FRASER RIVER
Action Plan

A Protocol for Evaluating the Quality of Trace Organic Data

CANADA'S GREEN PLAN
LE PLAN VERT DU CANADA

Canada

DOE FRAP 1993-25

Environment Canada Environnement Canada

A Protocol for Evaluating the Quality of Trace Organic Data

Prepared by

T.M. Fyles, B. King and P.R. West

UVic Organic Indicators Group
Department of Chemistry
University of Victoria
Box 3055, Victoria, B.C. V8W 3P6

for

Environment Canada
Environmental Conservation Directorate
Pacific and Yukon Region
224 West Esplanade
North Vancouver, B.C. V7M 3H7

December 1993

Fraser River Action Plan 1993-25

Disclaimer

This publication is the result of a project partially funded by Environment Canada. The ideas and opinions expressed herein do not necessarily reflect those of Environment Canada.

Summary

This protocol describes the evaluation of the quality of trace organic data. It was developed for evaluating organic data from the Fraser River Basin. The goal of this protocol is to derive a numerical ranking from 0 to 4 for each aspect of the sample collection, storage, analysis and data reduction process. A ranking of "0" would indicate serious flaws in the data while a ranking of "4" would indicate high quality data that could be suitable for direct comparison with data from independent sources and locations. The "3" ranking would indicate that the values are internally consistent while the "2" ranking would indicate that insufficient information was available to assess all aspects of the analysis process.

The protocol uses a set of "Decision Trees" to derive ratings for each step of the process: collection methodology, storage, analytical method, reference standard, and quality assurance/ quality control for the study. An overall rating is assigned by a "weakest link" approach as the lowest rating achieved among the individual categories.

Acknowledgements

The authors gratefully acknowledge the support of the Environmental Conservation Directorate of Environment Canada (Fraser River Action Plan), the B.C. Ministry of the Environment and the Science Council of B.C. (Aquatic Resources Research Project), and the Department of Fisheries and Oceans (Green Plan Toxic Chemical Initiative). The encouragement and criticism of collaborators and consultants at various stages of this project was very helpful in clarifying the issues. We particularly acknowledge the valuable insights and encouragement provided by Brian Smiley of the Institute of Ocean Sciences, Sidney, B.C. Cataloguing and data entry required the dedicated efforts of Vicky Carmichael, Ron Unger, Dana Watts, Allana Pryhitka, Paul Brett, and Blair King. The CODIS 1.0 program was written at AXYS Environmental Consulting, Sidney, B.C., by Martin Caldwell, Ann Blythe, Allison Peacock, and Lindsay Gilles.

The review of the report was coordinated by Cristina Baldazzi of Environment Canada. Cristina Baldazzi and Stephanie Sylvestre of Environment Canada edited the drafts.

Table of Contents

1. Introduction

Modern analytical methods coupled with intense interest in the environment have produced a vast body of results on the levels of various trace organic compounds in biota, water and sediments. Due simply to its size, it is inevitable that this body will have variations in quality. Some reports will be completely described and the values can be used with high confidence. Other reports will be less complete and useful under more restricted circumstances or with lower confidence. Still other reports will be insufficient in detail or in error in some obvious way and the values reported are of limited use.

Our primary goal was to establish a functional index of organic contaminants data in the Fraser River Basin. We therefore required some way to evaluate the quality of the preceding work to be incorporated in the index and to set standards for upcoming work. Data quality is a central issue for all users of data irrespective of their individual goals: regulatory, impact assessment, environmental toxicology or research on ecological interrelationships. Data quality has a direct effect on the confidence level of conclusions drawn from the data and on the kinds of questions that can be asked of the data.

Indices of data quality need to reflect a range of conditions:

- wrong result reported due to obvious error
- possible sources of error in report
- incomplete reporting of methods
- complete reports of limited transferability due to a lack of a certified standard
- complete reports including a certified reference.

The issue of a certified reference material is particularly acute for trace organic analysis. There are very few such reference materials; hence, the analytical accuracy of most reports is impossible to establish. However, data quality is not synonymous with accuracy. Accuracy is a measure of how close a measurement is to an absolute value. In the absence of a certified reference material, systematic errors in measurements cannot be detected; hence, data of apparently "good quality" (free of obvious errors, best available analytical methods) might still have some systematic error. Conversely some data of apparently "lower quality" (obvious sources of error, poorly controlled or not reported) might lack the systematic error and be closer to the unknown absolute value.

For practical purposes, data quality is frequently judged from the precision of a set of data. Precision is the measure of the random variations in results due to the experimental technique used. This variation can be derived from the comparison of replicates, the use of internal standards, and the use of internal "spikes" of the analyzed compound. A certified reference is not required to assess precision. Of course, data can be precise without being accurate.

Our analysis of quality is closely patterned after the approach taken in the Arctic Data Compilation and Appraisal Program (ADCAP) of the Institute of Ocean Sciences, Fisheries and Oceans Canada. This program has produced catalogues (twenty-two catalogues published to date) for all types of physical, chemical and biological oceanographic data in the Canadian Arctic, even those

collected in the 19th century. Using detailed tables and maps, these directories describe who measured what for whom, and where, when and how. The compilations attempt to examine all data regardless of their source and status.

The ADCAP chemistry catalogues, first prepared for the Beaufort Sea (Thomas et al. 1982) and recently revised and updated (Thomas et al. 1990) describe the completeness, reliability and availability of existing data for metals, hydrocarbons, nutrients, pigments and others in seawater, sediments and biota. Some statistics (mean, range of values for each constituent) are also reported. The data quality rating scheme, devised by Drs. David Thomas, Rob Macdonald and Alan Cornford, is of particular value. It offers an elementary but objective technique for users to judge the degree of correctness of existing data, independent of any judged suitability for different applications.

A subset of the ADCAP catalogued information has been computerized into an interactive, geo-referenced database called ODIS (Oceanographic Data Information System), which is accessible to users of the Institute's Micro Vax/Oracle system. Whether employing the hard copy catalogues or computer directory, users still need to consult the data reports themselves to derive the measurement values of interest. Even so, the comprehensive directories permit a quick "analysis of the data as data" by spotting their strengths and weaknesses, before proceeding with trend analyses and other applications. Consequently, confidence in assessment, regulatory and other management decisions are better assured with the ready availability of such compilations with appraisals.

We structured the index of organic contaminants in the Fraser River Basin, CODIS (Continental and Oceanographic Data Information System) using data quality index features similar to those used in ADCAP. The index consists of two functional units: a bibliography of datasets (unique reference number for the dataset, nature of data, location, physical form, and ownership of the data) and the index itself (reference number, sample location and date, matrix, compound, indices of data quality, and summary values if available (range, mean, number of samples, standard deviation)). The information in CODIS is sufficient to answer most questions about the data and will direct users to the specific dataset locations for further information.

