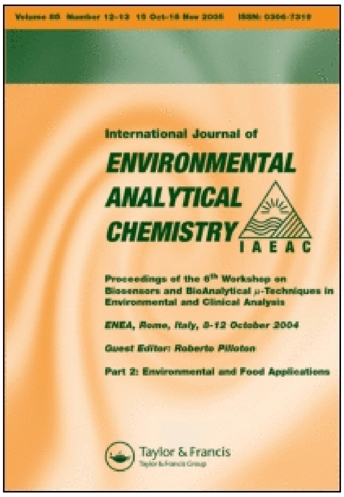

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ANALYTICAL INTERCOMPARISON EXERCISES AND HARMONIZATION WITHIN ENVIRONMENTAL LABORATORIES FROM DEVELOPING COUNTRIES

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Since the early 60's, the IAEA implements a Quality Assurance (QA) programme for the Member States. As part of this programme, the IAEA organized more than 150 analytical intercomparison exercises and produced more than 70 Certified Reference Materials for a wide range of determinands, encompassing radionuclides, trace elements, petroleum hydrocarbons, pesticides and PCBs. From the IAEA – Marine Environment Laboratory in Monaco, analytical Quality Assurance services are provided for non-nuclear contaminants in marine materials.

Results of recently organized worldwide intercomparison exercises using the sample materials IAEA-142 (mussel tissue homogenate) and IAEA-140 (seaweed homogenate), show that some progress was achieved worldwide in the analyses of the more common environmental contaminants. However, results also show that difficulties in obtaining accurate data for trace elements and especially for organic contaminants are still widespread, particularly in developing countries. Therefore, the success of international cooperative programmes as well as of many regional environmental monitoring programmes, depends on improved quality and comparability of data which has to be achieved still through reinforced Quality Assurance programmes. To this aim, the IAEA/UNEP/IOC-UNESCO inter-agency programme on marine pollution promotes the adoption of Reference Methods for harmonization of techniques used in developing and developed countries, organizes frequent intercomparison exercises, and produces certified marine Reference Materials which are made available to laboratories worldwide.

Keywords: Quality Assurance; intercomparison exercises; reference materials; organochlorine pesticides; PCBs; petroleum hydrocarbons; trace elements

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INTRODUCTION

Since the early 60s the International Atomic Energy Agency (IAEA) has been supporting programmes for improving analytical quality in the Member States. This has been achieved through organizing inter-laboratory comparison exercises, producing and supplying reference materials, and developing schemes for promoting Quality Assurance and Quality Control (QA/QC) in such diverse fields as Nuclear Physics, Health, Nutrition and Environment [1]. In total, the IAEA organized more than 150 analytical intercomparison exercises and produced more than 70 Reference Materials. In the last 20 years the IAEA – Marine Environment Laboratory in Monaco provided QA support to the measurement of contaminants in the marine environment through organizing 25 intercomparison exercises and producing 20 marine Reference Materials. Intercomparison samples and Reference Materials produced cover a variety of sample matrices such as sediments, mussels, fish, and seaweeds, as well as a wide range of analytes such as pesticides, PCBs, petroleum hydrocarbons, trace metals and natural and man-made radionuclides. A catalogue of Quality Assurance materials provided by the IAEA is also periodically published and distributed to laboratories around the world, and a data base is maintained on reference materials available from all international suppliers [2].

Quality Assurance programmes have been also started by other organizations and, today, the awareness for QA/QC in analytical laboratories is fairly widespread. Nevertheless, the results obtained through the IAEA Quality Assurance programmes show that the QA/QC effort has to be maintained. Furthermore, the current offer of intercomparison exercises and reference materials is probably not sufficient to meet the present and future needs of environmental laboratories.

This paper reviews the results of some recent analytical inter-laboratory exercises and identifies common limitations of worldwide analytical capabilities in the measurement of environmental contaminants. Furthermore, it identifies the need for strengthening inter-laboratory exercises and harmonization of analytical protocols.

QUALITY ASSURANCE AND INTER-LABORATORY COMPARISON EXERCISES

Quality Assurance protocols aim at ensuring the precision and accuracy of analytical results and include the regular participation in some kind of proficiency testing or inter-laboratory comparison, along with other prescribed procedures such as the frequent use of Certified Reference Materials in validation of techniques, the use of Quality Control Charts, and Good Laboratory Practice [3].

