Part 2A, Environmental Protection Act 1990
Technical Guidance Sheet (TGS) on normal levels of contaminants in English soils

Supplementary Information

MERCURY (Hg)

Technical Guidance Sheet Supplementary Information TGS07s, July 2012.

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Acknowledgments

When referring to this document the following bibliographic reference should be made:

Defra, 2012. Technical Guidance Sheet on normal levels of contaminants in English soils: Mercury – supplementary information. Technical Guidance Sheet No. TGS07s, July 2012. Department for Environment Food and Rural Affairs (Defra), Soils R&D Project SP1008. Available on-line from Defra project SP1008 web page.

The mercury Technical Guidance Sheet which this document supplements:

Defra, 2012. Technical Guidance Sheet on normal levels of contaminants in English soils: Mercury. Technical Guidance Sheet No. TGS07, July 2012. Department for Environment Food and Rural Affairs (Defra), Soils R&D Project SP1008. Available on-line from Defra project SP1008 web page.

Supplementary Information

Important soil sample and analytical information

Relative to other inorganic contaminants, there is a paucity of data for Hg in the topsoils of England. This is because the analytical method used to determine total inorganic element concentration for systematic soil surveys (X-ray fluorescence spectrometry, XRFS) is not suitable to determine the low levels of Hg found in most soils. Sample preparation also requires precautions that prevent volatile Hg being lost at high temperatures. The results used for Hg domain attribution are discussed by Ander *et al*. (2012) and summarised in Table 1. There is an inherent problem in that, other than the Soil Herbage Survey rural data, surveys have targeted specific geographical areas and/or land uses. It is therefore very difficult to establish the extent to which systematic bias arising from sample collection, preparation, digestion and analytical methods contribute to the apparent difference between these data sources. Although Hg was determined on both phases of NSI original samples, the method had a relatively high detection limit (0.1 mg/kg), with over 50% of the data falling below that detection limit, and the remainder of the data being reported to only one significant figure; these data were thus not used.

Data source	Sample depth, support and preparation	Digestion step	Instrument and Laboratory	Detection limit (mg/kg)
Countryside Survey 1998	15 cm deep (× 8 cm diameter) core. Single core. Drying temperature/ sieving not recorded.	not specified.	not specified.	not specified.
Countryside Survey 2007	15 cm deep. 15 cm deep (× 8 cm diameter) core. Single core. Air dried. Sieving not recorded.	*Aqua-regia* microwave digestion.	ICP-MS. Laboratory not specified.	0.067
UK Soil and Herbage Pollutant Survey	5 cm deep. 3 cores per sample, support not specified but 3 samples collected within a 20×20 m square. Stored 4°C. Not specified whether sieved/dried.	*Aqua-regia*.	Cold-vapour atomic absorption spectrometry (CV-AAS). EA Laboratory.	0.07
FOREGS	0-25 cm. 3-5 sample composite. Dried at 40°C, sieved <2 mm.	n/a. Heated to 850°C to drive off Hg.	Hg analyser. Hungarian Geological Survey laboratory.	0.0001
G-BASE London	15 cm deep. 5 augers in 20×20 m area. 30°C dried. <2 mm sieved and ground in agate.	n/a. Heated to 850°C to drive off Hg.	Hg analyser. Hungarian Geological Survey laboratory.	0.0001
G-BASE Stoke	15cm deep. 9 composite on 2×2m grid. Air dried. <2 mm sieved and ground in agate.	*Aqua-regia*.	CV-AAS. Bondar Clegg Laboratory, Canada.	0.01
GEMAS	0-20 cm on arable; 0-10 cm permanent pasture. Five spade-dug pits in 10 × 10 m, ~3.5kg sample collected. Air-dried and <2 mm sieved.	n/a. Heated to 850°C to drive off Hg.	Hg analyser. Hungarian Geological Survey laboratory.	0.0001
Tipping 2011	Generally 10 cm; range 9-19 cm. Single pit dug and sampled. Air-dry. <2 mm sieved.	*Aqua-regia*, microwave digestion.	ICP-MS	0.07

