	533	33.3
<b>mg/kg</b>	<b>LOND</b>	200	6782	99.7	<b>mg/kg</b>	<b>LOND</b>	0.5	6764	99.5	<b>mg/kg</b>	<b>LOND</b>	3.0	2684	41.9
<b>Indium</b>	<b>LRD</b>	0.5	8348	99.4	<b>Mercury</b>	<b>LRD</b>	0.5	6921	82.4	<b>Thallium</b>	<b>LRD</b>	0.5	6054	72.1
<b>In</b>	<b>SEEN</b>	0.5	1586	99.2	<b>Hg</b>	<b>SEEN</b>	0.5	1513	94.6	<b>Tl</b>	<b>SEEN</b>	0.5	1049	65.6
<b>mg/kg</b>	<b>LOND</b>	0.5	6762	99.4	<b>mg/kg</b>	<b>LOND</b>	0.5	5408	79.5	<b>mg/kg</b>	<b>LOND</b>	0.5	5005	78.2
<b>Sulphur</b>	<b>LRD</b>	2000	8243	98.1	<b>Tantalum</b>	<b>LRD</b>	1.0	7741	92.9	<b>Ytterbium</b>	<b>LRD</b>	1.5	2520	30.0
<b>S</b>	<b>SEEN</b>	2000	1586	99.2	<b>Ta</b>	<b>SEEN</b>	1.0	1368	85.6	<b>Yb</b>	<b>SEEN</b>	1.5	371	23.2
<b>mg/kg</b>	<b>LOND</b>	2000	6657	97.9	<b>mg/kg</b>	<b>LOND</b>	1.0	6373	93.7	<b>mg/kg</b>	<b>LOND</b>	1.5	2149	33.6

Table 5 Nested ANOVA results for the London Region Data topsoil duplicate and replicate sets. The number of sites indicate the number of locations with duplicate and replicate samples. Results below the lower limit of detection are excluded from the ANOVA analysis (Johnson et al., 2010<sup>[12]</sup>).

Elements are ordered according to their performance in the nested ANOVA test. Shaded elements were excluded from the atlas after this test.

Element	Between-site %	Within-site %	Within-sample %	Number of sites	Element	Between-site %	Within-site %	Within-sample %	Number of sites
<b>Nb</b>	94.5	4.2	1.3	171	<b>MnO</b>	84.2	13.1	2.7	171
<b>K<sub>2</sub>O</b>	93.3	6.4	0.3	171	<b>As</b>	83.8	13.4	2.8	171
<b>Rb</b>	93.1	6.6	0.3	171	<b>P<sub>2</sub>O<sub>5</sub></b>	82.5	16.6	0.9	171
<b>La</b>	92.0	6.0	2.0	171	<b>Ba</b>	82.3	15.3	2.4	171
<b>TiO<sub>2</sub></b>	91.6	7.1	1.3	171	<b>Na<sub>2</sub>O</b>	82.3	10.2	7.5	124
<b>Ce</b>	91.0	7.4	1.6	171	<b>Co</b>	82.1	10.6	7.3	171
<b>Ga</b>	90.7	6.3	2.9	171	<b>Cs</b>	81.7	4.5	13.7	171
<b>MgO</b>	90.7	8.4	0.9	168	<b>W</b>	80.1	5.5	14.4	166
<b>Y</b>	90.6	7.0	2.4	171	<b>Ni</b>	79.9	16.2	3.9	171
<b>Al<sub>2</sub>O<sub>3</sub></b>	90.5	8.7	0.7	171	<b>Cu</b>	79.6	17.8	2.6	171
<b>V</b>	90.5	8.3	1.2	171	<b>Zn</b>	77.0	20.9	2.0	171
<b>Th</b>	89.4	6.2	4.4	171	<b>Sc</b>	76.4	9.3	14.2	165
<b>Zr</b>	88.9	9.4	1.7	171	<b>Sb</b>	75.9	14.9	9.2	170
<b>CaO</b>	88.3	10.3	1.3	171	<b>Sn</b>	75.0	16.4	8.5	171
<b>Fe<sub>2</sub>O<sub>3</sub></b>	88.1	8.8	3.1	171	<b>U</b>	72.1	5.5	22.3	165
<b>Mo</b>	88.1	8.9	3.0	151	<b>Se</b>	66.7	14.9	18.4	171
<b>Sr</b>	88.0	10.5	1.5	171	<b>Cd</b>	62.9	24.7	12.4	108
<b>Nd</b>	86.6	7.5	5.9	170	<b>Ge</b>	62.3	17.8	20.0	168
<b>Br</b>	86.4	11.4	2.2	171	<b>Ag</b>	58.9	30.9	10.2	26
<b>Hf</b>	86.0	7.1	6.9	171	<b>Bi</b>	52.2	28.1	19.7	55
<b>Pb</b>	85.3	10.7	4.0	171	<b>Yb</b>	34.8	5.3	59.8	99
<b>I</b>	85.2	8.8	6.0	171	<b>Hg</b>	29.7	55.2	15.1	39
<b>SiO<sub>2</sub></b>	85.0	12.5	2.5	171	<b>Sm</b>	25.7	4.5	69.8	166
<b>Cr</b>	85.0	13.9	1.2	171	<b>Tl</b>	16.6	-8.6	91.9	65
					<b>Ta</b>	15.3	3.0	81.7	54

