

CHAPTER 4 LABORATORY ANALYSES

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4. LABORATORY ANALYSES

4.1 INTRODUCTION

4.1.1 Scope

This chapter provides information and guidance on method selection and quality control strategies for the analysis of the principal contaminants of concern from New Zealand timber treatment sites:

- copper, chromium, arsenic, boron
- pentachlorophenol and related chlorophenols
- polychlorinated dibenzodioxins and dibenzofurans (PCDDs and PCDFs).

A range of other organic contaminants could also be involved at particular sites, including organochlorine insecticides, phenols, cresols, polycyclic aromatic hydrocarbons, volatile aromatic hydrocarbons and petroleum hydrocarbons. Methodologies for these classes of contaminants will not be specifically discussed but are available in the compendiums of methods from the US-EPA and other agencies.

Soil or sediment samples will additionally require determination of dry matter content. Other parameters such as pH, cation exchange capacity, organic carbon content and particle size fractions may also require determination. Water samples may additionally require determination of pH, total dissolved solids, colour, turbidity and anion/cation balance. These tests are reasonably standardised in laboratories routinely undertaking analyses of soils or waters for agricultural purposes.

The intention in writing this chapter was, wherever possible, to adopt a non-prescriptive approach and give individual analysts maximum freedom in selecting appropriate analytical methods and analytical instrumentation. To achieve this goal, and in the first part of the chapter, emphasis has been placed on a description of strategies which ensure that analytical results are of known quality.

Guidance for the specific selection of analytical methods for both inorganic and organic contaminants is provided in the second part of the chapter. For organic contaminants a number of reference methods have been suggested as performance benchmarks against which new methods can be validated. For inorganic contaminants, methods are prescribed for the analysis of soluble boron and Cr(VI) in soils and sediments and also for the digestion of all other species. However, analysts may use their discretion in selecting an instrument for the determination stage.

4.1.2 Chapter Summary

The following aspects relating to analysis and sample handling are considered:

- Criteria for selection of an analytical method and an analytical laboratory.
- Definition of laboratory analysis quality control terms.
- Quality control strategies for sample handling and analysis, including:
 - sample storage;
 - instrumental calibration standard preparation and care;
 - analytical quality control steps, including laboratory reagent blanks, replicate analyses, reference control samples, and sample fortification with surrogate compounds and internal standards.
- Requirements for method performance in terms of detection limits.
- Recommended methods for inorganic contaminants (copper, chromium, arsenic and boron) in soils, sediments and waters.
- Recommended methods and other available methods for organic contaminants (pentachlorophenol and related chlorophenols and PCDDs and PCDFs) in soils, sediments and waters. (A brief summary and critique of methods for pentachlorophenol analysis is provided in Appendix A.)
- Recommendations for the style of reporting data.

4.2 SELECTION OF AN ANALYTICAL METHOD

There are many method options for the analysis of metals and organic contaminants in soil and water, options often differing in scope, specificity, sensitivity, rigour and complexity. With respect to timber treatment chemicals the rigour of extraction must be consistent with the techniques upon which the human health and environmental protection criteria are based. For soils and sediments (except where criteria are expressed in terms of leachable and soluble) this is usually “total” contaminant content. This indicates that for metals analysis, the enduring soil science techniques are to be preferred over more recently espoused mild-extractions which aspire to measure bio-available concentrations. For organic contaminants, this initial value judgement on method rigour is less contentious in that the aspiration of all method options is to measure total content. However, most standard extraction protocols, e.g. US-EPA SW-846 (Method 3540: Soxhlet extraction of soil/sediment) have not been rigorously tested for completeness of extraction of weathered field residues. Method acceptance criteria may need to be largely based on recovery of spikes and results of inter-laboratory reference samples.

When there are multiple methods available, the principal considerations used to select the most suitable one for the situation at hand include the following:

- availability of instrumentation,
- confidence level needed,

- detection limits,
- potential interferences,
- applicability of the method for the matrix,
- complexity and cost.

The priorities of the above will vary depending on each specific situation.

Certainly one of the first considerations must be availability of instrumentation. If, for example, the method selected requires a mass spectrometer for analysis and the laboratory does not have that instrument, then clearly either another method or another laboratory must be selected.

Another early consideration involves the matrix for which the method has been designed. Some methods are designed for aqueous matrices and others for solid matrices (soils or sediments). Aqueous matrix methods usually are subdivided into drinking water, raw source water for drinking water, and industrial waste waters. Both surface waters and groundwaters are sources for drinking water, so all methods that mention raw source waters should be applicable for either of these water types. Most methods differ in their application for various matrices only in sample preparation. Once a sample has been prepared correctly according to matrix requirements, the instrumental analytical protocols from most other related methods should be able to be used after proper verification of precision and bias.

The selectivity of some methods is better than others. This will affect the degree of confidence in the identification of specific analytes as well as the possibility of false positive detections. Note that there is an important difference between detection and identification. Detection involves determining whether a signal produced by using a specific method is from the sample instead of being an artefact from instrumental noise, background contamination, or other types of interferences. A signal that meets detection criteria and that has the characteristics of the analyte of interest (e.g. a peak in a gas chromatogram at the correct retention time for that analyte) is often assumed to also identify that analyte. This is not necessarily true. Multiple identification characteristics are required for an identification to be valid. In the example above, repeating the analyses using a different GC column, so that a second and different retention time of the analyte can be compared to a standard of it, is one way to verify an identification. An alternative would be to check for the presence of characteristic ions and their ratios to one another using mass spectrometric detection.

