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Meeting of the Ecosystem Approach Correspondence Group on Pollution Monitoring

Podgorica, Montenegro, 2-3 April 2019

Agenda item 5: Marine Pollution Monitoring Regional Data Base and Related Quality Assurance Issues; Data Standards and Data Dictionaries

Results of the Proficiency Tests on the Determination of Trace Elements and Organic Contaminants in Sediment and Biota Samples and related Training Courses

Note by the Secretariat

In 1986, the UN Environment Programme/Mediterranean Action Plan (UN Environment/MAP) established a cooperation with the Marine Environmental Studies Laboratory (MESL), a special section of the International Laboratory of Marine Radioactivity (ILMR) of the IAEA, regarding quality assurance of the monitoring programme related to contaminants and capacity building for MED POL designated laboratories.

Since 1987, a comprehensive and interactive strategy was developed, updated and exercised for enhancing the capacities of the Mediterranean laboratories and building up and maintaining more effective scientific groups at the national level in order to address marine pollution issues in national and regional context.

To date, the IAEA MESL in collaboration with MED POL implemented the following: i) 50 interlaboratory comparisons/proficiency tests for the analysis of trace elements and organic contaminants; ii) 60 training courses on the analysis of trace elements and organic contaminants in marine samples, with more than 350 analytical laboratory practitioners trained in the Monaco laboratories; and iii) 56 Recommended Methods specifically developed for the analysis of trace elements and organic contaminants in marine samples. Between 1986 and 2012, IAEA MESL had conducted 33 extended Quality Assurance missions to Mediterranean countries; 93 instrument service missions; and installed new instruments in the Mediterranean laboratories.

The present Progress Report aims at bringing to the attention of the Contracting Parties the present state of play with regards to implementation of the Proficiency Tests and Training Courses organized for trace elements and organic contaminants and initiating a discussion on a number of needs of national laboratories and their staff participating in national marine environment monitoring programmes within the implementation of MED POL Monitoring (Phase IV)/IMAP, with a view of providing recommendations to improve the quality and quantity of monitoring data in the decade to come.

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List of Abbreviations / Acronyms

COP	Conference of the Parties
CORMON	Correspondence Group on Monitoring
CRM	Certified Reference Material
EACs	Environmental Assessment Criteria
EQS	Environmental Quality Standard
IAEA	International Atomic Energy Agency
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectrometry
ILC	Interlaboratory Comparison
IMAP	Integrated Monitoring and Assessment Programme of the Mediterranean Sea and Coast and Related Assessment Criteria
MAP	Mediterranean Action Plan
MED POL	Programme for the Assessment and Control of Marine Pollution in the Mediterranean Sea
MESL	Marine Environment Studies Laboratory of the IAEA Environmental Laboratories in Monaco
OCPs	Organochlorine Pesticides
PCBs	Polychlorinated Biphenyls
PHs	Petroleum Hydrocarbons
PT	Proficiency Test
QA/QC	Quality Assurance/Quality Control
TC	Training Course
TE	Trace Elements
UN	United Nations

1. INTRODUCTION

1. In order to ensure comparability of analytical data for monitoring studies and assessment products, one essential aspect of quality assurance and quality control is the periodic external assessments of measurement performance via interlaboratory comparisons (ILCs) and proficiency tests (PTs). The participation in the ILCs and/or PTs is important not only for verifying the accuracy of the laboratories' analytical results, but also for evaluation of their analytical performance. Good laboratory practice (GLP) together with technical knowledge about the methods and instrumentation used to analyze marine matrix samples are necessary to accurately produce reliable monitoring results.

2. MAIN FINDINGS RELATED TO THE RESULTS OF THE PROFICINECY TESTS AND TRAINING COURSES ON TRACE ELEMENTS AND ORAGNIC POLLUTANTS

2. This chapter provides an overview of the results from the trace element; organic PTs and the GLP training course developed for the analysis of trace elements and organic contaminants in marine samples for the period between 2008 and 2018. Particular attention is given to the results of the last three years.

2.1. Proficiency tests (PTs)

3. Table 1 provides a representation of the number of laboratories that received samples and returned results in PTs organized for laboratories providing trace element and organic contaminant data for the MED POL monitoring programme. As can be seen, the response of laboratories is significantly less than 100%, i.e. between 56% and 87% for the trace element (TE) PT, and as low as 14% for PHs, 17% for PCBs and 36% for OCPs. This means that many of the nominated laboratories are either not capable or due to some other reasons did not produce and/or report results.

