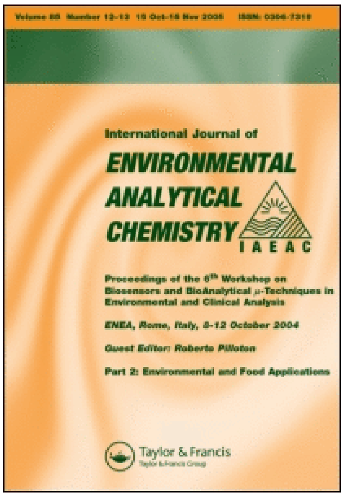

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# DETERMINATION OF ORGANOCHLORINE COMPOUNDS, PETROLEUM HYDROCARBONS, AND STEROLS IN A SEDIMENT SAMPLE, IAEA-383. RESULTS OF AN INTERCOMPARISON EXERCISE

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A worldwide interlaboratory analytical comparison exercise was organised using a lagoon sediment as sample material (IAEA-383). A total of 54 laboratories from 41 countries reported results for organochlorine pesticides, PCB congeners, aliphatic and aromatic petroleum hydrocarbons, and sterols. The statistical treatment of the data indicates that the accurate determination of these organic contaminants in sediments is still a delicate task for environmental laboratories and, for many compounds, the relative standard deviations of the mean concentration values are relatively large. The difficulties with analytical accuracy and precision are nearly the same in several regional programmes and they do not seem geographically biased. Thus, further progress is needed and may be achieved with analytical training and reinforced participation of the laboratories in proficiency testing schemes. Nevertheless, the statistical treatment of the data reported by the laboratories participating in this exercise allowed the assignment of reference values for many analytes. Based on the experience of previous exercises, the assigned reference values are likely a very good estimate of the true concentrations of analytes, although the confidence limits of those values are relatively broad. This sediment sample can now be used as a Reference Material in Quality Control and assist laboratories with assigning concentration values in environmental samples of similar matrix. In particular for sterols this is the first sediment material available with information on analyte concentrations.

*Keywords:* Intercomparison exercise; quality control; reference material; chlorinated hydrocarbons; petroleum hydrocarbons; PAHs; sterols

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## INTRODUCTION

The environmental monitoring of contaminants and pollution assessment depend upon accurate analytical determinations. This is usually achieved through the use of validated techniques and with the regular testing of data quality through participation in interlaboratory comparison exercises (round robin tests), and use of certified reference materials (CRMs). The accurate determination of contaminants is also increasingly requested in food and beverage control and, such as the environmental issues, may have implications on the international trade and public health. As a consequence, all the laboratories face a growing pressure to report analytical data of demonstrated quality.

To assist the Member States and, in particular, the developing countries to meet the standards of increased analytical quality, for many years the IAEA has been organising intercomparison exercises, producing reference materials and providing analytical training [1-3]. This paper describes the results of a recently organised international intercomparison exercise. A lagoon sediment sample, IAEA-383, was used as intercomparison material for the analyses of organic contaminants by laboratories currently implementing environmental surveillance programmes.

## ORGANIZATION OF THE INTERCOMPARISON EXERCISE

This intercomparison exercise, as previous ones of the same kind organised by the IAEA, followed very closely an internationally harmonised protocol for proficiency testing [4]. The intercomparison exercise targeted laboratories that routinely carry out research and monitoring of organic contaminants in environmental matrices. In many countries (e.g., USA, West Europe, Mediterranean countries) coastal sediments are routinely analysed for a wide range of contaminants [5,6]. Therefore, this exercise proposed a sediment sample to the laboratories for analysis of organic contaminants. The participants were requested to determine as many organochlorine compounds as possible including pesticides such as hexachlorobenzene (HCB), lindane. aldrin, dieldrin, 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 hydrocarbons, the participants were requested to report individual aliphatics, such as n-C17, n-C18, pristane, phytane, total resolved and unresolved aliphatics and all individual aromatic compounds (PAHs) which could be identified. The analysis of faecal sterols, which are common contaminants of coastal areas receiving sewage discharges, was also proposed to the participating laboratories.

