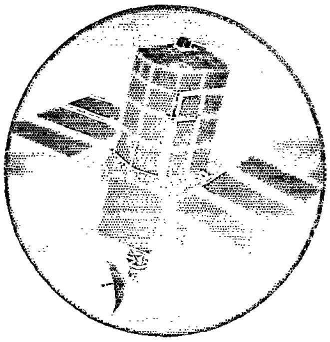
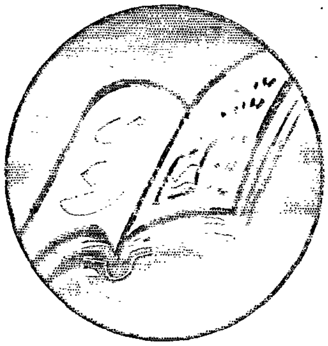
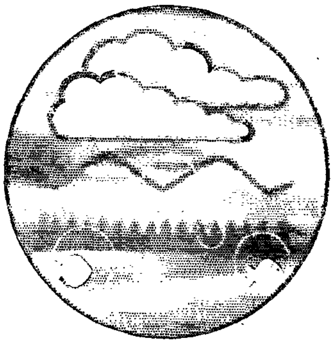
Methods for the Determination of Red List Substances in Waste Leachates







Research and Development

Technical Report

P242

ENVIRONMENT AGENCY

Methods for the Determination of Red List Substances in Waste Leachates

Technicl Report P242

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Research Contractor:
Analytical Services Group, AEA Technology

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Statement of use

This document contains guidance protocols for organisations which are charged with carrying out the determination of Red List substances in landfill leachates. The report also provides data on sensitivity and reproducibility when analysing leachates. Suggestions for method improvements and for further work are included. The report will be of interest to landfill operators, regulators, laboratory staff and analytical/environmental chemists. The Agency is taking forward this research under a further stage of development.

Research Contractor

This document was produced under R&D Project CLO223, Contract No. EPG 1/7/20 by:

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Executive Summary

This study was commissioned to produce a protocol or guidance manual for waste management and regulation organisations carrying out the determination of Red List substances in leachate. This was to comprise draft analytical methods based on current best practice for each substance, together with method performance data derived from round robin testing. Recommendations for the statistical interpretation of data were also required, including information on estimating the significance of measurements made at levels close to statutory limits. A range of quasi-reference materials with known analyte levels was needed for the study in order to carry out the round robin tests and for subsequent use by analysts determining Red List analytes in leachates. Analytes which were shown in the round robin tests to be impossible to measure at the required concentrations were to be identified so that future method development could be targeted on these analytes.

The requirements for this work arise from the new Waste Management Licensing system which came into force in May 1994, increasing the regulatory pressure on waste management. There are currently three routes for leachate to return to the environment:- (i) to rivers and estuaries, monitored by the NRA on behalf of HMIP, (ii) to sewers or sewerage treatment works, monitored by a water plc (England and Wales) or to (iii) underground strata from landfills, monitored by the waste regulators with advice from NRA. For legislative reasons, the concentrations of Red List analytes which may be discharged by these routes is often effectively "zero", and consequently the NRA, water plcs and waste regulators require analytical methodologies which, theoretically, can measure down to this level - in practice, the limit of detection of the best methods in current use. For this reason, it is important that the analytical methods used by these organisations for Red List analysis are compared, and information obtained about performance when measuring low concentrations of these analytes in leachates.

Of the waste regulator, waste operator and commercial laboratories which were approached, fifteen were selected as participants in the study. Surveys of the methods in use by these laboratories revealed that most used methods based on specific DoE "Blue Books" to cover the Red List analytes. Very few methods issued by other bodies were used, although several were derived from USEPA procedures. "In-house" procedures were used in some cases, particularly where new analytical technology has become available since a particular "Blue Book" was published or revised. Very often, a method was described as "Blue Book", although in fact it had been modified, usually by removal of the cleanup step to make it less time consuming and costly to perform.

A round robin using a series of samples based on river water and dilute, oxidised leachate revealed that the best performance was obtained using original "Blue Book" procedures which had not been simplified by the removal of the cleanup step; use of more sophisticated detection methods (eg GC-MS rather than GC-ECD) did not appear to be detrimental to the performance of the basic method.

A second round robin exercise was carried out in which participants were asked to use only the specific "Blue Book" and related methods which had worked well in the first round robin; it was stressed that the cleanup must not be omitted from the methodology. The samples in this second round robin were anaerobic, high-matrix leachates. Several of the laboratories with the lowest performance in the first round robin improved their performance in this round, although an overall reduction in performance occurred. This was due largely to the difficulties participants experienced during the solvent extraction step with some of the organochlorine compounds. A series of tests was carried out to improve the solvent extraction efficiency of these compounds from leachate, and an approach identified which gave quantitative results. The limitations of the methods available for each of the Red List analytes have been identified, and recommendations made where method development is still required. A summary of each method is given as a protocol, together with information on method performance as far as the analysis of leachates is concerned.

The main conclusions of the work are the following:

- "Blue Book" methods appeared to closely resemble the "best practice" compared with methods available from other sources;

- for mercury and cadmium, existing methods were satisfactory for all the matrices tested, achieving accurate results at low levels, and detection limits sufficient to meet EQS criteria;

- methods for atrazine, simazine, aldrin, dieldrin, endrin and trichlorobenzene worked well with water, and in some laboratories with leachate, although less laboratories achieved accurate results than did with the metals;

- current methods for some species such as DDT, PCBs, HCH and HCB worked well in water and oxidised leachate, but did not succeed in extracting the analyte species from the anaerobic leachate matrix. A series of bench tests carried out with PCBs identified a modification to the solvent extraction step of this method which overcame this problem;

- methods for most organophosphorus compounds worked well for the water matrix, but not for any of the leachates at the levels tested;

- more internal standards (^{13}C labelled or analogues) are required to allow for the wide range of chemical properties experienced with some classes of compounds.

CONTENTS

Appendices

Tables

1. INTRODUCTION

This work was commissioned by the Department of the Environment's Waste Technical Division under contract number EPG 1/7/20. The work was undertaken by the Analytical Services Group at AEA Technology over the period November 1994 to June 1995.

1.1 BACKGROUND TO PROJECT

The requirements for this work arise from the new Waste Management Licensing system which came into force in May 1994. This increased the regulatory pressure on waste management, for example with respect to the discharge of potentially toxic pollutants in leachate.

There are currently three routes for leachate from landfilling to return to the environment:- (i) to rivers and estuaries, monitored by the NRA on behalf of HMIP, (ii) to sewers or sewerage treatment works, monitored by a water plc (England and Wales) or (iii) to underground strata from landfills, monitored by the waste regulators with advice from NRA.

Potential water pollutants of international concern include the so-called List 1 and List 2 substances, of which 23 are regarded by the UK government as being the first priority for discharge minimisation; these substances are known collectively as the "Red List" (Appendix 1) and are the analytes of interest in this study. For legislative reasons, the concentrations of Red List analytes which may be discharged by the three routes listed is often effectively "zero", and consequently the NRA, water plcs and waste regulators require analytical methodologies which can measure down to this level - in practice, the limit of detection of the best methods in current use. Clearly, it is important that the methods in use by these organisations are compared and information obtained about method performance for low concentrations of Red List analytes in leachates. This study was designed to evaluate the current state-of-the-art of trace analysis for Red List analytes in waste leachates, so that advice can be given to waste managers and regulators on the best analytical approach to be adopted for the measurement of these substances before disposal of leachates.

1.2 OBJECTIVES

The principal objectives of the study were the following:-

(i) to identify 12 to 15 participant laboratories for the study (including AEA);

(ii) to identify the methods used by the selected laboratories for Red List analytes in leachate, and to obtain any performance data for these methods from external analytical intercomparison schemes;

(iii) to identify the best-available literature methods for the determination of Red List analytes in leachates, at levels down to the appropriate Environmental Quality Standard (EQS) concentrations (Appendix 2), to supplement the information obtained in (ii);

(iv) to produce intercomparison materials with a leachate matrix, to be used for a series of round robin tests;

(v) to conduct an initial round robin to test the methods used by participants, using the intercomparison materials with the simplest matrices;

(vi) to identify the methods which performed best in this round robin and to carry out a second round robin using these methods only;

(vii) to prepare protocols for each Red List analyte, detailing the preferred method and giving advice on the performance expected and on the statistical interpretation of results, based on performance in the second round robin;

(viii) to maintain a stock of reference standards/matrix to assist waste operators or regulators when undertaking Red List analyte determinations.

2. METHODS

2.1 SELECTION OF PARTICIPATING LABORATORIES

The list of potential participating laboratories (Appendix 3) was compiled in part from information supplied by the DoE, and included other laboratories which had tendered for this study or had expressed an interest. Other potential participants were identified from advertisements offering a service for Red List analysis placed in trade journals and from personal contacts. Two laboratories in excess of the number required were selected as possible reserves. The choice of laboratories was dictated in practice by the quite limited number of organisations able to offer a full Red List analytical capability.

Each potential organisation was telephoned to identify a contact point, and the purpose of the current study explained. If a full Red List analysis service was available, a quotation was requested for the two batches of test materials proposed for the round robin components of the study. As an inducement at this stage, a bonus payment of 20% was offered to laboratories which returned data within the requested time scale (n.b., in the event, only three laboratories were able to supply results within the fifteen working days requested). The price quoted per sample for a full Red List analysis is also included in Appendix 3. The requirements for the analytical samples (size, number, preservatives etc.) were also discussed at this stage, and an appointment made for a member of AEA's staff to visit the organisation to begin compiling method and performance data.

2.2 SURVEY OF RED LIST METHODOLOGIES

A protocol was designed which summarised the essential information relating to trace analysis of an environmental sample such as a leachate (Appendix 4). A member of AEA's staff took copies of the protocol to each of the proposed participating laboratories and, as far as possible, compiled one for each analyte or group of analytes. In the event, some information was not available due to commercial confidentiality, although more details were often obtained in subsequent telephone conversations, or as information attached to results during the round robin exercises. Performance data for analytical quality schemes was requested at the same time, but was only supplied by a limited number of participants.

Method data was extracted from the completed protocol forms and has been summarised in an analyte-by-analyte (or by group of analytes where this is more appropriate) format as Appendix 5. This is, in effect, a summary of current practice for the participating laboratories.

2.3 LITERATURE SURVEY

A literature search was carried out to complement the method information available from participants, and for the protocols (Appendix 12). One of the authors of this report (CJP) had previously carried out a literature survey of analytical methods for Annex II substances in solid waste (Pickford and Monaghan, 1993). This survey had looked at methods for each analyte which had been published by regulatory bodies such as DoE, BS, USEPA, DIN and ASTM. Literature sources had also been searched to complement "official" methods.

Sources which had been found in this review were brought up to date with a library search, including the use of the *"Analytical Abstracts"* CD-ROM information system, which was searched for the matrix including water, leachate, environmental samples, and for specific and generic analytes.

2.4 ROUND ROBIN STUDIES

2.4.1 Sample Matrices

A total of four basic materials were used for the analytical round robin exercises, comprising river water, an aged and oxidised leachate, and two anaerobic, freshly-collected leachates:-

(i) ***River Water***

River water was collected from the River Thames at Clifton Hampden, Oxfordshire. Samples were collected from the downstream flow by lowering 45 litre capacity carboys into the flow and allowing them to fill to the brim to exclude atmospheric air.

This sample was obtained to provide a reasonably "clean" environmental sample to use as a realistic matrix for the initial comparison of the analytical methodologies to be used.

(ii) ***Oxidised Leachate/Mixed Landfill Run-Off***

Samples of liquid were collected from a leachate/landfill run-off holding tank at Brogborough landfill, Bedfordshire, in early December 1994. This liquid was a composite of collected and aerobic leachate, and rainwater which had run off the surface of the landfill.

This liquid (which had been subject to atmospheric oxidation) represented a sample of intermediate "strength" between the relatively "clean" river water described above and the leachate from anaerobic landfilled waste.

(iii) Leachate from Anaerobic Landfilled Waste.

Samples of leachate were collected from two of the DoE-funded test cells located at the Brogborough landfill site. These were obtained from leachate sampling wells in Test Cells 2 (containing domestic waste) and 6 (containing mixed domestic/non-hazardous industrial wastes). Each well was pumped and purged for two entire well volume changes (approximately 20 minutes per volume change) prior to collection of the samples. Each sample was collected in 45 litre carboys which had been previously purged with carbon dioxide. To minimise residual head space, each carboy was filled to overflowing before sealing.

The materials were collected between December 1994 and mid-February 1995 and delivered to Analytical Services Group (ASG) in 45 litre carboys. TOC, pH and trace element data for each sample are tabulated in Annex 6; these parameters give some indication of the nature of the matrix of each sample. Samples containing a high loading of organic and inorganic matter are more likely to present difficulties to the analyst.

2.4.2 Containers

As part of the information gathering phase of the study, participants were asked to specify their normal sample bottle requirements. Using this information, a compromise container set was designed for the first round robin which would be acceptable to most participants. This consisted of three, 1 litre bottles (organophosphorus, organochlorine and organotin compounds), one 500 ml bottle (pentachlorophenols), a 250 ml glass bottle containing 10 ml of 5M nitric acid (mercury compounds), a 250 ml polythene bottle with the same preservative (cadmium) and a 40 ml septum vial for volatile organic compounds. A number of laboratories were supplied on request with an additional 1 litre glass bottle for triazine compounds.

In the second round robin, the vial for volatile compounds was omitted as this was essential for one analyte only (dichloroethane) which was added at spike concentrations (based on NRA EQS) well below existing limits of detection. The mercury and cadmium samples were combined in a single 500 ml polythene bottle with preservative to minimise the overall number of bottles; this was discussed and agreed with participating analysts with a specialist experience of sample preservation. Bottle sets for both round robins were supplied under contract by Yorkshire Water.

2.4.3 Spiked Sample Matrices

Preliminary discussions with analysts experienced at leachate analysis confirmed that natural levels of Red List analytes in the four basic samples would probably be well below the limits of detection for most analytes. Therefore, each sample was supplied to participants (i) "as sampled", and (ii) spiked with Red List analytes at levels just above EQS values. For this purpose, the EQS levels supplied by NRA were used (Appendix 2), as these were the only values available during the course of the study. However, values derived from the Surface Water Directive (SWD) were used for the evaluation of results, as these were more relevant to the needs of the DoE. The substantial differences in one or two cases between these two sets of values meant that unfortunately, for several analytes, the spiking levels were not appropriate to assess performance at concentrations close to the SWD EQS concentrations (e.g. dichloroethane).

The reason for supplying both unspiked and spiked samples was to derive true method blanks or detection limits from the data for the unspiked samples, and accuracy data from the results for the spiked samples.

The approach proposed for the addition of spikes was discussed with the participating laboratories at the start of the study and the decision made to supply samples with the analyte spikes already added. This approach has the advantage that the added analytes are in a "real" matrix and therefore the analytical procedures are tested under realistic conditions, although for several analytes (principally dichlorvos and malathion), there is the risk that decomposition will occur between spiking and analysis (n.b., in the "Aquacheck" analytical proficiency scheme, samples are supplied unspiked, but are accompanied by a spiking solution to be added before analysis).

Participants were recommended to take precautions to minimise the risk of loss of analytes to surfaces or to suspended solids, including washing the inside of the bottle with the solvent used for extraction and combination of the wash liquid with the extract(s) prepared subsequently. Advice was also given that filtration should be avoided, and that solvent or solid phase extraction, where carried out, should include any remaining suspended solids in the sample as supplied, or the filtered solids subject to a separate extraction. The leachate samples had been allowed to stand for some time before spiking and bottling to minimise the amount of suspended solids present in the supernate. The approach adopted with respect to filtration of the samples and treatment of suspended solids was discussed and agreed with both DoE and WRC.

The pure chemical standards used to make up the spike solutions are listed in Appendix 7, together with the concentrations in the mixed spike solutions. Wherever feasible, spikes were added as methanol or acetone solutions rather than in a solvent immiscible with water so that efficient mixing of spikes and samples could be obtained. The actual levels of the spikes added in the two round robins are listed in Appendix 8.

