BENZO[*a*]PRYRENE (BaP)

Technical Guidance Sheet Supplementary Information TGS04s, July 2012.

Contents

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Acknowledgments

This supplementary information for the benzo[*a*]pyrene Technical Guidance Sheet (TGS) is compiled with information derived mainly from the reports prepared for the Department for Environment Food and Rural Affairs (Defra) soil R&D project SP1008 by the British Geological Survey. This work has been led by Chris Johnson with assistance from Louise Ander, Mark Cave and Barbara Palumbo-Roe (all BGS, Keyworth) with additional contributions and comments from Murray Lark, Barry Rawlins, Don Appleton and Chris Vane (BGS Keyworth); Stephen Lofts (CEH Lancaster); and Paul Nathanial Land Quality Management Group, Nottingham. The authors also thank the Defra Soils Policy Team, the Project Steering Group and several Local Authority contaminated land officers who have given valuable advice to improve the content of this information sheet.

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: Benzo[*a*]pyrene – supplementary information. Technical Guidance Sheet No. TGS04s, 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 BaP Technical Guidance Sheet which this document supplements:

Defra, 2012. Technical Guidance Sheet on normal levels of contaminants in English soils: Benzo[*a*]pyrene. Technical Guidance Sheet No. TGS04, 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

There is a paucity of BaP data for English soils as this is not routinely measured by the large systematic national surveys which have focussed on inorganic elements. Therefore, all available BaP has to be considered for domain attribution and the criteria used to define data sets suitable for use in this work (see Ander *et al.* 2011) are less rigidly applied. This has meant that it is necessary to combine data from several studies with inherently different sampling and analytical protocols – these are summarised in Table 1. It should also be noted that these data have been collected over a period of time, during which considerable advances in sampling, sample preservation and analytical methodologies have also been achieved. No additional English studies in which sampling locations and information other than central tendency (mean, median) or range are identified (Ander *et al.* 2011), and so the low sample numbers for England has meant data from Scotland and Wales has been included, particularly to generate a NBC for urban areas in England (see Figure 2 of the BaP TGS).

Study	Depth (cm)	Composite (support) and preparation	Analytical method	Analytical instrument	n
UKSHS	0-5	3 cores per sample, support not specified but 3 samples collected within a 20×20m square. Stored 4°C. Not specified whether sieved/dried.	50:50 acetone:dichloromethane (DCM) extraction. ^{2}H labelled PAH addition.	Two stage clean up. HRGC-LRMS (high resolution gas chromatography – low-resolution mass spectrometry).	225
CS Heywood et al (2006)	0-8	5 cores 20 m apart, but not bulked and not all analysed. Stored at -20°C.	^{13}C labelled PAH addition. DCM microwave extraction.	Two-cleanup stages. HPLC separation of fractions. GCMS analysis.	201
Jones *et al* (1989a)	0-5	20 cores (area not given). Air-dried. Sieved to <2 mm.	DCM extraction. Full method given; Certified reference materials (CRMs) reported.	High-performance liquid chromatography (HPLC)	49
Cousins *et al* (1997)	0-2.5 – 0-25 (to match previous studies)	Support not reported. Stored -17°C, clasts and vegetation removed by hand (not sieved) and analysed wet.	Sodium sulphate added to enhance extraction. Hot DCM extraction. Full method given. Quality control reported.	HPLC	45

Table 1: Summary of sampling and analytical strategies for BaP data sets explored in this study.

Scale and use of Normal Background Concentrations

There are limitations in the reporting of site locations (easting and northing) for the Countryside Survey (CS) and UK Soil and Herbage Survey (UKSHS) datasets with locations being degraded to ±10 km. Those from the papers of Jones *et al* 1989(a,b) and Cousins *et al* (1997) are substantially better, at ±100 m. Interpolation of data is deemed inappropriate due to the relatively low sample numbers and the low numbers of samples from urban areas in England. These data should then be used either in conjunction with site specific properties reported by the original projects, or at a low-resolution national scale such as presented here (Figure 1). Further information is provided in Ander *et al (*2011).