Today environment laboratories are challenged with increasing requirements for accurate results in national monitoring programmes. For example, laboratories are frequently called to control contaminants in food, drinking water, and waste discharges and, hence, results have implications on quality of the environment, compliance of waste discharges, trade of foods and on public health. Furthermore, feed-back from laboratory data is needed to evaluate the effectiveness of measures taken to control and abate environmental pollution. Simultaneously, transboundary environmental pollution problems usually require the collaborative effort of international laboratory networks. This is the case, for example, with the implementation of the E.U. directives on micropollutants in drinking water and international rivers. Also, International agreements such as the UN Conference on the Law of the Sea, the Montreal Convention, the Global Programme of Action for the Protection of the Marine Environment from Land-based Activities, and regional agreements, stipulate the duty of the states to carry out monitoring programmes for assessing the contamination of the seas [4,5]. This global assessment of the health of the environment and of the oceans will depend upon the capacity of the states to implement the required monitoring programmes. Henceforth, it will depend upon the quality and comparability of data reported by laboratories worldwide, which has to be ensured. The organization of inter-laboratory comparison exercises is, thus, an essential tool to achieve this aim.

For the analysts involved with the determination of measurands in environmental materials, it is of capital importance to know how close their results are to the true concentration of analytes in the sample material. Although a number of self quality control procedures can be incorporated in the routine of the laboratory (e.g., Quality Control Charts, frequent analysis of a standard material prepared in the laboratory), for that purpose the analysts seek participation in unbiased tests of analytical performance. This is usually achieved with inter-laboratory comparisons which are carried out through analysis of identical samples of an homogeneous material distributed to the participants.

The preparation of an intercomparison sample requires the selection and handling of a large amount of suitable material. For instance, the preparation of a marine sediment may require 0.5 tonnes of wet sediment to obtain 100 kg of freeze-dried and sieved (<125μm) fine sediment. The material has to be thoroughly homogenized which may take 2–3 weeks in a shaking drum, tested for homogeneity and stability through measurements of several properties (e.g., grain size distribution, concentration of analytes), dispensed into apropriate bottles, labelled and dispatched to the laboratories for analysis. The results obtained by the analysts are then reported to the organizing laboratory which carries out the statistical analyses of the data and assesses the accuracy of results. This is frequently done through identification of outlying results and evaluation of the performance of individual laboratories with the help of Z-scores relative to the best estimate of the true concentration of the analytes[6]. At the completion of the exercise, a report is issued and laboratory data are presented under a confidential code number [7,8,9].

The organization of inter-laboratory comparison exercises is, therefore, a complex task which can only be successfully carried out by well equipped and trained laboratories able to ensure adequate preparation and testing of the sample material. Harmonized protocols for proficiency testing of chemical laboratories have been agreed and the organization of these exercises shall meet internationally accepted standards [6,10]. In addition, as the participants in the exercise seek demonstration of analytical competence and quality, frequently for accreditation purposes, the exercise organizer shall be an independent and idoneous organization (government laboratory, international organization, or other).

RESULTS OF WORLDWIDE INTERCOMPARISON EXERCISES AND CURRENT CAPABILITIES TO MEASURE ENVIRONMENTAL CONTAMINANTS

Worldwide inter-laboratory comparison exercises allow for self-assessment of the quality of analytical results obtained in individual laboratories and, at the same time, allow also for assessing the overall capability to measure specific environmental contaminants [11].

In recent exercises a mussel tissue homogenate was proposed as intercomparison sample (IAEA-142) for the analyses of organic contaminants and distributed to 245 laboratories worldwide [7]. Results of the exercise show that the laboratories around the world do not have comparable accuracy and precision in the analysis of the contaminants (Figure 1). Data reported by 84 laboratories from 54 countries interested in the analysis of organochlorine pesticides and PCBs indicate that very few laboratories were able to identify and quantify all the common persistent organic compounds proposed. Furthermore, a large number of the results reported were outliers rejected by data screening statistical tests, and only about 50% of the accepted results were within the 95% confidence interval of the best estimate of the true concentration of analytes. A similar spread of results was observed also for petroleum hydrocarbons. It is also interesting to note that individual laboratories able to analyse with accuracy one given compound (e.g., DDE), did not demonstrate the same capability in the analyses of other persistent organochlorine compounds (e.g., endosulfan or heptachlor).

