

SCOPING STUDY FOR MASQ

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This document is an assessment for the validity of an analysing a wide range of potential contaminants in soil as part of the Countryside Survey 2000 Monitoring and Assessing Soil Quality Project and will be used by the Agency to determine the programme of study that it will support financially.

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**MASQ: MONITORING AND ASSESSING SOIL QUALITY**

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**Module 6: Soils and Pollution**

**Scoping Study for MASQ**  
**Analyses of Heavy Metals and Organic Pollutants**  
**from the CS2000 Soil Samples**

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## 1. **Executive summary**

The Scoping Study was requested by The Environment Agency to assess the validity of analysing a wide range of metals, semi-metals, metalloids and organic compounds from the MASQ (CS2000) soil samples based on several criteria from national relevance to recommended analytical methods. Therefore, the aim of this scoping study is to determine, within the strict financial constraints of the project, what approach to sampling and analysis would best meet the regulatory and policy requirements of the Agency and the Department, and the scientific needs of CEH.

For metals/metalloids, the analytical list of Pb, Zn, Cu, Cd, Ni, Cr by ICP-OES with Hg by cold vapour AAS was recommended. Provisional analytical costs are provided for all options. Total metal concentrations were identified are the most appropriate given current status of standard analytical methods.

The study takes a practical approach to developing a satisfactory work plan for the organics analyses (MASQ-O). First, it compares the existing analytical capability at ITE Monks Wood with the Agency wish-list set out in the Introduction, and identifies which of the compounds in the wish-list can be quantitatively analysed in soil samples without undue time being devoted to method development. Approaching the problem in this way maximises the number of samples that can be analysed and minimises (but does not eliminate) methodological development. Arguments are then advanced to show that the “selective list” is a good match to the overall aims of MASQ-O. Analytical methods and their costs are then outlined.

Consideration is then given to the various factors that need to be taken into account in selecting which of the 1,000-odd soil samples should be analysed, and to the scientific strategy of MASQ-O. Finally, because the resources in MASQ-O will not permit all available soil samples to be analysed for the elective list of compounds, a tentative work plan is outlined to form the basis for a discussion with the Agency. This includes proposals for a modest amount of method development that might considerably increase either the number of squares analysed or the number of determinands.

## **2. Background**

The Environment Agency (EA) has requested that the Institute of Terrestrial Ecology carry out a Scoping Study for the analyses of metals, metalloids and organic compounds as part of the jointly funded MASQ project (CS2000 Soils module 6: Soils and Pollution; NERC, EA and DETR funded). This study will assess these substances for priority in analyses from the soils collected in the Countryside Survey 2000. These analyses will be used to produce baseline data-sets for metals/metalloids and organic pollutants from a uniform, stratified and distributed sampling of the range of land and land cover types in UK which have detailed supporting vegetation and environmental data. These datasets can then be used, in conjunction with the other MASQ soil components (e.g. biota, pH, LOI, type) in producing or addressing the following:

- I A national overview on the “state” of soils in the U.K.;
- II A baseline against which target values can be set and specific sites can be compared;
- III The first stage in the development of soil quality indices for the UK;
- IV An assessment of changes in soil quality;
- VI Critical loads for metals and persistent organic pollutants;
- VII Issues of contaminated land and land reclamation/restoration.

## **3. Specifications of the Scoping Study**

The following specification were provided by the Environment Agency (02/02/99):

“The Agency has supplied a list of elements and compounds that it would ideally like to have analysed from the CS2000 soils, if resources were not limited. Following initial discussion, this list has been shortened slightly but it is still too extensive for the available resource. The aim of the scoping study is to help the Agency to decide what is the optimum list of substances that it would like included. There is scope for the Agency to provide extra funds to have additional analyses done, beyond those to be agreed under the collaborative project. The Agency would like the scoping study to include more detail on each of the proposed analyses and their methods. It should include the following information, broken down for each substance or group of substances as appropriate, for those listed below.”

The additional information to be included in this assessment is:

- ◆ Potential groupings of substances - for ease and efficiency of analysis.
- ◆ Proposed methods for each analyses or group of analyses. To include a brief description of all parts of the analysis process (e.g. sample preparation, extraction and analysis). The Agency would prefer all methods used in the project to be standard and validated.
- ◆ A brief assessment of the suitability of each method (e.g. for preparation, extraction and analysis) for soil samples in general, and for the soil samples as taken and stored in CS2000.
- ◆ How do the storage methods used relate to the ideal method for particular applications and what are the resulting limitations?
- ◆ Cost, per sample or groups of samples. Preferably these costs should be broken down into costs for sample preparation, extraction, analysis and interpretation.
- ◆ Where ITE have no existing methods, do such methods exist in other laboratories? If so, is there a case for sub contracting those analyses? If not, the Agency needs to know that the proposed methods will be validated and quality assured in their laboratories, for instance using trials on “known” soil samples.
- ◆ Quality assurance and quality control methods proposed for each stage of the analysis process, to include a discussion of the likely confidence levels, detection limits or other potential areas of uncertainty
- ◆ Any other information that ITE think would support the proposed approaches and help in prioritising the substances for inclusion and deciding on the optimum list of substances for the available resource.
- ◆ Recommendations of which substances ITE think should be included, preferably with one or more options and a discussion of the advantages and disadvantages of each option.

A wide range of metals, metalloid and organic compounds are be considered significant environmental pollutants. A select set has been identified by the Environment Agency for relevance to the Agency’s priorities in the UK and as potential substances for analyses in the CS2000 Soils Module project (MASQ). This full list is given in Appendix 1. The main human sources of these elements and compounds are listed in Table 1.

Table 1: Potential contaminants associated with main industrial sectors. Adapted from USEPA, 1999.

<b>Sector</b>	<b>Example of contaminants</b>
<b>Gasworks</b>	<i>Coal tar creosote, phenol, Cyanide free/complex, sulphide/sulphate</i>
<b>Iron + Steel works</b>	<i>Metals copper, nickel, lead Acids sulphuric, hydrochloric Mineral oils - Coking works residues (as for gasworks )</i>
<b>Metal finishing</b>	<i>Metals cadmium, chromium, copper, nickel, zinc Acids sulphuric, hydrochloric Plating salts cyanide Aromatic hydrocarbons benzene Chlorinated hydrocarbons 1,1,1-Trichloroethane</i>
<b>Non ferrous metal processing</b>	<i>Metals copper, cadmium, lead zinc Impurity metals antimony, arsenic Other wastes battery acids</i>
<b>Oil refineries</b>	<i>Hydrocarbons various fractions Acids, sulphuric, Alkalies caustic soda, Insulation asbestos Spent catalysts lead, nickel, chromium</i>
<b>Paints</b>	<i>Metals lead, cadmium, barium Alcohols toluol, xylo Chlorinated hydrocarbons Methylene Chloride Fillers, extenders silica, titanium dioxide, talc</i>
<b>Petrochemical plants</b>	<i>Acids, alkalies sulphuric, caustic soda Metals copper, cadmium, mercury Reactive monomers styrene, acrylate, VCM Cyanide toluene di-isocyanate Amines analine Aromatic hydrocarbons benzene, Toluene</i>
<b>Petrol stations</b>	<i>Metals copper, cadmium, lead, nickel, zinc Aromatic hydrocarbons benzene Octane boosters lead, MTBE Mineral oil - Chlorinated hydrocarbons trichloroethylene Paint, plastic residues barium, cadmium, lead</i>
<b>Rubber processing</b>	<i>Metals zinc, lead Sulphur compounds sulphur, thiocarbonate Reactive monomers isoprene, isobutylene Acids sulphuric, hydrochloric Aromatic hydrocarbons xylene, Toluene</i>
<b>Semi-conductors</b>	<i>Metals copper, nickel, cadmium Metalloids arsenic, antimony, zinc Acids nitric, hydrofluoric Chlorinated hydrocarbons trichloroethylene Alcohols methanol Aromatic hydrocarbons xylene, Toluene</i>
<b>Tanneries</b>	<i>Acids hydrochloric Metals trivalent chromium Salts chlorides, sulphides Solvents kerosine, white spirit Cyanide methyl isocyanate Degreasers trichloroethylene Dyestuff residues cadmium, benzidine</i>
<b>Textiles</b>	<i>Metals aluminium, tin, titanium, zinc Acids, alkalines sulphuric, caustic soda Salts sodium hypochlorite Chlorinated hydrocarbons Perchloroethylene Aromatic hydrocarbons phenol Pesticides dieldrin, aldrin, endrine Dyestuff residues cadmium, benzidine</i>
<b>Wood processing</b>	<i>Coal tar creosote Chlorinated hydrocarbons pentachlorophenol Metalloids / metals arsenic, copper, chromium</i>
<b>Sewage sludge</b>	<i>Metals Copper, chromium, zinc, cadmium, arsenic, mercury, nickel, lead</i>
<b>Burning of Fossil Fuels</b>	<i>Metals / metalloids mercury, lead (petrol additive), copper, nickel , zinc, vanadium, chromium, cadmium, antimony, beryllium,</i>
<b>Waste incinerators</b>	<i>Metal/metalloids Zinc, chromium</i>

#### **4. Metals, metalloids, semi-metals and other compounds**

The “metals, metalloids and semi-metals” from the Agency’s specification are listed in Table 2 with current recommendations for analyses, soil protection limits and requirements for human health for each substance. Most of these metals/metalloids occur naturally, either as elements or various compounds, in the environment but anthropogenic sources result in the contamination of air, water and soil. A brief description of the natural and human sources of each of these metals and metalloids, and their potential environmental impacts, are given in Appendix Two. A mini-review of the relevance of heavy metals to soil microbial communities is to be found in Appendix Three; both of these were used in the prioritising exercise.