## Quality control

G-BASE<sup>[1]</sup> analytical results are subjected to rigorous quality control procedures described in detail elsewhere (Lister and Johnson, 2005<sup>[13]</sup>; Johnson, 2011<sup>[14]</sup>). The entire process, from field procedures to sample preparation and analysis in the laboratory is designed to minimise errors. Systematic errors are able to be checked because a randomised number is assigned to samples on collection.

Accuracy, precision and long-term analytical drift is assessed by including BGS XRF laboratory

primary and secondary certified reference materials (CRMs) along with every batch of 500 samples in the analytical runs. Secondary CRMs allow any between batch bias to be identified and corrected. Primary CRMs ensure that bias from the 'true' result is minimized. Primary and secondary reference materials have been used routinely to assess the quality of regional geochemical data since the UK national mapping programme commenced in the 1960s (Lister and Johnson, 2005<sup>[15]</sup>; Johnson et al., 2008<sup>[16]</sup>). This ensures a 'seamless' continuation of geochemical data across large regions for samples collected over many field campaigns and analysed by different analytical instruments. All data in this London Region Geochemical Dataset are levelled using four accredited reference materials (GSD-7, GSS-1, LKSD-1, LKSD-4). Certified values (in red) together with the values reported by the BGS XRF laboratory are shown in [Table 6](#).

A previously unrecognised analytical interference between high topsoil Pb concentration and U measurement in the London Earth<sup>[2]</sup> results, where high Pb was suppressing the U results, has been corrected in this London Region dataset.

The G-BASE<sup>[1]</sup> project also inserts field *duplicate* and laboratory *replicate* samples in every batch of fifty (urban) or one hundred (rural) samples. The laboratory *replicate* is a sub-sample of the *same sample* taken before analysis, whilst a field *duplicate* is a *second sample* collected in the field at the same location as a regular sample. These two control samples allow assessment of the analytical and sampling variability respectively and comparison to the total variability. This provides a check that the local (within-site) 'noise' is low enough so that the regional patterns (between sites) are distinguishable and reliable. This was achieved by performing a nested unbalanced analysis of variance (ANOVA) using these duplicate and replicate samples (Johnson, 2002<sup>[17]</sup>). The validity of the nested ANOVA depends on the representativeness of the duplicates and replicates, and it may not be valid if a large number of samples have element concentrations that are near or below the LLD. Nevertheless, results give an indication of the elements for which the natural geochemical variability is significantly higher than the variability related to the sampling and analytical procedures. The higher the percentage of total variability attributed between sites, the higher the confidence in the results ([Table 5](#)). For elements with a value above 80% the sampling and analytical methodology is considered suitable, as it does not introduce too much 'background noise'. As between-site variability decreases from 80% down to about 50%, increasing caution must be taken during statistical analysis and/or interpretation. Elements showing a between-site variability below 50% (Yb, Hg, Sm, Tl and Ta) are not considered further in the LRA, as already explained under the [Sample preparation and analysis](#) section of this atlas.