2. Dataset Definition

There is no standard definition of a "dataset". The McGraw-Hill Dictionary of Scientific and Technical Terms (4th ed) defined "dataset" as: "named collection of similar and related data records, recorded upon some computer-readable medium." The Concise Oxford Dictionary of Current English defines "data" as: "known facts or things *used as a basis for inference or reckoning.*" It defines "set" as: "a number of things grouped together according to a system of classification or *conceived as forming a whole.*" From these two standard sources, it is clear that the term "dataset" *must preserve the sense of internal consistency.*

While the Arctic Data Compilation and Appraisal Program does not define a dataset *per se* it does stipulate that: "Each dataset comprises sampling or chemical measurements taken during a single cruise, or during a sampling excursion usually by a single agency. It is assumed, then, that data within a given dataset have been collected uniformly and should be internally consistent in so far as sampling methodology is concerned."

Therefore, a "dataset" is defined as:

> A collection of measurements unified by one or more of the following characteristics: chemical species, biological species, physical matrix, geographical locations or sampling methodology. The measurements in a dataset must be treated uniformly, ideally by a single agent or agency, and should be internally consistent with respect to sampling methodology. Measurements in a dataset need not always be of the same type.

The division of a large report into datasets must strive to maintain the expectations of internal consistency of the original workers. The subdivision must also take into account some general realities.

1) When subdividing a large report into simpler datasets one should strive to maximize the size of the datasets.

2) When subdividing reports, the new datasets should be easy to derive from the original report.

3) Datasets should have uniform quality rankings. A large dataset could be fragmented to preserve high quality data ("3" or "4" rating) together while lower quality data ("0" or "1" rating) is placed in a separate subdivision.

The following example illustrates how a data source is subdivided into datasets.

Swain, L.G. and D.G. Walton. 1989. Fraser River Estuary Monitoring, Report on the 1988 Fish Monitoring Program. Fraser River Harbour Commission, B.C. Ministry of Environment. 147p.

This is a complicated data grouping. It contains the values obtained through a year long study of fish in the Fraser.

It contains seven relevant tables, each comprised of various subsections. In total there are:

3 geographical locations
7 fish species
2 major organs in each species
roughly 40 chemicals ranging from chlorophenols to phthalates
values derived from approximately 1000 individual fish.

The various possible methods to split this report into datasets are:

1) 1 overall data group
2) 7 tables divided by organ and general chemical species
3) 84 divisions by chemical and organ
4) 420 divisions by chemical, organ and species
5) 1260 divisions by chemical, organ, species and location
6) 3 divisions by location of collection
7) 5 divisions by species collected
8) 10 divisions by species and organ
9) 30 divisions by species, organ and location
10) 40 divisions by chemical

Of the possible choices:

1) is too general
3),4) and 5) result in too many datasets
6) is not necessarily internally consistent
9) and 10) are difficult to derive from the report as published

This leaves 2), 7) and 8). By the rule of maximum dataset size, option 2) is the best compromise.

This report will be indexed together using the dataset I.D. number 1989####. The seven individual datasets will be given the same 8 digit identifier plus extensions A, B . . etc.

3. Definition of Rating System

In order to carry out the data quality assessment, a standard methodology must be developed so that each dataset is treated in an identical fashion. Ideally this assessment should be totally objective, and is best dealt with through the use of a "Decision Tree". Each report containing data of interest to the study area and type (organic indicators in the Fraser River Basin) will be analyzed using this protocol and the quality of the data will be assigned a ranking on a scale from 0 to 4. The quality of the data will be assessed for each component of the sampling, storage and analysis process. The overall data quality is determined by the "weakest link" in the process. In essence, the overall data can be no better than the quality of the poorest component in the assessment.

Data quality is evaluated using the five level system previously applied in ADCAP. The overall rating value is defined as follows:

Rating	Data Quality
0	Data are found to be wrong. Report contains obvious errors.
1	Data are suspect because of poorly defined doubts. Patterns or trends within the data are probably not real.
2	Insufficient information is provided to assess the quality of the report.
3	Data are internally consistent. Patterns or trends within the data are probably real. Comparisons with other data sets may be difficult or impossible.
4	Data are internally consistent and are sufficiently standardized by means of a certified reference to permit comparison with other data.

Within each category discussed above, individual definitions of the values 0 to 4 are adjusted to preserve the final outcomes defined. Note that this is not strictly hierarchical: "2" is not "better" than "1" in any sense. As noted previously, the lack of certified reference materials will limit the accuracy of most studies. This will be reflected in the distinction between "4" -- potentially accurate and precise, -- and "3" -- potentially precise but of unknown accuracy.

The data quality index in the "overall" category assigns a confidence limit for the report. Data from a report ranked "4" can in principle be compared with data from other reports with the same "4" ranking. Data from a report ranked "3" are in principle internally consistent and can be used to establish trends. The user will determine what level of report is required for the question to

be answered, and will be able to search the data using the data quality indices as a guide to the availability of useful data.

We have broken down the evaluation of datasets into five categories: Collection, Storage, Analysis, Accuracy and Precision. In order to be generally useful, any report needs to provide information on all the above. The five categories were chosen to measure the confidence level in the full history of the sample from collection to final reporting. Each category is important, and relatively independent. A poor performance in any of these categories will be sufficient to diminish the overall quality of report, despite excellent performance in the other categories. For example, the goal of a collection program is to obtain a representative sample for the analytical laboratory, in a form which still reflects the unperturbed composition of the system sampled. Collection and storage of sediment samples for phthalate analysis in plastic buckets will probably result in exchange of components from the sample with the container. The sample analyzed is no longer representative of the original sediment, so the quality of the result for any practical purpose is limited. This will be true even if the accuracy and the precision of the analytical methods is very high. What follows is more information on the various groups.

Sample Collection:

The goal of sampling is to ensure that the constituents being evaluated are representative of their occurrence in the natural environment. The factors considered here are: How was collection carried out? Is the sample representative of the area sampled? Were appropriate procedures carried out to insure that the sample was not contaminated?

Sample Storage:

This section is used to ensure that proper precautions are taken to deliver the constituents in the samples to the analyst in the same representative proportions as at the collection site. The factors being considered are: How was the sample treated once it was collected? Was the sample stabilized? Was it stored in a non-reactive environment? Were precautions taken for volatiles so that, if present, they could be analyzed before breakdown? How was the sample stored? How long was the sample stored?

Sample Analysis:

The goal of the analysis step is to achieve a concentrated sample for instrumental analysis that is representative of the original sample in some defined way and to determine the level of a particular constituent in the matrix presented. Given the complexity of the sample matrices, interferences are the rule, rather than the exception; hence, the method chosen is critical to the quality of the results. Ideally, the method will extract all of the available compound from the sample without degradation (or augmentation), while the analysis will identify and quantify the species present. There is no single method suitable for all organics or all matrices. Moreover, there are numerous "correct" methods. The "Decision Tree" must rank all reasonable alternative methods.