In order to prepare the intercomparison material, about 30 kg of sediment were collected in the lagoon of Venice, Italy. The sediment was deep-frozen, freeze-dried, ground and sieved through a 250 μm stainless steel sieve. The sieved sediment was homogenised by mixing in a stainless steel rotating drum for two weeks. Then, aliquots of about 35 grams were packaged into glass bottles with aluminium screw caps and sealed with Teflon tape.

The homogeneity of the material for organochlorine compounds, petroleum hydrocarbons and sterols was checked by determining the concentration of these compounds in ten samples taken at random. A one way variance statistical test of the results of these analyses indicated that the material was homogeneous at $p<0.05$ and was, thus, suitable as intercomparison material.

The water content of the lyophilised material, determined by drying to a constant weight at 105 °C, was found to be 2.0 %. However, since the moisture content may change with the ambient humidity and temperature, it was recommended to the analysts to determine moisture again in a separate sub-sample (not taken for the analysis) by drying it at 105 °C for 48 hours.

In March 1997, 150 bottles with this sediment, labelled IAEA-383, were distributed to laboratories worldwide as the sample material for the analytical intercomparison exercise. Participants were requested to analyse chlorinated compounds, petroleum hydrocarbons and sterols by their usual technique. They were also requested to make preferably three separate determinations for each compound, and to report the results together with a short description of the method used (extraction, clean-up, gas chromatography conditions, confirmation method, Quality Control, etc). It was stated that concentrations should be reported as net values, i.e. after correcting for blank, moisture content, etc., leaving as many significant figures as justified by the precision of the method used. A suitable reporting form was attached to the information sheet for this purpose.

Results were received until end of June 1998, date of closure of the exercise. The data reported by the laboratories were compiled in data sets for each compound. In these data sets each laboratory is represented by the laboratory mean result. Compound after compound, the results were analysed by standard statistical procedures described elsewhere [7,8]. Exploratory statistics were carried out, including the identification of outliers which were removed using the Box-and-Whisker plot of Statgraphics 5.0, and the range, median, mean and standard deviation were recalculated for each compound.

For each analyte, the computed median value and the 95% confidence interval were retained as the best estimate (consensus value) of the true concentration of the analyte in the intercomparison sample. The evaluation of the accuracy of laboratory results is made through comparison of the laboratory results with the population median value and the 95% confidence interval.

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 robust 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 worldwide intercomparison run); and $s_b$ is the target standard deviation.

This score effectively expresses the difference between the robust mean of the laboratory and the assigned value in units $s_b$. Performance is acceptable if this difference is less than or equal to two. Performance is of unacceptable accuracy when $2 < |Z| < 3$ and the measurement is regarded as out of control when $|Z| \geqslant 3$. This score represent a simple method of giving each participant a normalised performance score for bias. This procedure has been accepted as a standard by ISO/IUPAC [4]. and has been used in previous reports by the IAEA-MEL [7].

The selection of the acceptable level of relative standard deviation (in %) depends on the monitoring objectives. For example, the criteria for PCB congeners is usually set so that laboratories should have at least a relative bias equal 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. Therefore, this should be included in the target value for bias according to the formula:

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

where $s_b$ is the target standard deviation and $s_{tu}$ is the uncertainty of the assigned value.

## RESULTS

A total of 54 laboratories from 41 countries reported results. Among the participants there are laboratories in developed and developing countries in several continents. A full list of participants, as well as a detailed compilation of the methods used and results reported is given in the IAEA report IAEA/AL/115, which can be obtained free of charge from the IAEA-MEL, Monaco [7]. In the report each laboratory is represented by a code number in order to preserve the anonymity of each result. In most cases, the analyses of the various groups of contaminants were performed using different tecniques and separate aliquots of the sample material. Only two laboratories used a combined analytical protocol for the sequential extraction of all groups of compounds. In general, the participating laboratories used well known and validated analytical methods, which are adequate to marine pollution studies. These methods are published in the UNEP/IAEA/IOC-UNESCO Reference Methods for Marine Pollution Studies [8–12]. Analyses of sterols were carried out according to methods published in the literature, which involve silylation of the compounds [13] and use of molecular markers as internal standards [14].