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National map showing the distribution of BaP in topsoils

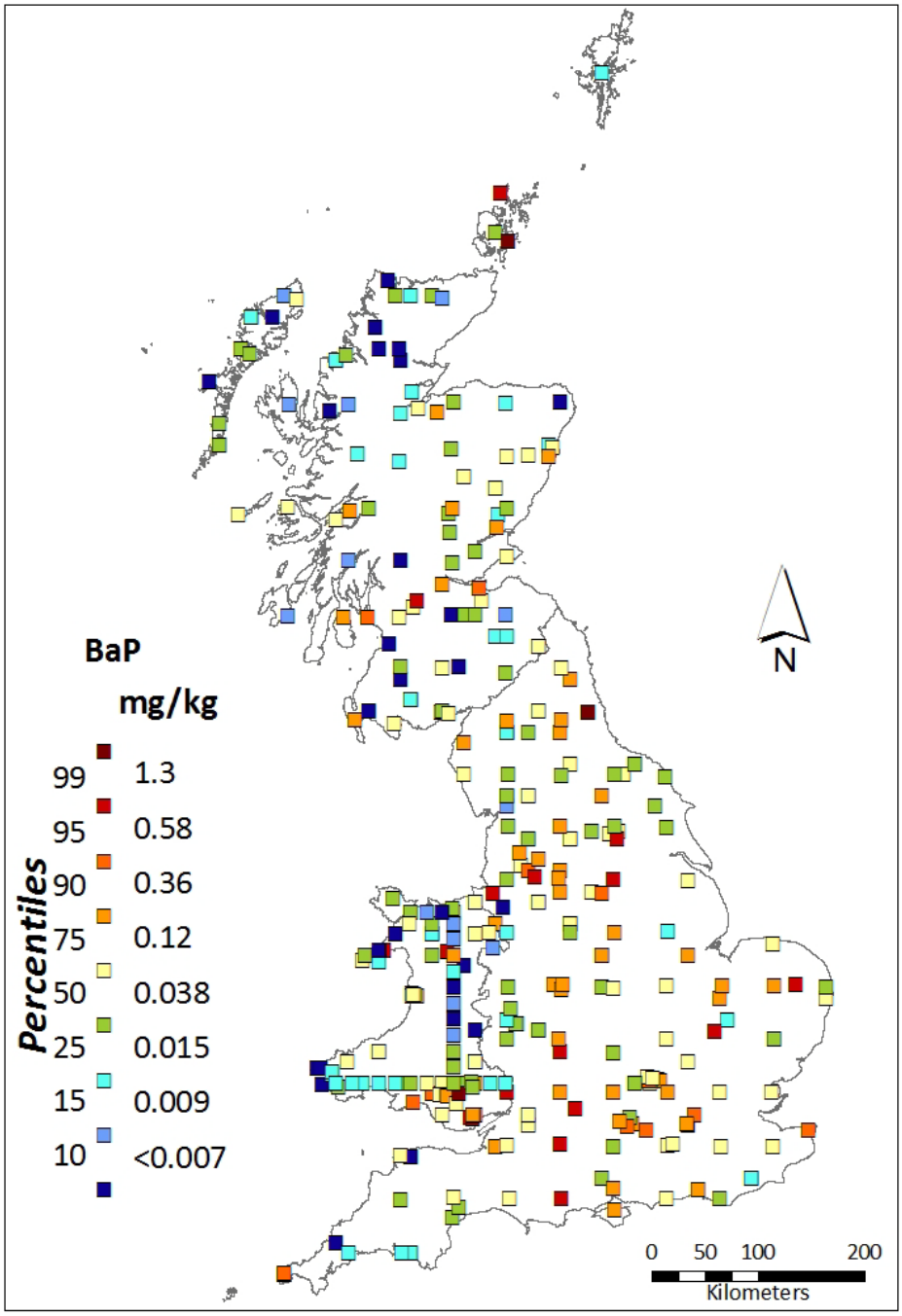

Figure 1: National map of BaP distribution in topsoils (see Figure 2 of the BaP TGS for source of data).