Accuracy:

Accuracy for our purposes is a determination based on use of certified reference materials. A certified reference material used must correctly reflect the interferences from the sample matrix. A suitable standard for PCBs in sediment would be inappropriate for PCBs in transformer oils, and vice versa. As well, if a methodology does not adequately pick up a standard, the sample should be treated as if no standard exists.

Precision:

When standards do not exist or do not supply adequate information, precision becomes the deciding step in quality measurements. The precision of the analysis is assessed by use of blanks, spiked samples and spiked "reference" materials (a "clean" sample of a typical matrix with the compound of interest deliberately added). The other factor being considered in precision is quality control. Quality control is a measure of how internally consistent is the methodology. This is done by testing blanks and spiked samples to insure that the results are reproducible.

4. Decision Trees

The detailed "Decision Trees" are outlined below. Each of the five trees has three sections: an overall flow of questions to be answered, a section of guidelines to assist in answering the questions, and a list of comments generated by the tree. The extensive notes with the Analysis Tree are given as summary guidelines only. The detailed procedures of these methods are available in a companion file. The intention is to provide guidance rather than prescription.

Collection Tree

1) Was the collection documented? (see guideline 1) →no→2

2) Were the collection apparatus and the materials suitable? (see guideline 2) →no→0

3) Were all utensils and containers suitably cleaned? (see guideline 3) →no→0

4) Was cross-contamination avoided? (see guideline 4) →no→0

5) For benthic samples: Was a suitable sampler used with disclosed mesh size? →no→1

6) For fish samples: Was a trap method and fish type indicated? →no→1

7) For PCDD, PCDF and related analytes: Were the containers pre-washed with the sample? →yes→1

8) For volatile analytes: Was head space left in sample? →yes→1

9) Exit with collection rating 4.

Guidelines to Collection Tree

Guideline 1: Documentation required

Sufficient information must be provided to answer questions 2-7. Ideally, this will include the sampling methods, and cleaning procedures, as well as the avoidance of cross-contamination.

Guideline 2: Suitable collection apparatus and materials

Suitable materials for sample containers and sampling apparatus are glass, stainless steel and PTFE (Teflon). Unsuitable materials include plastic, wood and tygon.

Guideline 3: Suitable cleaning procedure for collection materials

Puget Sound Protocols for cleaning utensils

Utensils (except for those used in collecting samples for analysis of volatile compounds) should be solvent-rinsed and air-dried before each use. Utensils used in collecting samples for the analysis of volatile compounds should be washed with detergent, rinsed once with tap water, rinsed at least twice with distilled water, and dried at $>105°$ C. A solvent rinse should be avoided because it may interfere with the analysis.

Puget Sound Protocols for cleaning containers

Sample bottles (for non- and semi-volatile compounds) should be washed with detergent and rinsed successively with tap water, distilled water, acetone, high-purity dichloromethane and oven dried. Glass bottle lids should be protected with PTFE to avoid contamination. The containers, screw caps, and cap septa (silicone vapour barriers) used for collecting samples with volatile compounds are washed with detergent, rinsed once with tap water, rinsed at least twice with distilled water, and dried at $>105°$ C. A solvent rinse should be avoided because it may interfere with the analysis.

Environment Canada Method for cleaning of utensils and containers

Utensils and containers should be washed with detergent and rinsed with tap water, distilled water or high purity deionized water. The cleaning method (for non- and semi-volatile compounds) proceeds with several rinses with acetone to remove any water followed by several rinses with (pesticide grade) hexane or methanol or petroleum ether to remove organics. Dichloromethane (pesticide grade) is used only for highly contaminated or dried on material, and should always be followed with several rinses of hexane. For volatile compounds, utensils should be rinsed several times with acetone then hexane, and the solvent evaporated in an oven at 125° C. Another cleaning method for volatiles and non-volatile compounds is oven baking at 325° C for 12 hours, at 350° C for 6 hours, or at 450° C for 4 hours. However, solvent washing is recommended. All equipment can be solvent washed in the field to prevent cross-contamination of samples between different sites. Solvent washing allows for consistency between field and lab cleaning procedures.

Guideline 4: Cross-contamination sources

Sources of cross-contamination include sampling gear, grease from ship winches or cables, ship engine exhaust, ship engine leaks, dust, and ice for cooling. The report must provide information explaining how such contamination was avoided.

Storage Tree

1) Were the sample storage conditions documented? (see guideline 1) →no→2

2) Was the sample stored in an appropriate container? (see guideline 2) →no→1

3) Was the sample stored in the dark? (see guideline 3) →no→1

4) Was the sample storage at an appropriate temperature? (see guideline 4) →no→1

5) Was the sample stored for acceptable time? (see guideline 4) →no→1

6) Were the samples treated correctly? (see guideline 5) →no→1

7) Exit with storage rating 4

Guidelines to Storage Tree

Guideline 1: Sufficient documentation is required to complete this tree.

Guideline 2: Suitable materials for sample storage

For storage of liquids, sediments and benthos, glass, stainless steel or PTFE (Teflon) containers are allowed. Glass amber containers are preferred. The lids must be Teflon or wrapped in solvent washed and air or oven dried aluminum foil. The lids must be wrapped so that the samples cannot come into contact with the unprotected portion of the lids.

Whole fish samples should be wrapped in solvent rinsed and air or oven dried aluminum foil and may then be put into plastic bags. The fish must be wrapped sufficiently to avoid contact with the plastic.

At no time may plastic or tygon containers be used.

Guideline 3: Suitable lighting for storage

All samples should be kept out of direct light, preferably in a dark storage area.

Guideline 4: Suitable storage temperatures for samples

Table 1 details the storage process for the following constituents: PCBs, organochlorine pesticides, chlorinated phenols, chlorinated catechols, guaiacols, syringols and vanillins, PAHs, phthalates, chlorinated hydrocarbons, antisapstains and volatile organics.

Table 1

Matrix	Storage Temperature	Maximum holding time	Maximum holding time of extract before analysis
Water	Between 0-4° C	7 days	40 days
Sediments	Between 0-4° C	14 days	40 days
	-20° C	14 days for volatiles 1 year for others	----- 40 days
Benthos	Between 0-4° C	7 days	40 days
	-20° C	14 days for volatiles 1 year for others	----- 40 days
Biota	-20° C	14 days for volatiles 1 year for others	---- 40 days

Table 2 defines the storage process for PCDDs, PCDFs, resin acids and fatty acids.

