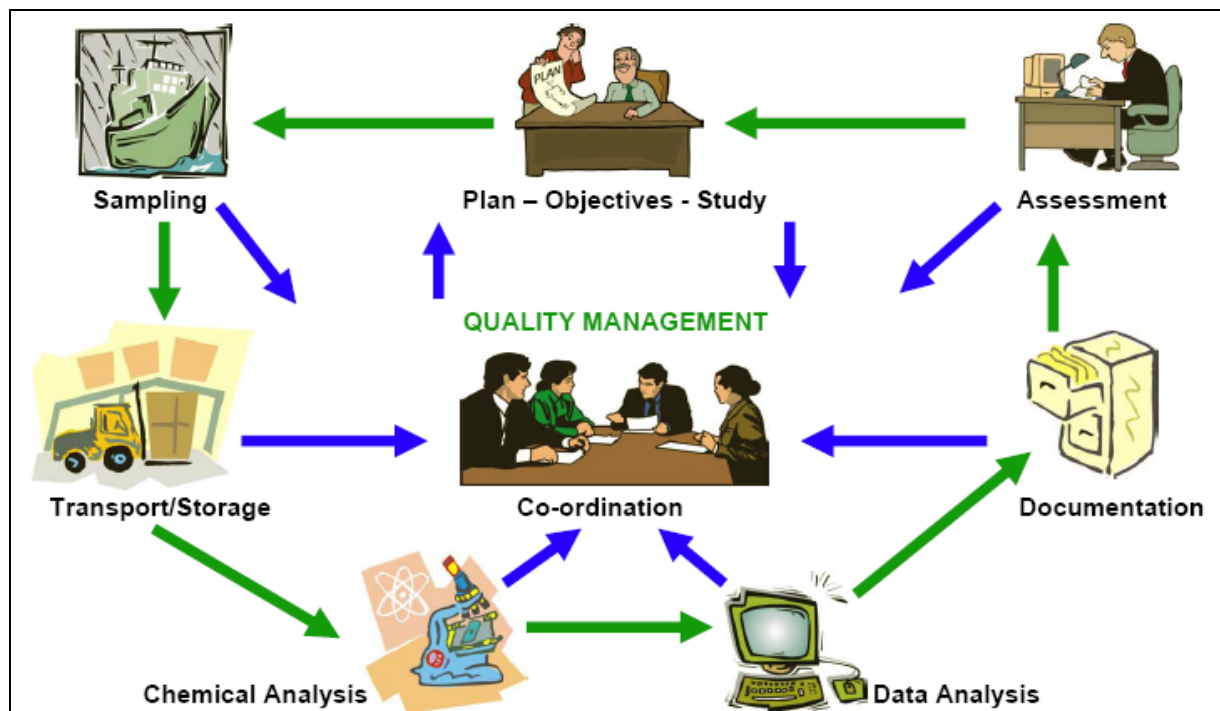




Guidance for Analysis of Persistent Organic Pollutants (POPs)



UNEP Chemicals Branch, DTIE

March 2007

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Pollutants (POPs)**

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This publication reflects the conclusions and recommendations as to analysis of POPs from the three Regional Workshops held within the UNEP/GEF Project "Assessment of Existing Capacity and Capacity Building Needs to Analyse Persistent Organic Pollutants (POPs) in Developing Countries". The project is financed by the Global Environment Facility and implemented by UNEP through UNEP Chemicals. Co-financing of the project is through the governments of Canada, Germany, and Japan, and with technical support from UNEP Chemicals.

The three workshops during the 1st phase of the project were held:

- 5-9 September 2005 for Latin American and Caribbean countries in Montevideo, Uruguay
- 4-6 October 2005 for African countries in Pretoria, South Africa, and
- 13-16 December 2005 for Asian and Central and Eastern European countries in Beijing, PR China