Table 1. Numbers of nominated laboratories receiving PT samples and returning analysis results for Trace Element (TE) analysis and Organic Contaminant analysis (Organochlorine Pesticides (OCP), Polychlorinated Biphenyls (PCB) and Petroleum Hydrocarbons (PH).

Year	**Trace Element PT**		**Organic Contaminants PT**			
	No. of labs receiving PT samples	Labs returning results	No. of labs receiving PT samples	Labs returning results for OCP	Labs returning results for PCB	Labs returning results for PH
2008	33	79%	26	62%	31%	42%
2010	25	56%	25	64%	28%	32%
2011	22	59%	19	47%	37%	37%
2012	32	59%	24	50%	42%	38%
2013	32	59%	28	36%	36%	14%
2014	36	67%	28	57%	50%	43%
2015	32	78%	32	56%	56%	47%
2016	38	82%	31	65%	65%	65%
2017	39	56%	31	52%	52%	35%
2018	39	87%	35	24%	27%	43%

4. The quality of the PTs data reported back to the MESL is categorized into acceptable, questionable and unacceptable results according to the z scores calculated as recommended in the ISO guide 13528 [1], where $z = \frac{x_{lab} - X_{ass}}{\sigma_p}$, with x_{lab} is the measurement result reported by the participant, X_{ass} is the assigned value and σp is the target standard deviation or standard deviation for proficiency assessment. An acceptable result has a z score of ≤ 2, questionable results score between $2 < |z| < 3$,

and unacceptable values having a z-score of ≥ 3. The target standard deviation is 12.5% from the assigned value. It is noted that for organic contaminants, target standard deviation has only been set to 12.5% from 2013 on (more detail presented below).

5. The z-score represents a simple method of giving each reported data a normalized performance score. The procedure has been accepted as a standard by ISO/IUPAC [1, 2, 3]. Z-scores can also be used to verify the performance of individual or country's laboratories.

6. Zeta score- information:

$$\text{zeta} = \frac{x_{lab} - X_{ass}}{\sqrt{u_{lab}^2 + u_{ass}^2}}$$

shows if the participant's result agrees with the assigned value within the respective uncertainties. The denominator of equation is the combined uncertainty of the assigned value and the measurement uncertainty reported by the participant.

7. Laboratories participating in PTs receive 2 reports. One, soon after the reporting has resumed, showing only their results in comparison to the certified or consensus analyte values. A second regional report is issued for the MED POL office, the MED POL Focal Points and the PT participants in which overall results of the PTs are given. This regional report is anonymized and only each laboratory knows their lab code. The full regional reports for 2017 and 2018 are provided in UNEP/MED WG.463/Inf.7.

8. Regarding the quality of results reported back to the MESL, in general trace element data is consistently better than organic contaminant data as can be seen in the following Figures 1 – 4.

9. Figure 1 provides a graphical representation of the quality of results (represented by reported z-scores) of PTs organized for laboratories providing trace elements (TE) data for the MED POL monitoring programme. A slow, but steady improvement of results can be observed (1.7% increase of acceptable results/year, r^2=0.52) for the last decade. It should also be noted that global PTs return similar percentage of acceptable results, e.g. a global fish PT in 2017 returned 81% of acceptable results. A full representation of TE PT results including the Zeta-scores for the last two years can be found in UNEP/MED WG.463/Inf.8.

10. Together with the results, laboratories are also asked to submit a survey that includes questions about the procedures used, the quality assurance procedures in place, the use of certified reference material (CRM), etc. It is noteworthy that still many laboratories do not have a proper QA/QC system in place (Figures 2 - 4), or do not use a suitable CRM. Most poorly performing laboratories would usually be within this group. In 2017, it was possible to correlate a negative bias of some trace elements results to the omission of hydrofluoric acid in the digestion of sediment. This is, despite the use of hydrofluoric acid was specifically recommended in the instructions to the PT.