Sensitivity can be an important consideration when concentration levels of the analytes of interest are likely to be very low. Sensitivity will vary among methods for most of the analytes. Instrument selection (e.g. ICP versus direct aspiration atomic absorption or electrothermal atomic absorption instruments) is important for metals. In the case of detectors for organic compound analyses, sensitivity and selectivity characteristics must be weighed against one another as both affect the method detection limits.

An important principle for method selection is the degree of generality. Preferred methods are those that share sample preparation and initial digestion or extraction steps with other methods being used on the samples. Similarly, methods that are suitable for both soils and sediment or surface and groundwaters will enhance productivity. A high degree of universality at the determination step can be useful e.g., ICP-MS or X-ray fluorescence for inorganics and high resolution gas chromatography with mass-spectrometric detection for organics. However, simpler determinative steps may be more cost-effective where a limited number of analytes are being covered.

Methods should be chosen which are internationally recognised and have been subjected to extensive validation and inter-laboratory study. In some cases existing methods may be unsuitable or modifications may be required for reasons such as improving cost-effectiveness on particular analytes. It is then necessary that the laboratory carry out detailed validation studies on the method as developed and applied. This validation data should be available for inspection by clients and auditing agencies along with other QC data produced during analysis of client samples. Full reporting of analytical data, on samples to which appropriate soil or water quality guidelines apply, is also important to allow clients to make correct judgements on the environmental significance of the concentrations observed. Where analyte concentrations are close to or below the method detection limit, clients will need to assess the reliability of the data. For example, data is only of quantitative significance when the concentrations reported are about four times higher than the MDL.

4.3 SELECTION OF AN ANALYTICAL LABORATORY

It is essential that a laboratory participating in studies have suitable equipment and staff experienced in the particular analyses required. The laboratory should have a comprehensive QA/QC programme in place which can prevent, detect and correct problems in the measurement processes so analytical data produced can be demonstrated to be of acceptable quality. Normally this will require that the laboratory meets ISO 9002 and ISO Guide 25 quality management standards.

A number of organisations are able to accredit and audit the more general ISO 9000 series standards. However, at present in New Zealand, TELARC is the organisation with the most experience in the ISO Guide 25 laboratory standards which include both a general audit of the quality management systems and a detailed assessment of particular analytical methods the laboratory chooses to register. It should be noted that not all the methods used in a laboratory need to be registered for TELARC accreditation. In many cases only the more routine and high-volume tests are covered. It is then incumbent on the client to ensure that an unregistered, perhaps more complex and specialised, method offered by the laboratory can be carried out to the required quality standards. This involves judgements on the experience of the analysts, the suitability of the method and its validation, and the QC analyses offered with that method.

4.4 DEFINITIONS

A range of terms is used as part of laboratory quality control procedures and as measures of data quality and method performance. It is desirable that a common set of terms is agreed upon and understood by all those involved in conducting site investigations or making decisions based on derived data. The following definitions largely follow those adopted by the US-EPA.

Internal standard: A pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component. In practice internal standards are added prior to the final instrumental determining stage.

Surrogate analyte: A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction and is measured with the same procedures used to measure other sample components. Where mass spectrometric detection is employed, internal standards or surrogate standards may be isotopically labelled analogues of one or more of the analytes.

Laboratory duplicates: Two sample aliquots taken in the analytical laboratory and analysed separately with identical procedures. Analyses of duplicates give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

Field duplicates: Two separate samples collected at the same time and placed under identical circumstances and treated exactly the same throughout field and laboratory procedures. These give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

Laboratory reagent blank (LRB): An aliquot of reagent water or quartz sand that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

Field control sample (FCS): A sample of field matrix which contains levels of the analytes of interest which are low compared to those expected in test samples. The FCS should otherwise be as similar as possible to the test samples. Aliquots of FCS, alone and fortified with analytes, carried through the complete method provide essential data on interferences, analyte recoveries and detection levels for a method as being applied in a given laboratory at a given time.

Laboratory performance check solution (LPC): A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

Laboratory fortified blank (LFB): An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analysed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

Laboratory fortified sample matrix (LFM): A portion of an environmental sample, usually a field control sample, to which known quantities of the method analytes are added in the laboratory and which is then analysed exactly like a sample. Its purpose is to determine whether the sample matrix contributes bias to the analytical results, i.e. whether the matrix causes interferences or reduced recoveries of the analytes. The background concentrations of the analytes in the sample matrix alone must be determined in a separate aliquot and used to correct the measured values in the LFM.

Stock standard solution: A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

Primary dilution standard solution: A solution of one or more analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

Calibration standard (CAL): A solution prepared from the primary dilution standard solution of the analytes and stock standard solutions of the internal standard(s) and surrogate analyte(s). The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

Quality control sample (QCS): A sample matrix containing method analytes, portions of which are regularly analysed to check that a method is in control. A QCS can be a fortified sample matrix (either laboratory or external). A thoroughly homogenised field sample with analytes present as weathered residues can also be used as a QCS. The QCS may be locally prepared from a bulk sample containing analytes in relevant concentration ranges (laboratory reference material) or from external sources where the QCS may have been carefully validated by an inter-laboratory collaborative study. These certified reference materials are available from US-NBS, European BCR and other national agencies but are expensive and may not contain priority timber treatment analytes in the relevant concentration ranges.

Accuracy: Closeness of a result or the mean of a set of results to the true value. Accuracy is assessed by means of laboratory fortified matrix samples or external QC samples.