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Abbreviations and Acronyms

°C	Degree Celsius
%	per cent
AOAC	Association of Official Analytical Chemists
ASTM	American Society for Testing and Materials
BAT	Best available techniques
BEP	Best environmental practices
COP	Conference of the Parties
DDE	Dichlorodiphenyldichloroethylene, metabolite of DDT
DDT	Dichlorodiphenyltrichloroethane
DTIE	Division of Technology, Industry and Economics
EC	European Commission
ECD	Electron capture detector
EPA	Environmental Protection Agency
EU	European Union
GEF	Global Environment Facility
GEMS	Global Environment Monitoring System
GPS	Global Positioning System
HPLC	High performance liquid chromatography
HRGC	High-resolution gas chromatography
HRMS	High-resolution mass spectrometry
LOD	Limit of detection
LOQ	Limit of quantification
MS	Mass selective (for detector)
ND	Not determined
OECD	Organisation for Economic Co-operation and Development
OHS	Overhead system
PCB	Polychlorinated biphenyls
PCDD	Polychlorinated dibenzo- <i>p</i> -dioxins
PCDE	Polychlorinated diphenyl ethers
PCDF	Polychlorinated dibenzofurans
PFE	Pressurized fluid extraction
POP(s)	Persistent organic pollutant(s)

QA	Quality assurance
QC	Quality control
SC	Stockholm Convention
SFE	Solid-phase extraction
SI	International System (of Units)
SIM	Selected ion monitoring
SOP	Standard Operating Procedure
SSC	Secretariat of the Stockholm Convention
UNEP	United Nations Environment Programme
US	United States
WHO	World Health Organisation

Units

kg	kilogram
g	gram
mg	milligram
µg	microgram
pg	picogram
fg	femtogram
mL	milliliter
µL	microliter
m ³	cubic meter
ppqt	parts-per-quadrillion
ppm	parts-per-million

Guidance for Analysis of Persistent Organic Pollutants (POPs)

1 INTRODUCTION

UNEP Chemicals is executing the medium-sized GEF-funded Project “Assessment of Existing Capacity and Capacity Building Needs to Analyse POPs in Developing Countries” (for further information, see <http://www.chem.unep.ch/pops/laboratory/default.htm>). Besides the GEF, the governments of Canada, Germany, and Japan contribute financially to this project. This 2-year project addresses country needs for laboratory analysis of POPs, pursuant to the Stockholm Convention, and conditions necessary to conduct such analysis in a sustainable manner. The project focuses on the analysis of the 12 POPs listed in Annexes A, B, and C of the Stockholm Convention. The needs for POPs analysis under the Stockholm Convention mainly arise from three areas:

1. Effectiveness evaluation of the implementation of the Stockholm Convention (Article 16) with the matrices ambient air, mother’s milk, and human blood for the first evaluation in 2008. These matrices are laid down in decision SC-2/13 from the second meeting of the Conference of the Parties of the Stockholm Convention (SC COP-2 2006);
2. Limit values for PCDD/PCDF (Article 5), for which the BAT/BEP Expert group suggested achievable levels in stack emissions (draft chapters of the revised guidelines for download from the Stockholm Convention WebPage http://www.pops.int/documents/batbep_advance/intersessional_work/draft_guide.htm, SSC 2006);
3. Provisional limit values for “low POP content” (Article 6) for POPs wastes (solid/liquid technical matrices and stack emissions) as established under the Basel Convention for the 12 POPs (for download, see <http://www.basel.int/techmatters/index.html> and follow language version, SBC 2006).

The outcomes of this UNEP/GEF project include:

1. A databank of operational laboratories worldwide according to their capabilities to analyze classes of POPs in different matrices. The data will be stored in a searchable and accessible databank;
2. Recommended criteria for:
 - (a) Sampling, identification, quantification of POPs;
 - (b) To operate POPs laboratories in a sustainable manner.

UNEP Chemicals Branch, DTIE, has established a POPs Laboratory Databank containing information on laboratories with experience in POPs analysis that were gathered through a questionnaire provided through this project. The databank is accessible at the project's WebPage.

From September to December 2005, three regional workshops were held and participants from four regions have proposed criteria that would generate high quality POPs data. The individual workshop reports (UNEP/GEF 2005) can be downloaded from <http://www.chem.unep.ch/pops/laboratory/workshops.htm>.

This report has been compiled as guidance for laboratories performing POPs analysis based on the outcomes from the three regional workshops and amended through experiences gained during the visits at the pilot laboratories that participate in this UNEP/GEF project and the training undertaken in the course of the project.

