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REPORT NO. 31

INTERCALIBRATION OF ANALYTICAL METHODS  
ON MARINE ENVIRONMENTAL SAMPLES

Results of MEDPOL II Exercise for the Intercomparison of Trace  
Element Measurements on Mussel Tissue Homogenate and  
Marine Sediment (MA-M-2/TM and SD-N-1/2/TM)

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## 1. INTRODUCTION

The pollution of the Mediterranean Sea is nowadays a potentially important problem and many laboratories in various Mediterranean countries are investigating this matter within the framework of the Mediterranean Action Plan (MEDPOL-Phase II).

Among the various possible forms of pollution, that caused by heavy metals is perhaps the most important one since these substances are accumulated in the marine food-web and are not destroyed with time.

Filter-feeding animals (e.g. mussels) and coastal sediments are often considered as contamination indicators of the marine environment. Mussels react quickly to the pollution of the surrounding sea water, while mechanisms of transfer and fixation of heavy metals into sediments often reflect long-term processes. Broadly speaking, it may be said that mussels act as a short-term "memory" of the pollution of sea water by heavy metals while sediments constitute a long-term "memory" of this pollution.

Many scientists, therefore, who study the contamination of the Mediterranean Sea are faced with problems of analysis of heavy metals in mussels and sediments. Since these analyses are often very difficult and require elaborate techniques, it was judged appropriate to provide the analysts working in institutes participating in MEDPOL Phase II with an opportunity for checking their analytical performances. One of the essential ways to achieve this aim is the simultaneous analysis of a homogeneous material by many laboratories working independently from each other and using various methods of analysis. For each element analysed, results are normally grouped around a central value which may be considered as the best estimation of the "true" concentration of the analysed element in the material. Each analyst can then evaluate the systematic error of his method by the deviation of the average of his own results from this value which is usually termed the "consensus value" in laboratory intercomparisons.

## 2. SCOPE OF THE INTERCOMPARISON

Each participant received a sample of lyophilised mussel tissue and/or a sample of coastal sediment. These samples originated from batches of homogenized materials which are described below. Each sample was accompanied by an information sheet and a report form. Participants were requested to determine as many as they could from among the following 15 elements: Ag, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, V and Zn.

In total 19 laboratories from 9 countries participated in this intercomparison run. Seven laboratories analysed the mussel sample only, 4 laboratories analysed the sediment sample and 8 laboratories analysed both samples. In the case of the MA-M-2 material (mussel) 120 laboratory means were reported for 15 elements but for 2 of them only isolated results (1 or 2 laboratory means) were supplied. In the case of the SD-N-1/2 material (sediment) 101 laboratory means were reported for 15 elements and for 5 of them only isolated results were obtained.

### 3. DESCRIPTION OF THE MATERIALS

#### a. Mussel MA-M-2/TM

Since this material was also used in other intercomparisons (e.g. worldwide intercomparisons for determination of trace metals and organochlorine compounds), a large amount (about 17 kg) of lyophilised mussel tissue was prepared and homogenized in the following way:

About 600 kg of Mediterranean mussels (*Mytilus galloprovincialis*) were purchased from a local supplier. Soft tissues were separated from the shells using stainless steel knives. The shells were discarded and soft tissues were lyophilised on aluminum trays covered with plastic sheets under a vacuum of  $10^{-1}$  Torr.

Lyophilised tissues were ground in a mixer made of stainless steel and glass only. The fraction of the material passing through a 150  $\mu\text{m}$  sieve was collected and the residue was again ground in a porcelain ball mill. After grinding, the resulting powder was again sieved and the fraction passing through a 150  $\mu\text{m}$  sieve was added to the first portion of powder.

Homogenization was done by mixing the entire quantity of powder having particle size  $< 150 \mu\text{m}$  in a stainless steel rotating drum for 100 hours. Then, aliquots of 25 g were packaged into glass bottles sealed with plastic screw caps.

The homogeneity of the material for trace elements was checked by determining the concentration of some typical heavy metals in ten 500 mg samples taken randomly from the bulk of the powder. The samples were mineralized by wet ashing with nitric acid and zinc was determined by flame atomic absorption spectroscopy while the flameless technique was applied to the determination of Cd, Cu, Mn and Pb. Each sample solution was analyzed 10 times. A one-way variance analysis showed that the variance between samples could be explained by the analytical variance for each element determined (at a significance level of 0.05). This material was, therefore, considered as homogeneous for the purpose of the intercalibration (at least for a sample weight  $\geq 500$  mg).

The water content of the lyophilised material as determined by drying to a constant weight at  $85^\circ\text{C}$  was found to be 6.5%. As, however, the water content may vary with changes in the ambient humidity and temperature, it was recommended that the water content of this material be always determined in a separate sub-sample (not that taken for analysis) by drying for 48 hours at  $85^\circ\text{C}$ . All results were to be reported on a dry-weight basis.

#### b. Sediment SD-N-1/2/TM

This material was also used in other intercomparison runs (e.g. worldwide intercomparisons for determination of trace metals and radionuclides). It was prepared in the following way:

Approximately 100 kg of surface sediment were collected in 1979 from the Scheldt Estuary (North sea) by the Delta Institute for Hydrobiological Research, Netherlands. After drying at  $105^\circ\text{C}$ , grinding and sieving, the powdered sediment was homogenized in a stainless steel rotating drum for one week. Then, aliquots of about 25 g of this material were dispensed into small polyethylene bottles with double seals.

The approximate mineral composition of the matrix is the following:

60% quartz	6% feldspar
20% calcite	3% NaCl (residual sea salts)
10% clay minerals	1-2% pyrite

Homogeneity tests were performed on a number of samples selected at random, by determining Cr, Cs, Fe, Hf and Eu in 100 mg - aliquots by instrumental neutron activation analysis. On the other hand, the concentrations of Cd, Cu, Mn, Pb and V were measured in 200-500 mg aliquots by flameless atomic absorption following sample decomposition by acids. In neither case did the relative standard deviation exceed 4%. The "between samples" variances showed no significant differences from the "within samples" variances for all the elements tested (at a significance level of 0.05).

The loss of weight on drying 1-2 g aliquots of this sample at 105-110°C was found to be about 1.5%.

All results were to be reported on a dry-weight basis.

#### 4. EVALUATION OF RESULTS

The data provided by laboratories participating in this intercomparison are presented in Tables 1-15 for the exercise on MA-M-2/TM (mussel) and in Tables 16-30 for the exercise on SD-N-1/2/TM (sediment). All results relevant to a given element are grouped in the same table. The terms used in the tables are defined as follows:

Unit: Units in which the concentration of an element to be determined is expressed. In this intercomparison, all results are expressed in  $\mu\text{g g}^{-1}$  (micrograms per gram) of dry-weight, except for iron in sediment, the concentration of which is expressed in  $\text{mg g}^{-1}$  (milligrams per gram) of dry-weight.