In the analysis of organochlorine compounds, 61% of the laboratories determined again the sample dry weight as recommended. The favourite extraction method was the Soxhlet (63%), and most of analysts used as solvent either hexane alone (26%) or hexane based mixtures (41%). Fractionation of the extracted compounds was performed either on Florisil or Silica gel columns. The majority of analysts (61%) added internal standards to the sample in order to correct for the yield of recovery, but still 33% used no internal standard. Compounds more frequently used as internal standards were PCB 29 plus ε-HCH, but many laboratories used only one internal standard, such as PCB 29 or PCB 209, α-HCH, or another. The analytical instrument of choice was GC-ECD (89%), followed by GC-MSD (6%). Most analysts used nitrogen as make-up gas (63%) or helium (4%) or another one (11%).

In the analysis of petroleum hydrocarbons, the analysts (63%) generally determined again the moisture of the sediment sample as requested. The majority of them used Soxhlet extraction (59%) and some reported other extraction methods using Dionex and SFE. Hexane or hexane based mixtures with either $MeCl_2$ or MeOH were generally used as solvents. Fractionation of the extracts was carried on Silica/Alumina columns. Internal standards, frequently 2 compounds, were used by 77% of the analysts to determine the yield of chemical recovery. Frequently used standards were C18 + C32, squalane, and dihydroantracene. Seven laboratories used a mixture of deuterated compounds as internal standards. The analytical instrument preferred by the analysts was GC-FID (40%), whilst some used GC-MSD (30%) and GC-MS (25%). As carrier gas the majority used helium (82%) and hydrogen (18%).

Sterols were recovered from the Silica/Alumina column with a mixture of methanol and dichloromethane, after elution of the petroleum hydrocarbon fractions, and derivatized with BSTFA N,O-bis(trimethylsilyl)trifluoracetamide). To quantify the yield of recovery three of the laboratories used internal standards such as α-androstane or 5α-androstan-3β-ol. The four laboratories performed confirmation of the compounds by GC-MS.

Most of the participating laboratories routinely use some Quality Assurance/Quality Control (QA/QC) procedures, being the quality control charts the more popular ones. Most of the laboratories have also been regular participants in previous exercises organised by the IAEA-MEL. However, only 10 out of the