2 POPs ANALYSIS

The purpose of this guidance is to provide information to laboratories and clients how to produce reliable data for concentrations of persistent organic pollutants (POPs) in various matrices. The application of this guidance should assist to generate results of comparable quality that form the basis for the mutual acceptance of data among countries. If customers can rely on analytical results developed in other countries or other laboratories, duplicate works and testing can be avoided thereby saving time and money. In most aspects, POPs analysis does not differ from any other chemical analysis for determination of the mass concentration of an analyte of interest in a given matrix. Therefore, this guidance includes elements of common sense practices such as aspects of the “Principles of Good Laboratory Practice” (OECD 1998) and descriptions found elsewhere or already being in place at laboratories because of other types of chemical analysis. Nevertheless, there are certain criteria specific for POPs analysis and these should be taken into consideration when performing analysis to serve the environmental multilateral agreements such as the Stockholm, Rotterdam or Basel Conventions. It should also be noted that there are steady improvements in analytical techniques and instrumentation and therefore, this guidance should be considered as a living document to be amended and recommended for consultation of further reading and other sources of information.

Further information on POPs analysis can be found in written materials prepared under this UNEP/GEF project such as in the training documents and workshop presentations.

As for any other chemical analysis, POPs analysis includes the following three main steps:

1. Sampling;
2. Transport and storage of the samples;
3. Analysis (extraction, purification, separation, identification, quantification and reporting).

Before the start of any POPs analysis, an adequate study design has to be established to ensure that the sampling and subsequent analysis will meet the objectives of the study. Therefore, close cooperation between the laboratory and the client needs to be established to understand the objectives of the study and adequately accommodate all needs. All of the activities mentioned above under (1) to (3) should be conducted by trained professionals, according to a well-designed plan and using internationally or nationally approved methods, carrying out the same method each time over the time span of the program. It should be understood that mistakes in sampling or analysis – and reporting or storage of data or any deviation from standard operational procedures can result in meaningless data or even program-damaging data.

Quality control and quality assurance are important factors in sampling and analysis. Any method performance must be verified through control tables where optimal operational ranges are defined, and the periodical analysis of certified reference materials, own laboratory reference materials, and blind or divided samples should be included in routine QA/QC (Note: the supply of such materials must be ensured). The inter-calibration exercises are an essential component in quality assurance of the results and are deemed indispensable in the implementation of a regional laboratory network. A recommendation would be that at least

once a year such an intercalibration study is performed for each matrix and POP of interest to the Region.

Laboratories may adopt EU / EPA / AOAC / ASTM, *etc.*, methods or other published methods for sample extraction, clean up, and analysis, and have to validate them within the laboratory. The most basic requirements are:

- The laboratory must be able to prove competence for infrastructure, instrumentation, and well-trained staff to conduct specific analyses;
- Validation of the analytical methods including in-house methods;
- Standard operating procedures (SOPs) for the validated methods, including all the laboratory equipment and consumables;
- Quality criteria for QA/QC described in the SOPs, *e.g.*, analysis of blank samples, use of reference materials, signal/noise ratio, and sensitivity of the analytical system.

Because there are numerous reasons for sampling and analysis of POPs and because there are also so many matrices and numerous methods that can be used, it is beyond the scope of this document to discuss these methods. In the next four sections, however, the key points for sampling, transport and storage, and analysis are considered.

2.1 Sampling

The objective of any sampling activity is to obtain a sample that can serve the objective of the study commissioned by the client. In this activity it is considered indispensable to ensure the representativeness and integrity of the sample during the whole sampling process. Additionally, quality requirements in terms of equipment, transportation, standardization, and traceability are indispensable. It is important that all sampling procedures are agreed upon and documented before starting a sampling campaign.

The analyte (= POPs of interest), matrix, sampling site, time or frequency, and conditions should be determined depending on the objective of the sampling.

Although it may be too expensive to get full accreditation for sampling, Quality Assurance/Quality Control (QA/QC) procedures for sampling should be put in place.

2.1.1 General Sampling Procedures

General sampling procedures include:

- Preparation of sampling equipment(s), eventually shipment of samplers;
- Establishment of criteria for acceptance of samples at the laboratory;
- Establishment of standard operation procedures for sampling;
- Establishment of quality assurance procedures, *e.g.*, field blanks, chain-of-custody.