Table 2

Matrix	Storage Temperature	Maximum holding time	Maximum holding time of extract before analysis
Water	Between 0-4° C	30 days	45 days
Sediments	Between 0-4° C	30 days	45 days
	-20° C	1 year	45 days
Benthos	Between 0-4° C	30 days	45 days
	-20° C	1 year	45 days
Biota	-20° C	30 days	1 year

NB: Recent work now indicates that the freezing of sediment and benthic samples is an acceptable way of lengthening acceptable storage times for non-volatile organics. This storage procedure is currently in use in Canada but, at the time of writing, had not been incorporated into EPA Standards.

Guideline 5: Other Procedures

Procedure for elimination of residual Chlorine

In liquid samples, residual chlorine should be removed with 3 mL of 10% sodium thiosulfate per gallon of sample.

Procedure for preservation of Vanillins

With vanillins in water, ascorbic acid must be added to prevent oxidation.

Procedure for preservation of Resin Acids

Resin acids in water, sediments and benthos must be adjusted to roughly pH 9 to avoid isomerization.

NB: Some newer methods suggest that if the sample is adjusted to pH 5 before analysis, it need not be preserved in the field.

Procedure for preservation of DDAC

With DDAC in water and benthos, 5 mL of Rexonic N25-7 solution (2,000 mg/L) and 10 mL of formaldehyde must be added to each litre of solution. In sediments, 2.5 mL of Rexonic N25-7 and 5 mL of formaldehyde must be added to each 100 grams of the sediment sample.

Procedure for fixing benthos

Formalin, not alcohol, should be used to fix benthos as the alcohol takes excessive time and allows for the breakdown of the samples.

Procedure for preserving Volatile Organics

Liquid samples that are being analyzed for volatile organics, should have 1 drop of concentrated hydrochloric acid for each 10 mL of sample.

Notes for storage of Phthalates

Storage at 4° C of aqueous samples at neutral pH and pH 2 is adequate for up to 7 days. Storage of water samples at pH 9, even at 4° C, should be avoided because most target compounds show more than a 50% decrease in concentration after 7 days of storage.

Analysis Tree

1) Was the complete methodology documented? (see guideline 1) →no→2

2) Was the methodology appropriate for the constituent? (see guideline 2) →no→0

3) Exit with analysis rating 4

Guidelines to Analysis Tree

Guideline 1: Documentation required

Sufficient information must be provided to allow future workers in the field to reproduce the entire analysis procedure. If the method is not a standard method as displayed in Table 3, it must have additional documentation indicating that the method used was at least as sensitive as the standard methods.

Guideline 2: Methodology by constituent

Table 3 lists some recommended methods for organic analysis. These are not the only methods and some may have been updated since publication. Newer methodologies may be available through updates in methods manuals while new EPA methods are generally published in the Journal of the Association of Official Analytical Chemists.

Abbreviations in Table 3:

GC	Gas Chromatograph
ECD	Electron Capture Detector
MS	Mass Spectrometer
FID	Flame Ionization Detector
HPLC	High Precision Liquid Chromatography
FPD	Flame Photometric Detector
TD	Thermionic Detector
EPA	Environmental Protection Agency (USA)
EC	Environment Canada Laboratories, Pacific and Yukon Region
EPS	Environment Canada, Environmental Protection Series Reference Method
HD	Halide specific Detector
PID	Photoionization Detector
NPD	Nitrogen-Phosphorus Detector

Table 3

Analysis methodology by constituent			
Constituent	Method	Note #	Reference
PCBs and Organochlorine pesticides	GC/ECD	1	EC Method Version 3.1 EPA Method 8080
PCDDs and PCDFs	GC/MS	2	EPA Method 8280 EPS Methods 1/RM/19 and 1/RM/23
Chlorinated Phenols	GC with FID or ECD	3	EC Method Version 3.0 EPA Method 8040
Chlorinated Catechols, Guaiacols, Syringols and Vanillins	GC/ECD	4	EC Method Version 1.0
Polycyclic Aromatic Hydrocarbons	GC/FID or GC/MS or HPLC	5	EC Method Version 1.1 EPA Method 8100 EPA Method 8310
Phthalates	GC/ECD or GC/FID	6	EPA Method 8060
Resin and Fatty Acids	GC/MS	7	EC Method Version 2.5
Volatile Organics	GC/HD or GC/MS or GC/FID or GC/PID	8	EPA Methods 601,624, 8010, 8015, 8020, 8030 EC Method Version 1.0 - Effluents & Version 1.0 - Sediments
Chlorinated Hydrocarbons	GC/ECD	9	EPA Method 8120
Antisapstains:DDAC	GC/MS GC/NPD	10	EC Method Version 2.0
Antisapstains:TCMTB and Metabolites	HPLC	11	EC Method Version 2.1
Antisapstains: CU-8	HPLC	12	EC Method Version 1.3
Chlorinated Herbicides	GC/ECD	13	EPA Method 8150
Organophosphorus Pesticides	GC/FPD or GC/TD	14	EPA Method 8140

Notes to Table 3

1. PCBs and Organochlorine Pesticides

Overview from Environment Canada Laboratories, Polychlorinated Biphenyls, Version 3.1, August 1993 (Environment Canada 1993a).

> Effluent (includes drinking water, receiving water and industrial effluents) and swap samples are extracted with hexane, the extract concentrated, and then treated using Florisil, concentrated sulphuric acid, activated copper and mercury (as required) to remove interferences. The samples are analyzed using megabore column gas chromatography with electron capture detection. Sediment and homogenized biota samples are acetone extracted using a wrist-action shaker, partitioned with 2% NaCl, then treated in the manner outlined for effluent and swap samples.

2. PCDDs and PCDFs

Overview from Advances in Chemistry Series 214, Organic Pollutants in Water, Sampling, Analysis, and Toxicity Testing. I.H. Suffet (ed.) 1987. p71.

> The sample is extracted with methylene chloride and solvent exchanged to hexane. Cleanup is accomplished by washing the extract with sodium hydroxide followed by sulphuric acid and water. The extract is concentrated and further cleaned by using either of the optional column chromatographic procedures, silica gel or aluminum oxide. These may be used individually or in series as needed. Determination is by capillary column GC-Selective ion monitoring MS.

Aqueous samples cannot be aliquoted from the sample containers. The entire sample must be used and the container is washed out with the extracting solution.

3. Chlorinated Phenols

Overview from Environment Canada Laboratories, Chlorinated Phenols, Version 3.0, August 1993 (Environment Canada 1993a).

> Effluent samples are acidified with dilute sulphuric acid and extracted with diethyl ether. After the samples are concentrated, the extract is methylated using ethereal diazomethane, then treated with Florisil, activated copper, concentrated sulphuric acid and mercury to remove interferences. The sample is then analyzed using High Resolution Gas Chromatography with electron capture detection (HRGC/ECD). Sediment and homogenized biota samples are acetone extracted using a wrist-action shaker, partitioned with 2% NaCl and hexane, methylated as required, then cleaned up and analyzed in the manner outlined for effluent samples.

