Worldwide quality control for measuring contaminants in the marine environment — 15 years of progress at the International Laboratory of Marine Radioactivity

A global team of analysts are working for a common aim

by L. Mee, V. Noshkin, and A. Walton

Only three decades ago, marine pollution was not an issue in the public eye. The threat of pollution by radionuclides arising from the large-scale atmospheric testing of nuclear devices was one of the factors which changed this situation. Indeed, it led to such widespread concern that in 1961 a unique facility was created by the IAEA in Monaco, the International Laboratory of Marine Radioactivity (ILMR).

During the early 1960s, the public suddenly became aware of many other forms of marine pollution following world press reports of major catastrophic incidents: The Torrey Canyon sinking (off the coast of England) made the public intensely aware of the grim consequences of oil pollution; the large-scale and tragic poisoning by methyl-mercury at Minamata, Japan, demonstrated the risks of heavy metals; and the evidence of bioaccumulation of DDTs and eggshell thinning by marine and terrestrial birds, shortly after the publication of Rachel Carson's *Silent Spring*, heightened public fears of chlorinated pesticides.

Three decades ago, however, adequate analytical techniques were not widely available for chemists to quantify contaminants causing pollution and to assess their impact. With increased concern for measuring potential pollutants in the marine environment, techniques were rapidly adapted from other areas of pure and applied chemistry and a large number of methodologies and data sets began to appear in scientific literature.

Some of the data sets initially published were not consistent, particularly at the lower background or "baseline" levels. In some cases, periodic modifications in analytical strategies brought spectacular changes in our knowledge of baseline concentrations: an apparent lowering in the baseline seawater concentrations of lead of three orders of magnitude in four decades; three orders of magnitude for tin in two decades; and one order of magnitude for mercury in one decade. Of course, all these changes were artifacts of increasing analytical accuracy as understanding of the problems of sample contamination and methodological interferences gradually improved.

Ensuring data quality

In order to evaluate spatial or temporal trends in contaminant concentrations, to define criteria (and in some cases legislation) for coastal water quality, and to interpret biological effect studies, there was a clear need for intercomparable data of the best generally available precision. The task of guaranteeing data quality was not an easy one and was beyond the domain of national organizations, especially where data on transboundary contamination was involved. As the only laboratory in the United Nations system capable of realizing marine pollution studies, ILMR was ideally suited to assume the role of organizing specialist intercalibration exercises on a worldwide scale.

The first intercalibration exercises, conducted from ILMR just over 18 years ago, addressed the measurement of radionuclides in marine biota and sediments. Radioactivity in the marine environment is dominated by the presence of naturally occurring radionuclides and great analytical care is required to discern the artificial radioactive contaminants and to accurately quantify them. This is particularly true in the case of alpha-emitting transuranic elements such as plutonium. Without careful chemical separation, the plutonium (239 and 240) signal can be completely masked by some naturally occurring uranium isotopes. Laboratories agreeing to participate in ILMR's exercises were sent

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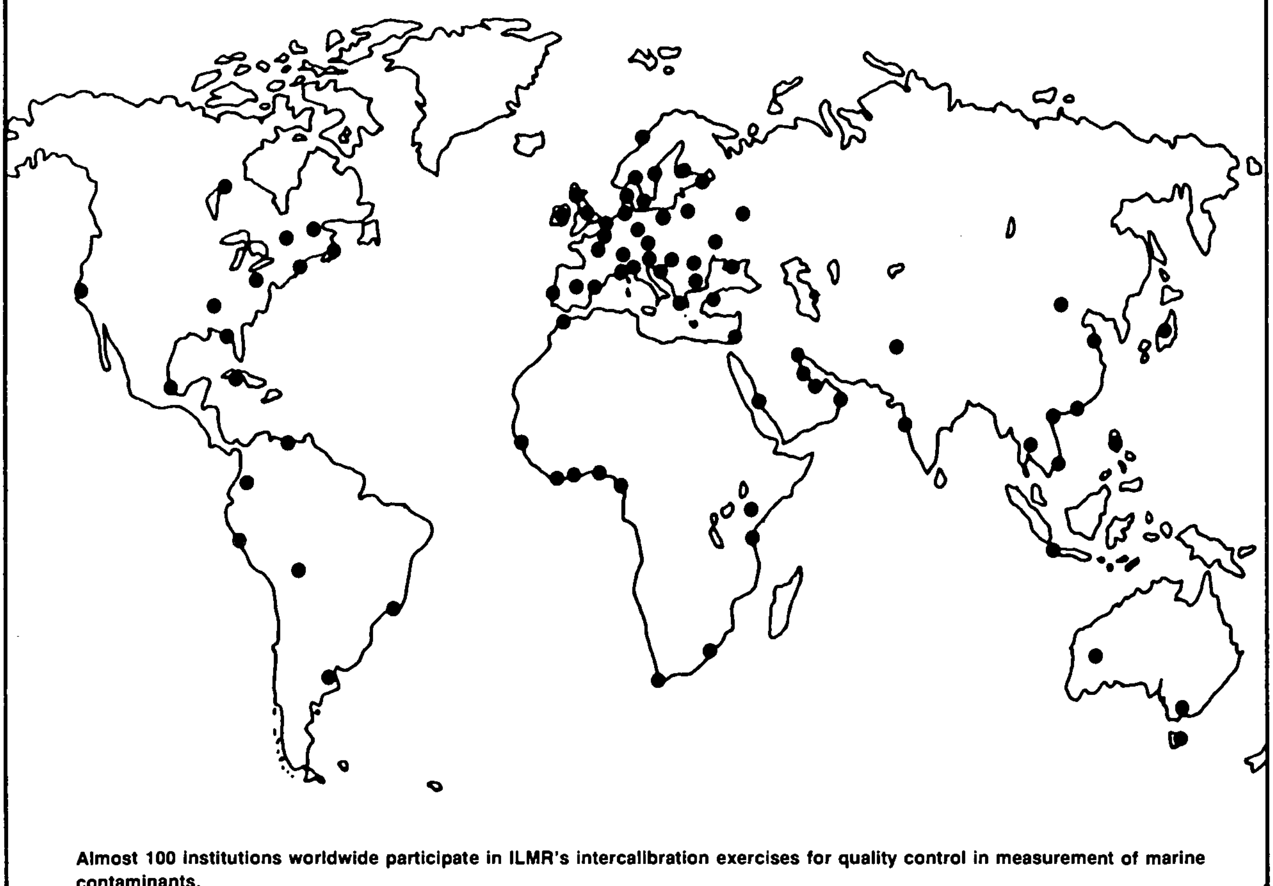
samples of materials which had been dried, ground, and carefully homogenized. Results of the analyses from each laboratory were collated and the full data set subjected to a statistical evaluation. From the consensus values for each parameter and the spread of the data around this value, analytical performance of each lab (and the group as a whole) could be evaluated. Where the data was well grouped (i.e., the consensus value was, to the best of our knowledge, an accurate measurement of the parameter in question), the material was "certified" and then could be used for reference purposes by other laboratories when checking their own analytical techniques for precision and accuracy.