The map of BaP distribution in topsoils is shown in (Figure 1). This map demonstrates the variability in BaP at a national scale and is also available to view on-line at the BGS project web page.. The map has been generated from available systematic and compatible data for BaP in soils from England, Wales and Scotland. 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.

Descriptive statistics for benzo[*a*]pyrene in topsoil

Benzo[*a*]pyrene Domain percentile classifications

Benzo[*a*]pyrene data for soils has been gathered from data sets as described in the BaP TGS and classified according to the most important domains as detailed by Ander *et al.* (2011). A percentile of a data distribution (in this case the distribution of BaP 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 BaP NBC for each domain is defined as the upper 95% confidence limit of the 95th percentile for the BaP topsoil concentrations that fall within that domain.** A summary of domain percentiles with their upper and lower limits is given in Table 2.

Percentile	Urban Domain (32)			Principal Domain (71)		
	lower	middle	upper	lower	middle	upper
50	0.18	0.27	0.43	0.031	0.037	0.042
55	0.21	0.32	0.50	0.038	0.044	0.051
60	0.25	0.38	0.58	0.045	0.053	0.061
65	0.29	0.44	0.68	0.054	0.064	0.075
70	0.34	0.53	0.81	0.067	0.078	0.092
75	0.41	0.64	0.99	0.082	0.10	0.11
80	0.50	0.79	1.2	0.10	0.12	0.15
85	0.62	1.0	1.6	0.13	0.16	0.20
90	0.81	1.4	2.2	0.19	0.23	0.29
95	1.2	2.2	**3.6**	0.31	0.39	**0.50**

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

Table 2: A summary of the BaP domain percentile classifications (to two significant figures). Domain NBCs shown in bold red. Concentrations in mg/kg. The NBC calculation is based on samples from England, Scotland and Wales.

Descriptive statistics BaP topsoil data set

Table 3 shows descriptive statistics for all the topsoil BaP based on data from the UK Soil and Herbage Pollutant Survey (Creaser *et al.* 2007); Countryside Survey (Black *et al.* 2002; Emmett *et al.* 2010); UK-wide rural (Cousins *et al.* 1997); and urban/industrial S Wales valleys (Jones *et al.* 1989a). Other data sets for other English cities may exist but they are not made publicly available and are not sampled and analysed to a nationally consistent standard.

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(a) All data	Number	Mean	Minimum	25th percentile	Median	75th percentile	Maximum	Skewness
All data	403	0.14	0.0001	0.015	0.038	0.121	3.7	6.32
(b) Data set type	**Number**	**Mean**	**Minimum**	**25th percentile**	**Median**	**75th percentile**	**Maximum**	**Skewness**
Rural	374	0.105	0	0.0128	0.0334	0.0991	3.14	7
Urban	32	0.536	0.026	0.103	0.356	0.614	3.7	3
(c) Data source	**Number**	**Mean**	**Minimum**	**25th percentile**	**Median**	**75th percentile**	**Maximum**	**Skewness**
Cousins *et al* 1997	45	0.134	0.0001	0.0145	0.04	0.15	1.2	3
CS	176	0.0806	0.0013	0.0136	0.0323	0.0932	1.44	6
EA_UKSHS	133	0.222	0.0023	0.0237	0.0616	0.207	3.14	4
Jones *et al* 1989a	49	0.138	0.003	0.009	0.016	0.0515	3.7	6

Table 3: Descriptive statistics of data for BaP in all topsoils. These are classified by various data set subgroups (concentrations in mg/kg methods shown in Table 1). Results cited to 3 significant figures.