Laboratory Code No.: Each laboratory was represented by a code number, which remains unchanged throughout the tables. These numbers, however, do not correspond to the sequence of laboratories in the list of participants given at the end of this report, so that anonymity is preserved. When a laboratory has used two different analytical procedures for the determination of the same element, the results are distinguished as different sets of data by the capital letter A or B added to the code number. The same procedure is applied when the same co-ordinator supervises two different laboratories which may use the same basic method for determination of the same element. The sets of results furnished by the two laboratories are still distinguished by the letter A or B added to the same code number.

Method: Participating laboratories were requested to give basic information on the analytical methods which they applied to the determination of trace elements. These methods are described in the Tables 1 - 30 by a code, namely:

INAA: neutron activation analysis (instrumental)  
RNAA: neutron activation analysis (with radiochemical separations)  
Flame-AAS: atomic absorption spectroscopy (flame technique)  
GF-AAS: atomic absorption spectroscopy (graphite-furnace technique)  
Hydride-AAS: atomic absorption spectroscopy (hydride generation technique)  
CV-AAS: atomic absorption spectroscopy (cold-vapour technique)  
ASV: anodic stripping voltammetry (or other voltammetric technique)

No. of determinations: The number of individual determinations of a given trace element, performed by a laboratory using the same analytical procedure.

Laboratory mean: The arithmetic mean computed from all individual results supplied by a laboratory for the determination of a given trace element. An asterisk next to a laboratory mean denotes that this mean was classified as an outlier and was not taken into account when computing the overall mean.

Coefficient of variation: The ratio (expressed in percent) of the standard deviation of the individual results of determination of a given trace element to the laboratory mean (the standard deviation is computed in the usual way). The coefficient of variation was not computed when less than 3 individual results were reported.

"Consensus values" established on the basis of worldwide intercomparisons for the determination of trace elements in the same materials are also given in Tables 1-30. These intercomparison runs were carried out in 1983-1985 and involved the participation of a large number of laboratories, namely 55 laboratories from 29 countries for the MA-M-2/TM exercise (mussel) and 98 laboratories from 42 countries for the SD-N-1/2/TM run (sediment). The results of these intercomparisons and the procedures for establishment of "consensus values" have been presented in reports issued by the International Atomic Energy Agency (1,2). Briefly, "consensus values" were established by a non-parametric procedure as follows:

1. For a given trace element, the laboratory means are computed and arranged by ascending order.
2. "Outliers" are eliminated by a distribution-free procedure (3).
3. The overall median of the set of the "accepted" results is computed in the usual way and its confidence limits are calculated using statistical tables (4).
4. The overall median is accepted as the most robust estimator of the "true" concentration value of this element in the intercomparison material, i.e., the median is chosen as the "consensus value" for this element.

## 5. DISCUSSION

It was not the purpose of this MEDPOL intercomparison to establish consensus values for trace element concentrations in the materials to be analysed. These values have been already established for most elements with a satisfactory degree of confidence on the basis of a large number of results provided by many laboratories using various methods of

analysis. In the case of the MEDPOL results, the number of reported data for a given element is in most cases much smaller than the number of results of the worldwide intercomparison for this element. The application of non-parametric statistics is not suitable in this case, since such procedures are indeed asymptotically distribution-free and give a too large confidence interval for the median when the size of the sample is small. In this exercise, therefore, outliers were identified by applying the t - test at the significance level  $\alpha = 0.01$  (two-sided) and by doing the assumption of a normal distribution of data for each element. The mean values of the sets of results obtained after elimination of outliers and their confidence intervals were then computed in the usual way, i.e.:

$$\bar{x} - t.S/\sqrt{n} < \mu < \bar{x} + t.S/\sqrt{n}$$

where:  $\mu$  = theoretical mean of the distribution of results  
 $\bar{x}$  = arithmetical mean of the distribution of results  
S = standard deviation of the "accepted" results  
n = number of "accepted" results  
t = Student's factor for (n - 1) degrees of freedom and a significance level  $\alpha = 0.05$  (two-sided)

In Table 31 (mussel) and Table 32 (sediment) these mean values are given together with their confidence intervals and they are compared to the "consensus values" resulting from the worldwide intercomparisons. The confidence intervals of the consensus values are also given (one can notice that these intervals are asymmetrical). In the case where the number of "accepted" results was smaller than five, no mean value was computed from the MEDPOL results. The range of the accepted results is given instead.

For some elements (Ag, Ni, Pb, Sb, V in mussel and Fe, Hg, Se in sediment) no certified consensus values could be derived from the worldwide intercomparisons, i.e. the median values could not satisfy the criteria chosen for their qualification (too large dispersion of results, disagreement between different methods, etc.). In such a case, a non-certified information value is given together with its confidence interval. If it was not even possible to derive an information value owing to data of too bad quality, only the range of the "accepted" results is given.

From the results given in Table 31 (mussel MA-M-2/TM), one can see that the overall agreement between the average of the MEDPOL results and the "consensus value" is good in the case of the determination of Cd, Co, Cr, Cu, Fe, Hg, Mn, Pb, Se and Zn. There is an overlapping of the confidence intervals of both central values for these elements. Taking into account the dispersion of results and the ranges of the reported data, the agreement appears to be not bad for Ag, As, Ni, Sb and V. For these elements, the "accepted" results, although not of very good quality, are at least of the same order of magnitude.

In the case of the sediment SD-N-1/2/TM (Table 32), the overall agreement between the results of the MEDPOL run and these of the worldwide exercise seems to be good for Ag, As, Cd, Co, Cu, Hg, Mn, Ni, Pb, Se and Zn. For these elements, there is an overlapping of the confidence intervals of both central values. For Cr and Fe, however, the overall means of the MEDPOL results significantly differ from the "consensus values" derived for these elements from the worldwide intercomparison. On the other hand, a single result only was provided in the MEDPOL run in the case of Sb and V and this result is for both elements significantly lower than the "consensus value".