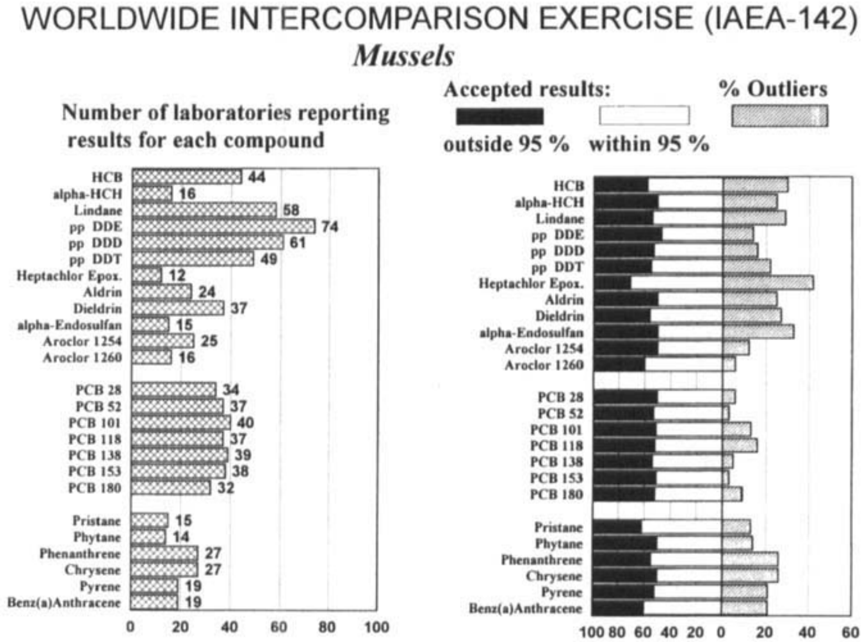

FIGURE 1 Results obtained in the worldwide intercomparison exercise completed in 1996 with the sample IAEA-142 (mussel tissue homogenate) for organic contaminants. From results reported by 84 laboratories for organochlorine compounds, approximately 35% were outliers and a further 50% were outside of the range of acceptable precision (95% confidence interval)

A similar inter-laboratory exercise was organized one year later, this time using as comparison material a seaweed *(Fucus)* sample (IAEA-140). The sample was distributed to 200 laboratories worldwide, mostly having analyzed also the mussel sample IAEA-142. Results for organochlorine compounds and petroleum hydrocarbons were reported by 80 laboratories from 51 countries [8]. The spread of results for each analyte in this sample, show again that only a relatively small percentage of the data were of acceptable accuracy (Figure 2). Furthermore, the bias in results indicate many too low values. Interestingly, laboratories which had obtained accurate results in the analyses of the mussel sample, showed in the intercomparison with the seaweed sample, poor performance due to matrix effects.

