APPENDIX H - GUIDELINES FOR STANDARD OPERATING PROCEDURE DEVELOPMENT

GUIDELINES FOR STANDARD OPERATING PROCEDURE DEVELOPMENT

Each agency participating in the IADN is required to develop written standard operating procedures detailing field and laboratory operations and data management procedures. The following is a list of minimum contents for SOPs (data management SOPs require only the items marked with a "*").

- Scope and application *
- Summary of method(s) *
- Definitions *
- Interferences (for lab SOPs)
- Safety precautions
- Apparatus
- Reagents/materials
- Sampling procedures
- Sample handling and tracking
- Calibration/standardization
- Analysis procedures (for lab SOPs)
- Calculations *
- Data reporting *
- Quality control checks *
- Corrective action *

APPENDIX I - LIST OF CURRENT STANDARD OPERATING PROCEDURES

LIST OF CURRENT STANDARD OPERATING PROCEDURES

Meteorological Service Of Canada

Environment Canada, *Laboratory Procedures for the Determination of Polycyclic Aromatic Hydrocarbons in Ambient Air Samples, September, 2000*.

Environment Canada. *Great Lakes Water Quality Agreement Annex 15 Integrated Atmospheric Deposition Network Sampling Protocol Manual*, June 1993. (Revision in progress.)

Environment Canada, *Laboratory Procedures for the Determination of PCBs and OC Pesticides in Ambient Air Samples, September, 2000*.

Vet, Robert, Sukloff, Bill, and Allan, Syd, *The Research Data Management and Quality Control System, User Manual*, Environment Canada, Atmospheric Environment Service, 4905 Dufferin Street, North York, Ontario. M3H 5T4

Ecosystem Health Division

Young, Cynthia *Quality Assurance Manual*, National Laboratory for Environmental Testing, NWRI, August 9, 1999, Version No. 4.0

National Laboratory for Environmental Testing, *Method for the Analysis of 9 Chlorobenzenes, 17 Organochlorine Pesticides, Total Polychlorinated Biphenyls and 16 Polynuclear Hydrocarbons in Water Using Liquid/Liquid Extraction and Gas Chromatography With Electron Capture and Mass Selective Detectors* (03-3251), Version 1.0, August 1997

National Laboratory for Environmental Testing, *Standard Operating Procedure for the Analysis of Metals in Surface, Ground and Precipitation Waters by Inductively Coupled Plasma Optical Emission Spectrometry With Ultrasonic Nebulisation and Direct Aspiration* (02-2001), Version 1.0, August 2000.

The National Laboratory for Environmental Testing, Protocol 06-013 - *Montreal Protocol For The Preparation, Packing And Extraction Of Resin Samples,* Version Number: 1.0 Date Authorised: October 2000

The National Laboratory for Environmental Testing, Protocol 06-016 - *Montreal Protocol for The Preparation of Dichloromethane Precipitation Field Extracts for Analysis of Organochlorines and PAHs,* Version Number: 1.1 Date Authorised: April 2001

The National Laboratory for Environmental Testing , Protocol 06-015 - *Protocol for the Preparation of Dichloromethane Precipitation Extracts for Analysis of Organochlorines and PAHs, V*ersion Number: 1.1 Date Authorised: April 2001

Ontario Ministry of the Environment

Shackleton, M.N. *Technical and Operating Manual: Toxics Deposition Monitoring Program*, Report No. ARB-254-89. May 1990.

Ontario Ministry of the Environment, Laboratory Services Branch; *The Determination of Chlorinated Benzenes (CBs), Polychlorinated Biphenyls (PCBs) and Organochlorines (OCs) in Ambient Air by Gas Chromatography-Mass Spectrometry (GC-MS)*, E3275B, June 12, 1997.

Ontario Ministry of the Environment, Laboratory Services Branch; *The Determination of Polychlorinated Biphenyls (PCBs) and Organochlorines (OCs) in Precipitation by Gas Chromatography-Mass Spectrometry (GC-MS)*, E3127B, June 12, 1997.

Ontario Ministry of the Environment, Laboratory Services Branch; *The Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air by Gas Chromatography-Mass Spectrometry (GC-MS)*, E3124C, June 12, 1997.

Ontario Ministry of the Environment, Laboratory Services Branch; *The Determination of Polycyclic Aromatic Hydrocarbons in Precipitation by Gas Chromatography-Mass Spectrometry (GC-MS)*, E3313A, June 12, 1997.