Precision: A measurement of the agreement of a set of replicate results amongst themselves without assumption of any prior information as to the true result. Laboratory precision is assessed by means of analysis of duplicate/replicate sub-samples.

Method Detection Level or Limit (MDL): The lowest concentration at which individual measurements for a specific analyte are statistically different from a laboratory blank with a specified confidence level for a given method and representative matrix.

For a 95% confidence interval $MDL = 3 S_B/M$

where M = Slope of calibration line for analyte

S_B = Standard deviation of the noise level or the background signal
(usually from a field control sample).

Reliable detection level (RDL): Lowest recommended concentration of analyte for making qualitative decisions based on individual measurements for a given method and representative matrix. Recommended to be 2 x MDL (CCME, 1993, Keith, 1991 a, b, c).

Reliable quantitation level (RQL): Lowest recommended concentration of analyte for making quantitative decision based on individual measurements for a given method and representative matrix. Recommended to be 4 x MDL (CCME, 1993, Keith, 1991 a, b, c).

4.5 LABORATORY QUALITY CONTROL

4.5.1 Importance of QA/QC

The basic features of laboratory quality assurance have been summarised in Chapter 2. These precepts are fundamental to providing a physical and managerial environment in which analytical systems of controlled quality may function. However, the mere use of approved methods in a facility operating a quality assurance programme does not guarantee adequate results. A wide range of unanticipated effects can cause inaccuracies. It is largely the QC components of each method as it is applied to test samples that allow the detection of these errors and that provide key validation of the data as reported.

A crucial factor for hazardous waste sites and their environs can be the concentration range of the analytes. Cross-contamination from dust, glassware or instruments will make it extremely difficult to obtain quality data from broader environmental samples in a laboratory that is also analysing highly contaminated site samples where analyte concentrations may be 3-5 orders of magnitude higher. Conversely, adequate sub-sampling and wide-ranging instrument calibration is more important for soil samples which are likely to be more heterogeneous, and exhibit wider variations in contaminant concentration, than other environmental samples such as water or sediment. QC procedures must be designed to cope with these extremes.

The following sections are not comprehensive and fuller information is available in preambles to documented environmental analytical methodologies (SWP-846, US-EPA 1986; CCME 1993). However, it is useful to highlight areas which are likely to be crucial to obtaining quality analytical data on samples from contaminated timber treatment sites or surroundings, whether by fully documented and approved methods or by newer, perhaps in-house, methods.

4.5.2 Sample Storage

Tables D1 and D2 in Chapter 2, Appendix D summarise storage conditions suitable for samples received for analysis of priority timber treatment contaminants. Sample containers for organic analytes should be glass with Teflon-faced cap seals. Waters should be acidified to pH 2 on receipt to minimise microbial growth using HNO₃ for inorganics and HCl for organics.

4.5.3 Sample Preparation and Sub-sampling

As the distribution of contaminants in soil or sediment is often heterogeneous, samples must be adequately mixed before taking portions for analysis to ensure sub-sampling errors are small with respect to other errors in the analytical procedure. There is a trend towards smaller test portions in order to minimise costs of reagents and waste disposal and to simplify glassware manipulations. Some attention to detail is obviously required if an analysis of a 0.5 g portion is to adequately represent a 1 kg field sample. It is recommended that all sample preparation, including mixing, be undertaken by the laboratory, minimising the potential for cross-contamination (refer to Chapter 3 for details of the sampling procedures).

Where analytical portions are 10 g or greater, field-moist samples can be used after removal of stones and other large particles and thorough mixing of the sample. Superficial water can be decanted from sediment samples prior to mixing. For volatile analytes field-moist sub-samples should be tested without drying.

For high-clay, clumpy samples or where smaller test portions are to be taken, it is necessary to air dry appropriate sub-samples and carry out grinding and sieving prior to taking analytical portions. The following procedure is recommended:

1. Obtain a representative sub-sample of the laboratory sample by riffler or cone-and-quarter technique. Take at least 50% of the sample or 200 g, whichever is smaller.
2. Remove the largest stones and vegetation. Do not discard (see Step 4).
3. Air dry the sample (30°C to 35°C, <65% RH, 16 hours or longer if required).
4. Grind (mortar and pestle) and sieve so less than 5% w/w retained on 2 mm sieve (store this retained fraction together with the larger particles (from Step 2) for possible future examination).

5. Homogenise the fraction <2 mm diameter. If small analytical portions (<10 g) are to be taken, grind at least 10 g of this to pass smaller sieves as shown in Table 4.1.
6. Store the ground and sieved sub-sample in suitable glass air-tight container. In some cases, for example PCDDs, PCDFs, and chlorinated phenols, it may be necessary to protect the sample from decomposition by sunlight by storing in the dark.

Table 4.1
Recommended Sieve Sizes

Mass of Sample Required for a Single Analysis	Sieve Size Recommended (mm)
Less than 1 g	0.15
Less than 2 g	0.5
2 to 9 g	1.0
10 g or greater	2.0

The preparation of samples for composite analysis should only entail the use of documented site samples as sub-samples for which the appropriate drying, grinding and sieving steps have been carried out. Each sub-sample from which the composite is compiled should contribute equally in mass. Prior to analysis the material should be thoroughly mixed to ensure the sample is homogeneous. The composite sample should not be composed of more than four sub-samples. This restriction ensures that the contaminants appearing in a single sub-sample will not be diluted below the method detection limit.