A survey of the results given in Table No. 20 (Cr in sediment) shows that all reported laboratory means are significantly lower than the consensus value ( $149 \mu\text{g g}^{-1}$ ) with the exception of the results given by Laboratory No. 2 ( $132.0 \mu\text{g g}^{-1}$ ) and Laboratory No. 19 ( $161.8 \mu\text{g g}^{-1}$ ). Both results were obtained by two different techniques (Flame-AAS and INAA, respectively). All other results were obtained by Flame-AAS and vary between  $25.2 \mu\text{g g}^{-1}$  and  $98.8 \mu\text{g g}^{-1}$ . These results are surprisingly low if one compares them with the data of the worldwide exercise (2). When one looks carefully at the results of the worldwide exercise, however, it appears that 65% of the results obtained by AAS (flame and graphite-furnace techniques together) are below the "consensus value" while 85% of the results obtained by INAA are above this value. It seems, therefore, that in this particular case, atomic absorption spectroscopy has a tendency to produce lower results than neutron activation analysis. This may be due to the fact that nuclear methods such as INAA are less sensitive to matrix effects than spectrochemical methods e.g. AAS. This tendency is again obvious in the MEDPOL exercise since 8 out of 9 results were produced by flame-AAS and were all lower than the single result obtained by INAA. Unfortunately, the number of results obtained by other methods in the worldwide intercomparison is too low to establish with certainty which method, AAS or NAA, gave the best results in that case.

As already mentioned, another discrepancy was found between the mean value of the MEDPOL results and the consensus value in the case of the determination of iron in the sediment SD-N-1/2. If one looks at the results of the MEDPOL exercise given in Table 22, one can see that a very low result ( $0.11 \text{ mg g}^{-1}$ ) was not detected as an outlier by the t-test at the 0.01 significance level. If this result is removed from the set, one gets a new mean value of  $26.5 \pm 6.6 \text{ mg g}^{-1}$  which still significantly differs from the consensus value  $36.4$  ( $35.3 - 37.8$ )  $\text{mg g}^{-1}$ . The results of the worldwide intercomparison, however, do not seem to indicate that flame atomic absorption spectroscopy has a tendency to give lower results than the other analytical techniques such as neutron activation, plasma-AES, etc. The reasons for which 7 out of 8 determinations of iron by flame-AAS seem to be too low in this case are, therefore, not clarified.

As far as the data reported for silver are concerned, the two results obtained by AAS in the case of the mussel sample are of the same order of magnitude as the single result reported by INAA (Table No. 1). This can be considered as satisfactory if one takes into account the very low level of concentration of this element in mussel (about  $50 \text{ ng g}^{-1}$ ). Only the result obtained by INAA, however, is in close agreement with the consensus value (not certified). In the case of the sediment sample, only one result was reported, which agrees quite well with the certified consensus value (Table 16). This result was also obtained by INAA.

Three results were reported for the determination of arsenic in the mussel sample (Table No. 2). Two of them seem to be in good agreement with the consensus value and were obtained by NAA (with radiochemical separation) and AAS (hydride generation technique). The third result, however, seems to be too low (by about a factor 2). It was obtained by hydride-AAS. Two results were reported for arsenic in the sediment sample (Table No. 17). They were obtained by hydride-AAS and NAA (with radiochemical separation) and both agree pretty well with the consensus value for this element.

Fifteen determinations of cadmium in the mussel sample were reported (Table No. 3) with two of them probably too low ( $0.35$  and  $0.55 \mu\text{g g}^{-1}$ ) and two of them obviously too high ( $2.71$  and  $9.68 \mu\text{g g}^{-1}$ ). The other results are well grouped ( $1.12 - 1.81 \mu\text{g g}^{-1}$ ) and are in good agreement with the certified consensus value ( $1.32 \mu\text{g g}^{-1}$ ). All results were obtained by three different techniques (AAS, NAA and ASV). It is interesting to notice that the four incorrect results were obtained by graphite furnace-AAS. Six good results, however, were reported by participants using this method. One cannot say, therefore, that this technique gave poor results in this case but it seems that some laboratories do not master well the analysis of cadmium in biological samples by graphite furnace - AAS. On the other hand, out of 12 determinations of cadmium in the sediment sample (Table No. 18), one is obviously too low ( $0.79 \mu\text{g g}^{-1}$ ) and another one somewhat too high ( $15.3 \mu\text{g g}^{-1}$ ). The other results are well clustered ( $10.4 - 13.9 \mu\text{g g}^{-1}$ ) and are in good agreement with the certified consensus value ( $11.0 \mu\text{g g}^{-1}$ ).

As far as the data obtained for cobalt are concerned, the seven results reported for the determination of this element in the mussel sample (Table No. 4) are spread over a fairly wide range ( $0.48 - 1.61 \mu\text{g g}^{-1}$ ) which, however, is relatively well centered on the certified consensus value ( $0.88 \mu\text{g g}^{-1}$ ). Two results, however, seem to be too low ( $0.48$  and  $0.50 \mu\text{g g}^{-1}$ ) and were obtained by ASV and Flame-AAS, respectively. Two other ones ( $1.29$  and  $1.61 \mu\text{g g}^{-1}$ ) seem to be too high and were obtained by graphite-furnace AAS. The determination of cobalt in the sediment sample (Table No. 19) gave also rise to a wide range of reported values ( $4.7 - 12.6 \mu\text{g g}^{-1}$ ) which were obtained by flame-AAS, ASV and NAA. When compared with the certified consensus value ( $12.1 \mu\text{g g}^{-1}$ ), two results obtained by flame-AAS were too low ( $4.7$  and  $8.4 \mu\text{g g}^{-1}$ ). Only the two results obtained by neutron activation analysis (either instrumental or with radiochemical separations) are in close agreement with the consensus value ( $11.1$  and  $12.6 \mu\text{g g}^{-1}$ ). It seems, therefore, that for both samples the best determinations of cobalt were done by neutron activation analysis.

The results for chromium in the mussel sample (Table No. 5) are relatively well grouped ( $1.05 - 1.89 \mu\text{g g}^{-1}$ ) with the exception of one result ( $2.45 \mu\text{g g}^{-1}$ ) which is probably too high. The reported values do not differ very much from the consensus value ( $1.25 \mu\text{g g}^{-1}$ ). Results were obtained by graphite furnace - AAS, flame - AAS and INAA. Systematic differences between the results of the different methods do not seem to exist. As previously discussed, results are not so satisfactory for chromium in sediment since the measurements done by atomic absorption were significantly lower than those obtained by neutron activation analysis (Table No. 20).