Ontario Ministry of the Environment, Laboratory Services Branch*; The Determination Of Trace Metals In Acid Precipitation And Low Volume Air Filters And Precipitation By Inductively-Coupled Plasma-Mass Spectrometer (ICP-MS)*, E3061A, November 18, 1998.

U.S. Environmental Protection Agency / Indiana University

Basu Ilora, *Analysis of PCBs, Pesticides, and PAHs in Air and Precipitation Samples - Sample Preparation Procedure*, Version 1.2, May 2000.

Basu, Ilora*, Analysis of PCBs and Pesticides in Air and Precipitation Samples - Gas Chromatography Procedure*, Version 1.2, July 2000

O'Dell, Matt and Basu, Ilora, *Collection of Air and Precipitation Samples - Standard Operating Procedure,* Version 1.1, May 2000

Wassouf, Micahsel, and Basu, Ilora, *Analysis of Total Suspended Particles (TSP) and Total Organic Carbon (TOC) in Air Samples*, Version 1.0 November 1995.

Cortes, Donald, *Instrumental Analysis and Quantitation of Polycyclic Aromatic Hydrocarbons,* Version 3.0, June 1997

Total Suspended Particle (TSP) in Air Samples from the Great Lakes Area: Integrated Atmospheric Deposition Network: Indiana University, January 18, 2000, Version 1.0.

APPENDIX J - IADN DATA REDUCTION PROTOCOL

IADN DATA REDUCTION PROTOCOL

Definitions of terms and statistics referred to in this section may be found in the Glossary (Appendix A) and Section 3.0 of the Data Quality Appendix (Appendix I).

1) Laboratory analytical data will be submitted to the Database Manager 18 months after the last sample of that calendar year has been analyzed. Data may be submitted at more frequent intervals if the data is available. The spreadsheet should contain the mass per sample for each chemical aligned in columns, with the sample records aligned in rows. Field sampling data will include start time, stop time for the sampling, total volume information for the air samples or precipitation volume for precipitation samples, plus comment codes for samples which may have been affected by an abnormal sampling condition or local event (ie. Grass mowing, field plowing in the area, etc..). In this way, the comment codes in the sampling data can be compared with analysis results in order to complete a first order quality assurance check on the sample. These data streams are to be merged such that the sampling data align with the laboratory analysis data. They may also be submitted in separate spreadsheets with a common sample number or code specific to each record. This will permit the database manager to link the two spreadsheets with the record sample number or code within RDMQ.

2) The laboratory data analysis file will contain:

   a) **Laboratory blank table** showing the analyte mass per analysis in the solvent, media blank, and a **field blank table**.

   b) Row-wise aligned field sampling **data table** (unique sample number, date and time on and off, total sample volume, calibration data, date of calibration, or any other data relevant to sample integrity) analyte mass (labeled μg, ng, pg per sample in the header) by sample, field comments and laboratory comments.

   c) A **recovery table** showing average recoveries per analyte for the period covered by the table.

   d) The Laboratory blanks, field blanks, recoveries, and active samples may be reported in the same spreadsheet as long as the sample number and code clearly indicated the record type. Within RDMQ, the records are labeled as:
      i) Lab Blank - LAB
      ii) Field Blank - BLNK
      iii) Active Sample - SMPL
      iv) Recovery - no code specified.. suggest REC

3) If possible, determine the Practical Detection Limit, PDL (Appendix I, Section 3.3.2), for each sample and blank taken. This defaults to the MDL, if available, or at a very minimum,

the IDL. This provides a laboratory minimum sensitivity in pg/sample which can be used to calculate level of detection (LOD). Whether the PDL, MDL, or IDL is used, a table of values which apply to each sample or blank must be available. For further steps in this procedure, we will call these results the **IDL table**. Calculate the **mean IDL plus 3σ**. The table is to be submitted at the same time as sample data is submitted. Clearly indicate the units of the IDL in the header.