Table 1: Summary of data sets used to establish Hg NBCs during the exploratory data analysis (after Ander *et al*. (2012))
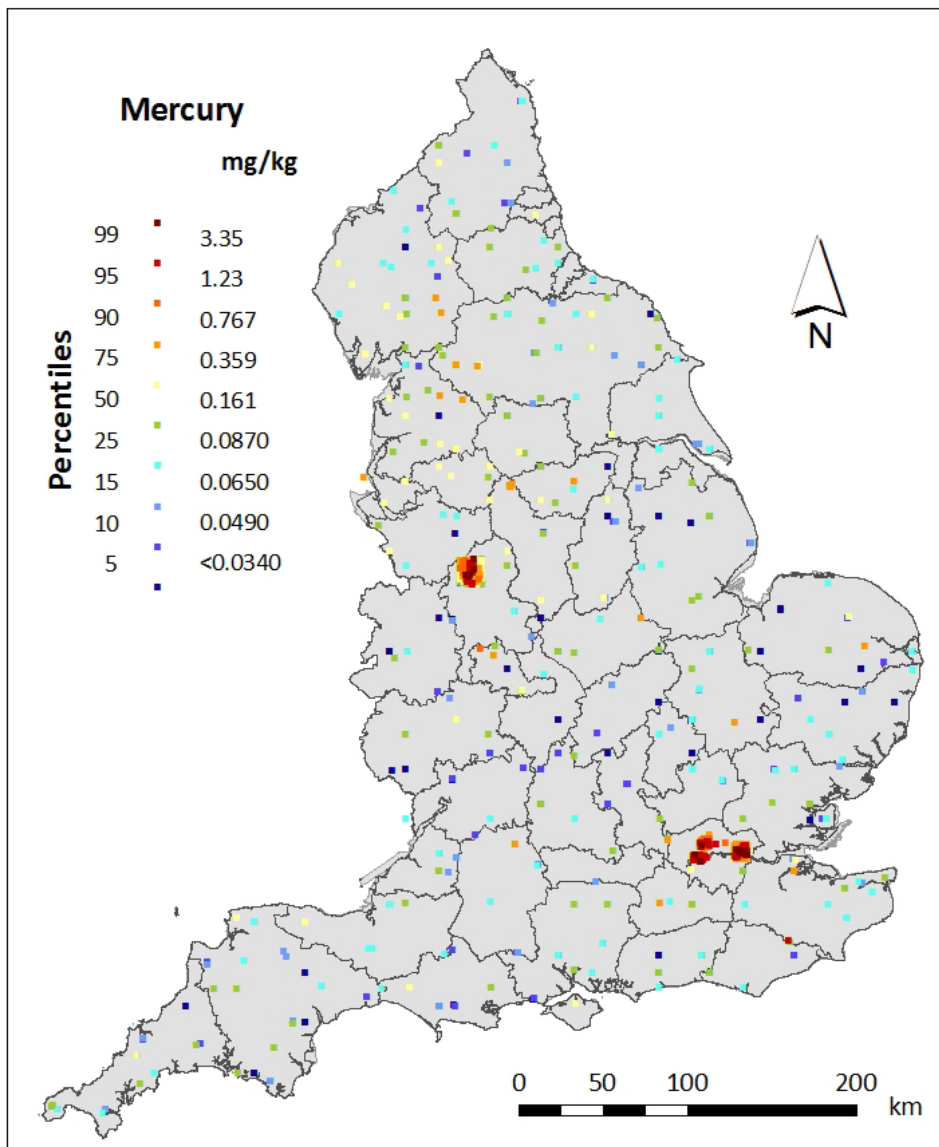
Figure 1: National map of mercury distribution in topsoils with county boundaries. Distribution of samples used in this interpolated map is shown in Figure 1 of the Hg technical guidance sheet.

Figure 1 demonstrates the variability in Hg at a national scale and is also available for on-line viewing on the BGS Project web page. The map has been generated from data for Hg in soils from England. The percentile classification is based on **all data** and differs from the domain data sets in which results are modelled to fit a normal distribution and outliers (representing point rather than diffuse pollution) are appropriately dealt with.

The most detailed systematic surveys for Hg in soils are those done in the Stoke-on-Trent and London areas (737 and 440 samples, respectively. The Stoke-on-Trent baseline geochemical mapping is reported by Fordyce and Ander (2003). The interpretation of the London Hg data is currently in progress.

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Descriptive statistics for mercury in topsoil data

Mercury Domain percentile classifications

Percentile	Urban Domain (512)			Principal Domain (1,126)		
	lower	middle	upper	lower	middle	upper
50	0.31	0.34	0.37	0.11	0.12	0.12
55	0.35	0.38	0.41	0.12	0.13	0.14
60	0.39	0.43	0.47	0.14	0.14	0.15
65	0.45	0.49	0.54	0.15	0.16	0.17
70	0.51	0.56	0.62	0.17	0.18	0.19
75	0.59	0.65	0.72	0.19	0.20	0.22
80	0.69	0.77	0.85	0.22	0.23	0.25
85	0.83	0.93	1.0	0.25	0.27	0.29
90	1.1	1.2	1.3	0.30	0.33	0.36
95	1.5	1.7	**1.9**	0.40	0.45	**0.50**

Figure in brackets represents the number of samples used in the domain calculation

Table 2: A summary of the mercury domain percentile classifications. Domain NBCs shown in bold red (concentrations in mg/kg, shown to 2 significant figures).