Table 6 Summary of primary reference material results for soil samples XRF analyses in the London Region Atlas of Topsoil Geochemistry. Units for elements shown as oxides are wt% and mg/kg otherwise.

#### Elements by XRF-ED

CRM ID	Cert Ag	Cert Ag	Cert Cd	Cert Cd	In In	Cert In	Sn Sn	Cert Sn	Sn Sn	Cert Sb	Cert Sb	I I	Cert I	I I	Cert Cs	Cert Cs	Ba Ba	Cert Ba	Ba Ba	Cert La	Cert La	Ce Ce	Cert Ce
<b>GSD-7</b>	1.4	1.1	0.9	1.1	not detected	no data	4.8	5.4	2.8	2.6	0.9	no data	5	6	740	720	45	45	82	78.0			
<b>GSS-1</b>	0.4	0.4	4.4	4.3	not detected	no data	5.9	6.1	1.0	0.9	1.9	1.9	9	9	587	590	34	34	68	70.0			
<b>LKSD-1</b>	0.5	0.6	1.1	1.2	0.5	no data	15.2	16.0	0.9	1.2	1.7	no data	1	2	396	430	14	16	25	27.0			
<b>LKSD-4</b>	0.1	0.2	1.9	1.9	not detected	no data	4.6	5.0	1.3	1.7	9.5	no data	2	2	262	330	21	26	38	48.0			