Extreme care should be taken to avoid cross-contamination during the sample preparation process and to minimise spread of dust in the laboratory. Equipment and containers used must be thoroughly cleaned before each sample to prevent cross-contamination. Cleaning procedures will vary according to the analytes being determined. Generally detergent washing, followed by deionised distilled water rinsing and oven drying will suffice. For trace metal analysis it may be necessary to incorporate soaking in dilute acid before distilled water rinsing. Solvent rinsing followed by air drying will normally be required prior to homogenising samples for organics analysis. Frequent laboratory reagent blank analyses will be required to check for contamination.

WARNING: Grinding of soils to fine dimensions may produce airborne particles which present a health hazard. Preparation should be performed in a fume hood, and appropriate respiratory protection should be worn.

4.5.4 Calibration Standards

Inter-laboratory check sample programmes have consistently shown that the most common source of major bias in analytical data is inaccurate concentrations, or even identifications, of analytes in calibration standards. Consequently laboratory QA/QC systems and quality audits must put great emphasis on this area. It is essential that detailed procedures are in place and followed by the analysts to manage and document the traceability and validity of reference materials and derived solution standards used in analytical methods. Documentation should include:

- A suitable coding system for uniquely identifying all primary and derived standards.
- Records of receipt for all primary reference compounds or certified standards including source, purity and expiry date.
- Records of preparation for all stock standard solutions including dates of preparation and expiry, weight of reference material, final volume and solvent of dilution, signature of check by laboratory manager or person responsible for quality assurance policy in the laboratory.
- Record of preparation for all primary dilution and calibration (working) standard solutions including aliquot volume(s) or weight(s) of stock standard(s), final volume and solvent of dilution, expiry date, signature of check by laboratory manager.
- Records of confirmation of identity and concentrations of analytes in standard solutions including GC-MS, comparisons of concentrations with those of previous standards and comparisons of concentrations with those of standard solutions exchanged with other laboratories.

For inorganic solution stock standards, solutions prepared in acid solution (stored at $<4^{\circ}\text{C}$) and chlorophenol or PCDD/PCDF solution standards prepared in organic solvents (stored at -18°C), the expiry dates can be long (at least 12 months) provided careful checks are made on the volumes. Running records of total weights before and after removing aliquots can be used to check for solvent losses during storage. These will be minimised by use of high-boiling solvents, e.g. ethyl acetate, toluene. Fresh calibration standard solutions should be prepared often and instrument responses compared to those for previous sets.

4.5.5 Recommended QC Procedures

It is recommended that the QC steps described in Chapter 1, "Quality Control" of "Test Methods for Evaluating Solid Water", USEPA Publication SW-846, be adopted for all soil analyses and are also applicable to most water analyses.

In particular, it is expected that analysts would implement the following QC steps with each analytical batch, or with each 20 samples, whichever is the smaller:

1. **Laboratory Reagent Blank:** at least one determination of a blank to establish the contribution to the analytical signal by reagents, glassware etc. The blank should be subtracted from the gross analytical signal for each analysis before calculation of sample analyte concentration.
2. **Replicate Analysis:** duplicate analysis of at least one sample from the batch. The variation between replicate analyses should be recorded for each batch to provide an estimate of the precision of the method.
3. **Quality Control Sample:** analysis of at least one control sample, which comprises either a standard reference material, a laboratory reference material or a control matrix fortified with analytes representative of the analyte class. Recovery check portions should be fortified at concentrations which are easily quantified but within the range of concentrations expected for real samples.
4. **Surrogate analytes:** surrogates should be added to all analyses for determinations where it is appropriate (e.g. chromatographic analysis of organics). Surrogate spikes are known additions **to each sample, blank and matrix spike or reference sample analysis**, of compounds which are similar to the analytes of interest in terms of:
 - (a) extraction,
 - (b) recovery through clean-up procedures, and
 - (c) response to chromatographic or other determinations, but which
 - (d) are not expected to be found in real samples,
 - (e) will not interfere with quantification of any analyte of interest, and
 - (f) may be separately and independently quantified by virtue of, for example, chromatographic separation or production of different mass ions in a GC/MS system.

Surrogates are added to the analysis portion **before extraction** to provide a means of checking, for every analysis, that no gross errors have occurred at any stage of the procedure leading to significant analyte losses.

In the case of organic analyses the surrogate analytes may be ^{13}C , deuterated, alkylated or halogenated analogues, or structural isomers of analyte compounds.

5. **Internal Standards:** use of internal standards is highly recommended for chromatographic analysis of organics. Internal standards are added, **after all extraction, clean-up and concentration steps**, to each final extract solution. The addition is a constant amount of one or more compounds with similar qualities to 4(d), 4(e) and 4(f) above.

Internal standards are used to check the consistency of the analytical step (e.g. injection volumes, instrument sensitivity and retention times for chromatographic systems) and provide a reference against which results may be adjusted in case of variation. The instrument is usually calibrated using the

ratio of peak height or area for analytes compared with that for the internal standard(s). Surrogates are treated as analytes for quantification.

Internal and surrogate standards are most useful for trace analyses where analyte losses during extraction or chromatography and small final volumes can give rise to considerable errors. They are of lesser utility for samples with very high concentrations of analytes as the responses of small quantities of added standards are likely to be swamped or to be lost in dilution of final extracts.

In addition to the above within-batch QC samples, it is also strongly recommended that the laboratory participate in inter-laboratory sample exchange and collaborative study programmes and periodically analyse certified reference materials. These QC activities provide invaluable experience and external reference to validate the analytical methodology and give confidence in the data produced.