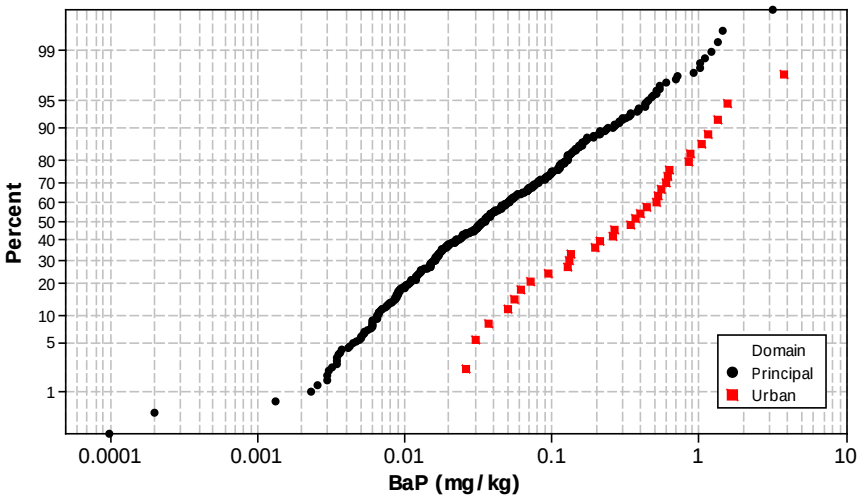

Figure 2: Probability plot of BaP in soil categorised by domains. Soil samples from England, Wales and Scotland are used in this plot (see Table 3 for data summary statistics)

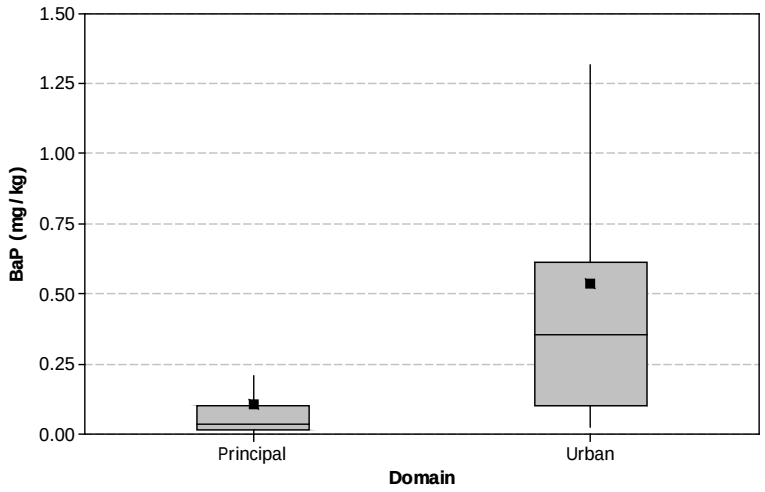

Figure 3: Boxplot of BaP in soil attributed to domains. Soil samples from England, Wales and Scotland are used in this plot (see Table 3 for data summary statistics)

Figure 2 and Figure 3 show the frequency distribution of results for soils over the Urban and Principal Domains defined for BaP using topsoil results from England, Wales and Scotland. 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 of the boxplot 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).

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Landscape data used to define contaminant domains