#### Elements by XRF-WDT

CRM ID	<u>K<sub>2</sub>O</u>	<b>Cert</b> K <sub>2</sub> O	<u>CaO</u>	<b>Cert</b> CaO	<u>TiO<sub>2</sub></u>	<b>Cert</b> TiO <sub>2</sub>	<u>MnO</u>	<b>Cert</b> MnO	<u>Fe<sub>2</sub>O<sub>3</sub></u>	<b>Cert</b> Fe <sub>2</sub> O <sub>3</sub>	S	<b>Cert</b> S	Cl	<b>Cert</b> Cl	<u>Sc</u>	<b>Cert</b> Sc
<i>GSD-7</i>	3.64	3.54	1.65	1.67	0.707	0.747	0.093	0.089	6.50	6.51	646	190	83	no data	13.7	14.6
<i>GSS-1</i>	2.53	2.59	1.75	1.72	0.766	0.805	0.238	0.227	5.18	5.19	847	310	114	78	10.4	11.2
<i>LKSD-1</i>	1.06	1.10	12.14	10.80	0.448	0.500	0.093	0.100	4.03	4.10	9306	1570	430	no data	6.5	9.0
<i>LKSD-4</i>	0.76	0.80	1.85	1.80	0.299	0.400	0.068	0.100	4.20	4.10	5952	999	215	no data	7.1	7.0
CRM ID	<u>V</u>	<b>Cert</b> V	<u>Cr</u>	<b>Cert</b> Cr	<u>Co</u>	<b>Cert</b> Co	<u>Ni</u>	<b>Cert</b> Ni	<u>Cu</u>	<b>Cert</b> Cu	<u>Zn</u>	<b>Cert</b> Zn	<u>Ga</u>	<b>Cert</b> Ga	<u>Ge</u>	<b>Cert</b> Ge
<i>GSD-7</i>	93.4	96.0	119.3	122.0	20.6	21.0	55.6	53.0	36.1	38.0	246.2	238.0	16.7	17.7	0.9	1.4
<i>GSS-1</i>	80.7	86.0	60.0	62.0	13.9	14.2	20.7	20.4	19.7	21.0	671.6	680.0	17.6	19.3	0.6	1.3
<i>LKSD-1</i>	47.8	50.0	27.0	31.0	11.0	11.0	16.0	16.0	40.6	44.0	322.4	331.0	9.0	no data	0.1	no data
<i>LKSD-4</i>	45.5	49.0	30.1	33.0	11.7	11.0	34.1	31.0	30.1	31.0	194.3	194.0	7.9	no data	0.5	no data
CRM ID	<u>As</u>	<b>Cert</b> As	<u>Se</u>	<b>Cert</b> Se	<u>Br</u>	<b>Cert</b> Br	<u>Rb</u>	<b>Cert</b> Rb	<u>Sr</u>	<b>Cert</b> Sr	<u>Y</u>	<b>Cert</b> Y	<u>Zr</u>	<b>Cert</b> Zr	<u>Nb</u>	<b>Cert</b> Nb
<i>GSD-7</i>	83.7	84.0	0.2	0.3	0.6	no data	146.4	147.0	222.4	220.0	24.9	24.0	156.9	162.0	15.1	17.0
<i>GSS-1</i>	35.8	33.5	0.1	0.1	2.5	2.9	137.9	140.0	156.6	155.0	24.9	25.0	250.1	245.0	14.7	16.6
<i>LKSD-1</i>	34.9	40.0	1.0	no data	10.3	11.0	22.7	24.0	259.4	250.0	20.9	19.0	132.8	134.0	4.0	7.0
<i>LKSD-4</i>	16.6	16.0	2.3	no data	50.6	49.0	25.0	28.0	121.0	110.0	22.2	23.0	101.3	105.0	4.3	9.0
CRM ID	<u>Mo</u>	<b>Cert</b> Mo	<u>Nd</u>	<b>Cert</b> Nd	<u>Sm</u>	<b>Cert</b> Sm	<u>Yb</u>	<b>Cert</b> Yb	<u>Hf</u>	<b>Cert</b> Hf	<u>Ta</u>	<b>Cert</b> Ta	<u>W</u>	<b>Cert</b> W	<u>Hg</u>	<b>Cert</b> Hg
<i>GSD-7</i>	1.3	1.4	34.1	37.0	4.4	6.1	2.2	2.6	5.0	4.9	0.8	1.4	6.5	5.5	-0.3	0.1
<i>GSS-1</i>	1.1	1.4	26.3	28.0	3.9	5.2	2.1	2.7	7.7	6.8	0.5	1.4	4.6	3.1	-0.8	0.0
<i>LKSD-1</i>	9.4	10.0	19.4	16.0	2.9	4.0	1.7	2.0	4.1	3.6	-0.2	0.3	1.7	<4	-0.6	0.0
<i>LKSD-4</i>	1.3	<5	27.1	25.0	4.3	5.0	2.1	2.0	3.1	2.8	-0.1	0.4	1.8	<4	-0.5	no data
CRM ID	<u>Tl</u>	<b>Cert</b> Tl	<u>Pb</u>	<b>Cert</b> Pb	<u>Bi</u>	<b>Cert</b> Bi	<u>Th</u>	<b>Cert</b> Th	<u>U</u>	<b>Cert</b> U						
<i>GSD-7</i>	0.7	0.9	361.1	350.0	0.6	0.7	12.6	12.6	3.4	3.5						
<i>GSS-1</i>	0.7	1.0	98.2	98.0	0.7	1.2	11.4	11.6	3.7	3.3						
<i>LKSD-1</i>	0.1	no data	83.7	82.0	0.6	no data	2.1	2.2	9.7	9.7						
<i>LKSD-4</i>	0.8	no data	97.3	91.0	0.0	no data	5.1	5.1	31.4	31						

### Elements by XRF-WDM

CRM ID	<u>Na<sub>2</sub>O</u>	<b>Cert</b> Na <sub>2</sub> O	<u>MgO</u>	<b>Cert</b> MgO	<u>Al<sub>2</sub>O<sub>3</sub></u>	<b>Cert</b> Al <sub>2</sub> O <sub>3</sub>	<u>SiO<sub>2</sub></u>	<b>Cert</b> SiO <sub>2</sub>	<u>P<sub>2</sub>O<sub>5</sub></u>	<b>Cert</b> P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	<b>Cert</b> SO <sub>3</sub>
<i>GSD-7</i>	1.2	1.2	4.3	3.1	14.6	13.4	67.3	64.7	0.21	0.19	not detected	no data
<i>GSS-1</i>	1.4	1.7	2.1	1.8	14.1	14.2	57.4	62.6	0.18	0.17	0.1	0.08
<i>LKSD-1</i>	1.6	2.0	1.8	1.7	5.6	7.8	31.5	40.1	0.16	0.20	2.6	no data
<i>LKSD-4</i>	0.5	0.7	1.0	0.9	5.2	5.9	45.2	41.6	0.36	0.30	2.1	no data



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