A percentile of a data distribution (in this case the distribution of Hg in soil for a given domain) is the value of a variable below which a certain percentage of observations fall. The 95th percentile, for example, is the value below which 95% of the observations may be found, *i.e.* it encompasses the majority of the data. The contaminant concentrations in the soil for a given domain are a subset of the total population of all possible soil concentrations and therefore any percentile calculation will only be an approximation of the true value. The uncertainty on the percentile increases as the number of samples used to calculate it decreases. Lower and upper limits can be statistically estimated for each percentile giving a confidence interval for that percentile. **The Hg NBC for each domain is defined as the upper 95% confidence limit of the 95th percentile for the Hg topsoil concentrations that fall within that domain** (Cave *et al.* 2012). A summary of domain percentiles with their upper and lower limits is given in Table 2.

Descriptive statistics mercury topsoil data set

Table 3 shows descriptive statistics for all the topsoil Hg results from a variety of data sets. The cities in Table 3(c) (Stoke-on-Trent and London) are those that have been sampled by the G-BASE project. Other data sets for English towns and cities may exist but they are not made publicly available and are not sampled and analysed to a nationally consistent standard.

(a) All data	Number	Mean	Minimum	25th percentile	Median	75th percentile	Maximum	Skewness
	1646	0.402	0.01	0.087	0.161	0.359	30.8	15
(b) Data source	Number	Mean	Minimum	25th percentile	Median	75th percentile	Maximum	Skewness
Countryside Survey 1998	36	0.13	0.03	0.069	0.111	0.192	0.304	0.7
Countryside Survey 2007	175	0.092	0.033	0.034	0.035	0.097	0.703	3
UK Soil and Herbage Pollutant Survey	61	0.108	0.07	0.072	0.089	0.12	0.562	5
UK Soil and Herbage Pollutant Survey	13	0.37	0.117	0.19	0.391	0.52	0.839	0.8
FOREGS	33	0.077	0.0112	0.05	0.067	0.087	0.274	3
G-BASE London	440	0.959	0.045	0.29	0.522	0.90	30.8	9
G-BASE Stoke	737	0.251	0.01	0.101	0.143	0.228	7.22	8
GEMAS	131	0.098	0.021	0.044	0.059	0.081	3.12	11
Tipping 2011	20	0.389	0.207	0.225	0.392	0.522	0.625	0.2

Table 3: Descriptive statistics of underlying primary data sets for Hg in all topsoils (results in mg/kg cited to 3 significant figures). Data sources are described in Ander et al. (2012).
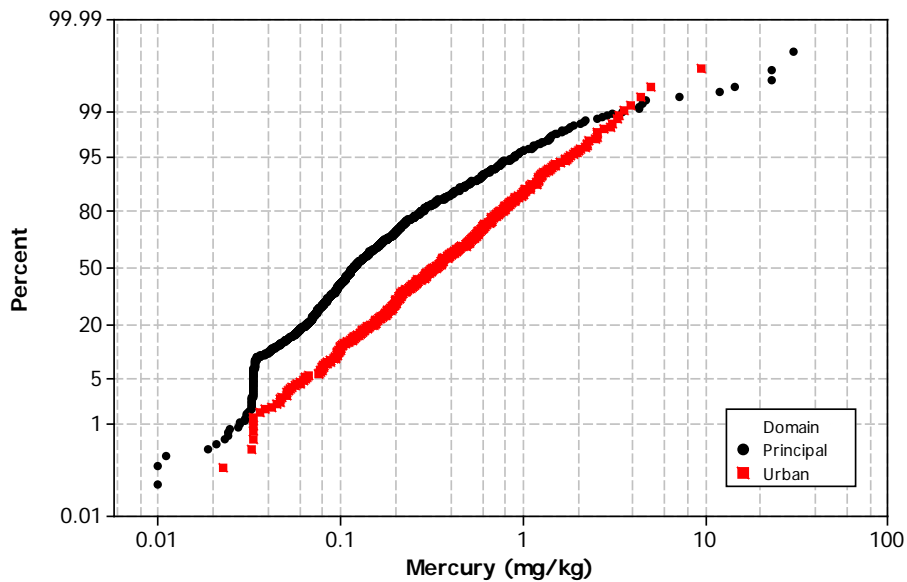
Data distributions