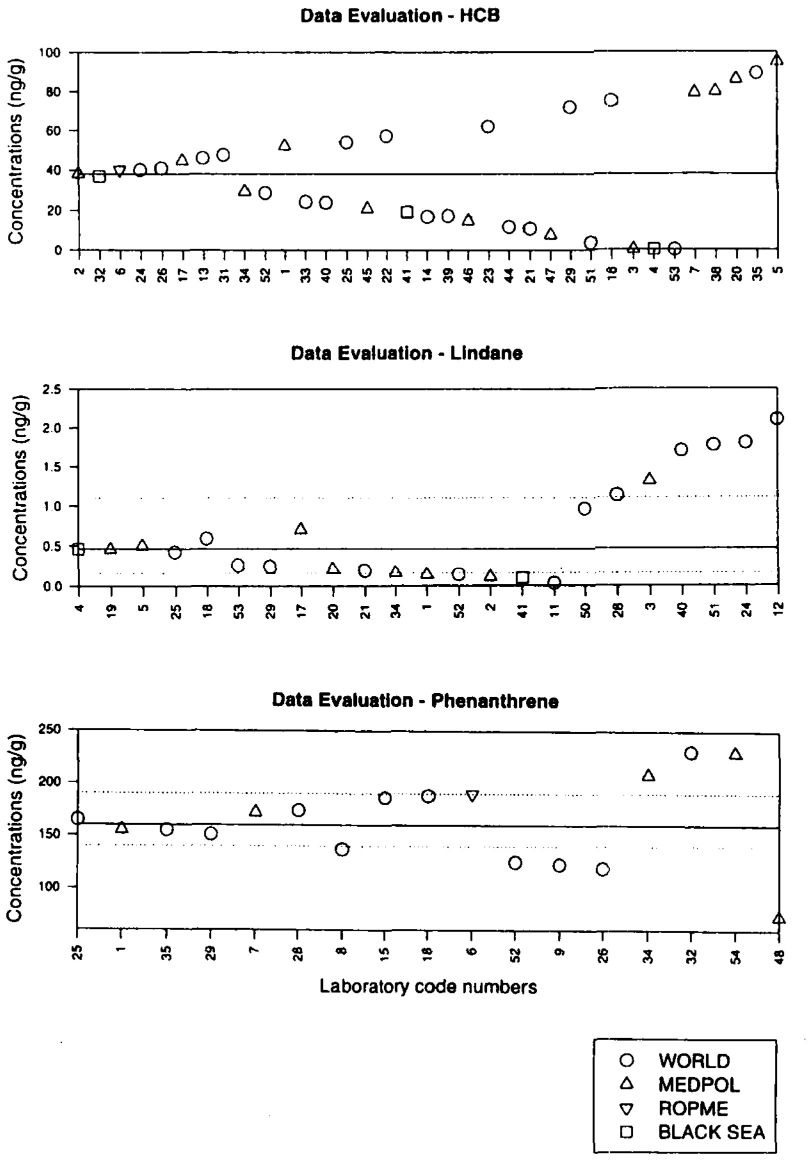

FIGURE 1 Assessment of the concentration values reported by laboratories against the assigned reference value for IAEA-383 (solid line) and 95% confidence interval (dotted lines) for selected compounds. Laboratories participating in specific regional programmes are identified with different symbols

54 laboratories reported the concurrent analysis of reference materials (RMs) with the sample IAEA-383. These laboratories generally obtained results for the reference materials within the range considered acceptable by the RM supplier, and their results in the analysis of the intercomparison sample IAEA-383 were generally also good. Among the reference materials used by the laboratories, several were supplied by the IAEA (SDM-2/OC, IAEA-142), and others by the NIST, USA (CRM 349, SRM 941a, SRM 1647c) and by the NRCC, Canada (HS).

The distribution of laboratory means for selected analytes are illustrated graphically in Figure 1. 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 (outliers being removed from the graphs). These graphic plots identify monitoring laboratories with specific UNEP's Regional Seas programme. It is interesting to note that the distribution of good results is generally homogeneous, and that there is no difference between laboratories from MEDPOL (Mediterranean Sea area), ROPME (Gulf Sea area), Black Sea or the Worldwide exercise.

Performance of the laboratories in terms of accuracy was assessed by Z-scores, which were calculated for each individual compound. Examples of Z-scores for some compounds are shown in Figure 2. Outliers are excluded in the graphical presentations and, in general, the distribution of Z-scores is very symmetric. The general impression is that a large number of the laboratories have achieved satisfactory performance. However, it should be emphasised that this is basically due to the substantial uncertainty, which resulted in broad confidential intervals.

For many analytes, the data is sufficiently well grouped to allow for assignment of reference values based on consensus values and statistical criteria. These values are shown in the Tables I, II, III and IV for the several classes of compounds. Concentration values and confidence intervals of compounds in class A are robust and reliable determinations which fully comply with the series of criteria. Concentration of compounds in class B are also reliable but met partly the criteria. Values for compounds in class C shall be regarded as information values only.

## DISCUSSION

In total 48 laboratories reported data for organochlorine compounds, of which 19 also reported data for PCBs. The number of laboratories with more than 50 % outlier data is relatively high for organochlorine pesticides (approximately 13 %). Compared to previous exercises (e.g. IAEA-357 and IAEA-351) coefficients