EPA Method 8040 requires "GC capable of on-column injections and a flame ionization detector (FID) or electron capture detector (ECD)"

4. Chlorinated Catechols, Guaiacols, Syringols and Vanillins

Overview form Environment Canada Laboratories, Chlorinated Catechols, Guaiacols, Syringols, and Vanillins, Version 1.0, October 1993 (Environment Canada 1993a).

> Effluent samples are acetylated "in situ" using acetic anhydride/potassium carbonate then extracted with dichloromethane. The extract is concentrated, exchanged into hexane, cleaned up as required and analyzed by HRGC/ECD.

Aldehydes are known to undergo hydration to form hydrates and, in the presence of alcohol, they form hemiacetals. For these reasons, alcohols should be avoided in the extraction stage. At neutral pH, hydration proceeds the least; therefore, after derivatization with acetic anhydride, the sample should be maintained at neutral pH with potassium carbonate solution in order to achieve quantitative extraction of the chlorovanillins.

5. Polycyclic Aromatic Hydrocarbons

Overview from Environment Canada Laboratories, Polycyclic Aromatic Hydrocarbons, Version 1.1 , February 1994 (Environment Canada 1993a).

> Effluent samples are extracted using Empore (TM) solid phase extraction disks. Just prior to the extraction, all samples are spiked with a mixture of five deuterated PAH compounds (d10-phenanthrene, d8-naphthalene, d12-chrysene, d10-acenaphthene and d12-perylene). The extracts are then spiked with a deuterated PAH internal standard (d10-anthracene) and analyzed using High Resolution Gas Chromatography/Low Resolution Mass Spectrometry (HRGC/LRMS). MS data is acquired in Total Ion Mode (TIM) and quantitated using selected mass ions and a multilevel internal standard procedure. Recovery efficiency is calculated from spiked deuterated PAH surrogates but the final results are not recovery corrected.

Hydrocarbons and fatty acids potentially create analytical problems in biota but GPC cleanup should remove most of these interferences. A GC/MS library Total Ion acquisition data search will provide identification confirmation.

Sulphur compounds will interfere with the GC/MS analysis and will not be removed by GPC. They must be removed by treatment with mercury and activated copper.

The use of rotary evaporation in the extract workup will preclude the reliable determination of naphthalene on a routine basis due to potential losses during evaporation.

The EPA has two methodologies accepted for analysis Methods 8100 and 8310. Method 8100 uses GC columns and a flame ionization detector. Method 8310 analyzes the samples by HPLC by using a reverse-phase HC-ODS Sil-X column with UV and fluorescence detectors.

6. Phthalates

Overview from EPA's Sampling and Analysis Methods Database Manual. L. Keith (ed.) 1990. Method 8060 Phthalates.

> These compounds are extracted with methylene chloride, concentrated, and solvent exchanged to hexane for Florisil or aluminum oxide column cleanup. They require a GC capable of on-column injections and a flame ionization detector (FID) or electron capture detector (ECD).

Modifications to this methodology as suggested under the "Single-Laboratory Validation Program" by Lopez-Avila and Milanes (1991) are summarized below.

> Extraction of water samples in a separatory funnel (Method 3510) was preferred over the continuous liquid-liquid extraction (Method 3520) because it gave good recoveries and repeatabilities for most target analytes, it greatly reduced the extraction time, and it minimized contamination. Concentration of the phthalates in aqueous samples on C18-membrane disks followed by extraction with acetonitrile gave good recoveries and repeatabilities, and was therefore incorporated as an option in the revised Method 8060. Alumina column cleanup is preferred over Florisil column cleanup mainly because it allows recovery of all target compounds by elution with hexane-diethyl ether (4+1). When the Florisil column cleanup was used, 3 of the 16 phthalates could not be recovered at all. A procedure that uses Florisil and alumina cartridges was incorporated in the revised method.

7. Resin and Fatty Acids

Overview from Environment Canada Laboratories, Resin Acids, Version 2.5, September 1991 (Environment Canada 1993a).

> Effluent samples are adjusted to pH 9 and extracted with diethyl ether. Sediment samples are extracted by shaking with methanol in a screw cap centrifuge bottle. The extracts are rotary evaporated and the resulting residues, containing the resin acids and other solvent soluble organics, are then redissolved in methanol, transferred to small glass vials, methylated with diazomethane then evaporated to dryness under nitrogen. The residue is re-dissolved in methyl t-butyl ether (MTBE) and injected in a High Resolution Gas Chromatograph/Low Resolution Mass Spectrometer (HRGC/LRMS) system for analysis. LRMS data is acquired in Total Ion Mode (TIM) and quantitation is performed using a single selected ion. Positive identification of the various resin acids is made on the basis of a comparison of absolute retention times to those of the external standards and mass spectral mass/intensity library searching and matching routines using up to 50 peaks.

Overlap between resin acid and fatty acid methyl esters is usually slight, but some minor fatty acids such as the C22, C24 and C26 saturated normal fatty acids potentially interfere with HRGC/FID determinations.

Evidence exists in the literature which suggests that storage at low or high pH could lead to different results for some compounds. In particular, neoabietic, palustric and levopimaric acids tend to undergo isomerization. Studies have shown they produce an equilibrium mixture consisting of 95% abietic acid and 2-3% each of neoabietic and palustric acids under acidic (pH 2) conditions. At present, it is deemed best to keep the samples cool ($<4°$ C) during transport to the laboratory and adjust the pH to 9 upon receipt thus avoiding the obvious problems associated with accurate control of pH adjustment under field conditions.

The current literature indicates that standard solutions of resin acids are not stable in methanol but are stable in MTBE.

Levopimaric and palustric acid co-elute, thus HRGC/LRMS is required to distinguish between these isomers. The available published information about their concentrations in pulp and paper mill effluents suggests that levopimaric acid should be a minor component relative to palustric acid (if it is present at all). They can easily be distinguished by examination of their mass spectra. Even if a mixture is present, the quantitation of each can be easily accomplished by selection of the appropriate quantitation ions for palustric acid (mass 301) and levopimaric acid (mass 146).

8. Volatile Organics

Volatile organic compounds (VOCs) are divided into two streams, chlorinated and non-chlorinated, and these two groups each have numerous methodologies. The overviews listed here are from the EPA's Sampling and Analysis Methods Database Manual. L. Keith (ed.) 1990.

The two methods below are limited to purgeable organics in liquid samples. In both methods, an inert gas is bubbled through a 5 mL water sample in a specially designed purging chamber. Here, purgeables are transferred from aqueous to gaseous phase, passed onto an absorbent column and trapped. The trap is heated and backflushed with inert gas to desorb purgeables onto a GC column, where purgeables are separated.

Methods 601
- covers 29 purgeable halocarbons.
- describes conditions for a 2nd GC column to confirm measurements made with primary column.