2.1.2 Infrastructure and Set-up

With respect to sampling indispensable requirements include:

- Equipment: To have adequate sampling instruments according to the type of matrix and POP (dredger, HiVol, water bottles, *etc.*);
- Materials: Sampling instrumentation that is analyte-compatible, including utensils, containers, *etc.* (stainless steel-glass, never plastic);
- Personal protection: Those in charge of the sampling must wear adequate protection outfits depending on the type of samples they will work with (gloves, rubber boots, goggles, *etc.*);
- Sample blanks: These allow for the assessment of potential contamination;
- Preservation: Samples and sample blanks will be preserved according to matrix and type of POP requirements;
- Transportation: Adequate transportation that minimizes the possibility to contaminate the sample, ensuring its integrity and conservation until it reaches de laboratory in charge of the analysis;
- Availability of “in situ” monitoring equipment: To measure relevant environmental parameters according to each environment. The environmental conditions should be registered;
- Geo-referencing and photographic registers: Availability of GPS to locate sampling sites with precision and ensure future location of the site;
- Standardized protocol: Well-established sampling procedures have to be applied. Such sampling protocols have been developed by institutions or organizations such as ASTM (American Society for Testing and Materials), EC (European Commission), US-EPA (Environmental Protection Agency), GEMS (Global Environment Monitoring System), WHO (World Health Organisation). However, it has to be noted that such protocols may have to be updated or adjusted if necessary;
- Labelling: Unambiguous labels are needed;
- Interface between sampling personnel and analytical laboratory: Close cooperation is crucial between project planners, the samplers, the analytical laboratory, and data users;
- Training of personnel: Personnel should be sufficiently trained and familiarized with the sampling techniques. An ecosystem expert is needed in the sampling group and some local people could act as guides;
- Storage capacity: The laboratory must have an adequate storage capacity, *i.e.*, refrigerators or freezers at sufficiently low and stable temperatures, to ensure the integrity of the samples. These temperatures should be monitored constantly and documented.
- Waste Treatment: Consideration of suitable treatment/handling of the waste generated during the sampling.

2.1.3 Standard Operating Procedure

A Standard Operating Procedure (SOP) has to be established for each type of matrix (note: several similar matrices can be combined). In these SOPs the following requirements must be addressed:

- The objective of the sampling exercise, including sampling protocols and specifications;
- Sample size in accordance with the analytical requirements and limitations in order to meet regulations or other objectives as given in the study;
- Description and geographic location of the sampling sites, preferentially with GPS coordinates;
- Guidelines for representative samples;
- Criteria for composite samples, *e.g.*, number of sub-samples, homogenization;
- Date, time of the sample taking;
- Conditions during sampling;
- Time intervals between sampling exercises;
- Specifications for the sampling equipment, including the operating, maintenance, and cleaning procedures;
- Identity of the person who has taken the sample;
- Full description of sample characteristics;
- Labelling (sample numbers should be assigned in the protocol and prepared labels taken into the field);
- Labelling of samples (in the field) and sample registration for further follow-up;
- Indication of expected level of POP concentration in the sample;
- Any additional observation that may assist in the interpretation of the results;
- Quality assurance procedures to prevent cross-contamination.

The SOP should also contain a section with details on personal protective equipment that must be worn and listing of other safety concerns as appropriate.

2.1.4 Sub-contracting a Sampling Laboratory

No general recommendation can be given with respect to whom should perform the sampling. Whereas for certain matrices, *e.g.*, human blood, there is no doubt that not the laboratory but a specialist, *i.e.*, medical doctor or nurse, has to take the sample. For human samples, also ethical considerations have to be respected. There are pros and cons for sub-contracting a laboratory specialist in sample taking:

- (a) Advantages: Sub-contracting the sampling can be an advantage to the laboratories that don't have the required personnel and equipment;
It could assure a more immediate answer in an emergency situation;

- (b) Disadvantages: The laboratory must be sure that the sampling was made within the established conditions;
If the laboratory is not present at the sampling location, it can reduce the added value to the analysis and its interpretation.