Cyanide and sulphur were also present in the metal/metalloid/semi-metal list received from the Agency. Cyanide has been included in the assessment exercise in this scoping study since it can cause environmental concern in certain industrial areas (see Appendix Two) but not in the costing exercise, as explained below. Sulphur has been excluded from the scoping study at this stage as has been considered of lower priority than the other substances. Atmospheric sulphur dioxide levels have been declining from the early 1970’s, principally due to the industrial pollution control measures with deposition now low enough to cause deficiencies in certain crops e.g. wheat, pasture grasses, oilseed rape and barley (McGrath and Withers, 1996; Jones et al., 1997). Point sources (fossil-fuel power stations without de-sulphurisation equipment) may produce levels of high deposition ( $>40 \text{ kg ha}^{-1}$ ), however these levels are rarely exceeded within the UK. It is recognised that certain soils, that have exceeded their critical load, may continue to cause acidifying problems for the foreseeable future or if drained. These soils have, however, been identified from critical load assessments. Site specific sampling would be the optimum method by which to obtain an appropriate soil sample for extractable sulphate or sulphide analyses.

Table 2: Potential metals, metalloids and other compounds for analyses in MASQ: CS2000 Soils Module: form, dietary requirements, analytical techniques and examples of soil protection levels.

Substance	Element form	Trace element requirements A = animals P = plants U = ultratrace <sup>5</sup>	Analytical techniques	Correlation of totals and extractables <sup>1</sup> R <sup>2</sup>	Soil protection limits <sup>2</sup> mg kg <sup>-1</sup> n.b. use dependant	Target and intervention values <sup>3</sup> mg kg <sup>-1</sup>	Soil protection limits <sup>4</sup> mg kg <sup>-1</sup>
Beryllium (Be)	Metal		ICP-OES				
Cadmium (Cd)	Metal	U	ICP-OES	0.78	3	0.8/12	0.3 - 1.5
Chromium (Cr)	Metal	A	ICP-OES	-	600	100/380	20 - 130
Copper (Cu)	Metal	A P	ICP-OES	0.64	140	36/190	20 - 70
Lead (Pb)	Metal	U	ICP-OES	0.68	300	85/530	25 - 100
Manganese (Mn)	Metal	A P	ICP-OES	0.69			
Mercury (Hg)	Metal		cold vapour AAS			0.3/10	0.1 - 2.1
Nickel (Ni)	Metal		ICP-OES	0.31	75	35/210	10 - 85
Vanadium (V)	Metal	A	ICP-OES				
Zinc (Zn)	Metal	A P	ICP-OES	0.21	300	140/720	60 - 200
Antimony (Sb)	Metalloid		ICP hydride elements				
Arsenic (As)	Metalloid	A	ICP hydride elements			29/55	
Boron (B)	Metalloid	P	ICP-OES				
Selenium (Se)	Metalloid	A P	ICP hydride elements				
Sulphur (S)	Non-metal				2- 30 ug m <sup>-3</sup> 6		
Cyanide (HCN)	Non-metal salt of HCN	U				1/20 free 5/50-650 complex	

1 = McGrath and Loveland (1992).

2 = CEC recommendations (agricultural soils mainly for sewage sludge input controls)

3 = Vries de and Bakker (1998)

4 = Haan de (1996)

5 = Hopkin (1989) and ASTDR (see appendix two).

#### 4.1 Potential groupings and an optimum list

In the process of prioritising and grouping substances for analyses from CS2000 soils, extensive literature searches were carried out using BIDS, BIOSIS, the WWW and the CEH library service. The literature was examined for data on emissions/sources, toxicity (human, plant, microbial and animal) and current recommendations/legislation (soil protection, human exposure, critical loads and land remediation) for each of the listed substances. It is recognised that certain substances, potentially significant pollutants, may have been excluded from this exercise. This is principally due to a lack of appropriate risk assessments and/or adequate toxicological data; there are insufficient toxicity or eco-toxicity data for preliminary OECD risk assessments for 50 to 75% of chemicals (CMA, 1998; EEA, 1998).

The results from these searches were used to produce a guide to what is known about each of the substances and to be able to produce a ranked order of priorities (Table 3). The results indicate the following list of priorities, from high to low; **Pb>Zn=Hg=Cu=Cd>Ni=Cr>As>Mn>B>V=Se=Sb=HCN=Be.**

Analytical techniques (Table 2) and sample requirements can be used to further prioritise these substances. A significant issue is the limited amount of soil available for analyses (140 CS2000 soil samples <50 g; the remaining >100g; min. 25 g to be retained). Subsequent analyses may be limited by the sample available. This is especially relevant for ICP-OES where one 5 g sample can be used for the analyses of all relevant metals. Therefore, it is recommended that all metals required by ICP-OES should be analysed from a single sample at the same time. Cyanide soil chemistry samples (air-dried) or the remaining soil microbial sample (frozen but too small). Site specific sampling and analyses could be carried out in conjunction with planned re-sampling for volatile organic compounds.

The options for groupings of metals and metalloids for analyses are presented in Table 4 along with analytical costs for each, based on analyses of all 800 samples from England and Wales. It is recommended that minimum analyses should be carried out on Option Three; **Hg, Pb, Zn, Cu, Cd, Ni, Cr.**

Table 3: Metals, metalloids and cyanide: a guide to what is known about each of the substances and a ranking of each according to these criteria.

Each criterion is scored 1 if it can be referred to individual substances.

Element/ compound	Listed on Aarhus Protocol	DETR UK Sustainable Development Indicators	Release in sewage sludge monitored by DETR	Used for soil protection/ critical loads	In: McGrath & Loveland (1992)	Data on soil faunal responses available	Data on soil microbial responses available: see appendix 3	Mammalian health risk data	Known to bio- accumulate	Phyto- toxicity data available	Ranked by all criteria
Beryllium (Be)								1		1	2
Cyanide (HCN)				1			1	1			3
Antimony (Sb)							1	1	1		3
Selenium (Se)								1	1	1	3
Vanadium (V)							1		1	1	3
Boron (B)						1	1	1	1	1	5
Manganese (Mn)					1	1	1	1	1	1	6
Arsenic (As)			1	1		1	1	1	1	1	7
Chromium (Cr)			1	1	1	1	1	1	1	1	8
Nickel (Ni)			1	1	1	1	1	1	1	1	8
Cadmium (Cd)	1	1		1	1	1	1	1	1	1	9
Copper (Cu)		1	1	1	1	1	1	1	1	1	9
Mercury (Hg)	1	1	1	1		1	1	1	1	1	9
Zinc (Zn)		1	1	1	1	1	1	1	1	1	9
Lead (Pb)	1	1	1	1	1	1	1	1	1	1	10

Table 4. Recommended options for groupings of metals and metalloids for analyses from CS2000 soil samples; costs calculated using the quotations given in Table 6.

Option 1	Option 2	Option 3	Option 4	Option 5	Option 6	Option 7	Option 8
Pb, Zn, Cu, Cd	Hg, Pb, Zn, Cu, Cd	Hg, Pb, Zn, Cu, Cd, Ni, Cr	Hg, Pb, Zn, Cu, Cd, Ni, Cr, Mn, B	Hg, Pb, Zn, Cu, Cd, Ni, Cr, As	Hg, Pb, Zn, Cu, Cd, Ni, Cr, Mn, B, As	Hg, 12 ICP-OES metals	Hg, 12 ICP-OES metals, As
£26,140	£40,456	£42,072	£43,688	£55,494	£57,110	£46,920	£60,342

Table 5: Analytical costs (£) for all potential groupings of metals and metalloids.

Number of metals for ICP-OES	4	6	8	12
Proposed priorities for metals and metalloids	Cd, Zn, Pb, Cu	Cd, Zn, Pb, Cu, Ni, Cr	Cd, Zn, Pb, Cu, Ni, Cr, Mn, B	Cd, Zn, Pb, Cu, Ni, Cr, Mn, B, V, Se, Be, Al
Cost £ (FEC)				
Metals only	26140	27756	29372	32604
Metals + Hg	40456	42072	43688	46920
Metals + As	39562	41178	42794	46026
Metals + Hg/As	53878	55494	57110	60342

Table 6: Analytical costs of each analyses (£): total cost and itemised for each step in the analysis. (not available for the EA cyanide analysis) provided by ITE Merlewood for ICP-OES and ICP-hydride, ITE Monkswood for cold vapour AAS.

