MEDITERRANEAN ACTION PLAN
MED POL

UNITED NATIONS ENVIRONMENT PROGRAMME

INTERNATIONAL ATOMIC ENERGY AGENCY

DATA QUALITY REVIEW FOR MED POL (1994-1995)

Evaluation of the analytical performance of MED POL laboratories during 1994-1995 in IAEA/UNEP laboratory performance studies for the determination of trace elements and trace organic contaminants in marine biological and sediment samples

By

M. Horvat, M. Coquery, J-P. Villeneuve and C. Catini

MAP Technical Reports Series No. 116

UNEP
Athens, 1997

Note: The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of UNEP concerning the legal status of any State, Territory, city or area, or of its authorities, or concerning the delimitation of their frontiers or boundaries.

P.O Box 18019, Athens, Greece

ISBN 92-807-1656-4

For bibliographic purposes this volume may be cited as:

UNEP/IAEA: Data Quality Review for MED POL (1994-1995) - Evaluation of the analytical performance of MED POL laboratories during 1994-1995 in IAEA/UNEP laboratory performance studies for the determination of trace elements and trace organic contaminents in Marine biological and sediment samples. MAP Technical Reports Series No. 116. UNEP, Athens, 1997.

Contents

Page

INTRODUCTION 1

PART I. Laboratory performance study for the determination of trace elements in marine sediment, SD-MEDPOL-1/TM and fish homogenate, MA-MEDPOL-1/TM 5

1. Introduction 5
2. Scope of the intercomparison 5
3. Description of the material 5
   3.1. Marine sediment 6
   3.2. Fish homogenate 7
4. Analyses and reporting 8
5. Evaluation of the results 8
6. Results and discussion 12
   6.1. Overview of the results 12
      6.1.1. Moisture content 12
      6.1.2. Reporting of the results 12
      6.1.3. Analytical methods 12
      6.1.4. Less than values 13
      6.1.5. Laboratory performances 13
   6.2. Laboratory performance for selected trace elements 15
      6.2.1. Arsenic 15
      6.2.2. Cadmium 15
      6.2.3. Chromium 18
      6.2.4. Copper 18
      6.2.5. Iron 19
      6.2.6. Mercury 19
      6.2.7. Manganese 20
      6.2.8. Nickel 20
      6.2.9. Lead 20
      6.2.10. Zinc 21
   6.3. Overall laboratory performance 21
      6.3.1. Sediment 21
      6.3.2. Fish 23
      6.3.3. Summary 23
7. Conclusions 23

PART II. The analytical performance study for the determination of chlorinated compounds and petroleum hydrocarbons in mussel tissue, IAEA-142 25

1. Introduction 25
2. Scope of the intercomparison 25
3. Description of the material 26
4. Homogeneity test 26
5. Moisture content 26
6. Sample dispatch and data return 26
7. Reference values for chlorinated pesticides, PCBs and petroleum hydrocarbons in IAEA-142 27
8. Evaluation of the results 31
   8.1. Organochlorine compounds 31
   8.2. Petroleum hydrocarbons 31
   8.3. Z-scores 31
9. Discussion 32
   9.1. Chlorinated pesticides and PCBs 32
   9.2. Petroleum hydrocarbons 32
10. Conclusions 35

RECOMMENDATIONS 37

REFERENCES 38

ANNEX I. Data report for SD-MEDPOL-1/TM 41
ANNEX II. Data report for MA-MEDPOL-1/TM 67
ANNEX III. List of participants (trace elements) 85
ANNEX IV. Data report for IAEA-142 93
ANNEX V. List of participants (organic compounds) 121

INTRODUCTION

It has long been recognized that measurements of chemical contaminants of the marine environment are often subject to large errors in terms of precision and accuracy. A major part of the analyst's work is to reduce these errors to a degree that the data become useful for assessing the changing state of the marine environment. Environmental chemists are required to validate their data by inter-comparing their results and by checking their measurements using materials of known composition. This should be a continuous and regular process in order to obtain maximum confidence in the data set.

Since the beginning of the Long-term Programme for Marine Pollution Monitoring MED POL Phase I, the Contracting Parties to the Barcelona Convention have expressed their concern regarding the quality of monitoring data used to conduct marine pollution assessments and have consequently given a high priority to Data Quality Assurance (QA) in its widest context. Analytical Data Quality Assurance can be broadly regarded as the mechanism for ensuring that the quality of the data is sufficiently reliable for its intended application. Analytical Data Quality Control (QC) which is a component of any QA strategy, is the day to day mechanism for keeping the data at the desired level of quality.

At the earliest stages of MED POL, the Quality Assurance Programme mainly consisted of workshops and intercomparison exercises. Since that time the demand has increased for more precise data covering a wider range of analytes. In response to this need, a more sophisticated and comprehensive data quality assurance programme was developed in 1987 integrating intercomparison exercises, instrument maintenance, technique development, training (encompassing measurement techniques, QA/QC, instrument maintenance) and joint monitoring exercises. This work is coordinated by the IAEA Marine Environment Laboratory (MEL) in Monaco which established a special section, the Marine Environmental Studies Laboratory (MESL) which acts *inter alia* as the regional analytical centre for MED POL.

Since 1987, MESL has conducted 33 extended QA missions, 93 instrument service missions, installed new instruments in 7 countries and received 102 MED POL trainees. It has also continued with its interactive intercomparison programme, produced 7 new reference materials and developed a bank of standards and standard reference materials freely available to all MED POL laboratories.

IAEA, together with UNEP and IOC, work closely with other producers of Reference Materials in order to assure a continuous supply of these vital compounds for QA/QC procedures. A bank of materials is maintained at MESL in Monaco and these are available free of charge to all MED POL monitoring laboratories. In recent years stronger links have been forged with other QA/QC programmes, notably those of the EU and ICES and mutual experience in this field is being exchanged.

The main source of information on Mediterranean analytical data quality is from the intercomparison exercises which have been conducted on a regular basis since 1973. These exercises are conducted by taking a very large single sample of an appropriate environmental

matrix (fish, mussel, sea plant, sediment, etc.) freeze drying and homogenizing it and distributing it amongst some 250 or so institutions world-wide.

The resulting data are then analyzed using parametric and non-parametric statistics. Where the consensus median is reasonable and a series of statistical criteria are fulfilled, the sample is issued as a reference material for use in quality control programmes. A full report on each exercise is issued, however, the identification of the individual participants remains strictly confidential. Laboratories doing badly in the intercomparison exercise are contacted by the relevant staff of MESL and asked whether they require any assistance in order to "trouble-shoot" and correct their analytical problems.

From the outset it should be stated that all Mediterranean laboratories, whether part of the official MED POL network or not, have been encouraged to participate in the data quality intercomparison exercises. All laboratories have been offered support with appropriate methodologies, standard reference materials and calibration standards. Additionally, all official MED POL laboratories from developing countries have been provided with instrument maintenance services and, where possible with state-of-the-art instruments, glassware and training. The Secretariat of the Mediterranean Action Plan (MAP) has sought to respond to the technical needs of these institutions within the constraints of the MED POL budget and has conducted regular promotional campaigns to encourage participation in the QA/QC work. The results of these efforts and, in many cases those of the Mediterranean scientists, are reflected in the encouraging statistics presented in the report reviewing the 19 years of progress [1]. The report has shown that data from intercomparison exercises were highly encouraging and compared well with laboratories in other regions. It was noted that there is considerable room for improvement in the analysis of trace organics, but this situation is a general problem world-wide and Mediterranean countries should be encouraged to become leaders in the field to remedy it. The report also stressed the importance of the vital role of the National Coordinators in individual countries and improvement in QA/QC should be high on the agenda for implementing national monitoring strategies. In addition, it has been proposed that monitoring data should not be accepted from laboratories that systematically fail to participate in intercomparison exercises. Furthermore, it is also important to note that the *UNEP/IAEA Consultation meeting on guidelines on analytical data quality assurance, Monaco, 21-23 October 1993 (UNEP(OCA) WG. 72/1, 23 October, 1993)* proposed that the QA programme should be mandatory and form an integral part of each MED POL Monitoring Agreement. Participation of MED POL laboratories in intercomparison exercises should therefore also be considered as mandatory.

This report details the progress towards the fore-mentioned goals. It describes the performance of Mediterranean laboratories in three intercomparison runs conducted during 1994 and 1995. Two exercises were organized for the determination of trace elements in marine sediment (SD-MEDPOL-1/TM) and fish homogenate (MA-MEDPOL-1/TM) and one was organized for the determination of trace organic contaminants in mussel homogenate (IAEA-142). The first two exercises were organized solely for the MED POL region and differ from previous exercises in that samples of certified composition were distributed. Data submitted are summarized and discussed in Part I of this report. The third exercise (IAEA-142)

was organized as a regular IAEA/UNEP world-wide intercomparison exercise and the results submitted for the MED POL region are summarized and discussed in Part II of the present report. Many Mediterranean laboratories participated in these exercises: 37 submitted data for trace metals and 32 for trace organic contaminants. This is the largest number of participants since our exercises commenced over 20 years ago!

A review of the performance of the laboratories for selected trace elements indicates that about 40% of the laboratories have achieved satisfactory performance for trace elements in both sediments and biota. In addition, 10% of the laboratories analyzed either the fish or sediment sample and reported satisfactory data. It is encouraging to note that for Cu, Hg and Zn, the majority of laboratories reported acceptable results. However, there is a need to improve the performance for Cd, Co, Cr, Fe, Mn, Pb and V. In general, results are much less satisfactory for the fish homogenate sample when compared to the sediment. This is probably because of the lower concentrations of most elements in biota samples, rendering analyses more vulnerable to contamination problems, faulty calibration and poor QA/QC practice.

A review of data for trace organics (IAEA-142) shows a significant improvement compared to previous exercises. A number of participating laboratories have achieved satisfactory performance for chlorinated pesticides and for PCBs. Data for petroleum hydrocarbons, however, still need to be improved.

In summary, the results are highly encouraging. They provide an estimate of the variability of data within the MED POL monitoring for 1994/95 and identify where future investments in technical support should be targeted. Continuation of the Analytical Quality Assurance programme is essential in order to maintain the performance achieved and to improve analyses in laboratories that are currently facing serious problems in achieving satisfactory results.

Further information concerning this report and the UNEP/IAEA quality assurance programme can be obtained by contacting the IAEA-MEL, Marine Environmental Studies Laboratory, P.O. Box No. 800, MC 98012, where the staff will be pleased to assist.

PART I

LABORATORY PERFORMANCE STUDY FOR THE DETERMINATION OF TRACE ELEMENTS IN MARINE SEDIMENT, SD-MEDPOL-1 /TM AND FISH HOMOGENATE, MA-MEDPOL-1/TM

M. Coquery and M. Horvat

1. INTRODUCTION

This study was intended to give laboratories responsible for trace element analyses of marine materials an opportunity for checking their analytical performance. Two reference materials were used: the certified reference material MESS-1 (Marine Sediment) obtained from National Research Council of Canada; and MA-ROPME-1 (Fish homogenate) which was previously used in a world-wide intercomparison exercise. The samples were sent to 76 Mediterranean laboratories. Results from 37 laboratories (15 countries) were received. Their performance was assessed by comparing reported results with certified (and recommended) values.

This report provides feed-back to the individual participants about their performance and should enable them to make appropriate modifications to their laboratory's analytical procedures where necessary. All results were treated as strictly confidential and each laboratory was identified with a code number.

2. SCOPE OF THE INTERCOMPARISON

Each participating laboratory received two lyophilized samples, one marine sediment and one fish homogenate, accompanied by an information sheet and a report form. These samples originated from batches of homogenized materials which are described below. Participants were requested to determine by their routine procedures as many trace elements as possible out of the following 17 elements: As, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Ni, Pb, Sb, Se, Sn, Sr, V and Zn. It was not the purpose of this MED POL intercomparison to establish consensus values for trace element concentrations in the materials to be analyzed. These values have been already established for most elements concerned with a satisfactory degree of confidence.

3. DESCRIPTION OF THE MATERIAL

Aliquots of approximately 13 g of Certified Reference Material MESS-1 (Marine Sediment: National Research Council of Canada) were packed into glass bottles with Teflon lined screw caps and sealed with Teflon tape. Aliquots of approximately 7 g of material MA-ROPME-1 (IAEA) were packed in a similar manner. One bottle of each material was sent to 76 Mediterranean laboratories in June 1995.

3.1. Marine sediment

This sample was collected from the Gulf of Saint-Lawrence (Miramichi River estuary), freeze dried, screened to pass through a 125 μm sieve, then thoroughly homogenized.

The average moisture content of the lyophilized sample, determined by drying to a constant weight at 105°C, was found to be 1.5%. Since the moisture content can vary with the ambient humidity and temperature, it was recommended that the water content of this material be determined in a separate subsample (not used for analysis) by drying to a constant weight (~24 hours) at 105°C just prior to analysis. Final results should always be reported on a dry weight basis.

Table I.1. Trace element concentrations in SD-MEDPOL-1/TM (MESS-1) (mean ± confidence interval at 95%)

ELEMENT	Concentration
Arsenic (As) (mg kg^{-1})	10.6 ± 1.2
Beryllium (Be) (mg kg^{-1})	1.9 ± 0.2
Cadmium (Cd) (mg kg^{-1})	0.59 ± 0.10
Chlorine (Cl) (g kg^{-1})	8.2 ± 0.7
Cobalt (Co) (mg kg^{-1})	10.8 ± 1.9
Chromium (Cr) (mg kg^{-1})	71 ± 11
Caesium (Cs) (mg kg^{-1})	[4]
Copper (Cu) (mg kg^{-1})	25.1 ± 3.8
Mercury (Hg) (mg kg^{-1})	0.171 ± 0.014
Manganese (Mn) (mg kg^{-1})	513 ± 25
Nickel (Ni) (mg kg^{-1})	29.5 ± 2.7
Lead (Pb) (mg kg^{-1})	34.0 ± 6.1
Antimony (Sb) (mg kg^{-1})	0.73 ± 0.08
Selenium (Se) (mg kg^{-1})	[0.4]
Strontium (Sr) (mg kg^{-1})	[89]
Vanadium (V) (mg kg^{-1})	72.4 ± 5.3
Zinc (Zn) (mg kg^{-1})	191 ± 17

[ ] Information value

Table I.1 gives trace element concentrations in MESS-1 for those constituents for which certified and recommended values have been established. Certified values are based on the results of measurements made by at least two independent methods of analysis. The uncertainties represent 95% tolerance limits for an individual sub-sample. That is, 95% of a sample (500 mg or greater) from any bottle would be expected to have concentrations within the specified range 95% of the time.

3.2. Fish homogenate

This sample was prepared from shark muscle tissue taken from specimens collected in the Persian Gulf. The sample was freeze dried and ground in a mixer made of stainless steel and glass. The coarse powder obtained was then ground in a porcelain ball mix. The resulting powder was passed through a 150 μm stainless sieve and thoroughly homogenized. The homogeneity was tested using a standard analytical and statistical protocol.

The average moisture content of the lyophilized sample, determined by drying to a constant weight at 85°C, was found to be about 7%. Since the moisture content can vary with the ambient humidity and temperature, it was recommended that the water content of this material always be determined in a separate subsample (not used for analysis) by drying to a constant weight (~24 hours) at 85°C just prior to analysis. Final results should always be reported on a dry weight basis.

Reference values were assigned on the basis of the results obtained by two different analytical techniques (ICP-MS and GF-AAS) from 6 different laboratories and are summarized in Table I.2.

Table I.2. Trace element concentrations in MA-MEDPOL-1/TM (MA-ROPME-1) (mean ± confidence interval at 95%)

ELEMENT	Concentration
Cadmium (Cd) (mg kg^{-1})	0.015 ± 0.012
Chromium (Cr) (mg kg^{-1})	0.28 ± 0.14
Copper (Cu) (mg kg^{-1})	0.62 ± 0.12
Iron (Fe) (g kg^{-1})	5.8 ± 0.7
Mercury (Hg) (mg kg^{-1})	2.69 ± 0.17
Nickel (Ni) (mg kg^{-1})	0.065 ± 0.032
Lead (Pb) (mg kg^{-1})	0.074 ± 0.015
Zinc (Zn) (mg kg^{-1})	16.80 ± 0.48

4. ANALYSES AND REPORTING

The participants were requested to analyze the trace metal concentration of the samples by their usual technique. They were requested to make at least 3, but preferably 6, separate determinations of each element and to report the results together with a short description of the method used on the report form attached to the information sheet. Other information requested included the drying procedure, the mineralization procedure, the instrumental parameters and the way in which calculation of results was performed. Also, a summary of quality control procedures routinely employed within the laboratory was requested.

All results were to be reported on a dry-weight basis. The concentrations were to be reported as net values (i.e., after correcting for the blanks, etc.), leaving as many significant figures as justified by the precision of the method used. For each element the participants were requested to report the average weight of the sample taken for analysis, the arithmetic mean and the standard deviation (s_{n-1}) of the analytical results and an estimate of any potential sources of error.

5. EVALUATION OF THE RESULTS

The complete data set is presented in Tables A1.1 to A1.47 of Annex I for SED-MEDPOL-1/TM (marine sediment) and in Tables A2.1 to A2.27 of Annex II for MA-MEDPOL-1/TM (fish homogenate). The terms used in the tables are defined as follows:

Laboratory Code Number: Each laboratory was represented by a code number which remains unchanged throughout the tables.

Method code number: Code number which enables the analytical method employed to be identified. A detailed description of the codification is given in Table I.3. The information given includes the pretreatment method, the acids used for mineralization of the samples and the instrumental technique employed.

Number of measurements: Number of individual determinations on a given element performed by a laboratory using the same analytical procedure.

Laboratory mean: Arithmetic mean ($\bar{x}$) computed from all individual results supplied by a laboratory for the determination of a given element. Laboratory means are arranged in ascending order in the tables. Results given as below the detection limit (DL) or not detectable (ND) are reported with the symbol "<" or ND, respectively.

Standard deviation (SD): This is the weighted (n-1) standard deviation (s_{n-1}) of the experimental data given as an absolute value.

Z-score: For the assessment of laboratory performance, a Z-score is calculated according to the formula:

$$Z = (x_i - x_a) / s_b$$

where x_i is the arithmetic mean of the reported value of the analyte concentration in the sample; x_a is the certified or assigned value; and s_b is the target standard deviation.

This score effectively expresses the difference between the mean of the laboratory and the assigned value in units s_b.

- Performance is considered to be acceptable if this difference is less than or equal to to 2: ($|Z| \leq 2$);
- The results are of questionable quality when: $2 < |Z| < 3$
- The measurement is regarded as out of the acceptable range when: $|Z| \geq 3$.

This type of score represents a simple method of giving each participant a normalized performance score for bias. This method of assessing laboratories has been accepted as a standard for ISO/IUPAC [2].

The selection of the correct target value depends on the monitoring objectives. The criteria used in this report have been set so that laboratories should have at least a relative bias equal to or better than 25% ($2s_b$, s_b=12.5%).

In case of cadmium, chromium, copper, nickel and lead in fish homogenate, the uncertainty of the assigned concentrations is substantially higher than the target precision and it has to be taken into account. This uncertainty was therefore included in the target value for bias according to the formula:

$$Z = (x_i - x_a) / (s_b^2 + s_a^2)^{0.5}$$

where x_i is the arithmetic mean of the reported value of the analyte concentration in the sample; x_a is the assigned value; s_b is the target standard deviation and s_a is the standard deviation of the assigned value.

P-score: P-score has been introduced for the assessment of laboratory precision and is defined as:

$$P = s_i / s_p$$

where s_i is the standard deviation of the determinations of each laboratory and s_p is the target precision (standard deviation).

It is assumed that:

- Values of $P \leq 2$ indicates a satisfactory precision;
- $2 < P < 3$ is questionable;
- $P \geq 3$ indicates an imprecise measurement.

Where the methodology or a laboratory performance cannot meet these targets, then action should be taken to improve that situation. It is recognized that this is a minimum criteria.

In addition to the tables of results given in Annex I and II, the distribution of laboratory means for selected parameters is illustrated graphically in Annex I for SED-MEDPOL-1/TM (marine sediment) and Annex II for MA-MEDPOL-1/TM (fish homogenate). Error bars

represent laboratory means ± standard deviation ($\bar{x} \pm s_{n-1}$). The horizontal lines on the figures indicate the mean value (solid line) and the 95% confidence intervals of the mean (hatched lines) for the certified or information values.

Table I.3. Method Codification

The "Method Code No." consists of a numerical code containing up to 7 digits. Each digit represents one information field which, when left blank, indicates the absence of reported information or its redundancy (e.g., there is normally no sample digestion with neutron activation analysis). This system was designed for all kinds of analytes but only information relevant to trace metal analyses is indicated here.

Field number:	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Alphanumerical Code:	**1**	**P**	**A**	**P1**	**P2**	**A1**	**A2**

- Field 1 has a numerical value of 1 (trace metal measurements);
- Fields 2 and 3 give basic information on pre-treatment method (P) and analytical instrument techniques (A), respectively;
- Fields 4 and 5 give details of the pre-treatment (sample mineralization);
- Fields 6 and 7 give details of the instrumental technique.

Pre-treatment (digestion) techniques

P =
- 0 · Not communicated
- 1 · No pre-treatment
- 2 · Dry ashing
- 3 Wet ashing

When P = 2

P1 =
- 0 . Not specified
- 1 . Muffle furnace
- 2 . Plasma (oxygen)

When P = 3

P1 =
- 0 · Not specified
- 1 · Normal pressure
- 2 : Pressure decomposition
- 3 . Microwave decomposition

When P = 3 and P1 = 0 - 3

P2 =
- 0 HNO_3
- 1 : HNO_3, HCl
- 2 · HNO_3, HCl, HF
- 3 : Aqua regia, HF
- 4 HNO_3, $HClO_4$, HF
- 5 : HNO_3, HCl, H_2O_2, HF
- 6 HNO_3, HF
- 7 · $HClO_4$, HF
- 8 HNO_3, $HClO_4$, H_2SO_4
- 9 Aqua Regia
- 10 . HNO_3, $HClO_4$
- 11 · HNO_3, H_2O_2
- 12 HNO_3, H_2SO_4
- 13 HNO_3, HCl, H_2O_2
- 14 HNO_3, H_2SO_4, H_2O_2
- 15 Other (no HF)

Table I.3. (continued)

Instrumental techniques

A =
- 0 : Not indicated
- 1 : Atomic absorption spectrophotometry (AAS)
- 2 : Emission spectrometry
- 3 : Neutron Activation Analysis (NAA)
- 4 : Polarography
- 5 : X-Ray Fluorescence
- 6 : Mass spectrometry

When A = 1

A1 =
- 0 : Not specified
- 1 : Flame technique
- 2 : Graphite furnace technique (GF-AAS)
- 3 : GF with Zeeman correction
- 4 : Hydride generation technique
- 5 : Cold vapour technique

When A = 2

A1 =
- 0 : Not specified
- 1 : Flame emission spectrometry
- 2 : Atomic emission spectrometry
- 3 : ICP AES
- 4 : DCP AES
- 5 : Microwave plasma AES

When A = 3

A1 =
- 0 : Not specified
- 1 : Instrumental NAA (INAA)
- 2 : NAA with radiochemical separation

When A = 5

A1 =
- 0 : Not specified
- 1 Energy dispersive XRF
- 2 · Wave length dispersive XRF
- 3 · Total reflection XRF

When A = 6

A1 =
- 0 . Not specified
- 1 : Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
- 2 · Thermal Ionisation Mass Spectrometry

When A = 1 and A1 = 1, 2, or 4

A2 =
- 0 : DBC not specified
- 1 : DBC yes
- 2 : DBC no

(DBC = Deuterium background correction).

When A = 1 and A1 = 5

A2 =
- 0 · Gold trap not indicated
- 1 . Gold trap yes
- 2 : Gold trap no

6. RESULTS AND DISCUSSION

6.1. Overview of the results

In total 37 laboratories from 15 countries participated in this intercomparison exercise (Annex III). Thirty five laboratories analyzed the marine sediment sample and 35 the fish homogenate, and 33 laboratories analyzed both samples. Three laboratories excused themselves for technical reasons: one from Algeria, one from Croatia and one from Turkey.

In the case of the SD-MEDPOL-1/TM material (sediment), laboratories provided analytical results for a total of 47 elements (Annex I). Z-scores were calculated for 15 elements (Table I.4) and enough data was available to allow plots for 14 elements to be made (Figure 1.1 to 1.14, Annex I).

For sample MA-MEDPOL-1/TM (fish homogenate) laboratories provided analytical results for a total of 27 elements (Annex II). Table I.5 presents Z-scores for 8 elements and the distribution of the results is illustrated for 12 elements (Figure 2.1 to 2.12, Annex II).

The largest number of results for both samples was reported for cadmium, chromium, copper, iron, manganese, mercury, nickel, lead and zinc. For 31 elements only a few results were obtained. These data are given in the tables of Annex I and II, but are not included in the detailed description nor in the figures.

6.1.1. Moisture content

It was required that the results be reported on a dry weight basis. The determination of the dry weight is indeed important, particularly in the case of the fish homogenate which has a relatively elevated moisture content (about 7%). Only 7 laboratories reported the moisture contents and the results are fairly scattered. It should be noted that the recommended procedure for its determination (i.e., 105°C for sediment and 85°C for fish respectively, until constant weight) was not always followed (e.g., too low temperature, very short drying time, etc.). Also, some laboratories did not measure the moisture content at all.

6.1.2. Reporting of the results

It is noteworthy that calculation and transcription of the data is still frequently the major source of erroneous data reported. Also, a number of laboratories gave too many significant figures as compared to the precision of their analytical methods. Some laboratories still used ppm units for reporting the concentrations. Results should be reported using S.I. units (e.g. mg kg^{-1}). It was also noticed that some laboratories calculated s_n instead of the weighted standard deviation s_{n-1}.

6.1.3. Analytical methods

The analytical techniques applied most frequently were flame atomic absorption spectrophotometry (flame-AAS) and graphite furnace atomic absorption spectrophotometry

(GF-AAS) followed by emission spectrometry (ICP-AES), mass spectrometry (ICP-MS), instrumental neutron activation (INAA) and X-Ray fluorescence. Cold vapour AAS was mainly used for mercury. Most laboratories used wet mineralization as the sample pretreatment procedure which is the preferred method for analysis by AAS and ICP. We noticed the increasing use of microwave-oven for mineralization (12 laboratories). Two laboratories using INAA used no pretreatment.

6.1.4. Less than values

Generally, only a few laboratories reported results as "less than the detection limit". However, up to about 28% of the laboratories for Cd and Cr, 30% for Pb and 45% for Ni reported concentrations to be below their detection limits in the fish sample. In some cases, the quoted detection limits are higher than the reference values (i.e., Cd, Cr, Cu, Ni, Pb). As the marine sediment and the fish homogenate contained concentrations typical of those found in the environment, it may be concluded that in some cases the methods being used do not have performance characteristics (particularly detection limit) necessary to undertake environmental monitoring for certain elements at the typical concentration range (e.g., ICP-AES; use of flame AAS instead of GF-AAS). Additionally, problems of contamination prevented some laboratories from obtaining low detection limits (e.g., for analyses by GF-AAS).

6.1.5. Laboratory performances

The performance for precision and accuracy was assessed by Z- and P-scores which were calculated for each element individually as indicated in section 5.

The P-scores indicate the performance of the laboratories precision. In general the precision is satisfactory for most laboratories and all elements analyzed in the marine sediment sample (i.e. $P \leq 2$) (Annex I). The situation is less satisfactory for the fish sample which contains much lower concentrations of most elements than the sediment. The precision is unsatisfactory for several laboratories in the case of Cd, Cr, Ni and Pb (Annex II). Seven laboratories have systematically bad precision for at least 2 of these elements in the fish sample (laboratories No 4, 13, 17, 22, 25, 31, 37).

Unfortunately, the evaluation of the accuracy (Z-score) shows that values reported by some laboratories are far from satisfactory (Table I.4 and I.5).

For the sediment sample, the complete data set included 230 reported concentrations of which 73 results (32% of the data set) are inaccurate (i.e., $|Z| \geq 3$). Elements for which more than 50% of the data set were unacceptable include Cd and Se (Table I.4.). Less than 25% of unacceptable results (i.e., $|Z| \geq 3$) were obtained for As, Cu, Mn, Ni and Zn.

In the case of the fish sample, 151 results were obtained and 60 of these (40% of the data set) were inaccurate. At least 50% of the results were unacceptable for Cr, Fe, Ni and Pb (Table I.5). Less than 25% of the data were considered inaccurate (i.e., $|Z| \geq 3$) only for Hg and Zn. Results are not as good as for the sediment sample and this is due to the much lower

elemental concentrations in the fish sample compared to the sediment for most elements considered here.

Results obtained for As, Cu, Ni, Zn in sediment and Zn in fish are relatively well clustered around the certified value with only a few erroneous values (Fig. 1.1, 1.5, 1.8, 1.13, and 2.8).

Asymmetrical distributions were obtained in the case of Cr, Mn and Sr in sediment and for Hg in fish, for which a strong negative bias (towards low values) was observed (Fig. 1.3, 1.7, 1.11, 2.5). In contrast, for Se in sediment, and Cd, Cr, Cu, Fe, Mn, Ni and Pb in fish, the distributions exhibit a positive bias (towards high values) (Fig. 1.10, 2.1 to 2.4, 2.6, 2.7, 2.10). In the case of Cd, Co, Hg, Pb and V in sediment, numerous erroneous values (high and lows) were reported (Fig. 1.2, 1.4, 1.6, 1.9, 1.12).

Evidently, good laboratory practice and quality control have not yet reached a number of laboratories. A total of 16 laboratories gave no information at all on their quality control procedures as was requested on the report form. Only 7 laboratories presented results obtained for reference materials analyzed together with the samples and 3 laboratories provided examples of control charts. In order to validate their results, all laboratories should systematically: (1) analyse reagent blanks to verify the quality of the purified water and reagents and to control other possible sources of contamination (e.g., from dirty laboratory ware, dusty environment, etc.) [6, 8]; (2) analyse standard reference material with a similar matrix and approximately the same concentration level as the samples analyzed. This should be done for each series of analysis (batch of digested samples), preferably in triplicates, and these digests should be analyzed at regular intervals during the measurements [8].

Laboratories with erroneous results will have to carefully check their laboratory procedures. First, they should check the calculation of their results, as a number of reported values were wrong by an order of magnitude (e.g., lab. No 4, 25, 26, 36). Erroneous calibration standards are another source of bias. For instance, losses can occur in low-concentration working standard solutions which would result in overestimates of the concentrations of elements in the samples, so they should not be stored for an extended period of time.

Excess results could also originate from contamination during sample pretreatment (e.g., mineralization) or analyses. The laboratories concerned should carefully check their analytical procedures (e.g., quality of purified water and reagents) and try to improve the cleanliness of their working environment as dust is the most common atmospheric source of contaminants for trace elements in laboratories. Filtration of solution digests should be avoided as it can result in contamination of samples. Laboratories should also develop an effective scheme for cleaning laboratory-ware which generally includes a soap wash, an acid wash and thorough rinsing with purified water free from trace elements [6].

Low results could be due to incomplete mineralization due to insufficient time and/or at too low temperature, or in the case of sediment, because HF was not used. All these factors can produce incomplete digestion and have been observed to give low results in previous intercomparison exercises [1, 3]. It is apparent that many laboratories still encountered difficulties with the analysis of trace elements by GF-AAS and obtained poor precision for low level measurements. Low results for Cd, Co, Cr, Mn, Pb, Sr, V could be caused by suppressive interferences due to components of the sample matrix. These remain a problem in case of poor optimization of electrothermal programmes for GF-AAS and/or if adequate matrix modifiers are not used where necessary. The use of such modifiers was seldom mentioned on the report forms. For Hg, low results can be related to volatilization losses during the digestion procedure (e.g., too high temperature), or improper preservation of digested samples (without oxidizing agent and/or for an extended period of time). Alternatively, low digestion temperature and weak oxidation can also be the source of low results in fish sample, as organic mercury is not completely destroyed thus cannot be reduced by $SnCl_2$.

6.2. Laboratory performance for selected trace elements

6.2.1. Arsenic

Most laboratories obtained concentrations of As in sediment in good agreement with the certified value. Arsenic was determined by AAS (hydride generation and GF), ICP-MS or INAA. Laboratories No 25 and 29 gave results with Z-scores >10; both laboratories used graphite furnace AAS (GF-AAS). One cannot say that this technique gave poor results in this case, but it seems that these laboratories have problems mastering the analysis of As in sediment samples by GF-AAS. These excess results could also arise from contamination of samples.

6.2.2. Cadmium

A total of 13 laboratories obtained $|Z|$-scores above 3 for Cd in sediment, thus 50% of the results are not acceptable. The majority of analyses was performed by GF-AAS (18 values) of which 10 were within (or close to) the acceptable range. Results obtained by flame AAS (4 values) were all incorrect, probably because the concentration of Cd in sediment is too low for this method of analysis.

For the fish sample, the relatively large number of values reported as below the detection limit (8 out of 30) can be explained by the low Cd concentration in this sample. Eleven laboratories reported a mean concentration within the 95% confidence interval of the certified value. Seven laboratories obtained Z-scores >3. As for the sediment sample, most analyses were performed by GF-AAS.

A number of laboratories reported correct values using GF-AAS, the most common method used for this exercise. It is apparent, however, that many laboratories still encountered difficulties with the analysis of Cd at low levels in sediment and biological samples by GF-AAS. The unacceptably high results indicate difficulties associated with contamination,

Table L4. Z-scores for SD-MEDPOL-1/TM (Marine sediment): Assessment of laboratory performance

Laboratory Code	As	Cd	Cr	Co	Cs	Cu	Hg	Mn	Ni	Pb	Sb	Se	Sr	V	Zn
1			-1.9			-0.5	0.6	0.1	-0.1	-1.4					-0.6
2						13		-1.0		13			0.4	3.4	-0.8
3		-3.5				0.4		0.3		-1.3					0.0
4		9.2	-0.4	19		0.9		0.1	6.2	11					-0.1
5	1.0	19	-5.3	3.3		3.0	1.4	-2.9	-2.3	-3.3			-5.3	4.4	-1.1
6			-4.1			-1.9		-3.6	-1.5						-0.9
7	-0.2	1.7				-0.5	1.7	-2.9	0.6	-2.3		-2.9			-0.7
8	-1.5	0.3		0.2		-1.2	2.3	-1.6	-0.5	0.0				-1.8	-0.7
9			-0.7	8.6		-0.2		-0.3	0.6				0.4	1.3	-1.3
11	-0.8	2.7	-1.5			0.8		0.0	-0.9	0.9		-1.6	0.2	0.0	-0.3
12		1.5				-0.4		-3.0		-1.5					-0.1
13	-1.9	3.2	-1.0	2.1		-1.1		-1.4	-0.8	-1.3		19.4	-6.4	-0.4	-0.6
14	-1.0		-0.5	0.5	1.5										
15		-1.6								-4.8					1.6
16						0.4		-0.3							
17		13	-0.8			-1.8	26	-1.7		-5.6					-1.8
18 (1)		1.3	-1.8			-0.7	2.0	-0.5	-1.4	-0.6					0.3
18 (2)						0.6									0.3
19	-2.2	0.9	-4.7	-1.3		-1.5	2.8	-3.0	-1.0	-2.4			-5.7	-4.3	-1.0
20		1.9								0.3					-1.7
22 (1)		67	-7.0			28	13			-4.8					
22 (2)		-3.4	-7.4			-1.8	24			-1.6					
23		19				0.1	1.4	-3.7	4.3	2.7					-3.0
24							1.2								
25	11	2.2	-7.3			4.4	-7.9	-2.4		77		121			3.2
26		-6.2				-8.0									8.0
27		0.8				-1.8	0.0			-0.7					
28 (1)	-0.3		0.0	0.2	0.4		-0.1	0.0			0.3		-0.4	0.4	-0.5
28 (2)							1.0								
29	20	2.5	-5.3	-6.4		0.4	1.6	-2.7	0.4	3.5		82		-3.5	19
30		-2.1	-5.3				-5.5			-4.8					
31		12	-7.2			-1.4				-1.8					-1.9
32		-1.6				-0.3	0.0			-4.7					
33		-3.8	-2.6			0.1	2.8	-0.1		-2.8					-1.1
34							-1.3								
35		-6.3				-0.7	9.2			-2.6					-2.0
36		-8.0					1.8	-3.5							-1.4
37		9.3				0.6	30			-3.2					-1.3

$|Z| \leq 2$: performance is acceptable

$2 < |Z| < 3$: measurements are of questionable quality

$|Z| \geq 3$ measurements are out of the acceptable range.