It is also recommended that a field control sample spiked with analytes in the mid-range of anticipated sample concentrations be analysed for every matrix type from a site assessment study. Such samples provide information on the potential of the matrix to cause positive or negative bias. For soil and sediment samples the spike should be applied to fresh material which has already been dried, ground and sieved. An unspiked duplicate sample must also be analysed to establish the naturally occurring analyte concentrations.

4.6 METHOD PERFORMANCE SPECIFICATIONS

Method specifications must be such as to allow assessment of compliance with the various health and environmental guidelines. In general, guidelines for protection of aquatic ecosystems are more stringent than those for other beneficial uses and may well require implementation of laboratory practices not required for the majority of tasks. For this reason – and because ecosystem guidelines are not formally proposed in this document – specifications are presented in two categories. Laboratories unable to meet the requirements for testing compliance with ecosystem guidelines are not then excluded from participation in site assessments that do not involve aquatic ecosystems. Furthermore, current methods have difficulty meeting the MDLs required to determine PCP and dioxins at aquatic ecosystem guideline levels, particularly as reliable quantitation can only be achieved at concentrations more than four times the MDL (refer Sections 4.4 and 4.8).

The method detection limits in Table 4.2 for aquatic ecosystems are illustrative and are presented only to guide analytical work. Where protection of aquatic ecosystems is not a significant consideration, the illustrative method detection limits presented in Table 4.3 may be more appropriate.

Table 4.2
Illustrative Sediment and Water Method Detection Limits
(for aquatic ecosystem protection)

Contaminant	Method Detection Limit for Sediments (mg/kg)	Method Detection Limit (mg/L)
Cu	4	0.001
Cr (total)	6.5	0.002
Cr (VI)		0.002
As	1.5	0.010
B (total)		
B (soluble)	2.5	2
PCP		0.01 µg/L
Dioxins		0.002 ng/L

Table 4.3
Required Method Detection Limits for Soils and Waters
for Beneficial Uses other than Ecosystem Protection

Contaminant	Min. Soil Guideline (mg/kg) ⁽¹⁾	Method Detection Limit (mg/kg)	Min. Water Guideline (mg/L) ⁽²⁾	Method Detection Limit (mg/L)
Cu	30	7.5	0.2	0.05
Cr (total)	600	150	0.1	0.025
Cr (VI)	10	2.5	0.05	0.015
As	10	2.5	0.012	0.003
B (total)	25	6.3	0.4	0.1
B (soluble)	3	0.75	(0.4)	(0.1)
PCP	0.1	0.025	0.003	0.00075
Dioxins (T.E.)			0.015 ng/L	0.0038 ng/L

Notes: (1) Refer to Chapter 5
(2) Refer to Chapter 6

4.7 METHODS FOR INORGANIC CONTAMINANTS

The methods nominated in this section seek to standardise the extraction rigour of a sample work-up. The prescription does not, in general, extend to dictating which instrumental technique is used in the final analysis step. So within the constraints of accuracy and specificity and the need to comply with the sensitivity requirements given in Table 4.3, there is sufficient flexibility for competent laboratories to apply techniques already in use. No method is described in full unless it is unpublished or not readily accessible.

4.7.1 Cu, Cr (total), As, B in Soils and Sediments

Sample is subjected to a mild acid digestion following the procedure set out in USEPA Method 200.2. The resultant solution is amenable to instrumental analysis using a number of modern techniques. If boron is analysed colorimetrically, the method must accommodate the presence of nitric acid in the digest. The Azomethine-H method is commonly used without problem, but use of Curcumin without adequate dilution of the test solution may attract interference from nitrate.

4.7.2 Soluble B in Soils and Sediments

There are several variants of this empirical soil test. Although all similar in concept, the operational differences are of significance in that the results obtained are very much a function of the extraction procedure. The method described in the Handbook on Reference Methods for Soil Analysis (Soil and Plant Analysis Council, 1992) is recommended, the essential details being consistent with procedures already in use in the major soil laboratories in New Zealand. The basis of the method is as follows:

- Mix 20 g of air-dry, 2 mm soil with 40 mL of water containing 0.5 mL of 10% CaCl_2 . Bring to boil and gently reflux for 10 minutes.
- Without cooling, filter or centrifuge a suitable volume of suspension.
- Analyse the clarified solution for B. Express results on sample dry-weight basis.

4.7.3 Cr(VI) in Soils and Sediments

A suitable method is that described by Page (1982), and requires a fresh, moist sample.

- Shake 3 g of moist sample with 25 mL of 0.1 M KH_2PO_4 for 5 minutes.
- Centrifuge or filter.
- Add 1 mL of S-diphenylcarbazide reagent to 8 mL of extract, mix and measure colour developed after 20 minutes.
- Express results on dry-weight basis.

NB. The diphenylcarbazide reagent differs from that in Standard methods 3500-Cr D and is as follows:

“Dissolve 0.4 g of S-diphenylcarbazide in 100 mL of ethanol, and mix this solution with 120 mL of 85% phosphoric acid diluted to 400 mL with water.”

4.7.4 Suitability for landfill disposal

The USEPA TCLP test as outlined in Appendix B of Chapter 7 is applied.

4.7.5 Cu, Cr, As, B in Water

Elements Cu, Cr(total), As, B are to be determined using any suitable method following sample preparation according to USEPA Method 200.2. Any colorimetric finish for boron must be able to accommodate the presence of nitric acid in the digest (refer to Appendix E of Chapter 2 for a discussion of sample field filtration and preservation requirements). The Azomethine-H method is suggested as suitable.