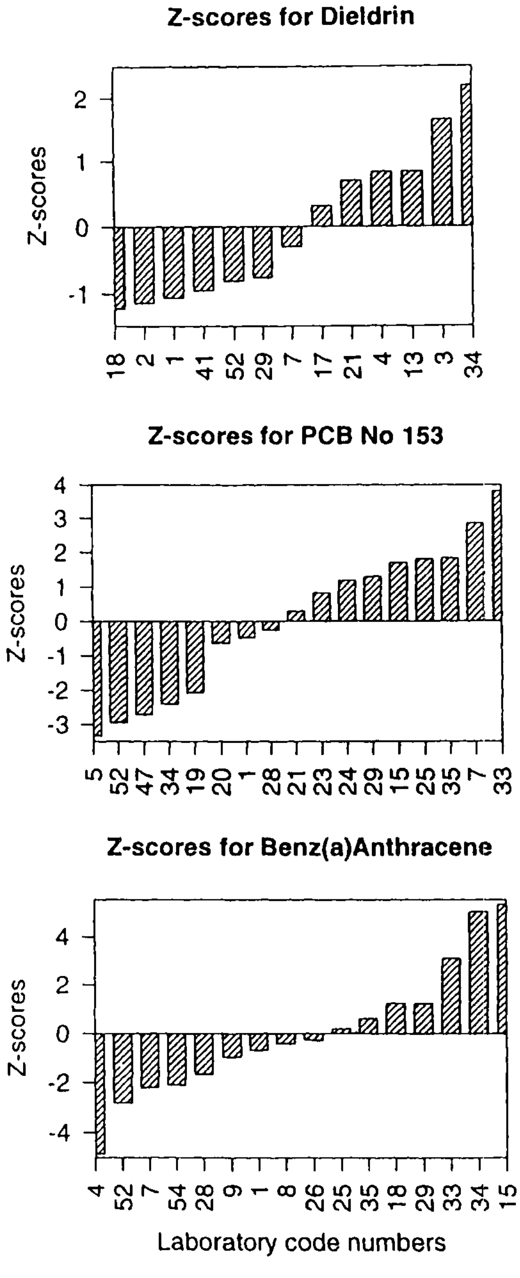

FIGURE 2 Performance of laboratories (Z-scores) in the analysis of selected compounds in the sample IAEA-383

of variation (CV) have not substantially improved for chlorinated pesticides and PCBs. The CV for chlorinated pesticides varied from 47 to 150 % with an average of 86 % while for individual PCB congeners it varied from 19 to 180 % with an average of 53 % (after removal of outliers). Clearly the data for pesticide measurements is inferior to that for PCB congeners (Tables I and II).

TABLE I Reference values for concentrations of chlorinated compounds in the sediment sample IAEA-383

| *Chlorinated compounds (ng/g dry weight)* | | | | |
|---|---|---|---|---|
| *Analyte* | *Concentration*[a] | *Confidence Interval*[b] | *N*[c] | *Class* |
| HCB | 38 | 17 – 57 | 35 | C |
| α-HCH | 0.29 | 0.13 – 3.7 | 8 | C |
| β-HCH | 0.57 | 0.26 – 9.7 | 5 | C |
| Lindane | 0.46 | 0.16 – 1.1 | 23 | C |
| pp'-DDE | 1.2 | 0.75 – 1.8 | 30 | A |
| pp'-DDD | 1.8 | 0.8 – 3.6 | 28 | C |
| pp'-DDT | 2.4 | 0.86 – 6.1 | 24 | C |
| op-DDE | 0.21 | 0.062 – 0.73 | 3 | C |
| pp-DDD | 1.2 | 0.54 – 2.5 | 6 | C |
| op-DDT | 0.39 | 0.067 – 0.82 | 3 | C |
| Heptachlor | 1 | 0.51 – 2.5 | 9 | C |
| Heptachlor Epoxide | 1.5 | 0.42 – 5.9 | 8 | C |
| Aldrin | 1.4 | 0.84 – 5.9 | 8 | C |
| Dieldrin | 0.27 | 0.1–0.57 | 13 | C |
| Endrin | 1.1 | 0.4 – 1.8 | 8 | C |
| α-Endosulfan | 0.31 | 0.15 – 0.57 | 6 | C |
| Endosulfan sulfate | 1.7 | 0.92 – 7.1 | 3 | C |
| α-Chlordane | 0.47 | 0.06 – 0.73 | 3 | C |
| γ-Chlordane | 1.4 | 0.8 – 1.9 | 3 | C |
| Aroclor 1254 | 36 | 24 – 48 | 10 | B |
| Aroclor 1260 | 22 | 14 – 34 | 10 | C |

a. Median value expressed on a dry weight basis

b. 95 % confidence intervals of the median

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

TABLE II Reference values for concentrations of PCB congeners in the sediment sample IAEA-383.