In case a laboratory will be sub-contracted to take the sample, it is recommended that the analytical laboratory establishes and provides the sampling protocol. Those in charge of the sampling process must apply security seals, as well as follow the preservation criteria to guarantee the integrity of the sample during transportation.

In some countries different government departments are responsible for the sampling of different matrices to comply with specific national or international regulations, *e.g.*, for the import / export of food commodities. In the countries where regulations do exist, qualified staff is appointed by the government of the country to do sampling. In other countries no procedures may be in place for sampling.

2.2 Transport and Storage

The SOP also includes the requirements for transport and storage. More specifically, these are:

- Transport and storage conditions for each sample matrix including adequate facilities and infrastructure to be provided present, *e.g.*, freezers;
- Preservation of integrity of samples during transport (temperature, light, *etc.*);
- Provisions for adequate storage. These conditions are dependent on the analyte and the matrix, but in general, the following conditions and times are proposed:
 - Water: Refrigerator at +4 °C
 - Biota and solids: Refrigerator at – 20 °C; possibly at -80 °C when considered necessary.
- Adequate storage also includes:
 - Registry of the performance of refrigerators and freezers, *e.g.*, registration and control of temperature;
 - Availability of automatic power-supply equipment in case of power cuts;
 - Recommended storage times are: ~ 2 weeks in the case of extraction, 40 days for the analysis, and several years for archiving samples.
- Preservation of individual samples for their re-analysis (counter-sample);
- Pre-analytical treatment of the sample: statistical criteria to obtain sub-samples and composite samples (pools) that are representative, homogenization of solids and tissue;

Note: there may be requirements for shipment to be addressed and respected. Especially in the case of international shipment, considerations for transport and customs' clearance must be taken into account since restrictions may exist.

2.3 Analysis

For information on general methodological considerations, among others, information is given in the guidance document as established for the Global Monitoring Plan (UNEP 2007).

Key steps to be considered are:

- Procedures and acceptance criteria for handling and preparation of the sample in the laboratory (*e.g.*, homogenization);
- Standard QA/QC procedures must be followed by the laboratory;
- Participation at international intercalibration studies, analysis of certified reference materials are essential.

2.3.1 Set-up and Infrastructure

POPs analysis may be performed on a large variety of matrices and concentrations in the samples may differ across many orders of magnitude; *e.g.*, from PCB in transformer oils in the mg/kg (ppm)-range to PCDD/PCDF in ambient air in the fg/m³ (ppqt)-range (twelve orders of magnitude). In order to guarantee preservation of the samples, control of potential cross-contamination, standardization of the technique, calibration, and good maintenance of instruments, the requirements listed below are considered indispensable. In general, the laboratory should be clean and safe, well organized, and have adequately trained staff to conduct the analysis. Having implemented the above mentioned measures will allow for accreditation in the medium run. The requirements include:

- General laboratory environmental conditions should ensure enough laboratory space for each step of the analysis and to avoid interference between individual samples. This includes:
 - Physical separation of standards and samples according to their origin (for example, industrial *versus* environmental) or
 - Expected POP concentration (minimize cross-contamination by separating highly contaminated samples from low contaminated samples)
 - Control of temperature and provision of air-conditioning;
 - Availability of extraction hoods;
 - Handling area of inflammable products;
 - Provisions for laboratory waste disposal
- Ensure the custody chain of the sample: verify the integrity and preservation of the samples (maintenance) in terms of temperature, containers, labels, registry, those responsible at each stage, establishment of acceptance criteria (conditions as well as quantity of material, according to analyte and matrix);
- Separation of aliquots: In the case of complementary analysis (for example, granulometry) prior to the freezing of the sample;
- Selection and validation of analysis method: Use method validation protocol according to the type of analyte and matrix (selectivity, repeatability, ability to reproduce, extraction efficiency, recovery, detection limit, quantification limit, accuracy). Quality of solvents and reagents (blanks). Clean glass material (avoid cross-contamination). Maintenance and calibration of auxiliary equipment (stoves, scales, test tubes, pipettes, glassware). Protocols and procedures must be clearly described and documented.