Analytical methods	Costs (£ FEC)			
	Total for all 800 samples	Itemised <i>Sample prep.</i> Agate mill grinding	Itemised <i>Extraction</i> Booking/ aqua regia/ moisture content	Itemised <i>Analyses</i>
Cold vapour AAS = Hg	14,316	4,194	9,018	14,316
ICP-OES = 4 metals	26,140	4,194	9,018	12,928
ICP-OES = 6 metals	27,756	4,194	9,018	14,544
ICP-OES = 8 metals	29,372	4,194	9,018	16,160
ICP-OES = 12 metals	32,604	4,194	9,018	19,392
ICP-hydride extraction = As	13,422		6,711	6,711
EA methods = cyanide	10,000			

Option 1 includes lead, zinc, copper and cadmium as these would be the first four metals to be analysed by ICP-OES, confirming the agreed list for the collaborative project. Two of these (Pb, Cd) are listed in the Aarhus protocol while these two with Cu and Zn are included in the DETR list of sustainable development indicators (Table 3).

Mercury is also listed in both the Aarhus Protocol and DETR list and is therefore included in Option 2; it is recommended that mercury be analysed by cold vapour AAS (see below). Nickel and chromium are then added to produce Option 3 as both these metals are released from sewage sludge in significant amounts (as monitored by DETR), used in soil protection and critical loads assessments and included in McGrath and Loveland's Geochemical Map of the UK (McGrath and Loveland, 1992). The fourth option includes manganese and boron to ensure optimum use of the soil samples in ICP-OES. Although arsenic ranked higher in priority than both B and Mn in Table 3, it would require analysis by ICP-hydride elements and is therefore included in Option 5. Arsenic is also monitored in sewage sludge by DETR and used in soil protection recommendations and analysed by ICP-hydride elements. The remaining two groups provide costs for further analyses of metals using ICP-OES.

#### **4.2 Analytical laboratories: metals and metalloids**

It is proposed that ICP-OES analyses would be carried out at ITE Merlewood and cold-vapour analyses at ITE Monkswood to utilise in-house expertise and equipment.

#### **4.3 Analytical costs**

Analytical costs have been calculated for the analyses of all 800 CS2000 soil samples from England and Wales from quotations provided by ITE Merlewood for ICP-OES and ICP-hydride and ITE Monkswood for cold vapour AAS. For reference, analytical costs have been given for cyanide analyses by the EA at Llanelli. The analytical costs of each Option (Table 4), the full range of groupings (Table 5) and for each analysis with a breakdown of costs into sample preparation, extraction and analyses, where available. Analyses costs for less than 800 samples can be calculated on a proportional basis.

#### **4.4 Analytical Priorities: Totals or exchangeables?**

The analysis of *total* metal or metalloid contents ( $\text{mg kg}^{-1}$ ) will remain the most reliable and meaningful environmental assessment until there are recognised standard methods for determining the available reactive content of metals or metalloids and the bioavailability of these “available” components is fully understood (Vries de and Bakker, 1998). In support of this, almost all current legislation and recommendations are based on total concentrations of metals and metalloids in soils since total concentrations are relatively easy to determine and incorporate into soil quality standards, compared to available concentrations. Working in the precautionary principle, totals at least identify soils with potential risks: the first stage of a risk assessment is to identify presence of a chemical and the next is to identify a compound’s behaviour (de Haan, 1996). Data from McGrath and Loveland (1992) indicate that relatively good relationships exist between totals and availables for several metals (Table 3) and these relationships, once more fully understood, may prove useful in predicting available metal contents in soils.

#### **4.5 Storage procedures for metals, metalloids**

All soil samples collected in 1999 have been put into long-term storage at ITE Merlewood. Every sample was treated according to the MASQ standard soil preparation protocol; air-dried, sieved in a 2 mm stainless steel mesh and all samples put into air-tight plastic containers. These samples are now in safe storage at ITE Merlewood. In the short-term, there will be no detectable change in metal or metalloid contents. Long-term storage effects are unknown. These could be assessed by the analyses of a sub-set of soil samples from the 1978 ITE Woodland Survey (pers. comm. R. Bunce).

#### **4.6 Analytical procedures and quality control: metals and metalloids**

##### **4.6.1 ICP-OES**

ICP-OES and ICP-MS can be regarded as complementary methods for analyses and each has its own advantages and disadvantages. ICP-MS offers the potential for better sensitivity with lower detection limits. However, with ICP-MS there are matrix problems associated with the analysis of acid digests of solid samples, as there is a limit on the dissolved salt content.

This means that the working detection limit may not be as good as the analysis by ICP-OES, because of the requirement to work with lower solid: liquid ratios. ICP-MS is available if the

analysis reveals concentrations in solution too low by ICP-OES and there is the option to analyse digests on the ICP-MS instrument.

#### **4.6.2 Cold-vapour AAS for mercury analysis**

Aqua-regia digestion for Hg is a standard method (MEWAM, as for other metals). Cold vapour AAS is one of the most sensitive methods for quantifying Hg. As regards, quality control, we will include certified reference material and samples from proficiency testing (ISE) to estimate accuracy and precision.

#### **4.7 Quality Assurance of Chemical Analysis at ITE**

The Environmental Chemistry Section at ITE Merlewood operates under the following QA policy: It is the aim of the analytical laboratories within ITE to provide analytical data fit for the purpose of studies in environmental research. To provide quality assurance, operations in the laboratories involve:

- sample management systems.
- use of modern equipment.
- use of validated methods.
- application of rigorous quality control procedures.
- employment of professionally qualified analysts.
- a commitment to training to maintain skills.
- careful organisation of laboratory accommodation for efficient use and to minimise contamination and
- good liaison between analysts, the project leader and the customer.

Quality assurance procedures ensure that there is a traceable link from certified reference material and validation through proficiency testing to the results of analysis. This is achieved through documented management of stock solutions, the use of rigorous internal quality control procedures, and where feasible, analysis of material with certified values, participation in inter-laboratory proficiency trials and recovery tests. Our laboratories are committed to participation in recognised proficiency testing schemes such as AQUACHECK (WRc) or University of Wageningen International Soil and Plant Exchange programmes in order to test performance against the wider analytical community.

The procedure proposed will adopt the following approach:

- Methods for the Determination of Metals in Soils, sediments, and sewage sludge and plants by hydrochloric-nitric acid digestion..... by Methods for the Examination of Waters and Associated Materials, 1986 HMSO.
- At the time of analysis we will analyse Certified Reference Material and samples from an international soil exchange scheme (ISE) to verify methods.
- Analysis will be traceable to Certified Reference Materials namely NBS Estuarine Sediment 1646 and BCR Lake Sediment No 280 through internal QC samples.
- With each batch of 25 samples, we will also analyse 2 internal laboratory, reference samples, blanks solutions and a random duplicate.

## **5. Organic pollutants**

### **5.1 An optimum list for analyses**

Although a lot is known about the way organic chemicals affect biota, how they move around the environment and are broken down (or persist) in different environmental compartments, there are still significant gaps in knowledge. One of these gaps is a lack of national and regional information about the way in which organic chemicals are distributed in soils. This type of information is needed to provide a background for regulatory decisions on contaminant releases and to help with policy formulation and development on issues such as soil health.

In the UK, there have been:

- (a) studies in and around individual sites on a number of compounds such as PAHs, PCBs and dioxins (Meharg et al 1997; Lovett et al 1998; Meharg et al 1998); further studies are just being reported to the Agency and are underway as part of the NERC URGENT programme;
- (b) modelled predictions of national distributions of selected pesticides in soils that have not been validated on a national scale;
- (c) a few studies on selected compounds in soil (PCBs, PAHs, dioxins) that have either a long-term temporal dimension or a large-scale spatial element (Creaser et al 1989; Cousins et al 1997; Lead et al 1997).

The long-term and large-scale studies are most relevant to MASQ-O but all have been limited in a variety of ways. For instance, in no previous case has it been possible to obtain national and regional information that can be related to physical geography, land use, soil type and biota – all potentially important variables that could determine contaminant distribution. CS2000 provides a framework within which, for the first time, a properly controlled study of national and regional patterns of soil contamination can be done for a selected range of contaminants. This is how the MASQ study differs from previous work, and because of this, it offers the possibility of establishing a national baseline. This may not have been attempted anywhere else in the world.

A wide range of organic chemicals is of potential interest. The Environment Agency have listed a number of groups of organic compounds it would like to see analysed within the MASQ element of CS2000.

These groups are:

- 18 PAHs
- 6+ organochlorine pesticides (plus isomers and stable metabolites)
- c 16 triazole fungicides
- 2+ triazine herbicides
- the chlorobenzenes
- the chlorotoluenes
- c 4 chlorophenols
- pentachlorophenol
- c 6 organometals
- 7 other organics
- 13 PCB congeners
- 17 dioxins and furans.

Analysing for all these determinands (c 90) in all the CS2000 soil samples would be prohibitively expensive; analysing for the dioxins and furans alone at commercial rates could cost up to £500,000; this is 5 times the total budget for MASQ-O.

## **5.2 Scope of analytical capacity at ITE Monks Wood**

Of the compounds listed by the Agency, the PAHs, PCBs, organochlorine pesticides and certain of the chlorophenols and other organics are routinely measured at the Monks Wood analytical facility.