4) The field blank is analyzed to determine the **mean field blank mass per sample by analyte, plus the standard deviations of the field blanks**. Field blanks will have a larger fraction of non-detected analytes than the field samples. Follow these steps:

   a) If the field blank table contains censored data (*i.e.*, "below detection limits" (bdl), "<", or missing values), these values must be labeled as 'bdl' within the spreadsheet. Other codes may be used to label or flag bdl values. This method must be clearly indicated in the header of the spreadsheet in order to flag the analyte correctly within the dataset.

   b) Values that are bdl will have zero values inserted within the database and in the blank table. When such a value is inserted in the blank table and within the database, it must be so identified with a flag and the method of replacement noted in the database. If the laboratory data system presents the user with a value of 0 for values less than the PDL, this value can be retained as an uncensored value. All values less than the PDL will be flagged as such.

   c) Previous data 1990-1996 was decensored using 2/3 of the PDL. This method was discontinued in June 2001 when the SC examined data from 1990 to 1998. If the sample was detected, this replacement issue was not significant, but for analytes with low detection, the 2/3 PDL decensoring method reported values for analytes that should have been reported as zero. This was especially relevant to the precipitation analytes such as Mirex that are never detected, yet the statistics showed a value reported, even if that value is below the PDL.
   DECISION from 2001 Data Workshop: Since the different censoring methods do not produce different results for high %detect substances and using 2/3 LOD overestimates the average for low %detect substances, it was decided that we will substitute zero for non-detects for all data in the future.

5) If the value in the blank or active sample table is missing because of a failure in analysis or some reason *other than low concentration*, the value can be flagged with -99 (or similar code) and excluded from the blank statistics. It should be flagged as a missing value.

6) Calculate the mean field blank for each analyte. Calculate the standard deviation of the analyzed blanks. **The level of detection (LOD) is the larger of the mean blank +3σ or the mean IDL plus 3σ (see step 2d). In no case should the LOD be less than the instrumental detection limit**.

7) Quality assure the blank table for statistically-deviating blank concentrations. Is a blank value greater than 3σ above the mean? Is that value realistic? A single high blank

concentration among few blanks can badly bias a blank corrected data set. If a reason exists to expect contamination in a blank value, judgement can be used to remove the value from the blank means and LOD computation. All values so excluded from the calculation must remain in the database, and be flagged (I05) as invalid (contaminated). Blank values which systematically deviate from previous analysis periods should be analyzed for cause and remedied, if possible.

8) Two computed **concentration (air) and loading tables (precipitation)** are to be prepared, **one blank corrected, and the other not blank corrected**. The basis data for these tables are from 2b above.

   a) If a data value is "bdl" or "<", an identical replacement procedure to step 3a should be used so that the statistical calculations take account of all valid samples. Replacement of the value by zero is acceptable, as long as the method is noted, as long as it is consistent with step 3a, and the replaced value is flagged in the data system.

   b) For air concentration data, divide the mass per sample by the sampler flow value to for the concentration table. For the blank-corrected values, divide the mass per sample minus the mean blank by the sampler flow volume. The mean blank mass is the value computed in step 3c above. For concentrations near the detection limit, the blank-corrected table may include negative concentrations. These negative values should be retained. In the seasonal and annual tables, these values will revert to 0.

   c) For precipitation data, the mass per sample should be divided by the surface area of the collector times the sampling period, to form a loading table in units of ng m^{-2} day^{-1}. Alternate units are acceptable as long as they are noted in the database header. Form two tables, one not blank-corrected and one blank-corrected.

   d) A second table for the precipitation data may be prepared of concentrations per sample period, which is the mass per sample divided by the standard gauge volume during the averaging period (season or annual). If the collected volume is used in this calculation, the collector efficiency (collector catch in litres divided by the standard gauge equivalent catch in litres) must be obtained.

   e) The method used in the loadings equation and within the database is to calculate a volume weighted mean which is the sum of the mass of sample collected over the season or year divided by the sum of the volume collected for analysis over the season or year. Units are to be reported in ng/l.

9) Report the following statistics on the concentration/loading data per analyte on a seasonal and annual basis:

Air samples:

   a) Number of samples taken
   b) Number of samples greater than the LOD
   c) Limit of detection (LOD) (pg/m3)
   d) %detection

e) Arithmetic mean value
f) Arithmetic standard deviation
g) Geometric mean value
h) Geometric standard deviation
i) Percentile concentrations for (lowest to highest concentration, annual statistics only):
    i) Minimum
    ii) 10%
    iii) 25%
    iv) 50%
    v) 75%
    vi) 90%
    vii) Maximum

j) For precipitation sampling, form a table of volume-weighted mean loadings by season and on an annual basis. The volume-weighted mean concentration is the total sample mass over an averaging period divided by the total volume collected over the averaging period.