As far as the results obtained for copper in the mussel sample are concerned (Table No. 6), one result seems to be too low ( $2.0 \mu\text{g g}^{-1}$ ) and another one too high ( $13.3 \mu\text{g g}^{-1}$ ) when compared with the other results which are pretty well grouped ( $6.0 - 10.0 \mu\text{g g}^{-1}$ ). The range of the "accepted" results is well centered on the consensus value ( $8.0 \mu\text{g g}^{-1}$ ). These results were obtained by atomic absorption spectroscopy (flame and graphite-furnace) and by neutron activation analysis. The two incorrect results were obtained by flame-AAS which, however, is usually a good technique for the determination of copper, as shown by the other results obtained by this technique. The determinations of copper in the sediment



(Table No. 21) are less satisfactory. One result obtained by flame-AAS is obviously too low ( $13.4 \mu\text{g g}^{-1}$ ) while the "accepted" results are spread on a relatively wide range ( $46.6 - 82.2 \mu\text{g g}^{-1}$ ). Eight out of the ten reported results are below the certified consensus value ( $72.2 \mu\text{g g}^{-1}$ ). All these results, except one, were obtained by flame-AAS. It seems, therefore, that a chemical interference due to the sediment matrix is responsible for the too low results obtained by flame-AAS in this particular case.

The results obtained for the determination of iron in the mussel sample (Table No. 7) are spread on a relatively large range of concentrations ( $182-338 \mu\text{g g}^{-1}$ ). Seven out of the 8 reported results are higher than the certified consensus value. Except one result ( $338 \mu\text{g g}^{-1}$ ) which is probably too high, all data are in good agreement with those of the worldwide intercomparison. These results were obtained either by flame-AAS or by graphite furnace-AAS and systematical differences do not appear. Results are not so satisfactory for iron in sediment (Table No. 22). As previously discussed, one result is obviously too low ( $0.11 \text{ mg g}^{-1}$ ) and all other results, except one, are significantly lower than the consensus value.

As far as the results obtained for the determination of mercury in the mussel sample are concerned (Table No. 8), it is noticeable that the range of the reported results is wide ( $0.35 - 1.85 \mu\text{g g}^{-1}$ ). This range, however, is well centered on the certified consensus value ( $0.95 \mu\text{g g}^{-1}$ ). One result is obviously too high ( $1.85 \mu\text{g g}^{-1}$ ) while two other ones ( $0.35$  and  $0.38 \mu\text{g g}^{-1}$ ), although not detected as outliers by the t-test, seem to be too low. All results, except one, were obtained by cold vapour atomic absorption spectroscopy. The results are not so good for the determination of mercury in sediment (Table No. 23). Their range is wide ( $0.13 - 2.14 \mu\text{g g}^{-1}$ ) and they are very dispersed, so that no outlier could be detected by the t-test. The range of reported results, however, is well centered on the information value derived from the worldwide intercomparison ( $1.46 \mu\text{g g}^{-1}$ ). This value, however, is not certified, owing to a strong dispersion of the results of the worldwide intercomparison. It appears from these results, therefore, that most laboratories do not master completely the determination of mercury in sediment samples.

Nine laboratories reported results of determination of manganese in the mussel sample (Table No. 9). They were all determined by AAS (flame and graphite-furnace) and by NAA. The range of the accepted results ( $63.2 - 77.0 \mu\text{g g}^{-1}$ ) is well centered on the certified consensus value ( $67.1 \mu\text{g g}^{-1}$ ). One result only seems to be too high and was obtained by graphite furnace - AAS ( $87.4 \mu\text{g g}^{-1}$ ). Results reported for the determination of manganese in the sediment sample (Table No. 24) are also satisfactory, although that 7 out of the 9 reported results are below the certified consensus value ( $777 \mu\text{g g}^{-1}$ ). All these results were obtained by flame-AAS. This technique seems, therefore, to have a tendency to produce results which are rather low, which is possibly due to a chemical interference related to the sediment matrix.

Only 5 laboratories reported values for the determination of nickel in the mussel sample (Table No. 10). One result obtained by flame-AAS is obviously too high ( $4.95 \mu\text{g g}^{-1}$ ). For the other results one can conclude that they appear to be reasonable when compared to the results of the worldwide intercomparison since no consensus value and no information value could be derived from this intercomparison. The results obtained for nickel in sediment (Table No. 25) are well grouped and in good agreement with the certified consensus value ( $31.0 \mu\text{g g}^{-1}$ ). Three of

them, however, seem to be a little too low (19.5, 22.0 and 22.1  $\mu\text{g g}^{-1}$ ). They were obtained by flame-AAS. Here also an uncorrected chemical interference may be the cause of this disagreement.

Thirteen laboratories reported results for the determination of lead in the mussel sample (Table No. 11). One of them is obviously too high and was found to be an outlier by the t-test (11.2  $\mu\text{g g}^{-1}$ ). The range of the "accepted" results is very wide (0.59 - 3.60  $\mu\text{g g}^{-1}$ ) but their dispersion is comparable to that of the results of the worldwide intercomparison from which no certified consensus value could be derived. It is interesting to notice that the central values of both exercises are close to each other (1.8 and 1.9  $\mu\text{g g}^{-1}$ ). Most results were obtained by graphite furnace-AAS and some of them by flame-AAS. No systematic difference between both techniques was found. As far as the lead determinations in the sediment sample are concerned (Table No. 26), one result is obviously too low (55.9  $\mu\text{g g}^{-1}$ ) and was detected as an outlier by the t-test. The other results are pretty grouped and their range is well centered on the certified consensus value (120  $\mu\text{g g}^{-1}$ ). Almost all determinations were performed by flame-AAS which is a sufficiently sensitive method at this concentration level.

The reported data for the determination of selenium in the mussel sample are satisfactory (Table No. 12). All results lie in the confidence interval of the certified consensus value (1.70 - 2.56  $\mu\text{g g}^{-1}$ ). They were obtained by NAA and AAS (hydride generation technique). Only two results of determination of selenium in the sediment sample were reported (Table No. 28). One result was obtained by AAS (hydride generation) and is close to the non-certified information value of the worldwide intercomparison (2.9  $\mu\text{g g}^{-1}$ ). The other result was obtained by NAA (instrumental) and seems to be too high (4.51  $\mu\text{g g}^{-1}$ ).

Fourteen results of determination of zinc in the mussel sample were reported (Table No. 15). One result is obviously too low (15.4  $\mu\text{g g}^{-1}$ ) and was found to be an outlier by the t-test. The "accepted" results are spread on a wide range which gives a factor 2 between the extreme values (107 - 214  $\mu\text{g g}^{-1}$ ). This is surprising because, in principle, zinc is easy to determine in biological materials. Since most of the determinations were done by flame-AAS, one can assume that uncorrected chemical interferences and possibly contamination errors during analysis are responsible for such a dispersion of the data. The range of reported results, however, is relatively well centered on the certified consensus value from the worldwide intercomparison (156.5  $\mu\text{g g}^{-1}$ ). As far as the results reported for the determination of zinc in sediment are concerned (Table No. 30), one can observe that they are also spread on a wide range. Two results are obviously too low (21.0 and 41.3  $\mu\text{g g}^{-1}$ ) but were not detected as outliers by the t-test at the  $\alpha = 0.01$  significance level, probably because all results are too much dispersed. All other results lie in the range 281 - 688  $\mu\text{g g}^{-1}$ , which is relatively well centered on the certified consensus value from the worldwide intercomparison (439  $\mu\text{g g}^{-1}$ ). The scatter of results, therefore, is more evident for the sediment sample than in the case of the mussel sample. Here, uncorrected chemical interferences and contamination errors during analysis are probably the cause of this dispersion since most results were obtained by flame-AAS.