2.4.4 Organisation Of Round Robins

As each matrix was supplied both unspiked and spiked, each participant received a total of 28 or 32 sample bottles in the first round and 20 in the second round, taking into account the requirement for individual samples for each group of analyte. This required total volumes of each leachate of 136 litres in the first round, and 120 litres in the second. In practice, more than this was required to allow for breakages and repeat samples.

The sets of bottles were packed with suitable material (mainly polystyrene chips) to minimise breakage, and sent to the participating laboratories by courier. Typically, the participant received the sample within 1 - 3 working days of the spike addition. In the first round, a minimal number of breakages occurred, although some participants asked for more sample. In the second round, a commercial courier was used rather than AEA Transport Services, resulting in a greater number of breakages.

Participants were asked to return data within 15 working days, allowing a reasonable margin over the expected time scales since most had claimed 5 to 10 days turnaround on quotations. In the event, much longer time scales were encountered, particularly in the second round robin; in some cases, many telephone calls or fax communications were necessary before data was received.

3. RESULTS AND OBSERVATIONS

3.1 ANALYTICAL METHODS

Most laboratories identified the principal procedures they used as being "Blue Book"; in some cases, these were modified to take into account advances in technology (e.g. the use of GC-MS in place of GC-FID or -ECD in an original method). However, in some laboratories, it was claimed that "Blue Book" methods were used, but in fact vital steps had been omitted from the procedures to reduce the time required and the complexity of the methodology. The steps most often removed were the clean-up procedures.

Very few methods from other sources were used. Non-"Blue Book" methods were most often quoted for the metals, e.g. (i) several participants used a bromine oxidation/AFS approach for mercury which was based on a literature method (but also incorporated into a "Blue Book"), and (ii) cadmium determination by ICP-MS was often attributed to USEPA, although the methods actually used were usually simplified versions of the USEPA procedure.

The literature review revealed that very few practical methods are explicitly suitable for matrices as complicated as landfill leachate; USEPA methods, although highly regarded and well tested, are usually designed for water and a large dilution must be used before materials such as leachate can be analysed. This would, in most cases, raise (worsen) the detection limit to a level much above the EQS level required for this current study. Literature methods which were identified as potentially useful are referenced for each analyte in the analytical protocols in Appendix 12.

3.2 PARTICIPATION IN ANALYTICAL PROFICIENCY SCHEMES

Most laboratories claimed that they participated in one or more external analytical proficiency schemes (usually Aquacheck or Contest). However, despite repeated requests, few provided data which could be used to draw any useful conclusions about laboratory performance. Of the fifteen laboratories, NRA provided summary data for each region for most analytes, Severn Trent and AEA provided data for different rounds for some of the Red List analytes and Birmingham City Council provided data for cadmium only. All of the information provided referred to water analysis (Aquacheck) which may be of limited value in the present exercise, bearing in mind the apparent difference in performance between water and leachate analysis (see below). Virtually all of the data provided were within ±50% of the laboratory mean or WRC spike concentrations (Aquacheck).

3.3 ROUND ROBINS

The full data reported by the participants for the first and second round robins are tabulated in Appendix 9. Overall means and standard deviations for these data have been calculated, together with the spike levels for the samples #.2, #.4, #.6 and #.8 (# is the individual laboratory number and the second number identifies the sample). After rejection of overt outliers, a summary of the mean, standard deviation, median and spike values is given in Appendix 10 for each spiked sample. Although guidelines for the conduct of analytical proficiency schemes were followed wherever practicable (Thompson & Wood, 1993), the preliminary nature of this study and the limited quality of the data submitted by participants restrict any statistical interpretation to a quite basic level. Nevertheless, a comparison of spike levels for each analyte/sample with the number of positive results, the mean and median values and the errors on these values enables some conclusions to be drawn about analytical performance.

To assist in the evaluation of techniques between the first and second round robins, a simple and arbitrary scoring system was used, in which a reported value between one half and twice the spike level was regarded as correct. The most successful methodologies were selected on the basis of the score in the first round robin. These are summarised in Appendix 11 and form the basis (modified in the light of experience in the second round robin) of the recommended method for each analyte given in the analytical protocols in Appendix 12. Participants were asked to use these methods only in the second round robin, although in practice this meant little or no change in methodology for most of the more successful laboratories.

3.3.1 Accuracy

Using the above scoring system as a basis, the performance of each laboratory for the spiked samples is summarised in Table 1:-

Table 1: Laboratory Scores for Round Robins 1 & 2

Lab	#.2	#.4	Total RR 1	Rank RR 1	#.6	#.8	Total RR 2	Rank RR 2
1	1	1	2	15	6	2	8	6
2	15	9	24	4	3	3	6	10
3	14	14	28	2	5	4	9	3
4	4	1	5	11				
5	9	5	14	9	3	4	7	9
6	2	2	4	13	4	6	10	1
7	5	5	10	10	0	0	0	13
8	15	3	18	8	4	5	9	3
9	16	15	31	1	6	4	10	1
10	18	3	21	7	4	5	9	3
11	15	11	26	3	1	4	5	11
12	13	10	23	5	4	4	8	6
13	2	3	5	11	0	3	3	12
14	3	1	4	13				
15	13	9	22	6	4	4	8	6
Mean	9.7	6.1	15.8		3.4	3.7	7.1	

The potential maximum score per sample for a laboratory is between 20 and 30, although in many cases not all analytes were reported. Overall, there is a clear deterioration in performance as the matrix becomes more complicated, although against this trend two laboratories improved in the second round robin. The large number of "less than" values reported in the second round robin (in one case, for every analyte) was stated to be a direct consequence of the complexity of the matrix.

Successful analyses for each Red List analyte expressed as a score are listed in Table 2:-

Table 2: Analyses Scored "Correct" For Each Analyte

Compound	Round 1 #.2 (River Water)	Round 1 #.4 (Oxidised Leachate)	Round 2 #.6 (Fresh Leachate)	Round 2 #.8 (Fresh Leachate)
Hg + cmpnds	8	5	8	10
Cd + cmpnds	6	8	6	5
All hexachlorocyclohexanes	9	5	0	3
All DDTs	5	2	0	1
Pentachlorophenol	4	7	1	0
Hexachlorobenzene	10	6	0	2
Hexachlorobutadiene	0	1	0	0
Aldrin	7	3	2	2
Dieldrin	9	6	5	8
Endrin	5	6	3	8
PCB 118	8	5	0	0
PCB 153	8	3	0	1
PCB 180	1	2	0	0
PCB 28	7	2	0	0
PCB 52	6	4	1	0
Dichlorvos	4	1	1	0
1,2 Dichloroethane	0	0	0	0
Trichlorobenzenes	4	5	5	2
Atrazine	9	3	3	0
Simazine	8	1	3	0
TB Tins (µg/l)	2(2 Tot)	0(2 Tot)	1(Tot)	2(Tot)
TP Tins (µg/l)	1	1	0	0
Trifluralin	5	5	0	0
Fenitrothion	3	1	1	1
Azinphos-methyl	6	1	2	1
Malathion	4	2	0	2
Endosulfans	6	4	0	1

*Values are scored "correct" if between 50% and 200% of the spike value.

Wth the exceptions of Hg, Cd, dieldrin and endrin (and perhaps trichlorobenzene), a marked deterioration in accuracy is evident as the matrix becomes more complicated. For many compounds, the methods only appear to work for the spiked river water sample, and are too matrix-dependent without modification to be used for leachate.

Some of the poor performance for some compounds may be a consequence of decomposition. Analytes for which decomposition has been reported include azinphosmethyl, fenitrothion, malathion and dichlorvos (Barcelo, 1993, Nicholson and Blaine, 1992 and Smith, 1995). However, in a study to produce Red List substances storage protocols (Nicholson, Shaw & Blaine, 1992) and to assess the stability of these analytes in water and trade effluent, loss from solution was not found to be a problem, even for sensitive analytes such as malathion.

3.3.2 Limits of detection

Median limits of detection for each analyte are summarised in Table 3, based on the "less than" values given for the unspiked samples in the second round robin exercise. These values were higher than those quoted by participants during the initial, assessment phase of the study, but they are likely to be more realistic (most of the quoted values in the initial survey were only applicable to water and were over-optimistic as far as leachate was concerned). Median rather than mean values are given as the ranges for each analyte are very large, despite methods being the same or very similar. The table also includes an estimate of the percentage of laboratories able to meet EQS limit of detection requirements for each analyte.

Table 3: Limits of Detection in Leachate and EQS Targets (ng/l)

Compound	**Limit of Detection** (Median from estimates by Participants)	**EQS Target Value (Surface Waters Directive)**	**% of Participants Achieving EQS Target LODs**
Hg + cmpnds	400	5000	77
Cd + cmpnds	5000	1000	54
HCHs	20	100	69
DDTs	20	10	15
Pentachlorophenol	200	2000	46
Hexachlorobenzene	20	30	54
Hexachlorobutadiene	22.5	100	62
Aldrin	20	30	62
Dieldrin	20	30	69
Endrin	22.5	5	15
PCBs (each)	22.5	-	-
Dichlorvos	150	1	8
1,2 Dichloroethane	3500	10000	15
Trichlorobenzenes	100	400	77
Atrazine	125	2000	ca. 54
Simazine	100	(Combined)	ca. 54
TB Tins (µg/l)	90(Combined)	20	-
TP Tins (µg/l)		20	-
Trifluralin	20	100	77
Fenitrothion	100	10	8
Azinphos-methyl	100	10	8
Malathion	87.5	10	8
Endosulfans	40	3	8

It was not possible to calculate a limit of detection in some cases, resulting in an underestimation of the percentage of laboratories meeting the EQS limit of detection requirements in the last column of Table 3. However, there were many cases where laboratories did not detect analytes present at levels considerably higher than their stated limit of detection, casting doubt on the meaningfulness of laboratories' own estimates. This problem may stem in part from the solvent extraction recovery problem discussed elsewhere for organochlorine compounds. If the analyst has not seen a response for a particular analyte, the assumption has often been made that the level is below the known limit of detection for the method, although in fact the first part of the method (extraction) has broken down.

3.3.3 Blanks

Some values greater than zero were reported by participants for the unspiked leachates (#.3, #.5 and #.7). In part, these may be due to genuine levels of analyte actually present in the sample (eg Hg, Cd and TCB), but in other cases probably represent artefacts associated with high blanks and/or determination at levels close to the (real) detection limit (eg with PCPs, atrazine, simazine and organophosphorus compounds).

3.4 METHOD PERFORMANCE

The methods available for Hg (mainly bromination, followed by AFS) and Cd (wet digestion followed by ETV-AAS or better, ICP-MS) work well and are clearly applicable even to the most complicated of the leachate matrices used in the round robin studies. A majority of the values reported for these two elements were essentially correct, and the detection limits achieved met EQS criteria.

Methods for dieldrin, endrin and trichlorobenzene (extraction, cleanup, GC-ECD or better GC-MS) work well in some cases, although there is evidence that one of the leachates presented more difficult than the other. There is no indication that low recovery was responsible for the relatively minor difficulties experienced with these analytes, as mean and median values compare reasonably well with spike levels.

Methods for DDT, aldrin, HCB, HCH and PCBs appeared to experience recovery problems with the leachate matrix. Very low values were found for these analytes, even though few interferences were reported if GC-MS was used. The relatively simple modification to the methodology proposed in

Appendix 13 may solve this problem, although it needs evaluation in a further round robin.

The methods for atrazine, simazine, pentachlorophenol, the organophosphorus compounds and the organotins worked sporadically, but are clearly not robust enough for this matrix, indicating that method development or new methods are required for these compounds.

The methods available specifically for the volatile organic compounds were not shown in the first round robin to be sensitive enough to meet the original EQS (NRA) needs, and these analytes were excluded from the second round robin. However, the SWD EQS is less exacting for dichloroethane than the NRA proposed EQS, and existing purge and trap methods appear to be sensitive enough. This has not been tested in this study with "real" leachate and a further round robin may be required to assess whether the methods actually work for leachate. The other two "volatile organic compounds" are actually involatile enough to be analysable as part of the organochlorine group (hexachlorobutadiene, B.P. 220°C and trichlorobenzenes, B.P. 208-220°C) without recourse to other methods.

3.5 Laboratory Performance

Although it was not the objective of this work to test individual laboratories, some useful observations can be drawn from laboratory performance in the two round robins. There was a slight but significant correlation in the first round between laboratory score and low analytical cost, indicating perhaps that the laboratories handling the most samples (and therefore probably also the lowest cost) were also the most accurate and/or experienced.

Despite the second round being more difficult than the first, several laboratories clearly improved their performance against the trend, hopefully as a result of the method recommendations made to them at the conclusion of the first round robin. This demonstrates the value of this kind of study, and perhaps highlights the need for an analytical proficiency scheme which includes leachates as matrix, and gives expert feedback on methods as well as simply reporting performance.

The most important single factor responsible for the overall drop in performance between the first and second round robins was the failure of the methods used to extract organochlorine compounds such as HCB, HCH and PCBs. The method of compensating for this problem suggested in Appendix 13 should be tested on a wider range of compounds, and in different laboratories.

3.6 Other Observations

Most laboratories stated that meeting the turnaround times required for the round robins should not present a problem. However, the following turnaround times (working days) were recorded in practice:-

Round 1	(after excluding Public Holidays)		
	Mean	22	(St Deviation 6)
	Range	14 - 32	
Round 2	Mean	26	(St Deviation 10
	Range	14 - 48	

Despite most laboratories stating at the start of the study that they had methods which were appropriate for landfill leachates, the commonly-expressed view during round 2 was that the samples were "too difficult", and that methods were not really applicable. For this reason, some laboratories did not return results as such, but stated that analytes were undetectable. In round 2, about half of the laboratories required frequent telephone or fax enquiries before results were obtained. A contrast was noted between the (optimistic) statements often made by the person supplying the quotation that "leachate was just another aqueous sample" and the analysts, that leachate was a very difficult matrix for which they had no adequate experience or methods.

At several laboratories, the person responsible for the analysis appeared to change several times, making it quite difficult to discuss results with a suitably-informed person. At one laboratory (which is very proud of its NAMAS accreditation), enquiries were passed to the actual analyst who cheerfully admitted that he had no training or experience of analytical chemistry at all, that he had only started the job last week and that the most rudimentary technical enquiries would have to be passed to the head of laboratory. In contrast, at several other laboratories, the analysts were extremely knowledgeable and helpful, and made a considerable technical contribution to the study.

Samples for the first round robin were sent to laboratories using AEA Technology's own specialist transport services. For the second round robin, a commercial express courier was used, at a slightly lower cost. However, in contrast to the first round (one breakage), five sets of samples were damaged in the second round, and one laboratory needed three successive deliveries before a complete set of sample bottles was obtained.

4.0 RECOMMENDATIONS

The following recommendations can be drawn from this study:-

- Blue Book methods make an excellent basis for leachate analysis; it may be that in some cases, they should be updated to take into account improved technology and perhaps the requirements of a matrix such as leachate. Registration as formal standards is desirable to promote acceptance;
- the improved solvent extraction procedure suggested in this study to overcome the severe chemical effects induced by the leachate matrix should be tested in a further round robin;
- a wider range of internal standards and/or ^{13}C standards should be used by participants than at present, to allow for compound-to-compound differences in chemical behaviour. This may mean that some compounds not currently available should be synthesised for this purpose;
- method development is required for some compounds such as the organophosphorus pesticides, if EQS criteria are to be met;
- an analytical proficiency scheme for leachate analysis should be set up to give more confidence in the reliability of the analyses that are being performed.

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We would like to acknowledge with gratitude the contribution made by members of AEA's staff who helped in this study, including Grant Baldwin (provision of leachates), Alicia Fox (statistics), Peter Ambidge (organic analysis) and Janice Haines (inorganic analysis).