| *PCBs (ng/g dry weight)* | | | | |
|---|---|---|---|---|
| *Analyte (IUPAC congener number)* | *Concentration*[a] | *Confidence Interval*[b] | *N*[c] | *Class* |
| 18 | 0.5 | 0.27 – 0.78 | 4 | C |
| 28 | 1 | 0.77 – 1.4 | 12 | A |
| 31 | 0.76 | 0.38 – 1.2 | 6 | B |
| 44 | 1.1 | 0.92 – 1.2 | 4 | C |
| 49 | 1.1 | 0.89 – 1.3 | 5 | C |
| 52 | 2.5 | 1.1 – 2.8 | 14 | A |
| 66 | 2 | 1.8 – 3.1 | 4 | C |
| 87 | 0.7 | 0.55 – 0.91 | 3 | C |
| 95 | 3.6 | 2.7 – 4.5 | 4 | C |
| 97 | 0.41 | 0.26 – 0.9 | 3 | C |
| 99 | 1.3 | 0.59 – 1.8 | 5 | C |
| 101 | 2.9 | 1.3 – 4.2 | 16 | A |
| 105 | 0.99 | 0.77 – 1.5 | 12 | A |
| 110 | 2.4 | 1.8–3.6 | 6 | B |
| 118 | 3.3 | 2.2 – 4.1 | 17 | A |
| 128 | 0.63 | 0.52 – 0.87 | 10 | B |
| 137 | 0.17 | 0.09 – 0.22 | 3 | C |
| 138 | 4.4 | 2.6 – 6.1 | 15 | A |
| 141 | 0.64 | 0.34 – 1.1 | 4 | C |
| 149 | 3.2 | 2.3 – 3.7 | 8 | B |
| 151 | 0.58 | 0.37 – 1.1 | 3 | C |
| 153 | 4.3 | 2.3 – 5.4 | 17 | A |
| 156 | 0.47 | 0.24 – 0.78 | 7 | C |
| 158 | 0.39 | 0.18 – 0.57 | 4 | C |
| 170 | 0.82 | 0.62 – 1.3 | 11 | A |
| 174 | 0.67 | 0.42 – 0.92 | 4 | C |
| 177 | 0.56 | 0.35 – 0.73 | 4 | C |
| 180 | 2.5 | 1.9 – 3.4 | 17 | A |
| 183 | 0.47 | 0.34 – 0.57 | 6 | B |
| 185 | 0.14 | 0.073 – 0.18 | 3 | C |
| 187 | 1.3 | 0.63 – 1.5 | 10 | B |
| 189 | 0.07 | 0.041 – 1.4 | 4 | C |

| *PCBs (ng/g dry weight)* | | | | |
|---|---|---|---|---|
| *Analyte (IUPAC congener number)* | *Concentration*[a] | *Confidence Interval*[b] | *N*[c] | *Class* |
| 194 | 0.54 | 0.31 – 0.73 | 7 | B |
| 195 | 0.24 | 0.13 – 0.29 | 5 | C |
| 199 | 0.091 | 0.01 – 0.35 | 3 | C |
| 200 | 0.16 | 0.051 – 0.22 | 3 | C |
| 201 | 0.71 | 0.28 – 0.74 | 3 | C |
| 205 | 0.033 | 0.027 – 0.05 | 3 | C |
| 206 | 0.48 | 0.44 – 1.1 | 5 | C |
| 207 | 0.094 | 0.05 – 0.19 | 3 | C |
| 209 | 2.1 | 1.2 – 3 | 7 | B |

a, b, c, See Table I.

For petroleum hydrocarbons 22 laboratories provided data (Table III). The percentage of laboratories with more than 50 % outlier data is only 4 % (only one laboratory). This laboratory was the only one to use a Supercritical Fluid Extractor for this exercise but they did not use any internal standard, which could explain the high number of outlier results that they reported. Comparison of the global results of this exercise with the results obtained in previous exercises shows hat, in general, there is no improvement in petroleum hydrocarbon data. The CV obtained (20–100 %) is about the same as for the previous exercise using the sediment sample IAEA-357 (5–91 %).

TABLE III Reference values for concentrations of petroleum hydrocarbons in the sediment sample IAEA 383

| *Petroleum hydrocarbons (dry weight basis)* | | | | | |
|---|---|---|---|---|---|
| *Analyte* | *Concentration*[a] | *Confidence Interval*[b] | *Units* | *N*[c] | *Class* |
| UVF Chrysene equivalent[a] | 13 | 1.8 – 2.8 | µg/g | 6 | C |
| UVF ROPME Oil[b] | 96 | 12 – 225 | µg/g | 7 | C |
| Total aliphatics | 52 | 14 – 85 | µg/g | 6 | C |
| Resolved aliphatics | 9.6 | 6.7 – 24 | µg/g | 9 | C |
| Unresolved aliphatics | 52 | 11 – 79 | µg/g | 7 | C |
| n-C17 | 380 | 330 – 470 | ng/g | 11 | A |
| Pristane | 87 | 36 – 240 | ng/g | 10 | C |
| n-C18 | 83 | 42 – 230 | ng/g | 10 | C |
| Phytane | 57 | 43 – 150 | ng/g | 9 | C |
| Σn-alkanes (C14-C34) | 6.1 | 5.3 – 6.8 | µg/g | 8 | C |