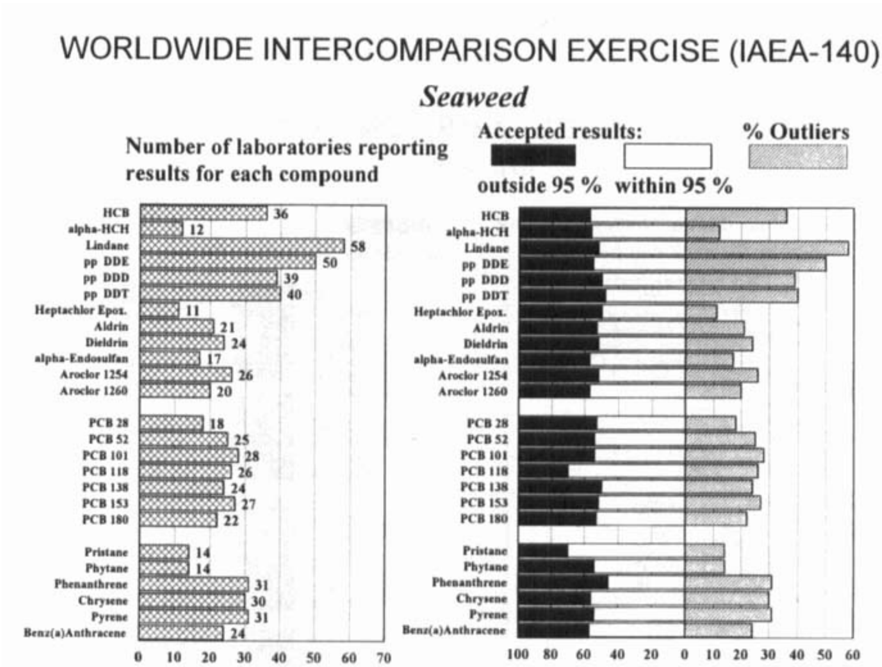

FIGURE 2 Results obtained in the worldwide intercomparison exercise completed in 1997 with the sample IAEA-140 (seaweed homogenate) for organic contaminants

A large number of laboratories carrying out environment measurements of trace metals, participated in the exercise with the seaweed sample IAEA-140 [9]. A total of 116 laboratories from 54 countries reported data for a total of 50 elements and methyl-Hg. On the whole, several sample preparation methods were used and the panoply of instrumental techniques included AAS, ICP-MS, INAA, ICP-AES and XRF. A summary of results for a selection of the 12 most commonly analyzed elements and 1 organo-metal compound is given in Figure 4. The results show that common elements such as Cu, may have a reduced number (8%) of statistical outliers, but only 22% of accepted results fall within the 95% confidence interval of the true concentration value. Other elements, such as Hg, showed a much higher percentage of statistical outliers but 46% of accepted results fall in the acceptable range of accuracy.

The graphic plot of the Z-scores of results reported for each element gives also information on the overall analytical performance and, in the case of metals such as copper and mercury, it indicates that many of the outliers may have poor performance due to contamination problems (Figure 5).

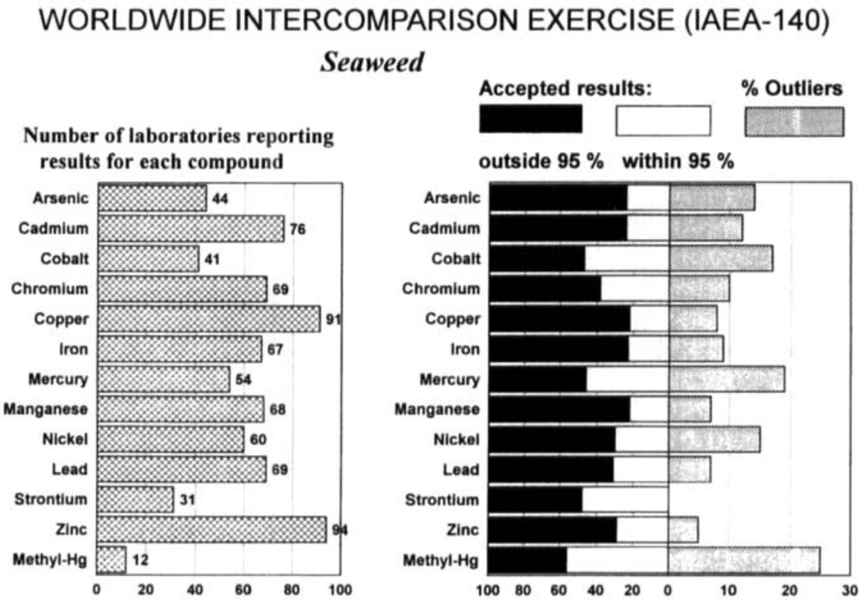

FIGURE 3 Results obtained in the worldwide intercomparison exercise completed in 1997 with the sample IAEA-140 (seaweed homogenate) for selected trace elements and methyl-mercury

The results obtained in the two inter-laboratory exercises (IAEA-142 and IAEA-140) carried out for organic contaminants with about a 1 year interval, show that little progress was achieved in the worldwide capability to measure these contaminants. However, progress is substantive in comparison with results of similar worldwide exercises carried out 10 or 15 years ago [12]. This indicates that the effect of QA and the feed-back of inter-laboratory exercises on analytical performance is a slow one.