Shaded areas represent unacceptable results ($|Z| \geq 3$).

Table I.5. Z-scores for MA-MEDPOL-1/TM (Fish homogenate): Assessment of laboratory performance

Laboratory Code	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Zn
1					-1.2			
2			50	91				5.0
3	0.2		-0.9				0.7	-0.2
4		28	45	35		417	328	2.5
5	240		0.6		-3.8			2.1
6				14				-0.4
7	-0.7		0.7	1.1	-0.7	7.5		0.5
8		0.8	-0.3	17	-1.2	2.7		0.4
9				5.0				1.0
10 (1)	-0.9	-0.3	4.5		-1.5		-1.1	-0.1
10 (2)	-0.4						5.8	
11		-1.6	-1.0	2.3				0.0
12	-1.1		0.3				-1.1	0.2
13	23	28	5.1	100			98	1.2
15	517							-2.0
17	9.5	8.2	2.1		-2.3		42	0.4
18			1.0	8.7	0.1			0.9
19	-0.9	0.1	2.0		0.2	3.4	0.0	1.4
20								-0.5
21 (1)	-0.8				-0.4		0.1	
21 (2)					0.4			
22 (1)	7.7	4.4	-1.3		-4.7		87	
22 (2)	6.5	4.6	-0.9		-2.9		408	
23			11		-3.4			1.3
24					-1.6			
25	25		32	65			55	13
26		40		-3.3				-7.9
27	2.9		-1.1		-0.6			
28 (1)		-0.7		3.4	-0.1			-0.2
28 (2)					0.7			
29	0.9	4.5	-0.7	4.2	-1.0	2.7	3.8	3.5
30	1.0	0.2			8.9		-1.2	
31	0.1	-0.6	-1.4	24		39	11	-1.8
32	2.4		0.9		-0.8		29	
33	0.2		-0.7	4.9	0.2			1.5
34					-2.4			
35	0.8		14		-2.5		38	-0.8
36					0.6			0.4
37	5.4		2.5		-6.1		18	1.3

$|Z| \leq 2$. performance is acceptable.
$2 < |Z| < 3$: measurements are of questionable quality
$|Z| \geq 3$: measurements are out of the acceptable range.
Shaded areas represent unacceptable results ($|Z| \geq 3$).

poor calibration and poor precision inherent to GF-AAS and other instrumental methods at such low Cd concentrations. Alternatively, analysis by GF-AAS without proper background correction can also result in positive bias. Indeed, laboratories using GF-AAS with Zeeman background correction obtained lower values than those using other methods for the fish homogenate. On the other hand, the unacceptably low results obtained for sediment could be caused by incomplete digestion or by suppressive interferences during measurement. These remain a problem in case of poor optimization of electrothermal programmes and/or if adequate matrix modifiers are not used where necessary (e.g. ammonium dihydrogeno-phosphate + magnesium nitrate; paladium nitrate).

6.2.3. Chromium

The majority of values reported for sediment are lower than the certified concentration. Z-scores were < -3 for 8 laboratories. In contrast, determination of Cr in fish is mainly biased towards higher values. Six laboratories obtained Z-scores > 3.

It seems, therefore, that many laboratories do not master the analysis of Cr by GF-AAS in marine sediment and at low concentration biological samples. For sediment, the substantial bias towards low values could result from matrix interference. As for Cd and Pb, interferences can produce underestimates of Cr in case of poor optimization of electrothermal programmes for GF-AAS and/or if adequate matrix modifiers (e.g. magnesium nitrate) are not used. In our previous intercomparison exercises, low values of Cr in sediment were attributed to poor digestion, in particular omission of HF [1, 3]. In this exercise, low values do not seem to be related to the mineralization acids used (i.e., with or without HF). However we cannot exclude the possibility that incomplete digestion (too low temperature or too short time) may be responsible for the low concentration results. In the fish sample, the bias towards high values could result from contamination, from erroneous calibration standards and poor precision inherent to GF-AAS at such low levels of Cr.

6.2.4. Copper

In sediment, the results generally show a good agreement with the certified value. Out of 29 data set, only 5 $|Z|$-scores were ≥ 3, showing that most laboratories are able to analyse Cu in sediment at this relatively high concentration. A majority of the determination was performed by AAS (flame or GF) and most of the laboratories appear to have mastered the technique in this case. The few elevated results are probably due to contamination (lab. No. 2, 5, 22, 25).

The agreement with the reference value is not as good for fish as for the sediment sample. This is certainly related to the much lower concentration in the fish sample. Out of 26 results, 16 were within the range (or very close) of the reference value. Z-scores were >3 for 7 laboratories. It is apparent from these results that the determination of Cu at these low concentrations presents difficulties for a number of laboratories using AAS techniques and also for laboratories using other instrumental techniques. All the concerned laboratories (No 2, 4, 10, 13, 23, 25, 35) should carefully check for the risks of contamination and the accuracy of their calibration standards.

6.2.5. Iron

No certified value exists for Fe in sediment, so results were compared to the mean ± s_{n-1} of 20 of the values (excluding 2 outliers, lab. No 4 and 26). Most laboratories fall within the defined range, but laboratories No 13 & 17 reported slightly low results and laboratories No 7, 11 and 29 obtained too high values. Most laboratories analyzed Fe by flame AAS. It should be emphasized that accurate measurement of iron at such high levels is not particularly difficult, especially by flame AAS.

A large number of the results in fish homogenate appears positively biased and only 2 out of 15 laboratories obtained Z-scores < 3. This could be explained by contamination problems because Fe concentration is relatively low in this fish sample. As for the sediment sample, most analyses were performed by AAS (flame or GF). Laboratories No 2, 4, 6, 8, 13, 25 and 31 reported concentrations more than double the consensus mean value (up to 10 times higher), thus suffer from acute problems of contamination.

6.2.6. Mercury

Results for sediment generally show a fairly good agreement with the certified value. Six out of 22 laboratories obtained $|Z|$-scores ≥ 3. Four laboratories reported seriously elevated concentrations that probably result from contamination (No 17, 22, 35, 37). Unfortunately, not enough data on the analytical protocols used was provided (e.g., reducing agent used) to explain the reason for their failure. Interferences occurring in the measurement step (reduction/aeration step) would likely result in values which are too low. This supports the conclusion that the high values are probably the consequence of contamination or poor calibration. Only 2 laboratories reported underestimates (No 25, 30) and they are probably related to volatilization losses during incorrect digestion procedure (e.g., too high temperature), or improper preservation of digested samples (without oxidizing agent, e.g., BrCl, $K_2Cr_2O_7$, and/or for an extended period of time). They could also result from the poor calibration of the instruments.

For the fish sample, 5 laboratories obtained $|Z|$-scores ≥ 3. Ten out of 27 results were too low compared to the reference value. The same observation has been made in previous intercomparison exercises for the determination of Hg in biological samples (e.g., [4]). This could be explained in different ways. First, low concentrations could result from the incomplete digestion of the matrix and in particular of methyl mercury (normally more than 80% of the total Hg in muscle tissue is in the methylated form). As a consequence, Hg in the digest solution is not completely reduced to the elemental form (Hg^0), particularly if $SnCl_2$ is used as a reducing agent, and consequently reported concentrations are too low. On the other hand, lower results could also be related to too strong digestion conditions or unsuitable preservation of samples after mineralization. It should also be mentioned that moisture content should always be determined in a separate aliquot, as drying of samples at high temperature can result in losses of Hg. All laboratories obtaining Z-scores < -2 are strongly advised to check their digestion and preservation procedures. As the information on pretreatment of samples and measurement techniques are incomplete, it is difficult to make any further comments.

6.2.7. Manganese

A majority of the 22 results reported for sediment tends to be biased towards low values compared to the certified concentration. Five laboratories obtained Z-scores < -3. It is surprising to see that many of the results for Mn are inaccurate, since the analysis of this element at such elevated concentration should not be of major difficulty. The systematic use of standard reference materials for quality control would prevent such a poor outcome. The quality of the results does not apparently depend on the instrumental method. Most laboratories used flame AAS and 3 used GF-AAS. It is important to note that the laboratories using a mineralization scheme which did not include HF obtained the lowest results (with the exception of laboratory No 23).

6.2.8. Nickel

The results for sediment are generally satisfactory. The two exceptions are laboratories No 4 and 23 who reported too high concentrations, with Z-scores > 3, probably due to contamination.

Only 6 laboratories reported detectable concentrations in the fish homogenate. These laboratories used GF-AAS or ICP-MS. All of them reported excess concentrations and 4 obtained Z-scores > 3. The mean reference concentration of Ni in the fish sample is fairly low and laboratories have to be extremely careful in order to avoid contamination.

6.2.9. Lead

Out of 27 laboratories, 11 obtained $|Z|$-scores ≥ 3 for the determination of Pb in sediment. Four laboratories reported excess concentrations compared to the certified value. The precision is also very poor for 3 of these results. In contrast, 7 laboratories reported too low values. Most laboratories used GF-AAS and 4 used flame AAS and the quality of the results does not appear to depend on the instrumental method.

A total of 25 results were reported for the fish sample and a majority were too high compared to the certified value, with 12 Z-scores > 3. Most laboratories used GF-AAS which is indeed a method of choice for the very low levels in this sample.

It seems, therefore, that many laboratories do not master the analysis of Pb by GF-AAS in marine sediment and at low concentration biological samples. For sediment, the substantial bias towards low values could result from matrix interference or erroneous calibration standards. The laboratories concerned should put more effort in the optimization of the GF programmes and use matrix modifiers when necessary (e.g., ammonium dihydrogenophosphate + magnesium nitrate; paladium nitrate). Low concentrations do not appear to be related to the mineralization acids used (i.e., with or without HF). However we cannot exclude the possibility that incomplete digestion may be responsible for the low concentration results. As in the case of Cd, Cr and Ni, the low concentration in the fish sample was problematic for many laboratories. Pb is an element particularly sensitive to sources of contamination and all laboratories with Z-scores ≥ 2 should check their analytical procedures in order to obtain valuable results.

6.2.10. Zinc

Most laboratories reported concentrations in sediment in fair agreement with the certified range. Only 4 laboratories had $|Z|$-scores ≥ 3. Even at this high level, 3 laboratories obtained excess results compared to the certified value (No. 15, 25, 29). A few laboratories using flame AAS reported too low values.

Results for the fish homogenate are also generally satisfactory and 12 laboratories reported concentrations in close agreement with the reference range. However, 4 laboratories had $|Z|$-scores ≥ 3 and a number of laboratories obviously have some problems due to contamination.

Even at relatively high Zn concentrations like in the sediment sample, precautions should be taken to avoid any risk of contamination, as zinc is a major contaminant in dust. Also, gloves with powder should never be used for the analysis of trace elements as the powder contains large amounts of zinc and other elements. Alternatively, in case of flame AAS, the presence of high concentrations of solids in the digested sample can cause non-specific absorption that has to be corrected (i.e., deuterium lamp). Indeed, laboratory No 25, who reported excess values in the sediment sample did not use the deuterium background correction. As for the low values obtained in sediment, the acids used for digestion are apparently not the problem as the use of HF made no systematic difference. The remaining possible explanation is the use of erroneous calibration standards.

6.3. Overall laboratory performance

The analyses of the two matrices (sediment and fish homogenate) were compared to allow assessment of the variability of trace element data within the MED POL region.

Table I.6 summarizes the performance of all laboratories. The proportion of Z-scores falling within $|Z| < 3$ and the number which falls within the band $2 < |Z| < 3$ are given. The percentage of satisfactory Z-scores ($|Z| < 3$) for each laboratory within each exercise is then used to assign the performance of each laboratory to a group level graded 1 to 4. We assigned criteria for group selection as follow:

- Group 1 laboratories with $|Z| < 3$ for $\geq 90\%$ of the data;
- Group 2 laboratories with $|Z| < 3$ for 75% to $< 90\%$ of the data;
- Group 3 laboratories with $|Z| < 3$ for 50% to $< 75\%$ of the data;
- Group 4 laboratories with $|Z| < 3$ for $< 50\%$ of the data.

6.3.1. Sediment

It is encouraging to note that 10 laboratories reported acceptable concentrations for all elements analyzed (i.e., $|Z| < 3$): No. 1, 7, 8, 11, 14, 16, 18, 20, 27, 28. Also, the two laboratories that reported results for Hg only (No 24 and 34) were within the acceptable range. In addition, laboratories No 3, 9, 12, 13, 32 and 33 reported less than 25% of unacceptable results. Thus 18 laboratories - about 50% of the laboratories involved in this exercise - reported results with less than 25% of outlier data (Group 1 and 2).

Table I.6. Overall assessment of the performance of the laboratories.

LAB No.	MARINE SEDIMENT				FISH HOMOGENATE			
	No $\|Z\|<3$	%	No $2<\|Z\|<3$	GROUP	No $\|Z\|<3$	%	No $2<\|Z\|<3$	GROUP
1	7/7	100	0	1	1/1	100	0	1
2	3/6	50	0	3	0/3	0	0	4
3	4/5	80	0	2	4/4	100	0	1
4	4/8	50	0	3	1/6	17	1	4
5	5/12	42	2	4	2/4	50	1	3
6	3/5	60	0	3	1/2	50	0	3
7	9/9	100	3	1	5/6	83	0	2
8	10/10	100	1	1	5/6	83	1	2
9	7/8	88	1	2	1/2	50	0	3
10					6/8	75	0	2
11	11/11	100	1	1	4/4	100	1	1
12	4/5	80		2	4/4	100	0	1
13	9/12	75	1	2	1/6	17	0	4
14	4/4	100	0	1				
15	2/3	67	0	3	1/2	50	0	3
16	2/2	100	0	1				
17	4/7	57	0	3	3/6	50	2	3
18	10/10	100	0	1	3/4	75	0	2
19	8/12	67	3	3	6/7	86	0	2
20	3/3	100	0	1	1/1	100	0	1
21					4/4	100	0	1
22	2/10	20	0	4	3/10	30	1	4
23	3/7	43	1	4	1/3	33	0	4
24	1/1	100	0	1	1/1	100	0	1
25	2/9	22	2	4	0/5	0	0	4
26	0/3	0	0	4	0/3	0	0	4
27	4/4	100	0	1	3/3	100	1	1
28	11/11	100	0	1	4/5	80	0	2
29	5/12	42	2	4	4/8	50	1	3
30	1/4	25	1	4	3/4	75	0	2
31	3/5	60	0	3	4/7	57	0	3
32	3/4	75	0	2	3/4	75	1	2
33	6/7	86	3	2	4/5	80	0	2
34	1/1	100	0	1	1/1	100	1	1
35	3/5	60	2	3	3/5	60	1	3
36	2/4	50	0	3	2/2	100	0	1
37	2/5	40	0	4	2/5	40	1	4

- Group 1 laboratories with $|Z| < 3$ for $\geq 90\%$ of the data;
- Group 2 laboratories with $|Z| < 3$ for 75% to $< 90\%$ of the data;
- Group 3 laboratories with $|Z| < 3$ for 50% to $< 75\%$ of the data,
- Group 4 laboratories with $|Z| < 3$ for $<50\%$ of the data.

However, 11 laboratories obtained at least 50% of inaccurate results (about 30% of the laboratories): No. 2, 4, 5, 22, 23, 25, 26, 29, 30, 36, 37. For each element, errors were not systematically in one direction, thus are probably the result of a combination of causes.

6.3.2. Fish

According to the Z-score values, 6 laboratories reported acceptable data for all elements analyzed ($|Z|<3$): No 3, 11, 12, 21, 27, 36. Also 4 laboratories reported acceptable concentrations for one element: No 1, 24 and 34 that measured Hg only and No. 20 that measured Zn only. Laboratories No 7, 8, 10, 18, 19, 28, 30, 32 and 33 reported less than 25% of unacceptable results ($|Z|\geq 3$). Thus 19 laboratories, or about 54% of the laboratories involved in this exercise, reported data with no, or less than 25% of outlier data (Group 1 and 2).

However, 14 laboratories (about 40% of the laboratories) reported at least 50% of inaccurate results ($|Z|\geq 3$): No. 2, 4, 5, 6, 9, 13, 15, 17, 22, 23, 25, 26, 29 and 37.

6.3.3. Summary

Fourteen laboratories (38% of all) have reported data with no or less than 25% outlier data for both sediment and fish homogenate samples (Group 1 and 2). These laboratories (No. 1, 3, 7, 8, 11, 12, 18, 20, 24, 27, 28, 32, 33, 34) deserve congratulations! In addition, 4 laboratories analyzed either the fish or the sediment sample and reported data with no or less than 25% outlier (lab. No 10, 14, 16, 21).

In contrast, 9 laboratories failed for both the sediment and the fish sample, as they reported at least 50% of outlier data (lab. No. 2, 4, 5, 22, 23, 25, 26, 29 and 37). Thus about 25% of the laboratories involved in this exercise were unable to produce reliable data for trace metal analyses. In addition, 7 laboratories produced at least 50% of outliers for one of the two matrices (lab. No. 6, 9, 13, 15, 17, 30, 36).

7. CONCLUSIONS

- The review of the laboratories performance for selected trace elements showed that 6 participating laboratories (16%) are capable of producing good data with 90% or more of all Z-scores within the target band of $|Z|< 3$ both for the marine sediment and the fish samples (Group 1). An additional 6 laboratories produced good data for sediment only and 2 laboratories for fish only. The within-laboratory precisions are generally very good.

- It is encouraging that for Cu, Hg and Zn the majority of laboratories reported acceptable results. However, more than half of the participating laboratories who reported values have serious problems in determining Cd, Co, Cr, Fe, Pb and V. Significant analytical problems still persist, since fairly scattered results were reported for these elements. Results are much less satisfactory for the fish sample, compared to the sediment, because concentrations were very low for these elements. The main deficiencies originate most probably from contamination problems, faulty calibration standards and/or from the inability to optimize sophisticated instruments for such low levels determination. It is also surprising to note that

elements normally easy to determine in sediment and biological matrices like Zn, Cu and Mn caused problems in some cases. It is unfortunate that there was little information given on the use of background correction and matrix modifiers for AAS and that so few laboratories reported their quality control data together with their results. This information could have enabled a better assessment of the problems encountered by the different laboratories.

- All aspects of Quality Assurance and Quality Control procedures should be implemented in order to improve the performance of the laboratories who failed in their analytical performance [8, 5]. These include the systematic use of reagent blanks and standard reference materials.

- Calculations should be checked more carefully as many errors were noticed (most of them were corrected afterwards by the laboratories), and only the proper number of significant figures should be reported. This number depends on the detection limit and on the precision of the determination.

- It is interesting to note that even though it is well known that total digestion (with HF) is essential for obtaining accurate results for the total trace element content, a number of laboratories still did not follow the recommended protocols for sediment sample digestion [5]. Effects of a partial digestion (using no HF) were indeed perceptible for Co and Mn.

- Another subject of concern is the very small number of results reported for Al: 3 for sediments and only one for fish. This is particularly disappointing, as Al is often used for "normalizing" sediment trace metal data, in order to differentiate anthropogenic contaminants from the same metal occurring naturally [5]. Future intercomparison exercises will address this problem.

- Therefore, if it is considered that some of these trace elements should be monitored for MED POL (e.g., Al, Cd, Cr, Cu, Hg, Pb, Zn), it is essential that the laboratories continue to improve their performance. Continuous support for training personnel in analytical methods should be provided. It is strongly recommended that additional regional training courses should be organized which will include all important steps such as sample collection, sample preparation, sample digestion, final detection by AAS and Quality Assurance/Quality Control protocols.

- Three invited countries did not participate in this exercise: Lebanon, Malta, which have MED POL monitoring agreements, and Libya. The first 2 cited countries are obliged to measure trace metals according to their monitoring agreement. Lebanon participated in 3 intercomparison exercises between 1977 and 1988, Malta participated in all the exercises since 1985 and Libya participated only once in 1987 [1]. On the other hand, new encouraging participation was noticed from countries that only recently started these exercises (Albania, Egypt) or were not so active in recent years (Tunisia, Turkey) [1]. A better response was also obtained from Morocco, which is probably due to recent investments in MED POL laboratories. Therefore, all effort should be made in order to achieve the participation of all MED POL laboratories in future exercises.

PART II

THE ANALYTICAL PERFORMANCE STUDY FOR THE DETERMINATION OF CHLORINATED COMPOUNDS AND PETROLEUM HYDROCARBONS IN MUSSEL TISSUE, IAEA-142

J.-P. Villeneuve, M. Horvat and C. Cattini

1. INTRODUCTION

This report describes the results of IAEA/UNEP Intercomparison run IAEA-142 for the chemical analysis of organochlorine compounds and petroleum hydrocarbons in a homogenized mussel sample. Staff of the Marine Environmental Studies Laboratory (MESL) of IAEA-MEL have conducted intercomparison exercises on trace organic compounds for over fifteen years as part of its contribution to IAEA's Analytical Quality Control Service and UNEP's Regional Seas Programme and occasionally in association with the Intergovernmental Oceanographic Commission (of UNESCO) GIPME programme. Results of previous exercises have revealed serious problems for many regional laboratories to obtain comparable data.

After the rather good results obtained during the previous intercalibration exercise (IAEA-357) with a relatively contaminated sediment [9] and encouraged by the results obtained within the MEDPOL area when comparing the data obtained after nineteen years [1], it was considered timely to undertake a new intercomparison exercise of regional and world wide dimension on a biological sample.

More than 200 samples of the mussel homogenate were distributed to monitoring laboratories. A total of 96 laboratories participated in the exercise, of which 32 were involved in the MED POL programme.

2. SCOPE OF THE INTERCOMPARISON

For the organochlorine part of the exercise the participants were requested to determine as many compounds as possible including: HCB, lindane, pp'DDE, pp'DDD, pp'DDT, Aroclor 1254 and Aroclor 1260. The participants were also requested to report the PCBs as individual congeners whenever possible. For the petroleum hydrocarbon part of the exercise, the participants were requested to report individual aliphatics, such as n-C17, n-C18, pristane, phytane, total resolved and unresolved aliphatics, and all of the individual aromatic compounds which could be identified. The IAEA, however, was also interested in receiving results for additional compounds.

3. DESCRIPTION OF THE MATERIAL

About 80 kg of deep-frozen mussel tissue (from Ireland) was purchased from a local supplier. These mussels were freeze-dried under a vacuum of 0.1 Torr. The freeze-dried material was then ground in a laboratory cutting mill. The resulting powder was sieved through a 250 µm stainless steel sieve. Only the fraction of the material passing through the sieve was kept. In this way it was possible to prepare about 16 kg of powder with a particle size of less than 250 µm. This was further homogenized by mixing in a rotating drum for one week. Then, aliquots of about 35 g were packed into glass bottles with aluminium screw caps and sealed with Teflon tape.

4. HOMOGENEITY TEST

The homogeneity of the material for organochlorine compounds and petroleum hydrocarbons was assessed by determining the concentration of some compounds (chlorinated pesticides and petroleum hydrocarbons) in 10 samples taken randomly in the bulk of the powder. A one way variance analysis indicated that the material could be considered as homogeneous.

5. MOISTURE CONTENT

The water content of the lyophilized material (as determined by drying to a constant weight at 105°C) was found to be 5.8 % ± 0.5. Since the moisture content may change with the ambient humidity and temperature, it is recommended that the water content of this material should always be determined in a separate sub-sample (not that taken for analysis) by drying for 48 hours at 105°C.

6. SAMPLE DISPATCH AND DATA RETURN

In March 1994, 245 bottles containing mussel homogenate sample (labelled IAEA-142) were distributed world-wide. 96 laboratories reported results. 29 provided data for both chlorinated and petroleum hydrocarbons, 56 provided results for organochlorine compounds and 11 laboratories provided data on petroleum hydrocarbons. As a part of the MED POL Quality Assurance Project, 51 bottles of the sample were sent to monitoring laboratories in the region. Results from 27 laboratories were received for chlorinated hydrocarbons and 18 laboratories reported results for petroleum hydrocarbons.

7. REFERENCE VALUES FOR CHLORINATED PESTICIDES, PCBs AND PETROLEUM HYDROCARBONS IN IAEA-142

The data obtained through the worldwide intercomparison for many of the parameters is sufficiently well grouped to permit provisional certification of the mussel homogenate as a reference material [10]. Recommended and informations values are reported below:

Recommended values for pesticides and PCBs
(Based on dry weight)

Analyte	Units	Concentration*	Confidence Interval **	N***
HCB	ng/g	0.48	0.32-0.70	31
Lindane	ng/g	0.97	0.5-1.5	41
α HCH	ng/g	0.43	0.21-0.65	12
pp' DDE	ng/g	8.2	5.4-10	64
pp' DDD	ng/g	4.3	2.8-5.8	51
pp' DDT	ng/g	2.0	1.0-3.1	38
Dieldrin	ng/g	3.4	1.5-5.0	27
Aroclor 1254	ng/g	56	33-83	22
PCB No 28	ng/g	1.3	0.82-2.4	32
PCB No 31	ng/g	0.90	0.57-1.4	8
PCB No 49	ng/g	2.3	1.6-3.4	5
PCB No 66	ng/g	1.8	1.1-2.0	8
PCB No 99	ng/g	4.3	2.7-5.4	6
PCB No 101	ng/g	3.1	2.7-5.0	35
PCB No 105	ng/g	1.4	1.1-2.1	24
PCB No 118	ng/g	3.0	2.5-4.1	31
PCB No 128	ng/g	1.5	0.74-1.8	11
PCB No 138	ng/g	5.6	4.2-7.1	37
PCB No 149	ng/g	3.7	2.8-6.9	10
PCB No 153	ng/g	6.4	4.9-8.7	37
PCB No 156	ng/g	0.50	0.28-0.60	13
PCB No 180	ng/g	0.75	0.55-1.4	29
PCB No 187	ng/g	2.4	2.1-3.7	11

* Median values expressed on a dry-weight basis

** 95% confidence intervals of the median

*** Number of accepted laboratory means which were used for calculation of recommended, information values and confidence intervals.

Recommended values for pesticides and PCBs
(Based on dry weight)

Analyte	Units	Concentration*	Confidence Interval **	N***
Resolved aliphatics	µg/g	9.2	6.2-16	11
Unresolved aliphatics	µg/g	100	61-130	10
n- C 17	ng/g	670	500-910	15
Pristane	ng/g	170	90-240	13
Phytane	ng/g	120	50-180	12
Σn-alkanes (C14-C34)	µ g/g	5.2	3.3-8.4	14
Total aromatics	µg/g	42	30-48	7
Unresolved aromatics	µg/g	27	25-38	5
Biphenyl	ng/g	7	4.8- 5.2	6
Phenanthrene	ng/g	60	41-82	20
1-methyl phenanthrene	ng/g	20	16-24	11
Anthracene	ng/g	4.3	1.8-6.4	14
Chrysene	ng/g	32	21-46	20
Fluoranthene	ng/g	73	59-94	20
Pyrene	ng/g	57	39-81	23
Benzo(b) fluoranthene	ng/g	19	14-30	8
Benzo(k) fluoranthene	ng/g	9.7	6.0-13	9
Benz(a) anthracene	ng/g	15	12-17	15
Perylene	ng/g	7.3	6.1-9.3	8
Benzo(e) pyrene	ng/g	27	22-30	14
Benzo(a) pyrene	ng/g	3.5	2.9-5.0	11
2 -Methyl naphthalene	ng/g	23	20-29	6
Naphthalene GC-MS[1]	ng/g	37	23-95	6
Naphthalene GC-FID[1]	ng/g	23	20-48	6
Benzo(ghi) perylene	ng/g	9.9	8.3-13	14
Indeno(123cd) pyrene	ng/g	6.5	5.5-7.9	8
Acenaphthene	ng/g	3.4	1.9-7.1	6
UVF-Chrysene	µg/g	5.4	4.6-5.8	9

* Median values expressed on a dry-weight basis

** 95% confidence intervals of the median

*** Number of accepted laboratory means which were used for calculation of recommended, information values and confidence intervals.

1 Two reference values are provided for naphthalene depending on the analytical instrumentation used for quantification.

Information values
(Based on dry weight)

Analyte	Units	Concentration*	Confidence Interval**	N***
Chlorinated Pesticides				
Heptachlor epoxide	ng/g	0.27	0.15-0.49	7
Aldrin	ng/g	1.4	0.79-5.4	18
α Endosulfan	ng/g	0.96	0.05-1.4	10
γ Chlordane	ng/g	0.29	0.22-0.59	8
PCBs				
Aroclor 1260	ng/g	36	12-69	15
PCB No 8	ng/g	1.0	0.7-2.4	7
PCB No 18	ng/g	0.97	0.34-1.5	6
PCB No 44	ng/g	1.9	1.0-5.2	11
PCB No 52	ng/g	3.0	1.8-7.3	36
PCB No 70	ng/g	2.3	1.6-4.3	6
Petroleum Hydrocarbon				
UVF-ROPME Oil	µg/g	59	32-89	14
Total aliphatics	µg/g	120	71-140	10
n- C 18	ng/g	200	100-450	13
Resolved aromatics	µg/g	9.8	3.1-82	11
2-methyl phenanthrene	ng/g	47	20-75	8
Fluorene	ng/g	8.7	6.1-11	8
1-methyl naphthalene	ng/g	15	13-17	6
2,6 dimethyl naphthalene	ng/g	10	8.5-11	3
Dibenz(ah) anthracene	ng/g	1.8	1.5-5.0	5
Acenaphthylene	ng/g	1.9	1.4-2.7	4

* Median value expressed on a dry weight basis

** 95% confidence intervals of the median

*** Number of accepted laboratory means which were used for calculation of recommended, information values and confidence intervals

Systematic numbering of PCB congeners

IUPAC No		IUPAC No	
	Dichlorobiphenyl		**Hexachlorobiphenyl**
8	2,4'	**128**	2,2',3,3',4,4'
		138	2,2',3,4,4',5'
	Trichlorobiphenyl	**149**	2,2',3,4',5',6
		151	2,2',3,5,5',6
18	2,2',5	**153**	2,2',4,4',5,5'
28	2,4,4'	**156**	2,3,3',4,4',5
31	2,4',5	**158**	2,3,3',4,4',6
	Tetrachlorobiphenyl		**Heptachlorobiphenyl**
44	2,2',3,5	**170**	2,2',3,3',4,4',5
49	2,2',4,5'	**180**	2,2',3,4,4',5,5'
52	2,2',5,5'	**183**	2,2',3,4,4',5',6
66	2,3',4,4'	**187**	2,2',3,4',5,5',6
70	2,3',4',5	**188**	2,2',3,4',5,6,6'
74	2.4,4',5		
77	3,3',4,4'		
	Pentachlorobiphenyl		**Octachlorobiphenyl**
87	2,2',3,4,5'	**200**	2,2',3,3',4,5',6,6'
97	2,2',3',4,5		
99	2,2',4,4',5		
101	2,2',4,5,5'		
105	2,3,3',4,4'		
110	2,3,3',4',6		
118	2,3',4,4',5		
126	3,3',4,4',5		

8. EVALUATION OF THE RESULTS

8.1. Organochlorine compounds

Results obtained for chlorinated pesticides and PCBs are presented in Annex IV (Table A4.1 and A4.2). 27 laboratories reported results for this part of the exercise (Annex V). The analytical protocols employed by the laboratories are summarized in Tables A4.4 and A4.5 (Annex IV).

In addition to the above tables, the distributions of laboratory means for selected parameters are illustrated graphically in Figures 4.1 to 4.10 (Annex IV). The selected data sets are: HCB, Lindane, pp' DDE, pp' DDD, PCBs 28, 52, 101, 118, 138 and 152. In these examples, a non-parametric approach was used with the horizontal lines on the figures indicating the median values and the 95 % confidence intervals of the median.

8.2. Petroleum hydrocarbons

Results reported for petroleum hydrocarbons together with reference values are listed in Annex IV (Table A4.3). 18 laboratories reported data (Annex V). The analytical protocols employed by the laboratories are summarized in Tables A4.6 and A4.7 (Annex IV).

8.3. Z-scores

For the assessment of laboratory performance, a Z-score is calculated according to the formula:

$$Z=(x_i-x_a)/s_b$$

where x_i is the mean of the reported values of the analyte concentration in the sample; x_a is the assigned value (a mean value of the acceptable results in the world-wide intercomparison run) [10]; and s_b is the target standard deviation.

This score effectively expresses the difference between the mean of the laboratory and the assigned value in units s_b. Performance is considered to be acceptable if this difference is less than or equal to two. The measurement is regarded as out of control when $|Z| > 3$. This score represents a simple method of giving each participant a normalized performance score for bias. This procedure has been accepted as a standard for ISO/IUPAC [2].

The selection of the right target value depends on the monitoring objectives. The criteria for PCB congeners is usually set so that laboratories should have at least a relative bias equal to or better than 25% ($2s_b$, s_b=12.5%).

For both chlorinated pesticides and petroleum hydrocarbons, the uncertainty of the assigned values is substantial and it has to be taken into account. This should therefore be included in the target value for bias according to the formula:

$$Z=(x_i-x_a)/(s_b^2 + s_a^2)^{0.5}$$

where s_b is the target standard deviation and s_a is the uncertainty of the assigned value.

9. DISCUSSION

The laboratories performance in terms of accuracy was assessed by Z-scores which are calculated for each compound individually. The performance is considered satisfactory if a relative bias is equal to or better than 25% (Z-score equal to or better than 2). Z scores from 2 to 3 indicate that the results are of questionable quality. All Z-scores equal to or higher than 3 indicate that the measurements are out of control.

9.1. Chlorinated pesticides and PCBs

In total, 27 MED POL laboratories reported data for chlorinated pesticides, and 14 reported data for individual PCB congeners. A summary of Z-scores is shown in Table II.1. Only ~ 17% of the data (26 out of 156) for chlorinated pesticides and ~8% (9 out of 108) for PCBs are considered to be unacceptable. This compares well with the achievement in the world wide exercise (18 % and 6 % of unacceptable results for chlorinated pesticides and PCBs respectively) [10]. This is likely to be related to the intensive technical support activities described in the introduction, especially in the case of good performance by official MED POL laboratories from the developing countries.