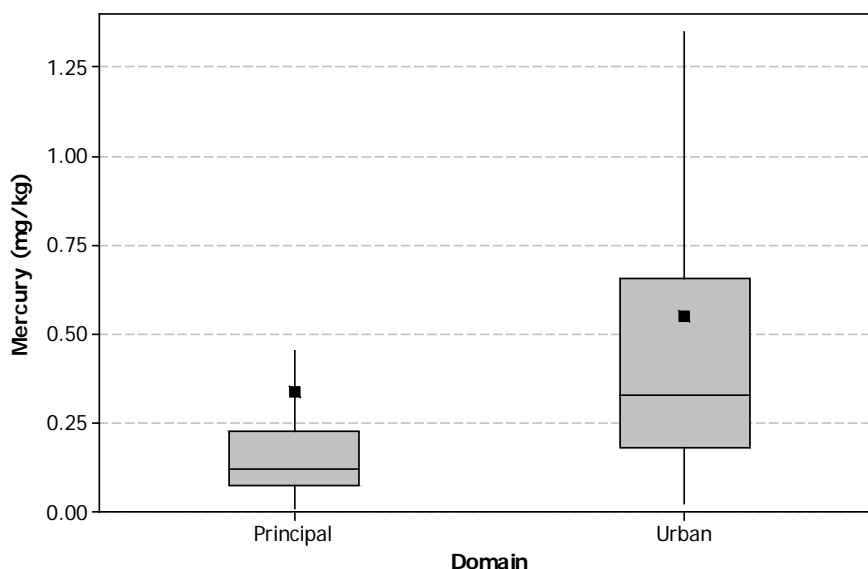Figure 2: Probability plot of topsoil Hg results categorised by domains.

Figure 3: Boxplot of Hg topsoil results attributed to domains.

Figure 2 and Figure 3 show the frequency distribution of results for soils over the two domains defined for Hg using results from a variety of data sets (see Table 3). These plots can be used in conjunction with any new results plotted in a similar way to compare distributions with the defined domains. The box represents the interquartile range (Q1, Q3), with the median (Q2) as a line within the box. The point symbol shows the mean value. The upper whisker = Q3 + 1.5(Q3-Q1); lower whisker = Q1-1.5(Q3-Q1).

Archer and Hodgson (1987) carried out a study of total and extractable trace element contents of agricultural soils (from a depth of 15 cm) in England and Wales, including Hg from selected areas of England. "Total" Hg analyses were done by flameless AAS following a digestion using nitric acids. They defined the normal range for trace element contents as that between twice the log-derived standard deviation above and below the mean; approximately 95% of the data range. For 305 agricultural topsoils they determined a Hg median of 0.09 mg/kg and a "normal" range of 0.02 - 0.04 mg/kg.

Tipping *et al.* (2011) present a comprehensive review of Hg in UK topsoils. In this, using some of the data sets used here, they report a median of 0.05 mg/kg and 95% value of 0.36 mg/kg for UK rural soils (898 samples).

Landscape data used to define contaminant domains

Rather than seeking to define a single Hg NBC for the whole of England, the project has, through its data exploration (Ander *et al.* 2012), determined the most significant domains that can be defined in order to capture the most significant controls on Hg distribution in soils. For Hg this has been identified as soils in urban areas. Spatial distributions were investigated in relation to some key landscape data sets within a GIS environment. Namely: the BGS Soil-Parent Material Model (SPMM) (Lawley, 2009) and a revised and digitally updated version of the Ove Arup (1990) Department of the Environment (DoE) Metalliferous Mining and Mineralisation data set.

Soil parent material

The Soil-Parent Material Model[1] (SPMM) has been developed by BGS, using as its basis the mapped boundaries of the national 1:50,000 superficial and bedrock geological data (DigMapGB-50[2]), and is used within a GIS environment. Soil 'Parent Material' is the first recognisably geological material found beneath a soil profile, and is the lithology on which that soil has developed. Soils thus inherit many properties, including chemical composition, from this material.

In the SPMM the geological data have been combined into one layer of information which indicates the rock/sediment formation mapped as directly underlying soil. Where this is a superficial deposit (such as alluvium, glacial deposits, peat), the data set also maintains the record of the solid geological formation first encountered beneath this surface sediment; such information is of benefit where the underlying solid geology imparts chemical (or other) characteristics into the overlying superficial deposits, and thus the soil. The information, which has historically routinely been attributed to the mapped digital polygons in DigMapGB, largely comprises lithological and chronological information. Augmenting this in the SPMM is additional information on texture, mineralogy and lithology, which is attributed in a hierarchical classification system. In the context of the present study this means that a higher level of aggregated characteristics can easily be applied to soil geochemical data than is possible solely using DigMapGB; for instance, retrieving all formations which are classed as 'ironstones' (irrespective of their formal name) and confers benefits from using the SPMM.

The scale of mapping for the soil parent material is also relevant – 1:50,000 is the scale at which much of the systematic soil sampling has been undertaken, and gives the user a reasonable feel for the degree of uncertainty on the data. Where geographical information is provided at other common scales, such as 1:250,000 or 1:625,000, the boundaries and number of polygons are simplified and aggregated in order to provide generalised information at the national-scale. More detailed mapping, such as 1:10,000, is not available in a consistent format or as part of the SPMM data, and would imply greater certainty in sample locations and polygon boundaries than is appropriate from the data. Soil mapping is available at a national-scale (see *e.g.* NSRI NATMAP[3]) but this is not systematically mapped at 1:50,000 and would require attribution with the latest geological mapping data in order to retrieve information on key formations, and so has not been used in this study.