4.7.6 Cr(VI) in Waters

Cr(VI) may be determined by the diphenylcarbazide colorimetric method. A suitable procedure is APHA Standard Methods 3500-Cr D.

The analysis should be performed on a sample filtered through a 0.45 µm membrane filter and acid-preserved at the time of sampling (refer Appendix E of Chapter 2). When separate analyses for total chromium and Cr(VI) are required, separate samples should be taken. A practical expedient is to analyse for Cr(VI) only if the result for Cr(total) indicates exceedance of the Cr(VI) guideline, although care is required to ensure maximum sample holding times (refer Appendix D, Chapter 2) for Cr(VI) are not exceeded.

4.8 REFERENCE AND SCREENING METHODS FOR ORGANIC CONTAMINANT ANALYSIS

Reference methods for analysis of pentachlorophenol (PCP) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs and PCDFs) in soils, sediments and waters are presented in Table 4.4. In some cases the complete method is sub-divided into extraction, clean-up and analysis (determination) stages, which are referenced separately themselves. These methods have been validated as being capable of producing quantitative analytical data in the concentration region of 4 times the quoted detection limits and above. The reference methods selected have been chosen on the grounds of their validation and inter-laboratory exchange history as well as international recognition. It should be emphasised that, provided suitable validation studies are conducted, other methods may prove to be more suitable, particularly for

screening. Appendix A summarises some of the characteristics of the various reference and screening methods for PCP.

Screening methods should be validated, typically by analysing an appropriate number of samples using a reference method and conducting a statistically based comparison.

Analyses for the highly toxic PCDDs and PCDFs are complex due to the very low levels that may be significant, the wide range of congeners (chlorination level) and positional isomers. The high selectivity, specificity and sensitivity provided by capillary GC-MS (selected ion mode) is essential to obtain reliable detection limits. Isotopically labelled internal and surrogate standards are extensively used for in-run QC. Due to the specialised nature of the analyses, the expensive equipment required and the expense/toxicity of standard materials, PCDD and PCDF analysis remains the province of very few laboratories.

The MDLs shown in Table 4.4 should be regarded as indicative values only. Individual laboratories will have to establish their own detection limits for analytes as specified in Section 4.4. For PCP analysis in soils and sediments and PCDD and PCDF analysis in water a five-fold improvement of the specified reference method detection limit is required to comply with the method performance standards suggested in Section 4.6. Several of the specified US-EPA methods for PCP were developed principally for neutral or weakly acidic contaminants and are unlikely to be able to produce reliable data for PCP at low detection limits. The validation data for the highly acidic PCP often showed poor precision and high MDLs. However, the methods do have value for analysis of a broad range of contaminants.

Table 4.5 shows a number of screening methods for the analytes in question. Screening methods are often considerably faster and cheaper to perform than the corresponding reference methods. In many cases these methods may also offer improved quality characteristics (MDL, precision). In many cases these methods only lack the full validation and interlaboratory study required of reference methods. However, screening methods may also provide analytical data which is qualified in some way. The qualification might be a possible positive bias and relatively low precision such as may occur with some of the immunoassay techniques for PCP. Also a method may have a lack of scope, such as with the DSIR OCDD screening analysis. This method can be used to provide quantitative data for hepta-chlorinated and octa-chlorinated dioxin and furan isomers substituted in the 2, 3, 7 and 8 positions, but is not suitable for the isomer-specific determination of tetra-chlorinated to hexa-chlorinated congeners.

Appendix A summarises some of the characteristics of the various reference and screening methods for PCP.

Analyses performed using screening methods should still be conducted according to the QA/QC requirements recommended in Section 4.5.5. Screening methods used under more relaxed circumstances, such as in the field, have some use for selection of contaminated areas for further sampling.

Table 4.4
Reference Methods for the Analysis of Pentachlorophenol
and Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans

Analyte and Matrix	Determination	Extraction	Clean-up	Method Detection Limit
Pentachlorophenol				
Soil/sediment	USEPA 8270	USEPA 3540 or 3550	USEPA 3650 or 8040	0.5-3 mg/kg
	USEPA 8040	USEPA 3540 or 3550	USEPA 8040	0.5 mg/kg
Water (contaminated)	USEPA 8270	USEPA 3510 or 3520	USEPA 3650 or 8040	0.6-50 µg/l
	USEPA 8040	USEPA 3510 or 3520	USEPA 8040	0.6 µg/l
Water (drinking or 0.08 µg/l ecosystem protective)	USEPA 515.1	USEPA 515.1	USEPA 515.1	0.08 µg/l
	USEPA 1653	USEPA 1653	USEPA 1653	0.28 µg/l
Polychlorinated dibenzodioxins and dibenzofurans				
Soil/sediment (contaminated)	USEPA 8280	USEPA 8280	USEPA 8280	2 µg/kg
Water (contaminated)	USEPA 8280	USEPA 8280	USEPA 8280	10 ng/l
Soil sediment (trace)	USEPA 8290	USEPA 8290	USEPA 8290	1 ng/kg
Water (trace)	USEPA 8290	USEPA 8290	USEPA 8290	0.010 ng/l

Table 4.5
Screening Methods for the Analysis of Pentachlorophenol and
Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans

Analyte	Matrix	Reference
Chromatographic Methods		
Pentachlorophenol	Soil or water	Stark (1969)
Pentachlorophenol	Soil or sediment	Lee et al (1987)
Pentachlorophenol	Water	Abrahamsson and Xie (1983) Lee et al (1984)
PCDDs and PCDFs	Soil	DSIR/ESR (1992)
Immunoassay Methods		
Soil or Water		Test packs : Millipore Corp Ohmicron Corp Ensy Corp

4.9 DATA REPORTING

Laboratories have a responsibility to provide reports that are complete, accurate and unambiguous so that clients can draw clear conclusions from the data without making any assumptions. Laboratories must also maintain full records of samples, methodology and experimental data so that auditing can be carried out at any time to verify the reported results. Particular attention must be given to the QC records in reports and filing.