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
B.P.	Boiling Point
DCE	1,2 Dichloroethane
DCM	Dichloromethane
DDT	Dichlorodiphenyltrichloroethane
DoE	Department of the Environment
ECD	Electron Capture Detector
ETV	Electrothermal Vaporisation
FPD	Flame Photometric Detector (of GC)
GC	Gas Chromatography
GC-MS	Gas Chromatography - Mass Spectrometry
GC-MSD	Gas Chromatography - Mass Spectrometry Detector
GF	Graphite Furnace
HCB	Hexachlorobenzene
HCBut	Hexachlorobutadiene
HCH	Hexachlorocyclohexane (Lindane)
HPLC	High Performance Liquid Chromatography
ICP-AES	Inductively Coupled Plasma - Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
MS	Mass Spectrometry
MWt	Molecular Weight

NPD	Nitrogen Phosphorus Detector (of GC)
PCB	Polychlorinated biphenyl
PCP	Pentachlorophenol
SE	Solvent Extraction
SPE	Solid Phase Extraction
TCB	Trichlorobenzene
TBT	Tributyltin
TOC	Total organic carbon
TPT	Triphenyltin
WRC	Water Research Centre

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Mercury in waters, effluents, soils and sediments etc., additional methods (1985) ISBN 0 11 751907 3

Determination of very low concentrations of hydrocarbons and halogenated hydrocarbons in water, (1984-5) ISBN 0 11 752004 7

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Appendix 1: The Red List

Cadmium & compounds

Mercury & compounds

Tributyl Tin Compounds
Triphenyl Tin compounds

1,2 Dichlorethane
1,2,4 Trichlorobenzene (each congener)
Hexachlorobutadiene

Hexachlorocyclohexane (HCH or Lindane)
Hexachlorobenzene (HCB)
DDT isomers
Aldrin
Dieldrin
Endrin
Endosulfan I & II (total)
Trifluralin
Polychlorinated Biphenyls
(PCBs) each of 7 congeners

Dichlorvos
Fenitrothion
Azinphos-methyl
Malathion

Atrazine
Simazine

Pentachlorophenol & compounds (PCPs)

Appendix 2
Red List Environmental Quality Standards (EQS) Values

Substance(s)	**EQS *ex* NRA (P Smith) (ng/l)**	**EQS ex ENDS (Surface Waters Directive) (ng/l)**
Cadmium & compounds	500	5000
Mercury & compounds	100	1000
Tributyl Tin Compounds	20	20
Triphenyl Tin compounds	20	20
1,2 Dichlorethane	10	10000
1,2,4 Trichlorobenzene (each congener)	100	400
Hexachlorobutadiene	10	100
Hexachlorocyclohexane (HCH or Lindane)	10	100
Hexachlorobenzene (HCB)	10	30
DDT isomers	10/15	10
Aldrin	25	30
Dieldrin	25	30
Endrin	25	5
Endosulfan I & II (total)	10	3
Trifluralin	100	100
Polychlorinated Biphenyls (PCBs) each of 7 congeners	10	-
Dichlorvos	200/10	1
Fenitrothion	10	10
Azinphos-methyl	200	10
Malathion	150	10
Atrazine	300	Combined 2000
Simazine	300	
Pentachlorophenol & compounds (PCPs)	1000	2000

Appendix 3: Participating Laboratories

The participation of the following laboratories is gratefully acknowledged*:-

> ACER Environmental, Analytical & Environmental Services Ltd. (AES), Birmingham City Council, Clayton Environmental Consultants, ECoS, Exeter, Llanelli & Nottingham NRA Laboratories, Laboratory of the Government Chemist, SAC Scientific Ltd, Science & Technology Scientific Centre (Wessex Water), Severn Trent, Water Quality Centre (Thames Water), Yorkshire Environmental Ltd (Yorkshire Water).

*Identities were disguised by using a random laboratory number (1 - 15).

Other laboratories approached but not included in the intercomparison studies were:-

> Ashtact, Butterworth, Cleanaway, CSL MAFF, Creme & Warner, FUGRO, GEOCHEM Group, Institute of Terrestrial Ecology, Intera, Ove Arup, Scottish Agricultural College, Southern Science, University of Lancaster, Water Research Centre, WS Atkins.

Quoted Costs per Sample Analysed:

Round 1:

Average cost:-	£362	Range:-	£200 - £544

Round 2:

Average cost:-	£424	Range:-	£200 - £930

Appendix 4: Analytical Methods Survey Protocol

Analyte Group:

Lab:

Analytes (DoE Red List):

Hg + cmpnds ....
Cd + cmpnds ....
All hexachlorocyclohexanes ....
All DDTs ....
Pentachlorophenol ....
Hexachlorobenzene ....
Hexachlorobutadiene ....
Aldrin ....
Dieldrin ....
Endrin ....
Others ....
....
....

PCBs ....
Dichlorvos ....
1,2 Dichloroethane ....
Trichlorobenzenes ....
Atrazine ....
Simazine ....
TB Tins ....
TP Tins ....
Trifluralin ....
Fenitrothion ....
Azinphos-methyl ....
Malathion ....
Endosulfan ....

Scope of Method:

Water Leachate Effluent Other.....................

Collection And Storage of Sample:

Preparation Or Extraction Procedure,

Solvent Extraction S/ Phase Extraction Wet Digestion
Other.........

Measurement Technique & Procedure,

GC GC-MS AASF.less AAS HPLC ICP-AES ICP-MS Other……

Column, detector etc:

Standardisation eg internal, external etc:

Accuracy Attainable:

Precision of Method:

Limit of Detection:

Range of Method:

Known Interferences And Matrix Effects:

Status Of Method:

DoE
EPA
In-house: Provisional Tested
Other............

Quality Control

References:

Appendix 5: Summary of Methods Used for Each Analyte/Group (Derived from Methods Questionnaire)

Lab. No.	Mercury
1	AD/CV-AAS
2	AD/ICP-MS
3	H2SO4/Permanganate digestion/CV-AAS
4	CV-AAS
5	AD-CV-AFS
6	
7	Acidification, CV-AFS
8	Bromination/CV-AAS
9	Bromination/CV-AAS
10	Microwave digestion/Bromination/CV-AAS
11	Samples sent to ACER
12	AD/CV-AFS
13	CV-AFS
14	
15	Bromination/CV-AFS

Lab. No.	Cadmium
1	AD/ICP-AES
2	AD/ICP-MS
3	AD/GF-AAS
4	MM/GF-AAS
5	AD/GF-AAS
6	
7	Acidification/ICP-MS
8	AD/ICP-MS
9	AD (M-wave)/ICP-MS
10	AD (M-wave)/ICP-MS
11	AD/SE/AAS
12	AD/GF-AAS
13	AD/ICP-AES
14	
15	AD/GF-AAS

Lab. No.	Organochlorine Compounds
1	SE with DCM/GC-MS on DB5 column
2	SE with DCM or hexane or SPE/GC-MS
3	SE with DCM/solvent exchange to hexane/GC-ECD on BP5
4	SE with Hexane/alumina-AgNO3 cleanup, silica PCB separation/GC-ECd on DB608 or BP5
5	SE (?)/GC-ECD on BP5
6	
7	SE with hexane or SPE/GC-MS with BX5 or GC-ECD
8	SE with hexane/alumina column cleanup/GC-MS or GC-ECD on DB5 or DB50.
9	SE with hexane/Florisil cleanup/GC-MS on HP5
10	SE with DCM, alkaline cleanup/GC-MS on BPX5
11	SE with hexane/Concentration with Sneider column/GC-ECD on SE54 or GC-MS
12	SE with hexane/alumina column cleanup/GC-ECD with twin columns (DB5, DB17)
13	SE with ?/GC-MS on DB1
14	
15	SE with hexane/SP cleanup/GC-ECD with twin columns.

Lab. No.	Organophosphorus Compounds
1	As organochlorine compounds.
2	SE with DCM/GC-MS on DB5
3	SE with DCM/Exchanged to hexane/GC
4	SE with hexane or DCM/GC with flame thermionic detector on DB608
5	SE with ?/GC with flame photometric detector on BP5
6	
7	SPE or SE with hexane/GC-MS on BP5
8	SE with DCM, double with pH control, GC-NPD with dual columns (azinphos methyl GC-MS)
9	SE with ?/GC-FPD or -NPD or -MS
10	SE with DCM, double with pH control/GC-MS on BPX5
11	
12	SE with DCM/exchanged to hexane/GC-FPD on DB5 or DB17
13	SE with ?/GC-MS on DB1
14	
15	

Lab. No.	Triazines
1	As organochlorine compounds
2	As organophosphorus compounds
3	SE with DCM/HPLC on reverse phase C18 column with UV detection.
4	SE with DCM from alkaline solution/GC-nitrogen detector on DB608
5	SE with ?/GC-NPD on BP20
6	
7	SPE or SE with DCM after pH adjustment/GC-MS on BP5
8	As organophosphorus compounds
9	As organophosphorus compounds
10	SE with DCM/SE with DCM from alkaline solution/GC-MS on BPX5
11	SE from alkaline solution with DCM/GC-NPD on BP5
12	SE with DCM/GC-MS
13	SPE/HPLC-MS
14	
15	SPE/GC-MS on D5

Lab. No.	**Volatile Organic Compounds**
1	1,2 DCE SE into iso-octane/GC-MS on DB5
2	TCB and HCBut as organochlorine compounds
3	Purge & Trap/GC-Ion Trap MS
4	Purge & Trap/GC-RCD on DB624
5	Purge & Trap/GC-MS or SE GC-ECD on BP5
6	
7	As organochlorine compounds
8	Purge & Trap/GC-ECD or -FID, photoionization.
9	Headspace analysis on JW624
10	Purge & Trap/GC-MS on DB624 or CPSil5 or Headspace GC-MS on DB624
11	SE with DCM or pentane/GC-ECD on BP5
12	1,2 DCE by Headspace analyser with ECD
13	Purge & Trap/GC-MS on DB1
14	
15	Headspace/GC-MS on JW DB624

Lab. No.	**Pentachlorophenol & Compounds**
1	SE with hexane/diazomethane derivatisation/GC-MS on DB5
2	As organochlorine compounds
3	Se with hexane/diazomethane derivatisation/GC-MS on DB5
4	SE with diethylether/methylation/GC-ECD on DB608 or DB624
5	SE with ?/pentafluorobenzoxyl chloride/GC-ECD on BP5
6	
7	SE with ?/? derivatisation/GC-ECD on CP8CB
8	SE & derivatisation with acetic anhydride and hexane/GC-ECD with dual columns (DB5 & DB50)
9	As 8
10	SE with diisopropylether/diazomethane derivatisation/GC-MS on phenylmethyl silicone column.
11	SE with DCM/GC-MS on HP5 or SE54
12	SE with diethylether/diazomethane derivatised/GC-MS
13	
14	
15	SE & acetylation/GC-MS on DB5

Lab. No.	**Organotin Compounds**
1	None
2	SE with toluene/AD ICP-MS (Total)
3	SE with toluene/AAS (Total)
4	SE with toluene/GF-AAS (Total)
5	SE/Grignard derivatisation/GC-Ion Trap on BP5
6	
7	SE with toluene/HPLC-ICP-MS
8	SE with hexane & tropolone/Grignard derivatisation/GC-FPD with tin filter
9	SE/Grignard derivatisation/GC-FPD or as 8
10	SE?/GF-AAS? (Total)
11	SE with toluene/GC-MS (Total)
12	SE with toluene, pentane & acetic acid/GF-AAS
13	SE/GC-MS with DB1
14	
15	SE with toluene/GF-AAS

A space implies that the information was not available.

Appendix 6: Parameters of Leachates & Riverwaters

	Riverwater	**Leachate (Oxidised)**	**Leachate (Cell 2)**	**Leachate (Cell 6)**
TOC (mg/l)	20	490	450	660
pH	8.41	8.05	8.62	8.54
Fe (mg/l)	<	2.3	2.3	2.4
Ca (mg/l)	110	70	20	25
K (mg/l)	5	400	950	850
Mg (mg/l)	5	38	100	83
Na (mg/l)	26	680	1100	1100
S (mg/l)	24	29	19	31
Si (mg/l)	5.5	20	29	32

Appendix 7: Source of Standard Materials

Analyte	Starting Material (P = Pure, S = Solution)	Working Solution (mg/l)	Spike Solution
Mercury	S (BDH, 1 g/l)	2	A
Cadmium	S (BDH, 1 g/l)	10	A
Tributyltins	P (Chem Services)	1000 and 1	B
Triphenyltins	P (Chem Services)	1000 and 1	B
1,2 Dichloroethane	P (May & Baker)	1000	C
1,2,4 Trichlorobenzene	P (Ultra Scientific)	246	C
Hexachlorobutadiene	P (Hopkin & Williams)	246	C
Hexachlorocyclohexane	P (ChemService)	1000	C
Hexachlorobenzene	P (Ultra Scientific)	1000	C
DDTs	P (Supelco)	492	C
Aldrin, Dieldrin & Endrin	P (Supelco)	250/500	C
Endosulfan I & II	P (Supelco)	500	C
Trifluralin	P (Labor Dr Ehrensdorfer)	400	C
PCBs	P (Labor Dr Ehrenstorfer)	100	D
Dichlorvos	P (Supelco)	500	E
Fenitrothion	P (Chem Services)	250	E
Azinphos-methyl	P (Labor Dr Ehrenstorfer)	500	E
Atrazine & Simazine	P (Labor Dr Ehrenstorfer)	500	E
Pentachlorophenols	P (Chem Sevices)	1000	F

Appendix 8: Spike Levels Used For The Intercomparison Materials

Substance(s)	#.2 (ng/l)	#.4 (ng/l)	#.6 (ng/l	#.8 (ng/l)
Cadmium & compounds	1190	1980	1500	4000
Mercury & compounds	100	240	300	800
Tributyl Tin Compounds	58000	92800	60	160
Triphenyl Tin compounds	52500	84000	60	160
1,2 Dichlorethane	25	40	30	80
1,2,4 Trichlorobenzene (each congener)	250	400	300	800
Hexachlorobutadiene	25	40	30	80
Hexachlorocyclohexane (HCH or Lindane)	25	40	30	80
Hexachlorobenzene (HCB)	25	40	30	80
DDT isomers	31	50	45	120
Aldrin	62	100	75	200
Dieldrin	62	100	75	200
Endrin	92	100	75	200
Endosulfan I & II (total)	25	40	30	80
Trifluralin	250	400	300	800
Polychlorinated Biphenyls (PCBs) each of 7 congeners	25	40	30	80
Dichlorvos	500	800	1600	600
Fenitrothion	25	40	80	30
Azinphos-methyl	489	783	1600	600
Malathion	375	599	1200	450
Atrazine	748	1197	2400	900
Simazine	707	1131	2400	900
Pentachlorophenol & compounds (PCPs)	2388	3980	8000	3000