Most of the outlying data were reported for lindane, where the results are influenced by the difficulty in obtaining good accuracy for this rather volatile and water-soluble compound. There is a need to improve its analysis. A number of laboratories have also produced unacceptable data for pp'DDD and pp'DDT, probably due to co-elution of chromatographic peaks (positive bias).

It is encouraging to note that 11 laboratories (No. 4, 5, 12, 28, 29, 32, 46, 51, 56, 69, 84) provided data with Z-scores below 3. However, 4 laboratories (No. 27, 65, 73 and 92) have submitted data which are almost all considered as unacceptable. All of the outlying data are too high. The reasons for discrepancy may lay in erroneous calibration standards, problems associated with removal of interfering lipid compounds, and/or problems associated with the chromatographic separation and quantification of individual compounds. For example laboratory No. 27 did not use a clean-up / fractionation procedure and it also omitted the use of internal standards which is essential for accurate correction of the results for the recovery through the analytical protocol. Laboratories No. 65 and 73 seemed to use appropriate analytical protocols and the reason for their bad performance may lay in erroneous calibration standards. Laboratory No. 92 did not provide sufficient data on their analytical protocols to allow investigation of their bad performance for both chlorinated pesticides and individual PCB congeners.

9.2. Petroleum hydrocarbons

In total, 16 laboratories provided data for petroleum hydrocarbons. Z-scores are shown in Table II.2. The overall performance of the laboratories is superior to that for chlorinated hydrocarbons. Over 24 % of data sets are considered as unacceptable (54 out of 224). Clearly, when comparing the data with the world-wide data set (15% unacceptable data), performance

Table II.1. Z-scores for chlorinated pesticides and PCB congeners

Analyte	Laboratory Code Number																									
	4	5	12	13	15	18	25	27	28	29	32	41	42	46	47	51	56	57	58	59	60	61	65	69	73	84	92
HCB	0 3	0 6	-0 5			0.6	-0.8	29	-0.8		-0.5				0.5	0 0			-0.2			3.6		-0.7	19		
Lindane	-0 9	0.1	0.2	-1.3	4.0	0.4	1.9	140	-1.0	0.7					1.9	-1.0	-0 7	3.7	0.7	8.2		-0.3		-0.6	27		14
α HCH			-0.1				1.6		-1.1						2.0							-0.7					50
pp' DDE	0 1	1.4	0 4		0 0	-0.5	0.5	1.5	0 2	-1 1	0.5	8.5		-0.4		0.1	-1.4	0.1	0.5	-1.5	-0.6	-1.2	-0.5	-2	0.3	-1.8	8.5
pp' DDD	0 4	1 6	2 4		0.1	-0.5	0.4		0.3	-0.9					-1.3	1 0	-1.3	3.9	-0.7		-0.8	-0.5	10	-1.8	7.4	-1.5	11
pp' DDT	-0 7	3.0	-0.9			0 7	-0 2		-0.7					-1.2		-0.7		0.1	4.4		3.4	-1.0	12	-1.5	22	-1.1	
Heptachlor			-0 8				-0 7	22										-0.6	2.2					-0.5			
Aldrin							-0.8	29										1.1	0.7	2.1		-0.7	-0.7		3.6		
Dieldrin			0 2				0 2			- 0 2							-0.7	-0 4	0.7				6.3				6.5
Aroclor 1254	-0.5		-1	0 7	-0 4					0.8		-1 4					-1.1		1.1		2.0	0.7		1.2		0.5	
Aroclor 1260			-0 8							0.5		-1.0					-0.9		-0.3					1.6		-0.6	
PCB No 28	2 0	-0 4	-1.1		20	1.0	0.7		-1.4	1 8	-0.3			-1.1		-1 4								-1.0			
PCB No 52	-0 5	-0 4	-0 9		-0.6	2.1	-0.4		-0.8	0 6	-0.4			-0.9										-0.9			
PCB No 66		0 4	-0.6			5.4	0 3																				
PCB No 101	-0.3	-0 3	-0 9		-0.3	1.0	-0.5		-0.4	0 6	-0.3			-0.9		-0 1	-1 6							-1.5			8.4
PCB No 105		-1 0	-1.0			0.7	3.8		0.1		0 1					-0.8											2.1
PCB No 118	0.6	-0.4	-1.3		-0.3	3.1	-1.0		1.2	-0.2	-0.3			-0.4		-0 2								-1.7			47
PCB No 138	1 0	-0 9	-0 7		-1.0	0.5	0 3		-0.5	0.9	0.3			-1.1		-0 4	-1.6							-1.0			19
PCB No 153	0.2	-0 8	-0.9		-0.3	0.9			-0.4	1.0	-0.4			-1.5		-0.2	-1 8							-0.8			8.6
PCB No 156									-1.2		1.0					-0.8								-0.2			-2.1
PCB No 180		-0.8	-0 8			4.6	-0 6		0 8	2 4	-0.3			0 6										-0.5			-1.7
PCB No 187		-0 9	-0 5			1.9	-0.3																				-2.5

$|Z| < 2$. performance is acceptable
$2 < |Z| < 3$: measurements are questionable
$|Z| > 3$ measurements are unacceptable

Shaded areas represent unacceptable performance.

Table II.2. Z-scores for petroleum hydrocarbons

Analyte	Laboratory Code Number															
	4	5	12	29	41	46	52	56	61	65	72	76	80	84	91	92
UVF-ROPME Oil	-0.5		1.8						0.0	-0.9			-0.1	-0.2		
UVF-Chrysene	1.6		17						0.1	-1.7			3.5	0.7	0.4	
Total Aliphatics	5.4	0.2	0.8				1.5	12			-1.4		-0.6		-0.2	
Resolved Aliphatics	-0.7	0.1	0.6			-0.3	1.8	7.3			-1.1	45	-0.4		-0.9	
Unresolved Aliphatics	1.1	0.3	0.9			-0.3	1.7	15			-1.7		-0.7		-0.1	
n- C 17	-0.9	-0.8	-0.2	6.5		-0.9	0.2	1.3			-1.5	26	0.7		1.3	
Pristane	-0.8	-1.4	-0.9			-0.9	0	0.7			1.2	28	0.4		0.0	
n- C 18	-0.3	-0.7	-1.0	5.8		-1.2	-0.4	1.7			-0.2	23	0.5		-0.8	
Phytane	-1.0	-1.1	-0.8			-0.7	0.5	1.8			0	21	-0.2		0.4	
Σ n-alkanes (C14-C34)	-1.0	-0.2	-0.8	2.2		-0.7	-1.0	13			-0.4	27	0.2		-0.5	
Total Aromatics			-0.3				7.9				0.5				0.2	
Resolved Aromatics	-0.8		-0.7				1.3				-0.6	0.9			-0.8	
Unresolved Aromatics			-0.2				3.8				0.8				0.9	
Naphthalene			-0.9				1.1	4.1							1.7	
1-Methyl Naphthalene		3.4	-1.5					14							33	
Fluorene		-1.2	0 6					5.8			120					
Phenanthrene	-1.0	-0.3	-0.3		4.3	-0.6	0.0	1.0			9.4	7.1	0.7		0.8	
2-Methyl Phenanthrene		-0.8	-0.3			-0.7	1.6					7.1			14	
1- Methyl Phenanthrene		-1.7	5.2			-0.9	9.1	1.7				16			43	
Anthracene		-0.7	0.6					0.9			180					
Fluoranthene	1.3	-1.8	0 7		-0.2	-0.4	36	0.3			9		0 3		43	-1.1
Pyrene	1.3	-1.8	0.9		-0.7	-0.3	3.5	-0.1			16	11	1.0		16	22
Chrysene	-0.1	-1.5	4.0			0.3	4.6	0.3			110	4.5	-0.6		2.3	25
Benz(a) Anthracene	0.7		0.5			0.4	0.9	0.2					0.7			2.9
Benzo(a) Pyrene	17		6.9			0.4	0.8	1.2					3.9			
Benzo(b) Fluoranthene			0.0					-0.4								-1.6
Benzo(e) Pyrene			0 5			4.2	-1.3	0.2			520		-0.8			1.2
Benzo(ghi) Perylene			-1.1			0.3	3.4	-1.7			190		0.7			

$|Z| < 2$: performance is acceptable
$2 < |Z| < 3$: measurements are questionable
$|Z| > 3$: measurements are unacceptable

Shaded areas represent unacceptable performance.

of the MED POL laboratories is inferior to world-wide performance [10]. Training programmes in the future will have to address this group of compounds with greater care.

The fact that all of the erroneous data have positive Z-score values indicate that the same sources of errors as described for chlorinated hydrocarbons can explain discrepancies in the data for this group of compounds (i.e., interfering peaks, etc.).

Three laboratories provided data on "total oil" using UVF measurements relative to standard chrysene and ROPME (Kuwait) crude oil. All three laboratories provided acceptable results.

For some individual aromatic compounds and PAHs (e.g., 1-Me phenanthrene, chrysene, fluoranthene, pyrene, benzo(a)pyrene, 1-Me naphthalene), most of the laboratories failed, probably due to identification and quantification problems. It is often necessary to perform confirmatory analyses using GC-MS (which most of the laboratories do not have) to validate data. Alternatively, and in the absence of GC-MS, laboratories should be encouraged to run analyses on two capillary columns with different polarity phases. This will provide confirmation of peak identification.

Five laboratories (No. 52, 56, 72, 76 and 91) provided more than 50 % outlier data. Laboratory No. 56 seems to have problems associated with impurities in the aliphatic fraction and in addition should use internal standards. Laboratories No. 52, 72 and 91 have reported acceptable data for the aliphatic fraction but their results for aromatics and PAHs are generally too high. The identification and quantification of chromatographic peaks and/or bad quality of calibration standards may explain the observed positive bias. Laboratory No. 76 has used packed chromatographic columns which cannot afford separation of individual compounds and would normally results in positive errors.

10. CONCLUSIONS

In summary, a review of the reported data shows that a number of participating laboratories have achieved satisfactory performance for chlorinated pesticides and PCBs. Data for petroleum hydrocarbons are inferior to that for chlorinated compounds. For MED POL monitoring purposes, it is essential that the laboratories improve their performance. As many of these compounds are toxic, carcinogenic and some tend to bioaccumulate, they belong to the Annex I of the Protocol for the Protection of the Marine Environment Against Pollution from Land-based Sources of the Barcelona Convention. Consequently they are monitored to provide accurate information for the implementation of Article 5 of the above mentioned protocol.

Laboratories that are involved in this demanding analytical task should be equipped with appropriate instrumentation and consumable materials in order to achieve successful work. Continuous support for the training of personnel in analytical methods should be provided and appropriate funding secured for its proper implementation. All other aspects of QA/QC procedures should also be implemented in order to maintain quality at an appropriate level and to improve the performance in those laboratories that continue to fail in their analytical performance.

It should be noted that 7 Mediterranean countries did not participate in this exercise: Algeria, Greece, Lebanon, Libya, Malta, Syria, and Tunisia. Among these, only Libya is not obliged to measure organic contaminants through their monitoring agreement. All efforts should be used in order to promote the participation of all MED POL laboratories in future exercises.

RECOMMENDATIONS

Intercomparison exercises represent only one aspect of data quality assurance and can only provide occasional indicators of data quality. The most valuable approach to quality assurance is through the regular analysis of standard reference materials, or even home-made working reference materials, and by plotting the resulting data on quality control charts. This provides a continuous feed-back to the analyst and is an essential tool for monitoring the quality of data and assuring accurate and comparable results in future exercises [8].

In addition, the participants are encouraged to refer to IAEA/UNEP/IOC Reference Methods in order to improve their analytical methods and their Quality Control procedures [5, 6, 7, 8, 11, 12, 13]. These methods are available free of charge from UNEP, Nairobi or from IAEA-MEL in Monaco. Furthermore, a complete catalogue of Standards and Reference Materials for Marine Science can be obtained free of charge from IAEA-MEL in Monaco [14].

Participants are recommended to review their data and to "score" them by evaluating whether the mean value obtained for each element/compound falls within a range of $|Z|$-score values lower than or equal to 2. This range is, of course, arbitrary and is presented as a simple guideline for the user. It should be reminded that it is a minimum criteria. The accuracy and precision required for data depend upon its final application - e.g., long term trend data or that used for geochemical monitoring must be much more accurate than that used for "hot spot" pollution monitoring or mineral prospecting. Nevertheless, the use of the Z-scores will help to identify and correct systematic errors in accuracy (e.g., from calibration errors, reagent contamination, incomplete digestion, erroneous use of separation protocols) and to optimize data quality.

It is essential that the MED POL laboratories continue to improve their performance for the determination of trace elements as well as organic compounds. Laboratories that are involved in these demanding analytical tasks should be equipped with appropriate instrumentation and consumable materials in order to achieve successful work. It is strongly recommended that continuous support for the training of personnel in analytical methods should be provided and appropriate funding secured for its proper implementation.

REFERENCES

1. UNEP/IAEA, 1994. Data quality review for MED POL: Nineteen years of progress. MAP Technical Report Series No 81. UNEP, Athens. *(by L.D. Mee, M. Horvat and J.P. Villeneuve).*

2. M. Thompson and R. Wood, 1993. The international harmonized protocol for the proficiency testing of (chemical) analytical laboratories. IUPAC/ISO/AOAC, *J. Pure. Appl. Chem.* 65: 2123-2144.

3. UNEP/IAEA/IOC, 1994. Report on the world-wide and regional intercomparison run IAEA-356 trace elements in polluted marine sediment. IAEA/AL/080, IAEA/MEL/56, UNEP, Nairobi.

4. UNEP/IAEA/IOC, 1992. Report on a world-wide and regional intercomparison run IAEA-350 trace elements in tuna fish homogenate. IAEA/AL/052, IAEA/MEL/53, UNEP, Nairobi.

5. UNEP/IAEA/IOC, 1996. Manual for the geochemical analyses of marine sediments and suspended particulate matter. Reference Method for Marine Pollution Studies No. 63, UNEP, Nairobi.

6. UNEP/IAEA/IOC, 1996. Reagent and laboratory-ware clean-up procedures for low-level contaminant monitoring. Reference Methods for Marine Pollution Studies No. 65, UNEP, Nairobi.

7. UNEP/IAEA/IOC, 1996. Determination of total cadmium, zinc, lead and copper in selected marine organisms by atomic absorption spectrometry. Reference Methods for Marine Pollution Studies No. 11, Rev (2), UNEP, Nairobi.

8. UNEP/IAEA/IOC, 1990. Contaminant monitoring programmes using marine organisms: Quality Assurance and Good Laboratory Practice. Reference Methods for Marine Pollution Studies No. 57. UNEP, Nairobi.

9. UNEP/IAEA/IOC, 1992. World-wide and regional intercomparison for the determination of organochlorine compounds and petroleum hydrocarbons in sediment sample IAEA-357. IAEA/AL/055, IAEA/MEL/51. UNEP, Nairobi.

10. UNEP/IAEA/IOC, 1996. Report on the world-wide and regional intercomparison run IAEA-142 organochlorine compounds and petroleum hydrocarbons in mussel homogenate. IAEA/AL/086, IAEA/MEL/59, UNEP, Nairobi.

11. UNEP/IAEA/IOC, 1992. Determination of petroleum hydrocarbons in marine sediments. Reference Methods for Marine Pollution Studies No. 20, UNEP, Nairobi.

12. UNEP/IAEA/IOC, 1996. Sample work-up for the analysis of chlorinated hydrocarbons in the marine environment, Reference Methods for Marine Pollution Studies No. 71, UNEP, Nairobi.

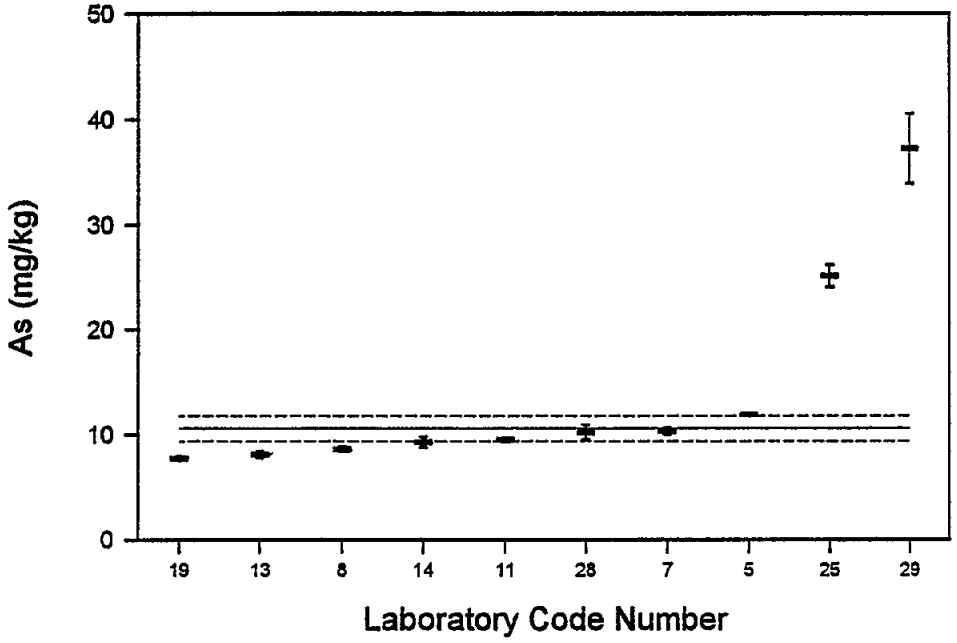
13. UNEP/IAEA/IOC, 1996. Determination of petroleum hydrocarbons in selected marine organisms. Reference Methods for Marine Pollution Studies No. 72, UNEP, Nairobi.

14. IOC/NOAA/IAEA/UNEP, 1993. Standard and Reference Materials for Marine Science. Revised edition, IOC Manuals and Guides 25, UNESCO, Paris.

ANNEX I

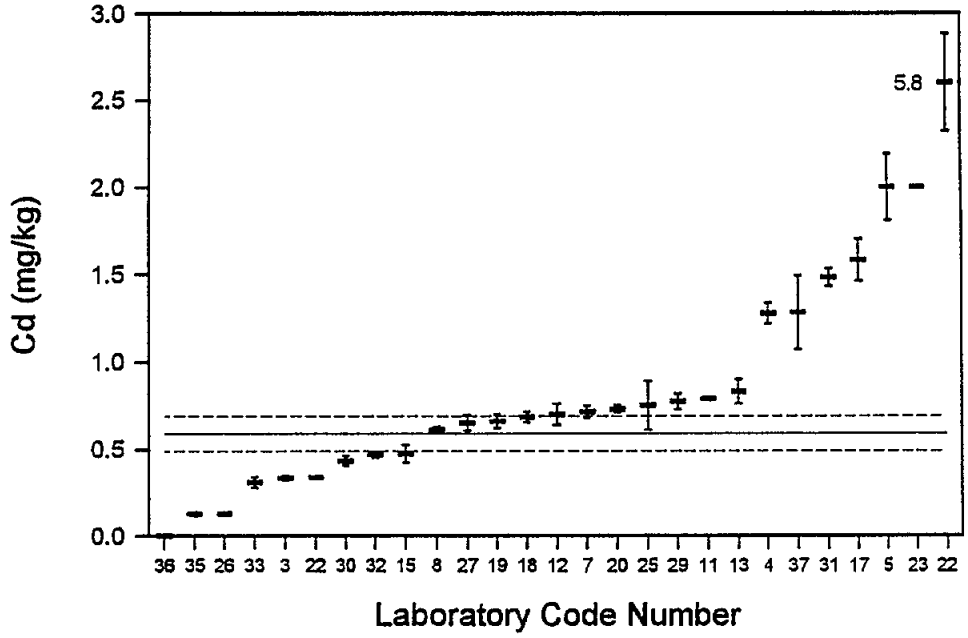
Total analyses data report
SD-MEDPOL-1/TM

Figure 1.1. Arsenic concentrations in Marine Sediment
SD-MEDPOL-1/TM
Laboratory Performance Study



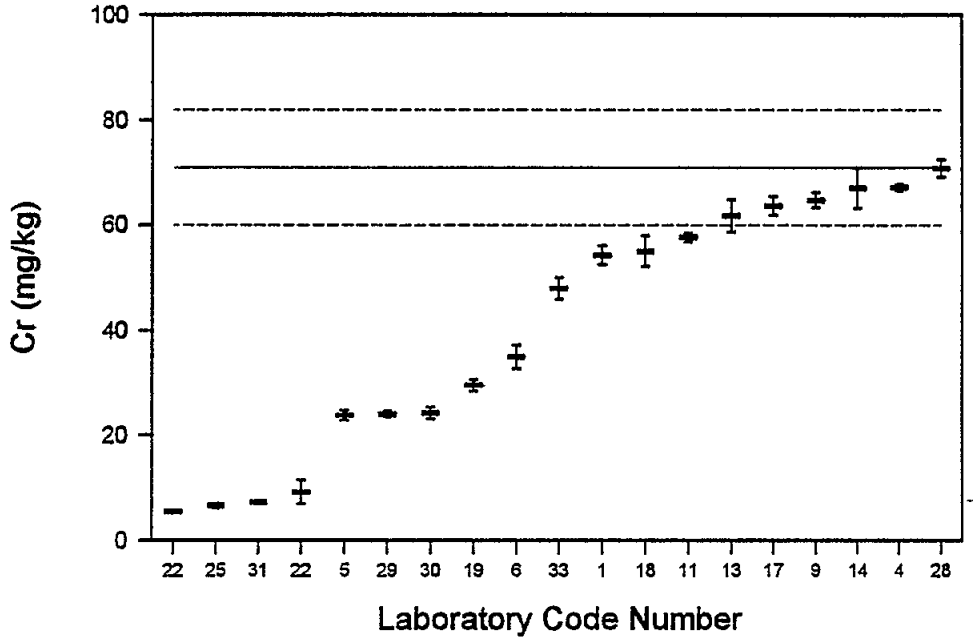
Error bar = mean ± 1 SD
Horizontal lines = Certified value ± 95% Confidence Interval (10 6 ± 1.2 mg/kg)

Figure 1.2. Cadmium concentrations in Marine Sediment
SD-MEDPOL-1/TM
Laboratory Performance Study



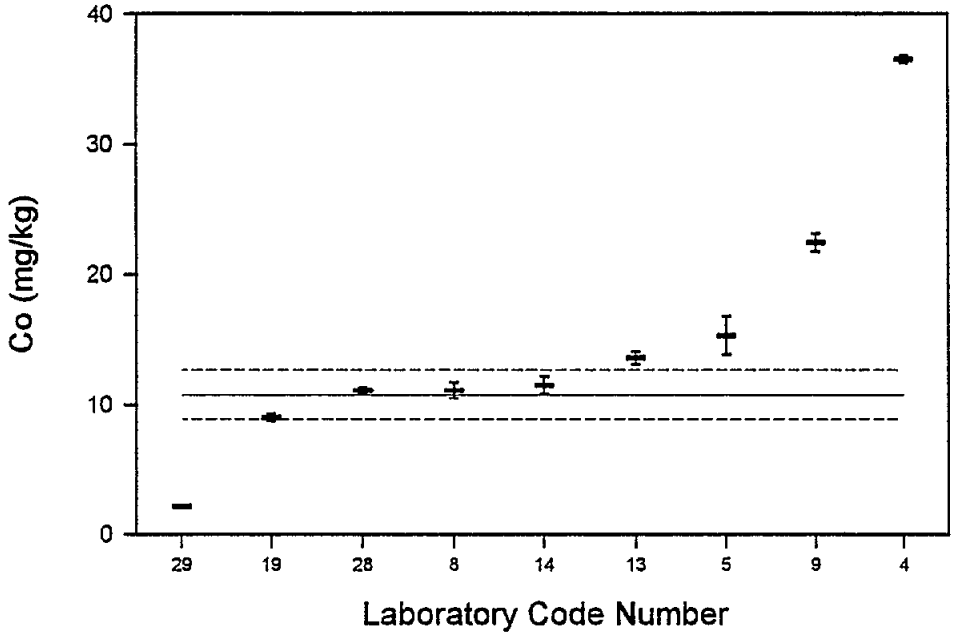
Error bar = mean ± 1 SD
Horizontal lines = Certified value ± 95% Confidence Interval (0 59 ± 0.10 mg/kg)

Figure 1.3. Chromium concentrations in Marine Sediment
SD-MEDPOL-1/TM
Laboratory Performance Study



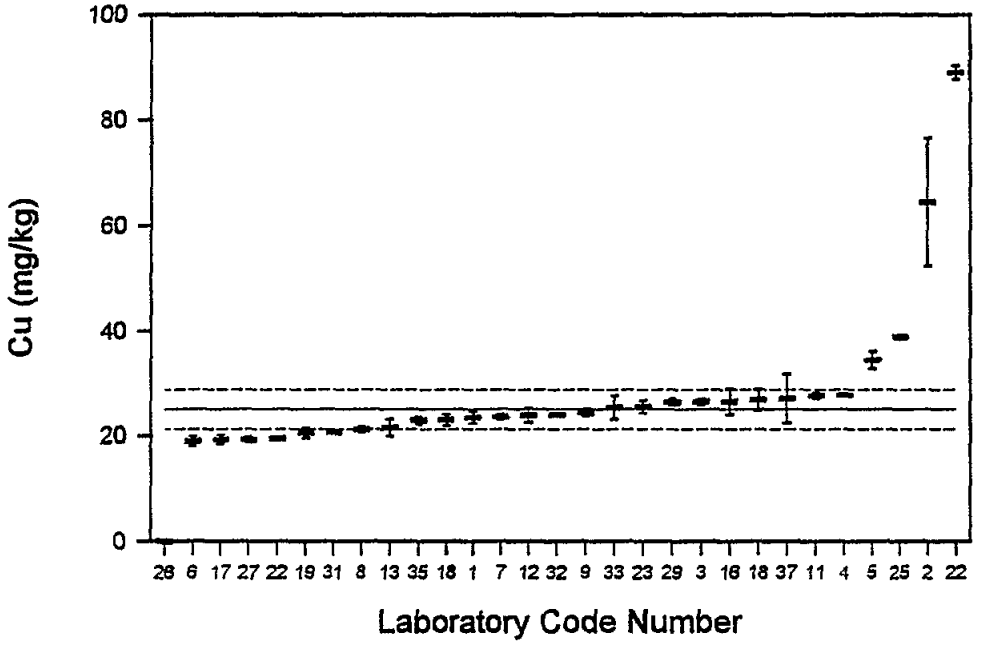
Error bar = mean ± 1 SD
Horizontal lines = Certified value ± 95% Confidence Interval (71 ± 11 mg/kg)

Figure 1.4. Cobalt concentrations in Marine Sediment
SD-MEDPOL-1/TM
Laboratory Performance Study



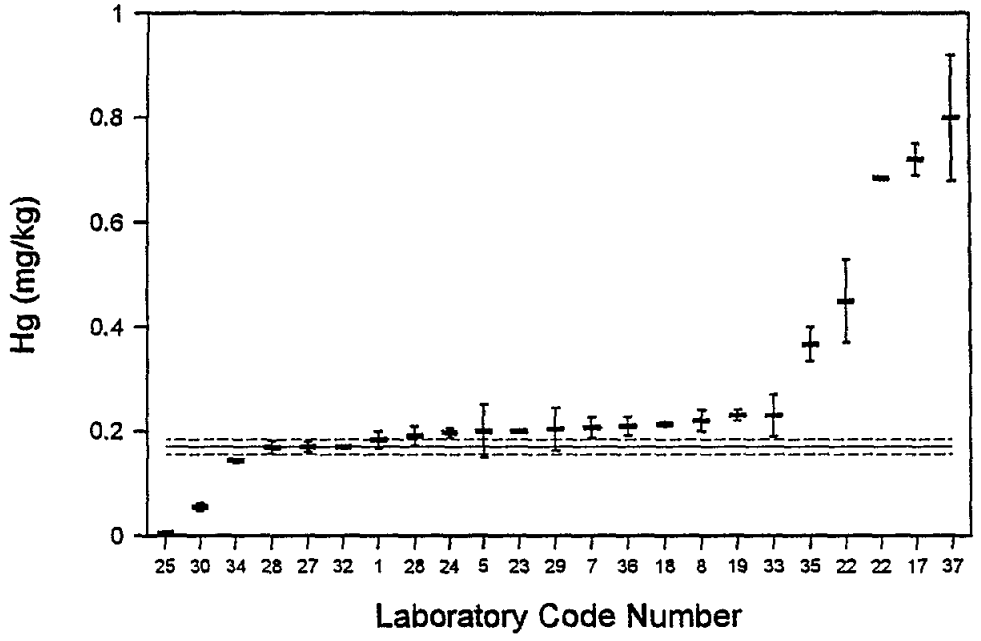
Error bar = mean ± 1 SD
Horizontal lines = Certified value ± 95% Confidence Interval (10 8 ± 1.9 mg/kg)

Figure 1.5. Copper concentrations in Marine Sediment
SD-MEDPOL-1/TM
Laboratory Performance Study



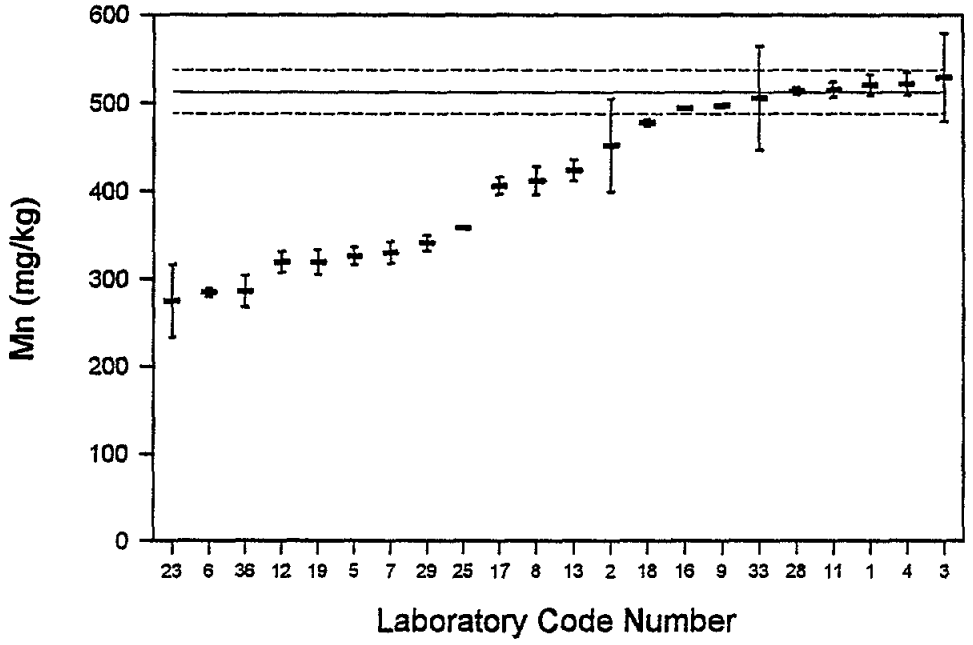
Error bar = mean ± 1 SD
Horizontal lines = Certified value ± 95% Confidence Interval (25 1 ± 3.8 mg/kg)

Figure 1.6. Mercury concentrations in Marine Sediment
SD-MEDPOL-1/TM
Laboratory Performance Study



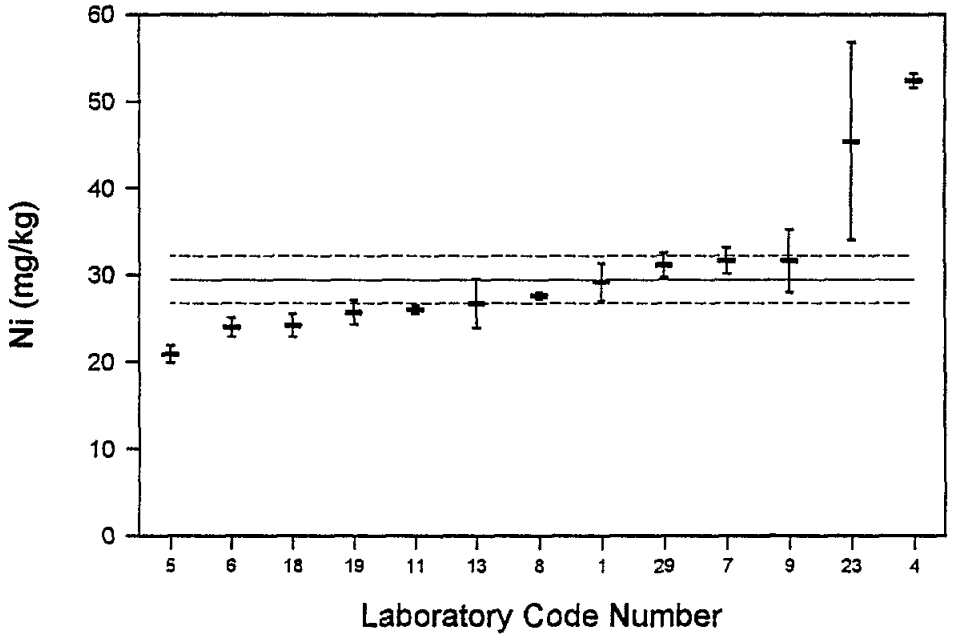
Error bar = mean ± 1 SD
Horizontal lines = Certified value ± 95% Confidence Interval (0 171 ± 0.014 mg/kg)

Figure 1.7. Manganese concentrations in Marine Sediment
SD-MEDPOL-1/TM
Laboratory Performance Study



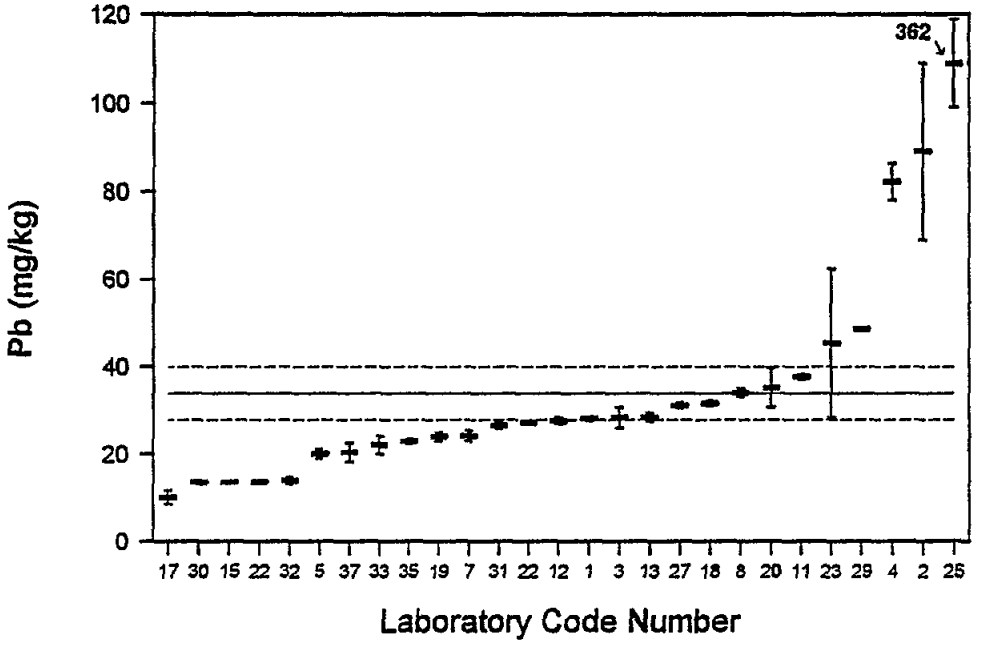
Error bar = mean ± 1 SD
Horizontal lines = Certified value ± 95% Confidence Interval (513 ± 25 mg/kg)