Reports must contain the following information:

- Sample I.D. (client and laboratory) and description.
- Date of receipt and conditions of storage.
- Date extraction commenced.
- Details of sample preparation and fraction of sample taken for analysis.
- Citation and summary of analytical procedure – may be just the title for a validated regulatory method. Any modifications to the protocol should be noted.
- Date of reporting and signature of laboratory manager or other authorised signatory.

It is recommended that results of analyses should be reported using the following conventions. Those for concentrations in the region of the detection limit follow recent trends in North America (Canadian NWQL, ASTM, ACS) which leave any censoring of data to the client but provide guidance on the quality of the data.

- No results are to be reported for analyses that were outside the calibration range of the instrument. Dilutions must be made to bring extracts/digests into the linear range. For analyses using derivatisation, smaller aliquots of extract must be taken through the procedure.
- Concentrations of analytes in soils or sediments should be presented on an oven dry (105°C) basis with moisture contents of the field samples presented separately if requested.
- Analyte concentrations should be corrected for the blank but not for recovery.
- Use SI units e.g. mg/kg, mg/L rather than ppm or ppb.
- No observed signal for the analyte – report as ND (not detected) at quoted Method Detection Limit (MDL).
- Analyte signal detectable but concentration less than the MDL – report concentration but flag as <MDL and in a region of high uncertainty. Terms such as “Trace” should be avoided.
- Analyte concentrations greater than MDL – report unflagged.
- Separate results should be presented for each field replicate.
- The MDL and analyte recovery (% from spikes) should be given based on actual QC samples run with the client samples and should not be estimates from previous method validation experiments. MDLs should be based on environmental control samples rather than laboratory blanks. If suitable control samples are not available then MDLs should be set on a conservative basis after a careful study of signals from field samples and blank samples.
- Results for laboratory replicates should be averaged and marked in the report with the number of measurements e.g. 0.31 (3). Sets of laboratory replicate data should be summarised in the form of confidence intervals to show within-laboratory precision.
- The mean and standard deviation of the recoveries for the surrogate analyte(s) across all samples should be reported.
- Results for all QC analyses (reagent blanks, field control samples, fortified laboratory matrix, QC samples) run with client samples should be reported with ranges, means and confidence intervals where appropriate.

4.10 REFERENCES

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APPENDIX A BRIEF DESCRIPTION AND CRITIQUE OF REFERENCE AND PROPOSED METHODS FOR PENTACHLOROPHENOL ANALYSIS

The principal target phenol from timber treatment sites is pentachlorophenol (PCP). However, a variety of lower-chlorinated phenols are also generally present, either from impurities in the PCP formulations or microbial degradation of PCP, with 2, 3, 4, 6-tetrachlorophenol predominating. It is desirable to use methods that analyse for a wide range of chlorophenols so a more complete inventory of site contamination and extent of PCP degradation can be obtained.

The following US-EPA methods are relevant to chlorophenol analysis.

SW-846 Method 8040A, rev. 1, 1990 (Phenols by gas chromatography).

This concentrates on the determination steps but indicates that chlorophenols can be recovered from waters by liquid-liquid partition (Method 3510 Separating funnel or Method 3520 Continuous liquid-liquid) or from solid waste by solvent extraction (Method 3540B Soxhlet or Method 3550B Sonication). Clean-up is by acid-base partitioning (Method 3650A) and, for low levels in soil, gel permeation chromatography (Method 3640A).

Reliable quantitation levels by packed column GC with flame ionisation detector (FID) are about 5 mg/L in waters and 0.5 mg/kg in soils for some di- and tri-chlorophenols and about a factor of 10 higher for PCP.

The specificity of packed column GC-FID is low and interferences from other acidic compounds may be expected. Also acidic phenols are liable to tailing and other adsorption effects in the GC, effects which can be variable and influenced by co-extractives and therefore lead to poor quantitation.

The method also provides for a derivatisation step to form pentafluorobenzyl-ethers of the phenols which have more reliable GC performance and give high responses to the electron capture detector (ECD). However, a time-consuming silica gel chromatographic clean-up is required to remove interferences including derivatised co-extractives. The method has been validated for a range of phenolics including cresols but a number of the relevant lower chlorophenols have not been formally included.

SW-846 Method 8270B (Capillary GC-MS for Semi-volatile Organics in Solid or Liquid Water).

This is a screen also based on solvent extracts prepared using the 3500 series protocols (see above). However, the low resolution mass spectrometric detection (full scan mode) covers a wider range of contaminants with higher selectivity than ECD or FID. The high resolution capillary column separation also improves selectivity and inertness in the analytical system. However, erratic performance of PCP at low levels will be a problem with crude extracts of

soils or waste waters. The method has not been validated for many of the chlorophenol isomers.

EPA-600 Method 525.1, rev. 2.2, 1991 (Determination of Organic Compounds in Drinking Water using Liquid/Solid Extraction and Capillary GC-MS).