APPENDIX 9: Round Robin 1 & 2 Data

	1.1	2.1	3.1	4.1	5.1	6.1	7.1	8.1	9.1	10.1	11.1	12.1	13.1	14.1	15.1	Mean	St Dev
Hg	180	<	<	<	<	<	<	<	30	33	<	<	<	<	<	81	86
Cd	<	530	730	1800	<	<	450	<	430	450	<	<	<		<	732	535
HCH gamma	<	<	<	4	<	<	<	6.7	9	<	<	<	<	900	6	185	400
DDT	<	<	70	<	<	<	<	<	<	<	<	<	<		<	70	
PCPs	<	590	104		300	<	<	88	<	68	<	<	<		140	215	202
HCB	<	<	<	4	<	<	<	<	<	<	<	<	<		<	4	
HC But	<	<	<	<	<	<	<	<	<	<	<	<	<		<		
Aldrin	<	<	20	<	<	<	<	<	<	<	<	<	<		<	20	
Dieldrin	<	<	30	5	<	<	<	<	<<	<	<	<	<		<	18	18
Endrin	<	<	30	<	<	<	<	<	<	<	<	<	<		<	30	
Tot PCB	<	<	<	<		<	<	<	<	<	<	<	<		<		
PCB 101	<	<	<		<		<	<	<	<	<	<	<		<		
118	<	<	,		<		<	<	<	<		<	<		<		
138	<	<	<		<		<	<	<	<		<	<		<		
153	<	<	<		<		<	<	<	<		<	<		<		
180	<	<	<		<		<	<	<	<		<	<		<		
28	<	<	<		<		<	<	<	<		<	<		<		
52	<	<	<		<		<	<	<	<		<	<		<		
Dichlorvos	<	<	<	<		20	80	<	<	<	<	<	<		<	50	42
Dichlorethane	<	<	<	<	<	<	960	<	<	<	<	<	<		<	960	
TCB 123	<	<	<	<	<		<	<	<	<	<	<	<		<		
124	<	<	<		<		<	<	<	<	<	<	<		<		
135	<	<	<		<		<	<	<	<	<	<	<		<		
Tot TCB	<	<	<	<		<	<	<	<	<	<	<			<		
Atrazine	<	38	<	<	100	30	60	47	<	53	<		50		50	54	21
Simazine	<	13	<	<	<	30	30	<	<	34	<	<	30		20	26	8
Tot Org ins(x2.7)	<		220				<	<	<	122	<	<			2300	881	1230
TP Tins	<		<		<	<		<	<	<	<			<	<		
TB Tins	<		<		<	<		<	9	<	<		<	350	<	180	241
Trifluralin	<	<	30	<	<	<	<	<	<	<	<	<	<		<	30	
Fenitrothion	<	<	<	<	<	<	<	<	<	<	<		<		<		
Azinphos-methyl	<	<	<		<	<	<	<	<	<	<	<	<		<		
Malathion	<	<	<	<	<	<	<	<	<	<	<	<	<		<		
Endosulfan a	<	<	40	<	<	<	<	<	<	<	<		<		<	40	
End Total	<								<	<	<						

	1.2	2.2	3.2	4.2	5.2	6.2	7.2	8.2	9.2	10.2	11.2	12.2	13.2	14.2	15.2	*Mean*	*Std Dev*	*Spike*
Hg	170	<	320	<	<	<	<		230	250	230	200	<	300	270	246	50	240
Cd	<	1800	2200	4400	<	<	3300		1650	1680	<	2200	<	1700	<	2366	986	1190
HCH gamma	<	40	<	23	24	<	<	30	28	28	36	13	<		30	28	8	25
DDT	<	19	90	<	10	<	<	16	8	21	27	<	<		45	30	27	31
PCPs	2560	746	2400		2100	<	510	1940	3030	1387	280	2200	140		2700	1666	1015	1000
HCB	<	21	20	28	22	<	<	37	45	33	34	31	<		30	30	8	25
HC But	<	6	<	<	<	<	<	8.5	<	<	<	<	<		8	8	1	25
Aldrin	<	21	50	14	40	55	<	34	48	29	33	15	<		38	34	14	62
Dieldrin	<	46	70	<	40	76	<	43	55	46	46	24	<		44	49	15	62
Endrin	<	31	70	<	50	<	60	43	53	45	53	36	<		45	49	11	92
Tot PCB	<			1000		<							<			1000		=125
PCB 101	<	<	<		<		<	<	<	<	<	<	<		<			
118	<	17	40		<		<	25	25	17	35	16	<		32	26	9	25
138	<	<	<		<		<	<	<	<	<	<	<		<			
153	<	24	40		10		<	29	20	18	45	19	<		37	27	12	25
180	<	10	<		10		<	12	<	8	<	<	<		15	11	3	25
28	<	13	20		<		<	<	30	17	30	13	<		26	21	7	25
52	<	11	<		<		<	23	26	14	31	15	<		22	20	7	25
Dichlorvos	<	423	290	80		<	3220	330	223	320	112	<	<		1100	678	999	500
Dichlorethane	<		<	<	<	<	1000	<	<	<	<		<		<	1000		25
TCB 123	<		<	<			<	<	<	<	26		<		<	26		
124	<	82	<				150	112	<	13	170	158	<		<	114	59	250
135	<		<				<	<	<	<	20		<		<	20		
Tot TCB	<			<	80	<							<	190		135	78	=250
Atrazine	<	660		950	380	170	1190	574	1080	784	360	370	580		770	656	313	748
Simazine	<	634		2600	280	50	1820	643	1410	1003	750	500	410		820	910	718	707
Tot Org Tins	<		1E+05							67500					12530	63343	48868	=110000
TP Tins	410				62000	<		33000			550			1200		19432	27599	52500
TB Tins	1800				26000	<		35000	15700		560		20880	3900		14834	13303	58000
Trifluralin	<	41	180	<	120	<	<	6.4	211	172	180	152	<			133	73	250
Fenitrothion	<	26	20	<		10	140	<	<	13	<		<		<	42	55	25
Azinphos-methyl	<	370	670		150	20	300	424	320		171	400	<		4500	733	1336	490
Malathion	<	455	150	<	300	30	4540	163	171	157	56	200	<		220	586	1316	375
Endosulfan a	<		40	26			60	6.4	9	15	<		<		<	26	21	25
End Total	<				50	70			17		25					41	24	=25

	1.3	2.3	3.3	4.3	5.3	6.3	7.3	8.3	9.3	10.3	11.3	12.3	13.3	14.3	15.3	Mean	St Dev
Hg	2400	<	110	<	<	<	<		70		280	<	<			715	1127
Cd	<	800	1200	7000	<	<	350		730	770	<	3200	<	700		1844	2263
HCH gamma	<		<	<	<	<	<	4	<	<		<	<		5	5	1
DDT	<		40	<	<	<	<	0.5	<	<		<	<			20	28
PCPs	<		230		<	<	140	79	63	232		270	<		200	173	81
HCB	<		<	<	<	<	<	<	<	<		<	<				
HC But	<		<		<	<	<	<	<	<		<	<				
Aldrin	<		<	<	<	<	<	<	<	<		<	<				
Dieldrin	<		20	<	<	<	<	6.3	<	<		15	<			14	7
Endrin	<		20	<	<	<	<	<	<	<		<	<			20	
Tot PCB	<			1300		<	<			<			<			1300	
PCB 101	<	40	40		<		<	20	75	<	89	33	<		17	45	27
118	<	4	30		<		<	15	40	<	77	24	<		11	29	24
138	<	4	20		<		<	11	<	<	79	18	<		<	26	30
153	<	3	<		<		<	10	40	<	49	15	<		<	23	20
180	<	11	<		<		<	<	<	<	25	<	<		<	18	10
28	<	14	20		<		<	<	150	<	1900	63	<		54	367	753
52	<	6	<		<		<	33	74	<	88	54	<		30	48	30
Dichlorvos	<		30	<	<	<	<	10	<	<		<	<			20	14
Dichlorethane	<		<	<	<	<	1600	<	<	<		<	<			1600	
TCB 123	<		<		<		<	<	<	<	28		<			28	
124	<		<	<	<		<	<	<	<		<	<				
135	<		<		<		<	<	<	<			<				
Tot TCB	<				90	<	<		<	2150			<			1120	1457
Atrazine	<	51			<	60	<	<	<	2150		<	100			590	1040
Simazine	<	42			<	68	<	159	<	<	3900	800	20			832	1532
Tot Org Tins	<		1680				<			245					780	902	725
TP Tins	<				<	<	<	<		<	<			5800		5800	
TB Tins	<				<	<	<	210	<	<	<		8340	<		4275	5749
Trifluralin	<		20	<	<	117	<	<	<	<	<	<	<			69	69
Fenitrothion	<		60	<	<	<	<	<	<	<			<			60	
Azinphos-methyl	<		30		<	<	<	<	<	<		<	<			30	
Malathion	<		<	<	<	<	<	<	<	<		<	<				
Endosulfan a	<		30	<	<		<	<	<	<		<	<			30	
End Total	<					74										74	

	1.4	2.4	3.4	4.4	5.4	6.4	7.4	8.4	9.4	10.4	11.4	12.4	13.4	14.4	15.4	Mean	St Dev	Spike
Hg	<	<	350	400	900	<	<		350		<	200	<		350	425	242	400
Cd	<	2700	3400	12800	1900	<	2200		2400	2600	<	1300	<	2600	<	3544	3519	1980
HCH gamma	<		20	<	40	<	<		53	<	47	<	<		42	40	12	40
DDT	<		50	<		<	<		<	<	64	<	<		20	45	22	49.5
PCPs	4590	220	3200		1700	<	1890	3540	4070	1819	150	3600	2990		2800	2547	1418	3980
HCB	<	19	30	<	30	<	<		66	<	61	48	<		33	41	18	39.6
HC But	<	20	<	<	<	<	<		<	<	<	<	<		9	15	8	39.9
Aldrin	<		40	<	<	60	<		62	<	62	22	<		20	44	20	100
Dieldrin	<		60	<	<	60	<		88	<	83	62	<		67	70	12	100
Endrin	<		60	<	<	<	80		73	<	79	59	<		62	69	10	100
Tot PCB	<					<				<			<					=200
PCB 101	<	70	60		<		<		77	<	34	37	<		20	50	23	
118	<	80	60		<		<		63	<	94	45	<		23	61	25	40
138	<	55	30		<		<		<	<	73	21	<		10	38	26	
153	<	90	40		<		<		56	<	85	32	<		13	53	30	40
180	<	33	<		<		<		<	<	28	<	<		<	31	4	40
28	<	70	40		<		<		182	<	<	83	<		82	91	54	40
52,	<	60	<		<		<		110	<	71	75	<		50	73	23	40
Dichlorvos	<		350	7800		30	<	170	970	<	<	<	<		10700	3337	4682	800
Dichlorethane	<		<	<	<	<	1700	<	<	<	<	<	<			1700		40
TCB 123	<		<			<	<		<	<	<		<					
124	<	330	<				250		<	<	570	505	<			414	149	400
135	<		<				<		<	<	<		<					
Tot TCB	<			<	280	<				<			<			280		=400
Atrazine	<	52			60	306	<	966	2430	2400	<	380	970		2900	1163	1120	1200
Simazine	<	30			60	490	<		3310	8100	4200	570	610		3500	2319	2716	1200
Tot Org Tins	<		1E+05							1E+05			<		15400	97467	71158	=180000
TP Tins	<				11000	<		29900		<	<		<	2800		14567	13898	84000
TB Tins	210				45000	<		84700	2380	<	<		32990	7200		28747	32823	92800
Trifluralin	<	276	170	<	220	<	280		306	<		<	<		226	246	50	400
Fenitrothion	<		60	90	<	<	<	<	<	<	260		<			137	108	40
Azinphos-methyl	<	360	30		100	<	<	<	1090	<	<	<	<			395	485	783
Malathion	<	530	60	110	<	<	<	195	325	<	<	<	<			244	189	600
Endosulfan a	<		30	<	<		70		58	<	31	<	<		10	40	24	40
End Total	<					250			110		81					147	90	=40

	1.5	2.5	3.5	4.5	5.5	6.5	7.5	8.5	9.5	10.5	11.5	12.5	13.5	14.5	15.5	Mean	St Dev
Hg	400	1000?	190		<	170		120	140	220	<	400	<		170	226	111
Cd	<	250	3600		1800	<		500	674	790	<	1700	<		<	1331	1161
HCH gamma	<	<	<		<		<	0.9	<	<	<	39	<		<	20	27
DDT	<	<	<		<	<	<	<	<	<	<	<	<		<	#DIV/0!	#DIV/0!
PCPs	<				4400	5	<	<	<	<	<	<	<		<	2203	3108
HCB	<	2			<		<	1.2	<	<	<	<	<		<	2	1
HC But	<	<	<		<		<	<	<	<	<	<	<		<	#DIV/0!	#DIV/0!
Aldrin	<	<	<		<	<	<	<	<	<	<	<	<		<	#DIV/0!	#DIV/0!
Dieldrin	<	<	<		<	<	<	<	<	<	<	210	<		<	210	#DIV/0!
Endrin	<	<	<		<	<	<	<	<	<	<	<	<		<	#DIV/0!	#DIV/0!
Tot PCB	<					<	<	<		<			<			#DIV/0!	#DIV/0!
PCB 101	<		<		<		<	<	<	<	<	<	<		<	#DIV/0!	#DIV/0!
118	<	<	<		<		<	<	<	<	<	<<	<		<	#DIV/0!	#DIV/0!
138	<	<	<		<		<	<	<	<	<	<	<		<	#DIV/0!	#DIV/0!
153	<	<	<		<		<	<	<	<	<	<	<		<	#DIV/0!	#DIV/0!
180	<	<	<		<		<	<	<	<	<	<	<		<	#DIV/0!	#DIV/0!
28	<	4	<		190		<	<	<	<	<	<	<		<	97	132
52	<		<		<		<	<	<	<	<	<	<		<	#DIV/0!	#DIV/0!
Dichlorvos	<	<	240		<	<	<	<	<	9.5	<	<	<		<	125	163
Dichlorethane	10000				<		<	<	<	<		<	<		<	10000	#DIV/0!
TCB 123		27	<		<		<	<	<	<	<	<	<		<	27	#DIV/0!
124		161	<		<		<	642	630	150	190	320	40		<	305	241
135		48	<		<		<	<	<		100		<		<	74	37
Tot TCB	170				<		<	<	<				<		<	170	#DIV/0!
Atrazine	<	<	<		<	<	<	<	<	<	<	<	<		<	#DIV/0!	#DIV/0!
Simazine	<	<	38000		<	<	<	<	<	<	<	<	<		<	38000	#DIV/0!
Tot Org Tins###	<	2900?			<	<	<	<		<		120	<		920	520	566
TP Tins					<			<	<				<			#DIV/0!	#DIV/0!
TB Tins					<			<	<				<			#DIV/0!	#DIV/0!
Trifluralin	<	<	<		<	<	<	<	<	<	<	<	<		<	#DIV/0!	#DIV/0!
Fenitrothion	<	<	100		<	<	<	<	<	<	<	<	<		<	100	#DIV/0!
Azinphos-methyl	<		2100		<	<	<	<	<	<	<	<	<		<	2100	#DIV/0!
Malathion	<	<	40		<	<	<	<	<	<	<	<	<		<	40	#DIV/0!
Endosulfan a	<	<	<		<	<	<	4	<	<	<	<	<		<	4	#DIV/0!
End Total		<													<	#DIV/0!	#DIV/0!