11. In summary, PT results for trace elements analysis in marine samples are showing, that the quality of analysis, as verified through the participation in PTs has improved significantly over the last 10 years. Furthermore, the majority of laboratories that participate in the TE PTs organized by IAEA MESL in collaboration with UNEP/MAP - MED POL monitoring programme perform well. However, in the last three years, up to 44% of nominated laboratories that received PT samples did not return PT results (see Table 1). Additionally, it is not known whether all laboratories providing data to the UNEP/MAP - MED POL monitoring programme have been nominated to participate in the TE PTs. Thus, how representative the results shown in Figure 1 are, compared to all laboratories providing data to the MED POL monitoring programme cannot be verified. This information should be additionally assessed and considered in the plan for further improvement of quality of measurement results.

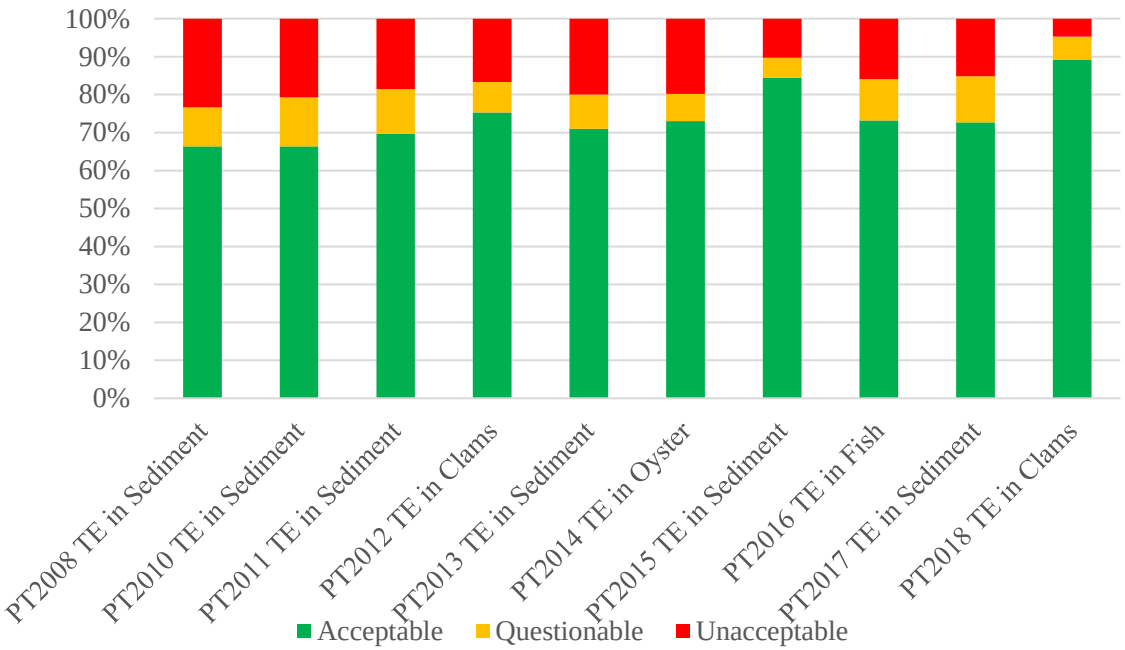

Figure 1. Acceptable (z-score ≤ 2), questionable (2 < z-score < 3), and unacceptable (z-score<3) analysis results from trace element proficiency tests in different matrices between 2008 and 2018.

12. The second PT is organized to verify the performance of laboratories providing organic contaminants monitoring data to MED POL. Figures 2, 3 and 4 provide graphical representation of the quality of results of organic contaminants PT based on the z-score.

13. Figure 2 shows the results of laboratories providing organochlorinated pesticides (OCP) data for the MED POL monitoring programme.