Precipitation sample statistics:

a) Number of samples taken
b) Number of samples greater than the LOD
c) Limit of detection (ng/l)
d) % detection
e) Arithmetic volume weighted mean value (ng/l)

2) The seasonal and annual statistics are based on the sample data start. Each season is calculated based on the following months:
    a) Winter = December (of previous year), January, February
    b) Spring = March, April, May
    c) Summer = June, July, August
    d) Fall = September, October and November

For certain networks that sample over a 14 day duration, the sample date start and end period may start in one month and season and end in the next month and season. (i.e. November 20 to December 4) the start date will determine which season that sample is included.

3) Perform an agency level quality assurance check on the concentration/loading tables in step 3d. Outliers (greater than 3σ above the mean sample) can be excluded from statistical analysis given valid cause and flagged as such. All data, including invalidated data, should be retained in the database. Principle Investigators/Laboratory managers should insert/include a comment and/or code stating the reason for invalidating a data point. (i.e. interference, broken sample, sample went to dryness, not enough volume for analysis, etc..)

4) The IADN Steering Committee is responsible for assuring the overall integrity of the IADN database. Agency LODs, adherence to the IADN QAPP, and interagency comparability will be used for determining the quality of each data set. The SC has the responsibility for

inclusion or exclusion of any data set from the IADN database and the data status will be reported to the Program Managers on an annual basis.

to facilitate the above, a Data Workshop is coordinated on a biennial basis to review 2 years of data (95-96, 97-98, 99-00, etc..) in preparation for loading reporting in accordance with the Implementation Plan timeline. The database manager will prepare necessary spreadsheets, reports and analysis for the Steering Committee to review. Prior to the data workshop, each Principle Investigator will have reviewed the statistical summaries prepared and distributed by the database manager.

APPENDIX K – INTEGRATED ATMOSPHERIC DEPOSITION NETWORK (IADN) DATA RELEASE GUIDELINE

INTEGRATED ATMOSPHERIC DEPOSITION NETWORK (IADN)
DATA RELEASE GUIDELINE

Background: Differences between the U.S. and Canadian Approach to IADN Data

In the U.S., IADN data is generated by cooperative agreement between U.S.EPA and a university. The grantee is the university. The Principal Investigator (PI) is the head researcher and acts as a representative of the university. The grantee and U.S.EPA have similar but independent interests in the data. *Preliminary data* is defined as data that has not yet been verified by the IADN data manager. The preliminary data is simultaneously the property of the PI and the U.S.EPA. The PI is given time to publish the preliminary data prior to general availability. Data is verified by the IADN data manager via the Research Data Management and Quality Control System (RDMQ™) prior to submittal into the IADN database. If data is requested prior to verification, it is released as confidential with a disclaimer. In addition, U.S.EPA is required by the Freedom of Information Act to provide government-generated data to the public upon request. Since the U.S. EPA funds IADN research, it is the owner of the data. However, the grantee has the right of intellectual property to the data and can use the data for their own purposes (student theses, journal publications, etc.)

In Canada, the data is generated by PIs in government laboratories, or contractors to government laboratories, and is the property of the Canadian Federal and Provincial government. Contract laboratories also maintain the right of intellectual property to the data. Data is verified via RDMQ™ and NAtChem (National Atmospheric Chemistry Database And Analysis System) and is provided by request to the public via the IADN data manager. All data is subject to Freedom of Information Act requests and, therefore, is considered to be public information. The Federal and Provincial government agencies, however, will provide only quality assured and controlled data sets. All value-added products (summary statistics, loadings estimates, quality assurance tables, etc.) are public information.

Data Release Guideline

Preliminary Data: *Preliminary data* may be released, upon request, by all PIs. A disclaimer

should accompany the U.S. *preliminary data*[1] and the *individual agency data*[2].

Data Submittal to RDMQ™:

Data will be submitted for verification in RDMQ™ within 12 to 15 months from the sample collection date. Verified data (fully flagged and screened) will be available within 6 months of submittal to RDMQ™. This verification process will involve 3 months of RDMQ™ analysis, 2 months for revision/clarification of data errors or problems by the originating PI, and 1 month to finalise the data for submission and inclusion in NAtChem.

NAtChem:

After verification through RDMQ™, and with agreement from the PI, the data will be released to NAtChem. Data from NAtChem will be released to users on a request basis. The request form for data will be widely available via the WWW.