2.3.2 Extraction

There are various methods for extraction, which include Soxhlet, SFE, PFE, liquid-liquid, *etc.* After extraction, the extract will be concentrated. In order to do so, the technique should be optimized to avoid excessive loss of the analyte. Typically, this step includes: evaporation under vacuum or with nitrogen (Note: control of temperature, flow of nitrogen, and vacuum are essential). Complete drying of the extract should be avoided.

- Before or during extraction, water, lipids, proteins, and sulfur should be eliminated. This can be done by:
 - Elimination of water by drying of the sample with sodium sulphate or equivalent demonstrated acceptable drying procedure
 - Elimination of lipids with sulfuric acid or permeation in gels after extraction)
 - Denaturation of proteins with oxalate
 - Elimination of sulfur with activated copper or by gel permeation after extraction.
- Extraction should be standardized with respect to standardization of extraction times, type of solvent, performance of auxiliary equipment, *etc.*;
- Before extraction, internal standards should be added to control the extraction efficiency;
- The recoveries of the extraction standards differ with POP to be analyzed and matrix. Based on current experiences (from international calibration studies) as a general rule:
 - For PCB and pesticides: 80 %-120 % (for tetra- and penta-chlorinated PCB, recoveries down to 60 % can be accepted)
 - For PCDD/PCDF: 50 %-130 % (for hepta- and octa-chlorinated PCDD/PCDF 40 %-150 % can be accepted)

2.3.3 Purification:

Purification is done to remove interfering substances/materials from the analyte in order to obtain unambiguous results. Purification should be efficient enough so that the chromatographic retention is not influenced by the matrix (especially when no labelled internal standards are used or no mass-specific detection is present).

Purification is being performed with various types of adsorbents with different solvents depending on selectivity, conditioning, and column flow. During purification the following aspects need to be controlled or maintained:

- Verification that profile/pattern (relative amounts within the sample) of the analytes is maintained throughout the whole purification procedure. In other words that at a satisfying recovery the pattern/profile of the analytes at the original composition are obtained;
- An internal standard is added at a concentration signal/noise at a minimum level with at least 20/1; with fixed concentrations of internal standards from sample to sample in order to obtain adequate response factors;
- Control fraction cut.

2.3.4 Separation

Separation of POPs will be conducted through gas chromatography with electronic capture detector (ECD), mass selective detector (MS detector) or, if available, high-resolution mass spectrometry (HRMS). Presently, only high-resolution gas chromatography (= capillary gas chromatography) can achieve sufficient separation. Packed columns (GC) or other separation techniques such as HPLC were not found adequate.

- In general, an appropriate GC phase has to be selected and enough GC peak separation must be achieved to allow accurate quantification (general numeric criteria cannot be given, but the use of capillary columns with lengths of 30-60 m, internal diameters of 0.15-0.25 mm, a film thickness of 0.1-0.3 μm , and helium or hydrogen as a carrier gas should ensure sufficient resolution) (note: hydrogen cannot be used together with MS detection);
- Separation of critical isomer pairs and congeners has to be verified, *e.g.*, pairs of PCB 28 and 31, 118 and 149, *etc.*; in dioxin analysis separation of PCDD/PCDF from polychlorinated diphenyl ethers (PCDE) should be checked;
- Identification:
 - For ECD (or more general, for non-MS detectors), confirmation of peaks should be performed on a second column with different polarity. Alternatively, analyte additions can be used;
 - For MS detection, confirmation of peaks on a second column with different polarity can be advisable;
- For PCB analysis and ECD detection, a minimum of two internal standards - one eluting at the beginning and one at the end of the chromatogram – should be used. It is recommended to also use one PCB congeners that elutes in the middle of the chromatogram. Thus, the following three congeners are recommended: PCB #112, #155, and #198. These three congeners are quite stable and typically not found in commercial PCB mixtures. Note: decachlorobiphenyl (PCB #209) is not recommended because it tends to precipitate easily in standard solutions and due to long retention times, the peaks tend to be broad and have tailings. PCB #209 has also be identified in environmental samples and could not be quantified if this congener is selected as an internal standard.
- Adequate handling and preservation of all standards and reference materials;
- Verification of chromatographic conditions include:
 - Resolution, symmetric peak shape
 - Reproducibility of retention times
 - Purity of gases
 - Use of second column of different polarity as confirmation column
 - Verification of the linear range of the instrument.
- Calibration
 - Standard solutions should be prepared and stored on w/w basis rather than w/v (weight-to-weight rather than weight-to-volume);
 - Multi-level calibration curves of at least 5 points;
 - Periodical calibration (for example 1-2 times a week) and verification with daily intermediate level standard (define a rejection criterion of, for example, $\pm 10\%$).
 - Calibration of the detector: The instrumental MS detector detection limits needed are a few (1-3) $\text{pg}\cdot\mu\text{l}^{-1}$; for HRMS the instrument detection limit is 0.1-3 $\text{pg}\ \mu\text{l}^{-1}$;