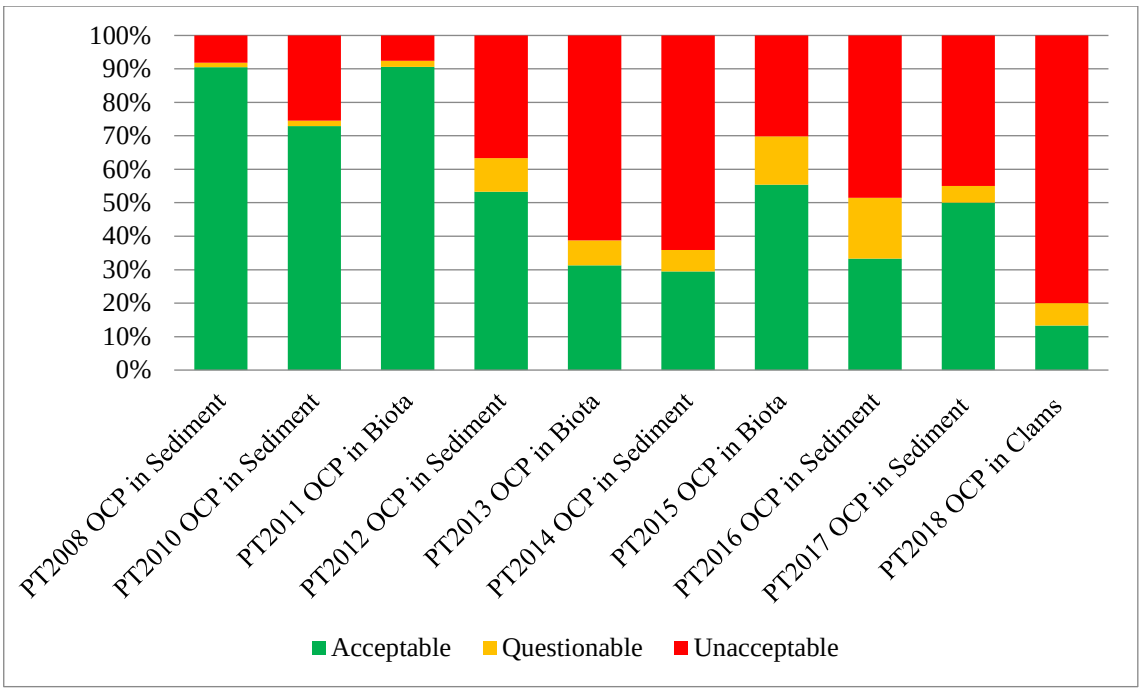

Figure 2. Acceptable (z-score ≤ 2), questionable (2 < z-score < 3), and unacceptable (z-score<3) analysis results from organochlorine pesticides (OCP) proficiency tests in different matrices between 2008 and 2018. For 2018 only 2 OCPs were certified.

14. Figure 3 provides a graphical representation of the quality of results of PTs organized for laboratories providing PCB congeners data for the MED POL monitoring programme.