## 6. CONCLUSIONS

With the exception of the determination of two elements in the sediment sample, one can state that the results of these MEDPOL intercomparison runs do not show any significant difference from the results of the corresponding worldwide exercises. The quality of the results is approximately the same in both situations. With some exceptions it seems, therefore, that at present the analytical work of Mediterranean institutes has reached a level of quality comparable to that of laboratories located in other parts of the world, as far as the analysis of trace metals in marine biological and geological materials is concerned.

It should be noted, however, that the number of analytical methods which were used in these MEDPOL intercomparisons was rather limited. In the case of the mussel MA-M-2/TM, about 85% of the reported results were obtained by AAS in its various forms (flame, graphite furnace, etc.) while approximately 12% of the determinations were done by NAA (instrumental or radiochemical) and 3% by ASV. In the case of the sediment SD-N-1/2/TM, about 83% of the reported results were obtained by AAS, 13% by NAA and 4% by ASV. No determinations were reported for other analytical techniques of trace element determinations such as X-ray fluorescence or plasma atomic emission spectroscopy.

The within-laboratory precision is satisfactory as shown by the following figures:

For the mussel MA-M-2/TM, 65% of the reported coefficients of variation lie between 0 and 10%, 25% are between 10 and 20%, 9% between 20 and 30% and only 1% higher than 30%. In the case of the sediment SD-N-1/2/TM, 90% of the reported coefficients of variation lie between 0 and 10% and the remaining 10% are between 10 and 20%. The overall within-laboratory precision is, therefore, better in the case of the SD-N-1/2/TM exercise. This could be expected, since the trace element concentrations are higher in the sediment sample than in the mussel sample.

The total number of outliers is moderate (9.2% of all results in the case of MA-M-2/TM and 3.0% in the case of SD-N-1/2/TM). The number of outlying results by participating laboratory varied between 0 and 4. Five laboratories produced 1 outlier, two laboratories reported 2 outliers and one laboratory produced 4 outliers (for 11 reported results). This laboratory should carefully revise its analytical procedures for trace element analysis.

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TABLE NO. 1.

RESULTS OF INTERCOMPARISON FOR Ag (MUSSEL MA-M-2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	15	Flame-AAS	6	0.022	18.8%
2	19	INAA	3	0.060	18.6%
3	14	GF-AAS	10	0.188	2.2%

No certified consensus value from the worldwide intercomparison information value (worldwide intercomparison): 0.054 microgram/gram

Confidence interval: 0.045 - 0.062 microgram/gram.

TABLE NO. 2

RESULTS OF INTERCOMPARISON FOR As (MUSSEL MA-M-2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	14	Hydride-AAS	10	6.9	4.2%
2	19	RNAA	6	13.3	1.6%
3	1	Hydride-AAS	6	14.2	1.8%

Certified consensus value (worldwide intercomparison): 12.8 microgram/gram

Confidence interval: 11.8 - 14.4 microgram/gram

TABLE NO. 3

RESULTS OF INTERCOMPARISON FOR Cd (MUSSEL MA-M-2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	14	GF-AAS	9	0.35*	1.0%
2	8	GF-AAS	2	0.55*	-
3	9	GF-AAS	4	1.12	2.7%
4	1	ASV	6	1.37	7.9%
5	7	Flame-AAS	6	1.42	4.9%
6	19	RNAA	6	1.42	3.1%
7	4	GF-AAS	6	1.43	14.0%
8	16A	GF-AAS	5	1.50	12.9%
9	15	Flame-AAS	6	1.55	1.7%
10	3	GF-AAS	6	1.57	1.9%
11	12	Flame-AAS	6	1.63	7.9%
12	16B	GF-AAS	5	1.65	16.5%
13	6B	GF-AAS	6	1.81	12.9%
14	6A	GF-AAS	6	2.71*	10.6%
15	17	GF-AAS	5	9.68*	21.1%

Certified consensus value (worldwide intercomparison): 1.32 microgram/gram

Confidence interval: 1.16 - 1.54 microgram/gram.

TABLE NO. 4

RESULTS OF INTERCOMPARISON FOR Co (MUSSEL MA-M-2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	1	ASV	6	0.48	2.9%
2	5	Flame-AAS	1	0.50	-
3	19A	INAA	4	0.94	19.8%
4	16A	GF-AAS	5	0.98	14.5%
5	19B	RNAA	6	1.10	5.7%
6	16B	GF-AAS	5	1.29	7.1%
7	14	GF-AAS	9	1.61	6.5%

Certified consensus value (worldwide intercomparison): 0.88 microgram/gram

Confidence interval: 0.75 - 1.07 microgram/gram



TABLE NO. 5

RESULTS OF INTERCOMPARISON FOR Cr (MUSSEL MA-M-2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	17	GF-AAS	5	1.05	25.4%
2	19	INAA	4	1.22	17.7%
3	16A	GF-AAS	5	1.47	20.1%
4	6B	GF-AAS	6	1.55	23.8%
5	7	Flame-AAS	6	1.72	8.2%
6	16B	GF-AAS	5	1.78	36.1%
7	6A	GF-AAS	6	1.89	17.6%
8	15	Flame-AAS	6	2.45	9.1%

Certified consensus value (worldwide intercomparison): 1.25 microgram/gram

Confidence interval: 0.95 - 1.62 microgram/gram.

TABLE NO. 6.