*Petroleum hydrocarbons (dry weight basis)*

| *Analyte* | *Concentration*[a] | *Confidence Interval*[b] | *Units* | *N*[c] | *Class* |
|---|---|---|---|---|---|
| Total aromatics | 8.8 | 1.5 – 22 | µg/g | 5 | C |
| Resolved aromatics | 2.5 | 0.4 – 6 | µg/g | 7 | C |
| Unresolved aromatics | 6.6 | 1.1 – 16 | µg/g | 5 | C |
| Naphthalene | 96 | 52 – 110 | ng/g | 12 | A |
| 1-methyl naphthalene | 14 | 11 – 28 | ng/g | 6 | B |
| 2-methyl naphthalene | 36 | 26 – 43 | ng/g | 4 | C |
| Biphenyl | 6.1 | 19 – 30 | ng/g | 3 | C |
| 2.6 dimethyl naphthalene | 13 | 7.1 – 23 | ng/g | 4 | C |
| Acenaphthylene | 26 | 31 – 59 | ng/g | 8 | B |
| Acenaphthene | 5.3 | 13 – 21 | ng/g | 8 | B |
| Fluorene | 27 | 24 – 34 | ng/g | 9 | B |
| Phenanthrene | 160 | 140 – 190 | ng/g | 17 | A |
| 2-methyl phenanthrene | 31 | 24 – 38 | ng/g | 7 | B |
| 1-methyl phenanthrene | 24 | 18 – 28 | ng/g | 10 | B |
| Fluoranthene | 290 | 260 – 350 | ng/g | 16 | B |
| Pyrene | 280 | 210 – 350 | ng/g | 19 | A |
| Benz(a)anthracene | 105 | 83 – 130 | ng/g | 16 | A |
| Anthracene | 30 | 25 – 34 | ng/g | 9 | B |
| Chrysene | 170 | 20 – 220 | ng/g | 16 | A |
| Benzo(b)fluoranthene | 150 | 96 – 190 | ng/g | 8 | B |
| Benzo(k)fluoranthene | 73 | 48 – 76 | ng/g | 8 | B |
| Benzo(e)pyrene | 160 | 20 – 210 | ng/g | 12 | A |
| Benzo(a)pyrene | 120 | 77 – 140 | ng/g | 16 | A |
| Perylene | 58 | 41 – 130 | ng/g | 7 | B |
| Indeno(123cd)pyrene | 29 | 130 – 160 | ng/g | 8 | C |
| Dibenz(ah)anthracene | 20 | 18 – 41 | ng/g | 5 | C |
| Benzo(ghi)perylene | 110 | 69 – 230 | ng/g | 16 | A |

a, b, c, See Table I.

a. PH-Chrysene equivalent is a UVF measurement relative to that of standard chrysene.

b. PH-ROPME Oil is a UVF measurement relative to that of ROPME (Kuwait) crude oil.

For sterols only 4 laboratories reported results for the intercomparison sample (Table IV). These laboratories used the same techniques and the results reputed are in fairly good agreement. This was, however, the first time that the IAEA-MEL proposed the analysis of these compounds. The follow up of municipal waste discharges in coastal areas is likely to encourage more laboratories to develop capabilities to measure these contaminants and participation in future exercises may increase.

TABLE IV Information values on concentrations of sterols in the sediment sample IAEA-383

| *Sterols (dry weight basis)* | | | | | |
|---|---|---|---|---|---|
| *Analyte* | *Concentration*[a] | *Confidence Interval*[b] | *Units* | *N*[c] | *Class* |
| Coprostanol | 590 | 340–840 | ng/g | 4 | C |
| Cholesterol | 1150 | 1050–1250 | ng/g | 3 | C |
| Cholestanol | 840 | 580–1100 | ng/g | 3 | C |
| Beta-Sistosterol | 700 | 490–910 | ng/g | 3 | C |
| Campesterol | 270 | 60–480 | ng/g | 3 | C |

a, b, c, See Table I.