- The signal to noise ratio must be equal or higher than 3:1;
- Injection:
 - Ensure cleanliness and superficial inertia of injector (deactivated glass insert, evaluate activity with an acceptance criterion, for example, for DDE/DDT < 20 %)
 - Verify the split/splitless relation, flows and state of septum
 - Repeatability must be ensured (for example, criterion < 5 %), and
 - Injection sequence for each group of samples analyzed as follows: blanks, control samples, duplicates, verification standards;
- Registration and traceability of services and performance of equipment.

2.3.5 Identification

- Retention time should match between sample and internal standard;
- Identification criteria include:
 - Positive identification should be done on isotopic ratios within 20 % of theoretical value (for SIM);
 - For positive identification with MS detection, the retention time of the labeled internal standard to the native compound should be within 3 seconds;
 - Retention time ± 0.2 min for ECD or a specified percentage of the retention time of the labelled internal standard for MS detectors;
- Matrix spikes (or co-injection) are recommended to verify components and check the quantification;
- Integration: select the basic level and the adequate signal to noise relation of integration according to the type of sample, verify the general form of the chromatogram, the form of the peaks and manually verify integration.
- The use of MS libraries is useful (if full scan);

For HRGC-ECD combinations, the following specific recommendations are given:

- Deactivated inlet liner in injectors has to be used;
- Criteria for the type and purity of carrier gas for the column. Helium, compared to nitrogen, is a better choice to achieve the desired separation of pesticide POPs and PCB. The best carrier gas to achieve the required separation is hydrogen but it has some safety risk. If all the precautions and safety procedures are in place a hydrogen generator may be considered;
- Criteria for the purity of nitrogen as detector make-up gas;
- Sample clean-up procedures should be efficient to prevent contamination of the ECD.

For HRGC-MS detection combinations, the following specific recommendations are given:

- Helium as carrier gas (the only choice);
- Deactivated inlet liner in injectors has to be used;
- Vacuum conditions of instrument;
- Mass calibration and tuning of instrument;

- Positive identification criteria: isotopic ratio should be within 15 % of theoretical value.

2.3.6 Quantification

For general aspects, please consult the Guidance Document on Global Monitoring Plan (UNEP 2007).

In general, quantification of the analyte should be done according to the internal standard methodology. For PCDD/PCDF and dioxin-like PCB, typically additional requirements are needed. The following requirements are considered to be indispensable:

- For preparation and maintenance of standard solutions and especially under not stable laboratory atmospheric conditions, it is recommended to use w/w basis rather than w/v (weight-to-weight rather than weight-to-volume);
- At least one standard representative for the POPs analyte group analyzed should be added at the normal level of quantification;
- For quantification it must be assured that the concentration of the compounds/analytes is within the previously determined linear range of the detector (Note: Not necessary when multi-level calibration is performed!);
- Verification that the concentration of blanks is significantly lower than the samples; recommendation: < 10-times; and
- Noise should be defined as close as possible to the peak of interest;
- The stipulated reporting concentration has been reached;
- For mass spectrometry (MS detectors), at least 10 data-points should be sampled across a mass peak for quantification (Note: Some instruments do so automatically);
- The performance for each sample to be achieved should be:
 - LOD for PCDD/PCDF of at least 1/5
 - LOQ of 1/5 for all other POPsof the regulatory value to be controlled/to get meaningful results;
- Criteria should be set to define lower-bound and upper-bound concentrations (see also 2.3.8 "Definitions" at end of this section);
- The reporting value and therefore the limit of quantification should be at least 1/5 of the regulatory limit or level of interest or baseline concentration (also covered under section 2.3.7 "Reporting");
- Calibration:
 - Labelled internal standards are an added value;
 - Multi-point calibrations should be carried out;
 - [Daily] calibration checks in connection with analyzing a series of samples should be done (for large batches calibration drifts have to be checked during the run).