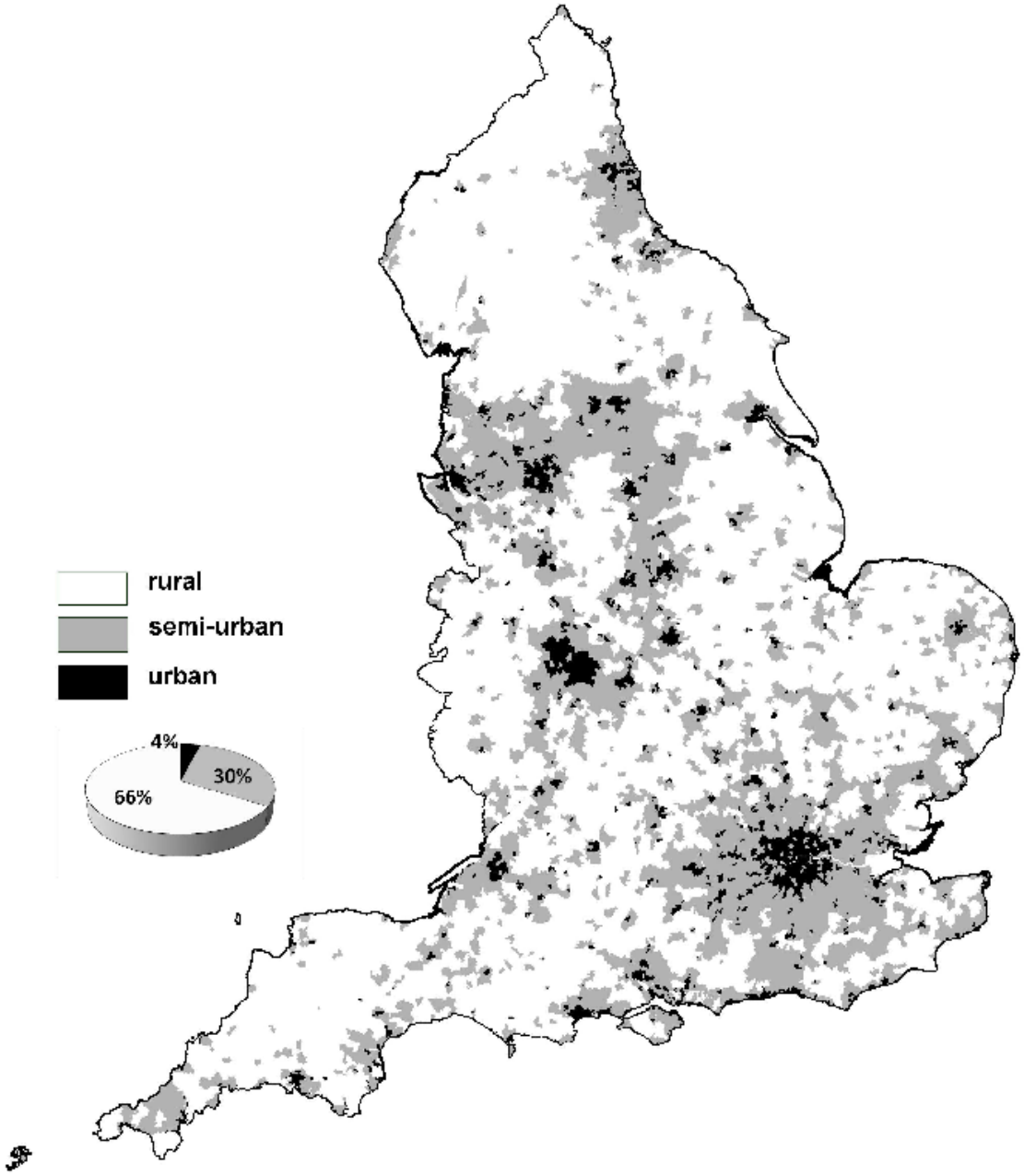
Rather than seeking to define a single BaP NBC for the whole of England, the project has, through its data exploration (Ander *et al.* 2011), determined the most significant domains that can be defined in order to capture the most significant controls on BaP distribution in soils. For BaP urbanisation is identified as the most important controlling factor. The principal data set used for defining urban areas has been the Generalised Land Use Database (GLUD) Statistics for England 2005 (Communities and Local Government 2007). Other key data sets used for other contaminants, 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 were not utilised for this contaminant.

Generalised Land Use Database (GLUD) Statistics for England 2005

The definition of normal levels of contaminant concentrations in soils includes the contribution from diffuse pollution. In the case of BaP this is the major contribution. BaP diffuse pollution will be associated with built-up regions, so defining areas of urbanisation to create an urban domain is most important in the attribution of a NBC to BaP. 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[1], 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. The ready availability and quantitative outputs of the Generalised Land Use Database (GLUD) Statistics for England 2005 (Communities and Local Government 2007[2]) make this particularly suitable for implementing a measure of urbanisation. Using the land use data from the 8850 Census Area Statistical Wards (CASW) an urbanisation index can be determined as described in Ander *et al.* (2011). This index can be 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.