This screen is similar to SW846 8270B in the determination of a wide range of contaminants using capillary GC-MS except that reversed phase adsorbents (column or disk) are used to concentrate contaminants from water samples. However, poor GC performance of the acidic PCP resulted in a method detection limit of 48 µg/L versus 0.03-0.5 µg/L for most neutral contaminants tested. No lower chlorophenols have been validated through the method.

EPA-600 Method 515.1, rev. 4.0, 1988 (Determination of Chlorinated Acids in Water by GC-ECD).

Solvent extraction of the water sample is followed by derivatisation with diazomethane to form the methyl esters/ethers. Chlorophenol methyl ethers are detected by capillary GC-ECD along with methyl esters of chlorinated and other electron capturing acids. A Florisil Chromatographic clean-up is used to reduce interferences but no data is provided on performance of the method on soil extracts. The method has been validated for PCP with a method detection limit of 0.08 mg/L but no data is provided for other chlorophenols.

EPA Method 1653 (Chlorinated phenolics in wastewater by *in-situ* acetylation and GC-MS).

Chlorophenolics in water are extracted with hexane after *in situ* acetylation with acetic anhydride at pH 9-11.5. After volume reduction to 0.5 mL the compounds are separated and determined by high resolution gas chromatography with mass spectrometry. Detection limits are 0.5-1 µg/L. This method covers a wide range of chlorophenols and apart from the GC-MS detection is simple and direct. Detection limits can be improved by selected ion monitoring (SIM).

None of these USEPA regulatory methods has the simplicity to recommend it as the first choice for screening of chlorophenols in soil or water. Method 515.1 seems likely to perform well for lower chlorophenols in water as well as PCP and it is probable that solvent extracts of soils could also be analysed after acid/base partition, methylation and Florisil clean-up. However, the procedure is relatively complex and diazomethane is a carcinogenic reagent. The soil extraction procedures using neutral conditions are likely to be relatively ineffective at removing weathered residues of chlorophenols due to ionic binding. Several of the methods use GC-MS detection which raises the cost of the assays and the equipment is not available in some laboratories. GC with electron capture detection is the preferred technique for screening of the tri- through to pentachlorophenols. Some of the following alternative approaches seem more promising for development into fully validated methods for screening of chlorophenols in soil or water.

Analysis of Pentachlorophenol Residues in Soil, Water and Fish (Stark, 1969).

Soils are extracted with 0.1 M potassium hydroxide solution and an aliquot is buffered to pH 6.5-7.0 using boric acid and mineral acid before partitioning with toluene. Acidified water samples are partitioned with toluene directly. The toluene extracts are treated with diazomethane and PCP methyl ether determined by GC-ECD. Use of the PCP-trimethyl silyl (TMS) derivative was recommended for confirmation. Detection limits for PCP in soil of less than 1 mg/kg were reported.

This method has been adopted by the Victorian Environmental Protection Agency (ANZECC, 1993) with minor modifications including a toluene wash prior to acidification to remove base-neutral co-extractives and use of the TMS derivative rather than methyl ether for primary GC quantitation.

Graysons Laboratories, Auckland have also made available an in-house method which is related to the above methods. An aqueous base soil extract is rinsed with dichloromethane, acidified to pH 2 and chlorophenols extracted with dichloromethane. Chlorophenols are determined as TMS derivatives using HRGC-ECD (split injection) with detection limits in soil of 0.1 mg/kg.

Although a base extraction of soils can be expected to be efficient for chlorophenol residues, substantial quantities of humic acids will be solubilised. These are likely to give rise to problems of gels and emulsions at the acid partitioning step, overcome to some extent by the buffering in the Stark procedure. The TMS derivatisation is not attractive as the reagent and derivatives are unstable to hydrolysis and silicone polymer impurities can be formed. These effects are liable to lead to interferences and contamination of the sensitive ECD. The extracts can also be derivatised using diazomethane to form the more suitable methyl ether derivatives.

Direct Determination of Trace Amounts of Chlorophenols in Fresh Water, Waste Water and Sea Water (Abrahamsson and Xie, 1983).

This remarkably simple method uses extractive acetylation to selectively transfer chlorophenols as their acetates from water (pH adjusted to 9) plus acetic anhydride into hexane. A range of chlorophenols (di- to penta-) were determined with minimal interferences and high recoveries at levels of below 0.1 mg/L using capillary GC-ECD.

Analysis of 15 Chlorophenols in Natural Waters by In Situ Acetylation (Lee et al., 1984).

This method is very similar to the above, using 0.5% potassium carbonate as the alkaline buffer. All 16 possible di- to penta-chlorophenols were extracted and analysed as their acetates by GC-ECD. Method detection limits in lake water were below 0.1 µg/L. This method forms the basis for EPA Method 1653.

Determination of Pentachlorophenol and 19 other Chlorinated Phenols in Sediments
(Lee et al., 1987).

This method extends the acetylation procedure in the previous paper to the analysis of solvent extracts of sediments. Sediments were acidified to pH 1 and Soxhlet extracted with acetone/hexane. Partitioning/clean-up into 2% aq. potassium carbonate solution was followed by extractive acetylation and clean-up by silica gel chromatography. Method detection limits for chlorophenols were below 1 mg/kg using capillary GC-MS in selected ion mode (mono- to penta-) or using capillary GC-ECD (tri- to penta-). A dibromo-phenol was recommended as a surrogate analyte or internal standard. The method was not reliable for phenol itself or chloro methyl phenols and so it is unlikely to be applicable to cresols.