There are some differences of detail between the lists of PAHs and PCBs requested by the Agency and the lists routinely quantified at Monks Wood. Of the PAHs, Monks Wood does not analyse for benzo[e]pyrene and benzo[j]fluoranthene, which have been named by the Agency but not given their CAS numbers. There may be only limited value in identifying non-standard PAHs, although the analytical method used at Monks Wood is probably detecting a range of PAHs that are not quantified at present. These may include the 2 non-standard PAHs. The reverse situation applies to the PCBs where Monks Wood routinely analyses for about 8 PCB congeners in addition to those on the Agency list. These are congeners of some environmental importance as they may help identify sources, and would aid interpretation (eg of where high levels of dioxins might be found). Results for the heavier

4 of these congeners could be reported. Data for the other 4 would also be quantified but not necessarily reported. Reporting of these will depend on critical appraisal of the final data set.

The standard organochlorine data set also varies from the Agency list in its detail. Routinely, analysis is done for alpha- and gamma-HCH, HCB, and DDE in soils. If DDT is present (as it still is in some environmental samples), this too is normally quantified. HEOD (the environmentally stable member of the “drins” group) is unstable with the current clean-up method, but could be reported using an alternate well-established procedure.

In addition, organometals could be analysed depending on the level of detail required in the analysis (ie total organic element vs quantification for individual compounds). Methods for certain other compounds (eg pentachlorophenol, mirex, toxaphene etc) would need to be established *de novo*, although some have been analysed for certain matrices in the past. Dioxins and furans would be best contracted-out to a specialist laboratory, although costs would be substantial (up to £800 per sample). A university department has agreed in principle to co-operating on such specialist analysis if necessary; their costs per sample might be lower than the figure in parantheses above.

At present, Monks Wood has analytical capabilities for chlorophenols (about 16 are regularly quantified by an HPLC method) and chlorobenzenes (about 6 compounds comprise the standard set by GCMS). However, these methods have not been worked up for soils. The chlorobenzene method could be developed relatively easily, although the chemicals may be too volatile to make the effort worthwhile. The chlorophenol methods are dedicated for research projects and would need considerable development.

There have been two equipment enhancements at Monks Wood that are potentially of considerable importance to MASQ-O. One is purchase of a microwave digestion unit, and the other is the acquisition of a CEH LCMS facility. Respectively, these two pieces of equipment (a) should considerably speed-up sample preparation, allowing more samples to be processed, and (b) could increase the range of determinands being looked for.

### **5.3 Choice of analyte suite**

There are a number of constraints on the choice of analyte suite. Amongst these are costs, analytical methodology and the amount of soil available for analysis. Most important,

however, are the constraints applied by the objectives of and deliverables from the work, and the way soil samples have been collected from the field sites.

The main deliverable required is a mapping of the contamination of soil by a range of organic compounds that reflects the degree to which human activity has affected / is affecting soil health. Information on this can be obtained by choosing determinands that reflect the main types of human activity. From the list of contaminants produced by the Agency, the most appropriate substances to meet the needs of the project would seem to be:

- 1) PAHs, because they are (a) produced as a result of a very wide range of industrial, commercial domestic and accidental combustion processes and (b) affect key biological functions;
- 2) PCBs, because they (a) remain widespread having entered the open environment from a wide variety of mainly industrial sources and (b) may not be declining evenly across the country (especially in certain terrestrial biota);
- 3) Selected pesticides, because they (a) reflect agricultural and commercial pressures, at least in those parts of the country dominated by agriculture or textile processing, (b) persist for some time with attendant environmental risks;
- 4) Chlorotoluenes, chlorobenzenes and chlorophenols because (a) as a group they reflect commercial activities across quite a wide range of industrial and commercial sectors, and (b) they are being found surprisingly widely distributed in the environment.

The main practical constraint imposed by the sampling regime that had to be used to collect the samples is that the more volatile substances could have been lost. This could have happened either (a) during the transfer from the field to ITE Merlewood, or (b) during sample processing at Merlewood (although this would be little different to any processing of samples that would need to be done at Monks Wood for soil samples). To limit losses of volatile materials special collection conditions would have to be applied involving sampling and mixing with drying agents and solvents in the field. Such procedures have not been developed for soils in this country and would have been too expensive at this stage in the development of thinking on soil health issues. The current approach used at Monks Wood s to collect soils in the field in sealed containers and return these to the laboratory where they are stabilised by mixing with a solvent before addition of drying agents and solvents for extraction. This

approach was impractical in CS2000, but could be considered for MASQ-O if resources were set aside for selective re-sampling of MASQ soil plots.

These sampling constraints make it likely that to provide the soil health deliverables most effectively the following substances should definitely be quantified:

- the heavier PAHs;
- the more highly chlorinated PCB congeners; and,
- selected persistent organochlorine compounds (OCs).

An additional advantage of choosing these determinands is that there has been a limited amount of previous work on these substances in the country, although nothing as comprehensive as being attempted in the MASQ-O module of CS2000 (see Introduction). This previous work will act as a point of reference for the studies in MASQ. Moreover, mapping these determinands may reveal relative hotspots that warrant further study, perhaps for the more difficult and expensive determinands.

#### **5.4 Outline of Analytical Methods**

Analytical methods for these determinands are solvent based extraction of contaminants from the soil matrix (hexane for PCBs and OCs; dichloromethane for PAHs) followed by either GCECD or GCMS. It is important to use analytical methods that are sensitive so as to avoid problems in interpretation arising from the presence of too many non-detected analytical returns. GCECD is a very sensitive method for PCB and OC analysis, and experience over the past few years at Monks Wood has shown the GCMS is a powerful approach to environmental PAH analysis across a wide range of environmental matrices and concentrations. It has distinct QA advantages over more routine approaches to PAH analysis. These may prove important in MASQ. Further details of analytical methods are given in Annex 1. Note that limits of detection refer to limits in the material injected on the machine not to limits in the sample, and are based (conservatively) on about four times the noise. Limits in samples bear no direct relationship to machine measures of sensitivity but need to be calculated on a project by project basis. Calculations will be made at the outset of the MASQ studies to set sample preparation and analytical parameters at levels that minimise non-detected returns.

In all cases, analytical QA/QC procedures are similar to those that would be run under NAMAS or other accreditation schemes. The core of the procedures is the frequent use of analytical standards, internal standards, sample blanks, and standardised reference materials. Because standardised reference materials (especially international ones) are only rarely comparable to real environmental matrices it is sometimes difficult to make full use of such international QA schemes as exist. This is compensated for to some degree by exchanging samples between laboratories with similar interests or preparing in house reference material. It may be wise to prepare such a sample (or group of samples) at the outset of the MASQ organics study.

Experience of past programmes of study suggests the use of standard methodologies is only helpful in cases where standard, consistent, matrices are being used (eg a particular kind of food). It is an integral part of MASQ-O that very variable matrices are being examined. The best approach in these circumstances is to devote time at the outset of the project to the development of an appropriate methodology, and then to employ QA procedures that ensure consistent results are obtained within the project. Certified reference materials would be used for comparative rather than fully quantitative purposes. One difficulty is that certified materials may not exist for samples of the wider environment; reference materials are often composed of relatively contaminated material.

ITE, Monks Wood runs a standard approach to QA/QC issues that includes the rejection of samples that fall outside statistically determined confidence intervals for those types of analysis for which adequate certified or in-house reference materials exist. It may be possible to establish such a system for certain of the MASQ-O determinands

### **5.5 Outline of Cost per sample**

Costs per sample at Monks Wood using the standard in-house methods are currently:

**£74** for a suite including 20+ PCB congeners and certain organochlorine pesticides (eg DDT derivatives, HCH isomers) done by GCECD, with confirmatory analysis on GCMS in difficult cases. These costs may need to be increased for some of these soils, as exhaustive soxhlet extraction may be required for some samples. Current costs can be broken down into staff time, equipment and consumables, and QA/QC costs that are respectively £55, £10, £9.

**£123** for 19/20 PAHs using the standard methodology on GCMS. These costs may need to be increased for some of these soils, as exhaustive soxhlet extraction may be required for some samples. Current costs can be broken down into staff time, equipment and consumables, and QA/QC costs that are respectively £85, £16, £20.

Thus, the cost per sample for a complete suite of persistent PCBs, PAHs and organochlorine compounds would be some **£190 - £200 per sample**, including costs of QC/QA, which constitutes about 14% of the effort in sample preparation and analysis.

If the Agency and the Department agree, some methodological work could be done that, if successful, could reduce costs per sample substantially and increase the information that could be derived from MASQ-O.

Within ITE, Monks Wood has been allocated £50K per annum for each of 2 years to complete organic analysis for MASQ (total available funds £100K). These costs are made up by funds from EA, DETR and CEH core science budget and include sample preparation, contaminant extraction, clean-up, quantitative analysis (with QA/QC). At c £200 per sample there is scope for the analysis of 500 samples without interpretation. However, interpretation of data will be important within MASQ because it is establishing a national baseline. It seems wise to reserve about one third of the total effort for interpretation and report preparation (c £30K). In these circumstances, the maximum number of samples that could be analysed is about 350. It would seem unwise to consider the analysis of fewer samples, especially as some developmental work may become necessary if difficult soil matrices are encountered.