Evaluation of the analytical performance by regions shows, likely without surprise, that accuracy is generally poorer in laboratories in Asia, Africa and Latin America (Figure 6). This generalization for trace metals analyses in Africa, Latin America and North America is, however, somewhat impaired because of weaker participation of laboratories from these regions in comparison with Europe. This geographic distribution of analytical difficulties suggests that more attention should be paid in those regions to Quality Assurance and Quality Control.

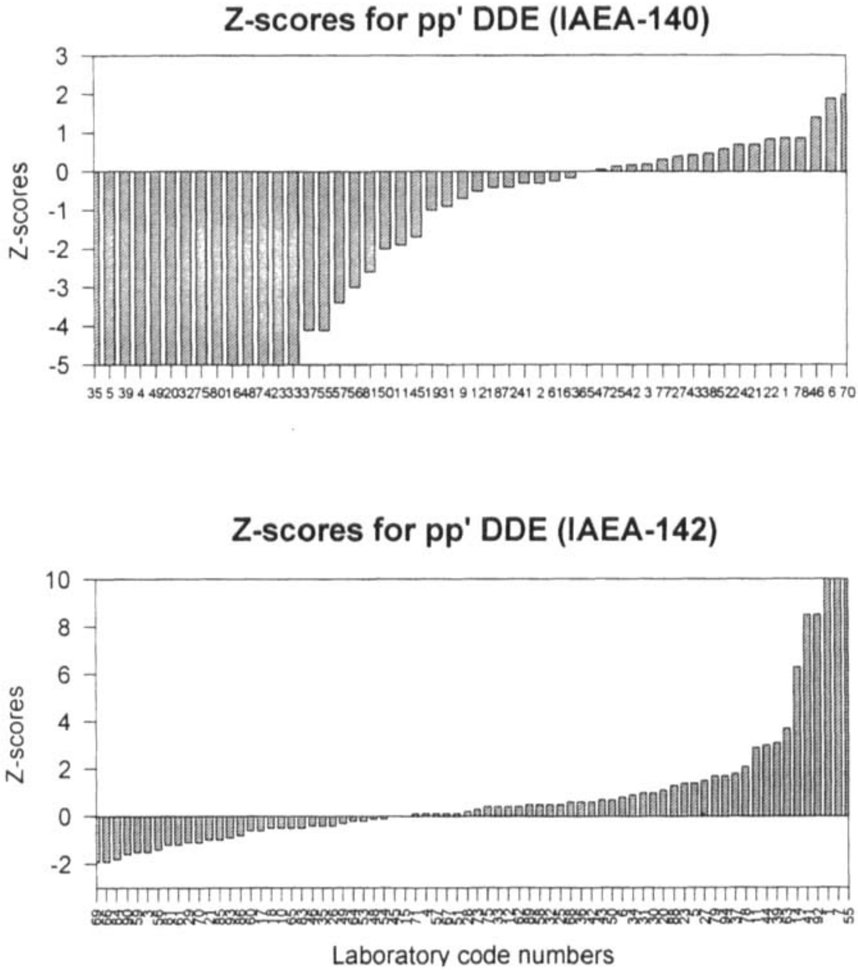

FIGURE 4 Results of intercomparison exercises with samples IAEA-142 (mussel) and IAEA-140 (seaweed). Data for individual participants in the analyses of pp'DDE are presented as Z-scores [7,8] and plotted in increasing order to Z-values. Z-scores between −2 and +2 correspond to acceptable accurate results

ANALYTICAL DIFFICULTIES OF THE LABORATORIES AND HARMONIZATION OF PROTOCOLS

The identification of the causes of inaccurate results and sources of error (inadequate blank values, calibration problems, random errors, etc.) is generally carried out as part of the evaluation of the exercise results[7, 8, 9], and is a valuable aid to the analyst for improving the data quality.