Figure 1.8. Nickel concentrations in Marine Sediment
SD-MEDPOL-1/TM
Laboratory Performance Study



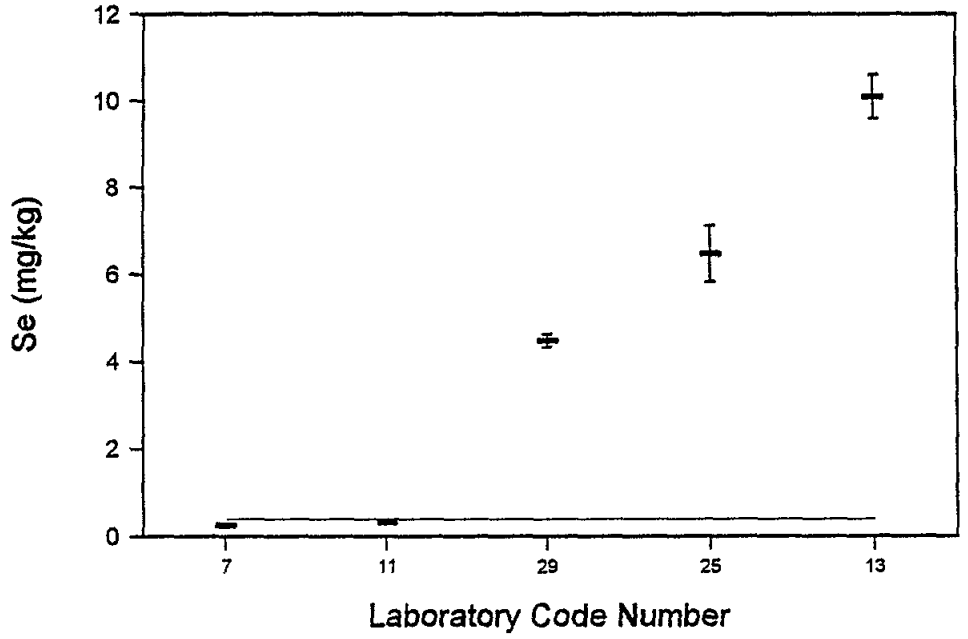
Error bar = mean ± 1 SD
Horizontal lines = Certified value ± 95% Confidence Interval (29 5 ± 2 7 mg/kg)

Figure 1.9. Lead concentrations in Marine Sediment
SD-MEDPOL-1/TM
Laboratory Performance Study



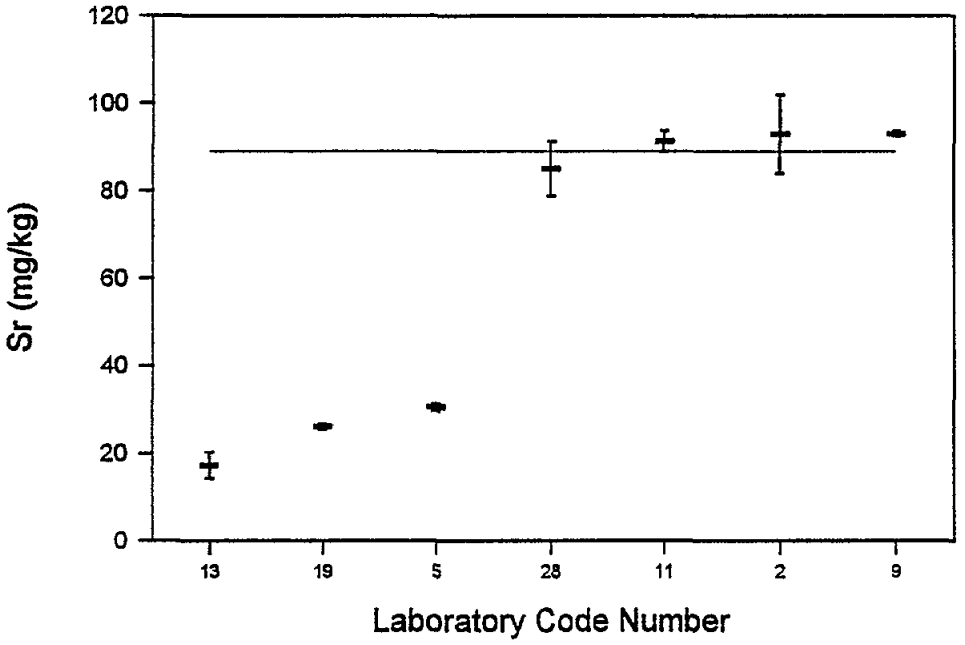
Error bar = mean ± 1 SD
Horizontal lines = Certified value ± 95% Confidence Interval (34.0 ± 6.1 mg/kg)

Figure 1.10. Selenium concentrations in Marine Sediment
SD-MEDPOL-1/TM
Laboratory Performance Study



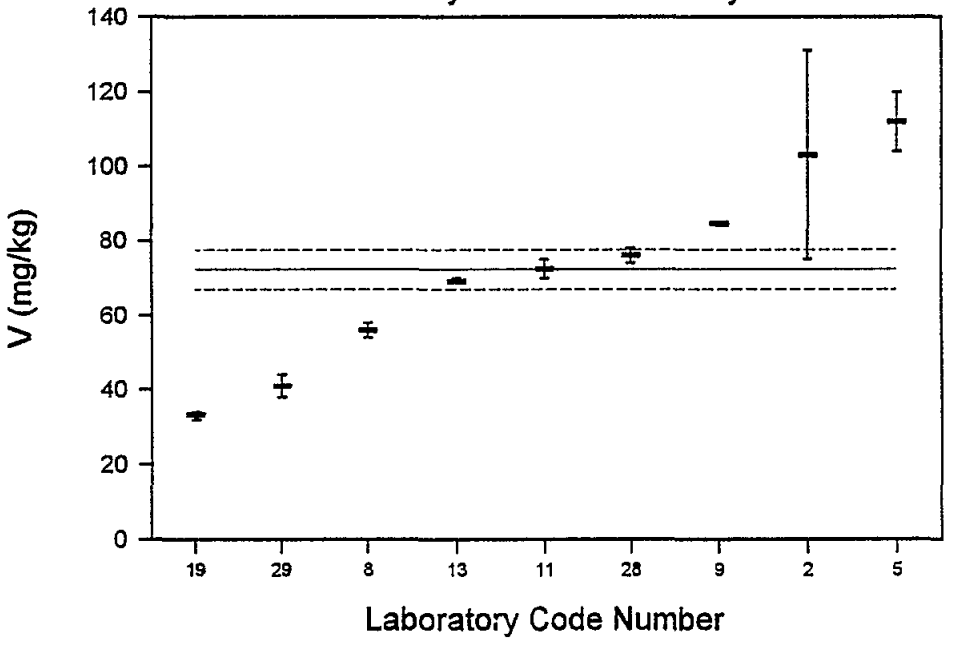
Error bar = mean ± 1 SD
Horizontal line = Information value (0.4 mg/kg)

Figure 1.11. Strontium concentrations in Marine Sediment
SD-MEDPOL-1/TM
Laboratory Performance Study



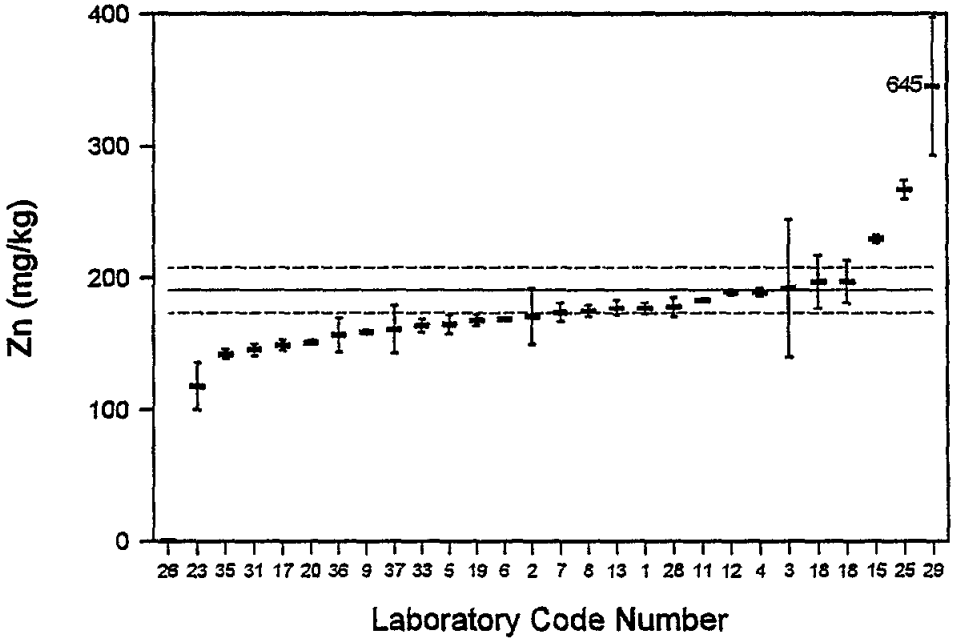
Error bar = mean ± 1 SD
Horizontal line = Information value (89 mg/kg)

Figure 1.12. Vanadium concentrations in Marine Sediment
SD-MEDPOL-1/TM
Laboratory Performance Study



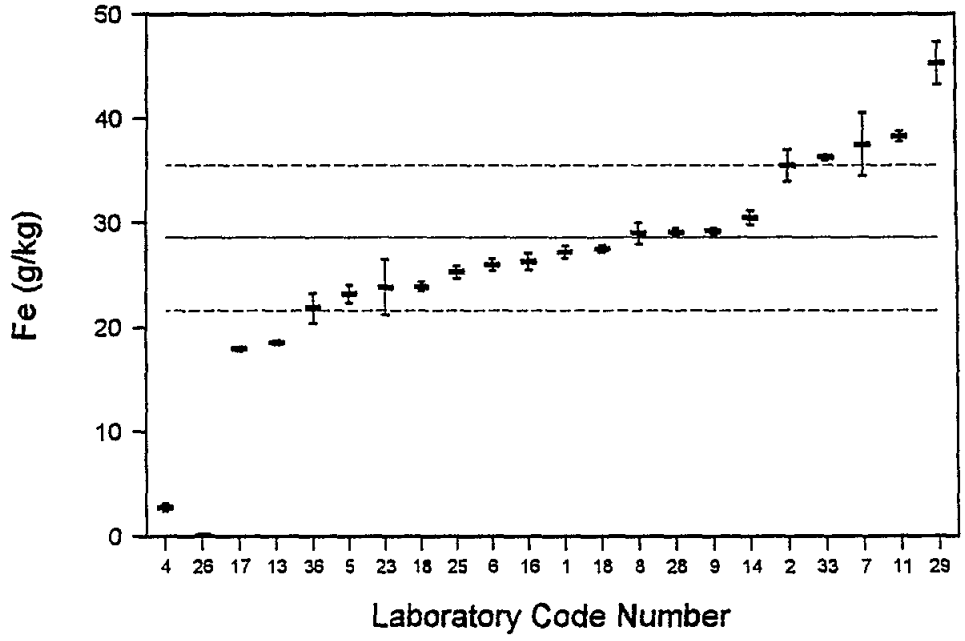
Error bar = mean ± 1 SD
Horizontal lines = Certified value ± 95% Confidence Interval (72 4 ± 5 3 mg/kg)

Figure 1.13. Zinc concentrations in Marine Sediment
SD-MEDPOL-1/TM
Laboratory Performance Study



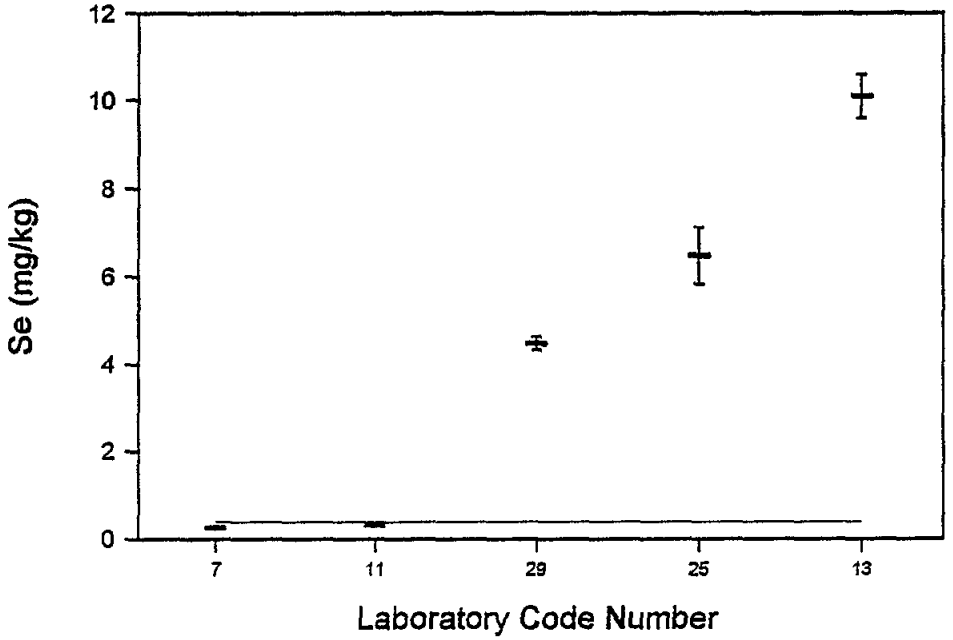
Error bar = mean ± 1 SD
Horizontal lines = Certified value ± 95% Confidence Interval (191 ± 17 mg/kg)

Figure 1.14. Iron concentrations in Marine Sediment
SD-MEDPOL-1/TM
Laboratory Performance Study



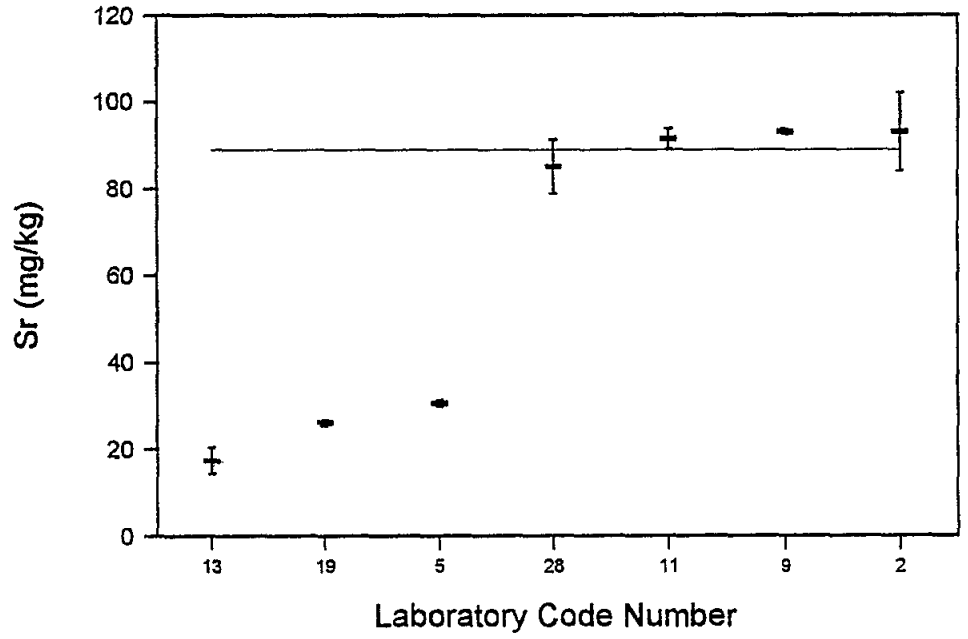
Error bar = mean ± 1 SD
Horizontal lines = Mean value ± 1 SD (28 6 ± 7 0 g/kg; except outliers lab #4 and 26)
(Semi-quantitative value = 30 g/kg)

Figure 1.15. Selenium concentrations in Marine Sediment
SD-MEDPOL-1/TM
Laboratory Performance Study



Error bar = mean ± 1 SD
Horizontal line = Information value (0.4 mg/kg)

Figure 1.16. Strontium concentrations in Marine Sediment
SD-MEDPOL-1/TM
Laboratory Performance Study



Error bar = mean ± 1 SD
Horizontal line = Information value (89 mg/kg)

Table A1.1. ALUMINIUM (Al) in SD-MEDPOL-1/TM
Units: g kg^{-1} Semi-quantitative value[a] = 80 g kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
18	1	3	1	0	HF	0	2	5	58.4	0.4
25	1	3	1	1	9	2	2	6	5.19	0.13
28	1	0	3			1		3	57.2	0.7

[a] Guideline information only (within a factor of 3 of true value).

Table A1.2. ARSENIC (As) in SD-MEDPOL-1/TM
Units: mg kg^{-1} Certified value[b] = 10.6 ± 1.2 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD	**Z-score**	**P-score**
	1	P	A	P1	P2	A1	A2					
5	1	3	1	1	0	4	0	6	11.9	0.1	**1.0**	**0.1**
7	1	3	1	3	0	4	0	6	10.3	0.3	**-0.2**	**0.2**
8	1	3	1	2	9	3		5	8.60	0.20	**-1.5**	**0.2**
9	1	3	2	3	2	3			<DL[c]			
11	1	3	1	3	2	3		3	9 48	0 17	**-0.8**	**0.1**
13	1	3	1	3	1	2	0	6	8.10	0.30	**-1.9**	**0.2**
14	1	1	3			1		6	9.26	0.52	**-1.0**	**0.4**
19	1	3	2	1	0	4		6	7.70	0.20	**-2.2**	**0.2**
25	1	3	1	1	9	2	1	6	25.1	1.0	**11**	**1**
28	1	0	3			1		4	10.2	0.7	**-0.3**	**0.5**
29	1	3	1	2	0	2	0	6	37.2	3.3	**20**	**3**

[b] Mean ± confidence interval (95%); [c] DL= detection limit.

Table A1.3. GOLD (Au) in SD-MEDPOL-1/TM
Units: µg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
28	1	0	3			1		3	1.49	0.26

Table A1.4. BARIUM (Ba) in SD-MEDPOL-1/TM
Units: mg kg^{-1} Semi-quantitative value[a] = 270 mg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
2	1	1	5			1		2	1688	350
14	1	1	3			1		6	324	30
19	1	3	2	1	0	4		6	44 2	1 3
25	1	3	1	1	9	2	2	6	58 7	6 6
28	1	0	3			1		4	283	12

[a] Guideline information only (within a factor of 3 of true value)

Table A1.5. BROMINE (Br) in SD-MEDPOL-1/TM
Units: mg kg^{-1} Semi-quantitative value[a] = 200 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
2	1	1	5			1		6	72.0	5.0
14	1	1	3			1		6	73.6	3.8
28	1	0	3			1		4	60.2	0.5

[a] Guideline information only (within a factor of 3 of true value).

Table A1.6. CALCIUM (Ca) in SD-MEDPOL-1/TM
Units: g kg^{-1} Semi-quantitative value[a] = 10 g kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
2	1	1	5			1		6	14.86	0 86

[a] Guideline information only (within a factor of 3 of true value).

Table A1.7. CADMIUM (Cd) in SD-MEDPOL-1/TM
Units: mg kg^{-1} Certified value[b] = 0.59 ± 0.10 mg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD	**Z-score**	**P-score**
	1	P	A	P1	P2	A1	A2					
3	1	3	1	3	4	2	0	6	0 333	0.012	**-3.5**	**0.2**
4 (1)	1	3	1	1	4	1	0	6	0 0103	0 0010	**-7.8**	**0.0**
4 (2)	1	3	1	1	4	2	0	4	0.0108	0.0060	**-7.8**	**0.1**
5	1	3	2	1	0	3		6	2 00	0 19	**19**	**3**
7	1	3	1	3	0	2	0	6	0.713	0.034	**1.7**	**0.5**
8	1	3	1	2	9	3		6	0 610	0 020	**0.3**	**0.3**
9	1	3	2	3	2	3			<DL[c]			
11	1	3	1	3	2	3		3	0.790	0.010	**2.7**	**0.1**
12	1	3	1	0	1	3		6	0.700	0.060	**1.5**	**0.8**
13	1	3	1	3	6	2	0	6	0.830	0 070	**3.2**	**0.9**
15	1	3	4	1	4			3	0 473	0.050	**-1.6**	**0.7**
17	1	3	1	1	4	2	0	3	1.58	0.12	**13**	**2**
18	1	3	1	0		0	1	5	0.684	0.029	**1.3**	**0.4**
19	1	3	2	1	0	4		6	0 660	0.040	**0.9**	**0.5**
20	1	3	1	2	10	2	0	3	0 730	0 020	**1.9**	**0.3**
22 (1)	1	3	1	1	3	2	1	2	5 53	0.28	**67**	**4**
22 (2)	1	3	1	1	3	2	1		0 337		**-3.4**	
23	1	3	1	1	6	1	0	5	2.00	0 00	**19**	**0**
25	1	3	1	1	9	2	1	6	0.750	0 140	**2.2**	**1.9**
26	1	3	1	3	14	1	0	6	0.128	0 003	**-6.2**	**0.0**
27	1	3	1	0	13	3		3	0 650	0 044	**0.8**	**0.6**
29	1	3	1	2	0	2	0	6	0 773	0 046	**2.5**	**0.6**
30	1	3	1	0	0	2	0	6	0.432	0 028	**-2.1**	**0.4**
31	1							2	1 48	0 049	**12**	**1**
32	1	3	1	3	4	2	1	6	0.468	0 018	**-1.6**	**0.2**
33	1	3	1	3	4	2	1	6	0 310	0 030	**-3.8**	**0.4**
35	1								0 126	0 008	**-6.3**	**0.1**
36	1	3	1	2	0	1	1	12	0 0011	0 0001	**-8.0**	**0.0**

[b] Mean ± confidence interval (95%), [c] DL= detection limit

Table A1.8. CERIUM (Ce) in SD-MEDPOL-1/TM
Units: mg kg^{-1} Semi-quantitative value[a] = 60 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
2	1	1	5			1		4	27.0	8.0
14	1	1	3			1		6	86.0	7.7
28	1	0	3			1		4	80.4	3.5

[a] Guideline information only (within a factor of 3 of true value).

Table A1.9. CHLORINE (Cl) in SD-MEDPOL-1/TM
Units: g kg^{-1} Certified value[b] = 8.2 ± 0.7 g kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD	**Z-score**	**P-score**
	1	P	A	P1	P2	A1	A2					
28	1	0	3			1		3	8.75	0.13	**0.5**	**0.1**

[b] Mean ± confidence interval (95%).

Table A1.10. COBALT (Co) in SD-MEDPOL-1/TM
Units: mg kg^{-1} Certified value[b] = 10.8 ± 1.9 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD	**Z-score**	**P-score**
	1	P	A	P1	P2	A1	A2					
4 (1)	1	3	1	1	4	1	0	6	0.362	0.010	**-7.7**	**0.0**
4 (2)	1	3	1	1	4	2	0	6	0.347	0.019	**-7.7**	**0.0**
5	1	3	2	1	0	3		6	15.3	1.4	**3.3**	**1.1**
8	1	3	1	2	9	1	0	6	11.1	0.6	**0.2**	**0.4**
9	1	3	2	3	2	3		6	22.4	0.7	**8.6**	**0.5**
13	1	3	1	1	6	2	0	6	13.6	0.5	**2.1**	**0.4**
14	1	1	3			1		6	11.5	0.7	**0.5**	**0.5**
19	1	3	2	1	0	4		6	9.00	0.30	**-1.3**	**0.2**
28	1	0	3			1		4	0.0111	0.0002	**-8.0**	**0.0**
29	1	3	1	2	0	2	0	6	2.13	0.08	**-6.4**	**0.1**

[b] Mean ± confidence interval (95%).

Table A1.11. CHROMIUM (Cr) in SD-MEDPOL-1/TM

Units: mg kg^{-1} Certified value[b] = 71 ± 11 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD	**Z-score**	**P-score**
	1	P	A	P1	P2	A1	A2					
1	1	3	1	2	4	1	0	3	54.2	1.8	**-1.9**	**0.2**
4 (1)	1	3	1	1	4	1	0	6	0.671	0.006	**-7.9**	**0.0**
4 (2)	1	3	1	1	4	2	0	6	0.252	0.129	**-8.0**	**0.0**
5	1	3	2	1	0	3		6	23.8	0.9	**-5.3**	**0.1**
6	1	3	1	3	0	2	0	4	35.0	2.2	**-4.1**	**0.2**
9	1	3	2	3	2	3		6	64.7	1.4	**-0.7**	**0.2**
11	1	3	1	3	2	3		3	57.6	0.8	**-1.5**	**0.1**
13	1	3	1	1	6	2	0	6	61.7	3.1	**-1.0**	**0.3**
14	1	1	3			1		6	67 0	3.8	**-0.5**	**0.4**
17	1	3	1	1	4	1	0	3	63.6	1.8	**-0.8**	**0.2**
18	1	3	1	0		2	2	5	54 9	2.9	**-1.8**	**0.3**
19	1	3	1	1	0	4		6	29.6	1.1	**-4.7**	**0.1**
22 (1)	1	3	1	1	3	2	2	2	9.11	2.23	**-7.0**	**0.3**
22 (2)	1	3	1	1	3	2	2		5 43		**-7.4**	
25	1	3	1	1	9	2	2	6	6.53	0 49	**-7.3**	**0.1**
28	1	0	3			1		4	70.8	1.7	**0.0**	**0.2**
29	1	3	1	2	0	2	0	6	24.0	0.6	**-5.3**	**0.1**
30	1	3	1	0	0	2	0	6	24 3	1.1	**-5.3**	**0.1**
31	1							2	7 19	0.14	**-7.2**	**0.0**
33	1	3	1	3	4	1	2	6	47 9	2.0	**-2.6**	**0.2**

[b] Mean ± confidence interval (95%)

Table A1.12. CAESIUM (Cs) in SD-MEDPOL-1/TM

Units: mg kg^{-1} Informative value = 4 mg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD	**Z-score**	**P-score**
	1	P	A	P1	P2	A1	A2					
14	1	1	3			1		6	4 76	0 29	**1.5**	**0.6**
28	1	0	3			1		4	4 21	0 12	**0.4**	**0.2**

Table A1.13. COPPER (Cu) in SD-MEDPOL-1/TM

Units: mg kg^{-1} Certified value[b] = 25.1 ± 3.8 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD	Z-score	P-score
	1	P	A	P1	P2	A1	A2					
1	1	3	1	2	4	1	0	3	23.5	1.1	-0.5	0.4
2	1	1	5			1		6	64.5	12.1	13	4
3	1	3	1	3	4	2	0	6	26.5	0.6	0.4	0.2
4 (1)	1	3	1	1	4	1	0	6	0.279	0.002	-7.9	0.0
4 (2)	1	3	1	1	4	2	0	6	0.263	0.019	-7.9	0.0
5	1	3	2	1	0	3		6	34 5	1.7	3.0	0.5
6	1	3	1	3	0	2	0	4	19.0	0.9	-1.9	0.3
7	1	3	1	3	0	1	0	6	23.6	0.4	-0.5	0.1
8	1	3	1	2	9	1	0	6	21.2	0.5	-1.2	0.2
9	1	3	2	3	2	3		6	24.4	0.6	-0.2	0.2
11	1	3	1	3	2	1	0	3	27.7	0.6	0.8	0.2
12	1	3	1	0	1	3		6	23.9	1.4	-0.4	0.4
13	1	3	1	3	1	2	0	6	21.6	1.6	-1.1	0.5
16	1	3	1	1	4	1	0	4	26.5	2.5	0.4	0.8
17	1	3	1	1	4	2	0	3	19.3	0 9	-1.8	0.3
18 (1)	1	3	1	0		0	2	5	23.0	1 1	-0.7	0.3
18 (2)	1	3	1	0	HF	0	2	5	26.9	1.9	0.6	0.6
19	1	3	2	1	0	4		6	20 5	0.9	-1.5	0.3
22 (1)	1	3	1	1	3	2	2	2	89.0	1.3	20	0
22 (2)	1	3	1	1	3	2	2		19.5		-1.8	
23	1	3	1	1	6	1	0	5	25.5	1.2	0.1	0.4
25	1	3	1	1	9	1	2	6	38.9	0.4	4.4	0.1
26	1	3	1	3	4	1	0	6	0.0720	0.0090	-8.0	0.0
27	1	3	1	0	13	3		3	19 3	0.5	-1.8	0.1
29	1	3	1	2	0	2	0	6	26.4	0.6	0.4	0.2
31	1							2	20.7	0.1	-1.4	0.0
32	1	3	1	3	4	2	2	6	24.0	0.2	-0.3	0.1
33	1	3	1	3	4	1	2	6	25.4	2.2	0.1	0.7
35	1								22.9	0.7	-0.7	0.2

[b] *Mean ± confidence interval (95%).*

Table A1.14. DYSPROSIUM (Dy) in SD-MEDPOL-1/TM

Units: mg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
28	1	0	3			1		3	7 28	0 71

Table A1.15. EUROPIUM (Eu) in SD-MEDPOL-1/TM

Units: mg kg^{-1} Semi-quantitative value[a] = 1 mg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
14	1	1	3			1		6	1 20	0 10
28	1	0	3			1		4	1 36	0 02

[a] *Guideline information only (within a factor of 3 of true value)*

Table A1.16. IRON (Fe) in SD-MEDPOL-1/TM

Units: g kg^{-1} Semi-quantitative value[a] = 30 g kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
1	1	3	1	2	4	1	0	3	27.2	0.6
2	1	1	5			1		6	35.5	1.5
4	1	3	1	1	4	1	0	6	0 0274	0 0000
5	1	3	2	1	0	0		6	23 2	0.9
6	1	3	1	3	0	1	0	4	26.0	0.5
7	1	3	1	3	0	1	0	4	37.5	3.0
8	1	3	1	2	9	1	0	6	29 0	1.0
9	1	3	2	3	2	3		6	29.2	0.3
11	1	3	1	3	2	1	0	3	38 3	0.5
13	1	3	2	3	1	3		6	18.6	0.2
14	1	1	3			1		6	30.5	0.7
16	1	3	1	1	4	1	0	4	26 3	0.8
17	1	3	1	1	4	1	0	3	18.0	0.2
18 (1)	1	3	1	0		0	1	5	23.9	0.4
18 (2)	1	3	1	0	HF	0	1	5	27 5	0.4
23	1	3	1	1	6	1	0	5	23.8	2.6
25	1	3	1	1	9	1	2	6	25.3	0 6
26	1	3	1	3	4	1	0	6	0.160	0 002
28	1	0	3			1		4	29 1	0.4
29	1	3	1	2	0	2	0	4	45.3	2.0
33	1	3	1	3	4	1	2	6	36 3	0 3
36	1	3	1	2	0	1	2	14	21.9	1.4

[a] Guideline information only (within a factor of 3 of true value).

Table A1.17. GALLIUM (Ga) in SD-MEDPOL-1/TM

Units: mg kg^{-1} Semi-quantitative value[a] = 20 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
28	1	0	3			1		5	12.9	2 3

[a] Guideline information only (within a factor of 3 of true value)

Table A1.18. HAFNIUM (Hf) in SD-MEDPOL-1/TM

Units: mg kg^{-1} Semi-quantitative value[a] = 20 mg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
14	1	1	3			1		6	15 5	0 8
28	1	0	3			1		4	15 5	0 9

[a] Guideline information only (within a factor of 3 of true value)

Table A1.19. MERCURY (Hg) in SD-MEDPOL-1/TM

Units: mg kg^{-1} Certified value[b] = 0.171 ± 0.014 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD	Z-score	P-score
	I	P	A	P1	P2	A1	A2					
1	1	3	1	2	1	5	0	5	0.184	0.016	**0.6**	**0.8**
5	1	3	1	1	0	5	0	6	0.200	0.050	**1.4**	**2.4**
7	1	3	1	3	0	5	0	6	0.207	0.020	**1.7**	**1.0**
8	1	3	1	2	9	5	0	6	0.220	0.020	**2.3**	**1.0**
13	1	3	2	3	1	3		6	<2			
17	1	3	1	1	4	5	0	3	0.720	0.030	**26**	**1**
18	1	3	1	0		5	0	5	0.213	0.004	**2.0**	**0.2**
19	1	3	2	1	0	5	0	6	0.230	0.010	**2.8**	**0.5**
22 (1)	1	3	1	1	3	5	0	2	0.450	0.080	**13**	**4**
22 (2)	1	3	1	1	12	5	0		0.684		**24**	
23	1	3	1	1	6	5	0	5	0.200	0.000	**1.4**	**0.0**
24	1	3	1	1	12	5	2	3	0.197	0.009	**1.2**	**0.4**
25	1	3	1	1	9	5	2	6	0.00543	0.00040	**-7.9**	**0.0**
27	1	3	1	0	13	5	0	3	0.170	0.010	**0.0**	**0.5**
28 (1)	1	1	3			1		5	0.169	0 012	**-0.1**	**0.6**
28 (2)	1	3	1	0		5	0	5	0.191	0 019	**1.0**	**0.9**
29	1	3	1	2	0	5	0	4	0.204	0 041	**1.6**	**2.0**
30	1	3	1	0	0	2	0	6	0.0555	0 0075	**-5.5**	**0.4**
32	1	3	1	3	4	5	2	6	0 170	0 003	**0.0**	**0.1**
33	1	3	1	3	4	5	2	5	0 230	0.040	**2.8**	**1.9**
34	1	3	1	1	10	5	0	4	0.144	0.003	**-1.3**	**0.1**
35	1								0.367	0.033	**9.3**	**1.6**
36	1	3	1	2	0	5	1	14	0 210	0.018	**1.8**	**0.9**

[b] Mean ± confidence interval (95%).

Table A1.20. IODINE (I) in SD-MEDPOL-1/TM

Units: mg kg^{-1} Semi-quantitative value[a] = 40 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	I	P	A	P1	P2	A1	A2			
28	1	0	3			1		3	23 6	3.3

[a] Guideline information only (within a factor of 3 of true value).

Table A1.21. POTASSIUM (K) in SD-MEDPOL-1/TM

Units: g kg^{-1} Semi-quantitative value[a] = 30 g kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	I	P	A	P1	P2	A1	A2			
2	1	1	5			1		6	12 3	4 3
25	1	3	1	1	9	0		6	2 40	0.30
28	1	0	3			1		4	17 1	0 2

[a] Guideline information only (within a factor of 3 of true value)

Table A1.22. LANTHANUM (La) in SD-MEDPOL-1/TM
Units: mg kg^{-1} Semi-quantitative value[a] = 30 mg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
14	1	1	3			1		6	40.4	3.0
28	1	0	3			1		4	36.0	1.1

[a] Guideline information only (within a factor of 3 of true value).