	1.6	2.6	3.6	4.6	5.6	6.6	7.6	8.6	9.6	10.6	11.6	12.6	13.6	14.6	15.6	Mean	Std Dev	Spike
Hg	440	1000	400		<	750		500	360	380	<	300	2E+05		420	19455	59924	300
Cd	<	1700	2500		1500	<		2000	1990	2080	<	<	<		<	1962	343	1500
HCH gamma	<	<	<		<		<	<	<	107	<	<			<	107	#DIV/0!	30
DDT	<	<	<		<	11	<	<	<	20	<	<			<	16	6	45
PCPs	<		590		4700	108	<	<	<	22	<	<			<	1355	2244	8000
HCB	<	2			<		<	1	<	<	<	<			<	2	1	30
HC But	<	<			<		<	<	<	<	<	<			<	#DIV/0!	#DIV/0!	30
Aldrin	<	96	<		<	114	<	5	<	<	<	<			<	72	58	75
Dieldrin	74	271	<		30	80	<	50	<	277	<	93			56	116	99	75
Endrin	<	617	<		<	101	<	40	<	201	<	78			<	207	237	75
Tot PCB	140		<		<	50	<	<	<		<	<				95	64	
PCB 101		3	<		<		<	<	<	5	<	<			<	4	1	
118		5	<		<		<	<	<	<	<	<			<	5	#DIV/0!	30
138		3	<		<		<	<	<	4	<	<			<	4	1	
153		8	<		80		<	<	<	12	<	<			<	33	40	30
180		3	<		<		<	<	<	3	<	<			<	3	0	30
28		10	<		350		<	<	<	<	<	<			<	180	240	30
52		5	<		<		<	<	<	39	<	<			<	22	24	30
Dichlorvos	<	<	800		<	22	<	<	<	4.9	<	<			<	276	454	1600
Dichlorethane	<				<		<	<	<	<	<	<			<	#DIV/0!	#DIV/0!	30
TCB 123		22	<		<		<	<	120		<	<			<	71	69	
124		185	<		<		<	1140	170	306	280	520			<	434	368	300
135		26	<		<		<	<	<		<	<			<	26	#DIV/0!	
Tot TCB	260				<		<	<	<							260	#DIV/0!	300
Atrazine	2170	66	<		200	150	<	<	2040	<	150	<			2300	1011	1088	2400
Simazine	1340	32	48000		1600	100	<	<	<	235	370	<			2800	6810	16671	2400
Tot Org Tins	<	2600?			<	300	<	<		<		280	<		420	333	76	
TP Tins	<				<			<	<			<				#DIV/0!	#DIV/0!	60
TB Tins					1600			<	36			<				818	1106	60
Trifluralin	<	<	<		<	20	<	<	<	<	<	<			<	20	#DIV/0!	300
Fenitrothion	<	<	120		<	10	<	<	<	<	<	<	<		<	65	78	80
Azinphos-methyl	<		2300		720	20	<	<	1680	<	<	<			<	1180	1010	1600
Malathion	<	<	<		<	60	<	<	<	<	<	<			<	60	#DIV/0!	1200
Endosulfan a	<	<	<			<	<	4	<	<	<	<	<		<	4	#DIV/0!	30
End Total		<			180					164						172	11	

	1.7	2.7	3.7	4.7	5.7	6.7	7.7	8.7	9.7	10.7	11.7	12.7	13.7	14.7	15.7	Mean	St Dev
Hg	<	1000	190		<	400		120	130	390	<	<	<		150	340	314
Cd	<	250	1100		1000	<		<	493	600	<	1200	<		<	774	380
HCH gamma	<	<	<		<		<	1	<	<	<	<	<		<	1	####
DDT	<	<	<		<	7	<	1	<	<	<	<	<		<	4	4
PCPs	<		460		8000	55	<	<	<	<	<	<	<		<	2838	4475
HCB	<	<	<		<		<	<	<	<	120	<	<		<	120	####
HC But	<	<			<		<	3	<	<	<	<	<		<	3	####
Aldrin	<	<	<		<	6	<	3	<	<	<	<	<		<	5	2
Dieldrin	<	<	<		<	<	<	<	<	<	<	<	<		<	####	####
Endrin	<	<	<		<	50	<	<	<	<	<	<			<	50	####
Tot PCB	<		<		<	<	<	<	<	<	<		<		<	####	####
PCB 101		<	<		<		<	<	<	<	<	<	<		<	####	####
118		<	<		<		<	<	<	<	<	<	<		<	####	####
138		<	<		<		<	<	<	<	<	<	<		<	####	####
153		<	<		<		<	<	<	<	<	<	<		<	####	####
180		<	<		<		<	<	<	<	<	<	<		<	####	####
28		7	<		<		<	<	<	<	<	<	<		<	7	####
52		<	<		<		<	<	<	<	<	<	<		<	####	####
Dichlorvos	<	<	50		<	<	<	<	<	21	<	<			<	36	21
Dichlorethane	<	<			<		<	<	<	<	<	<			<	####	####
TCB 123	<	31			<		<	<	<	<	<		<		<	31	####
124	<	48			<		<	135	240	28	<	45	20		<	86	86
135	<	10			<		<	<	<	<	<		<		<	10	####
Tot TCB	<				<		<	<	<	<	<				<	####	####
Atrazine	<	<	16000		<	20	<	<	<	<	<	<			<	8010	11300
Simazine	<	<	79000		<	<	<	<	<	<	150	<			<	39575	55755
Tot Org Tins	<	1800			<	<	<	<		<		640	<		240	893	810
TP Tins	<				<			<	<	<					<	####	####
TB Tins	<				<			<	<	<					<	####	####
Trifluralin	<	<	<		<	<	<	<	<	<	<	<			<	####	####
Fenitrothion	<	<	100		<	<	<	<	<	<	<	<			<	100	####
Azinphos-methyl	<	<	1600		<	<	<	<	<	<	650	<			<	1125	672
Malathion	<	<	540		<	<	<	<	<	<	<	700			<	620	113
Endosulfan a	<	<	<		<	<	<	<	<	<	<	<			<	####	####
End Total		<													<	####	####

	1.8	2.8	3.8	4.8	5.8	6.8	7.8	8.8	9.8	10.8	11.8	12.8	13.8	14.8	15.8	Mean	St Dev	Spike
Hg	700	1700	960		1400	1010		900	740		<	400	90000		440	9825	28173	800
Cd	<	10000	4800		23000	1760		4500	3640	3950	<	2500	<		<	6769	7010	4000
HCH gamma	<	<	110		<		<	3	378	61	<	<	<		71	125	147	80
DDT	<	<	<		<	104	<	8	<	<	<	<	<		<	56	68	120
PCPs	460		370		9400	551	<		<	<	20	<			<	2160	4052	3000
HCB	<	32			<		<	36	<	64	140	<	<		37	62	46	80
HC But	<	<			<		<		361	<	<	<	30		22	138	193	80
Aldrin	90	#	20		<	451	<	13	103	14	<	<	103		19	102	147	200
Dieldrin	160	247	80		40	113	<	177	609	387	230	<	360		173	234	164	200
Endrin	<	178	80		<	201	<	182	290	392	230	<	360		181	233	98	200
Tot PCB	<		<		<	110	<				<					110	#DIV/0!	
PCB 101		1	<		<		<		<	2	<	<	<		<	2	1	
118		7	<		<		<		<	20	<	<	<		<	14	9	80
138		<	<		<		<		<		<	<	<		<	#DIV/0!	#DIV/0!	
153		9	<		110		<		<	11	<	<	<		<	43	58	80
180		4	<		<		<		<	30	<	<	<		<	17	18	80
28		18	<		<		<		<	21	<	<	<		<	20	2	80
52		9	<		<		<		<	17	<	<	<		<	13	6	80
Dichlorvos	<	<	250		<	50	<		<	6.2	<	<			<	102	130	600
Dichlorethane	<				<		<		<	<	<	<			<	#DIV/0!	#DIV/0!	80
TCB 123		15			<		<		<		<	<	10		<	13	4	
124		65			<		<	1465	260	331	520	110			<	459	519	800
135		7			<		<		<		<				<	7	#DIV/0!	
Tot TCB	370				<		<				<					370	#DIV/0!	
Atrazine	<	68	28000		<	230	<		<	<	<	<			<	9433	16080	900
Simazine	<	120	1E+05		<	220	<		<	<	<	<			<	33447	57637	900
Tot Org Tins	<	1800			<	400	<			<		880	<		1100	1045	582	=320x
TP Tins					<				<							#DIV/0!	#DIV/0!	160
TB Tins					<				26							26	#DIV/0!	160
Trifluralin	<	4	110		<	50	<	13	<	<	<	<	<		<	44	48	800
Fenitrothion	<	<	90		<	30	<		<	<	<	<	<		<	60	42	30
Azinphos-methyl	<		1900		790	30	<		<	<	<	<			<	907	940	600
Malathion	<	<	390		<	80	<		<	<	<	700			<	390	310	450
Endosulfan a	<	<	<		<	30	<	4	<	<	<	<	<		<	17	18	80
End Total	<	<			60											60	#DIV/0!	

Appendix 10: Mean, Median & Spike Values, and Summary Statistics.

Riverwater Compound	Total Number of Results	Number of below threshold results	Number of outlier results	N	Mean	Standard Deviation	SE Mean	Median	Spike	Median as % of spike
	TOTAL VALUES			Values above threshold, excluding outliers						
Hg	14	6	0	8	246.25	49.84	17.62	240	240	100%
Cd	14	6	0	8	2366.25	986.46	348.77	2000	1190	168%
HCH gamma	14	5	0	9	28	7.76	2.59	28	25	112
DDT	14	6	0	8	29.5	27.03	9.56	20	31	64.5%
PCPs	13	1	0	12	1666.08	1014.73	292.93	2020	1000	202%
HCB	14	4	0	10	30.1	7.81	2.47	30.5	25	122%
HC_but	14	11	0	3	7.5	1.32	0.76	8	25	32%
Aldrin	14	3	0	11	34.27	13.78	4.16	34	62	55%
Dieldrin	14	4	0	10	49	14.91	4.71	46	62	74%
Endrin	14	4	0	10	48.6	11.33	3.58	47.5	92	52%
PCB 118	12	4	0	8	25.88	9.08	3.21	25	25	100%
PCB 153	12	3	0	9	26.89	11.67	3.89	24	25	96%
PCB 180	12	7	0	5	11	2.65	1.18	10	25	40%
PCB 28	12	5	0	7	21.29	7.43	2.81	20	25	80%
PCB 52	12	5	0	7	20.29	7.20	2.72	22	25	88%
Dichlorvos	13	4	2	7	254	123.42	46.65	290	500	58%
Dichlorethane	12	11	-	1	1000	-	-	1000	25	4000%
TCB 123	10	9	-	1	26	-	-	26	-	-
Data 124	11	5	0	6	114.17	59.32	24.22	131	250	52.4%
Data 135	9	8	-	1	20	-	-	20	-	-
Tot TCB	6	4	0	2	135	77.8	55	135	=250	54%
Atrazine	13	1	0	12	656	313	90	620	748	83%
Simazine	13	1	0	12	910	718.5	207.4	696.5	707	99%
Tot Org Tins	4	1	0	3	63343	48868	28214	67500	=110000	61%
TP_tins	6	1	0	5	19432	27599	12343	1200	52500	2%
TB_tins	8	1	0	7	14834	13303	5028	15700	58000	27%
Trifluralin	13	5	0	8	132.8	72.75	25.72	162	250	65%
Fenitrothion	12	7	1	4	17.25	7.18	3.59	16.5	25	66%
Azinphos-methyl	12	2	1	9	313.89	188.21	62.74	320	490	65%
Malathion	14	3	1	10	190	120.49	38.1	167	375	45%
Endosulfan	10	4	0	6	26.07	20.72	8.46	20.5	25	82%
End_total	5	1	0	4	40.5	24.17	12.09	37.5	=25	150%

Stab. Leachate Compound	Total Number of Results	Number of below threshold results	Number of outlier results	N	Mean	Standard Deviation	SE Mean	Median	Spike	Median as % of spike
	TOTAL VALUES			Values above threshold, excluding outliers						
Hg	12	6	1	5	330	75.83	33.91	350	400	87.5%
Cd	14	5	1	8	2387.5	617.45	218.30	2500	1980	126%
HCH gamma	12	7	0	5	40.4	12.46	5.57	42	40	105%
DDT	11	8	0	3	44.67	22.48	12.98	50	49.5	101%
PCPs	13	1	0	12	2547.42	1417.89	409.31	2895	3980	73%
HCB	13	6	0	7	41	17.63	6.66	33	39.6	83%
HC_but	13	11	0	2	14.5	7.78	5.5	14.5	39.9	36%
Aldrin	12	6	0	6	44.33	19.9	8.12	50	100	50%
Dieldrin	12	6	0	6	70	12.38	5.05	64.5	100	64.5%
Endrin	12	6	0	6	68.83	9.66	3.94	67.5	100	67.5%
PCB 118	11	5	0	6	60.83	25.12	10.25	61.5	40	154%
PCB 153	11	5	0	6	52.67	30.37	12.40	48	40	120%
PCB 180	11	9	0	2	30.5	3.54	2.5	30.5	40	76.3%
PCB 28	11	6	1	4	68.75	20.06	10.03	76	40	190%
PCB 52	11	6	0	5	73.2	22.77	10.19	71	40	177%
Dichlorvos	12	6	2	4	380	414.57	207.28	260	800	32.5%
Dichlorethane	12	11	-	1	1700	-	-	1700	40	4250%
TCB 123	8	8	-	0	-	-	-	-	-	-
Data 124	9	5	0	4	413.75	148.96	74.48	417.5	400	104%
Data 135	7	7	-	0	-	-	-	-	-	-
Tot TCB	6	5	-	1	280	-	-	280	=400	? 70%
Atrazine	12	3	0	9	1162.67	1119.55	373.18	966	1200	80.5%
Simazine	11	2	1	8	1596.25	1748.62	618.23	590	1200	49%
Tot Org Tins	5	2	0	3	97467	71158	41083	135000	=180000	? 75%
TP_tins	8	5	0	3	14567	13898	8024	11000	84000	13%
TB_tins	9	3	0	6	28747	32823	13400	20095	92800	22%
Trifluralin	12	6	0	6	246.33	50.01	20.42	251	400	63%
Fenitrothion	11	8	1	2	75	21.21	15	75	40	187 %5
Azinphos-methyl	12	8	1	3	163.33	173.88	100.39	100	783	13%
Malathion	13	8	0	5	244	188.79	84.43	195	600	32%
Endosulfan	11	6	0	5	39.8	24.00	10.73	31	40	78%
End_total	4	1	0	3	147	90.37	52.18	110	=40	? 275%

Cell 2 Leachate Compound	Total Number of Results	Number of below threshold results	Number of outlier results	N	Mean	Standard Deviation	SE Mean	Median	Spike	Median as % of spike
	TOTAL VALUES			Values above threshold, excluding outliers						
Hg	12	2	1	9	505.56	225.34	75.11	420	300	140%
Cd	12	6	0	6	1961.67	342.84	139.96	1995	1500	133%
HCH gamma	11	10	0	1	107	-	-	107	30	356%
DDT	12	10	0	2	15.5	6.36	4.5	15.5	45	34%
PCPs	11	7	1	3	240	306.14	176.75	108	8000	1.3%
HCB	10	8	0	2	1.5	0.71	0.5	1.5	30	5%
HC_but	10	10	0	0	-	-	-	-	30	-
Aldrin	12	9	0	3	71.67	58.43	33.74	96	75	128%
Dieldrin	12	4	2	6	63.83	22.86	9.33	65	75	87%
Endrin	12	7	1	4	105	68.77	34.38	89.5	75	119%
PCB 118	10	9	0	1	5	-	-	5	30	17%
PCB 153	10	7	1	2	10	2.83	2	10	30	33%
PCB 180	10	8	0	2	3	0	0	3	30	10%
PCB 28	10	8	1	1	10	-	-	10	30	33%
PCB 52	10	8	0	2	22	24.04	17	22	30	73%
Dichlorvos	12	9	1	2	13.45	12.09	8.55	13.45	1600	0.8%
Dichlorethane	9	9	0	0	-	-	-	-	30	-
TCB 123	9	7	0	2	71	69.30	49	71	-	-
Data 124	10	4	1	5	292.2	140.23	62.71	280	300	93%
Data 135	9	8	0	1	26	-	-	26	-	-
Tot TCB	5	4	0	1	260	-	-	260	300	87%
Atrazine	12	5	0	7	1010.86	1087.58	411.07	200	2400	8.3%
Simazine	12	4	1	7	925.29	1033.25	390.53	370	2400	15.4%
Tot Org Tins	9	6	0	3	333.33	75.72	43.72	300	-	-
TP_tins	5	5	0	0	-	-	-	-	60	-
TB_tins	4	2	1	1	36	-	-	36	60	60%
Trifluralin	12	11	0	1	20	-	-	20	300	6.7%
Fenitrothion	13	11	0	2	65	77.78	55	65	80	81%
Azinphos-methyl	11	7	0	4	1180	1010.21	505.11	1200	1600	75%
Malathion	12	11	0	1	60	-	-	60	1200	5%
Endosulfan	12	11	0	1	4	-	-	4	30	13%
End_total	3	1	0	2	172	11.31	8	172	-	-