There was no significant spatial correlation identified with any of the soil-parent material model data as has been identified for some other contaminants.

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[1] http://www.bgs.ac.uk/products/onshore/soilPMM.html
[2] http://www.bgs.ac.uk/products/digitalmaps/digmapgb_50.html
[3] http://www.landis.org.uk/data/natmap.cfm

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Metalliferous mining and mineralisation

The data set which has been examined in this project is that of non-ferrous Metalliferous Mineralisation and Mining database, originally produced in hard-copy by Ove Arup (1990) for DoE (Department of Environment), but which has been 'cleaned' and turned into a polygon layer by BGS. The data for England has been further attributed for this project by giving a name to the major ore fields allowing soil sample sites and geochemical data to be joined to the ore fields and separately analysed for typical soil concentrations. This mapping is generalised to 0.5 km grid squares, which is a suitable level of spatial resolution for this type of data. Therefore, it should be expected that not every occurrence of mineralisation/mining has been captured within this GIS layer. Where soil chemical data is encountered that is located outside a given mineralisation domain, but of a concentration expected for that contaminant within the local mineralisation domain, and lies over the parent material which is known to be affected by mineralisation in that ore field, then that high soil concentration could relate to either natural processes, or historical mining.

There was no significant spatial correlation identified with any of the metalliferous mining and mineralisation data as has been identified for some other contaminants, though there is insufficient Hg results available from soils systematically collected over non-ferrous metalliferous mineralisation to satisfactorily investigate any spatial correlations.

Definition of urban areas

The definition of normal levels of contaminant concentrations in soils includes the contribution from diffuse pollution. As much diffuse pollution is associated with built-up regions, defining areas of urbanisation to create an urban domain is important in the attribution of NBCs. The definitive database for land use in England is the Ordnance survey MasterMap® (Ordnance Survey, 2011), however, this is a licensed product with a great amount of detail. The CEH Land Cover Map (LCM2000[4], and more recent version) are digital data sets that provide substantial land use information at a high resolution, again a product requiring a licence to use it. However, the ready availability and quantitative outputs of the Generalised Land Use Database (GLUD) Statistics for England 2005 (Office for National Statistics, 2011) make this particularly suitable for implementing a measure of urbanisation. Using the land use data from the 8850 Census Area Statistical Wards (CASW) and urbanisation index can be determined as described in Ander *et al*. (2011). This index can be used to define the map used to define urban domains (Figure 4). The urban classification map of England is available as a GIS layer from the BGS Project web page.

In our exploration of spatial correlations it was the correlation of high Hg with urban areas that identified the only significant domain.