Table A1.23. LITHIUM (Li) in SD-MEDPOL-1/TM
Units: mg kg^{-1} Semi-quantitative value[a] = 60 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
5	1	3	2	1	0	3		6	33.1	0.8
9	1	3	2	3	2	3		6	42.2	0 9
13	1	3	2	1	6	3		6	36.8	0 4
19	1	3	2	1	0	4		6	30 1	1.0

[a] Guideline information only (within a factor of 3 of true value)

Table A1.24. LUTETIUM (Lu) in SD-MEDPOL-1/TM
Units: mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
14	1	1	3			1		6	0.520	0.045

Table A1.25. MAGNESIUM (Mg) in SD-MEDPOL-1/TM
Units: g kg^{-1} Semi-quantitative value[a] = 7 g kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
28	1	0	3			1		3	34 0	0.5

[a] Guideline information only (within a factor of 3 of true value)

Table A1.26. MANGANESE (Mn) in SD-MEDPOL-1/TM

Units: mg kg^{-1} Certified value[b] = 513 ± 25 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD	Z-score	P-score
	1	P	A	P1	P2	A1	A2					
1	1	3	1	2	4	1	0	6	521	12	**0.1**	**0.2**
2	1	1	5			1		6	452	53	**-1.0**	**0.8**
3	1	3	1	3	4	2	0	6	529	50	**0.3**	**0.8**
4	1	3	1	1	4	1	0	6	5.22	0.13	**-7.9**	**0.0**
5	1	3	2	1	0	3		6	326	10	**-2.9**	**0.2**
6	1	3	1	3	0	1	0	4	285	5	**-3.6**	**0.1**
7	1	3	1	3	0	1	0	6	330	12	**-2.9**	**0.2**
8	1	3	1	2	9	1	0	6	412	16	**-1.6**	**0.3**
9	1	3	2	3	2	3		6	497	2	**-0.3**	**0.0**
11	1	3	1	3	2	1	0	3	515	9	**0.0**	**0.1**
12	1	3	1	0	1	3		6	319	12	**-3.0**	**0.2**
13	1	3	2	1	6	3		6	424	12	**-1.4**	**0.2**
16	1	3	1	1	4	1	0	4	494	1	**-0.3**	**0.0**
17	1	3	1	1	4	1	0	3	406	10	**-1.7**	**0.2**
18	1	3	1	0	HF	0	1	5	478	4	**-0.5**	**0.1**
19	1	3	2	1	0	4		6	319	14	**-3.0**	**0.2**
23	1	3	1	1	6	1	0	5	275	42	**-3.7**	**0.7**
25	1	3	1	1	9	1	2	6	358	0	**-2.4**	**0.0**
28	1	0	3			1		3	514	4	**0.0**	**0.1**
29	1	3	1	2	0	2	0	6	341	9	**-2.7**	**0.1**
33	1	3	1	3	4	1	2	4	506	59	**-0.1**	**0.9**
36	1	3	1	2	0	1	1	14	286	18	**-3.5**	**0.3**

[b] Mean = confidence interval (95%).

Table A1.27. SODIUM (Na) in SD-MEDPOL-1/TM

Units: g kg^{-1} Semi-quantitative value[a] = 10 g kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
14	1	1	3			1		6	18.0	0.3
25	1	3	1	1	9	1	2	6	7.19	0 16
28	1	0	3			1		4	17.5	0.1

[a] Guideline information only (within a factor of 3 of true value)

Table A1.28. NEODYMIUM (Nd) in SD-MEDPOL-1/TM

Units: g kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
28	1	0	3			1		4	37.8	1 9

Table A1.29. NICKEL (Ni) in SD-MEDPOL-1/TM

Units: mg kg^{-1} Certified value[b] = 29.5 ± 2.7 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD	Z-score	P-score
	1	P	A	P1	P2	A1	A2					
1	1	3	1	2	4	1	0	3	29.2	2.2	**-0.1**	**0.6**
4 (1)	1	3	1	1	4	1	0	6	0.525	0.009	**-7.9**	**0.0**
4 (2)	1	3	1	1	4	2	0	3	0.661	0 020	**-7.8**	**0.0**
5	1	3	2	1	0	3		6	20.9	1.0	**-2.3**	**0.3**
6	1	3	1	3	0	2	0	4	24.0	1.1	**-1.5**	**0.3**
7	1	3	1	3	0	1	0	6	31.6	1.5	**0.6**	**0.4**
8	1	3	1	2	9	1	0	6	27.6	0.4	**-0.5**	**0.1**
9	1	3	2	3	2	3		6	31.6	3.6	**0.6**	**1.0**
11	1	3	1	3	2	3		3	26.0	0.5	**-0.9**	**0.1**
13	1	3	1	1	6	2	0	6	26.7	2.8	**-0.8**	**0.8**
18	1	3	1	0		0	1	5	24.2	1.3	**-1.4**	**0.4**
19	1	3	2	1	0	4		6	25.7	1.4	**-1.0**	**0.4**
23	1	3	1	1	6	1	0	5	45.4	11.4	**4.3**	**3.1**
29	1	3	1	2	0	2	0	4	31 1	1 4	**0.4**	**0.4**

[b] Mean ± confidence interval (95%)

Table A1.30. LEAD (Pb) in SD-MEDPOL-1/TM

Units: mg kg^{-1} Certified value[b] = 34 0 ± 6 1 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD	Z-score	P-score
	1	P	A	P1	P2	A1	A2					
1	1	3	1	2	4	2	0	4	28.1	0 5	**-1.4**	**0.1**
2	1	1	5			1		2	89 0	20 0	13	5
3	1	3	1	3	4	2	0	6	28 3	2.4	**-1.3**	**0.6**
4 (1)	1	3	1	1	4	1	0	6	0 559	0 013	**-7.9**	**0.0**
4 (2)	1	3	1	1	4	2	0	6	0.822	0.042	**-7.8**	**0.0**
5	1	3	2	1	0	3		6	20 0	1 0	**-3.3**	**0.2**
7	1	3	1	3	0	2	0	6	24.2	1 2	**-2.3**	**0.3**
8	1	3	1	2	9	1	0	6	34 0	1 0	**0.0**	**0.2**
9	1	3	2	3	2	3			<DL[c]			
11	1	3	1	3	2	3		3	37 7	0 6	**0.9**	**0.1**
12	1	3	1	0	1	3		6	27 6	0 7	**-1.5**	**0.2**
13	1	3	1	1	6	2	0	6	28 4	1.0	**-1.3**	**0.2**
15	1	3	4	1	4			3	13.6	0.2	**-4.8**	**0.1**
17	1	3	1	1	4	2	0	3	10 1	1.6	**-5.6**	**0.4**
18	1	3	1	0		0	2	5	31 6	0 6	**-0.6**	**0.2**
19	1	3	2	1	0	4		6	24 0	1 0	**-2.4**	**0.2**
20	1	3	1	2	10	2	0	3	35 2	4 5	**0.3**	**1.1**
22 (1)	1	3	1	1	3	2	1	2	13 6	0.2	**-4.8**	**0.0**
22 (2)	1	3	1	1	3	2	1		27 2		**-1.6**	
23	1	3	1	1	6	1	0	5	45 4	17 1	**2.7**	**4.0**
25	1	3	1	1	9	2	1	6	362	9 9	**77**	**2**
27	1	3	1	0	13	3		3	31 1	0 6	**-0.7**	**0.1**
29	1	3	1	2	0	2	0	4	48 7	0 2	**3.5**	**0.0**
30	1	3	1	0	0	2	0	6	13 6	0 4	**-4.8**	**0.1**
31	1							2	26 6	0.7	**-1.8**	**0.2**
32	1	3	1	3	4	2	1	6	13 9	0.8	**-4.7**	**0.2**
33	1	3	1	3	4	1	2	5	22 1	2.0	**-2.8**	**0.5**
35	1								22 9	0 5	**-2.6**	**0.1**

[b] Mean ± confidence interval (95%), [c] DL= detection limit

Table A1.31. RUBIDIUM (Rb) in SD-MEDPOL-1/TM

Units: mg kg^{-1} Semi-quantitative value[a] = 100 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
2	1	1	5			1		6	101	12
14	1	1	3			1		6	98	5.7
19	1	3	2	1	0	4		6	19 8	1.6
28	1	0	3			1		4	92 3	1.7

[a] Guideline information only (within a factor of 3 of true value).

Table A1.32. ANTIMONY (Sb) in SD-MEDPOL-1/TM

Units: mg kg^{-1} Certified value[b] = 0.73 ± 0 08 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD	**Z-score**	**P-score**
	1	P	A	P1	P2	A1	A2					
13	1	3	2	3	1	3		6	<5			
28	1	0	3			1		4	0.755	0 033	**0.3**	**0.4**

[b] Mean ± confidence interval (95%).

Table A1.33. SCANDIUM (Sc) in SD-MEDPOL-1/TM

Units: mg kg^{-1} Semi-quantitative value[a] = 20 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
14	1	1	3			1		6	10 7	0.5
28	1	0	3			1		4	10 1	0.1

[a] Guideline information only (within a factor of 3 of true value).

Table A1.34. SELENIUM (Se) in SD-MEDPOL-1/TM

Units: mg kg^{-1} Information value = 0.4 mg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD	**Z-score**	**P-score**
	1	P	A	P1	P2	A1	A2					
7	1	3	1	3	0	4	0	6	0 256	0 020	**-2.9**	**0.4**
11	1	3	1	3	8	3		3	0.320	0 010	**-1.6**	**0.2**
13	1	3	1	3	1	2	0	6	10 1	0.5	**194**	**10**
25	1	3	1	1	9	2	1	6	6.47	0.65	**121**	**13**
29	1	3	1	2	0	2	0	4	4.48	0.15	**82**	**3**

Table A1.35. SAMARIUM (Sm) in SD-MEDPOL-1/TM
Units: mg kg^{-1} Semi-quantitative value[a] = 8 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
14	1	1	3			1		6	7.96	0.47
28	1	0	3			1		4	7.17	0.31

[a] *Guideline information only (within a factor of 3 of true value)*

Table A1.36. TIN (Sn) in SD-MEDPOL-1/TM
Units: mg kg^{-1} Semi-quantitative value[a] = 6 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
13	1	3	2	3	1	3		6	5.20	0.40
29	1	3	1	2	0	2	0	4	0.216	0 046

[a] Guideline information only (within a factor of 3 of true value)

Table A1.37. STRONTIUM (Sr) in SD-MEDPOL-1/TM
Units: mg kg^{-1} Information value = 89 mg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD	**Z-score**	**P-score**
	1	P	A	P1	P2	A1	A2					
2	1	1	5			1		6	93	9	**0.4**	**0.8**
5	1	3	2	1	0	3		6	30.6	0.8	**-5.3**	**0.1**
9	1	3	2	3	2	3		6	93.0	0.6	**0.4**	**0.1**
11	1	3	2	3	2	3		3	91 3	2.4	**0.2**	**0.2**
13	1	3	1	3	1	2	0	6	17 3	3 0	**-6.4**	**0.3**
19	1	3	2	1	0	4		6	26.1	0 7	**-5.7**	**0.1**
28	1	0	3			1		4	85.0	6 2	**-0.4**	**0.6**

Table A1.38. TANTALUM (Ta) in SD-MEDPOL-1/TM
Units: mg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
28	1	0	3			1		4	1.42	0.04

Table A1.39. TERBIUM (Tb) in SD-MEDPOL-1/TM
Units: mg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
14	1	1	3			1		6	1.36	0 10
28	1	0	3			1		4	0 957	0.021

Table A1.40. THORIUM (Th) in SD-MEDPOL-1/TM
Units: mg kg^{-1} Semi-quantitative value[a] = 20 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
14	1	1	3			1		6	13.8	1 4
28	1	0	3			1		4	12.4	0 6

[a] Guideline information only (within a factor of 3 of true value).

Table A1.41. TITANIUM (Ti) in SD-MEDPOL-1/TM
Units: g kg^{-1} Semi-quantitative value[a] = 7 g kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
2	1	1	5			1		6	5.00	0 57
28	1	0	3			1		3	4 88	0.15

[a] Guideline information only (within a factor of 3 of true value).

Table A1.42. TAMARIUM (Tm) in SD-MEDPOL-1/TM
Units: mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
28	1	0	3			1		4	1 14	0.03

Table A1.43. URANIUM (U) in SD-MEDPOL-1/TM
Units: mg kg^{-1} Semi-quantitative value[a] = 5 mg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
14	1	1	3			1		6	4 10	0 66
28	1	0	3			1		4	4.26	0.24

[a] Guideline information only (within a factor of 3 of true value)

Table A1.44. VANADIUM (V) in SD-MEDPOL-1/TM

Units: mg kg^{-1} Certified value[b] = 72.4 ± 5.3 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD	**Z-score**	**P-score**
	1	P	A	P1	P2	A1	A2					
2	1	1	5			1		6	103	28	**3.4**	**3.1**
5	1	3	2	1	0	3		6	112	8	**4.4**	**0.9**
8	1	3	1	2	9	3		6	56.0	2.0	**-1.8**	**0.2**
9	1	3	2	3	2	3		6	84 6	0.9	**1.3**	**0.1**
11	1	3	2	3	2	3		3	72.5	2.6	**0.0**	**0.3**
13	1	3	2	3	1	3		6	69.2	0.4	**-0.4**	**0.0**
19	1	3	2	1	0	4		6	33.3	0.9	**-4.3**	**0.1**
28	1	0	3			1		3	76 1	2.0	**0.4**	**0.2**
29	1	3	1	2	0	2	0	4	41 0	3 1	**-3.5**	**0.3**

[b] Mean ± confidence interval (95%).

Table A1.45. YTTERBIUM (Yb) in SD-MEDPOL-1/TM

Units: mg kg^{-1} Semi-quantitative value[a] = 6 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
14	1	1	3			1		6	3 95	0.25
28	1	0	3			1		4	4 00	0 24

[a] Guideline information only (within a factor of 3 of true value)

Table A1.46. ZINC (Zn) in SD-MEDPOL-1/TM
Units: mg kg^{-1} Certified value[b] = 191 ± 17 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD	**Z-score**	**P-score**
	1	P	A	P1	P2	A1	A2					
1	1	3	1	2	4	1	0	5	177	4	**-0.6**	**0.1**
2	1	1	5			1		6	171	21	**-0.8**	**0.9**
3	1	3	1	3	4	2	0	6	192	52	**0.0**	**2.2**
4	1	3	1	1	4	1	0	6	1.89	0 03	**-7.9**	**0.0**
5	1	3	2	1	0	3		6	165	7	**-1.1**	**0.3**
6	1	3	1	3	0	1	0	4	169	1	**-0.9**	**0.0**
7	1	3	1	3	0	1	0	6	174	7	**-0.7**	**0.3**
8	1	3	1	2	9	1	0	6	175	4	**-0.7**	**0.2**
9	1	3	2	3	2	3		6	159	2	**-1.3**	**0.1**
11	1	3	1	3	2	1	0	3	183	1	**-0.3**	**0.0**
12	1	3	1	0	1	3		6	189	2	**-0.1**	**0.1**
13	1	3	2	1	6	3		6	177	6	**-0.6**	**0.2**
15	1	3	4	1	4			3	229	3	**1.6**	**0.1**
17	1	3	1	1	4	1	0	3	149	4	**-1.8**	**0.2**
18	1	3	1	0		0	1	5	197	20	**0.3**	**0.8**
18	1	3	1	0	HF	0	1	5	197	16	**0.3**	**0.7**
19	1	3	2	1	0	4		6	168	4	**-1.0**	**0.2**
20	1	3	1	2	10	1	0	3	151	1	**-1.7**	**0.1**
23	1	3	1	1	6	1	0	5	118	18	**-3.0**	**0.7**
25	1	3	1	1	9	1	2	6	267	7	**3.2**	**0.3**
26	1	3	1	3	4	1	0	6	0 538	0.064	**-8.0**	**0.0**
28	1	0	3			1		4	178	7	**-0.5**	**0.3**
29	1	3	1	2	0	2	0	4	645	52	**19**	**2**
31	1							2	146	4	**-1.9**	**0.2**
33	1	3	1	3	16	1	1	6	164	5	**-1.1**	**0.2**
35	1								142	3	**-2.0**	**0.1**
36	1	3	1	2	0	1	1	14	157	13	**-1.4**	**0.6**

[b] Mean ± confidence interval (95%)

Table A1.47. ZIRCONIUM (Zr) in SD-MEDPOL-1/TM
Units: mg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
2	1	1	5			1		3	509	181
28	1	0	3			1		4	595	51

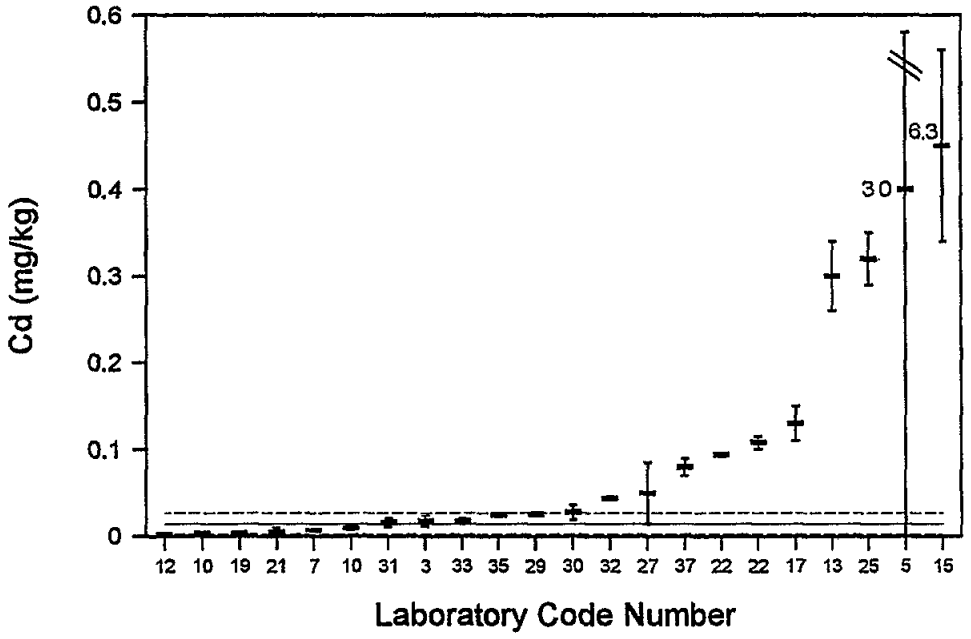
ANNEX II

Total analyses data report
MA-MEDPOL-1/TM

Figure 2.1. Cadmium concentrations in Fish Homogenate

MA-MEDPOL-1/TM

Laboratory Performance Study



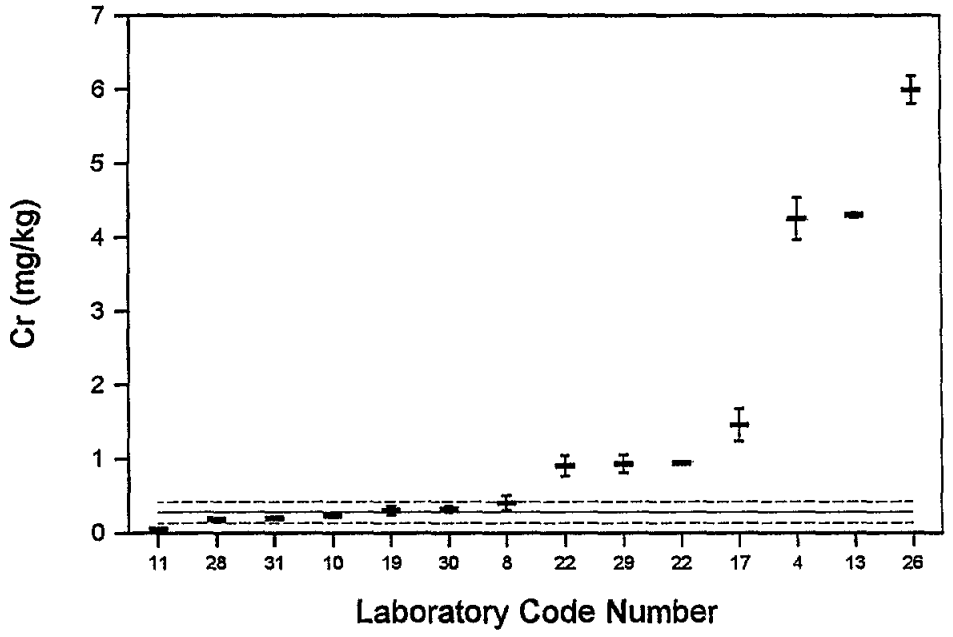
Error bar = mean ± 1 SD

Horizontal lines = Certified value ± 95% Confidence Interval (0.015 ± 0.012 mg/kg)

Figure 2.2. Chromium concentrations in Fish Homogenate

MA-MEDPOL-1/TM

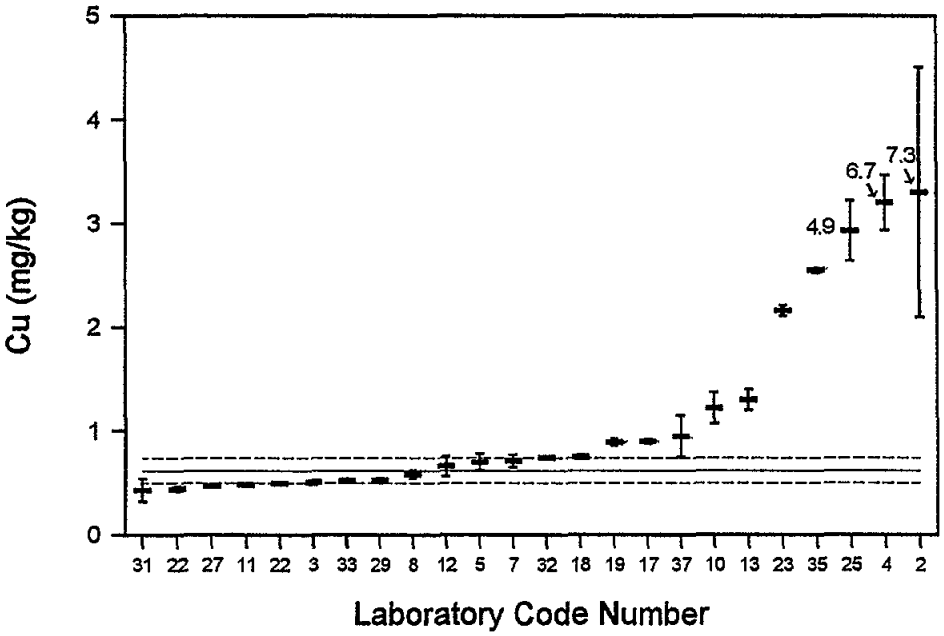
Laboratory Performance Study



Error bar = mean ± 1 SD

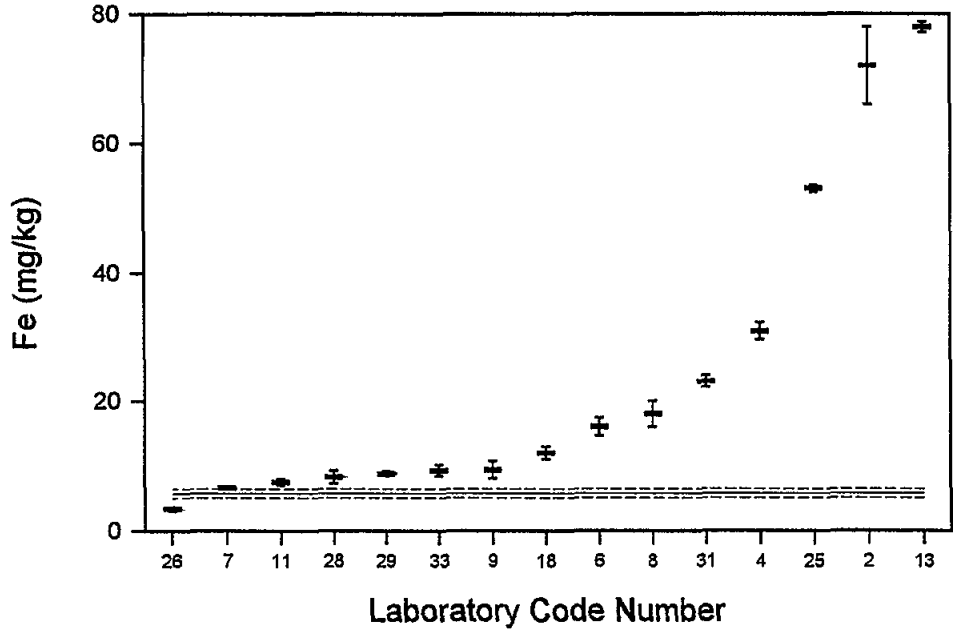
Horizontal lines = Certified value ± 95% Confidence Interval (0.28 ± 0.14 mg/kg)

Figure 2.3. Copper concentrations in Fish Homogenate
MA-MEDPOL-1/TM
Laboratory Performance Study



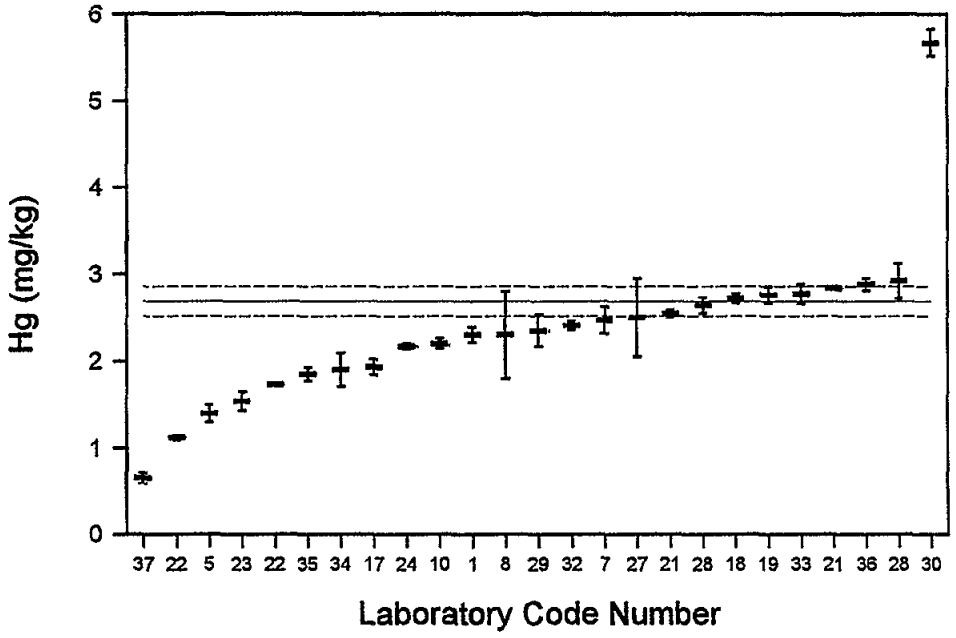
Error bar = mean ± 1 SD
Horizontal lines = Certified value ± 95% Confidence Interval (0 62 ± 0 12 mg/kg)

Figure 2.4. Iron concentrations in Fish Homogenate
MA-MEDPOL-1/TM
Laboratory Performance Study



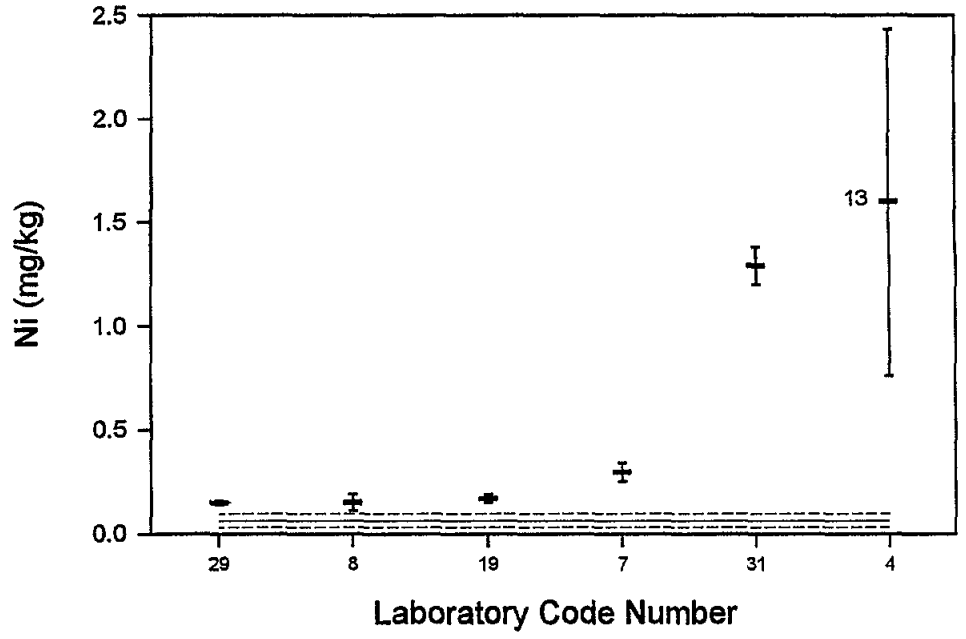
Error bar = mean ± 1 SD
Horizontal lines = Certified value ± 95% Confidence Interval (5 8 ± 0.7 mg kg)

Figure 2.5. Mercury concentrations in Fish Homogenate
MA-MEDPOL-1/TM
Laboratory Performance Study



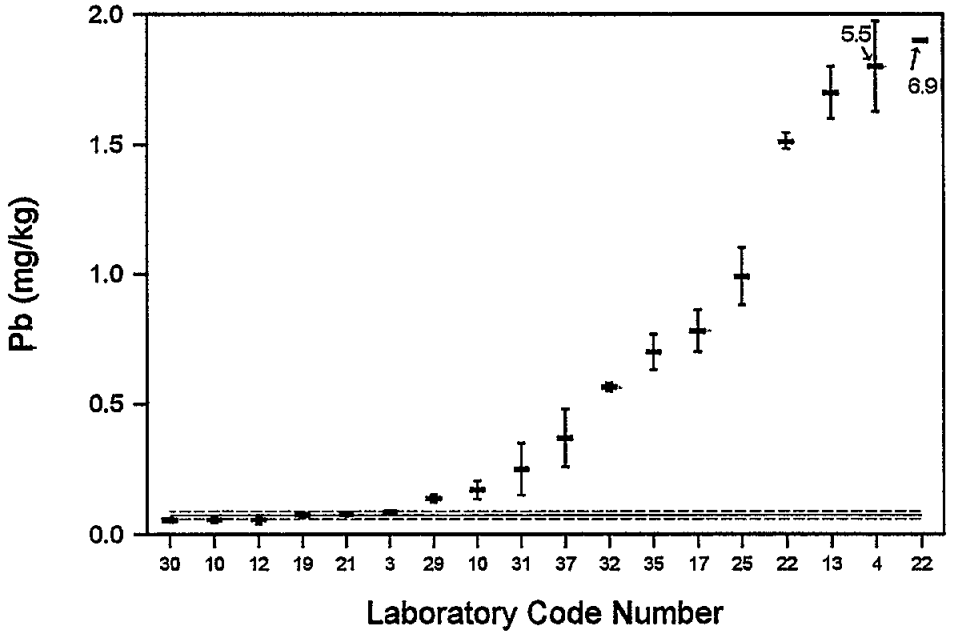
Error bar = mean ± 1 SD
Horizontal lines = Certified value ± 95% Confidence Interval (2.69 ± 0 17 mg/kg)

Figure 2.6. Nickel concentrations in Fish Homogenate
MA-MEDPOL-1/TM
Laboratory Performance Study



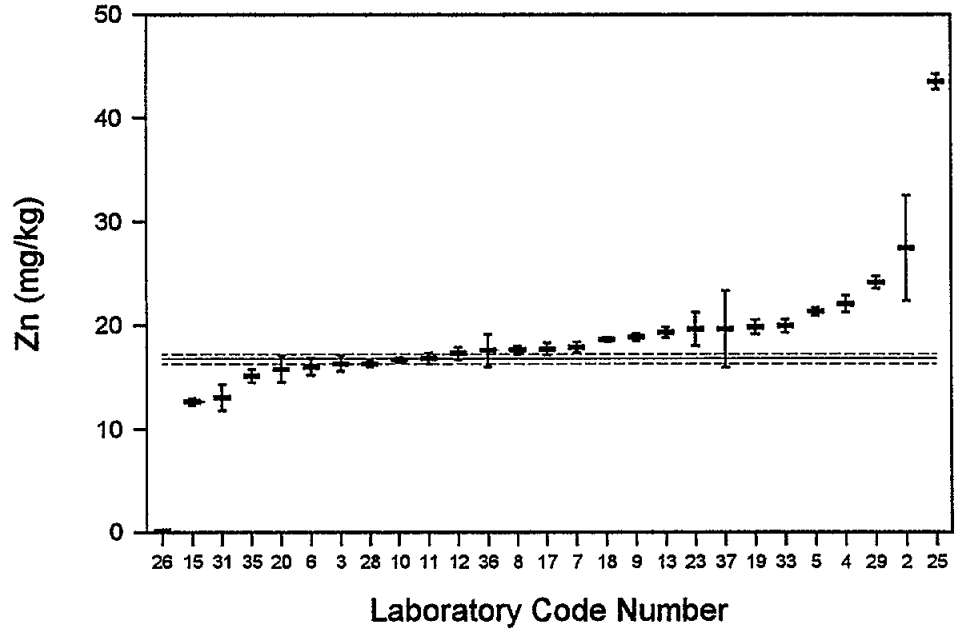
Error bar = mean ± 1 SD
Horizontal lines = Certified value ± 95% Confidence Interval (0 065 ± 0.032 mg/kg)

Figure 2.7. Lead concentrations in Fish Homogenate
MA-MEDPOL-1/TM
Laboratory Performance Study



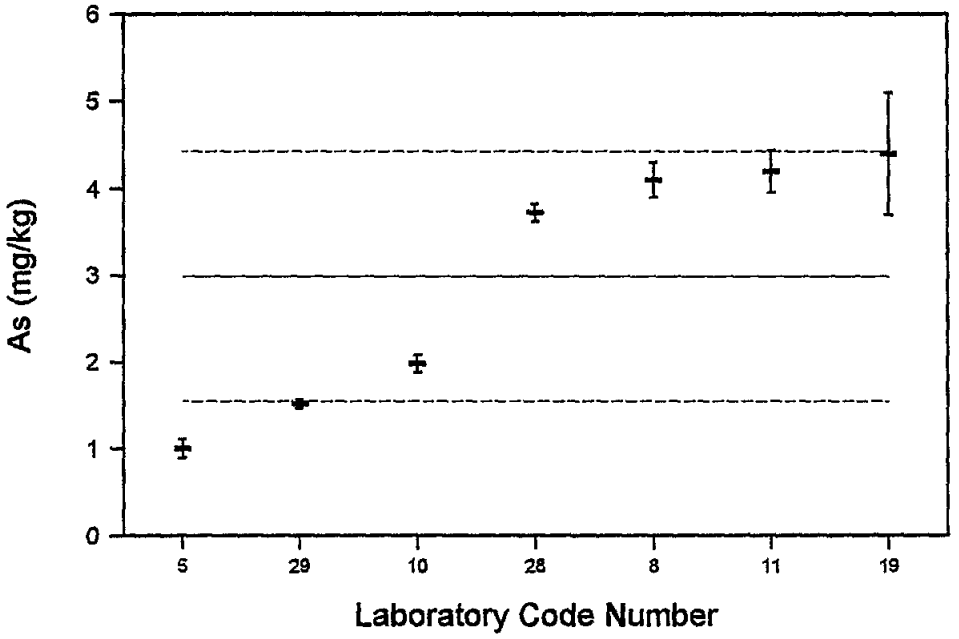
Error bar = mean ± 1 SD
Horizontal lines = Certified value ± 95% Confidence Interval (0.074 ± 0.015 mg/kg)