RESULTS OF INTERCOMPARISON FOR Cu (MUSSEL MA-M-2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	5	Flame-AAS	1	2.00*	—
2	4	Flame-AAS	6	6.05	4.9%
3	14	Flame-AAS	10	7.00	0.0%
4	19	RNAA	6	8.01	2.4%
5	7	Flame-AAS	6	8.38	2.6%
6	1	GF-AAS	6	8.40	4.5%
7	15	Flame-AAS	6	8.41	1.4%
8	16A	GF-AAS	5	8.48	13.8%
9	3	Flame-AAS	7	8.60	1.2%
10	16B	GF-AAS	5	8.67	23.7%
11	12	Flame-AAS	6	10.0	3.7%
12	9	Flame-AAS	4	13.3*	6.5%

Certified consensus value (worldwide intercomparison): 7.96 microgram/gram

Confidence interval: 7.53 - 8.44 microgram/gram

TABLE NO. 7

RESULTS OF INTERCOMPARISON FOR Fe (MUSSEL MA-M-2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	5	Flame-AAS	1	181.8	—
2	6A	Flame-AAS	6	257.1	9.6%
3	7	Flame-AAS	6	257.8	1.6%
4	16A	GF-AAS	5	271.8	2.4%
5	6B	Flame-AAS	6	285.8	12.4%
6	4	Flame-AAS	6	296.2	4.5%
7	16B	GF-AAS	5	300.0	13.2%
8	14	Flame-AAS	10	338.0	1.2%

Certified consensus value (worldwide intercomparison): 256.2 microgram/gram

Confidence interval: 229.2 - 268.2 microgram/gram

TABLE NO. 8

RESULTS OF INTERCOMPARISON FOR Hg (MUSSEL MA-M-2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	8	CV-AAS	2	0.35	—
2	7	CV-AAS	5	0.38	15.0%
3	9	CV-AAS	4	0.76	12.4%
4	12	CV-AAS	6	0.83	1.4%
5	16A	CV-AAS	5	0.88	10.2%
6	19	RNAA	6	0.89	2.1%
7	16B	CV-AAS	5	1.00	8.0%
8	1	CV-AAS	6	1.03	2.2%
9	4	CV-AAS	6	1.06	5.0%
10	6B	CV-AAS	6	1.08	1.8%
11	3	CV-AAS	7	1.08	3.2%
12	15	CV-AAS	6	1.18	3.5%
13	18	CV-AAS	1	1.18	—
14	6A	CV-AAS	5	1.31	12.1%
15	14	CV-AAS	10	1.85*	9.3%

Certified consensus value (worldwide intercomparison): 0.95 microgram/gram

Confidence interval: 0.85 - 1.06 microgram/gram

TABLE NO. 9

RESULTS OF INTERCOMPARISON FOR Mn (MUSSEL MA-M-2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	19	RNAA	3	63.2	2.6%
2	7	Flame-AAS	6	66.1	2.2%
3	3	Flame-AAS	9	67.0	3.7%
4	6B	Flame-AAS	6	68.4	2.8%
5	6A	Flame-AAS	6	72.5	8.4%
6	16A	GF-AAS	5	73.1	4.5%
7	4	Flame-AAS	6	73.3	4.9%
8	14	Flame-AAS	10	77.0	0.6%
9	16B	GF-AAS	5	87.4*	11.8%

Certified consensus value (worldwide intercomparison): 67.1 microgram/gram

Confidence interval: 60.7 - 75.3 microgram/gram

TABLE NO. 10

RESULTS OF INTERCOMPARISON FOR Ni (MUSSEL MA-M-2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	15	Flame-AAS	6	0.63	14.2%
2	1	ASV	6	1.33	6.1%
3	16A	GF-AAS	4	1.53	19.6%
4	16B	GF-AAS	4	1.76	23.2%
5	7	Flame-AAS	6	4.95*	11.1%

No certified consensus value from the worldwide intercomparison range of accepted laboratory means (worldwide intercomparison): 0.78 - 2.49 microgram/gram.

TABLE NO. 11

RESULTS OF INTERCOMPARISON FOR Pb (MUSSEL MA-M-2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	14	GF-AAS	8	0.59	4.6%
2	7	GF-AAS	6	0.70	10.0%
3	16A	GF-AAS	6	0.87	22.2%
4	5	Flame-AAS	1	1.30	—
5	9	GF-AAS	4	1.64	3.1%
6	16B	GF-AAS	6	1.72	25.2%
7	3	GF-AAS	5	2.03	1.5%
8	4	GF-AAS	6	2.20	15.4%
9	15	Flame-AAS	6	2.24	8.6%
10	1	GF-AAS	6	2.29	4.5%
11	6B	GF-AAS	6	2.34	19.6%
12	6A	GF-AAS	4	3.60	16.0%
13	12	Flame-AAS	6	11.20*	6.2%

No certified consensus value from the worldwide intercomparison information value (worldwide intercomparison): 1.92 microgram/gram confidence interval: 1.53 - 2.50 microgram/gram

TABLE NO. 12

RESULTS OF INTERCOMPARISON FOR Se (MUSSEL MA-M-2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	19B	RNAA	5	1.94	5.7%
2	19A	INAA	4	2.24	5.5%
3	4	Hydride-AAS	6	2.40	26.4%
4	3	Hydride-AAS	6	2.40	4.2%
5	1	Hydride-AAS	6	2.56	2.4%

Certified consensus value (worldwide intercomparison): 2.27 microgram/gram

Confidence interval: 1.70 - 2.56 microgram/gram

TABLE NO. 13

RESULTS OF INTERCOMPARISON FOR Sb (MUSSEL MA-M-2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	19	RNAA	6	0.038	6.6%

No certified consensus value from the worldwide intercomparison information value (worldwide intercomparison): 0.027 microgram/gram

Confidence interval: 0.026 - 0.030 microgram/gram



TABLE NO. 14

RESULTS OF INTERCOMPARISON FOR V (MUSSEL MA-M-2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	16A	GF-AAS	2	1.75	—
2	16B	GF-AAS	2	2.29	—

No certified consensus value from the worldwide intercomparison

Range of accepted laboratory means (worldwide intercomparison): 0.84 - 2.18 microgram/gram

TABLE NO. 15

RESULTS OF INTERCOMPARISON FOR Zn (MUSSEL MA-M-2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	5	Flame-AAS	1	15.4*	—
2	19B	RNAA	6	107.3	1.7%
3	19A	INAA	4	116.8	5.3%
4	6B	Flame-AAS	6	149.6	5.3%
5	9	Flame-AAS	3	159.2	0.8%
6	12	Flame-AAS	6	159.8	10.3%
7	7	Flame-AAS	6	160.5	3.3%
8	1	ASV	6	167.8	6.5%
9	3	Flame-AAS	9	177.0	1.7%
10	16B	Flame-AAS	6	178.2	24.6%
11	14	Flame-AAS	10	182.7	1.1%
12	16A	Flame-AAS	6	183.4	3.4%
13	4	Flame-AAS	6	197.7	5.6%
14	6A	Flame-AAS	5	214.3	10.5%