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[4] http://www.ceh.ac.uk/LandCoverMap2000.html
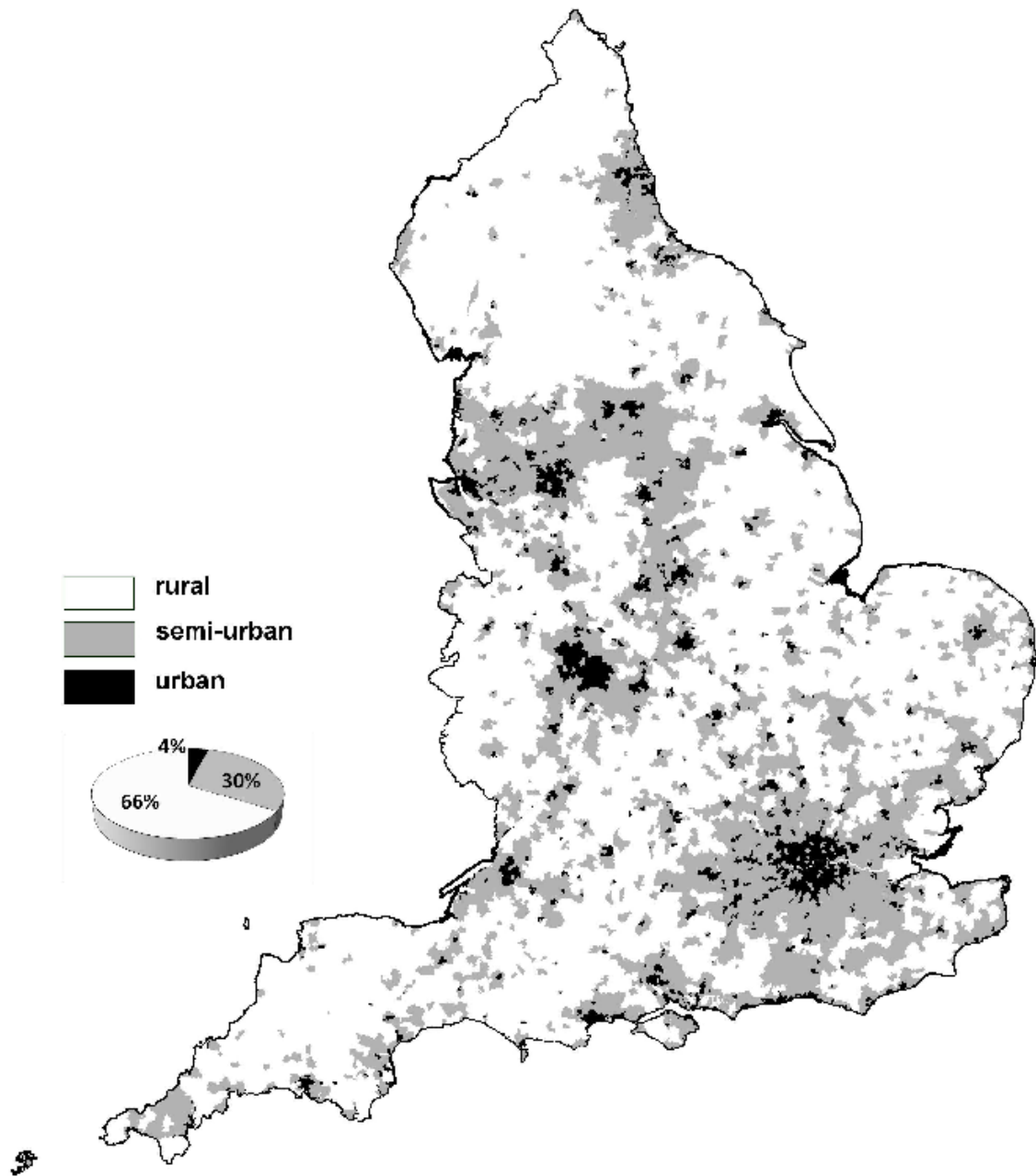
Adapted from data from the Office for National Statistics licenced under Open Government Licence v.1.0.

Figure 4: A map of England showing urban, semi-urban and rural areas of England defined from an urbanisation index using the GLUD database

Supplementary Information

Summary of statistical procedure to determine NBCs

Figure 5: Flow chart for the calculation of the NBC for a given contaminant domain (OS and SC are octile skew and skewness coefficient, respectively. MAD = median absolute deviation). See text for explanation, continued overleaf.