In the recent IAEA intercomparison exercises, the more common causes for the inaccurate results reported by laboratories were:

1. Use of inadequate or non-validated techniques. This is particularly obvious in the case of analysis of organic contaminants, in which several laboratories used inadequate sample extraction and extract clean-up procedures. Many laboratories that reported inaccurate results apply techniques which were not validated and thus failed to report on repeatibility, reproducibility, limit of detection and limit of quantitation.
2. Limited use of certified reference materials. Although the use of these materials is essential to validate the methods and to check and correct for matrix effects, many laboratories are not using them as yet. It is recognized, however, that in some cases (e.g., organic compounds in IAEA-140) there were no RMs available of a similar matrix to run at the time of the intercomparison exercise. In the analysis of trace metals, frequent sources of bias were contamination (e.g., Hg, Cd, Pb) and calibration problems.
3. Lack of analytical training. In many laboratories in developing countries, the analysts do not properly apply a given analytical technique or use a given instrument by lack of adequate training.

This evaluation of the sources of error based on the intercomparison exercises is in agreement with the answers to a questionnaire sent by the IAEA-MEL in 1997 to 350 laboratories around the world to assess QA procedures in use and to evaluate the need for further QA/QC support. The 117 answers received indicate that laboratories in developing countries have serious difficulties with the proper maintenance of expensive equipment, lack of training for analysts, request supply of reference materials and need advice on reference methods to facilitate the improvement of their work. It is also interesting to note that in the answers to the Questionnaire, there is a consensus – and request – amongst the analysts for organization of more frequent intercomparison exercises. Participation in these exercises is perceived as essential to "realize the difficulties" and "to motivate for enhanced accuracy".

In the work carried out by laboratories in developing countries, the selection of an adequate technique is frequently also a major difficulty. Advice in this matter is provided by the UNEP, IAEA, IOC-UNESCO Reference Methods series on Marine Pollution which includes about 70 titles and is supplied free-of-charge by UNEP. Adoption of the Reference Methods is intended to facilitate the harmonization of analytical protocols by environmental laboratories.