The GLUD data is only available for England, so for the samples from Wales and Scotland a classification of the data as urban or rural is based on the authors' descriptions of the sampling sites.

[1] http://www.ceh.ac.uk/LandCoverMap2000.html
[2] http://www.communities.gov.uk/publications/planningandbuilding/generalisedlanduse



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

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Summary of statistical procedure to determine NBCs

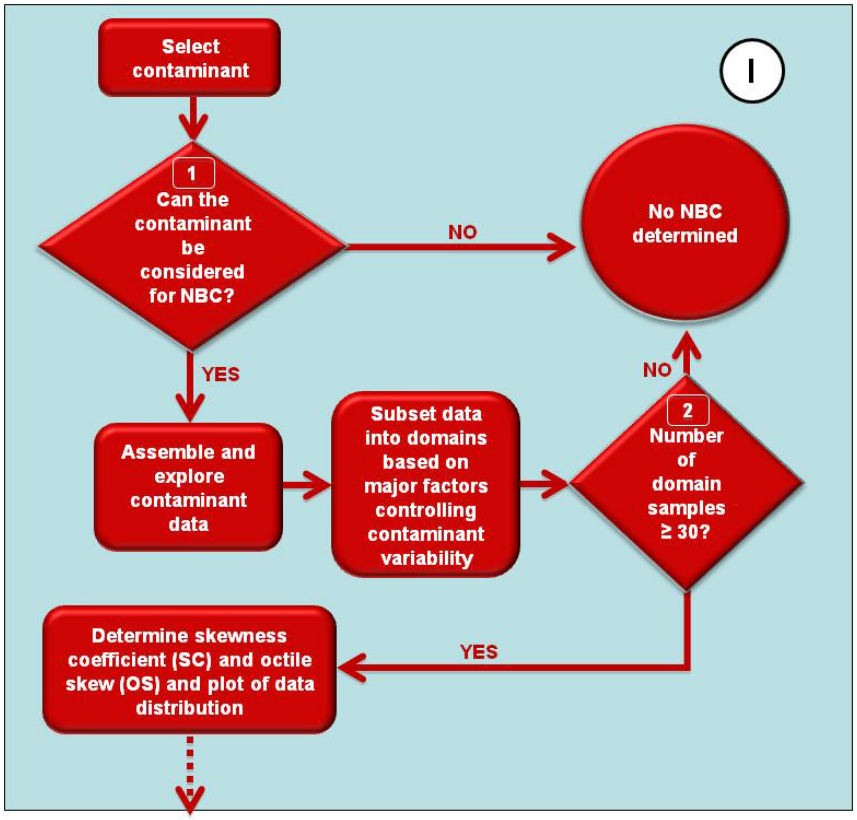

Figure 5: Flow chart for the calculation of the NBC for a given contaminant domain (OS and SC are octile skew and skewness coefficient, respectively. MAD = median absolute deviation). See text for explanation, continued overleaf.