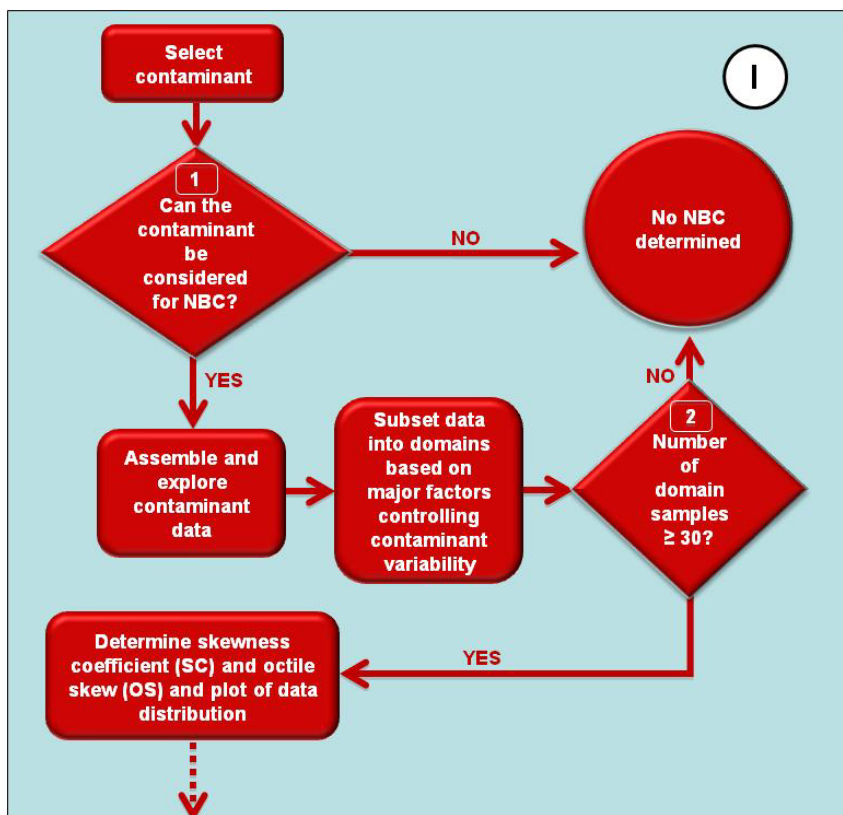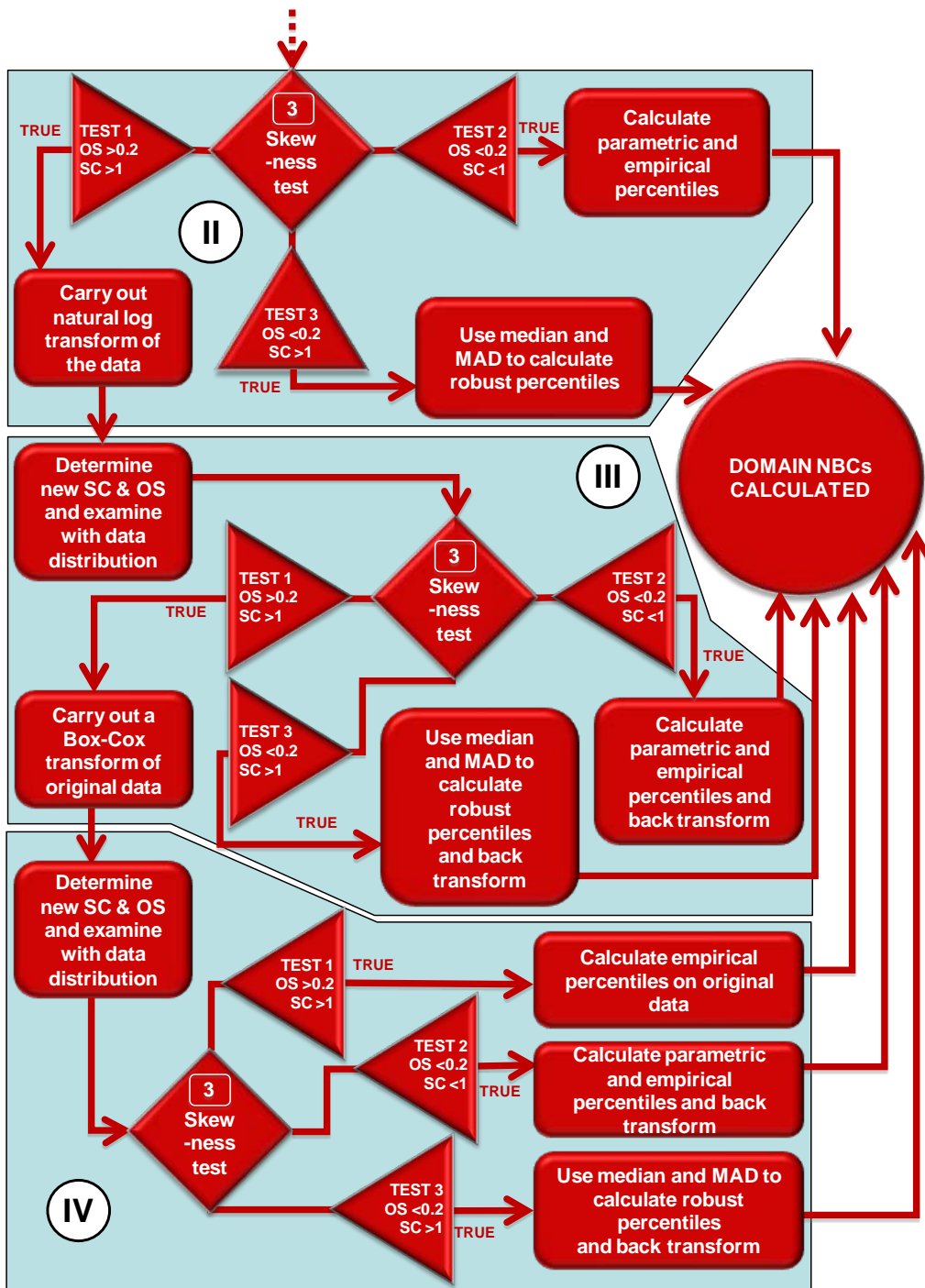Figure 5 continued. Flow chart for the calculation of the NBC for a given contaminant domain (OS and SC are octile skew and skewness coefficient, respectively. MAD = median absolute deviation). See text for explanation.

Figure 5 summarises the statistical procedure used to determine contaminant NBCs (see Cave *et al.* 2012). Part I essentially represents the data gathering and exploration phase of the project (WP1&2) in which domain areas are identified. Question 1 asks if the contaminant is suitable for a NBC. Asbestos and manufactured organic contaminants with no natural origin, for example, fail this question. The data exploration (Ander *et al.*, 2012) identifies the areas (domains) where there are clearly identifiable controls on high concentrations of a specified contaminant. The contaminant data set is then subdivided into domain data sets. In Question 2 (Figure 5), a minimum of 30 results are considered necessary to determine a NBC (see Cave *et al.*, 2012).