Figure 2.8. Zinc concentrations in Fish Homogenate
MA-MEDPOL-1/TM
Laboratory Performance Study



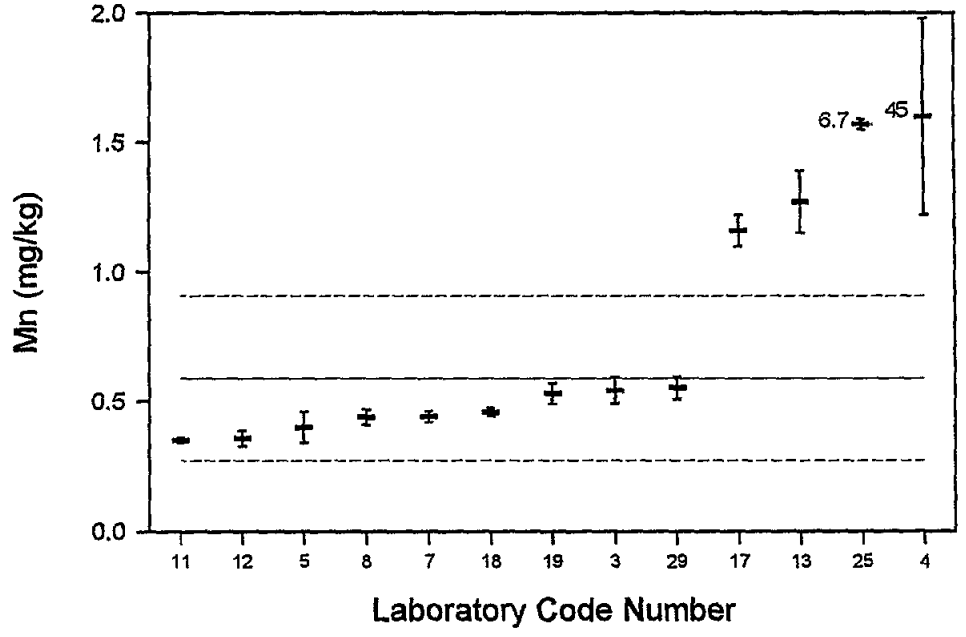
Error bar = mean ± 1 SD
Horizontal lines = Certified value ± 95% Confidence Interval (16 80 ± 0.48 mg/kg)

Figure 2.9. Arsenic concentrations in Fish Homogenate
MA-MEDPOL-1/TM
Laboratory Performance Study



Error bar = mean ± 1 SD
Horizontal lines = Mean value ± 1 SD (2.99 ± 1.44 mg/kg)

Figure 2.10. Manganese concentrations in Fish Homogenate
MA-MEDPOL-1/TM
Laboratory Performance Study

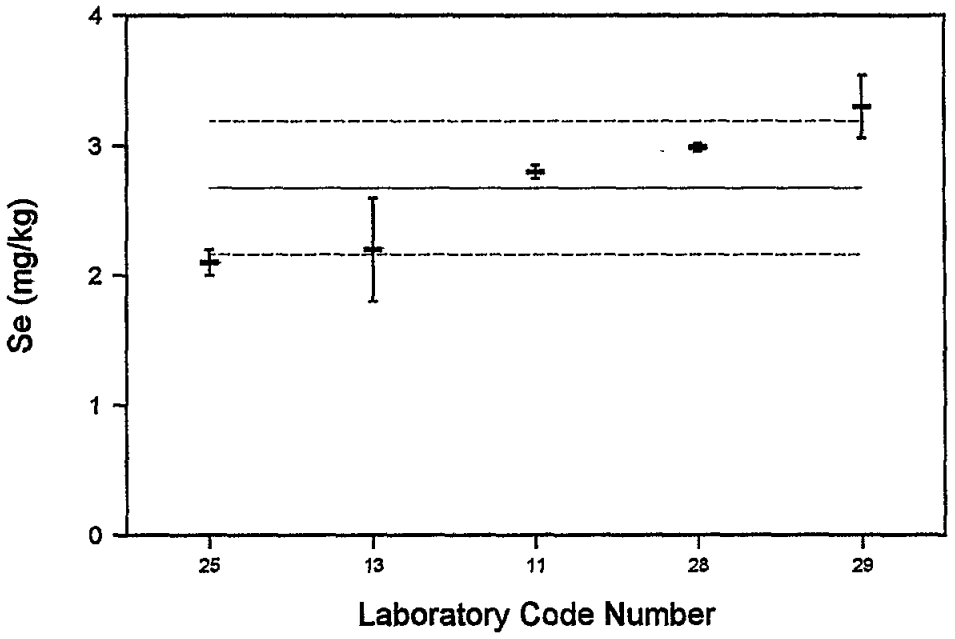


Error bar = mean ± 1 SD
Horizontal lines = Mean value ± 1 SD (0.59 ± 0.32 mg/kg; except outliers lab #4 and 25)

Figure 2.11. Selenium concentrations in Fish Homogenate

MA-MEDPOL-1/TM

Laboratory Performance Study

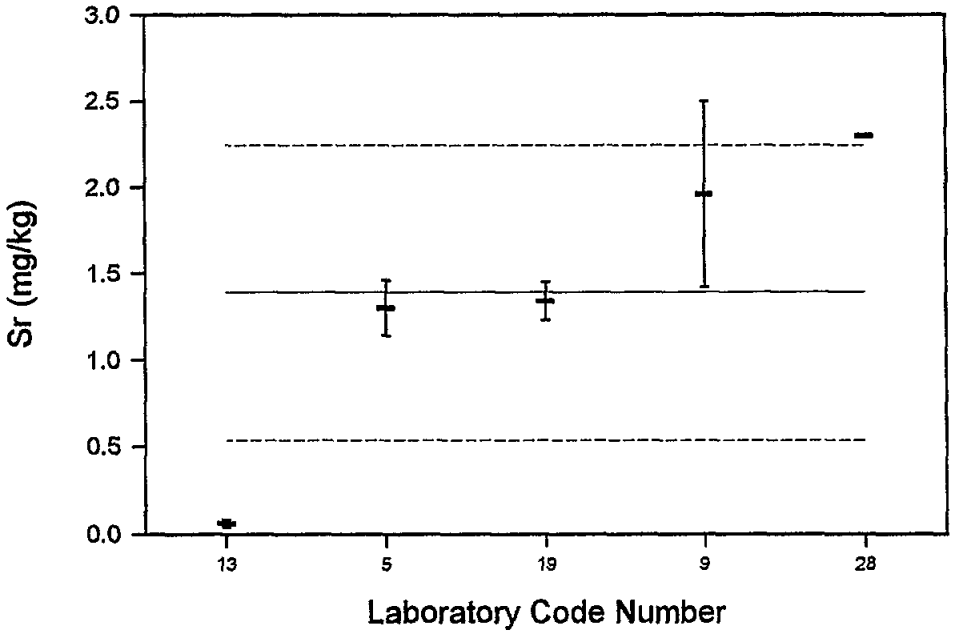


Error bar = mean ± 1 SD
Horizontal lines = Mean value ± 1 SD (2.68 ± 0.51 mg/kg)

Figure 2.12. Strontium concentrations in Fish Homogenate

MA-MEDPOL-1/TM

Laboratory Performance Study



Error bar = mean ± 1 SD
Horizontal lines = Mean value ± 1 SD (1.72 ± 0.49 mg/kg, except outlier lab #13)

Table A2.1. ALUMINIUM (Al) in MA-MEDPOL-1/TM
Units: g kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
25	1	3	1	1	14	2	2	6	0.0700	0.1400

Table A2.2. ARSENIC (As) in MA-MEDPOL-1/TM
Units: mg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
5	1	3	1	1	0	4	0	6	1.00	0.11
8	1	3	1	2	9	3		6	4.10	0 70
9	1	3	2	3	0	3			<DL[c]	
10	1	3	1	3	14	4	0	6	1.98	0.24
11	1	3	1	3	11	3		3	4.20	0.10
13	1	3	1	1	6	2	0	6	<0.5	
19	1	3	2	1	0	4		6	4.40	0 20
25	1	3	1	1	14	2	1	6	<DL[c]	
28	1	0	3			1		4	3.73	0.05
29	1	3	1	2	0	2	0	4	1 52	0 10

[c] DL= detection limit

Table A2.3. GOLD (Au) in MA-MEDPOL-1/TM
Units: µg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
28	1	0	3			1		4	0 667	0 116

Table A2.4. BARIUM (Ba) in MA-MEDPOL-1/TM
Units: mg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
19	1	3	2	1	0	4		6	0.110	0 020
25	1	3	1	1	14	2	2	6	11 4	0.6

Table A2.5. BROMINE (Br) in MA-MEDPOL-1/TM
Units: mg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
28	1	0	3			1		4	12.5	0.1

Table A2.6. CALCIUM (Ca) in MA-MEDPOL-1/TM
Units: mg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
2	1	1	5			1		6	113	15
28	1	0	3			1		3	367	49

Table A2.7. CADMIUM (Cd) in MA-MEDPOL-1/TM
Units: mg kg^{-1} Certified value[a] = 0.015 ± 0.012 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD	**Z-score**	**P-score**
	1	P	A	P1	P2	A1	A2					
3	1	3	1	3	10	2	0	6	0 018	0 006	**0.2**	**3.2**
4	1	3	1	1	12	2	0	6	ND[c]			
5	1	3	1	1	0	2	0	6	3.00	0.97	**238**	**511**
7	1	3	1	3	0	2	0	5	0 0070	0 0005	**-0.6**	**0.3**
8	1	3	1	2	9	3		6	<0.02			
9	1	3	2	3	0	3			<DL[b]			
10 (1)	1	2	2	0		4		4	0.0035	0.0006	**-0.9**	**0.3**
10 (2)	1	2	1	0		2	0	5	0.010	0.003	**-0.4**	**1.4**
11	1	3	1	3	11	3		3	<0.005			
12	1	3	1	0	0	3		6	0 0021	0.0007	**-1.0**	**0.4**
13	1	3	1	1	6	2	0	6	0 300	0.040	**22.7**	**21**
15	1	3	4	1	0			3	6.30	0 11	**501**	**58**
17	1	3	1	1	0	2	0	3	0 130	0.020	**9.2**	**11**
18	1	3	1	0		0	1	6	<0 100			
19	1	3	1	1	0	2	0	3	0 0039	0 0004	**-0.9**	**0.2**
20	1	3	1	2	0	2	0	3	<0 1			
21	1	3	1	3	11	3		5	0.0054	0.0047	**-0.8**	**2.4**
22 (1)	1	3	1	1	0	2	1	2	0.108	0.007	**7.4**	**3.7**
22 (2)	1	3	1	1	0	2	1		0.0940		**6.3**	
23	1	3	1	1	14	1	0	6	ND[c]			
25	1	3	1	1	14	2	1	6	0 320	0.030	**24**	**16**
26	1	3	1	3	4	1	0	6	<DL[b]			
27	1	3	1	0	11	3		3	0 050	0 035	**2.8**	**18**
29	1	3	1	2	0	2	0	4	0.026	0.0014	**0.9**	**0.7**
30	1	3	1	0	0	2	0	6	0.028	0 008	**1.0**	**4.4**
31	1							2	0 016	0.005	**0.1**	**2.6**
32	1	3	1	3	0	2	1	6	0 044	0.002	**2.3**	**1.1**
33	1	3	1	3	10	2	1	4	0.018	0 003	**0.2**	**1.6**
35	1								0.025	0 001	**0.8**	**0.7**

[a] Mean ± confidence interval (95%), [b] DL= detection limit; [c] ND = not detectable

Table A2.8. COBALT (Co) in MA-MEDPOL-1/TM
Units: mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
4 (1)	1	3	1	1	12	1	0	6	0.038	0.001
4 (2)	1	3	1	1	12	2	0	6	0.030	0.001
5	1	3	1	1	0	2	0	6	ND[c]	
9	1	3	2	3	0	3			<DL[b]	
13	1	3	1	1	6	2	0	6	<0.4	
19	1	3	2	1	0	4		6	0 022	0 005
29	1	3	1	2	0	2	0	4	0 070	0.007

[b] DL= detection limit; [c] ND = not detectable.

Table A2.9. CHROMIUM (Cr) in MA-MEDPOL-1/TM
Units: mg kg^{-1} Certified value[a] = 0.28 ± 0.14 mg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD	**Z-score**	**P-score**
	1	P	A	P1	P2	A1	A2					
4 (1)	1	3	1	1	12	1	0	6	0.0425	0 0029	**-1.6**	**0.1**
4 (2)	1	3	1	1	12	2	0	4	0.0407	0.0003	**-1.6**	**0.0**
5	1	3	1	1	0	2	0	6	±0 1			
6	1	3	1	3	0	2	0	2	<1			
8	1	3	1	2	9	3		5	0 400	0.100	**0.8**	**2.9**
9	1	3	2	3	0	3			<DL[b]			
10	1	2	2	0		4		4	0.233	0.027	**-0.3**	**0.8**
11	1	3	1	3	11	3		3	0.0550	0.0080	**-1.5**	**0.2**
13	1	3	2	1	6	3		6	4.30	0.03	**27**	**0.9**
17	1	3	1	1	0	2	0	3	1.45	0.22	**7.8**	**6.3**
19	1	3	2	1	0	4		6	0.30	0.06	**0.1**	**1.7**
22 (1)	1	3	1	1	0	2	2	2	0 901	0.140	**4.2**	**4.0**
22 (2)	1	3	1	1	0	2	2		0 934		**4.4**	
25	1	3	1	1	14	2	2	6	<DL[b]			
26	1	3	1	3	4	1	0	6	5 99	0 19	**38**	**5.4**
28	1	0	3			1		3	0.178	0.008	**-0.7**	**0.2**
29	1	3	1	2	0	2	0	3	0.927	0.123	**4.3**	**3.5**
30	1	3	1	0	0	2	0	6	0.316	0.044	**0.2**	**1.3**
31	1							2	0.200	0.020	**-0.5**	**0.6**
33	1	3	1	3	10	1	2	4	ND[c]			

[a] Mean ± confidence interval (95%); [b] DL= detection limit; [c] ND = not detectable

Table A2.10. CAESIUM (Cs) in MA-MEDPOL-1/TM
Units: mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
28	1	0	3			1		4	0 0844	0 0011

Table A2.11. COPPER (Cu) in MA-MEDPOL-1/TM

Units: mg kg^{-1} Certified value[a] = 0.62 ± 0.12 mg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD	Z-score	P-score
	1	P	A	P1	P2	A1	A2					
2	1	1	5			1		4	7 30	1.20	**47**	**15**
3	1	3	1	3	10	2	0	6	0.504	0.021	**-0.8**	**0.3**
4 (1)	1	3	1	1	12	1	0	6	0.0673	0.0030	**-3.9**	**0.0**
4 (2)	1	3	1	1	12	2	0	6	0.0595	0.0020	**-3.9**	**0.0**
5	1	3	1	1	0	2	0	6	0.700	0.080	**0.6**	**1.0**
6	1	3	1	3	0	2	0	3	<1			
7	1	3	1	3	0	2	0	6	0.709	0.061	**0.6**	**0.8**
8	1	3	1	2	9	3		6	0.580	0 040	**-0.3**	**0.5**
9	1	3	2	3	0	3			<DL[b]			
10	1	2	2	0		4		4	1.22	0.15	**4.2**	**1.9**
11	1	3	1	3	11	3		3	0.48	0.01	**-1.0**	**0.1**
12	1	3	1	0	0	3		6	0.66	0.10	**0.3**	**1.2**
13	1	3	1	1	6	2	0	6	1.30	0.10	**4.8**	**1.3**
17	1	3	1	1	0	2	0	3	0.900	0.020	**2.0**	**0.3**
18	1	3	1	0		0	2	6	0.748	0 019	**0.9**	**0.2**
19	1	3	2	1	0	4		6	0.890	0.030	**1.9**	**0.4**
22 (1)	1	3	1	1	0	2	2	2	0.441	0.023	**-1.3**	**0.3**
22 (2)	1	3	1	1	0	2	2		0.494		**-0.9**	
23	1	3	1	1	14	1	0	6	2.16	0.05	**11**	**0.6**
25	1	3	1	1	14	1	2	6	4.93	0.29	**30**	**3.7**
27	1	3	1	0	11	3		3	0.470	0.015	**-1.1**	**0.2**
29	1	3	1	2	0	2	0	4	0.523	0.021	**-0.7**	**0.3**
31	1							2	0 430	0.110	**-1.3**	**1.4**
32	1	3	1	3	0	2	2	6	0 744	0.009	**0.9**	**0.1**
33	1	3	1	3	10	1	2	6	0 520	0 020	**-0.7**	**0.3**
35	1								2.55	0.02	**14**	**0.3**

[a] Mean ± confidence interval (95%); [b] DL= detection limit.

Table A2.12. IRON (Fe) in MA-MEDPOL-1/TM

Units: mg kg^{-1} Certified value[a] = 5 8 ± 0 7 mg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD	Z-score	P-score
	1	P	A	P1	P2	A1	A2					
2	1	1	5			1		6	72	6	**91**	**8.3**
4	1	3	1	1	12	1	0	6	0 309	0.014	**-7.6**	**0.0**
6	1	3	1	3	0	2	0	2	16	1	**14**	**1.9**
7	1	3	1	3	0	2	0	6	6.6	0.2	**1.1**	**0.2**
8	1	3	1	2	9	1	0	6	18	2	**17**	**2.8**
9	1	3	2	3	0	3		6	9.4	1.4	**5.0**	**1.9**
11	1	3	1	3	11	3		3	7 5	0.5	**2.3**	**0.7**
13	1	3	2	1	6	3		6	78	1	**100**	**1.1**
18	1	3	1	0		0	1	6	12	1	**8.7**	**1.3**
23	1	3	1	1	14	1	0	6	ND[c]			
25	1	3	1	1	14	1	2	6	53	1	**65**	**0.7**
26	1	3	1	3	4	1	0	6	3.4	0.3	**-3.3**	**0.4**
28	1	0	3			1		4	8.3	1.0	**3.4**	**1.4**
29	1	3	1	2	0	2	0	3	8.8	0.4	**4.2**	**0.5**
31	1							2	23	1	**24**	**1.2**
33	1	3	1	3	10	1	2	4	9 3	0.8	**4.9**	**1.1**

[a] Mean ± confidence interval (95%), [b] DL= detection limit, [c] ND = not detectable

Table A2.13. MERCURY (Hg) in MA-MEDPOL-1/TM
Units: mg kg^{-1} Certified value[a] = 2.69 ± 0.17 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD	Z-score	P-score
	1	P	A	P1	P2	A1	A2					
1	1	3	1	0	15	0		5	2.30	0.09	-1.2	0.3
5	1	3	1	1	0	5	0	6	1.40	0.10	-3.8	0.3
7	1	3	1	3	0	5	0	5	2.47	0 15	-0.7	0.4
8	1	3	1	2	9	5	0	6	2.30	0.50	-1.2	1.5
10	1	3	1	3	14	5	0	6	2.20	0.06	-1.5	0.2
13	1	3	2	1	6	3		4	<2			
17	1	3	1	1	0	5	0	3	1.93	0.09	-2.3	0.3
18	1	3	1	0		5	0	6	2.72	0 05	0.1	0.1
19	1	3	2	1	0	5	0	6	2.76	0.09	0.2	0.3
21 (1)	1	3	1	3	11	5	0	6	2.54	0.04	-0.4	0.1
21 (2)	1	3	1	1	12	5	2	6	2.84		0.4	
22 (1)	1	3	1	1	0	5	0	2	1.12	0.03	-4.7	0.1
22 (2)	1	3	1	1	12	5	0		1.73		-2.9	
23	1	3	1	1	14	5	0	5	1.54	0.11	-3.4	0.3
24	1	3	1	1	12	5	2	3	2.17	0 03	-1.6	0.1
25	1	3	1	1	14	5	2	6	<DL[b]			
27	1	3	1	0	11	5	0	3	2.50	0.45	-0.6	1.3
28 (1)	1	1	3			1		5	2.64	0.09	-0.1	0.3
28 (2)	1	3	1	0		5	0	5	2 92	0 20	0.7	0.6
29	1	3	1	2	0	5	0	5	2.35	0.18	-1.0	0.5
30	1	3	1	0	0	2	0	6	5 67	0 16	8.9	0.5
32	1	3	1	3	0	5	2	6	2.41	0 05	-0.8	0.2
33	1	3	1	3	11	5	2	5	2.77	0.11	0.2	0.3
34	1	3	1	1	12	5	2	4	1.90	0.19	-2.4	0.6
35	1								1.85	0 08	-2.5	0.2
36	1	3	1	2	0	5	1	14	2.88	0.07	0.6	0.2

[a] Mean ± confidence interval (95%), [b] DL= detection limit.

Table A2.14. POTASSIUM (K) in MA-MEDPOL-1/TM
Units: g kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
2	1	1	5			1		6	2.28	0 25
25	1	3	1	1	14	1	2	6	1.54	0.21
28	1	0	3			1		4	17.9	0.1

Table A2.15. LITHIUM (Li) in MA-MEDPOL-1/TM
Units: mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
5	1	3	1	1	0	2	0	6	ND[c]	
9	1	3	2	3	0	3			<DL[b]	
13	1	3	2	1	6	3		6	<2	
19	1	3	2	1	0	4		6	0.038	0 003

[b] DL= detection limit, [c] ND = not detectable

Table A2.16. MANGANESE (Mn) in MA-MEDPOL-1/TM
Units: mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
3	1	3	1	3	10	2	0	6	0.542	0.051
4	1	3	1	1	12	1	0	6	0.453	0.004
5	1	3	1	1	0	2	0	6	0.400	0.060
6	1	3	1	3	0	2	0	3	<1	
7	1	3	1	3	0	2	0	6	0 441	0 020
8	1	3	1	2	9	3		6	0.440	0.030
9	1	3	2	3	0	3			<DL[b]	
11	1	3	1	3	11	3		3	0.350	0.010
12	1	3	1	0	0	3		6	0 358	0 0299
13	1	3	1	1	6	2	0	6	1 27	0.12
17	1	3	1	1	0	2	0	3	1 16	0.06
18	1	3	1	0		0	1	6	0.459	0.016
19	1	3	2	1	0	4		6	0.530	0.040
23	1	3	1	1	14	1	0	6	ND[c]	
25	1	3	1	1	14	1	2	6	6 67	0.02
29	1	3	1	2	0	2	0	4	0.552	0.043

[b] DL= detection limit; [c] ND = not detectable.

Table A2.17. SODIUM (Na) in MA-MEDPOL-1/TM
Units: g kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
25	1	3	1	1	14	1	2	6	1 68	0.19
28	1	0	3			1		4	1.60	0 01

Table A2.18. NICKEL (Ni) in MA-MEDPOL-1/TM
Units: mg kg^{-1} Certified value[a] = 0.065 ± 0.032 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD	**Z-score**	**P-score**
	1	P	A	P1	P2	A1	A2					
4	1	3	1	1	12	1	0	6	0.130	0.008	**1.9**	**1.0**
5	1	3	1	1	0	2	0	6	<0.3			
6	1	3	1	3	0	2	0	3	<2			
7	1	3	1	3	0	2	0	5	0 297	0.044	**6.8**	**5.5**
8	1	3	1	2	9	3		5	0 150	0.040	**2.5**	**5.0**
9	1	3	2	3	0	3			<DL[b]			
13	1	3	2	1	6	3			<DL[b]			
19	1	3	2	1	0	4		6	0 170	0.020	**3.1**	**2.5**
23	1	3	1	1	14	1	0	6	ND[c]			
29	1	3	1	2	0	2	0	4	0 149	0 011	**2.5**	**1.4**
31	1							2	1.29	0.09	**36**	**11**

[a] Mean ± confidence interval (95%), [b] DL= detection limit; [c] ND = not detectable

Table A2.19. LEAD (Pb) in MA-MEDPOL-1/TM
Units: mg kg^{-1} Certified value[a] = 0.074 ± 0.015 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD	Z-score	P-score
	1	P	A	P1	P2	A1	A2					
3	1	3	1	3	10	2	0	6	0.0850	0.0060	**0.6**	**0.7**
4 (1)	1	3	1	1	12	1	0	6	0.130	0.004	**3.1**	**0.4**
4 (2)	1	3	1	1	12	2	0	6	0.0553	0 0020	**-1.0**	**0.2**
5	1	3	1	1	0	2	0	6	ND[c]			
7	1	3	1	3	0	2	0	1	<0.080			
9	1	3	2	3	0	3			<DL[b]			
10 (1)	1	2	2	0		4		4	0.0560	0.0096	**-1.0**	**1.1**
10 (2)	1	2	1	0		2	0	5	0.170	0.035	**5.4**	**3.9**
11	1	3	1	3	11	3		3	<0.02			
12	1	3	1	0	0	3		5	0.0561	0 0154	**-1.0**	**1.7**
13	1	3	1	1	6	2	0	6	1.70	0.10	**91**	**11**
17	1	3	1	1	0	2	0	3	0.78	0.08	**39**	**8.9**
19	1	3	1	1	0	2	0	6	0.0740	0.0090	**0.0**	**1.0**
20	1	3	1	2	0	2	0	3	<0.5			
21	1	3	1	3	11	3		6	0.0762	0.0077	**0.1**	**0.9**
22 (1)	1	3	1	1	0	2	1	2	1.51	0 03	**80**	**3.4**
22 (2)	1	3	1	1	0	2	1		6.87		**379**	
23	1	3	1	1	14	1	0	6	ND[c]			
25	1	3	1	1	14	2	1	6	0.990	0 110	**51**	**12**
27	1	3	1	0	11	3		3	<0.1			
29	1	3	1	2	0	2	0	6	0.138	0 013	**3.6**	**1.4**
30	1	3	1	0	0	2	0	6	0.0545	0 0078	**-1.1**	**0.9**
31	1							2	0.250	0.100	**9.8**	**11**
32	1	3	1	3	0	2	1	6	0 564	0 014	**27**	**1.6**
35	1								0 699	0 068	**35**	**7.6**

[a] Mean ± confidence interval (95%); [b] DL= detection limit, [c] ND = not detectable

Table A2.20. RUBIDIUM (Rb) in MA-MEDPOL-1/TM
Units: mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
2	1	1	5			1		6	13 8	3 3
19	1	3	2	1	0	4		6	4 32	0 33
28	1	0	3			1		4	3.53	0.10

Table A2.21. ANTIMONY (Sb) in MA-MEDPOL-1/TM
Units: mg kg^{-1}

Laboratory code number	Method code							Number of Meas	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
13	1	3	2	1	6	3		6	<5	
28	1	0	3			1		4	0 0082	0.0017

Table A2.22. SCANDIUM (Sc) in MA-MEDPOL-1/TM
Units: µg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
28	1	0	3			1		4	0.777	0.099

Table A2.23. SELENIUM (Se) in MA-MEDPOL-1/TM
Units: mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
11	1	3	1	3	8	2	0	3	2 80	0 05
13	1	3	1	1	6	2	0	6	2.20	0.40
25	1	3	1	1	14	2	1	6	2 10	0.10
28	1	0	3			1		4	2.99	0.03
29	1	3	1	2	0	2	0	4	3.30	0 24

Table A2.24. TIN (Sn) in MA-MEDPOL-1/TM
Units: mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
8	1	3	1	2	9	3		5	<1	
13	1	3	2	1	6	3		6	<5	
29	1	3	1	2	0	2	0	4	0.416	0.022
31	1							2	0.860	0.110

Table A2.25. STRONTIUM (Sr) in MA-MEDPOL-1/TM
Units: mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD
	1	P	A	P1	P2	A1	A2			
5	1	3	1	1	0	2	0	6	1 30	0.16
9	1	3	2	3	0	3		5	1 96	0 54
13	1	3	1	1	6	2	0	6	0.060	0.020
19	1	3	2	1	0	4		6	1 34	0 11
28	1	0	3			1		1	2.30	

Table A2.26. VANADIUM (V) in MA-MEDPOL-1/TM
Units: mg kg^{-1} Information value = 1.78 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD	**Z-score**	**P-score**
	1	P	A	P1	P2	A1	A2					
9	1	3	2	3	0	3		6	<DL[b]			
13	1	3	2	1	6	3		6	<2			
19	1	3	2	1	0	4		6	0.029	0.008	**-7.9**	**0.0**
29	1	3	1	2	0	2	0	3	0.045	0.009	**-7.8**	**0.0**
31	1							2	<0.30			

[b] DL= detection limit.

Table A2.27. ZINC (Zn) in MA-MEDPOL-1/TM
Units: mg kg^{-1} Certified value[a] = 16 80 ± 0.48 mg kg^{-1}

Laboratory code number	Method code							Number of Meas.	Laboratory Mean	SD	**Z-score**	**P-score**
	1	P	A	P1	P2	A1	A2					
2	1	1	5			1		6	27.40	5 10	**5.0**	**2.4**
3	1	3	1	3	10	2	0	6	16 30	0.74	**-0.2**	**0.4**
4	1	3	1	1	12	1	0	6	0.220	0.008	**-7.9**	**0.0**
5	1	3	2	1	0	3		6	21 30	0.37	**2.1**	**0.2**
6	1	3	1	3	0	2	0	3	16.00	0.80	**-0.4**	**0.4**
7	1	3	1	3	0	1	0	6	17.90	0.50	**0.5**	**0.2**
8	1	3	1	2	9	1	0	5	17 60	0.40	**0.4**	**0.2**
9	1	3	2	3	0	3		6	18.84	0 34	**1.0**	**0.2**
10	1	2	2	0		4		4	16.67	0 22	**-0.1**	**0.1**
11	1	3	1	3	11	3		3	16 80	0 50	**0.0**	**0.2**
12	1	3	1	0	0	3		3	17 30	0 60	**0.2**	**0.3**
13	1	3	2	1	6	3		6	19.30	0 50	**1.2**	**0.2**
15	1	3	4	1	0			3	12.66	0 34	**-2.0**	**0.2**
17	1	3	1	1	0	1	0	3	17.70	0 60	**0.4**	**0.3**
18	1	3	1	0		0	1	6	18.60	0 17	**0.9**	**0.1**
19	1	3	2	1	0	4		6	19 80	0.70	**1.4**	**0.3**
20	1	3	1	2	0	2	0	3	15.80	1 27	**-0.5**	**0.6**
23	1	3	1	1	14	1	0	6	19.62	1 60	**1.3**	**0.8**
25	1	3	1	1	14	1	2	6	43 50	0.74	**13**	**0.4**
26	1	3	1	3	4	1	0	6	0.124	0.005	**-7.9**	**0.0**
28	1	0	3			1		4	16.30	0 30	**-0.2**	**0.1**
29	1	3	1	2	0	2	0	4	24 10	0 60	**3.5**	**0.3**
31	1							2	13 07	1 25	**-1.8**	**0.6**
33	1	3	1	3	10	1	1	4	19 90	0 64	**1.5**	**0.3**
35	1								15.15	0.65	**-0.8**	**0.3**
36	1	3	1	2	0	1	1	14	17 59	1 55	**0.4**	**0.7**

[a] Mean ± confidence interval (95%)

ANNEX III

List of participants

SD-MEDPOL-1/TM
MA-MEDPOL-1/TM

LIST OF PARTICIPANTS

Participating Laboratory	Responsable Analysts
ALBANIA	
Laboratory of Analytical Chemistry University of Tirana Faculty of Natural Sciences Tirana	A. Cullej, D. Babe, & V. Celo
ALGERIA	
Ministère de l'enseignement supérieur et de la recherche scientique Centre de Developpement des Techniques Nucléaires 2, Bd. Frantz Fanon, Alger	Dr. M.A. Benamar & I. Toumert
CROATIA	
Institute of Oceanography and Fisheries Setaliste I. Mestrovica, 63 P.O. Box 500, 21000 Split	N. Odzak
CYPRUS	
Department of Fisheries 13, Aeoloy Street, Nicosia	Mrs. P. Loizides
EGYPT	
National Institute of Oceanography Laboratory of Marine Chemistry Alexandria	M. H. El-Mamoney
National Institute of Oceanography and Fisheries Inland Waters and Aquaculture 101 El-Kars El-Ainy St., Cairo	Dr. Ezzat A. Ibrahim & H. E. Toulibah & A. Konsowa
FRANCE	
Institut Européen de l'Environnement de Bordeaux (IEEB) rue du Professeur Vèzes 33000 Bordeaux	P. Hocquellet

COGEMA Service d'Etudes de Procédés et d'Analyses B.P. 71 87250 Bessines sur Gartempe	Roche & P. Nardoux
Service d'Ecotoxicologie Faculté de Pharmacie, Université de Nantes 1, rue Gaston Veil 44035 Nantes Cedex 01	Dr. J.-C. Amiard
Ministère de l'Agriculture, de la Pêche et de l'Alimentation, Centre National d'Etudes Vétérinaires et Alimentaires (CNEVA-Paris) 43, rue de Dantzig, 75015 Paris	A. Soubelet & G. Schitzer

GREECE

National Centre for Scientific Research "Demokritos" Radioanalytical Laboratory Aghia Paraskevi Attikis, POB 60228 15310 Athens	Dr. G.D. Kanias
University of Athens Department of Chemistry Section III, Panepistimiopolis 15771 Athens	A. Pavlidou & M. Dassenakis
Laboratory of Applied Geochemistry Department of Geology University of Patras 26100 Patras	Prof. S.P. Varnavas
Laboratory of Analytical Chemistry Department of Chemistry Aristotle University 54006 Thessaloniki	Drs. G. Vasilikiotis, I. Stratis & G. Zachariadis

ISRAEL

Israel Oceanographic and Limnological Research Ltd., P.O. Box 8030, Tel Shikmona, 31080 Haifa	Dr. B. Herut, G. Feinstein, N. Kress & H. Hornung

ITALY

Dipartimento di Igiene e Sanità Pubblica Università Degli Studi di Cagliari Via G.T. Porcell, 4 09124 Cagliari	Dr. M. Schintu
Centro Ricerche Marine Viale A. Vespucci, 2 44042 Cesenatico (FO)	Drs. A. Milandri & A. Ceredi
P.M.P. - U.L.S.S. n. 12 sez Chimica Ambientale Via della Montagnola, 2 30170 Mestre (VE)	M. Gerotto & M. Palonta

MONACO

Service de l'Environnement 3 Ave. de Fontvieille 98000 Monaco	A. Veglia

MOROCCO

Institut Scientifique des Pêches Maritimes 2, rue de Tiznit, Casablanca	A. Chafik
Université Mohamed Ier Département de Chimie Faculté des Sciences d'Oujda Oujda	B. Hacht
Ministère de la Santé Publique Institut National d'Hygiène 27 Ave. Ibn. Batouta B.P. 769 Agdal, Rabat	Dr. L. Idrissi & A. Elabidi
Direction Laboratoire de Qualité des Eaux Office National de l'Eau Potable B.P. Rabat Chellah	Dr. M. Idrissi
Ministère de l'Environnement Laboratoire National d'Etude et de Surveillance de la Pollution et des Nuisances 36 Av. Abfal, Rabat	Y. Sabhi

SLOVENIA

National Institute of Biology
Marine Station Piran
66330 Piran
Fornace 41

R. Planinc

University of Ljubljana, "Jozef Stefan" Institute
Department of Environmental Sciences
Laboratory for Radiochemistry
Jamova 39, POB 100
61111 Ljubljana