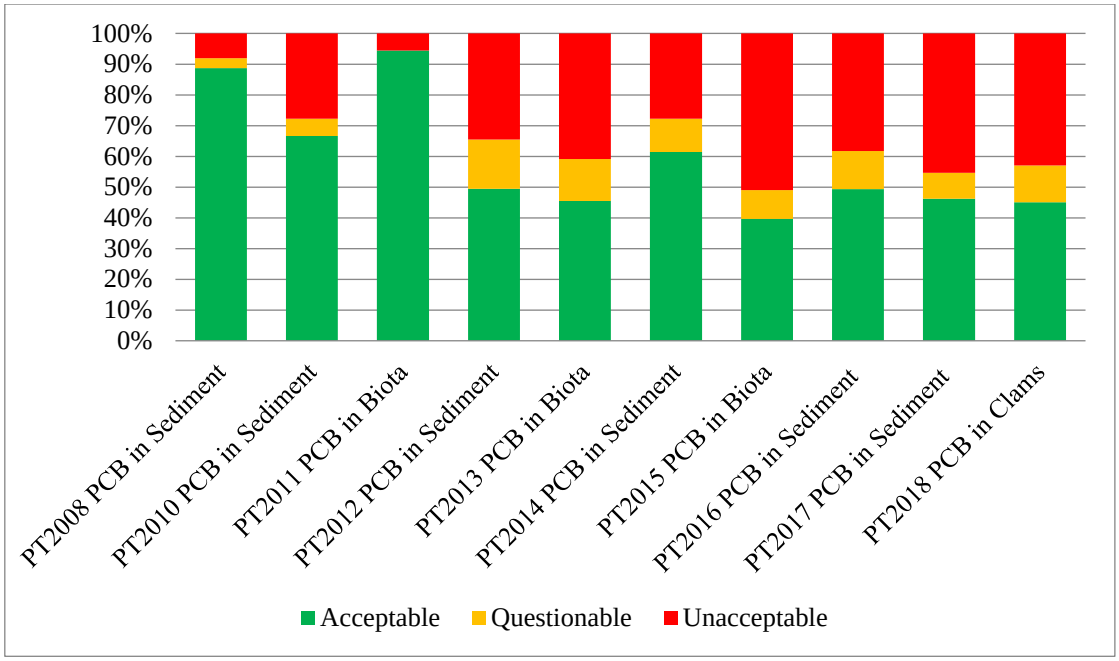

Figure 3. Acceptable (z-score ≤ 2), questionable (2 < z-score < 3), and unacceptable (z-score<3) analysis results from polychlorinated biphenyls (PCB) proficiency tests in different matrices between 2008 and 2018.

15. Figure 4 provides a graphical representation of the quality of results of PTs organized for laboratories providing petroleum hydrocarbons (PH) data for the MED POL monitoring programme.

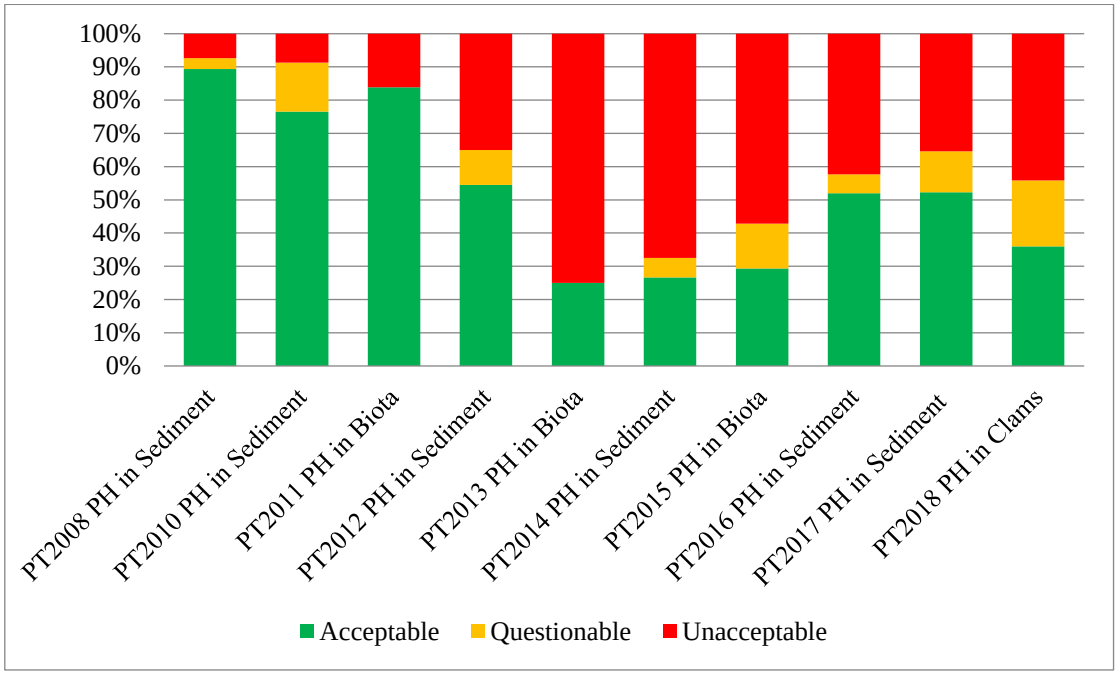

Figure 4. Acceptable (z-score ≤ 2), questionable (2 < z-score < 3), and unacceptable (z-score<3) analysis results from petroleum hydrocarbons (PH) proficiency tests in different matrices between 2008 and 2018.

16. The concentration levels of PT samples are usually considerably lower than the Environmental Quality Standards (EQS) values for food safety. However, for marine environmental monitoring (sediments and biota), the concentration levels of the PTs are in the normal to low range of typical environmental concentrations but are still measurable.