Cell 6 Leachate Compound	Total Number of Results	Number of below threshold results	Number of outlier results	N	Mean	Standard Deviation	SE Mean	Median	Spike	Median as % of spike
	TOTAL VALUES			Values above threshold, excluding outliers						
Hg	11	1	1	9	916.67	422.85	140.95	900	800	112%
Cd	12	4	2	6	3525	1177.79	480.83	3795	4000	95%
HCH gamma	12	7	1	4	61.25	44.21	22.11	66	80	83%
DDT	13	11	0	2	56	67.88	48	56	120	47%
PCPs	10	5	1	4	350.25	232.24	116.12	415	3000	14%
HCB	11	6	1	4	42.25	14.66	7.33	36.5	80	46%
HC_but	10	7	1	2	26	5.66	4	26	80	33%
Aldrin	12	4	1	7	51.71	44.20	16.71	20	200	10%
Dieldrin	13	2	0	11	234.18	163.87	49.41	177	200	89%
Endrin	13	4	0	9	232.67	98.38	32.79	201	200	100.5%
PCB 118	10	8	0	2	13.5	9.19	6.5	13.5	80	17%
PCB 153	10	7	0	3	43.33	57.74	33.34	11	80	14%
PCB 180	10	8	0	2	17	18.38	13	17	80	21.3%
PCB 28	10	8	0	2	19.5	2.12	1.5	19.5	80	24%
PCB 52	10	8	0	2	13	5.66	4	13	80	16.3%
Dichlorvos	11	8	1	2	28.1	30.97	21.9	28.1	600	4.7%
Dichlorethane	8	8	0	0	-	-	-	-	80	-
TCB 123	8	6	0	2	12.5	3.54	2.5	12.5	-	-
Data 124	9	3	1	5	257.2	182.43	81.59	260	800	33%
Data 135	6	5	0	1	7	-	-	7	-	-
Tot TCB	4	3	0	1	370	-	-	370	-	-
Atrazine	11	8	1	2	149	114.55	81	149	900	17%
Simazine	11	8	1	2	170	70.71	50	170	900	19%
Tot Org Tins	9	5	0	4	1045	582.04	291.02	990	=320x	? 309%
TP_tins	2	2	0	0	-	-	-	-	160	-
TB_tins	2	1	0	1	26	-	-	26	160	16%
Trifluralin	13	9	0	4	44.25	48.14	24.07	31.5	800	3.9%
Fenitrothion	12	10	0	2	60	42.43	30	60	30	200%
Azinphos-methyl	10	7	0	3	906.67	940.44	542.97	790	600	132%
Malathion	11	8	0	3	390	310	178.98	390	450	87%
Endosulfan	13	11	0	2	17	18.38	13	17	80	21%
End_total	3	2	0	1	60	-	-	60	-	-

Appendix 11: Best Performing Methods from Round 1*

1. Mercury

Lab	Method
3	Digestion with sulphuric permanganate, Cold Vapour AAS.
4	Bromate/bromide oxidation, reduction with hydrox. hcl and tin chloride, F-AAS
9	Fix with dichromate/nitric, bromination followed by tin chloride reduction, cold vapour AFS.
12	Acid digestion, tin chloride reduction cold vapour AFS
15	Digestion with bromide/bromate, cold vapour AFS.

2. Cadmium

Lab	Method
2	Acid digestion, ICP-MS using In as internal standard and standard additions.
3	Acid digestion, flameless AAS.
5	Acid digestion, flameless AAS
7	Acid addition, ICP-MS
9	Acid digestion in microwave, ICP-MS
10	Acid digestion in microwave, ICP-MS
12	Acid digestion, flameless AAS
14	?

* Summary of methods actually used for the leachate round robin samples, as compared with the methods identified from the analytical questionnaire (Appendix 5)

3. Organochlorine Compounds.

Lab	Method
2	SPE, followed by GC-MS.
3	DCM extraction, solvent exchange cleanup, GC-ECD on BP5
9	Hexane extraction, Florisil-Sepak cartridge cleanup, GC-MS on HP5 column
11	Hexane extraction, cleanup, GC-ECD
12	Hexane extraction, alumina-silver nitrate column cleanup, GC-ECD using dual column system (DB5, DB17)
15	Hexane extraction, solid phase cleanup, GC-ECD with dual columns.

4. Organophosphorus Compounds and Triazines

Lab	Method
9	Extraction with DCM, GC-FPD or NPD, or GC-MS. (Both OPs and Triazines)
13	SPE extraction, HPLC-MS (Triazine only)

5. Volatiles: TCBs, HCBt only (DCE unsatisfactory)

Lab	Method
2	SPE followed by GC-MS
7	SPE/DCM extraction followed by GC-MS
11	Hexane extraction? Cleanup? GC-ECD
12	With organochlorine compounds: Hexane extraction, silver nitrate/alumina cleanup, GC-ECD

6. Pentachlorophenols

Lab	Method
1	Hexane extraction, diazomethane derivatisation, GC-MS
3	Hexane extraction, diazomethane derivatisation GC-MS
8	Hexane extraction, acet. anhy. derivatisation, GC-ECD
9	Hexane extraction, acet. anhy. derivatisation, GC-MS
12	Diethylether extraction, diazomethane derivatisation, GC-MS
13	?
15	Hexane extraction, acetic anhy acetylation, GC-MS

7. Organotins

Lab	Method
3	Total
8	Hexane/tropolone extraction, Grignard derivatisation, GC-FPD
9	Total

Appendix 12: Analytical Protocols

Compound: Mercury and compounds.

EQS Value: 5000 ng/l

Structure(s):

$Hg(0)$, Hg^+, Hg^{++}, $(CH_3)_2Hg$ etc

Methods Available:

Very many procedures have been published for this trace element, although most are only suitable for waters with a low organic loading. EPA methods 7470 and 7471 are applicable for a range of liquid and solid wastes, with detection limits down to 200 ng/l. The methods use the principle of cold vapour AAS, with tin chloride and potassium permanganate as reagents. Both methods have been fully validated by EPA. The DoE "Blue Book" 0 11 751326 1 (1978) is generally applicable, and is said to work for both solid and liquid wastes. The principle of cold vapour AAS is used (tin chloride reductant) after oxidation of the sample with nitric and sulphuric acids, and addition of potassium permanganate. The EPA and the DoE method are essentially the same.

The DoE "Blue Book" ISBN 0 11 751907 3 (1985) has essentially replaced the earlier publication; it contains a number of different methods, of which method C is the most appropriate for leachates. Acidic bromine oxidation of the sample is used, followed by reduction with tin chloride and detection by AFS (Atomic Fluorescence Spectrometry). The limit of detection is 0.5 ng/l without preconcentration, and it has been shown to work even for sewage sludge.

Current practice uses one of the component methods of this Blue Book, with AFS being used for detection in most cases (usually with a commercial analyser made by PS Analytical), although sometimes AAS detection of the liberated mercury vapour is used.

Recommended Method (ISBN 0 11 751907 3, 1985, Method C):

Pre-treatment of Sample

500 ml of sample is treated upon receipt with bromate/bromide reagent and hydrochloric acid added. All reagents used in the procedure must be cleaned to remove trace mercury.

Separation Method

If required, the sample is preconcentrated into a brominating solution to increase sensitivity.

Method of Determination

The brominated sample (or preconcentrated solution) is placed in the AFS apparatus, and mercury vapour generated by the addition of acidified 10% tin chloride reductant. The mercury vapour is detected by atomic fluorescence at 253.7 nm.

Performance of Method

Limit of Detection

Stated in the method to be 0.5 ng/l without preconcentration (matrix not defined). With leachates, all the samples analysed were positively detected, indicating that detection limits of better than 100 ng/l were reached in practice.

Accuracy & Precision

Interlaboratory mean values and standard deviations for the laboratories using the above method are as follows:-

Material	Spike Level (ng/l)	Mean Found (ng/l)	Standard Deviation (ng/l)	n
Riverwater #.2	240	246	50	8
Stab. Leachate #.4	400	330	76	5
Cell 2 Leachate #.6	300*	505	225	9
Cell 6 Leachate #.8	800*	917	425	9

*Unspiked samples appear to contain between 150 and 300 ng/l.

Scope of Method

The method works well for each of the matrices tested, with more than 50% of participants submitting accurate data. There is no conclusive evidence that the nature of the matrix influences the performance of the method.

Compound: **Cadmium and compounds.**

EQS Value: **1000 ng/l**

Structure(s): **Mainly Cd^{++}**

Methods Available:

Cadmium is very readily determined by flame AAS (eg EPA 7130 and "Blue Book" ISBN 0 11 751908 1) in most environmental matrices, but the exacting requirements of the EQS level set for this element make flameless AAS methods more appropriate. EPA 7131 is applicable to a wide range of wastes, sludges etc. It uses acid digestion of the sample followed by flameless AAS with background correction; the detection limit is stated to be 100 ng/l. There appear to no suitable "Blue Book", ASTM or BS methods for flameless AAS of this element in a matrix such as leachate.

EPA 200.8 (1989, Draft V3.1) uses acid digestion followed by ICP-MS for wastewaters, sludges etc. A detection limit of 100 ng/l is achieved (interpolated). A draft "Blue Book" method uses essentially the same approach, but no detection limit is given.

A wide range of techniques are used in current practice including acid digestion ICP-AES, flameless AAS without sample pretreatment, acid digestion flameless AAS, solvent extraction flame AAS, ICP-MS and acid digestion ICP-MS. The two most common techniques are acid digestion flameless AAS and acid digestion ICP-MS.

The laboratories that analysed the leachate samples in the first round robin most successfully all used acid digestion followed by either flameless AAS or ICP-MS. The accuracy and interlaboratory precision demonstrated by the latter technique was superior, but the relatively high cost of the instrumentation may limit the acceptability of the technique in some cases. A number of laboratories using flameless AAS performed poorly for the leachate samples, whereas all of the laboratories using ICP-MS performed well.

Recommended Method (Based on ISBN 0 11 750950 & 0 11 751615 5):

Pre-treatment of Sample

Oxidative digestion of the sample with nitric acid in either an open tube or in a microwave digestor. In most cases, it is sufficient to acidify (1% nitric acid) the sample and heat it at 80°C for 6 hours. If internal standards are used (ICP-MS), these should be added at the start of digestion.

Method of Determination (Preferably ICP-MS, or flameless AAS if not available)

(a) Flameless AAS

In the round robins, successful methodologies were based on two "Blue Book" methods. The first, (ISBN 0117516155) was used as a general method for preparation of sewage sludge samples for AAS, and the second (ISBN 011750950) is a general method for trace elements by flameless AAS, based on an original publication by Perkin-Elmer. A Varian version of this was also used. Palladium nitrate-magnesium nitrates were used as matrix modifiers to retain cadmium during the ashing step and to promote oxidation of the matrix where necessary. Background correction was essential. Detection limits quoted were in the range 20 to 1000 ng/l.

(b) ICP-MS

Methods used were "in-house" although the new draft "Blue Book" method should provide a useful guide when available. Samples should contain less than 0.1% total dissolved solids (TDS) to avoid matrix suppression effects. Rhodium or indium were used as internal standards to correct for drift, and quantitation is carried out by the method of standard additions. Results were calculated as the mean for several Cd isotopes.

Performance of Method

Limit of Detection

(a) Flameless AAS: 20 to 1000 ng/l (typically 100 ng/l)
(b) ICP-MS: 100 to 500 ng/l (typically 100 to 200 ng/l)

Accuracy & Precision

Interlaboratory mean values and standard deviations for the above method (round 2) are as follows:-

Material	Spike Level (ng/l)	Mean Found (ng/l)	Standard Deviation (ng/l)	n
Riverwater #.2 (Unspiked estimated = 500)	1190	2370	990	8
Stab. Leachate #.4 (Unspiked, estimated = 700)	1980	2390	620	8
Cell 2 Leachate #.6 (Unspiked, estimated = 1500)	1500	1962	343	6
Cell 6 Leachate #.8 (Unspiked, estimated = ca. 1000)	4000	3525	1180	6

Interferences

Both methods are affected by high salt contents in solution (TDS). This results in signal suppression in ICP-MS, which can be overcome by signal ratioing using the internal standard. With flameless AAS, the effects are more difficult to predict, although a common consequence is worsened precision. Wetting agents (soaps, detergents etc) are also likely to be present in leachates, and to cause some problems with flameless AAS.

Scope of Method

The method with detection by flameless AAS appears to work well in river water and in the stabilised and oxidised leachate, but substantially less well in the fresh leachates. If ICP-MS is used for detection, the method appears to work in all of the matrices tested.

Organochlorine Compounds

Compounds:

Applicable to hexachlorocyclohexane (lindane), DDT, hexachlorobenzene, aldrin, dieldrin, endrin, polychlorinated biphenyls, trichlorobenzene and dichlorvos.

EQS Value: see individual compounds

Structure(s): see individual compounds

Methods Available:

Few validated methods are available for these compounds in leachate matrix. Although EPA methods are fully validated and are in some cases applicable to the analysis of leachate, they require extensive and skilled sample preparation and analysis and are therefore costly if performed correctly. In many cases, the dilution factors which must be applied for leachate raise (i.e. worsen) the limit of detection to levels above the EQS requirements. Method 8080 is the most general method for this class of compound. In current practice, most methods are variations of the "Blue Book" method below:-

Recommended Method (Blue Book ISBN 0 11 751373 3, 1978):

Separation Method

Suitable internal standards are added to the sample before extraction. Compounds used include deuterated polycyclic aromatic hydrocarbons such as phenanthrene and naphthalene, deuterated triazines (atrazine and simazine), deuterated ethyl parathion as well as isotopically labelled $^{13}C_{12}$ PCBs and hexachlorobenzene. Native hexabromobenzene, decachlorobiphenyl and desmetryn(2-isopropylamino-4-methylamino-6-methylthio-1,3,5-triazine) have also been used

The sample is extracted with hexane in a separating funnel. If substantial quantities of solid are present, these are extracted separately (small amounts of solid matter may be suspended in the sample by shaking, before extracting with hexane). Occasionally, dichloromethane is used in place of hexane.

The hexane extract is dried by passage through a column of anhydrous sodium sulphate, which is washed with more hexane. The hexane extract and washings are combined and evaporated to a low volume. It is important for the evaporation process to be carried out carefully to avoid loss of the more volatile organochlorine compounds.

The hexane extract is cleaned up before determination of individual analytes either by passage down a column of alumina-silver nitrate, or by solvent exchange to dichloromethane (either method appears to work equally well).

Method of Determination

In the original method, determination was carried out using GC-ECD, a variety of columns and conditions being given. If this approach is used, separation of the chlorinated insecticides from PCBs is required, if interferences are to be avoided. In practice, many laboratories use GC-MS for detection and quantitation in place of GC-ECD, which avoids the need to separate the two classes of compounds. Columns in use include DB5, BP5, BX5, DB50, BPX5 and DB1. Other variants include the use of a twin capillary GC with two ECDs.

The best-performing laboratories for the samples with the most complex matrix (fresh leachates) mainly used hexane extraction followed by GC-MS.

Performance of Method

Limit of Detection

Limits of detection claimed in the original Blue Book are typically 3 to 15 ng/l (PCBs 106 ng/l). It seems that these values refer to a riverwater matrix. It is not clear if the PCB value refers to individual values or a sum.

Typical limits of detection found by participants for the fresh leachates were 1 to 25 ng/l for all compounds except PCBs (10 to 50 ng/l). A median value of typically 20 ng/l was quoted for the anaerobic leachate.

Accuracy & Precision See individual compounds.

Interferences

If an ECD is used for detection, the method states that PCBs and the other chlorinated compounds must be separated, if interference is to be avoided. With GC-MS, there was no evidence for any interferences occurring at the mass ranges used for quantification; however the chemical matrix of the two fresh leachates was sufficiently concentrated to impede extraction of these compounds into hexane, resulting in extraction efficiencies of 5 to 10 % in some cases and reported values much below the known spike levels.

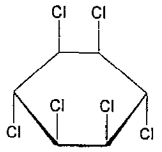
Scope of Method

Appears to work well with the riverwater, less well with the oxidised leachate and rather poorly with the two fresh leachates, with the possible exceptions of dieldrin, endrin and trichlorobenzene which were determined reasonably accurately in each of the matrices tested. Suggested improvements to the extraction process (Appendix 14) may solve this problem, if shown to be generally applicable.