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Once the data has been subsetted into domains, then skewness testing and inspection of frequency distribution plots can be done to select the appropriate data transform and method of calculating percentiles (Parts II – IV). Question 3, the skewness test, has three possible outcomes. TEST 1 (OS > 0.2 and SC >1) is true if the data distribution is skewed and not suitable for fitting to a Gaussian model and the data need to be transformed to using either a logarithmic or Box-Cox transform. If TEST 2 (OS < 0.2 and SC <1) is true then the data are consistent with the assumption of a Gaussian distribution and the parametric percentiles are fitted based on the mean and standard deviation of the data. Finally, TEST 3 (OS < 0.2 and SC >1) means the data show a mostly symmetrical distribution but with potential outliers. Here the data are consistent with the assumption of a Gaussian distribution and the parametric percentiles are fitted using median and the median absolute deviation (MAD) in place of the mean and standard deviation as these measures are robust to outliers.

Access to data and information resources used to calculate NBCs

Project Reports and information

These resources are available from the BGS project web page [5] and include:

Data Exploration Reports (BGS report No. CR/11/145 and CR/012/041); Methodology Report (BGS report No. CR/12/003); Final Project Report (BGS report No. CR/12/035); Technical Guidance Sheets and supplementary information; MS Access Database summary of available data; Project Bibliography (Endnote bibliography); R code scripts used to determine NBCs; and GIS Resources served as WMS files (Domain polygons; the urbanisation index polygons defined from GLUD database; and the national contaminant interpolated image maps).

Web map services (WMS) are an industry standard protocol for serving georeferenced images across the web. They were developed and first published by the Open Geospatial Consortium (OGC) in 2000. Since this date WMS have had a steady uptake and are being increasingly used in traditional desktop based GIS, web-based GIS systems (including Google Earth), and the latest Smartphone 'apps'. BGS holds the data on their servers and publish it openly via the BGS project web page.

Principal contaminant data sets for England

Intellectual Property Rights for the raw soil data sets resides with the organisations responsible for those data sets. In the case of the G-BASE and NSI (XRFS) data is made freely available subject to certain licensing terms and conditions. For large data sets there will also be a data handling fee. Enquiries should be sent to enquiries@bgs.ac.uk .

Other data sets providing information on soil chemistry are summarised in Appendix 2 of Ander *et al.* (2011) and this includes contact and links to web sites.

Soil parent material

The BGS Soil-Parent Material Model is described on a BGS web page (SPPM) and this contains information regarding further information and pricing.

Land use data including metalliferous mining and mineralisation

The Generalised Land Use Database (GLUD) Statistics for England 2005 is available for free from the Communities and Local Government website. Users interested in the detailed maps at land parcel level who hold the appropriate public sector licence to use OS MasterMap® can request to see the GLUD data at this large scale level (gis@communities.gsi.gov.uk).

The Ove Arup Mineralisation and mines data updated and modified by BGS is available from BGS subject to terms and conditions (see the BGS project web page).

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[5] http://www.bgs.ac.uk/gbase/NBCDefraProject.html

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Supplementary Information

Further Reading

The following is a list of bibliographic references that provide more detailed information regarding the distribution and behaviour of mercury in the surface environment. Some of these references are referred to in this supplementary information section.

Ander, E.L., Cave, M.R., Johnson, C.C. and Palumbo-Roe, B. 2011. Normal background concentrations of contaminants in the soils of England. Available data and data exploration. *British Geological Survey Commissioned Report*, CR/11/145. 124pp.

Ander, E.L., Cave, M.R., Johnson, C.C. and Palumbo-Roe, B. 2012. Normal background concentrations of contaminants in the soils of England. Results of the data exploration for Cu, Ni, Cd and Hg. *British Geological Survey Commissioned Report*, CR/12/041. 88pp.

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Fordyce, F.M. and Ander, E.L. 2003. *Urban soils geochemistry and GIS-aided interpretation : a case study from Stoke-on-Trent.* Nottingham, UK, British Geological Survey, 183pp. (IR/01/035) (Unpublished). Available online: http://nora.nerc.ac.uk/7018/1/IR01035.pdf last access 10th June 2012.

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Ordnance Survey, 2011. OS MasterMap Topography Layer. OS MasterMap® Topography Layer. http://www.ordnancesurvey.co.uk/oswebsite/products/os-mastermap/index.html last accessed 29th March 2012.

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Yin, Y., Allen, H.E., Li, Y, Huang, C.P. and Sanders, P.F. 1996. Adsorption of mercury (II) by soil: effects of pH, chloride, and organic matter. *Journal of Environmental Quality*, 25, 837-844.