### **5.6 Squares to analyse**

About 250 CS2000 squares (of the total of c 1210) have been sampled for soils and this means all squares could be analysed for PAHs, PCB and organochlorine pesticides. This would leave capacity for targeting additional collections (eg near towns or industrial sites) or for doing additional QA/QC procedures (e.g. to be conducted on within and between square heterogeneity), or for doing additional analysis on other determinands in selected squares.

However, within each of the CS2000 squares sampled for soils, 5 soil samples have been obtained from the range of soil and vegetation types present in the square. It will be necessary to test the heterogeneity of contaminant concentrations within each square to see if this is less

than or greater than the between square heterogeneity. Equally it will be necessary to check the within soil type and vegetation type heterogeneity, using squares with uniform soil and vegetation types. This type of preliminary work will be necessary before embarking on the main phase of analysis.

Before proceeding even to the first stage of analysis, it is worth considering the environmental variables that can affect contaminant distribution in the environment in case this influences the choice of squares to sample for the preliminary work outlined in the paragraph above.

There are four key factors, as far as the present study is concerned: the physicochemical (and environmental) properties of the contaminant, the soil type, the type of overlying vegetation and land management regime. Each is considered in turn:

Physicochemical and environmental properties: Resistance to biological breakdown makes some chemicals persist in soils for many years. For example, the rate of loss for DDT derivatives may be less than 1% per annum so that material applied to soils in the 1950s may persist well past the middle of the next century. On the other hand, some materials are lost from soil quickly due to their volatility or their susceptibility to biological decomposition (often achieved by the soil microbial community). Water solubility and the tendency to bind irreversibly to soil are two other, somewhat opposing, influences. All these factors combine in different proportions in different soils to affect what proportion of the inputs to soils will be available for analysis within a project like MASQ. These factors may be important considerations when interpreting the results from MASQ organics analysis. They should not however unduly affect the choice of squares to sample as the aim of MASQ is to quantitatively map the current state of play following a period in history when chemical use was less sustainable than it will need to be in the future.

Soil and vegetation type: These two factors will have a considerable bearing on the amounts of material entering the soil and, possibly, on the amount of what has entered it being extracted for analysis. Soil type is important for a number of reasons. For example, when chemicals enter soil a process known as “aging” begins whereby residues become increasingly more difficult to extract as time passes. This is thought to be the result of the chemical becoming physically incorporated into soil particles or attached to the humic fraction of soil in ways that make it difficult to extract. The biological and environmental significance of this process of aging is not understood. For example, it is not certain that such

aged material is unavailable to biota. Certainly, it becomes more difficult to extract material by chemical means. Further, since aging processes differ between soil types, extractability may vary similarly thus making comparisons between soils rather more complex than would be ideal for a country-wide mapping programme.

Soil type may also affect the analytical procedures in other ways. For instance, soil types differ markedly in composition of naturally occurring organic materials and there are a number of ways in which these can interfere with chemical analysis. The importance of this will have to be determined at the outset of the organics part of the MASQ exercise.

Vegetation type is important because variations in vegetation type will influence the way chemicals will reach the soil after being scavenged from the atmosphere by plants. Put simply, a solid object has a tendency to deflect air currents around it, whilst a finely divided object can act as more of a collector of material in the atmosphere. This is part of the reason why conifer woodland acts as a collector of organic pollutants. Chemicals adsorbed onto plant surfaces can reach the soil either after the plant becomes senescent or through stem flow or leaf-fall. The importance of this factor should also be checked at the outset of the organics part of MASQ.

The combined influence of soil and vegetation type on the organic content of soils could be established as part of the initial phase of work on the MASQ organics module. This could be done either by making some special collections of material, or by examining variation between different plots collected from within a set of 1 km squares.

Land management: This could be important to the scientific strategy of the MASQ organics module, because soils that are disturbed by ploughing and undisturbed soils will have quite different concentrations of chemicals. This will need to be taken into account when choosing which samples to analyse for.

## **5.7 Scientific strategy**

As a jointly funded project between DETR, EA and CEH it is important that the scientific strategy of the MASQ organics module is clear and that the scientific deliverables are such that scientific understanding on the residence of organic chemicals in the environment can be seen to have advanced.

The large scale sampling programme of CS2000 makes it possible to test the hypothesis that organic chemical distribution in the country's environment is taking place in accordance with the theory of "global distillation". Under this hypothesis, over time periods of decades or longer, clines in contamination will develop such that lighter more volatile substances will progressively migrate towards the poles whilst heavier less volatile materials will become proportionately enriched in temperate latitudes. Testing this hypothesis would help advance understanding about the behaviour and fate of chemicals in the national and global environment and should be the prime scientific objective of the work. If global distillation is occurring then, within comparable environments at similar altitudes, lighter congeners of PCBs should be found in higher proportions in northerly squares than in southerly ones. Provided local PCB sources are not too dominant and marine influences are not too great then it should be possible to detect clines within the UK, as the models predicting such distributions have working scales made up from 150 km boxes. ITE has evidence of temporal trends in biota that are consistent with the global distillation hypothesis but as yet there is only limited spatial data relating to soils. It seems certain that the distillation process is very dynamic, with volatilisation processes occurring on a daily basis depending on temperature (amongst other factors).

### **5.8 Sampling strategy**

One great advantage of CS2000 is the large amount of information that exists about each of the CS2000 sample squares and, additionally, about each of the soil sampling plots (X-plots) within each of the 250 1 km squares sampled for soils. All told there are about 1000 X-plots that could be sampled. This means it should be possible to select from amongst these enough plots to draw up country-wide maps whilst at the same time controlling for the range of factors that could influence the concentrations of contaminants in soil. However, preliminary study of the distribution of vegetation and soil types suggests that even within the range of sites available it may prove difficult to obtain sufficient samples across the country to prepare maps meeting the strictest scientific criteria. Additional sampling may be necessary to fill in gaps.

### **5.9 Proposed work plan**

There are a number of options available. Two are presented, with the first option being the preferred one:

### *Option 1*

- Meet with EA to:

Discuss scoping study;

Set out analytical limitations on study and decide on validation steps required before commencing analysis of MASQ samples;

Agree contingency plans (ie do further sample collections) if validation exercise produces data that is unsatisfactory;

Agree on any refinements of methodology (eg development of unified sample preparation and clean-up procedures for PAH and PCBs; inclusion of HEOD in OC list);

Agree, within sampling constraints set out above, the list of MASQ-O samples to be analysed (including consideration of the need to pool samples)

Consider need for supplementary analysis near sites of particular interest.

- Validate and refine methods

Refine methods for range of soil types and determinands within MASQ-O

Validate these against existing methods and certified reference samples

Meet with EA to discuss validation and refinement exercise

Agree final analytical programme with EA

- Proceed with analysis of 250 (or more) MASQ-O samples

Complete OC / PCB analysis

Complete PAH analysis

Report raw data to EA

Interpret results

Meet EA to discuss outcomes and implications

Map data

Meet EA to discuss outcomes and implications

Draft final report

Feedback from EA

Prepare final project report

Comments on draft from EA

Submit final report on MASQ-O.

## *Option 2*

- Meet with EA to:

Discuss scoping study;

Set out analytical limitations on study;

Agree to use of standard, existing Monks Wood methods

Agree, within sampling constraints set out above, the list of MASQ-O samples to be analysed (including consideration of the need to pool samples)

Consider need for supplementary analysis (eg near sites of particular interest).

- Proceed with analysis of 250 (or more) MASQ-O samples

Complete OC / PCB analysis on MASQ-O samples selected by ITE

Complete PAH analysis on MASQ-O samples selected by ITE

Report raw data to EA

Interpret results

Map data

Prepare final project report.

No matter what option is considered best to follow there are a number of issues that must be agreed before work commences if all involved are to maximise the likelihood that the project will have a successful conclusion. The issues are the acceptability of:

- 1) the suite of analytes.....ITE proposes PAHs and PCBs with selected OCs
- 2) the analytical methods.....ITE proposes the use of existing in house methods and QA /QC procedures or development of a project specific amendment
- 3) the field sampling protocol.....ITE may wish to consider re-sampling to strengthen scientific rigour
- 4) the MASQ plots to be sampled for organic analysis.....ITE is currently working up appropriate scenarios to present at a project meeting.

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## Appendix One

### The Agency's wish list of substances

#### Metals/semi metals/metalloids

Cadmium	Copper	Nickel	Vanadium
Lead	Mercury	Arsenic	Beryllium
Zinc	Antimony	Boron	Chromium
Manganese	Selenium	Sulphur	Cyanide

#### Polycyclic Aromatic Hydrocarbons (PAHs)

CAS No.	PAH	CAS No.	PAH
120-12-7	Anthracene	129-00-0	pyrene
86-73-7	Fluorene	218-01-9	chrysene
91-20-3	Naphthalene	56-55-3	benz[a]anthracene
85-01-8	Phenanthrene	205-99-2	benzo[b]fluoranthene
191-24-2	benzo[ghi]perylene	207-08-9	benzo[k]fluoranthene
208-96-8	Acenaphthylene	50-32-8	benzo[a]pyrene
83-32-9	Acenaphthene	53-70-3	dibenz[ah]anthracene
206-44-0	Fluoranthene	193-39-5	indeno[1,2,3-cd]pyrene
??	Benzo[e]pyrene	??	Benzo[j]fluoranthene

#### Organic pesticides

##### Drins, including:

Aldrin  
Dieldrin  
Endrin

##### OCs, including:

Chlordane  
DDT (and breakdown products?)  
HCH, (total or gamma etc.?)