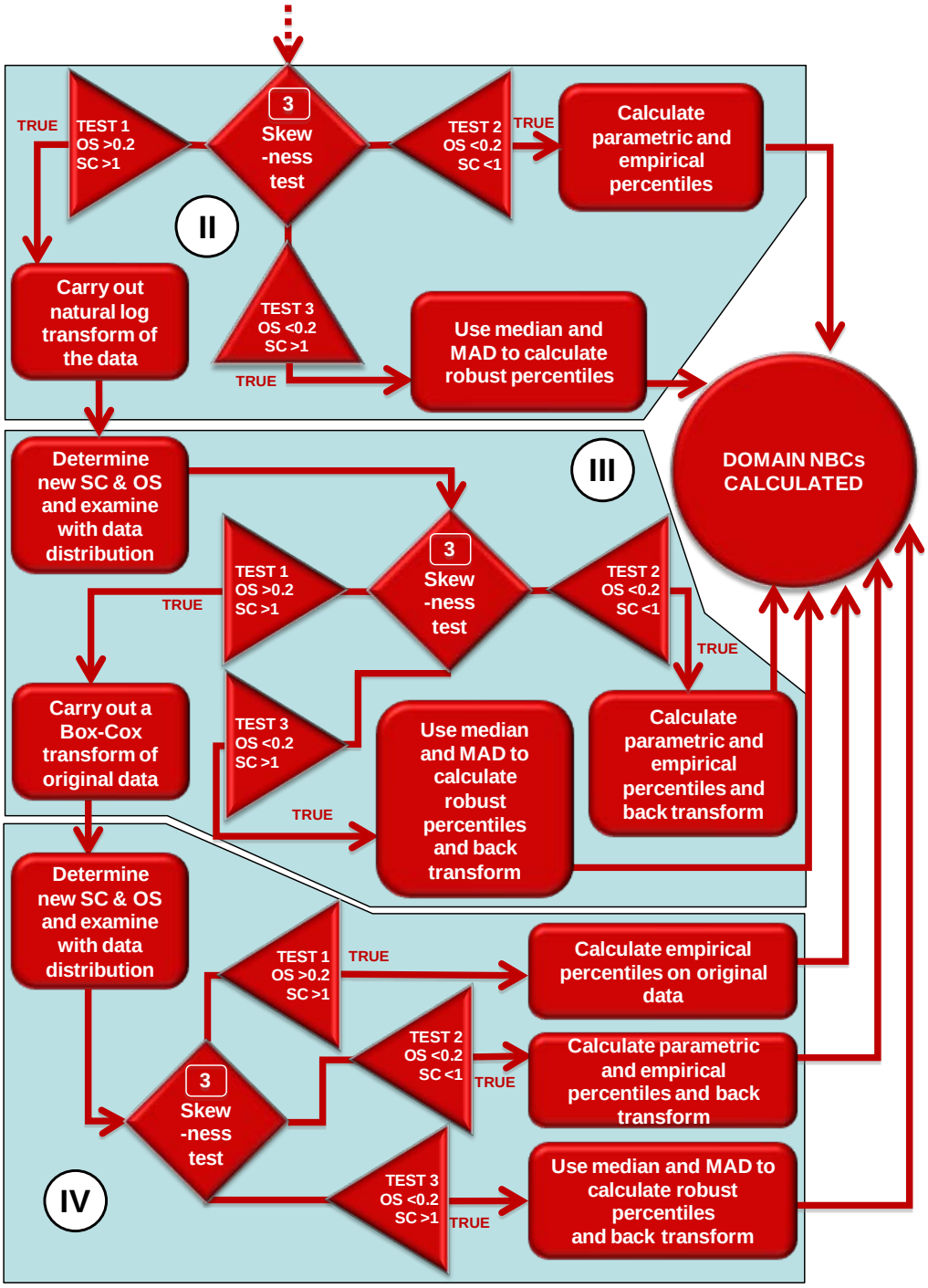

Figure 5 continued. Flow chart for the calculation of the NBC for a given contaminant domain (OS and SC are octile skew and skewness coefficient, respectively. MAD = median absolute deviation). See text for explanation

Figure 5 summarise 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*., 2011) 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

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(Figure 5), a minimum of 30 results are considered necessary to determine a NBC (see Cave *et al*., 2012). 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 [3] and include:

Data Exploration Reports (BGS report No. CR/11/145 and CR/12/041); 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.
Information regarding the data sets providing information for BaP are summarised in Appendix 2 of Ander *et al*. (2011) and this includes contact and web site links.

Soil parent material

The BGS Soil-Parent Material Model is described on a BGS web page (SPPM)[4] 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.[5] 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).

[3] http://www.bgs.ac.uk/gbase/NBCDefraProject.html
[4] http://www.bgs.ac.uk/products/onshore/soilPMM.html
[5] http://www.communities.gov.uk/publications/planningandbuilding/generalisedlanduse

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Further Reading

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

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