Compound: **Hexachlorocyclohexane congeners (Lindanes)**

EQS Value: **100 ng/l**

Structure(s):



Methods Available: See generic method

Recommended Method: See generic method

Performance of Method

Limit of Detection Median value of 20 ng/l quoted for leachate.

Accuracy & Precision

The interlaboratory mean values and standard deviations for the laboratories using the above method (second round robin) are as follows:-

Material	Spike Level (ng/l)	Mean Found (ng/l)	Standard Deviation (ng/l)	n
Riverwater #.2	25	28	8	9
Stab. Leachate #.4	40	40	12	5
Cell 2 Leachate #.6	30	107	-	1
Cell 6 Leachate #.8	80	61	44	4

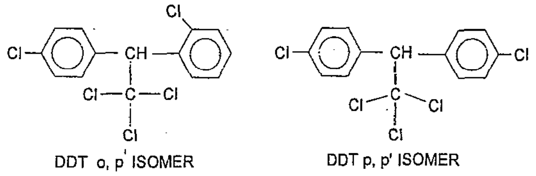
Scope of Method

The method is very matrix sensitive, giving good results for riverwater, degraded accuracy for the stabilised leachate and for the anaerobic leachate. There was some evidence that there was a difference in performance between the two anaerobic leachates.

Compound: DDT congeners

EQS Value: 10 ng/l

Structure(s):



Methods Available: see generic method.

Recommended Method: see generic method.

Performance of Method

Limit of Detection A median value of 20 ng/l is quoted for leachate.

Accuracy & Precision

Interlaboratory mean values and standard deviations for laboratories using the above method (2nd round robin) are as follows:-

Material	Spike Level (ng/l)	Mean Found (ng/l)	Standard Deviation (ng/l)	n
Riverwater #.2	31	30	27	8
Stab. Leachate #.4	49.5	45	22	3
Cell 2 Leachate #.6	45	15.5	-	2
Cell 6 Leachate #.8	120	56	-	2

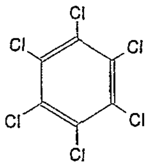
Scope of Method

On the basis of performance in the two round robins, the method is not suitable for anaerobic leachate, although suggested improvements to the solvent extraction step may extend the applicability (see HCH).

Compound: **Hexachlorobenzene**

EQS Value: **30 ng/l**

Structure(s):



Methods Available: see generic method.

Recommended Method: see generic method.

Performance of Method

Limit of Detection A median value of 20 ng/l is quoted for leachate.

Accuracy & Precision

Interlaboratory mean values and standard deviations for the round robins using the above method (2nd round robin only) are as follows:-

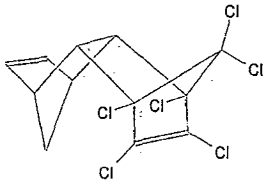
Material	Spike Level (ng/l)	Mean Found (ng/l)	Standard Deviation (ng/l)	n
Riverwater #.2	25	30	8	10
Stab. Leachate #.4	40	41	18	7
Cell 2 Leachate #.6	30	1.5	-	2
Cell 6 Leachate #.8	80	42	15	4

Scope of Method see HCH.

Compound: **Aldrin**

EQS Value: **30 ng/l**

Structure(s):



Methods Available: see generic method.

Recommended Method: see generic method.

Performance of Method

Limit of detection Median value of 20 ng/l quoted for leachate.

Accuracy & Precision

Interlaboratory means and standard deviations for laboratories using the above method (round 2) in the round robins are as follows:-

Material	Spike Level (ng/l)	Mean Found (ng/l)	Standard Deviation (ng/l)	n
Riverwater (#.2)	62	34	14	11
Stab. Leachate #.4	100	44	20	6
Cell 2 Leachate #.6	75	72	58	3
Cell 6 Leachate #.8	200	52	44	7

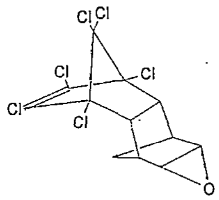
Scope of Method

The method was successfully used for the riverwater sample, but suffered from low recovery of the analyte for two of the three leachates samples. Interlaboratory precision deteriorated for the leachate samples.

Compound: **Dieldrin**

EQS Value: **30 ng/l**

Structure(s):



Methods Available: see generic method.

Recommended Method: see generic method.

Performance of Method

Limit of detection A median value of 20 ng/l was quoted for leachate.

Accuracy & Precision

Interlaboratory mean values and standard deviations for the round robins using the above method (for round 2) are as follows:-

Material	Spike Level (ng/l)	Mean Found (ng/l)	Standard Deviation (ng/l)	n
Riverwater (#.2)	62	49	15	10
Stab. Leachate #.4	100	70	12	6
Cell 2 Leachate #.6	75	64	23	6
Cell 6 Leachate #.8	200	234	164	11

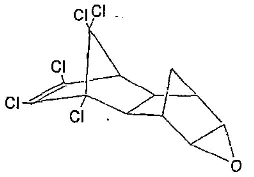
Scope of Method

The method appeared to work for all the matrices tested.

Compound: **Endrin**

EQS Value: **5 ng/l**

Structure(s):



Methods Available: see generic method.

Recommended Method see generic method.

Performance of Method

Limit of detection A median value of 22.5 ng/l was quoted for leachate.

Accuracy & Precision

Interlaboratory means and standard deviations for each sample using the above method (2nd round robin) are as follows:-

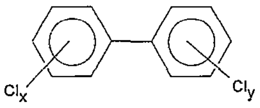
Material	Spike Level (ng/l)	Mean Found (ng/l)	Standard Deviation (ng/l)	n
Riverwater #.2	62	49	11	10
Stab. Leachate #.4	100	69	10	6
Cell 2 Leachate #.6	75	105	69	4
Cell 6 Leachate #.8	200	234	164	11

Scope of Method as Dieldrin.

Compound: **Polychlorinated biphenyls (PCBs)**

EQS Value: **None (suggested 10 ng/l for each)**

Structure(s):



x+y= 1 to 5

The seven specific isomers measured are as follows:-

2,4,4-T_3CB (28)
2,5,2,5-T_4CB (52)
2,4,5,2,5-P_5CB (101)
2,4,5,3,4-P_5CB (118)
2,3,4,2,4,5-H_6CB (138)
2,4,5,2,4,5-H_6CB (153)
2,3,4,5,2,4,5-H_7CB (180)

Methods Available:

EPA Methods 8080 and 505 for the determination of OC pesticides and PCBs are based on DCM extraction from neutral solution, solvent exchange to hexane and GC-ECD. The "Blue Book" method for OC pesticides and PCBs in turbid waters (ISBN 0 11 751913 8) is a GC-ECD procedure which separates OC pesticides and PCBs (see generic OC method).

Both of the above procedures can be modified with the use of GC-MS and isotopically-labelled internal standards for PCBs.

Recommended Method: see generic OC method.

Separation Method

After the addition of internal standards (preferably a ^{13}C labelled cocktail of appropriate PCBs if GC-MS is being used), the samples are extracted with DCM from neutral solution (acid solution if OC pesticides are extracted simultaneously). The extracts are dried over sodium sulphate, concentrated by evaporation and solvent exchanged to hexane. If GC-ECD is used, chemical cleanup is essential, using silica, alumina or chemically-modified adsorbents. If PCBs are being determined alone (without OC pesticides) by GC-MS, it is advantageous to use an alkaline silica column for cleanup.

Method of Determination

See generic OC method.

Performance of Method

Limit of detection	A median value of 22.5 ng/l for each congener was reported for leachate.
Accuracy & Precision	Interlaboratory means and standard deviations using the above method variants (round 2) were as follows:-

Material	Spike Level (ng/l)	Mean Found (ng/l)	Standard Deviation (ng/l)	n
Riverwater #.2				
PCB28	25	21	7	7
PCB52	25	20	7	7
PCB118	25	26	9	8
PCB153	25	27	12	9
Stab. Leachate #.4				
PCB28	40	69	20	4
PCB101	40	50	23	6
PCB118	40	61	25	6
PCB138	40	38	26	5
PCB153	40	53	30	6
Cell 2 Leachate #.6				
PCB28	30	10	-	1
PCB101	30	4	-	2
PCB118	30	5	-	1
PCB138	30	3	-	2
PCB153	30	10	-	2
Cell 6 Leachate #.8				
PCB28	80	19.5	-	2
PCB101	80	1.5	-	2
PCB118	80	13.5	-	2
PCB138	80	-	-	0
PCB153	80	43	58	3

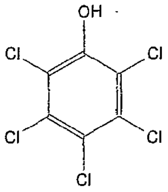
Scope of Method

Method applicable for the riverwater analysis; slightly less successful for the stabilised leachate and inapplicable to the fresh leachates without modification (see Appendix 14).

Compound: **Pentachlorophenol and compounds**

EQS Value: **2000 ng/l**

Structure(s):



Methods Available:

Gas chromatographic measurement of this compound is beset by many problems due to its property of being able to adsorb onto surfaces easily, resulting in poor peak shape or no peaks at all. Therefore, most methods involve derivatisation after solvent extraction of pentachlorophenol from the acidified (pH 2) sample matrix. The most common derivatisation is methylation using diazomethane as described in "Blue Book" ISBN 0 11 751886 7 (1985), but acetylation using acetic anhydride and derivatisation with pentaflurobenzoyl chloride have also been used.

Recommended Method (Blue Book ISBN 0 11 751886 7, 1985)

Separation

If GC/MS is the method of choice, a known amount of isotopically labelled $^{13}C_{12}$ pentachlorophenol is added to the sample as an internal standard. The sample is acidified with sulphuric acid and extracted with hexane. If GC/ECD is to be used, the isotopically labelled internal standard is not used. Another compound is used as internal standard or an external calibration is employed. The hexane extract is dried over anhydrous sodium sulphate and concentrated to a volume of approximately 1 ml.

The derivatisation reagent is prepared by collecting diazomethane which has been generated in ether solution; various procedures and diazomethane generation apparatus kits are available for this, based on a similar principles.

The derivatisation is carried out by mixing equal volumes of the hexane sample extract and the diazomethane reagent, allowing time for the reaction (15-20 minutes) and then removal of the ether under a stream of nitrogen.

Method of Determination

The derivative produced is stable and can be measured by GC with mass spectrometric detection using the PCP internal standard. Alternatively, GC with electron capture detection and external standards can be used. Columns used for the separation include DB5, BP5, BPX5 and HP5.

Performance of Method

Limit of detection	A median limit of detection of 200 ng/l was reported for leachate.

Accuracy & Precision

Interlaboratory mean values and standard deviations are tabulated for each of the spike values, using the above method (round 2 only):-

Material	Spike Level (ng/l)	Mean Found (ng/l)	Standard Deviation (ng/l)	n
Riverwater #.2	1000	1670	1015	12
Stab. Leachate #.4	3980	2550	1420	12
Cell 2 Leachate #.6	8000	240	310	3
Cell 6 Leachate #.8	3000	350	230	4

Scope of Method

On the basis of the round robins, the method is accurate for the riverwater and stabilised leachates, although the interlaboratory precision is very poor. Results for the anaerobic leachate suggest that the material has not been successfully extracted from this matrix.

Volatile Organic Compounds

Compound: **1,2 Dichloroethane**

EQS Value: **10 000 ng/l**

Structure(s):

$CH_2Cl.CH_2Cl$

Methods Available:

The procedures available are:- EPA 264 purge-and-trap GC with electron capture (ECD), EPA 524.2 purge-and-trap GC with mass spectrometer (MS) detection or GC headspace analysis using ECD or MS detection The 1984-5 Blue Book procedures (ISBN 0 11 7520047) describes a static headspace GC-ECD technique for this compound; alternatively pentane extraction followed by GC-ECD has been used. A valuable review of methods for isolating and preconcentrating these compounds from water is available (Namiesnik et al, 1990). Some of these may be applicable for leachate.

Recommended Method:

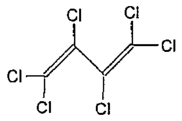
The results indicate that the use of purge/trap or headspace GC-ECD was successful for simple matrices but did not work so well with fresh leachates. No method is recommended due to the lack of performance data.

Limit of detection	A median LOD of 3500 ng/l is quoted for leachate.
Accuracy & Precision	No meaningful data.
Scope of Method	No meaningful data.

Compound: **Hexachlorobutadiene**

EQS Value: **100 ng/l**

Structure(s):



Methods Available: see generic VOC and OC methods

Recommended Method: see generic OC compound method.

Performance of Method

Limit of Detection A median value of 22.5 ng/l is quoted for leachate using the generic OC method.

Accuracy & Precision

There are too few data to allow a meaningful estimate of accuracy and precision to be made.

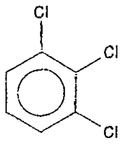
Scope of Method

The methods used were not sensitive enough to meet the original EQS (NRA) or to detect the spike levels added (which were based on the NRA EQS), and no real information about the scope of the method is available.

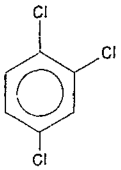
Compound: **Trichlorobenzene congeners**

EQS Value: **400 ng/l for each.**

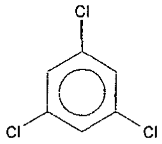
Structure(s):



1,2,3



1,2,4



1,3,5

Methods Available: see generic method for OC compounds.

Recommended Method: see generic method for OC compounds.

Performance of Method

Limit of detection A median value of 100 ng/l was quoted for leachate.

Accuracy & Precision Interlaboratory means and standard deviations using the above method (round 2) are as follows:-

Material	Spike Level (ng/l)	Mean Found (ng/l)	Standard Deviation (ng/l)	n
Riverwater #.2	250	114	59	6
Stab. Leachate #.4	400	414	149	4
Cell 2 Leachate #.6	300	292	140	5
Cell 6 Leachate #.8	800	257	182	5

Scope of Method

Moderately successful for riverwaters, stabilised leachate and Cell 2 leachate; inapplicable for cell 6 leachate due to low recovery (see Appendix 14).

Organophosphorus Pesticides, Atrazine and Simazine.

Compound: Dichlorvos, Fenitrothion, Azinphos-methyl, Malathion, Atrazine and Simazine.

EQS Value: see individual compounds

Structure(s): see individual compounds

Methods Available:

One commonly-used standard procedure for the determination of nitrogen and phosphorus containing pesticides in water is by GC with a nitrogen phosphorus detector (NPD), after dichloromethane solvent extraction (EPA Method 507). The DoE "Blue Book" (1985 ISBN 0 11 751912) procedure of sequential extraction in hexane and DCM, followed by GC flame photometric detection after alumina cleanup is another commonly-used method.

The "Blue Book" method for triazines involves a DCM extraction from alkaline solution (2 ml ammonia per litre of drinking water) followed by GC-NPD.
Each of these three methods is applicable to clean water samples only and has not been validated for leachates.

The triazines can be measured successfully after DCM extraction by GC-NPD (EPA 507), which is also recommended in the "Blue Book", but it is also possible to complete the measurement by high performance liquid chromatography (HPLC) using C18 reverse phase columns with UV detection.

Another alternative reported for the triazines is simultaneous measurement with the organophosphorus pesticides using GC-MS with internal, isotopically-labelled standards.

Recommended Method: (Based on EPA 507 and Blue Book ISBN 0 11 751912 X, 0 11 751660 0 & 0 11 751886 7 Methods).

Separation method

The best performance (as with the organochlorine compounds) was obtained with hexane or dichlomethane extraction and GC-MS detection with some form of internal standard. The variant recommended is dichloromethane extraction from alkaline solution, followed by cleanup using solvent exchange to hexane to remove polar co-extractants.

A number of different internal standards are used in current practice. Deuterated atrazine and simazine, and desmetryn are the most popular for the triazines and deuterated ethyl parathion and native crufomate (4-tert-butyl-2-chlorophenylmethyl methylphophoramidate, a superseded pesticide) are used most commonly for organophosphorus pesticides. The best standardisation is likely to be obtained by using a range of suitable deuterated analogues.

Method of Determination

Although GC-MS appeared to provide the best performance and is recommended if it is available, the method of determination recommended in the "Blue Book" and used by many participants in this study for organophosphorus compounds is GC with nitrogen phosphorus, flame thermionic or flame photometric detection. The columns used in current practice include DB5, BPX5, DB17 and DB608.