17. It can be observed (Figures 2 to 4) that the apparent quality of results of organic contaminants PTs significantly worsened between 2012 and 2013. This is an artifact related with a change in the way the z-scores were calculated. Before 2013, the target standard deviation used to calculate the z-scores was taken as the standard uncertainty from the reference material report, which are often much higher than the 12.5% target standard deviation that was assigned from 2013 onwards. Data are therefore difficult to compare with each other. However, the 12.5% target standard deviation is used commonly for trace elements PTs and ILC at MESL and is also recommended in UNEP documentation. While the assignment of the 12.5% target standard deviation follows recommendations of ISO 17043, it should be noted, that the uncertainty of the assigned value of the PT sample and the measurement uncertainty reported by the participant are not taken into account in this representation, and given the low concentrations of some organic contaminants, notably the OCPs, the uncertainties are often more in the order of 40% rather than 12.5%. The z-score would deal with this issue; however, only a very small number of laboratories that participate in the organic contaminant PT organized for the UNEP/MAP - MED POL monitoring programme report measurement uncertainty (e.g. only 3 out of 18 in 2018). This shows a lack of appreciation for QA/QC and metrology (measurement science) issues in general.

18. About 70% of the 2018 participants returning results reported to have a QA/QC system in place and to use internal standards. About half of the participants reported using validated methods. Only three Laboratories reported their QA/QC data along with the test results, as is requested. Most laboratories among the worst performing reported neither having a QA/QC system in place nor using internal standards.

19. A direct comparison of PT results is further difficult as the participating laboratories change from year to year, and good laboratories may be replaced by not so well performing and vice versa.

20. In summary, it is worrisome that for organic contaminants, no improvement of analysis quality can be seen, and the lack of reporting uncertainties (and appropriate QA/QC systems) is definitely representing a large part of the problem.

21. The poor performance of laboratories in organic PTs compared to trace elements may also be related to i) the larger number of analytes to be analyzed; ii) the complexity of the analytical purification procedures to avoid matrix interferences within the detection of the target organic contaminants by gas chromatography technique; and iii) the low concentration of organic contaminants in the matrix PT samples distributed as also discussed in §20. The limited participation rate of laboratories, especially for the organic contaminant PT, ~~,~~ is also a matter of concern (see Table 1).

22. For both, trace elements and organic contaminants, designated reporting Laboratories must be made aware of the importance of establishing and maintaining a solid QA/QC system in their laboratory. The use and reporting of certified reference material (CRM) in the production of monitoring data as well as during the participation in PTs and ILCs is imperative in order to produce monitoring results that are comparable with those of other laboratories. Laboratories without a verified QA/QC system should not be able to report data.

23. A considerable part of MED POL designated laboratories, reporting results to the IAEA MESL have very limited knowledge in the basic principles of metrology (the science of measurement), and this may be considered as part of the assistance MED POL can give in the future.

24. The steady improvement of trace elements PT results is encouraging and demonstrates the success of MED POL/MESL-IAEA`s efforts. However, for organic contaminant PTs such a success cannot be reported. While some good laboratories, all of which with appropriate QA/QC system in place, report mainly acceptable results, there are in each organic PT many poor performing laboratories. Some report data that is orders of magnitude above the actual contaminant concentration. Very bad performing laboratories never have an appropriate QA/QC system in place.

2.2. Good laboratory practices and training courses on trace elements and organic pollutants

25. The MED POL together with the MESL are making their decision by taking into consideration country distribution and overall merit of the nominees, as additional criteria to those presented in§21.

26. Since 1986, sixty Training Courses on the analysis of trace elements and organic pollutants in marine samples were organized, with more than 350 analytical laboratory practitioners having been trained in the MESL's laboratories. The statistics about participation of laboratory practitioners from different countries in the last decade is shown in Figure 5. The gender distribution in the period between 2008 and 2018 was 36% male and 64% female.