##### Azoles

##### Triazines

**Aromatic halocarbons**

Chlorobenzenes

Chlorotoluenes

**Chlorinated phenols**

Chlorophenols (not penta)

Pentachlorophenol

**Organometallics**

Organolead compounds

Organotin compounds

**Other organics:** Chlordecane, Hexabromobiphenyl, Mirex, Toxaphene, Acetone, Phenol, Oil/Fuel hydrocarbons

**Polychlorinated Biphenyls (PCBs)**

IUPAC NO.	Structure	TEF
non-ortho:		
77	3,3',4,4'-tetrachlorobiphenyl	0.0005
126	3,3',4,4',5-pentachlorobiphenyl	0.1
169	3,3',4,4',5,5'-hexachlorobiphenyl	0.01
mono-ortho:		
105	2,3,3',4,4'-pentachlorobiphenyl	0.0001
114	2,3,4,4',5-pentachlorobiphenyl	0.0005
118	2,3',4,4',5-pentachlorobiphenyl	0.0001
123	2',3,4,4',5-pentachlorobiphenyl	0.0001
156	2',3,3',4,4',5-hexachlorobiphenyl	0.0005
157	2,3,3',4,4',5-hexachlorobiphenyl	0.0005
167	2,3',4,4',5,5'-hexachlorobiphenyl	0.00001
189	2',3,3',4,4',5,5'-heptachlorobiphenyl	0.00001
di-ortho		
170	2,2',3,3',4,4',5-heptachlorobiphenyl	0.0001
180	2,2',3,4,4',5,5'-heptachlorobiphenyl	0.00001

**Dioxins**

Congener	I-TEF	Congener	I-TEF
2,3,7,8-TCDD	1	1,2,3,7,8-PeCDF	0.05
1,2,3,7,8-PeCDD	0.5	1,2,3,4,7,8-HxCDF	0.1
1,2,3,4,7,8-HxCDD	0.1	1,2,3,7,8,9-HxCDF	0.1
1,2,3,7,8,9-HxCDD	0.1	1,2,3,6,7,8-HxCDF	0.1
1,2,3,6,7,8-HxCDD	0.1	2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDD	0.01	1,2,3,4,6,7,8-HpCDF	0.01
OCDD	0.001	1,2,3,4,7,8,9-HpCDF	0.01
2,3,7,8-TCDF	0.1	OCDF	0.001
2,3,4,7,8-PeCDF	0.5		

(Where: T=tetrachloro; Pe=pentachloro; Hx=hexachloro; Hp=heptachloro; and O=octachloro)

## Appendix Two

### **Brief assessments of the toxicological and environmental risks of select metals, metalloids and cyanide**

Data presented in this appendix have been summarised from two main sources: US Department of Health and Human Service, Agency for Toxic Substances and Disease Registry = Toxicological Profiles and ATSDR ToxFAQs factsheets.

*Antimony:* Antimony is found naturally in the environment and ores are mined for use in metal alloys for a range of metal products e.g. pewter, batteries, pipes and bearings and paint products. It is released into the environment through particle release from incinerators, smelters and fossil fuel burning. When in soil, it binds with particles containing iron, manganese or aluminium. Exposure to high levels can lead to organ damage and fertility problems. USEPA = 0.006 ppm in drinking water

*Arsenic:* In nature, it is found in low levels mainly as inorganic arsenic compounds. Less toxic, organic compounds are found in animals and plants. Inorganic compounds are used as wood preservatives, insecticides and herbicides. Arsenic enters the environment when materials and waste are burned. Most arsenic compounds are soluble and can transfer to groundwater from soil. They bioaccumulate in aquatic organisms but are generally not toxic in fish. Inorganic arsenic is a human toxin and high levels in food or water can be fatal. Lower levels can cause tissue damage and breathing difficulties. USEPA = 0.05 ppm

*Beryllium:* Can be found in some rocks, soil and volcanic dust and compounds are commercially mined. The metal is used in electrical parts, machine parts, ceramics, aircraft parts, nuclear weapons and mirrors. It gets into the environment from natural sources and through burning of fossil fuels and industrial waste disposal. Once in soils, most beryllium remains there. Fish do not bioaccumulate beryllium. Low levels of beryllium can cause hypersensitivity or allergy while high levels can cause lung damage.

*Boron:* boron is found in nature and boron compounds (mainly borates) are mined for the production of glass, fire retardants, leathers, cosmetics, photographic materials, soaps and

cleaners, high energy fuels and wood preservatives and insecticides. It is released into the environment from natural sources (volcanic eruptions, oceans, geothermal steam) and is released from industries that use it. No information exists on the residence of boron in soil, water or air and does not bioaccumulate in animals. Boron does accumulate in plants. Little information is available on boron toxicity.

*Cadmium:* In nature, cadmium most commonly occurs as stable compounds with Cl, S or O. It is mainly used in metal plating, paint pigments, batteries and plastics and is produced as a by-product of zinc, lead or copper ore smelting. Release into the environment is caused through the use of phosphate fertilisers and sewage sludge, burning of fossil fuels, emissions from smelters and waste disposal. High levels of cadmium can cause irritation of the lungs and digestive system. Exposure to low levels over a long period of time may cause kidney and lung damage, lung cancer or high blood pressure. USEPA = 0.005 mg l<sup>-1</sup> in drinking water

*Chromium:* has three main forms, Cr(0), (III) & (VI) of which only Cr(III) is stable and naturally occurring. Although all forms are toxic at high levels, Cr(VI) is the most toxic and certain compounds containing this form are recognised carcinogens. Cr(III) is believed to help insulin maintain normal glucose levels. It is used in making steel and other alloys, bricks in furnaces, dyes and pigments, chrome plating, leather tanning and wood preservatives. It enters the environment through disposal of Cr containing products or chemicals or burning of fossil fuels. Cr settles from air in less than 10 days and adheres strongly to soil particles, with only a small amount moving from soil to groundwater. It is not taken up or stored in fish tissue. USEPA = 100 ug l<sup>-1</sup> in drinking water

*Copper:* It occurs naturally in plants and animals and is an essential element for all living organisms. Many copper compounds occur naturally and are mined extensively throughout the world. Copper is primarily in the manufacturing of wire, pipe, sheet metal and other metal products. Other manufactured products and uses include pesticides, preservatives and water treatment. It is a significant metal constituent of sewage sludge. Most copper compounds bind readily and strongly to soil particles. The major sources in the environment are from mining, smelters and copper industries waste and sewage sludge disposal to land or sea. Large levels of copper can lead to liver and kidney damage

while long-term exposure can cause headaches, dizziness, nausea, diarrhoea, irritation to eyes, lungs and mouth.

*Cyanide:* is generally found in combination with other chemicals in the environment. The most common substances found in the environment are hydrogen cyanide (HCN), sodium cyanide (NaCN) and potassium cyanide (KCN). Certain bacteria, fungi, algae and plants produce cyanide in biosynthetic pathways. Cyanide, and its compounds, is most frequently used in the production of organic compounds photographic development, fumigation, some mining processes, electroplating and metal treatment. The major sources in the environment are from waste treatment plants, iron and steel works and organic chemical plants while cyanide can also enter the groundwater from land-fills. High levels of exposure for short periods can cause harm to the central nervous system, respiratory system and cardiovascular system and, at worse, coma and/ or death. Low levels of cyanide can cause breathing difficulties, convulsions and/or loss of consciousness. However, as Vitamin B12, cyanide is an essential compound in the human diet. USEPA = 0.2 mg l<sup>-1</sup> in drinking water

*Lead:* Lead and its compounds can be found extensively in the environment. It is released into the environment through vehicle and industrial emissions (especially iron and steel works), industrial and municipal waste incinerators, lead batteries, sewage sludge applications to land and smelting. It is mined from ores and is used in the production of many chemicals and metal products, petrol additives, paint and batteries. Lead bioaccumulates in plants and animals. Excess lead in humans can lead to defects in unborn children and, reduce IQ, slow growth and cause hearing problems in young children, and cause organ damage in adults. USEPA = 0.015 mg l<sup>-1</sup> in drinking water

*Manganese:* Occurs naturally in the environment in combination with oxygen, sulphur and chlorine as various ores in rock. It is also required daily in small amounts by humans to maintain health. These ores are mine to produce manganese metal that is mixed with iron to make steel. Manganese compounds are also used in the production of batteries, ceramics, pesticides, fertilisers and some dietary compounds. Sources in the environment include smelters, steel works, fossil fuel burning plants and vehicle exhaust fumes. Exposure to high levels of certain manganese compounds can cause mental and physical disturbances (e.g. “manganism”). In extreme cases, permanent injury is caused to the

brain. At lower levels of exposure, manganese can cause respiratory problems or impotence in men.