Dr. A. R. Byrne
& R. Vadimovic

SPAIN

Universitad de Alicante
Facultad de Ciencias, F.-II
Carretera de San Vicente del Raspeij s/a
Alicante

P. Blasco, C. Santana
& J. Muñoz

CETS Institut Químic de Sarrià
Via Augusta, 390
08017 Barcelona

Dr. Obiols & D. Blanco

Universitat Autonoma de Barcelona
Dept. de Química
08193 Bellaterra (Barcelona)

A. Rosell & M. Valiente

Laboratorios de Contaminacion y Toxicologia
S.A. Contox, C/. Cronos, 8
28037 Madrid

D. de Hita

Instituto Español de Oceanografia
Centro Oceanografico de Murcia
Magallanes, S/N. P.O. Box 22
30740 San Pedro del Pinatar, Murcia

C. Rodriguez, J. Guerrero
& A. Jornet

SYRIA

Scientific and Environmental Research Center
Mazzal - Westren Villas
P. O. Box 36782 Damascus

F. El-Ok

Marine Research Institute
Tishreen University, Latakia

N. Youssef

TUNISIA

I.N.S.T.O.P.
Laboratoire des Métaux Traces
2060 La Goulette

H. Amara & A. El Abed

TURKEY

METU - Institute of Marine Science
P.O. Box 28
33731 Erdemli, Icel

Dr. S. Yemenicioglu
& S. Ergin

Ege University, Faculty of Science
Chemistry Department
35100 Bornova, Izmir

Dr. E. Henden
& S. Goulding

Dokuz Eylul University
Institute of Marine Sciences & Technology
Iskele 35440 Urla, Izmir

Dr. F. Kucuksergin

ANNEX IV

Data report
IAEA 142

Fig. 4.1 : Data Evaluation - HCB - IAEA-142

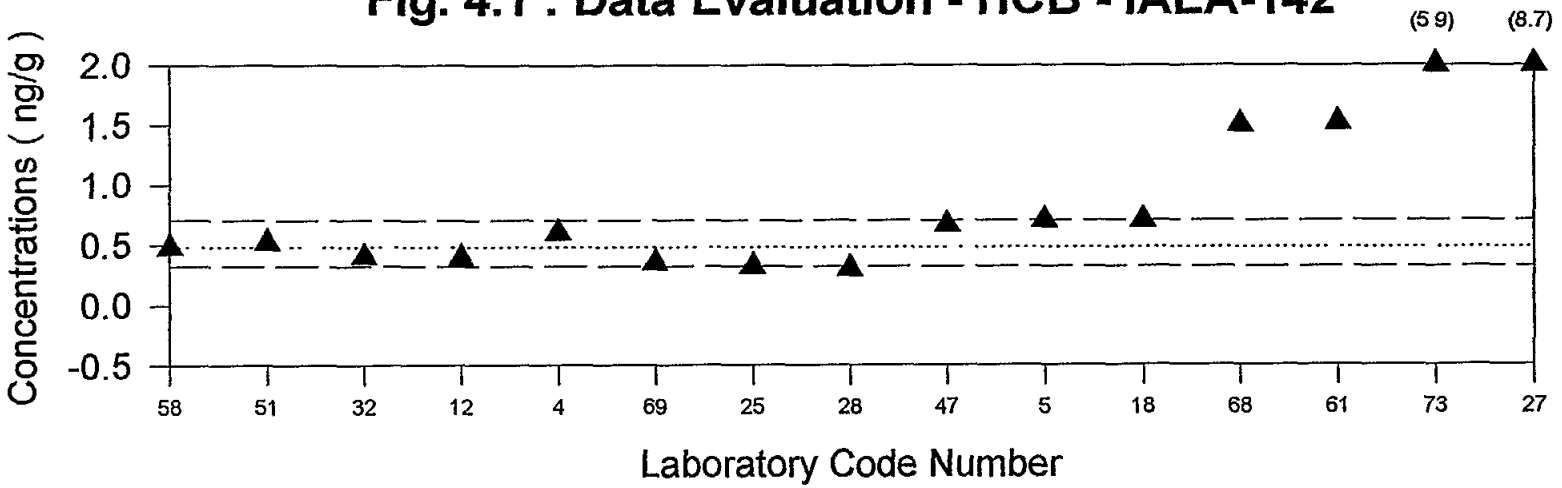


Fig. 4.2 : Data Evaluation - Lindane - IAEA-142

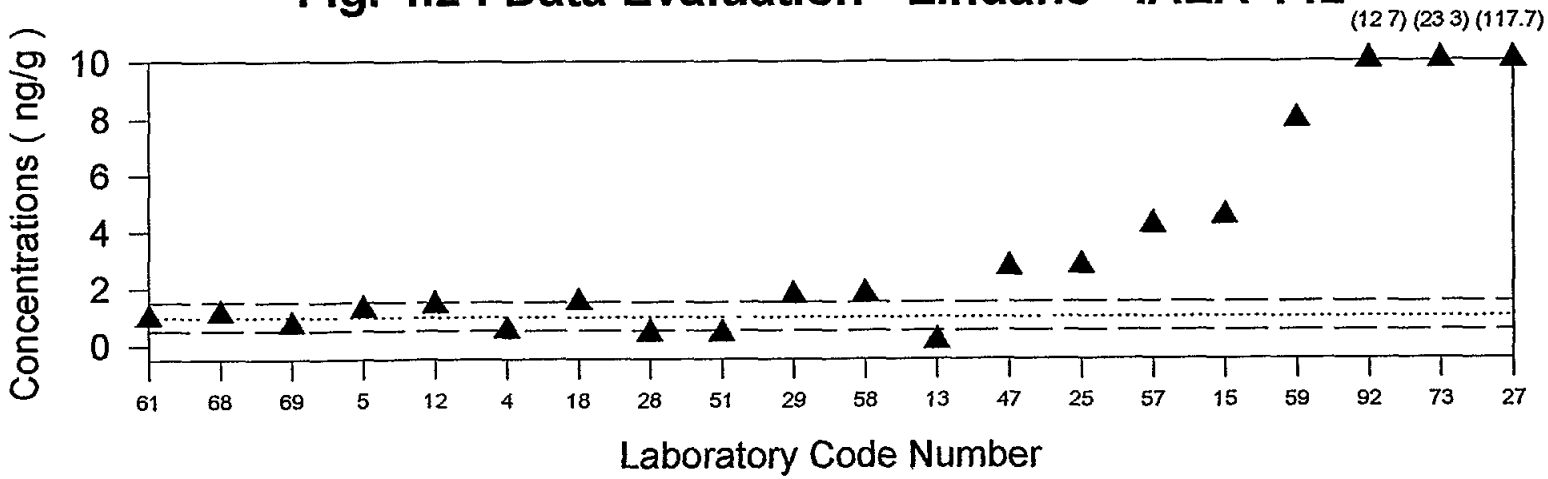


Fig. 4.3 : Data Evaluation - pp' DDE - IAEA-142

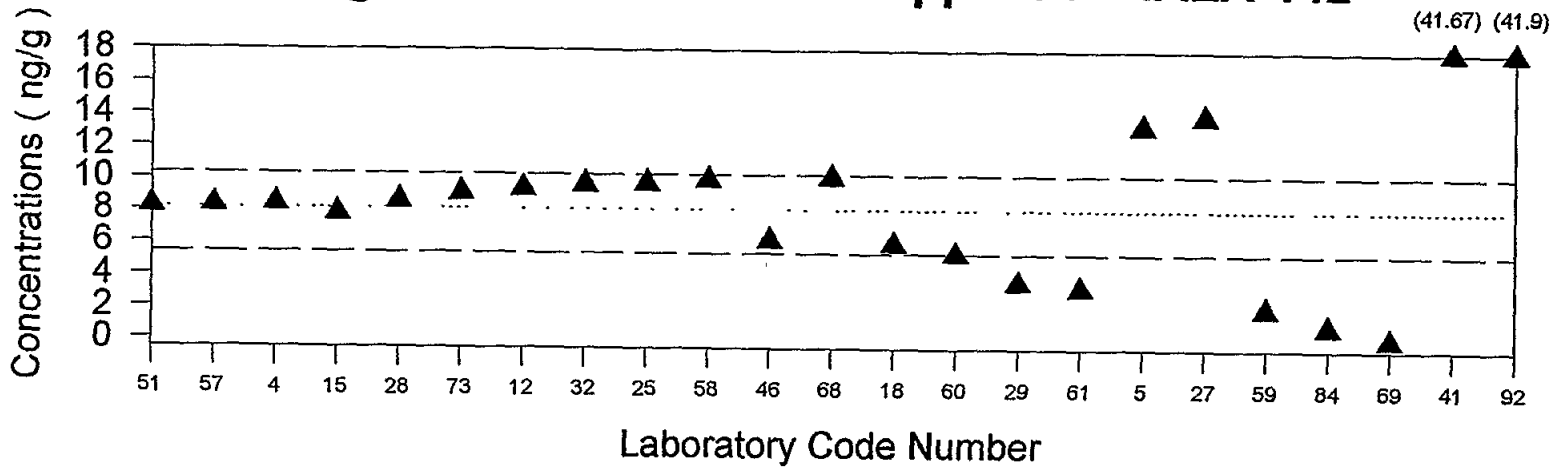


Fig. 4.4 : Data Evaluation - pp' DDD - IAEA-142

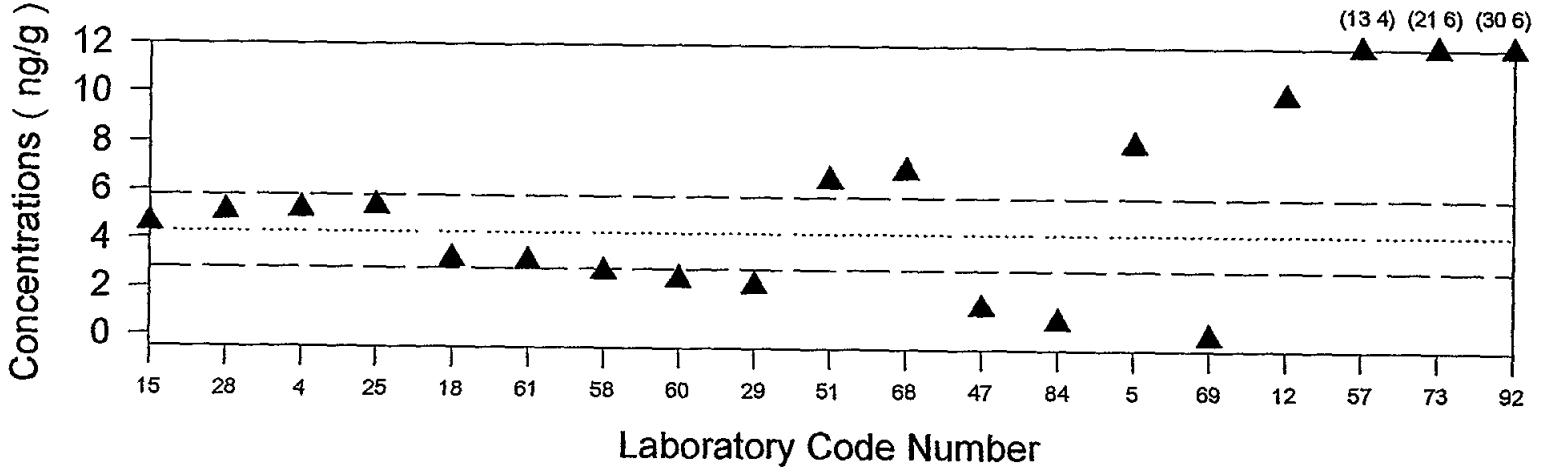


Fig. 4.5 : Data Evaluation - PCB 28 - IAEA-142

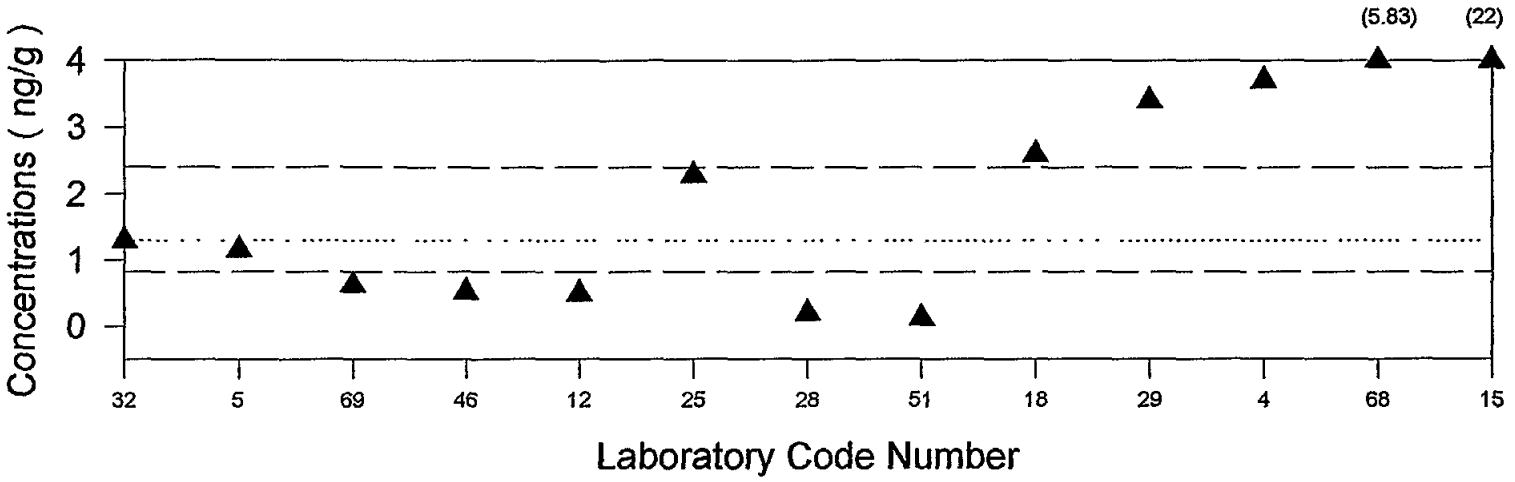


Fig. 4.6 : Data Evaluation - PCB 52 - IAEA-142

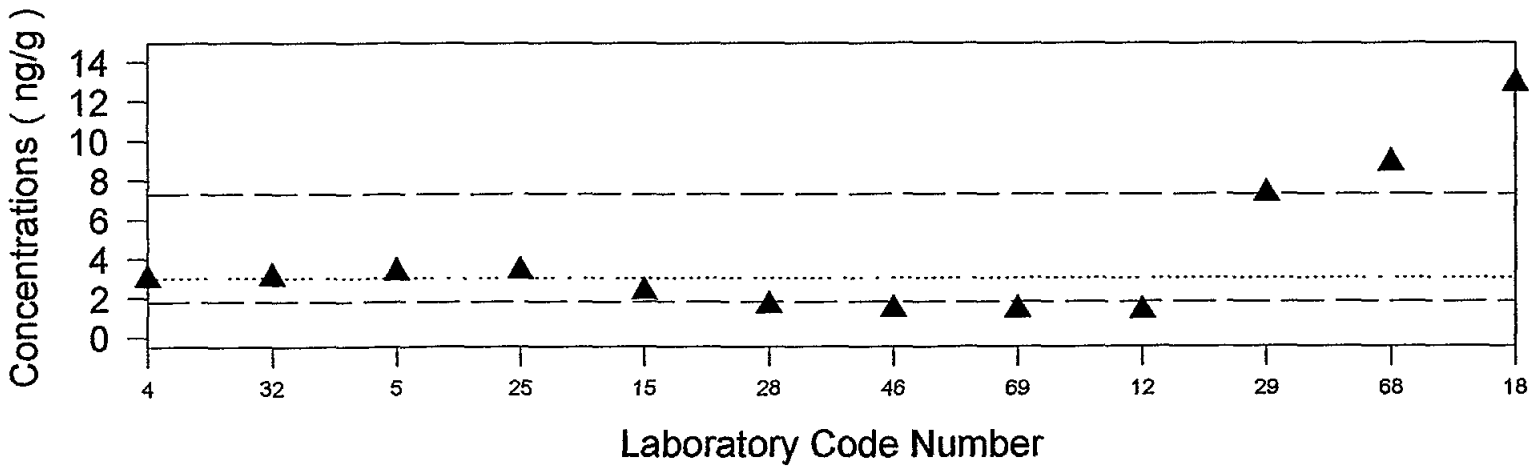


Fig. 4.7 : Data Evaluation - PCB 101 - IAEA-142

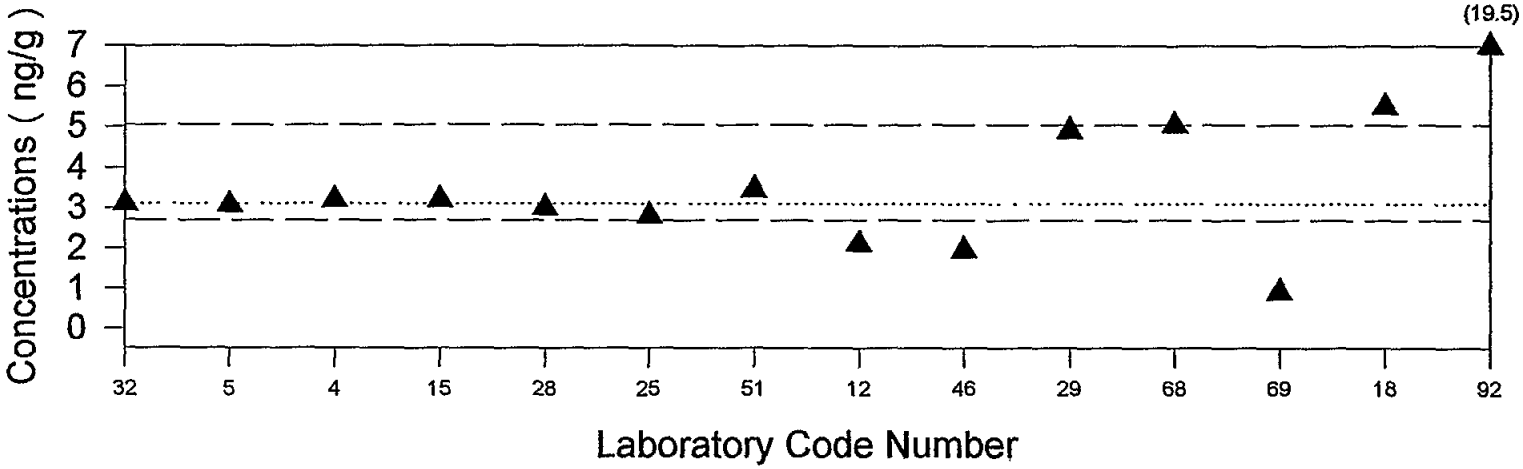


Fig. 4.8 : Data Evaluation - PCB 118 - IAEA-142

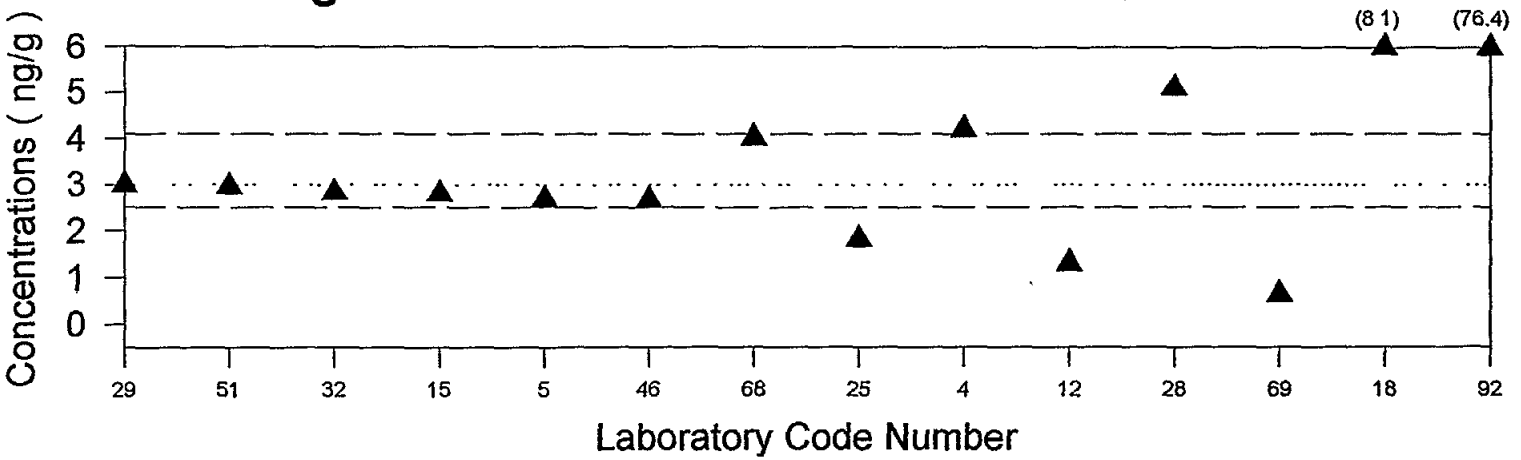


Fig. 4.9 : Data Evaluation - PCB 138 - IAEA-142

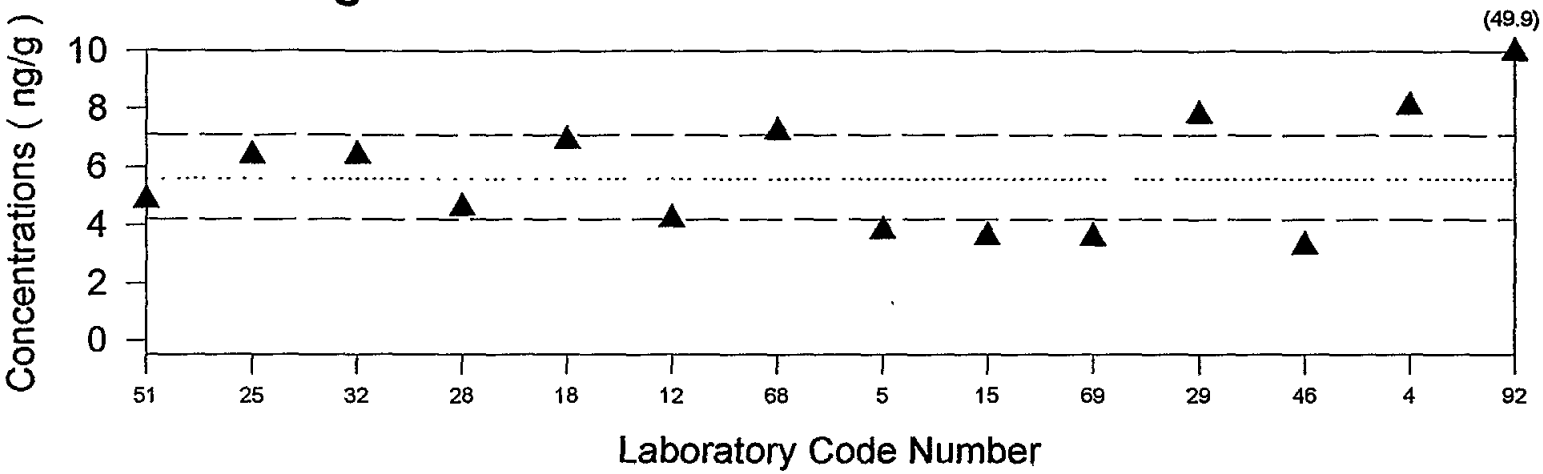


Fig. 4.10 : Data Evaluation - PCB 153 - IAEA-142

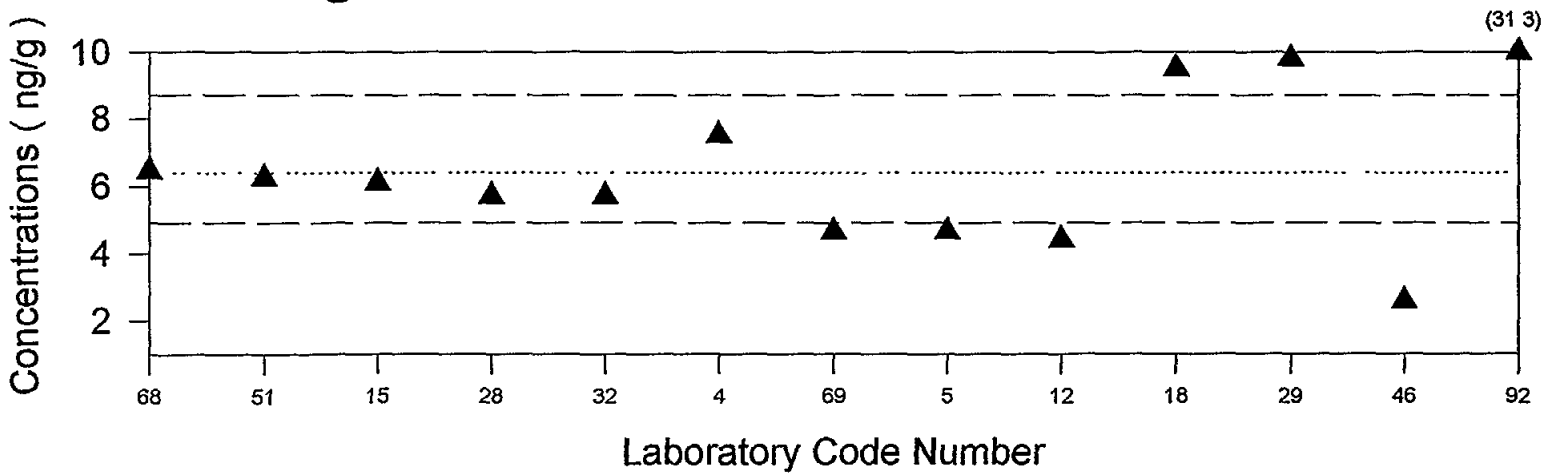


Table A4.1. Results of chlorinated pesticides in IAEA-142 sample

Laboratory Code Number	HEOM (mg/g)	HCB (ng/g)	alpha HCH (ng/g)	beta HCH (ng/g)	Lindane (ng/g)	pp' DDE (ng/g)	pp' DDD (ng/g)	pp' DDT (ng/g)
4	65.7	0.6	< 0.500	-	0.5	8.4	5.2	1.2
5	-	0.7	-	-	1.25	13.37	8.03	6.87
12	73	0.39	0.47	0.56	1.4	9.4	10	1
13	44	N.D.	-	-	0.11	N.D.	N.D.	N.D.
15	15.6	< 1	-	-	4.5	7.8	4.6	< 3
18	68.25	0.7	-	-	1.5	6	3.2	3.4
25	15	0.32	1.11	1.78	2.75	9.78	5.33	1.98
27	-	8.7	-	-	117.7	14	< 10	< 10
28	57.9	0.3	0.1	-	0.4	8.6	5.1	1.3
29	46.7	< 0.200	-	-	1.73	3.6	2.16	< 0.300
32	-	0.4	< 0.500	-	< 0.500	9.7	< 0.500	< 0.500
41	42.6	< 10	-	-	< 10	41.67	< 10	< 10
46	9.59	-	-	-	-	6.24	-	0.44
47	-	0.663	1.267	-	2.712	-	1.272	-
51	5.9	0.52	-	-	0.39	8.21	6.52	1.31
56	-	< 0.500	-	-	0.67	2.43	1.37	< 0.500
57	-	N.D.	-	-	4.2	8.3	13.4	2.5
58	57	0.48	-	-	1.79	9.99	2.7	9.03
59	56	-	-	-	7.94	2.01	-	-
60	40.3	-	-	-	-	5.4	2.4	7.4
61	-	1.52	0.232	-	0.963	3.268	3.09	0.766
65	-	-	-	-	-	6	28	21
69	107	0.35	-	-	0.7	0.14	0.07	0.07
73	-	5.9	-	-	23.3	9.1	21.66	35
84	32	-	-	-	-	0.9	0.7	0.7
92	-	< 1.100	19.1	-	12.7	41.9	30.6	-
96	41.2	0.163	-	-	0.493	13.6	24.2	22.6
Median *	5	0.48	0.43	6.8	0.97	8.2	4.3	2
Confidence Limits *	31--72	0.32--0.7	0.21--0.65	1.8--43	0.5--1.5	5.4--10	2.8--5.8	1--3.1

" - " not reported

* : obtained through the world-wide intercomparison.

N.D : not detected.

Table A4.1. continued.

Laboratory Code Number	op DDD (ng/g)	op DDT (ng/g)	Heptachlor (ng/g)	Heptachlor epoxide (ng/g)	Aldrin (ng/g)	Dieldrin (ng/g)	Endrin (ng/g)
4	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-
12	1.3	-	0.035	-	N.D.	4.1	N.D.
13	-	-	N.D.	-	N.D.	N.D.	N.D.
15	-	-	< 1	-	< 1	< 3	< 3
18	-	0.5	-	-	-	-	-
25	-	-	0.5	0.67	0.6	4.17	N.D.
27	-	-	103	-	93.3	< 10	< 10
28	-	-	-	-	-	N.D.	-
29	-	-	< 0.200	6.13	< 0.200	2.76	-
32	-	-	-	-	-	< 5	-
41	-	-	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
46	-	-	-	-	-	-	-
47	-	-	-	-	-	-	-
51	-	-	-	-	-	-	-
56	-	-	< 0.500	< 0.500	< 0.500	0.97	< 0.500
57	-	-	1	7.7	6.6	2.2	4
58	-	-	13.45	< 0.060	5.44	5.75	-
59	-	-	-	-	9.64	-	4.81
60	-	-	-	-	-	-	-
61	-	-	N.D.	-	0.899	-	-
65	-	-	-	-	1	25	2
69	-	-	1.46	N.D.	-	-	-
73	-	-	-	-	14.3	-	-
84	-	-	-	-	-	-	-
92	-	-	-	-	-	25.9	-
96	-	-	0.657	0.1	0.117	-	-
Median *	2.7	0.91	1	0.27	1.4	3.4	2
Confidence Limits *	1.1- -4.2	0.5- -6.1	0.54- -6.5	0.15- -0.49	0.79- -5.4	1.5- -5	0.94- -4.8

" - " : not reported
* : obtained through the world-wide intercomparison.
N.D. : not detected.

Table A4.1. continued.

Laboratory Code Number	alpha Endosulf (ng/g)	beta Endosulf. (ng/g)	Endosulf. Sulfate (ng/g)	alpha Chlordane (ng/g)	gamma Chlordane (ng/g)	Aroclor 1254 (ng/g)	Aroclor 1260 (ng/g)
4	-	-	-	-	-	40.5	-
5	-	-	-	-	-	-	-
12	12	N.D.	N.D.	0.44	0.068	22	12
13	N.D.	N.D.	N.D.	-	-	83	-
15	< 5	< 5	-	< 5	< 5	43	< 50
18	-	-	-	-	-	-	-
25	N.D.	N.D.	N.D.	3.54	N.D.	-	-
27	25	548.7	-	-	-	< 50	< 50
28	-	-	-	-	-	-	-
29	-	-	-	-	-	84	69
32	-	-	-	-	-	-	-
41	< 0.010	< 0.010	-	-	-	6.65	6.94
46	-	-	-	-	-	-	-
47	-	-	-	-	-	-	-
51	-	-	-	-	-	-	-
56	< 0.500	< 0.500	< 0.500	< 0.500	< 0.500	19	8.5
57	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
58	< 0.110	< 0.060	1.18	< 0.150	-	95.21	35.73
59	-	-	-	-	-	-	-
60	-	-	-	-	-	127.8	-
61	-	-	-	-	-	81	N.D.
65	-	-	-	-	-	-	-
69	-	-	-	0.21	-	100	115
73	-	-	-	-	-	-	-
84	-	-	-	-	-	74.1	22.1
92	-	-	-	-	-	-	-
96	0.334	-	-	-	-	83.5	139
Median *	0.96	1.3	2.7	0.54	0.29	56	36
Confidence Limits *	0.05- -1.4	1.2- -2.9	1.2- -9	0.44- -3.5	0.22- -0.59	33- -83	12- -69

" - " : not reported
* : obtained through the world-wide intercomparison.
N.D. : not detected.

Table A4.2. Results of PCBs in IAEA-142 sample

Laboratory Code Number	PCB 8 (ng/g)	PCB 18 (ng/g)	PCB 28 (ng/g)	PCB 31 (ng/g)	PCB 44 (ng/g)	PCB 52 (ng/g)
4	-	-	3.7	-	-	3
5	0.7	0.34	1.16	-	1.48	3.33
12	-	-	0.49	-	1.02	1.3
15	-	-	22	-	-	2.3
18	-	-	2.6	-	-	12.9
25	-	-	2.29	-	1.17	3.37
28	-	-	0.2	0.5	-	1.6
29	-	-	3.4	-	-	7.3
32	-	-	1.3	-	-	3.06
46	-	-	0.52	-	-	1.4
51	-	-	0.12	0.14	-	-
56	-	-	< 0.5	-	-	< 0.5
69	-	-	0.62	-	-	1.37
92	-	-	< 2.7	< 3.6	-	< 3.8
Median *	1	0.97	1.3	0.9	1.9	3
Confidence Limits *	0.7- -2.4	0.34- -1.5	0.82- -2.4	0.57- -1.4	1- -5.2	1.8- -7.3

Table A4.2. continued.

Laboratory Code Number	PCB 66 (ng/g)	PCB 77 (ng/g)	PCB 87 (ng/g)	PCB 99 (ng/g)	PCB 101 (ng/g)	PCB 105 (ng/g)
4	-	-	-	-	3.2	-
5	1.9	-	1.3	-	3.07	0.8
12	1.2	-	-	-	2.1	0.81
15	-	-	-	-	3.2	-
18	5.4	-	7.8	-	5.5	2.2
25	1.84	9.3	-	9.4	2.8	4.68
28	-	-	-	-	3	1.7
29	-	-	-	-	4.9	-
32	-	-	-	-	3.1	1.7
46	-	-	-	-	1.95	-
51	-	-	-	-	3.46	0.97
56	-	-	-	-	0.69	-
69	-	-	-	-	0.9	-
92	-	-	-	-	19.5	3.3
Median *	1.8		2.8	4.3	3.1	1.4
Confidence Limits *	1.1- -2		1.3- -7.8	2.7- -5.4	2.7- -5	1.1- -2.1

" - " : not reported

* : obtained through the world-wide intercomparison.

N.D. : not detected.

Table A4.2. continued.

Laboratory Code Number	PCB 110 (ng/g)	PCB 118 (ng/g)	PCB 126 (ng/g)	PCB 128 (ng/g)	PCB 138 (ng/g)	PCB 149 (ng/g)
4	-	4.2	-	-	8.1	-
5	-	2.68	-	0.74	3.8	-
12	3.63	1.3	-	1	4.2	1.3
15	-	2.8	-	-	3.6	-
18	-	8.1	7.1	4.6	6.9	-
25	-	1.81	N.D.	-	6.38	-
28	-	5.1	-	-	4.6	-
29	-	3	-	-	7.8	-
32	-	2.83	-	-	6.4	-
46	-	2.67	-	-	3.28	-
51	-	2.96	-	-	4.85	-
56	-	-	-	-	2.2	-
69	-	0.63	-	-	3.57	-
92	-	76.4	-	-	49.9	-
Median *	4.9	3		1.5	5.6	3.7
Confidence Limits *	2.1- -7.6	2.5- -4.1		0.74- -1.8	4.2- -7.1	2.8- -6.9

Table A4.2. continued.