Certified consensus value (worldwide intercomparison): 156.5 microgram/gram

Confidence interval: 152.8 - 166.7 microgram/gram

TABLE NO. 16

RESULTS OF INTERCOMPARISON FOR Ag (SEDIMENT SD-N-1/2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	19	INAA	4	2.21	4.8%

Certified consensus value (worldwide intercomparison): 2.3 microgram/gram

Confidence interval: 2.0 - 3.2 microgram/gram

TABLE NO. 17

RESULTS OF INTERCOMPARISON FOR As (SEDIMENT SD-N-1/2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	1	Hydride-AAS	6	55.8	2.3%
2	19	RNAA	6	61.6	3.9%

Certified consensus value (worldwide intercomparison): 50.0 microgram/gram

Confidence interval: 42.4 - 60.0 microgram/gram

TABLE NO. 18

RESULTS OF INTERCOMPARISON FOR Cd (SEDIMENT SD-N-1/2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	8	GF-AAS	1	0.79*	--
2	10	Flame-AAS	1	10.4	--
3	1	ASV	6	10.7	4.4%
4	13	Flame-AAS	5	11.0	2.8%
5	19	RNAA	6	11.0	3.6%
6	7	Flame-AAS	6	11.1	3.1%
7	16	GF-AAS	6	11.8	4.4%
8	6B	Flame-AAS	6	12.4	1.2%
9	2	Flame-AAS	4	12.6	2.0%
10	6A	GF-AAS	6	13.4	10.4%
11	11	Flame-AAS	6	13.9	10.4%
12	17	Flame-AAS	6	15.3	3.4%

Certified consensus value (worldwide intercomparison): 11.0 microgram/gram

Confidence interval: 10.0 - 12.0 microgram/gram

TABLE NO. 19

RESULTS OF INTERCOMPARISON FOR Co (SEDIMENT SD-N-1/2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	5	Flame-AAS	1	4.7	-
2	2	Flame-AAS	4	8.4	5.9%
3	11	Flame-AAS	6	10.1	11.5%
4	16	Flame-AAS	6	10.4	5.6%
5	1	ASV	6	10.5	10.7%
6	19A	INAA	4	11.1	7.7%
7	19B	RNAA	6	12.6	5.4%

Certified consensus value (worldwide intercomparison): 12.1 microgram/gram

Confidence interval: 11.2 - 12.7 microgram/gram

TABLE NO. 20

RESULTS OF INTERCOMPARISON FOR Cr (SEDIMENT SD-N-1/2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	11	Flame-AAS	6	25.2	4.2%
2	16	Flame-AAS	6	48.1	2.9%
3	17	Flame-AAS	6	52.5	5.4%
4	13	Flame-AAS	5	71.5	3.6%
5	7	Flame-AAS	6	76.5	7.4%
6	6A	Flame-AAS	6	77.5	13.7%
7	6B	Flame-AAS	6	98.8	1.6%
8	2	Flame-AAS	4	132.0	1.3%
9	19	INAA	4	161.8	5.4%

Certified consensus value (worldwide intercomparison): 149 microgram/gram  
Confidence interval: 125 - 161 microgram/gram

TABLE NO. 21

RESULTS OF INTERCOMPARISON FOR Cu (SEDIMENT SD-N-1/2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	5	Flame-AAS	1	13.4*	—
2	11	Flame-AAS	6	46.6	2.5%
3	13	Flame-AAS	5	55.0	9.9%
4	19	RNAA	6	66.5	5.3%
5	2	Flame-AAS	4	66.9	3.8%
6	10	Flame-AAS	3	67.0	2.6%
7	6	Flame-AAS	6	69.5	4.4%
8	7	Flame-AAS	6	70.0	2.3%
9	1	GF-AAS	6	77.3	6.1%
10	16	Flame-AAS	6	82.2	5.3%

Certified consensus value (worldwide intercomparison): 72.2 microgram/gram

Confidence interval: 68.1 - 75.2 microgram/gram

TABLE NO. 22

RESULTS OF INTERCOMPARISON FOR Fe (SEDIMENT SD-N-1/2/TM)

Unit: Milligram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	5	Flame-AAS	1	0.11	--
2	11	Flame-AAS	6	15.2	5.8%
3	6A	Flame-AAS	6	24.0	11.7%
4	6B	Flame-AAS	6	24.8	3.5%
5	2	Flame-AAS	4	25.0	0.8%
6	16	Flame-AAS	6	28.8	6.0%
7	7	Flame-AAS	6	29.0	4.5%
8	13	Flame-AAS	5	39.0	5.5%

No certified consensus value from the worldwide intercomparison information value (worldwide intercomparison): 36.4 milligram/gram

Confidence interval: 35.3 - 37.8 milligram/gram



TABLE NO. 23

RESULTS OF INTERCOMPARISON FOR Hg (SEDIMENT SD-N-1/2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	8	CV-AAS	1	0.13	—
2	13	CV-AAS	5	0.73	7.1%
3	7	CV-AAS	4	0.85	11.4%
4	16	CV-AAS	6	1.21	8.7%
5	19	RNAA	6	1.54	4.1%
6	1	CV-AAS	6	1.73	0.6%
7	10	CV-AAS	6	1.78	4.9%
8	6B	CV-AAS	6	1.95	0.8%
9	6A	CV-AAS	6	2.14	6.8%

No certified consensus value from the worldwide intercomparison.

Information value (worldwide intercomparison): 1.46 microgram/gram

Confidence interval: 0.06 - 1.72 microgram/gram

TABLE NO. 24

RESULTS OF INTERCOMPARISON FOR Mn (SEDIMENT SD-N-1/2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	16	Flame-AAS	6	603.2	4.3%
2	11	Flame-AAS	6	644.8	2.1%
3	7	Flame-AAS	6	699.0	3.0%
4	10	Flame-AAS	3	742.0	4.4%
5	6A	Flame-AAS	6	764.0	6.8%
6	6B	Flame-AAS	6	769.0	3.5%
7	13	Flame-AAS	5	771.6	3.2%
8	2	Flame-AAS	4	800.8	2.0%
9	19	RNAA	6	830.5	2.3%

Certified consensus value (worldwide intercomparison): 777 microgram/gram

Confidence interval: 728 - 801 microgram/gram

TABLE NO. 25

RESULTS OF INTERCOMPARISON FOR Ni (SEDIMENT SD-N-1/2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	11	Flame-AAS	6	19.5	5.8%
2	5	Flame-AAS	1	22.0	—
3	16	Flame-AAS	6	22.1	5.5%
4	7	Flame-AAS	6	26.2	4.2%
5	2	Flame-AAS	4	27.1	1.3%
6	10	Flame-AAS	3	28.5	4.6%
7	13	Flame-AAS	5	31.4	2.8%
8	1	ASV	6	36.3	2.3%