*Mercury*: this is a naturally occurring metal which has several forms. It combines with several elements to form inorganic “salts” (e.g. Cl, S, O) and carbon to form organic mercury compound. The most common of these is methyl-mercury, produced from biological processing of mercury compounds in soil and water and bio-accumulates in animal tissue. Mercury and its compounds are used in the production of chlorine gas and caustic soda, in thermometers, dental filling, batteries, skin-lightening creams and antiseptic creams. Inorganic mercury enters the environment from mining ore deposits, burning coal, waste incineration, manufacturing plants and mercury-containing fungicides. Exposure to high levels of mercury, in most forms, can permanently damage vital organs, especially in young children. USEPA = 2ppb (WHO = no safe limits).

*Nickel*: This is a very abundant element found in all soils. Nickel and its compounds are used in alloys, colouring, plating, batteries and catalysts and is released into the environment by particle release and deposition. It adheres readily with iron and manganese in soils and does not appear to bioaccumulate. Humans can become sensitive to nickel and high levels can cause inflammation in the lungs. USEPA = 0.04 mg l<sup>-1</sup> in drinking water

*Selenium*: This element is common in soils and rocks, mainly in sulphide mineral or in combination with silver, copper, lead or nickel. Selenium compounds are used in dandruff shampoos and gun blueing. It enters the environment through particle release and deposition and bioaccumulates in aquatic organisms. Selenium is rapidly transferred from soils to ground-water due to its highly soluble nature. Selenium is an essential element in humans with deficiencies resulting in heart and pain problems. High levels of selenium have a wide range of effects from dizziness and fatigue to bronchitis. USEPA = 50ppb

*Vanadium*: Vanadium and its compounds can be found in rocks, some iron ores and crude petroleum deposits. It is used, with other metals, to produce specialist alloys and as vanadium oxide in specialist steel, car parts, springs and ball bearings. It mainly enters

the environment through natural sources and the burning of fossil fuels. Once in soil, water or air, it is resident for a long time as it does not readily dissolve in water.?

*Zinc*: this is one of the most common elements in the earth's crust and is found in air, soil and water and present in all foods. It has many commercial uses from alloys, rust proof coatings, dry cell batteries to paints, dyes and wood preservatives. It is released into the environment through mining, steel production, coal burning and incineration of waste. Most zinc in soil remains bound to soil particles but some also leaches into groundwater. Zinc accumulates in animals but not plants. It is an essential dietary element for growth and the immune system while excess zinc can have detrimental effects on the immune system and growth. USEPA = 5 ppm.

## Appendix Three

### A mini-review of heavy metals and the soil microbial community

Nisha Parekh, ITE Merlewood, March 1999

Within the context of the CS2000 survey, multivariate statistical analysis will be used to detect relationships between changes in the substrate utilisation responses of microbial communities extracted from the soil samples, soil fauna and soil properties such as pH, organic matter content, levels of organic pollutants and heavy metal content. Heavy metals pose particular risks to the environment due to their persistence and potential toxicity. Whilst many metals are required by microbial cells as essential micronutrients for growth (see Table 1), certain chemical forms of most of the heavy metals are toxic to microorganisms (see Table 2).

Table 1: Classification of Heavy metals according to their requirement for the growth of microorganisms (from Pirt 1985).

Frequently essential for growth	Rarely essential for growth	Potentially rarely essential for growth
Mn, Fe, Co, Cu, Zn	B, Al, Si, V, Cr, Ni, As, Se, Mo, Sn	Be, F, Sc, Ti, Ga, Ge, Br, Zr, W

These elements are required in trace quantities (0.001 to 0.015g/100g dry biomass) for microbial growth and nutrition. Some metals are needed for the synthesis of particular molecules (e.g. cobalt forms part of vitamin B<sub>12</sub>), some are required as cofactors of enzymes (e.g. iron for haem containing cofactors of redox function enzymes such as cytochromes).

The chemical forms in which metals occur, soil texture and soil pH have been widely found to influence the concentrations at which toxicity occurs to micro-organisms (Babich and Stotsky, 1993). Higher pH, and increased contents of clay and organic matter considerably reduces metal toxicity. Soil pH has the largest influence due to its strong effects on solubility and speciation of metals both in the soil as a whole and particularly in soil solution. Plant root exudates, binding of metals to bacterial or fungal cell walls and the actions of micro-organisms, e.g. localised acidification by iron-oxidising bacteria, can also effect metal availability in soils (Giller *et al.*, 1998).

Table 2: Classification of heavy metals according to their potential toxicity (from Duxbury, 1985).

Noncritical	Potentially toxic and relatively accessible	Potentially toxic but insoluble and rare
Fe	Hg, Zn, Cu, Cd, Cr, Ni, Pb, Mo, Ag, Sb, Bi, Pt, Au, Mn, Sn, Pd, Tl	Hf, Ta, Os, Zr, Re, Rh, W, Ga, Ir, Nb, La, Ru

Disturbances caused by heavy metals to microbial biomass and activity and the consequent effects on decreased litter decomposition and less efficient nutrient cycling have been extensively reviewed (Tyler, 1981; Bååth, 1989; Duxbury, 1985 and Giller *et al.*, 1998). Soils receiving sewage sludge in a long-term field experiment were found to have 50% smaller biomass than that in adjacent low metal soils (Brookes and McGrath, 1984). High amounts of lead have also been shown to inhibit microbial respiration and dehydrogenase activity in polluted soils (Doelman and Haanstra, 1979). Hattori (1992) looked at the effects of five metals (Cd, Cr, Cu, Ni and Pb) on organic decomposition in gley and andosol soils and showed that Cd and Cu had the greatest inhibitory effect although all metals inhibited the evolution of CO<sub>2</sub>. Inhibition of microbial activity has been shown to lead to a retardation of tree growth due to deficiencies in plant micronutrients (Tyler *et al.*, 1989). Tyler *et al.*, (1989) reported that the normal decomposition of conifer litter and recycling of plant nutrients was inhibited in a forest surrounding a brass foundry which had emitted large amounts of Cu, Zn and other metals as aerosols for many years.

Several studies have also demonstrated heavy-metal induced changes in specific parts of the soil microbial community. Toxicity affecting *Rhizobium leguminosarum* bv. *trifolii* of metals, from long term sewage sludge applications in a UK field experiment, had a marked inhibitory effect on symbiotic nitrogen fixation in the roots and vesicular-arbuscular mycorrhizal infections of white clover (Koomen *et al.*, 1990; Chaudri *et al.*, 1992b). *In vitro* experiments in the same study showed a decreasing order of toxicity as being Cd > Zn > Cu > Ni. More recent field experiments concluded that numbers of *Rhizobia* in sewage sludge contaminated soils were low due to the inhibitory effect of Zn because this metal is present in high concentrations in sludges and sludged soils (Chaudri *et al.*, 1993). However, other workers concluded that Cd was more inhibitory to *Rhizobia* (Obbard and Jones, 1993). The high organic matter content of soils examined in the latter study may have served to reduce the bioavailability of metals. Studies of metal toxicity effects on nitrogen fixing bacteria in the USA have failed to show the same degree of

inhibition as those conducted in the UK (Angle and Chaney, 1991). McGrath *et al.*, (1995) summarised the data from long-term field experiments in the UK, Sweden, Germany and the USA with sewage sludge applications to land; some of the main findings are shown in Table 3.

Table 3 Summary of results from a study of the effects of long-term sewage sludge application on soil microorganisms (McGrath *et al.*, 1995)

Function or parameter inhibited or reduced	Heavy metals soil concentrations (mg kg <sup>-1</sup> )					
	Zn	Cd	Cu	Ni	Cr	Pb
Nitrogen fixation by free-living heterotrophic bacteria	127	3.4	37	21	52	71
Nitrogen fixation by free-living cyanobacteria	114	2.9	33	17	80	40
Numbers of <i>Rhizobium leguminosarum</i> bv. trifolli	130-200	0.8-1.0	27-48	11-15		
	Free metal ion concentrations (µg l <sup>-1</sup> )					
Long term toxicity to microorganisms	1.5-10	0.3-0.4	0.6-2.7	5000-10,000		

In conclusion, although Cu and Cd have been shown by most workers to be most toxic to soil bacteria, especially *Rhizobia*, Zn may constitute the greatest problem because of its presence in high concentration in sewage sludge. Although Zn does not appear to inhibit the growth of crop plants on sludged soils, the fact that numbers of *Rhizobia* are significantly reduced within the UK and EC limits for Zn (300mg kg<sup>-1</sup>) is a cause for concern (Chaudri *et al.*, 1993; MAFF Report PB 1561, 1993).