The triazines are also best determined by GC-MS with triazine internal standards, although high performance liquid chromatography (HPLC) using a C18 reverse phase column with UV detection or GC with nitrogen phosphorus detector (NPD) also appears to work well.

Performance of Method see individual compounds.

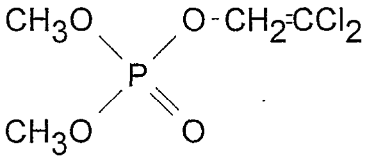
Scope of Method

Works well with riverwater and to some extent with the stabilised leachate and Cell 2 leachate; not applicable for Cell 6 leachate. The source methods are for water only, and more method development is required on cleanup and suitable internal standards if leachate is to be analysed successfully (the suggestions in Appendix 14 may also be applicable).

Compound: **Dichlorvos**

EQS Value: **1 ng/l**

Structure(s):



Methods Available: see generic method.

Recommended Method: see generic method.

Performance of Method

Limit of detection A median value of 150 ng/l was reported for leachate.

Accuracy & Precision Interlaboratory means and standard deviations for the above method variants (round 2 only) are as follows:-

Material	Spike Level (ng/l)	Mean Found (ng/l)	Standard Deviation (ng/l)	n
Riverwater #.2	500	254	123	7
Stab. Leachate #.4	800	380	414	4
Cell 2 Leachate #.6	1600	13	12	3
Cell 6 Leachate #.8	600	28	31	2

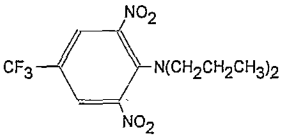
Scope of Method

Method moderately successful (low recovery) with riverwater; but not apparently applicable to leachates without modification.

Compound: **Trifluralin**

EQS Value: **100 ng/l**

Structure(s):



Methods Available: see generic method.

Recommended Method: see generic method.

Performance of Method

Limit of detection A median value of 20 ng/l was quoted.

Accuracy & Precision Interlaboratory mean values and standard deviations using the above method variants (round 2 only) are as follows:-

Material	Spike Level (ng/l)	Mean Found (ng/l)	Standard Deviation (ng/l)	n
Riverwater #.2	250	133	73	8
Stab. Leachate #.4	400	246	50	6
Cell 2 Leachate #.6	300	20		1
Cell 6 Leachate #.8	800	44	48	4

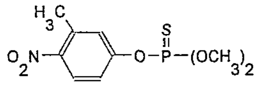
Scope of Method

Works moderately well with riverwater and stabilised leachate (low recovery), but not with fresh leachate.

Compound: **Fenitrothion**

EQS Value: **10 ng/l**

Structure(s):



Methods Available: see generic method.

Recommended Method: see generic method.

Performance of Method

Limit of detection A median value of 100 ng/l was quoted for leachate.

Accuracy & Precision Interlaboratory means and standard deviations for the above method (round 2 only) are as follows:-

Material	Spike Level (ng/l)	Mean Found (ng/l)	Standard Deviation (ng/l)	n
Riverwater #.2	25	17	7	4
Stab. Leachate #.4	40	75	-	2
Cell 2 Leachate #.6	80	65	-	2
Cell 6 Leachate #.8	30	60	-	2

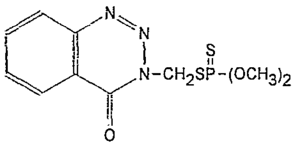
Scope of Method

Appears to work with riverwater, although there are too few data to assess performance with leachate.

Compound: **Azinphos-methyl**

EQS Value: **10 ng/l**

Structure(s):



Methods Available: see generic method.

Recommended Method: see generic method.

Performance of Method

Limit of detection A mean value of 100 ng/l quoted for leachate.

Accuracy & Precision Interlaboratory mean values and standard deviations using the above method (round 2 only) are as follows:-

Material	Spike Level (ng/l)	Mean Found (ng/l)	Standard Deviation (ng/l)	n
Riverwater #.2	490	314	188	9
Stab. Leachate #.4	783	163	174	3
Cell 2 Leachate #.6	1600	1180	1010	4
Cell 6 Leachate #.8	600	907	940	3

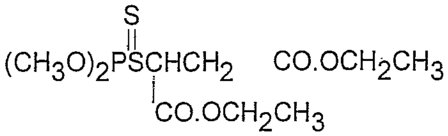
Scope of Method

Without further development, the method appears to be applicable to riverwater, and may work in leachates although this is not clear from the evidence available.

Compound: **Malathion**

EQS Value: **10 ng/l**

Structure(s):



$(CH_3O)_2\overset{\overset{S}{\|}}{P}S\underset{\underset{CO.OCH_2CH_3}{|}}{C}HCH_2\quad CO.OCH_2CH_3$

Methods Available: see generic method.

Recommended Method see generic method.

Performance of Method

Limit of detection A median value of 87.5 ng/l was reported for leachate.

Accuracy & Precision Interlaboratory means and standard deviations for the above method (round 2 only) are as follows:-

Material	Spike Level (ng/l)	Mean Found (ng/l)	Standard Deviation (ng/l)	n
Riverwater #.2	375	190	120	10
Stab. Leachate #.4	600	244	189	5
Cell 2 Leachate #.6	1200	60	-	1
Cell 6 Leachate #.8	450	390	310	3

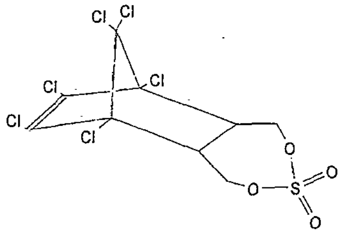
Scope of Method

Works moderately well with riverwater and stabilised leachate (with a low recovery?); less successful with anaerobic leachates.

Compound: **Endosulfan**

EQS Value: **3 ng/l total**

Structure(s):



Methods Available: see generic method.

Recommended Method: see generic method.

Performance of Method

Limit of detection A median value of 40 ng/l was quoted for leachate.

Accuracy & Precision Interlaboratory mean values and standard deviations for the above method (round 2 only) are as follows:-

Material	Spike Level (ng/l)	Mean Found (ng/l)	Standard Deviation (ng/l)	n
Riverwater #.2	25	26	21	6
Stab. Leachate #.4	40	40	24	5
Cell 2 Leachate #.6	30	4	-	1
Cell 6 Leachate #.8	80	17	-	2

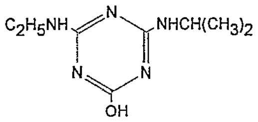
Scope of Method

Works with riverwater and stabilised leachate, but not with fresh leachates.

Compound: **Atrazine**

EQS Value: **2000 ng/l (combined with simazine)**

Structure(s):



Methods Available: see generic method.

Recommended Method see generic method.

Performance of Method

Limit of detection A median value for leachate of 125 ng/l was quoted.

Accuracy & Precision Interlaboratory mean values and standard deviations using the above method (round 2 only) are as follows:-

Material	Spike Level (ng/l)	Mean Found (ng/l)	Standard Deviation (ng/l)	n
Riverwater #.2	748	656	313	12
Stab. Leachate #.4	1200	1163	1120	9
Cell 2 Leachate #.6	2400	1011	1088	7
Cell 6 Leachate #.8	900	149	-	2

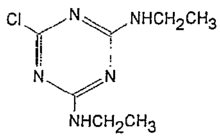
Scope of Method

Works well with riverwater and to some extent (poorer precision) with the stabilised leachate and Cell 2 leachate; not applicable for Cell 6 leachate.

Compound: **Simazine**

EQS Value: **2000 ng/l (combined with atrazine)**

Structure(s):



Methods Available: see generic method.

Recommended Method: see generic method.

Performance of Method

Limit of detection A median value of 100 ng/l was quoted for leachate.

Accuracy & Precision Interlaboratory mean values and standard deviations using the above method (round 2 only) are as follows.

Material	Spike Level (ng/l)	Mean Found (ng/l)	Standard Deviation (ng/l)	n
Riverwater #.2	707	910	719	12
Stab. Leachate #.4	1200	1596	1748	8
Cell 2 Leachate #.6	2400	925	1033	7
Cell 6 Leachate #.8	900	170	-	2

Scope of Method

As atrazine.

Organotin Compounds

Compound: Tributyltin and Triphenyltin compounds

EQS Value: see individual compounds

Structures: **$(Bu)_3Sn.X$ where X = OH, Cl etc**
$(Ph)_3Sn.X$ where X = OH, Cl etc

Methods Available:

There are few official methods for the determination of this class of compound in matrices as complex as leachates, with the exception of the "Blue Book" (ISBN 0 11 752360 7) which details a total of six methods for tin. These include methods for total organotin based on extraction followed by GF-AAS, and GC based methods following reduction of organotins to hydrides and solvent extraction.

Literature methods fall into three groups, including methods for total organotins similar to the above method, methods based on reduction - GC again similar to one variant of the above method, and methods in which organotins are converted to Grignard derivatives, and separated by GC, with or without FPD (Maguire & Huneault, 1981). This latter method is known to be affected by the presence of significant concentrations of organics, and like all published methods, seems mainly intended for the marine environment. Although there appear to be no appropriate USEPA procedures for this matrix, various papers have been published by EPA authors describing the use of LC-MS. Many papers describe speciation measurements (mainly seawater or marine biota) using HPLC/ICP-MS. The applicability of this kind of approach to leachate analysis is uncertain.

Participants in the current study used mainly the total organotin or SE/GC methods from the above "Blue Book". Several laboratories used the Maguire & Hunault procedure with GC-FPD or GC-MS, and one laboratory used a published variant of the "Blue Book" total organotin procedure.

Recommended Method (Blue Book ISBN 0 11 752360 7):

On the basis of performance in the first round robin, the "Blue Book" solvent extraction - GF-AAS (or ICP-AES/ICP-MS) was chosen. Because of sensitivity considerations, the method for water is more appropriate than the method for sludge and solids. Although the method does not enable individual compounds to be reported, unlike the chromatographic procedures, it does (on the basis of the first round robin) appear to be more resistant to matrix problems.

Pre-treatment of Sample

The sample is pre-acidified with glacial acetic acid for preservation.

Separation method

Solvent extraction with toluene in a bottle, using a shaking machine. This may be repeated if necessary. If GF-AAS is to be used, the extract may be evaporated in a stream of nitrogen to increase the concentration of the tin species.

Method of Determination

Normally carried out by GF-AAS using a wavelength of 286.3 nm, and pre-treated carbon tubes to overcome the spreading and adsorption problems associated with the direct analysis of organic solutions by GF-AAS. Alternatively, the extract can be evaporated to dryness, redissolved in acid and analysed by ICP-AES or ICP-MS (n.b., this latter route theoretically offers the possibility of the use of isotopically-labelled compounds as internal standards to improve the reliability of the analysis).

Performance of Method

Limit of detection	A median value of 90 ng/l was quoted for total organotins; there was some confusion amongst participants in the round robins as to whether this was quoted with respect to "total compound" or as tin.
Accuracy & Precision	Interlaboratory means and standard deviations using the above method (both round robins) are as follows:-

Material	Spike Level (ng/l)	Mean Found (ng/l)	Standard Deviation (ng/l)	n
Riverwater #.2	110000	63300	48900	3
Stab. Leachate #.4	180000	97500	41080	3
Cell 2 Leachate #.6	120	333	75	3
Cell 6 Leachate #.8	320	1045	580	4

Scope of Method

The method appeared to give consistently low results with the riverwater and stabilised leachate; this may be partially attributable to confusion amongst participants as to whether "total compound" or "tin equivalents" were being quoted as results. The relatively poor accuracy in round 2 may be due to this, to the presence of these compounds in the unspiked leachates or to poor statistics (too few results, too near to the LOD). More data is required.

Appendix 13: Recovery Tests For Organochlorine Compounds In Leachate

During the second round robin, it became apparent that most analysts participating in the exercise could not extract some compounds from the leachate matrix. This problem was confirmed in our own laboratory. Extraction efficiencies of less than 20% were obtained for compounds such as the PCBs, HCH and HCB, and values obtained for these analytes after normalisation for the ^{13}C spikes added as recovery standards were much lower than the anticipated levels. These compounds had been extracted satisfactorily from river water and dilute, oxidised leachate during the first round robin exercise.

A series of six extraction tests was set up in order to identify an improved solvent extraction methodology for any future work, using 100 ng quantities of PCBs as model compounds. The tests comprised:-

(i) 1 litre of leachate pre-spiked (10 days) with 100 ng quantities of 6 PCBs, spiked with ^{13}C recovery standards in methanol solution just before analysis, extracted with 3 x 50 ml aliquots of methylene chloride and analysed by GC-MS (Test C);

(ii) as (i), but with the ^{13}C recovery spikes added 10 days before extraction (Test D);

(iii) as (i), but using 0.33 litre of leachate which had been diluted to 1 litre (Test E);

(iv) as (i), with the leachate pre-adjusted to pH 2 with 5N sulphuric acid (Test F);

(v) as (i), with 200 g NaCl dissolved in the leachate (Test G);

(vi) as (i), with 50 ml of ethyl acetate added to the leachate (Test H).

A test similar to (i) was also carried out using tap water rather than leachate (Test B). An accuracy check was carried out (Test A) to compare the spiking standards with the analytical standards.

The following conclusions can be drawn:-

- the standardisation was accurate (Test A);
- extraction efficiencies from water (Test B) measured using the ^{13}C spikes were typically 75%. Data for the ^{12}C compounds (normalised using the ^{13}C values) were accurate;
- extraction of the leachate by the normal procedure resulted in extraction efficiencies of less than 50%. Data for the ^{12}C PCB congeners corrected for ^{13}C recovery were low and variable;
- pre-spiking with the ^{13}C PCBs gave correct values for the ^{12}C congeners (Test D). This implies that the ^{13}C and ^{12}C PCBs require a finite time to establish

chemical and/or physical equilibrium in the leachate, before accurate yield correction is obtained;

- dilution (Test E) and addition of ethyl acetate (Test H) raised overall recoveries somewhat, but low values were obtained for the ^{12}C PCBs;
- both acidification (Test F) and the addition of salt (Test G) worsened recovery;
- with the exception of the pre-spiking test, there was a marked tendency for the PCB congeners to show lower recoveries as MWt increased. This demonstrated that the use of one compound only as a recovery standard for a whole range of compounds may not be appropriate with a leachate matrix.

The conclusions of these tests are twofold; (i) that internal standards used for yield correction should be added well in advance of the solvent extraction, and thoroughly mixed with the leachate to allow some form of equilibrium to be established with the analyte compounds and (ii) it may be necessary to use a range of ^{13}C spikes or internal standard compounds to take into account the different chemical properties of apparently similar compounds. Current practice in many laboratories is the addition of a single compound immediately before solvent extraction as yield monitor.

Table 4: Solvent Extraction Recovery Tests for PCBs in Leachate

PCB	A	B	C	D	E	F	G	H
^{12}C (ng) Normalised								
PCB28	104	124	85	102	91	69	84	83
PCB52	98	119	77	102	78	60	66	58
PCB101	103	99	57	100	64	50	65	67
PCB138	101	86	51	113	64	58	66	59
PCB153	101	86	45	99	48	38	58	54
PCB180	101	82	36	97	41	35	53	51
Mean	**101**	**99**	**59**	**102**	**64**	**52**	**65**	**62**
^{13}C Recovery (%)								
PCB28	100	72	63	70	84	49	31	76
PCB52	100	74	50	59	74	40	21	79
PCB101	100	74	45	54	65	38	18	51
PCB138	100	75	42	52	68	37	17	50
PCB153	100	72	43	54	69	39	18	50
PCB180	100	77	43	52	74	40	19	51
Mean	**100**	**74**	**48**	**57**	**72**	**41**	**21**	**60**

Letters A to H identify the test. Numerical values in the bottom half of the table are effectively the true recoveries of the ^{13}C spikes for each test; values in the top half of the table are the apparent recoveries of the ^{12}C compounds, corrected for the ^{13}C recovery.