Method 624
- covers 31 purgeable organics.
- provides GC/MS conditions appropriate for the qualitative and quantitative confirmation of results.

In the four methods below, which are differentiated by specific columns and styles of detectors used, samples are analyzed using direct injection or purge and trap methods. Groundwater must be analyzed by the purge and trap method. This method provides an optional GC column which is used for analyte confirmation and that may help resolve analytes from interferences.

Method 8010 - designed for 39 halogenated VOCs
Method 8015 - designed for 6 nonhalogenated VOCs
Method 8020 - designed for 8 aromatic VOCs
Method 8030 - designed for 3 non halogenated VOCs

9. Chlorinated Hydrocarbons

Overview from EPA's Sampling and Analysis Methods Database Manual. L. Keith (ed.) 1990
Method 8120 Chlorinated Hydrocarbons

> This method is for chlorinated compounds other than those classified as pesticides, PCBs or purgeables. This method has difficulties with hexachlorocyclopentadiene which is unstable in the extracting solution (methylene chloride); thus recoveries for this compound are variable and low.

Modifications to this methodology, as suggested under the "Single-Laboratory Validation Program" by Lopez-Avila et al. (1989), are stated below.

> The two packed gas chromatographic columns specified in Method 8120 were replaced with two megabore fused-silica open tubular columns chemically bonded with trifluoropropylmethyl siloxane and polyethylene glycol, respectively. The list of target compounds was expanded from 15 to 22 to include all possible trichlorobenzenes, and hexachlorobenzene (BHC) isomers. The Florisil clean-up procedure was modified to allow quantitative recovery of 20 of the 22 target compounds. A procedure that uses 1 g Florisil disposable cartridges and hexane-acetone (9:1) eluant was developed.

10. Antisapstains: DDAC

Overview from Environment Canada Laboratories, Didecylmethylammonium Chloride, Version 2.0 , November 1993 (Environment Canada 1993a).

> Samples are first field preserved by adding Rexonic N25-7, and ethoxylated alcohol, and formaldehyde. Effluent samples are solvent extracted with dichloromethane. The extract is dried over anhydrous sodium sulphate, the solvent removed by rotary evaporation and the sample volumized with acetone. Sediment samples are solvent extracted with an acidified methanol solution and extracted similarly. The samples are then analyzed and quantitated by High Resolution Gas Chromatography using Nitrogen-Phosphorus detection (NPD-HRGC). The GC method is based on the reproducible thermal decomposition of DDAC in the GC injector with the resulting formation of tertiary amines and alkyl chlorides. A High Resolution Gas Chromatograph/Low Resolution Mass Spectrometer (HRGC/LRMS) system is used for target compound confirmation, if required.

Sample loss due to DDAC adsorption on sample container surfaces is potentially a serious

problem. Studies have shown that with UNPRESERVED samples, surface adsorption occurred with both glass and plastic containers and that the adsorption progressed with time. Use of an ethoxylated alcohol, such as Rexonic N25-7, will minimize or eliminate adsorption problems.

Clays can contain significant levels of polymeric silicates that carry negative charges and act in much the same manner as cation exchange resins. It is necessary to use an acidified methanol solution for sediment extraction to effect complete removal of the DDAC.

The NPD-GC and GC/MS injector liners should be checked frequently for contaminant buildup from sample decomposition products.

Avoid the use of halogenated solvents, nitrogen-containing solvents and methanol in NPD injection solutions as they can affect the sensitivity and stability of the detector and drastically reduce the life of the Rubidium bead.

Avoid the use of silyl reagents, which can also reduce the life of the NPD Rubidium bead.

The use of Total Ion Mode on the HRGC/LRMS system essentially eliminates potential interference problems in target compound identification by providing positive identification.

11. Antisapstains: TCMTB and Metabolites

Overview of Environment Canada Laboratories, 2-(Thiocyanomethylthio)benzothiazole, Version 2.1, October 1993 (Environment Canada 1993a).

> The sample is first extracted with methylene chloride then the extract is filtered, concentrated and the residue dissolved in acetonitrile. The sample is then analyzed for TCMTB and its metabolites MBT, MMBT and BT using High Performance Liquid Chromatography (HPLC).

12. Antisapstains: CU-8

Overview from Environment Canada Laboratories, 8-Hydroxy Quinoline, Version 1.3, October 1993 (Environment Canada 1993a).

> This method is applicable to the determination of 8-hydroxy quinoline (8-HQ) in effluents, treated materials and sediments. The 8-HQ detection limit is 10 *u*g/L in effluents and sediment detection limits are currently under evaluation. The concentration of bis-(8-quinolinato) copper ("copper-8-quino-linolate") is calculated from the 8-Hydroxy Quinoline concentration using a stoichiometric conversion factor of 1.212 . The sample is extracted with methane sulphonic acid:acetonitrile:water then cleaned up using solid phase extraction techniques (SPE). The sample is then analyzed by High Performance Liquid Chromatography (HPLC).

13. Chlorinated Herbicides

Overview from EPA's Sampling and Analysis Methods Database Manual. L. Keith (ed.) 1990
Method 8150 Chlorinated Herbicides

> This method is used for the analysis of 10 chlorinated herbicides. Samples are extracted, hydrolysed with potassium hydroxide, and extraneous organics are removed by a solvent wash. After acidification, the acids are extracted, concentrated and converted to their methyl esters using diazomethane. They are analyzed using direct injection into a gas chromatograph/electron capture detector or halogen specific detector.

The following paragraph describes modifications to this methodology as suggested under the "Single-Laboratory Validation Program" by Gurka et al. (1986).

> The extraction procedure was modified to use methylene chloride and sonification with an acidic buffer in place of the jar extraction of acidified wastes with acetone. Methylene chloride was used in place of ether in the liquid-liquid extraction. Methylation was carried out in mixed solvent in which isoctane was added as a keeper to decrease evaporation losses, and methanol was added to increase the reactivity of diazomethane. Capillary column gas chromatography using electron capture detection allowed the determination of the herbicide analytes as the methyl derivatives in a single, 20 min. gas chromatography run.

14. Organophosphorus Pesticides

Overview from EPA's Sampling and Analysis Methods Database Manual. L. Keith (ed.) 1990
Method 8140 Organophosphorus Pesticides

> This method is used for the analysis of 21 organophosphorus pesticides. Samples are extracted, concentrated and analyzed using direct injection of both neat and diluted organic liquid into a gas chromatograph. The use of Florisil cleanup materials may produce low recoveries. Elemental sulphur may interfere with some compounds when using a flame photometric detector.

Accuracy Tree

1) Was there documentation on standards? (see guideline 1) →no→2

2) Was a suitable standard available for use? (see guideline 2) →no→3

3) Was the appropriate standard used? →no→1

4) Did the methodology adequately quantify the constituent in the standard sample? →no→1

5) Exit with accuracy rating 4

Guidelines to Accuracy Tree

Guideline 1: Documentation on standards

A reference to any standard reference material is required. It must be stated if no reference was used.