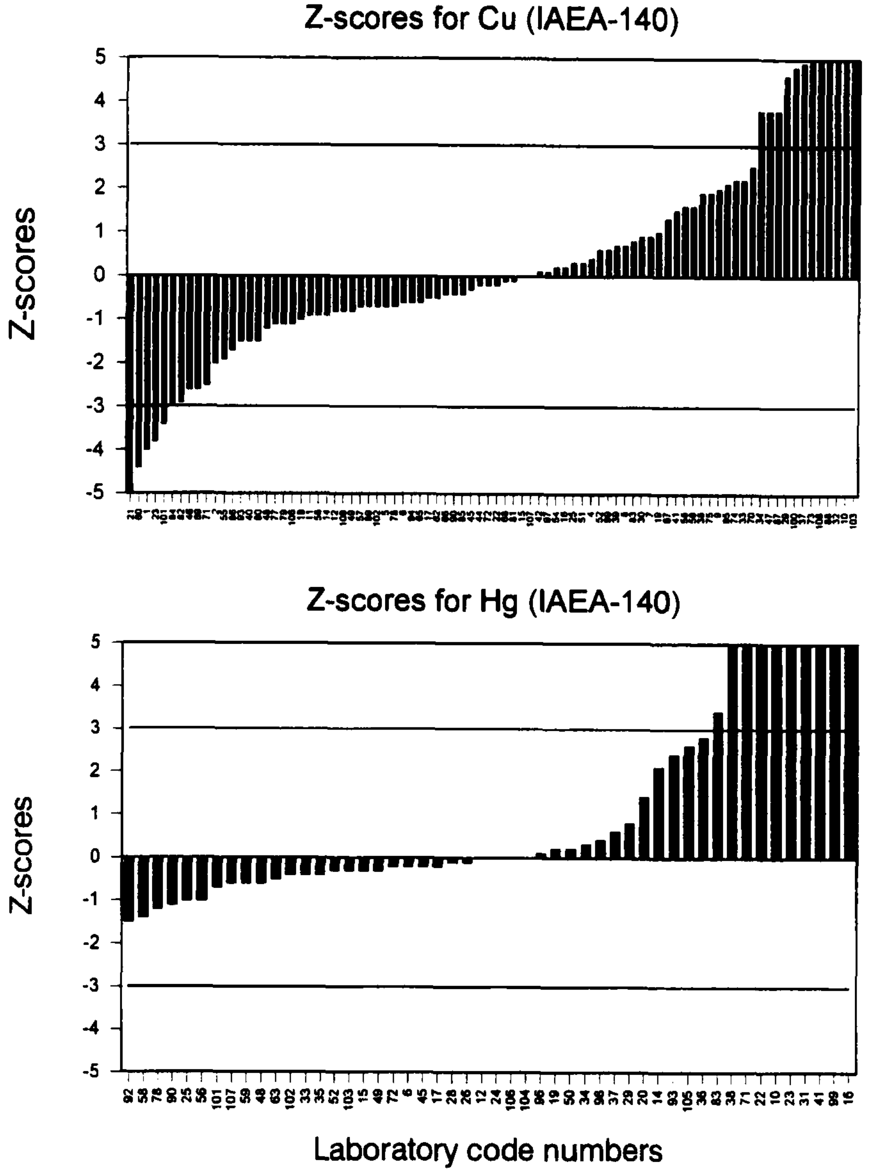

FIGURE 5 Results of the intercomparison exercise with sample IAEA-140 (seaweed). Data for individual participants in the analysis of Cu and Hg are represented as Z-scores [9]. Z-scores between −3 and +3 were considered as of acceptable accuracy

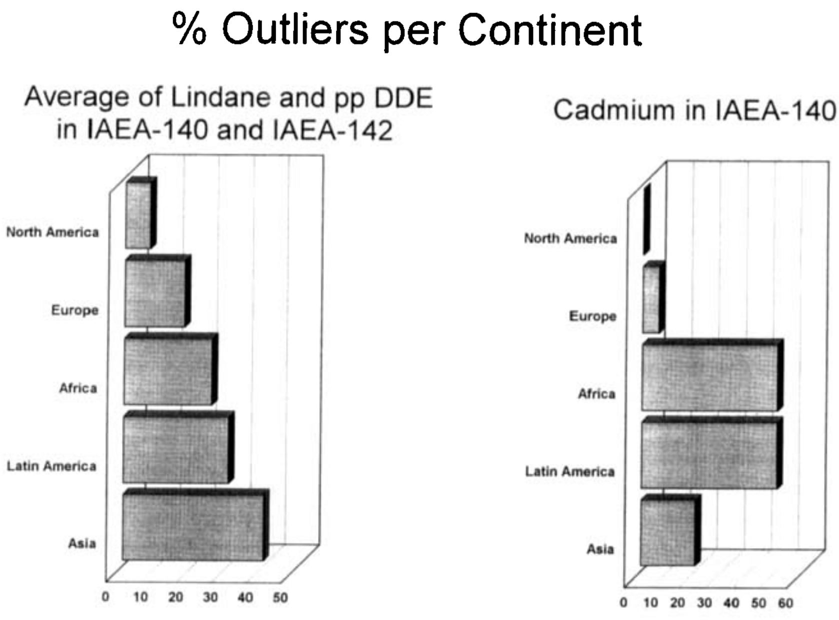

FIGURE 6 Geographic distribution of outlier results for laboratories which participated in intercomparison exercises for organic contaminants and trace metals

CONCLUSIONS

The results of worldwide intercomparison exercises indicate that substantive progress in the analyses of environmental contaminants has still to be achieved. Furthermore, the answers to the MEL Questionnaire confirm that QA/QC needs to be better understood and more widely adopted. Although Quality Assurance and Quality Control concern all the analytical laboratories, the geographic distribution of the current analytical difficulties indicates that QA/QC needs are greater in developing countries. Many of the laboratories in these regions cannot afford the costs for purchasing commercial Reference Materials and participation in commercially available proficiency tests. The costs of this effort have thus to be met largely by regional cooperative agreements and international organizations. The Inter-Agency Programme (UNEP, IAEA, IOC-UNESCO) on Marine Pollution contributes to this end through the QA services provided from the IAEA Laboratory in Monaco [13]. As part of these services, intercomparison exercises are regularly organized free-of-charge to participant laboratories.

Progress in analytical data quality can be fostered with more frequent inter-laboratory comparison exercises. These should include organic contaminants such as pesticides, herbicides, organo-metallic compounds, sterols, trace metals and other sample matrices of interest to the environmental laboratories and international programmes. The success of the effort for improved quality of analytical data do not depend, however, on the multiplication of intercomparison exercises only. Implementation of comprehensive Data Quality Assurance programmes, including production and supply of reference materials, training of analysts and adoption of harmonized and tested analytical methods, is also necessary.

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