Many of the changes in microbial activity, biomass or number in previous studies have been noted at relatively high metal concentrations. Subtle effects of heavy metals on the diversity and function of microorganisms in soils may decrease the resilience of the soil ecosystem or lead to less efficient soil nutrient cycling. Several studies using physiological profiling (e.g. using the BIOLOG system), thymidine incorporation and phospholipid fatty acid (PLFA) analysis suggest that subtle changes are brought about in the composition of soil microbial communities at sub critical levels (Reber, 1992; Kelly and Tate, 1998; Díaz-Raviña *et al.*, 1994; Pennanen *et al.*, 1996). Such changes are likely to precede more chronic changes such as the decrease in soil biomass due to chronic metal stress. Physiological profiling is a culture-based method that gives an indication of changes in the functional response of the soil microflora. A decrease in the number of

substrates that can be utilised by and/or a decrease in the respiration activity of a microbial community may lead to a reduction in its efficient exploitation of all ecological niches. Thus a decrease in functional diversity and activity of a soil microbial community may explain the decrease in the size of the biomass in soils from polluted sites (Reber, 1992; Giller *et al.*, 1998).

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## Appendix Four

### Outline of Analysis of PCB and Organochlorine Pesticide Residues in CS2000 MASQ Soils by GC-ECD

#### Scope

This procedure covers the preparation of sediment samples for analysis of PCBs by GC-ECD.

#### Sample Preparation

Samples would be sieved and dried at ITE Merlewood and transported to ITE Monks Wood. A dried sample would be weighed into a soxhlet thimble for extraction by either hexane. Residual moisture would be removed by sodium sulphate. Extraction would be by exhaustive soxhlet extraction for 8 hours.

#### Sample Clean-up

After extraction and reduction in a Kerdena-Danish system, clean up is achieved by addition of sulphuric acid and alumina column chromatography.

### Analysis by GC-ECD

Quantitative analysis is performed with a Varian Model 3400 fitted with a Varian 8200CX autosampler, and electron capture detector.

Chromatographic conditions: Injector temperature: 200°C; Split flow: 50 ml/min; Detector temperature: 300°C. Detector make-up gas: Nitrogen at 25 ml/min; Column: HT8 50m x 0.22 mm i.d. column connected fitted with a 3m x 0.22mm methyl deactivated retention gap. Manufacturer: Scientific Glass Engineering (UK) Ltd; Carrier gas: Hydrogen. (Distillers MG Grade 5.0); Carrier gas velocity: 45 cm s<sup>-1</sup>  
Column oven program is shown in Table 1; the initial temperature is 60°C (for 2 minutes).

**Table 1: Oven program details**

Level	Rate (°C/min)	Final Temp (°C)	Final Time (min)
1	45.0	170	2.5
2	2.5	200	5.0
3	2.0	280	0.0
4	40.0	320	2.0

**Calibration:** The GC is calibrated using the internal standard method. Dichlobenil is the internal standard. The internal standard is added to both standards and samples to give a concentration of 0.04µg/mL. Two separate calibration runs are used:

organochlorine pesticides and PCB congeners in hexane  
arochlor 1254 in hexane at a concentration of 4.0µg/ml.

Multilevel calibrations for organochlorine pesticides are carried out after every 4 batches of samples analysed.

### **Compound identification**

The identity of a chromatographic peak is found by comparison of its relative retention time with the relative retention times of peaks in the organochlorine standard. This operation is performed automatically by the EZCHROM chromatography data system. A visual check is made of the assigned peak identities, by overlaying sample, blank and standard chromatograms using the Overlay v5.0 in-house software.

## **Quality assurance**

A sample blank is run with every batch of samples. A 5g sample of Monks Wood sieved and oven dried soil is spiked with OCs and PCB congeners. This is analysed with a sample of unspiked soil to calculate recoveries throughout the lab procedures.

## **Limits of Detection**

The instrument limit of detection is calculated as follows (see Table 2 for actual values):

$$\text{LoD} = (\text{Noise}_{\text{Average}} + (\text{SD}_{\text{Noise}} \times 3.5)) \times C_{\text{WS}} / \text{PH}_{\text{WS}}$$

$\text{Noise}_{\text{Average}}$	The average baseline noise from six sample blanks.
$C_{\text{WS}}$	Concentration of the working standard.
$\text{PH}_{\text{WS}}$	Peak height of the working standard.
$\text{SD}_{\text{Noise}}$	Standard deviation of the noise from six sample blanks.

**Table 2: Instrument LoDs**

Compound	LoD ng/ml
HCB	0.09
a-HCH	0.09
g-HCH	0.11
DDE	0.36
TDE	0.50
DDT	0.67
PCB 8	1.03
PCB 18	1.30
PCB 28	0.57
PCB 31	0.64
PCB 52	2.10
PCB 77	1.11
PCB 101	0.70
PCB 105	0.50
PCB 114	0.38
PCB 118	0.35
PCB 123	0.56
PCB 126	0.60
PCB 128	0.51
PCB 138	0.47
PCB 149	0.74
PCB 153	0.47
PCB 156	0.42
PCB 157	0.52
PCB 167	0.33
PCB 169	0.30
PCB 170	0.44
PCB 180	0.40
PCB 209	0.65

## **Appendix Five**

### **Outline of Method for Analysis of Soil Samples for the Determination of PAH Residues by GC-MS for the CS2000 Study**

#### **Scope**

This procedure covers the preparation of soil samples for analysis of polycyclic aromatic hydrocarbons (PAHs) by GC-MS.

#### **Sample preparation, extraction and clean-up**

These procedures are similar to those described for OCs and PCBs, save that the extractant is dichloromethane.

#### **Analysis By GC-MS**

The GC-MS system used for this analysis is a Hewlett Packard 5890 series II Plus gas chromatograph fitted with a Hewlett Packard 7673B auto-sampler, interfaced to a 5972A series Mass Selective Detector (MSD); Column: 25m x 0.22mm fused silica column coated with 0.25um BPX5 joined by a fused silica press-fit connector (Supelco) to a 5m x 0.22mm methyl deactivated retention gap.

Chromatographic conditions: Column inlet: Cold on-column injection. The inlet is held at an initial temperature of 35°C for 1min, then ramped at 100°C/minute to 300°C and then held at 300°C for 20 minutes. Column oven: The initial temperature is 35°C, which held for 1 minute and then ramped at 8°C/minute to 320°C. Carrier gas: The carrier gas is helium held at a constant flow of 2ml/minute by electronic pressure control.

MSD: The MSD is operated in select ion mode with an interface temperature of 280°C, and an EI+ source with an electron energy of 70eV. The instrument was tuned for maximum sensitivity using PFTBA. The ions monitored are given in Table 4. Where possible, 3 ions were monitored for each compound. The most abundant ion (target) was used for quantification.

## Compound identification

The identity of a chromatographic peak is found by comparison of its relative retention time and ion ratios, with the relative retention times and ion ratios of peaks in the calibration standard. This operation is performed automatically by the GC-MS data system but is also checked manually, by overlaying the sample and calibration standard chromatograms. The most abundant ion (target ion) is used for quantification, the other ions for confirmation.

## Quality Control

Every batch of samples includes a sample blank, certified reference material (Coal gas site soil, Laboratory of the government Chemist) and a spiked soil sample (similar to that described for OCs and PCBs).

## Limits of detection

The instrumental limit of detection (Table 5) is calculated by  $y = y_B + 3 s_B$ , where  $y$  is the instrument response for the lower limit of determination (LLD),  $y_B$  is the blank signal and  $s_B$  is the standard deviation of the blank value.  $y_B$  and  $s_B$  are obtained from the regression line of a multilevel calibration and are the calculated  $y$  intercept and the standard error of the estimate  $S_{y/x}$  respectively. The value obtained for  $y$  is then converted to a concentration using the regression equation. The signal for the smallest qualifier ion is used.

**Table 4: SIM ions**

Compound	Target ion	Qualifier ion 1	Qualifier ion 2
Perylene-d12	264.2	260.2	265.2
Naphthalene	128.2	127.2	
Acenaphthylene	152.2	153.2	
Acenaphthene	153.2	152.2	154.2
Fluorene	166.2	165.2	167.2
Phenanthrene	178.2	176.2	179.2
Anthracene	178.2	176.2	179.2
Pyrene	202.2	200.2	203.2
Fluoranthene	202.2	200.2	203.2
Chrysene	228.2	226.2	229.2
Benzo[a]anthracene	228.2	226.2	229.2
Benzo[b]fluoranthene	252.2	250.2	253.2
Benzo[k]fluoranthene	252.2	250.2	253.2
Benzo[a]pyrene	252.2	250.2	253.2
Ideno[1,2,3-cd]pyrene	276.2	277.2	
Dibenzo[a,h]anthracene	278.2	276.2	277.2
Benzo[g,h,i]perylene	276.2	277.2	

**Table 5: Instrument LoDs**

Compound	Limit of detection (ug/ml)
Naphthalene	0.079
Acenaphthylene	0.090
Acenaphthene	0.073
Fluorene	0.082
Phenanthrene	0.067
Anthracene	0.107
Fluoranthene	0.114
Pyrene	0.106
Benzo[ <i>a</i> ]anthracene	0.152
Chrysene	0.097
Benzo[ <i>b</i> ]fluoranthene	0.161
Benzo[ <i>k</i> ]fluoranthene	0.096
Benzo[ <i>a</i> ]pyrene	0.156
Ideno[1,2,3- <i>cd</i> ]pyrene	0.175
Dibenz[ <i>a,h</i> ]anthracene	0.347
Benzo[ <i>g,h,i</i> ]perylene	0.081