IADN website:

IADN data will also be available on the IADN website (U.S. [www.epa.gov/glnpo/iadn] and Canadian [www.msc-smc.ec.gc.ca/iadn/] versions). Seasonal and annual average concentrations and loadings will be available in table form on the website. Raw timeseries data will be available via a data request form on the website.

Data Format and Reports:

Data reports will be available, on request through the IADN web sites, in standard NAtChem format. Reports will contain necessary meta data and chemical data in one comma separated variable (csv) file. Each data product will contain data for all sites, for one particular year and component (air or precipitation), for a group of parameters (PAH, OC, PCB, metals, meteorological).

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1 Disclaimer: Although this data collection effort has been funded by the U.S. Environmental Protection Agency through (contract or assistance agreement and number) to (name), the data has not been subjected to Agency review. Therefore, it does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

2 The preliminary data used in the IADN loadings estimates will undergo rigorous QC routines using RDMQ and data analysis. This data has not been Quality Controlled or Assured according to the QAPP standards or RDMQ.

Data Levels:

DATA LEVEL	LEVEL 0	LEVEL 1	LEVEL 2
Description	RDMQ™ flagged and unfiltered data set for use by experienced users who know how to handle data with many qualifiers and corrections for BDLs. Processed Comma Separated Variable (CSV) files and Excel (XLS) files.	RDMQ™ flagged and filtered data set. Filtered Comma Separated Variable (CSV) and Excel (XLS) files. Calculations of means and statistics should match Level 2 summary tables and loadings report.	Summary tables, statistical products, charts, reports. Available on U.S./Canada IADN websites. Tables as HTML web products, WORD 6.1 format (DOC) files, and ASCII text files. Graphical files will be in JPEG or GIF format.
Type	Both blank and non-blank corrected	Data less than the LOD will have substituted values (2/3 LOD). All invalidated data will be removed and replaced by an alphanumeric "I" code that cannot be interpreted as a numeric value (i.e. a zero or missing value). The user will be provided with sufficient description through the QAPP to be able to reconstruct the Level 2 value added products.	Seasonal and annual average data tables (for loadings and fluxes), QC reports, BDL summaries, completeness statistics.
Users	IADN Steering Committee, atmospheric deposition research community	General public, average sophisticated user (science or engineering training)	General public, all requestors of data

Data Release Procedure:

The user will submit the request to the IADN data manager. The data manager will then inform the Program Directors, and appropriate Principal Investigators, of the data request. Program Directors and Principal Investigators will approve the data release before the data manager services the request.

Statement (to be added to the data request form, and signed by the requester):

The user agrees that the IADN data shall not be used for profit or commercial ventures.

The IADN Steering Committee requests that the following citation be included in all publications and reports of IADN data.

"The Integrated Atmospheric Deposition Network, established in 1990, is implemented by the Canadian Federal (Environment Canada) and Provincial (Ontario Ministry of the Environment) governments and the U.S. Environmental Protection Agency as mandated in Annex 15 of the Great Lakes Water Quality Agreement (GLWQA)."

1APPENDIX L - OUTLINE OF SUGGESTED AUDIT PROTOCOL CONTENTS

OUTLINE OF SUGGESTED AUDIT PROTOCOL CONTENTS

A. The Audit Planning Phase

1. Assign the auditing responsibility.
2. Select and notify the lead auditor.
3. Conduct the preliminary review of EDCAs.
4. Summarize the preliminary review.
5. Select the data collection projects for detail review.
6. Select the audit team.
7. Prepare the audit checklist.
8. Prepare the audit agenda.

B. The Audit Phase

1. Notify the auditee (and the auditee's management).
2. Conduct entrance interviews and review QA documents, data, information, and reports.
3. Conduct audit team meetings.
4. Prepare the draft report on findings (positive and otherwise).
5. Conduct exit interviews and report preliminary audit findings with the auditee and the auditee's management.

C. Report Preparation Phase

1. Prepare the draft audit report.
2. Review the draft audit report.
3. Prepare the final audit report.
4. Distribute the audit report (normally restricted).
5. Review and file the auditee's response to the audit report.

D. Follow-up Audit Phase

1. Request detailed information on corrective actions.
2. Evaluate corrective actions.
3. Prepare follow-up audit agenda (if necessary).
4. Conduct formal follow-up audit session.
5. Prepare the follow-up audit report.
   a. Document areas of agreement.
   b. Document areas of disagreement.

E. Audit Closure Phase

1. Prepare closeout memorandum (notice of no further follow-up).
2. Forward closeout memorandum to appropriate manager.