Certified consensus value (worldwide intercomparison): 31.0 microgram/gram

Confidence interval: 27.0 - 34.0 microgram/gram

TABLE NO. 26

RESULTS OF INTERCOMPARISON FOR Pb (SEDIMENT SD-N-1/2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	5	Flame-AAS	1	55.9*	-
2	10	Flame-AAS	3	108.7	1.9%
3	16	Flame-AAS	6	108.8	3.9%
4	13	Flame-AAS	5	112.6	4.7%
5	2	Flame-AAS	4	114.0	0.6%
6	6B	Flame-AAS	6	128.6	3.3%
7	7	Flame-AAS	6	134.5	16.4%
8	11	Flame-AAS	6	136.8	3.5%
9	1	GF-AAS	6	139.9	2.7%
10	6A	Flame-AAS	6	150.0	8.3%

Certified consensus value (worldwide intercomparison): 120 microgram/gram

Confidence interval: 112 - 132 microgram/gram

TABLE NO. 27

RESULTS OF INTERCOMPARISON FOR Sb (SEDIMENT SD-N-1/2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	19	RNAA	6	2.04	17.1%

Certified consensus value (worldwide intercomparison): 3.62 microgram/gram  
Confidence interval: 3.20 - 3.95 microgram/gram

TABLE NO. 28

RESULTS OF INTERCOMPARISON FOR Se (SEDIMENT SD-N-1/2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	1	Hydride-AAS	6	2.78	2.6%
2	19	INAA	4	4.51	6.8%

No certified consensus value from the worldwide intercomparison information value (worldwide intercomparison): 2.90 microgram/gram  
Confidence interval: 2.30 - 3.78 microgram/gram

TABLE NO. 29

RESULTS OF INTERCOMPARISON FOR V (SEDIMENT SD-N-1/2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	16	GF-AAS	6	20.6	7.7%

Certified consensus value (worldwide intercomparison): 77.7 microgram/gram

Confidence interval: 65.0 - 80.7 microgram/gram

TABLE NO. 30

RESULTS OF INTERCOMPARISON FOR Zn (SEDIMENT SD-N-1/2/TM)

Unit: Microgram/gram (dry-weight)

No.	Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	16	Flame-AAS	6	21.0	1.7%
2	5	Flame-AAS	1	41.3	—
3	19A	INAA	4	281.0	8.8%
4	19B	RNAA	6	330.0	3.1%
5	11	Flame-AAS	6	369.8	2.1%
6	7	Flame-AAS	6	372.5	4.5%
7	1	ASV	6	419.3	4.5%
8	6B	Flame-AAS	6	433.3	2.6%
9	13	Flame-AAS	5	460.2	4.2%
10	10	Flame-AAS	2	553.0	—
11	2	Flame-AAS	4	586.5	7.6%
12	6A	Flame-AAS	5	688.5	5.2%

Certified consensus value (worldwide intercomparison): 439 microgram/gram

Confidence interval: 423 - 452 microgram/gram.

TABLE NO. 31

OVERALL MEANS OF THE MEDPOL RESULTS COMPARED TO THE CONSENSUS VALUES  
(MA-M-2/TM)

Concentration unit:  $\mu\text{g.g}^{-1}$  (of dry-weight)

ELEMENT	MEDPOL RESULTS (mean value)	WORLDWIDE RESULTS (consensus value)
Ag	(0.022-0.188)*	0.054 (0.045 - 0.062)**
As	(6.9 - 14.2)*	12.8 (11.8 - 14.4)
Cd	1.50 $\pm$ 0.12	1.32 (1.16 - 1.54)
Co	0.99 $\pm$ 0.38	0.88 (0.75 - 1.07)
Cr	1.64 $\pm$ 0.36	1.25 (0.95 - 1.62)
Cu	8.20 $\pm$ 0.74	7.96 (7.53 - 8.44)
Fe	273.6 $\pm$ 38.0	256.2 (229.2 - 268.2)
Hg	0.93 $\pm$ 0.16	0.95 (0.85 - 1.06)
Mn	70.1 $\pm$ 3.9	67.1 (60.7 - 75.3)
Ni	(0.63 - 1.76)*	(0.78 - 2.49)**
Pb	1.79 $\pm$ 0.54	1.92 (1.53 - 2.50)**
Se	2.31 $\pm$ 0.29	2.27 (1.70 - 2.56)
Sb	(0.038)*	0.027 (0.026 - 0.030)**
V	(1.75 - 2.29)*	(0.84 - 2.18)**
Zn	165.7 $\pm$ 17.8	156.5 (152.8 - 166.7)

\* Range of "accepted" results (insufficient number of data)

\*\* No certified consensus value. An information value or the range of "accepted" results is given instead.

NOTE: Confidence intervals are given for a significance level  $\alpha = 0.05$

TABLE NO. 32

OVERALL MEANS OF THE MEDPOL RESULTS COMPARED TO THE CONSENSUS VALUES

(SD-N-1/2/TM)

Concentration unit:  $\mu\text{g.g}^{-1}$  (of dry-weight) except Fe which is expressed in  $\text{mg.g}^{-1}$  of dry-weight.

ELEMENT	MEDPOL RESULTS (mean value)	WORLDWIDE RESULTS (consensus value)
Ag	(2.21)*	2.3 (2.0-3.2)
As	(55.8 - 61.6)*	50.0 (42.4 - 60.0)
Cd	12.1 $\pm$ 1.0	11.0 (10.0 - 12.0)
Co	9.7 $\pm$ 2.4	12.1 (11.2 - 12.7)
Cr	82.7 $\pm$ 32.8	149 (125 - 161)
Cu	66.8 $\pm$ 8.2	72.2 (68.1 - 75.2)
Fe	23.2 $\pm$ 9.6	36.4 (35.3 - 37.8)**
Hg	1.34 $\pm$ 0.51	1.46 (0.06 - 1.72)**
Mn	736.1 $\pm$ 56.8	777 (728 - 801)
Ni	26.6 $\pm$ 4.6	31.0 (27.0 - 34.0)
Pb	126.0 $\pm$ 11.8	120 (112 - 132)
Sb	(2.04)*	3.62 (3.20 - 3.95)
Se	(2.78 - 4.51)*	2.90 (2.30 - 3.78)**
V	(20.6)*	77.7 (65.0 - 80.7)
Zn	379.7 $\pm$ 126.3	439 (423 - 452)

\* Range of "accepted" results (insufficient number of data)

\*\* No certified consensus value. An information value or the range of "accepted" results is given instead.

NOTE: Confidence intervals are given for a significance level  $\alpha = 0.05$



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