Guideline 2: Reference to Certified Reference Materials

Currently we have on record the following standards:

NRC HS-3,HS-4, HS-5 and HS-6 all of which are Harbour Sediment References for Polycyclic Aromatic Hydrocarbons
NRC SES-1 Estuarine Sediment Research Material for Polycyclic Aromatic Hydrocarbons
NRC CS-1, HS-1 and HS-2 Marine Sediment Reference Materials for PCBs
EC-1 PAH, EC-2 PAH, EC-3 PAH, EC-4 PAH, EC-5 PAH, EC-6 PAH, and EC-7 PAH are all PAHs in freshwater sediments
EC-1 PCB, EC-2 PCB, EC-3 PCB, EC-4 PCB, EC-5 PCB, EC-6 PCB, and EC-7 PCB are all PCBs in freshwater sediments
EC-2 CHLO, EC-3 CHLO, EC-6 CHLO and EC-7 CHLO are all chlorobenzenes in freshwater sediments

Other certified reference materials will be added as we identify them.

Precision Tree

1) Was QA/QC documented? (see guideline 1) →no→2

2) Was the hardware subjected to regular QA analysis? (see guideline 2) →no→1

3) Was the sample subject to regular QC during analysis? (see guideline 3) →no→1

4) Exit with precision rating of 4

Guidelines to Precision Tree

Guideline 1: QA/QC documentation

Sufficient reference to QA/QC in methodology is required so that outside observers can be confident that an active QA/QC program was in force. Documentation must include detection limits of each constituent.

Guideline 2: QA for instrumentation

Sufficient information must be provided on methods to insure instrumentation calibration. Full documentation of recommended instrument performance control checks are provided in Chapter VII of "Quality Assurance in the National Water Quality Laboratory" by Haig Agemian.

Guideline 3: QC for samples

The following is a list of suitable quality control steps as suggested by the EPA in the "Recommended Guidelines for Measuring Selected Environmental Variables in Puget Sound."

Analysis Type	Recommended Minimum Frequency of Analysis
Surrogate Spikes	Required in every sample PCB/Pesticides - one per sample Volatiles - three per sample Semi-volatiles - three per sample for the neutral fraction plus three per sample for the acid fraction
Method blank	Semi-volatiles: one per extraction batch Volatiles: one per extraction batch or one per 12-hour shift, which ever is more frequent

Reference Materials	<50 samples: one per set of samples submitted to testing >50 samples: one per 50 samples analyzed
Matrix spikes	<20 samples: one duplicate per set of samples analyzed >20 samples: 5% of the total number of samples
Spiked method blanks	As many as required to establish confidence in method before analysis of sample
Duplicate analyses	<20 samples: one per set of samples analyzed >20 samples: additional duplicates for a minimum of 5% total replication
Field replicates	at discretion of tester
Field blanks	at discretion of tester

Also needed are specific QC points for special compounds.

5. Glossary

Accuracy	The intercomparability of an array of data. Also the closeness of a measured or computed value to a known absolute or real value. Accuracy is determined by comparing results with those obtained using Certified Reference Materials.
Aroclor	Trade Name (Monsanto) for a series of commercial PCB and polychlorinated terphenyl mixtures marketed in the North America.
Batch	The number of samples that can be prepared or analyzed at one time. A typical commercial batch is 5-20 samples for extraction of organic compounds from sample matrices. Batch size varies according to the complexity of the procedure.
Blank-Corrected Result	The concentration of a chemical in a sample adjusted for the concentration of that chemical in the method blank. The method blank must be carried through the procedure concurrently with the sample (comparison of sample and method blank results must take into account the weight, final volume, and any other dilution factor).
Benthic Organisms	Organisms that live in or on the bottom of a body of water (does not include fish that merely feed on the bottom of a body of water).
Biota	The animals, plants and microbes that live in a particular location or region.
CAS Registry Number	A unique number assigned by Chemical Abstracts Service to each unique chemical compound or defined mixture.
Calibration	The determination of the relationship between response from an instrument and concentration of the analyte.
Certified Reference Material	A reference material accompanied by, or traceable to, a certificate stating the concentration of constituents contained in the material. The certificate is issued by an organization, public or private, that routinely certifies such materials (e.g., National Research Council). Certified Reference Materials are used to assess the accuracy of results in analytical testing.
Collection	The action of obtaining a sample for the purposes of a measurement.

Consensus Reference Material	A reference material that, while not certified, has been assessed through round-robin testing and as a result the constituents are known with a high degree of accuracy. A consensus reference material can be used for comparison of analytical results but the reported concentrations are not certified.
Data	Known facts or things used as a basis for inference or reckoning, also numerical or qualitative values derived from scientific experiments.
Data source	A group of datasets collected as a unit. A data source can be divided into datasets.
Dataset	A group of measurements sharing certain traits (see full definition in section 2). A dataset can be rated.
Detection Limit	Established as three times the standard deviation of the blank or background response adjusted for the amount of sample typically extracted and the final extract volume of the method. When there is no blank response, the detection limit can be estimated based on the standard deviation of low-level matrix spike responses, adjusted for typical sample amounts and the final extract volume of the method.
Duplicate Analysis	A second analysis made on the same sample of material to assist in the evaluation of measurement variance.
External Standard	Standards for calibration which are not added to the sample extract.
Field Blank	A simulated sample that is taken through all phases of sample collection, transportation, preparation, and analysis. Results of field blank analyses are used to assess the contribution of analytes from all sources associated with collection, transportation, preparation, and analysis of the sample.
Florisil	Trade name (Floridin Company) for a synthetic magnesium silicate used for liquid chromatographic cleanup.
Internal Standard	A standard added in a known amount to a sample at some stage of analysis in order to determine the concentration of analyte from the analytical response relative to the internal standard. The internal standard can correct for some bias and random error affecting sample results.
Matrix	The medium from which the sample being determined must be liberated for analysis.