2.3.7 Reporting

Data compilation and reporting together with data storage are the final steps in analysis. The report form must include:

- Reporting should be done in accordance to regulation(s);
- The report has to include date, name of the sample and description (sampling, *etc.*), method used, the name of staff that has performed analysis, and signature of person in charge of the POPs laboratory;
- Only SI units (International System) should be used and should be verified before clearing the report;
- Clear references to the material must be given, *e.g.*, fresh weight, dry matter, lipid based;
- Data should be reported as "<LOQ value" or other bound as per regulatory requirements (and not as ND);
- Recovery efficiency should be reported;
- Uncertainty: Information on uncertainty should be made available;
- The reporting value should be at least 1/5 of the regulatory limit or level of interest or baseline concentration (also covered under Quantification);
- The difference between lower-bound and upper-bound value at the regulatory level should be less than 20 %;
- Reported values should not be corrected for percentage of recovery since the internal standard methods does so automatically;
- Criteria should be built in to guarantee that sensitivity/recovery issues do not impact the reporting values. Enough assurance should be given that the used reporting limits are fully guaranteed;
- It should be demonstrated that the blank is 10-times lower than the value that is reported. Reporting values should not be corrected by laboratory blanks (Note: There may be high fluctuations for laboratories' blanks, *e.g.*, for PCB 118). Handling of all blanks needs written documentation; in the case of high laboratory blanks; handling of such cases and justification should be clearly indicated in the SOP;

2.3.8 Definitions

- Limit of detection and limit of quantification are defined as follows:
 - LOD should be at least $\text{signal/noise} = 3$
 - LOQ should be 2-3 times the LOD
- An example with a definition specific to a particular regulation is the European Food/Feed regulation (EC 2002) with the following definition: $\text{signal:noise } 6:1 \text{ or } 9:1$;

- In the context of regulatory limit values or for reporting measured concentrations, there is no general rule how to treat results below LOQ. Very often, the regulations or laws define the way of reporting results. For reporting, the following definitions should be taken into account:
 - Lower-bound: Non-quantifiable peaks are set to zero
 - Upper-bound: Full LOQ included in presentation of result
- There are two methods available to provide information on uncertainty:
 - Quantification of uncertainty for each step
 - Overall uncertainty derived from inter- and intra-laboratory results.

2.4 Further Important Issues to Consider

2.4.1 Maintenance of Equipment

The maintenance of the analytical equipment is considered as one of the most important aspects in POPs analysis. It is very expensive to have service contracts for all the maintenance and therefore it is important to train the laboratory personnel to do the basic maintenance when the QA/QC results are unacceptable.

Laboratories must arrange for proper training, including basic maintenance, when new equipment is installed in the laboratories.

2.4.2 Training of Laboratory Staff

Human resources are crucial for any analytical work. The following specific problems need to be addressed and resolved:

- The lack of skilled laboratory personnel to conduct the analytical work was identified as one of the critical problems;
- The training requirements. Two levels of training exist:
 - Training of people to follow the analytical procedures and to report the results;
 - Training of people to do troubleshooting and conduct the necessary maintenance when the QA/QC criteria fail;
- Countries with experienced personnel should assist other countries with training of laboratory personnel;
- There is a need in the region for training courses and annual training workshops for the transfer of technology know-how;
- Although difficult to estimate, about 20% of the time spent on the analyses should be dedicated to QA/QC.

2.4.3 Housing

For POPs laboratories there are certain requirements as to housing. These include:

- Proper environmental conditions (humidity is most critical factor) for instrumental analysis but also for sample preparation;
- Minimization of vibration;
- Temperature control for helium carrier gas used with ECD;
- At certain locations, incoming air has to be cleaned (from dust, PCB, naphthalene);
- OHS venting;
- Environmentally sound/safe disposal of laboratory wastes and highly contaminated samples must be guaranteed.

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