In general, wrong results reported by the laboratories are associated with the analytical procedures and can be traced to various causes, including unsuitable extraction and clean-up procedures, erroneous calibration, and poor optimisation of chromatographic conditions. Furthermore, the laboratories, which did not use any internal standard to compute the yield of recovery, rarely have acceptable results [7,15,16].

Seventeen MEDPOL laboratories from 11 Mediterranean countries participated in this analytical exercise and reported data. This reflects the importance recognised to Quality Assurance in this region. which has been encouraged by the Mediterranean Action Plan. Although the participation from other regions has been comparatively poorer, the analytical performances shown by laboratories (Figure 1) indicate that the quality of data reported is similar to the performance of Mediterranean laboratories. Nevertheless. it is necessary to further promote the adoption of QA/QC procedures nearly everywhere.

The overall performance of laboratories in the analysis of the intercomparison sample is shown in Figure 3. Only a few laboratories could report accurate data for a wide range of contaminants. Although the number of outliers, in percent of responses per compound, is generally small, amongst the accepted results only about half are of adequate accuracy (within the 95% confidence interval) and the other half are of non-acceptable accuracy.

## CONCLUSIONS

The results of this exercise show that there is still a large spread of laboratory results in the analyses of organochlorine compounds and petroleum hydrocarbons. Many laboratories had demonstrated better accuracy in previous exercises, which was not confirmed in the current exercise with a sediment sample. This result highlights that maintenance of high standards of analytical performance requires a continuous effort by the analysts. The exercise organisers directly con-

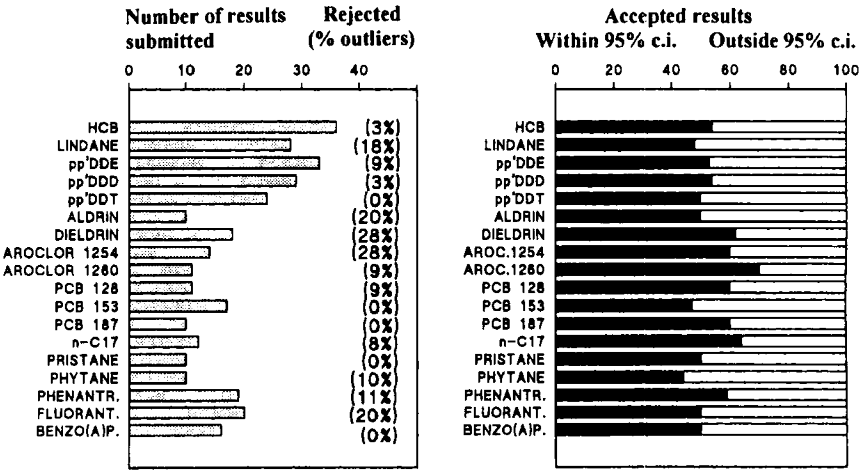

FIGURE 3 Overall assessment of the analytical accuracy of participants in the analysis of the sediment sample IAEA-383

tacted participants who performed poorly and analytical advice was provided. Furthermore, for the laboratories participating in regional co-operative programmes (MEDPOL, Black Sea), analytical training courses were organised.

In a closer look into the laboratories' performance, most of them employ well established and validated analytical methods, including those published and recommended by the UNEP/IAEA/IOC in the Reference Methods for Marine Pollution Studies or other methods [1,8–12, 15–17]. Many amongst the participants also follow Quality Assurance/Quality Control procedures, including the use of quality control charts, analysis of Reference Materials from various producers, and periodic participation in intercomparison exercises. Therefore, at the outcome of this exercise, the consensus values obtained and the assigned reference values are traceable to other reference materials produced by the IAEA, NRCC and NIST. Nevertheless, in the absence of an absolute method for certification of the concentrations of organic contaminants in this sample. the SI units are not realised through an unbiased and unbroken chain of analytical operations. Therefore, although we assign reference concentration values to this sample material, certification can not be ensured at the highest metrological level [18,19].

This new reference material (IAEA-383) is suitable to check the accuracy of analytical measurements when samples of similar matrix are analysed for the purpose of environmental monitoring. The sample can be obtained from the IAEA.

## *Acknowledgements*

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