Laboratory Code Number	PCB 153 (ng/g)	PCB 156 (ng/g)	PCB 170 (ng/g)	PCB 180 (ng/g)	PCB 187 (ng/g)	PCB 200 (ng/g)
4	7.5	-	-	-	-	-
5	4.64	-	-	0.55	1.84	-
12	4.4	-	0.31	0.52	2.3	0.5
15	6.1	-	-	<1	-	-
18	9.5	-	2.5	3.9	5.1	2.9
25	-	N.D.	N.D.	0.69	2.58	-
28	5.7	0.2	-	1.5	-	-
29	9.8	-	-	2.5	-	-
32	5.7	0.67	-	0.87	-	-
46	2.56	-	-	1.4	-	-
51	6.25	0.29	-	-	-	-
56	1.9	-	-	-	-	-
69	4.65	0.42	-	0.75	-	-
92	31.3	< 2.6	-	< 2.3	-	-
Median *	6.4	0.5	0.6	0.75	2.4	
Confidence Limits *	4.9- -8.7	0.28- -0.6	0.3- -1.6	0.55- -1.4	2- -3.7	

" - " · not reported.
* . obtained through the world-wide intercomparison.
N.D. not detected.

Table A4.3. Results of petroleum hydrocarbons in IAEA-142 sample

Laboratory Code Number	Extract.Org. Matter (mg/g)	PH Chrysene (µg/g)	PH ROPME (µg/g)	Total aliphatics (µg/g)	Resolved aliphatics (µg/g)	Unresolved aliphatics (µg/g)
4	65.7	7.5	45.9	447	7.598	440
5	-	-	-	123.4	12.85	109.2
12	41	29	140	160	16	140
13	44	-	-	-	-	-
29	46.7	-	-	-	-	-
41	42.6	-	-	-	-	-
46	9.59	-	-	-	-	80.56
52	-	-	-	201	24	177
56	224	-	-	870	59.5	810
61	68.6	5.5	67.6	-	-	-
65	-	3	28	-	-	-
72	53.6	-	-	22.685	4.878	17.785
76	42	-	-	-	306.1	-
80	25.52	10.08	62.11	70.52	9.19	61.33
84	32	6.2	56.7	-	-	-
91	28.5	5.8	-	98.7	6.2	92.7
Median *	43	5.4	59	120	9.2	100
Confidence Limits *	27- -66	4.6- -5.8	32- -89	71- -140	6.2- -16	61- 130

Table A4.3. continued.

Laboratory Code Number	n-C 17 (ng/g)	Pristane (ng/g)	n-C 18 (ng/g)	Phytane (ng/g)	Sum. of alkanes (µg/g)	Total aromatics (µg/g)
4	463	90	195	44	2.937	-
5	502	30	120	31	5.45	-
12	670	79	71	56	3.3	32
29	2600	-	1400	-	14	-
46	644.05	80.66	23.02	69.47	3.854	-
52	787	166	181	171	2.668	178
56	1100	240	595	290	53	-
72	281	291	221	130	4.866	47.513
76	8266	2917	4767	2043	99.3	-
80	906	211	355	113	6.78	-
91	1100	167	100	167	4.633	41.9
Median *	670	170	200	120	5.2	42
Confidence Limits *	500- -910	90- -240	100- -450	50- -180	3.3- 8.4	30- -48

" - " . not reported
* · obtained through the world-wide intercomparison
N.D. . not detected.

Table A4.3. continued.

Laboratory Code Number	Resolved aromatics (µg/g)	Unresolved aromatics (µg/g)	Biphenyl (ng/g)	Phenanthr. (ng/g)	2-methyl phenanthr. (ng/g)	1-methyl phenanthr. (ng/g)
4	0.407	-	-	31	-	-
5	-	-	-	52	11	9
12	6.6	25	5.2	52	36	55
27	-	-	-	< 10	-	-
41	-	-	-	190.17	-	-
46	-	-	-	43.16	16.81	14.13
52	100	78	-	62	115	81
56	-	-	-	93.5	-	31
72	9.783	37.73	-	346	-	-
76	82.4	-	-	275	355	125
80	-	-	-	84	-	-
91	3.11	38.8	-	86.7	656	323
92	-	-	-	< 1	-	-
Median *	9.8	27	7	60	47	20
Confidence Limits *	3.1- -82	25- -38	5.2- -8.3	41- -82	20- -75	1.6- -24

Table A4.3. continued.

Laboratory Code Number	Anthracene (ng/g)	Chrysene (ng/g)	Fluorene (ng/g)	Fluoranth. (ng/g)	Pyrene (ng/g)	Benzo(b) fluoranth. (ng/g)
4	-	30	-	112	92	-
5	2	7	5	16	10	-
12	6.4	98	11	94	82	21
13	-	-	-	N.D.	N.D.	N.D.
27	-	< 20	-	< 10	< 10	-
41	-	< 1	-	65.5	38.83	-
46	-	36.43	-	59.76	51.04	-
52	-	107	-	1206	152	-
56	7.5	37.5	28.5	83	56	16.5
72	631	1863	418	356	485	-
76	-	106	-	-	348	-
80	-	23	-	82	85	-
91	-	70	-	1430	487	-
92	-	452	-	40	665	0.97
Median *	4.3	32	8.7	73	57	19
Confidence Limits *	1.8- -6.4	21- -46	6.1- -11	59- -94	39- -81	14- -30

" - " : not reported
* : obtained through the world-wide intercomparison.
N.D. : not detected.

Table A4.3. continued.

Laboratory Code Number	Benzo(k) fluoranth. (ng/g)	Benz(a) anthracene (ng/g)	Perylene (ng/g)	Benzo(e) pyrene (ng/g)	Benzo(a) pyrene (ng/g)	1-methyl naphthal. (ng/g)
4	-	17	-	-	26	
5	-	-	6	-	-	3
12	-	16	N.D.	30	13	9.8
13	N.D.	N.D.	N.D.	N.D.	N.D.	-
27	-	< 40	-	< 10	< 10	-
41	-	< 1	-	-	< 1	-
46	-	15.61		52.99	4.45	-
52	-	18	-	19	5	-
56	15.5	15	9.5	28	5.5	65
72	-	-	-	-	676	-
80	-	17	-	22	9	-
91	-	-	-	-	-	306.7
92	-	26.9	-	34.4	< 0.15	-
Median *	9.7	15	7.3	27	3.5	15
Confidence Limits *	6- -13	12- -17	6.1- -9.3	22- -30	2.9- -5	13- -17

Table A4.3. continued.

Laboratory Code Number	2-methyl naphthal. (ng/g)	Naphthal. (ng/g)	Benzo(ghi) perylene (ng/g)	Ind.(123cd) pyrene (ng/g)	Acenaph- thylene (ng/g)	Acenaphth. (ng/g)
4	-	< 2	-	-	-	-
5	-	-	-	-	2	1
12	21	18	5	6	-	N.D.
13	-	-	N.D.	N.D.	-	-
27	-	< 40	< 40	-	-	-
41	-	< 1	< 1	-	-	-
46	-	-	11.34	-	-	-
52	-	48	25	-	-	-
56	90	94.5	2.5	-	31	9.5
72	-	< 0.1	863	-	-	-
80	-	-	13	-	-	-
91	-	56.7	-	-	-	-
92	-	-	< 1.7	< 6.4	-	-
Median *	23		9.9	6.5	1.9	3.4
Confidence Limits *	20- -29		8.3- -13	5.5- -7.9	1.4- -2.7	1.9- -7.1

" - " : not reported.
* : obtained through the world-wide intercomparison.
N D : not detected.

Table A4.4. Chlorinated compounds and PCBs - treatment of samples

Laborat. No	Drying Procedure	Extraction Procedure		Used	Internal Standard
		Instrument	Solvent	Time	
4	105 °C 24 hours	Soxhlet	Hexane	8 hours	2,4,5 TCB
5	None	Glass Ampoule	Ethyl Ether 80 °C	Not indic.	2,4,5 TCB
12	110 °C 24 hours	Soxhlet	Hexane	8 hours	2,4,5 TCB and ε HCH
13	103 °C 4 hours	Soxhlet	Hexane/ Acetone(3/1)	11 hours	Octachl. and tetrachl.Napht.
15	105 °C 48 hours	Ultrasonic	Hexane	16 hours	None
18	Oven	Soxhlet	Hexane	Not ind.	Mirex
25	Not indicated	Mixer	Acetone	2 minutes	PCB 4
27	105 °C 48 hours	Ultrasonic Bath	Petroleum ether	5 times	None
28	105 °C Overnight	Soxhlet	MeCl2/Pentane (1:1)	Not indic.	PCB 155
29	105 °C 48 hours	Ultrasonic	Hexane/Acetone (2: 1)	30 min.	None
32	105 °C const. weight	Soxhlet	Hexane/Acetone (50:50)	Not indic.	PCB 209
41	Not indicated	Soxhlet	Hexane	Not indic.	None
46	None	Soxhlet	Methanol	Not indic.	Not indicated
51	60 °C 48 hours	Not indicated	Hexane/Acetone (80:20)	Not indic.	Tetrachloro Naphthalene
56	Not indicated	Ultrasonic	Cyclohex/MeCl2 Hex (2 : 2 : 6)	Not indic.	None
57	None	Soxhlet	Hexane	Not indic.	2,4,5 TCB
58	Na2SO4	Soxhlet	Hexane	10 hours	Mixed Standard
59	None	Not indic.	Acetonitrile	Not indic.	None
60	105 °C 24 hours	Soxhlet	Hexane	8 hours	None
61	Freeze-Dried	Soxhlet	Hexane	8 hours	2,4,5 TCB
65	Not indic.	Soxhlet	Hexane	8 hours	2,4,5 TCB
73	Not indic.	Soxhlet	Hexane	8 hours	2,4,5 TCB
92	None	Bligh and Dyer Method	Not indicated	Not indic.	PCB 53 and Desmetryne
96	105 °C 48 hours	Mixer	Hexane	8 hours	2,4,5 TCB

Table A4.4. continued.

Laboratory No	Clean-up Procedure	Fractionation Procedure	Method for Confirmation
4	Sulfuric Acid for lipids	Silica Gel (1 g) 2 fractions	Relative Retention Times . For DDTs : dehydrochlorination
5	Sulfuric Acid for lipids	Florisil 2 fractions	GC/MS
12	Sulfuric Acid for lipids	Florisil (14 g) 3 fractions	Standard Retention Times + GC/MS Engine HP - NCI
13	Florisil	None	Injection on DB 1701 and DB 5
15	Sulfuric Acid	C 18 Petrol.Ether/ EthylEther(8:2)	Standard Retention Times (3 columns)
18	Sulfuric Acid	None	Dehydrochlorination
25	Florisil	Florisil(F1,F2,F3)	2 columns + GCMS
27	None	None	Standard Retention Times
28	Alumina/Silica	F1: isooctane F2:isooct/MeCl2	2 columns (CPSIL 19 CB)
29	OC: Liq/Liq part. PCB:Sulfur.Acid	OC : Florisil PCB : Silica gel	Standard Retention Times
32	Sulfuric Acid	Alumina/Silica 2 fractions	Use of 2 columns
41	Gel Permeation	Not indicated	GC/MS SIM
46	Saponification	Silica/Alumina	Stand. Ret. Times
51	Sulfuric Acid	Florisil	Standards Retention Times
56	Florisil/sea sand Celite/DMSO	None	Standards Retention Times
57	Sulfuric Acid	Florisil - 2 fractions EthylEther/Hexane	Not indicated
58	Sulfuric Acid	Silica Gel - Hex./ Diet.Ether : Hex.	Internal Standard Saponification
59	Liq.Liq partition. with hexane	Florisil - hex/ Hex/MeCl2 (7:3)	Retention Times and GC/MS Library
60	Sulfuric Acid	Silica Gel 2 fractions	Saponification
61	Sulfuric Acid	Florisil / 3 fractions	Stand. Ret. Times
65	Sulfuric Acid	Florisil	None
73	Not indicated	Florisil	Stand. Ret. Times
92	Alumina	Florisil	2 Columns JW-1701 and HP-5
96	Conc. Sulfuric Acid	Florisil	Standard Retention Times

Table A4.5. GC conditions - chlorinated compounds and PCBs

Laboratory No	Instrument Type	Detector Type	Injection Technique	Injector Temperature
4	C.Erba FV4160	ECD-Ni	Splitless	280
5	HP 5890 series II	ECD-Ni	Splitless	280
12	HP 5880 A	ECD-Ni	Splitless	250
13	Varian 3400	ECD-Ni	On Column	85
15	HP 5890 Carlo-Erba LMB-1	ECD-Ni ECD-Ni ECD-Ni	Split On column Tete de Colonne	250 140 220
18	Varian 3400	ECD-Ni	On Column	60
25	V 3400 CX	ECD-Ni	On Column	50 to 250 150 °C/min.
27	HP 5890	ECD-Ni	Split/Splitless	200
28	Perkin Elmer 8700	ECD-Ni	Splitless	270
29	Varian 3700	ECD-Ni	Splitless	240
32	Varian 3400	ECD-Ni	Splitless	270
41	GC/MS	Electr. Magn.	Splitless	250
46	HP 5890	ECD-Ni	Automatic 7673	280
51	Fisons GC 8000 HP 5890	ECD-Ni ECD-Ni	On Column On Column	75 75
56	HP 5890 series II	ECD-Ni	Splitless	250
57	Varian 3700	ECD-Ni	Splitless	240
58	Varian 3700	ECD-Ni	Packed column	210
59	Shimadzu GC 14A	ECD-Ni	Splitless	200
60	HP 5730 A	ECD-Ni	Splitless	250
61	VARIAN 3400	ECD-Ni	Splitless	210
65	Perkin Elmer 8700	ECD-Ni	Not indic.	Not indic.
73	VARIAN 3400	ECD-Ni	Splitless	220
92	CE HRGC 5300	ECD-Ni	On-Column	N/A
92	VARIAN 3300	ECD-Ni	Not indic.	270

Table A4.5. continued.

Labor. No	Injection Volume	Splitter closing time	Carrier Gas		Split Ratio
			Type	Flow rate	
4	2 µl	30 min.	Hydrogen	2 ml/min.	(1:10)
5	2 µl	1 min.	Helium	20 cm/sec.	N/A
12	1-3 µl	0.5 min.	Nitrogen	1.5 ml/min.	N/A
13	0.8 µl	N/A	Hydrogen	33 ml/min.	N/A
15	3 µl	Not indic.	Nitrogen	3.56 ml/min.	(5.6:1)
	0.2 µl	N/A	Hydrogen	1.5 ml/min.	N/A
	5 µl	Not indic.	Nitrogen	40 ml/min.	N/A
18	1 µl	N/A	Helium	2 ml/min.	N/A
25	1 µl	N/A	Helium	2 ml/min.	N/A
27	1 µl	Not indic.	Nitrogen	Not indicated	Not indic.
28	1 µl	3 min.	Helium	0.9 ml/min.	11
29	3 µl	1 min.	Nitrogen	1.7 ml/min.	(1:65)
32	1 µl	5 min.	Hydrogen	28-30 cm/sec	N/A
41	2 µl	1 min.	Helium	0.82 ml/min.	N/A
46	2 µl	0.5 min.	Helium	50 ml/min.	Not indic.
51	2 µl	N/A	Hydrogen	1.5 ml/min.	N/A
	1 µl	N/A	Hydrogen	1.5 ml/min.	N/A
56	2 µl	0.6 min.	Nitrogen	Not indicated	(46:1)
57	0.5 µl	Not indic.	Nitrogen	12 ml/min.	N/A
58	5 µl	N/A	Nitrogen	25 ml/min.	N/A
59	1 µl	0.2 min.	Nitrogen	1.5 ml/min.	N/A
60	2 µl	Not indic.	Nitrogen	2 ml/min.	N/A
61	1 µl	0.5 min.	Arg./Meth.	1.5 ml/min.	N/A
65	0.5 µl	Not indic.	Nitrogen	Not indic.	Not indic.
73	2 µl	Not indic.	Nitrogen	2 ml/min.	N/A
92	1 µl	N/A	Hydrogen	0.84 ml/min.	N/A
96	1 µl	0.75 min.	Nitrogen	Not indic.	Not indic.

Table A4.5. continued.

Laboratory No	Column				
	Type	Length	Diametre	Phase	Film Thickness
4	Capil.	30 m	0.32 mm	SE-54	0.3 μm
5	Capil.	50 m	0.32 mm	HP-5	0.17 μm
12	Capil.	25 m	0.2 mm	SE-54	0.32 μm
13	Capil.	60 m	0.25 mm	DB-1701	0.25 μm
15	Capil. Capil. Pack.	30 m 25 m 2 m	0.53 mm 0.52 mm 4 mm	DB-608 SE-54 10%Surchr.	0.83 μm 0.52 μm N/A
18	Capil.	60 m	0.32 mm	DB-5	0.25 μm
25	Capil.	50 m	0.32 mm	CPSIL 5 CB CPSIL 8 CB	0.25 μm
27	Capil.	50 m	0.25 mm	DB-1	0.12 μm
28	Capil.	50 m	0.2 mm	CPSIL 8 CB	0.33 μm
29	Capil.	30 m	0.25 mm	SE-54	0.25 μm
32	Capil.	60 m	0.25 mm	DB5/DB1701	0.25 μm
41	Capil.	30 m	0.25 mm	DB-5	0.25 μm
46	Capil.	30 m	0.25 mm	DB-5	Not indicat.
51	Capil. Capil.	60 m 60 m	0.25 mm 0.25 mm	DB-1701 DB-5	0.25 μm 0.25 μm
56	Capil.	25 m	0.32 mm	SE-54	0.17 μm
57	Capil.	25 m	0.53 mm	BP-5	1 μm
58	Pack.	2 m	2 mm	1.5% OV17 1.95% OV210	N/A
59	Capil.	30 m	0.32 mm	SE-54	0.52 μm
60	Capil.	25 m	0.2 mm	SE-54	0.11 μm
61	Capil.	30 m	0.32 mm	Not indic.	1 μm
65	Capil.	25 m	0.25 mm	BP-1	Not indic.
73	Capil.	25 m	0.32 mm	BPX-5	0.25 μm
92	Capil.	60 m	0.25 mm	DB - 1701	0.25 μm
96	Capil.	30 m	0.32 mm	DB-1	0.25 μm

Table A4.5. continued.

Labor.	Temperature Programme									
No	In.Temp	Isoth.	1st rate	to :	Isoth.	2nd rate	to :	Isoth.	3rd r.	to :
4	80	2 min.	4	280	15 min.					
5	60	4 min.	30	100	0 min.	2	280	10 min.		
12	60	0 min.	3	260	20 min.					
13	150	3 min.	3	260	30 min.					
15	140	0 min.	20	210	0 min.	5	270	20 min.		
	140	2 min.	10	240	3 min.	30	270	15 min.		
	220									
18	60	2 min.	6	120	5 min.	2	280	20 min.		
25	100	2 min.	20	220	10 min.	3	260	5 min.		
27	100	1 min.	6	180	5 min.	6	260	10 min.		
28	90	3 min.	30	215	30 min.	5	275	20 min.		
29	60	1 min.	12	230	30 min.					
32	80	2 min.	20	200	20 min.	5	320	3 min.		
41	60	3 min.	30	150	0 min.	5	280			
46	80	1 min.	6	280	15 min.					
51	75	2 min.	30	190	0 min.	2.5	290	5 min.		
	75	2 min.	30	180	0 min.	2.5	280	5 min.	5	300
56	125	1 min.	3	180	1 min.	1.3	260	1 min.		
57	180	5 min.	5	220	25 min.					
58	190									
59	200	5 min.	2	250	15 min.					
60	110	0 min.	8	220						
61	70	2 min.	3	250	40 min.					
65	70	2 min.	5	260	15 min.					
73	70	2 min.	3	260	15 min.					
92	100	1 min.	40	140	0 min.	2.5	270	30 min.		
92	70	2 min.	3	250						

Table A4.5. continued.

Laboratory No	Detector Temperature	Make-up Gas	Make-up Flow	Recorder Integrator
4	320	Nitrogen	35 ml/min.	HP 3396
5	350	Nitrogen	30 ml/min.	HP
12	300	Nitrogen	40 ml/min.	HP GC Terminal
13	300	Nitrogen	30 ml/min.	Computer (soft : Waters)
15	300 300 260	Nitrogen Nitrogen Nitrogen	40 ml/min. 30 ml/min. 40 ml/min.	HP-3396 HP-3396 HP-3390
18	300	Nitrogen	25 ml/min.	IBDH - Varian
25	300	Nitrogen	30-40 ml/min.	Minichrom VG instrument Fisons
27	300	Nitrogen	60 ml/min.	PC 486/33
28	360	Argon/Methane	60 ml/min.	Software "Gold"
29	300	Nitrogen	24 ml/min.	Spectra Physics 4400
32	310	Argon/Methane	18 ml/min.	Not indicated
41	Source : 200	N/A	N/A	not indicated
46	Not indicated	Not indicated	66.4 ml/min.	Not indicated
51	330 300	Argon/Methane Argon/Methane	Not indicated Not indicated	SP 4270 Chrom Card HP Chemstation
56	280	Nitrogen	40 ml/min.	HP 3396 II
57	300	Nitrogen	30 ml/min.	Varian 4270
58	280	Nitrogen	25 ml/min.	Varian 4290
59	280	Nitrogen	30 ml/min.	Computing System
60	350	Nitrogen	30 ml/min.	HP 3380 A
61	300	Argon/Methane	30 ml/min.	VARIAN 4290
65	300	Nitrogen	60 ml/min.	Not indicated
73	300	Nitrogen	30 ml/min.	Axxion Data System
92	300	Nitrogen	Not indicated	Integr. D25000 Merck
96	Not indic.	Not indic.	30 ml/min.	VA 4400I

Table A4.6. Petroleum hydrocarbons - treatment of samples.

Laborat. No	Drying Procedure	Extraction Procedure		Used	Internal Standard
		Instrument	Solvent	Time	
4	105 °C 24 hours	Soxhlet	n-Hexane	8 hours	n-C 24
5	not indicated	Glass Ampoule	Hexane 80 °C	24 hours	Squalane,HCH,HCB Dieldr.Perth.Methox.
12	110 °C 24 hours	Soxhlet	Methanol	8 hours	n-C32 , C18.1 9,10 dihyd.Anthrac.
13	103 °C 4 hours	Soxhlet	Hexane/ Acetone(3/1)	11 hours	None
27	105 °C 48 hours	Ultrasonic Bath	Methylene Chloride	5 times	None
29	105 °C 48 hours	Stirring	Hexane	10 min.	None
41	Not indic.	Soxhlet	Hexane	Not ind.	None
46	Not indicated	Not indicated	KOH/MeOH Hex/MeCl2	Not indicat.	None
52	105 °C overnight	Soxhlet	Methanol	6 hours	C18.1 / C 32 9,10 dihyd.Anthrac.
56	105 °C 24 hours	Soxhlet	Methylene Chloride	Not indic.	Chrysene d-12
61	Freeze dried	Soxhlet	Methanol	8 hours	None
65	None	Soxhlet	Methanol	8 hours	None
72	100 °C 24 hours	Soxhlet	Hex/MeCl2 (1:1)	8 cycles	C11-C30
76	Not indic.	Not indic.	Not indic.	Not indic.	Not indic.
80	Not indic.	Ultrasonic	Diethyl Ether	Not indic.	indeno(123cd)fluorant C18:1
91	Not indic.	Soxhlet	Methanol	12 hours	C18:1/C32
92	None	Bligh and Dyer Method	Not indic.	Not indic.	PCB 53 and Desmetryne

Table A4.6. continued.

Laborat. No	Clean-up Procedure	Fractionation Procedure	Method for Confirmation
4	Aliphatic : Conc. Sulf. Acid	Silica/Alumina 2 fractions	Aromatic : HPLC/Fluoresc. Detect.
5	Saponification	Silica Gel 2 fractions	Selected Ion monitoring
12	Saponification	Silica/Alumina 3 fractions	Standard Retention Times + GC/MS HP Engine NCI
13	Florisil	None	None
27	None	None	Comparison UV spectra and Retention times
29	Florisil (6 % Ether in Hexane)		GC/MS
41	Gel Permeation	Not indicated	GC/MS SIM
46	Not indicated	Liq. chromat. silica/ alumina . 3 fractions	Retention Times GC/MS
52	Saponification 2 hours	Silica/Alumina 2 fractions	Not indicated
56	Saponification	Silica/Alumina	GC/MSD SIM
61	Alumina	Silica Gel	None
65	Saponification	Silica/Alumina	None
72	Not indicated	Florisil 2 fractions	Standards Retention Times
76	Not indic.	Not indic.	Not indic.
80	Saponification	Alumina/Silica	Use of Relative Retention Times
91	Saponification	Alumina/Silica	Stand. Ret. Times
92	Not indicated	Alumina/Florisil	Standards Retention Times

Table A4.7. GC conditions - petroleum hydrocarbons.

Laboratory No	Instrument Type	Detector Type	Injection Technique	Injector Temper.
4	C.Erba FV 4160	FID	Splitless	280
5	Shimadzu QP1000	MD/EI	Splitless	280
12	Fisons 8000	FID	On-Column	35
29	HP 5890 series II	FID	Direct	290
41	GC/MS	Elect.Magn.	Splitless	280
46	PAH : MD 800 Fisons PH : C. E. Mega 5300	E.I. mode FID	Splitless Splitless	280 280
52	Fisons Mega serie II	FID	On Column	Not indic.
56	HP 5971 GC/MSD	MSD	Splitless	250
72	DANI 3800HR	FID	Split/Splitless	270
76	Not indic.	Not indic.	Not indic.	Not indic.
80	HP 5890 Series II	FID	Splitless	250
91	HP 5890	FID	On Column	63

Table A4. 7. continued.

Laborat. No	Injection Volume	Splitter closing time	Carrier Type	Gas Flow rate	Split Ratio
4	2 µl	0.5 min.	Hydrogen	1.8 ml/min.	(1:10)
5	2 µl	3 min.	Helium	1 ml/min.	N/A
12	0.5 µl	N/A	Helium	1.5 ml/min.	N/A
29	1 µl	N/A	Nitrogen	20 ml/min.	N/A
41	2 µl	1 min.	Helium	0.82 ml/min.	N/A
46	1 µl 1 µl	0.8 min. 0.58 min.	Helium Hydrogen	P= 14 psi 2 ml/min.	N/A N/A
52	1 µl	N/A	Helium	2.4 ml/min.	N/A
56	2 µl	0.75 min.	Helium	40 ml/min.	N/A
72	1 µl	Not indic.	Helium	3 ml/min.	(1:2.5)
76	Not indic.	Not indic.	Not indic.	Not indic.	Not indic.
80	1 µl	1 min.	Helium	0.72 ml/min.	(1:40)
91	1 µl	N/A	Helium	2 ml/min.	N/A

Table A4.7. continued.

Laboratory No	Column				
	Type	Length	Diametre	Phase	Film Thickness
4	Capil.	30 m	0.32 mm	SE-54	0.3 μm
5	Capil.	50 m	0.2 mm	HP-1	0.17 μm
12	Capil.	25 m	0.32 mm	SE 54	0.17 μm
29	Capil.	10 m	0.53 mm	HP-1	2.65 μm
41	Capil.	30 m	0.25 mm	DB-5	0.25 μm
46	Capil.	30 m	0.25 mm	SE-54	Not indic.
	Capil.	30 m	0.25 mm	SE-54	Not indic.
52	Capil.	30 m	0.32 mm	DB-5	0.25 μm
56	Capil.	30 m	0.25 mm	SE-54	0.25 μm
72	Capil.	25 m	0.3 mm	RSL200	0.3 μm
76	Packed	Not indic.	Not indic.	Not indic.	Not indic.
80	Capil.	25 m	0.25 mm	SE-54	0.25 μm
91	Capil.	25 m	0.32 mm	SE-54	0.17 μm

Table A4.7. continued.

Labor. No	Temperature Programme							
	Init. Temp	Isoth.	1st r.	to :	Isoth.	2nd r.	to :	Isoth.
4	80	2 min.	4	280	20 min.			
5	60	4 min.	30	100	0 min.	2	310	0 min.
12	70	0 min.	3	290	20 min.			
29	60	5 min.	15	310	50 min.			
41	90	3 min.	10	290	17 min.			
46	90	0 min.	15	110	0 min.	6	300	15 min.
	90	0 min.	15	110	0 min.	6	300	15 min.
52	60	0 min.	3	290	25 min.			
56	55	0.1 min.	18	180	0.1 min.	10	280	13 min.
72	80	1 min.	4	280	2 min.			
80	50	1 min.	5	290	20 min.			
91	60	0 min.	3	290	13 min.			

Table A4.7. continued.

Labor. No	Detector Temperature	Make-up Gas	Make-up Flow	Air Flow	Hydrogen Flow	Recorder Integrator
4	280	Nitrogen	40 ml/min.	300 ml/min.	30 ml/min.	HP 3396
5	280	N/A	N/A	N/A	N/A	GC/MS
12	300	N/A	N/A	Not indicat.	Not indicat.	CR5A Shimadzu
29	300	Not indic.	Not indicat.	400 ml/min.	30 ml/min.	HP 3369 A
41	Source : 200	N/A	N/A	N/A	N/A	Not indicated
46	330 330	N/A Nitrogen	N/A 30 ml/min.	N/A 350 ml/min.	N/A 25 ml/min.	Fisons Data Station Not indicated
52	300	Helium	10 ml/min.	430 ml/min.	30 ml/min.	Recorder
56	280	N/A	N/A	N/A	N/A	Not indicated
72	280	Nitrogen	65 ml/min.	200 ml/min.	50 ml/min.	Shimadzu CR3A
80	325	Nitrogen	27 ml/min.	640 ml/min.	57 ml/min.	Chemstation
91	300	Nitrogen	30 ml/min.	300 ml/min.	20 ml/min.	HP 3396

ANNEX V

List of participants
IAEA 142

Participating Laboratory	Responsible Analyst	Data Reported *
ALBANIA		
Tirana University Chair of Organic Chemistry TIRANA	Dr. K. KOCI	OC , PH
CROATIA		
Institute of Oceanography and Fisheries set. I. Mestrovica 68 58000 SPLIT	Mr. J. DUJMOV	OC , PH
Institute of Public Health Vukovarska 46 58000 SPLIT	Ms. S. CULIN Ms. J. PAVLOV	OC
Rudjer Boskovic Institute Center for Marine Research 52210 ROVINJ	Dr. M. NAJDEK	OC
Rudjer Boskovic Institute Center for Marine Research 41001 ZAGREB	Dr. M. PICER	OC , PH
Institute of Public Health B. Kidrica 52/A 51000 RIJEKA	Dr. SANTIN	OC
CYPRUS		
Ministry of Agriculture and Natural Ressources Department of Fisheries NICOSIA	Dr. P. LOIZIDES	OC
EGYPT		
NIOF , Kayet Bay ALEXANDRIA	Mr. Y. A. SHABAN	OC

*** OC organochlorine compounds**
PH petroleum hydrocarbons

FRANCE

Service des Eaux de l'Institut Pasteur de Lille B.P. 245 59019 LILLE Cedex	Mr. P.M. DUDERMEL	PH
Laboratoire Municipal et Region de Rouen 29 rue Bourg l'Abbe 76000 ROUEN	Dr. A. FRANCO	OC
IFREMER Centre de Brest B.P. 70 29287 PLOUZANE	Dr. A. ABARNOU	OC
Institut Bouisson Bertrand Parc Euromedecine 34196 MONTPELLIER Cedex 5	Dr. M. GHELFENSTEIN	OC , PH
Institut Europeen de l'Environnement de Bordeaux rue du Professeur Vezes 33300 BORDEAUX	Mr. J. FAURE	OC
Faculte de Pharmacie Laboratoire d'Hydrologie 27 Blvd J. Moulin 13385 MARSEILLE Cedex 5	Dr. J. MONOD	OC
Laboratoire Municipal de Chimie , de Recherches et d'Analyses 8 rue Hotel des Postes 06000 NICE	Mr. L. DOMINIQUE	OC , PH
CNEVA-LCHA 43 rue de Dantzig 75015 PARIS	Mr. F. BORDET	OC
Laboratoire Municipal de Brest 16 rue A. Ribot 29287 BREST	Mr. J. DUSSAUZE	OC , PH

ISRAEL

The Israel Institute of Petroleum and Energy 69975 Ramat Aviv TEL AVIV	Ms. J. BEN ASHER	PH

ITALY

Istituto di Biologia del Mar, CNR Riva 7 Martiri 1364/A I-30122 VENEZIA	Dr. V. U. FOSSATO	OC , PH
Presidio Multinazionale di Prevenzione USL No 31 Ferrara Corso Giovecca No 168 44100 FERRARA	Dr. S. COPPI	OC , PH

MOROCCO

Office National de l'Eau Potable 6 bis rue Patrice Lumumba RABAT	Dr. M. ASSAFI	OC
ISPM B.P. 21 2 rue de Tiznit CASABLANCA	Mr. A. CHAFIK	OC , PH

MONACO

IAEA-MEL/MESL B.P. No 800 MC-98012 MONACO	Ms. C. CATTINI	OC , PH

SLOVENIA

Public Health Institute of Slovenia Trubarjeva 2 61000 LJUBLJANA	Dr. J. JAN	OC , PH
Marine Biological Station Fornace 41 66330 PIRAN	Mr. O. BAJT	PH

Public Health Institute Environmental Protection Institute Prvomajska 1 62000 MARIBOR	Mr. E. VONCINA	OC , PH
Laboratorio de Contaminacion Toxicologia CONTOX Cronos 8 28037 MADRID	Dr. D. De HITA	OC
Instituto Espanol de Oceanografia Magallanes s/n , Lo Pagan 30740 SAN PEDRO DEL PINATAR	Dr. A. FRANCO	OC
Centro de Estudios Avanzados Instituto de Quimica Bio-Organica c/ Jorge Girona Salgado 10 BARCELONA 08034	Dr. J. ALBAIGES	OC , PH
Grupo Interlab Maria Tubau s/n Ed. Auge III , 3e A-1 28050 MADRID	Dr. P. ASPEITIA	PH
Consejo Superior de Investigaciones Cientificas Instituto de Ciencias del Mar Paseo Juan de Borbon s/n 08039 BARCELONA	Dr. J. SANCHEZ	PH

TURKEY

Department of Marine Sciences Middle East Technical University P.O. Box 28 33731 ERDEMLI-ICEL	Dr. I. SALIHOGLU	OC

UNEP

Issued and printed by:

Mediterranean Action Plan
United Nations Environment Programme

Additional copies of this and other publications issued by
the Mediterranean Action Plan of UNEP can be obtained from:

Coordinating Unit for the Mediterranean Action Plan
United Nations Environment Programme
Leoforos Vassileos Konstantinou, 48
P.O.Box 18019
11610 Athens
GREECE

PNUE

Publié et imprimé par:

Plan d'action pour la Méditerranée
Programme des Nations Unies pour l'Environnement

Des exemplaires de ce document ainsi que d'autres
publications du Plan d'action pour la Méditerranée
du PNUE peuvent être obtenus de:

Unité de coordination du Plan d'action pour la Méditerranée
Programme des Nations Unies pour l'Environnement
Leoforos Vassileos Konstantinou, 48
B.P. 18019
11610 Athènes
GRECE