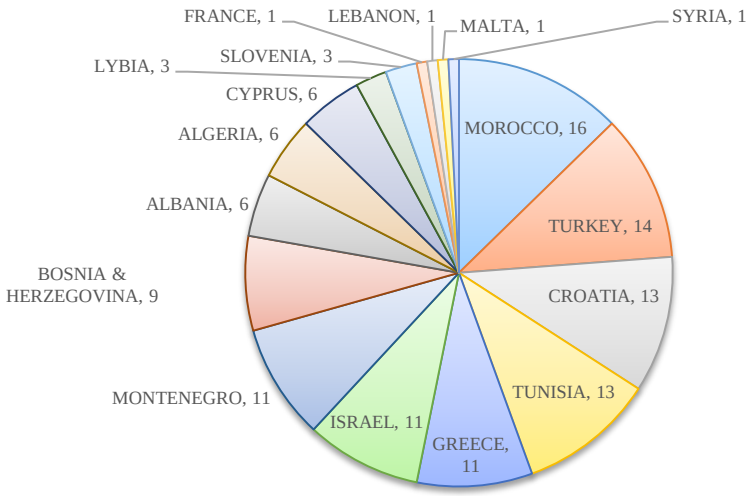

Figure 5. Pie chart showing the country of laboratories sending participants to trace element and organic contaminant training courses organized by IAEA MESL between 2008 and 2018.

27. The training courses comprise the lectures on recommended methodology for sampling, sample preparation and analysis, and on data evaluation. The lectures are supported by practical components during sampling field trips and in the chemical and computer laboratories. Special focus is given to QA/QC procedures necessary and recommended by ISO guide 17025 [4]. By the end of the course participants should have been aware of good laboratory practice necessary to produce reliable monitoring results for the respective contaminants. This includes the correct choice of certified reference material, use of verified methodology, reporting of measurement uncertainties and other measures to assure the quality of the produced data.

28. Based on the surveys that included questions about the quality of organization and new themes to be addressed in the future, the participants are usually very satisfied with the training courses. Asked about their interest in similar workshops with other topics, 33% of participants in the last 3 years respectively 2016, 2017 and 2018 in courses on trace elements TC indicated that a specific course on ICP-MS would be useful, 47% were interested in an ICP-OES course and 13% were specifically interested in a QA/QC course.

29. There has been a continuous interest by laboratory practitioners in the two training courses on trace elements and organic pollutants offered specifically for MED POL laboratories in the past. More nominations than spaces are usually received for the trace element training course, e.g. 10-12 per year, so the most suitable participants can be selected, taking into consideration selection criteria, including country distribution and merit of the nominees. For organic contaminants TC, there is usually less interest and the number of nominated practitioners is smaller than, or equals the spaces available, i.e. 6. This means that unless nominees are not very unsuitable, they are accepted to participate in the course. This has led to the participation of practitioners that have insufficient English proficiency, or that have little or no previous expertise with the analysis of organic contaminants in their home laboratory. The resulting heterogeneousness is often causing problems and makes the course less effective as it could be if participants would be at a similar level. However, the lack of nominations from practitioners in charge of the analysis of organic contaminants may likely reflect the situation in many countries providing monitoring data for the MED POL programme, i.e. the lack of laboratories and personnel to perform the analysis required.

30. Discussions during the present Meeting of CorMon on Pollution and efforts for some fact finding should be supported in the future to find out why the quality of laboratories providing data for organic contaminants is still unsatisfying and what could be done to improve the situation.

3. KEY PROBLEMS AND CHALLENGES

31. In line with the results presented above, key problems and challenges related to realization of the PTs and TCs are summarized herein and pointed out for consideration of the Meeting of CorMon on Pollution as follows:

a. No information available how designated laboratories were selected to participate in PTs and TCs and what is their role in implementation of MED POL IV/IMAP. A subsequent analysis, if the laboratories most in need of assistance are addressed by MED POL/MESL-IAEA`s efforts is needed;
b. Contribution of designated laboratories receiving PTs samples is often limited (< 50% in some years for some contaminant classes);
c. Quality of PTs results for organic contaminants not satisfying and not improving over the last decade, including the last three years. The lack of implementation and reporting of QA/QC measures remains a big challenge. Further, consideration on what that means for the quality of actual monitoring data is needed;
d. The knowledge on basic principles of metrology (measurement science), e.g. method validation, traceability and uncertainty of measurement results, are very limited and further action is requested.
e. Many laboratories do not seem to have appropriate CRMs at hand for the PT and likely neither for the actual monitoring programme;
f. Some participants in TCs have insufficient English knowledge;
g. Some participants in TCs, especially for organic contaminants do not have sufficient background in organic contaminant analysis and are overwhelmed in TC course;
h. Some laboratories do not seem to have the infrastructure (instrumentation) to provide good quality analysis. Alternative ways of funding the infrastructure should be discussed;
i. There is often not enough awareness of the TCs participants about the MED POL monitoring programme, which may lead to a lack of interest in the data produced, as well as to apply the knowledge learned during the TCs for improving quality of data produced within respective national monitoring programmes;
j. At present, a link between national designated laboratories that participate in PTs and those that send nominees to TCs is not clear. The participants in TCs should come from the laboratories designated to participate in PTs;
k. So far there is no mechanism to check if new knowledge acquired in the TCs is applied in the home laboratory, as well as if laboratories of course participants take part in the PTs. A better