Matrix Spike	A QA/QC sample created by adding a known amount of a chemical of interest to an actual sample, usually prior to extraction or digestion. The matrix spike is then analyzed using the normal analytical procedures. A comparison of results from the matrix spike with results from a replicate, unspiked sample enables an evaluation of the effect of the particular sample matrix on the recovery of the compound of interest.
Method Blank	A QA/QC sample created by proceeding through all phases of the analysis procedure with an aliquot of an analytically pure material (usually water). A method blank can be used to measure the contribution of analytes from all laboratory sources external to the sample.
Measurement	A single determination of some variable.
Precision	The degree of agreement between independent measurements as the result of repeated applications of a method under specified conditions.
Quality Assurance	The totally integrated program for assuring the reliability of monitoring and measurement data. A system for integrating the quality planning, quality assessment, and quality improvement efforts to meet user requirements.
Quality Control	The routine application of procedures for obtaining prescribed standards of performance in the monitoring and measurement process.
Quantification Limit	The minimum concentration of an analyte required to be measured and allowed to be reported without qualification as an estimated quantity for samples without substantial interferences. The quantification limit is based on the lowest concentration of the initial calibration curve. Typically 3-5 times the detection limit.
Replicate	One of several identical experiments, procedures, or samples. Duplicate is a special case of replicates consisting of two samples or measurements.
Reproducibility	The ability to produce the same results for a measurement. Often measured by calculation of relative percent difference or coefficient of variation.
Sensitivity	Capability of a method or instrument to discriminate between samples having differing concentrations of a chemical. The degree to which an instrument responds to low concentrations of a chemical.
Silica Gel	Granular form of silicic acid (H_2SiO_3).
Spiked Method Blank	A method blank to which a known amount of surrogate standards and analytes have been added.

Standard	A substance or material, the properties of which are believed to be known with sufficient accuracy to permit its use to evaluate the same property of a sample. In chemical measurements, a standard often describes a solution of chemicals , commonly prepared by the analyst, to establish a calibration curve or the analytical response function of an instrument.
Surrogate Spike Compound	A compound that has characteristics similar to that of a compound of interest, added to the sample prior to extraction. The surrogate compound can be used to estimate the recovery of chemicals in the sample.
Storage	The process of preserving a sample until analysis.

6. Bibliography

Agemian, H. 1988. Quality Assurance in the National Water Quality Laboratory. Environment Canada, Canada Centre for Inland Waters, Burlington, Ontario. 104p.

American Public Health Association. 1985. Standard Methods for the Examination of Water and Wastewater, Sixteenth Edition. American Public Health Association, Washington, D.C. 1268p.

Clark, M.J.R. 1980. A Compilation of Water Quality Criteria. Waste Management Branch, British Columbia Ministry of Environment.

Environment Canada. 1993a. Updates from the Analytical Methods Manual. Environment Canada Laboratories, Pacific and Yukon Region.

Environment Canada. 1993b. Summary of Sample Preservation, Container Type and Container Preparation. National Laboratory for Environmental Testing, Burlington, Ontario.

Environment Canada. 1993c. ENVIRODAT, Dictionary of Codes (Provisional). Surveys and Information Systems Branch, Ottawa, Ontario.

Environment Canada. 1992a. Reference Method for the Determination of Polychlorinated Dibenzo-para-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) in Pulp and Paper Mill Effluents. Environment Canada EPS Report 1/RM/19.

Environment Canada. 1992b. Internal Quality Assurance Requirements for the Analysis of Dioxins in Environmental Samples. Environment Canada EPS Report 1/RM/23.

Environment Canada. 1990. Standard Operating Procedure for Labware Cleaning. Version 1.2, September 1990. Environment Canada Laboratories, Pacific and Yukon Region.

Environment Canada. 1979. Analytical Methods Manual. Environment Canada, Inland Waters Directorate, Water Quality Branch, Ottawa.

Erickson. M.D. 1986. Analytical Chemistry of PCBs. Butterworth Publishers, Toronto. 508p.

Gurka, D.F., F.L. Shore and S-T, Pan. 1986. Single-Laboratory Validation of EPA Method 8150 for Determination of Chlorinated Herbicides in Hazardous Waste. J. Assoc. Off. Anal. Chem. 69(6):970-975.

Hanssen H.W. and N.D. Henderson. 1991. A Review of the Environmental Impact and Toxic Effects of 2-MBT. B.C. Ministry of Environment, Environmental Protection Division. 31p.

Hanssen H.W., N.D. Henderson and J.E.H. Ward. 1991. A Review of the Environmental Impact and Toxic Effects of TCMTB. B.C. Environment, Environmental Protection Division. 47p.

Hazardous Contaminants Coordination Branch. 1988. The MISA Effluent Monitoring Priority Pollutants List (1987). Ontario Ministry of the Environment.

Jones, P.A. 1981. Chlorophenols and their Impurities in the Canadian Environment. Environment Canada, Environmental Protection Service, Ottawa, Ontario. EPS 3-EC-81-2. 434p.

Jones, P.A. 1984. Chlorophenols and their Impurities in the Canadian Environment. 1983 Supplement. Enviroment Canada, Environmental Protection Service, Ottawa, Ontario. EPS 3-EP-84-3. 93p.

Keith, L.H. (ed). 1990. EPA's Sampling and Analysis Methods Database Manual (computer file). Lewis Publishers Inc., Boca Raton, Florida.

Krahn, P.K. and R. Strub. 1990. Standard Leaching Test For Antisapstain Chemicals. Environment Canada, Environmental Protection, Pacific and Yukon Region. North Vancouver, B.C. Regional Program Report 90-10.

Lopez-Avila, V. and June Milanes. 1991. Single-Laboratory Evaluation of Method 8060 for the Determination of Phthalates in Environmental Samples. J. Assoc. Off. Anal. Chem. 74(5):793-807.

Lopez-Avila, V., N.S. Dodhiwala and June Milanes. 1989. Evaluation of EPA Method 8120 for Determination of Chlorinated Hydrocarbons in Environmental Samples. J. Assoc. Off. Anal. Chem. 72(4):593-602.

National Research Council. 1982. Chlorinated Phenols, Criteria for Environmental Quality. National Research Council of Canada, Subcommittee on Pesticides and Industrial Organic Chemicals. Ottawa. 191p.

Puget Sound Estuary Program. 1991. Recommended Guidelines for Measuring Selected Environmental Variables in Puget Sound. Prepared for U.S. Environmental Protection Agency, Region 10, Office of Puget Sound, Seattle, Washington.

Suffet, I.H. (ed). 1987. Advances in Chemistry Series No 214, Organic Pollutants in Water, Sampling, Analysis, and Toxicity Testing. American Chemical Society, Washington, D.C.

Thomas, D.J., R.W. Macdonald and A.B. Cornford. 1982. Arctic Data Compilation and Appraisal. Volume 2. Beaufort Sea: Chemical Oceanography. Can. Data Rep. Hydrogr. Ocean Sci. No. 5. 243p.

Thomas, D.J., F. Noone, A. Blythe and B.D. Smiley 1990. Arctic Data Compilation and Appraisal. Volume 20. Beaufort Sea: Chemical Oceanography-Hydrocarbons, Metals, Pigments, Nutrients, Oxygen and Others. Revised and updated to include 1950 through 1987. Can. Data Rep. Hydrogr. Ocean Sci. No. 5 Vol. 20 (two part report), Part 1, 347p., Part 2, 171p.

Williams, S. (ed). 1984. Official Methods of Analysis of the Association of Official Analytical Chemists. Association of Analytical Chemists, Arlington, Virginia.