link between PTs participation and TCs participation should be introduced and followed up; and

l. ISO standard recommendations on the confidentiality of PT participants and their results currently restrict availability of names of laboratories to MED POL Focal Points, unless according to 4.10.4 of ISO 17043, designated laboratories will be notified that the results will be revealed, in such a case they may hold their right to refuse this approach

4. WAY FORWARD AND POSSIBLE RECOMMENDATIONS

32. Based on the results of the PTs and TCs, expert missions to national designated laboratories participating in national marine environment monitoring programmes for MED POL IV/IMAP should be organized and aimed at laboratories with greatest needs to improve their QA/QC and data quality. Given the fact that some laboratories need to build up expertise and infrastructure to be able to provide good quality data especially for organic contaminants, where the biggest problems seem to be, this should include the identification of technical (e.g. acquisition of laboratory equipment) and knowledge needs. These missions should be supported by the MED POL Focal Points to reinforce the importance and motivation.

33. MED POL Focal Points should follow up more closely with national laboratories participating in implementation of MED POL IV/IMAP monitoring programme and experts participating respectively in the PTs and TCs organized for trace elements and organic compounds, with a view of further supporting national efforts to implement the QA/QC measures in order to warrant good quality of monitoring data reported to MED POL.

34. MED POL Focal Points should make all possible efforts to ensure nominated participants of the TCs are with adequate background and from laboratories actively participating in national marine environment monitoring programmes within the implementation of MED POL IV/IMAP. Similarly, additional efforts are needed to ensure the laboratories participating in TCs are those taking part in PTs in order to make the most of the training received.

35. Laboratories should be able to purchase standards and matrix certified reference material (CRM). It is recommended that the MESL in consultations with MED POL will propose CRM that is most relevant for the MED POL monitoring programme with regards to matrix, contaminant presence and contaminant concentration in line with IMAP requirements. For laboratories struggling with the purchase, further possibilities of funding such CRM would be assessed.

36. Given the unsatisfactory performance of the laboratories participating in the organic contaminants PTs, unsatisfactory quality of PTs results and marine environment monitoring data must be significantly improved. It has to be noted that all data to be reported to MED POL should be delivered by laboratories which demonstrate their proficiency either through the MED POL organized PTs or through global PTs or inter laboratory comparisons (ILCs). This requirement is recommended to be strictly followed for nomination of the participants for future PTs.

37. Noting challenges described in §31.l on the confidentiality of PT results, national laboratories may need to agree on a waiver of this confidentially towards MED POL Focal Points. This would allow regional full reports on PTs provided by the MESL to participating laboratories and MED POL, which passes them to MED POL Focal Points, then to be supplemented with specific reports showing problems with specific or a number of laboratories in one country. Like in the past, laboratories will also continue to receive a preliminary report on their PTs results directly after the PTs have been evaluated. If this approach is not acceptable, MED POL will continue to communicate the results of PTs to MED POL Focal Points based on the findings presented in regional and national reports in which codes are assigned to respective participating laboratories.

38. In order to further support capacity building of national laboratories to perform QA/QC measures, the results of the PTs and TCs should guide further actions within the quality assurance

programme of UN Environment/MAP – MED POL towards i) improvement of the trends in laboratory performances and results of training courses; ii) addressing the most relevant gaps, needs and challenges per each Contracting Party; and iii) identification of specific knowledge and technical needs of individual laboratories aimed at gradual improvement of their performances to apply good laboratory practices.

39. In a view of IMAP Pollution cluster monitoring was expanded to offshore areas, a regional sampling and analysis effort can be planned for the future. Such missions could also be an additional way of training laboratory practitioners in sampling, sample preservation and preparation and building networks between practitioners to help each other if needed.

Annex I
References

References

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