A "global club" of analysts

Over the years, the number of regular participants in ILMR's intercalibration exercises gradually grew as a "global club" of analysts. Nuclear techniques can be applied to other analyses of marine contaminants, particularly trace metals (for example, by neutron activation analysis) and the "club" quickly extended to these parameters as well. This led to a unique opportunity for laboratories using conventional (non-nuclear) analytical techniques to compare their data with colleagues who had facilities for the more sophisticated nuclear techniques. By the end of the last decade, ILMR thus had become firmly established as a worldwide data quality centre for marine contaminants. Other UN agencies — particularly the United Nations Environment Programme (UNEP) and the Intergovernmental Oceanographic Commission (IOC) of the United Nations Educational, Scientific and Cultural Organization (UNESCO) — asked for ILMR's help in organizing data quality assurance programmes for organic contaminants (pesticides, petroleum hydrocarbons, etc.). At the present time, the "global club" has extended to almost 100 institutions and over 300 participants. *(See accompanying map.)*

Running intercalibration exercises for so many participants is not a trivial matter. For mussel tissue samples, for example, this involves collecting over half a ton of mussels, shelling them, drying, shredding, and mixing the tissue to such an extent as to be able to guarantee that any two samples of a half gram from the mixture are chemically identical to one another. Testing for homogeneity is a rigorous time-consuming process and samples are not released until 10 sub-samples, each

Institutions participating in quality control exercises of the International Laboratory of Marine Radioactivity



Almost 100 institutions worldwide participate in ILMR's intercalibration exercises for quality control in measurement of marine contaminants.

analysed 10 times for four different trace metals, show homogeneity (to 95% probability).

Some intercalibration exercises are much more complicated to organize, especially where ultra-trace levels of contaminants are being measured or where the contaminant would suffer major chemical alterations during transport and storage. Intercalibrating fission products in seawater involved sending 50 litre drums of water around the world from Monaco (as well as resolving the problems of collection of such large samples at sea). For the intercalibration of organotin contaminants (highly toxic components of some antifouling boat paints) in seawater, it proved more cost effective to transport the group of scientists to Monaco to conduct a joint sampling and sample pretreatment exercise.

Global results

Results of the worldwide exercises allow us to evaluate progress of the scientific community in the analysis of contaminants to ascertain how individual laboratories perform against this background and whether some analytical techniques introduce bias to the data they are generating. Of course, some results are obviously incorrect (often due to calculation errors), and are excluded from the data set classified as "outliers". In such cases, the laboratories are requested to carefully review their analytical and handling procedures.

For some 33 exercises conducted in the past 10 years for metals and organic contaminants, over 20 000 measurements include results from a wide variety of materials such as fish, sea plants, mussels, oysters, coastal and deep-sea sediments, and zooplankton. Many of these materials are now available as "standard reference materials" (having certified concentrations of a wide variety of parameters) through the IAEA's Analytical Quality Control Service (AQCS) programme.

The precision of analyses of contaminants in environmental samples partly depends on the nature of the material being analysed and the concentration of the analyte (generally speaking, the lower the concentration, the more difficult the analysis). Each material, or "matrix" as analysts prefer to call them, presents its own particular difficulties (and chemical interferences with the analysis). It is not sufficient to calibrate instruments with an ideal standard solution and expect the results for a real sample to fall on the calibration curve. Measurements must be validated using "real" materials of known composition. This is where the IAEA reference materials are particularly useful and permit the analyst to check his data quality at regular intervals. Some scientific journals now are insisting that specific mention is made of the use of reference materials before data is considered as publishable.

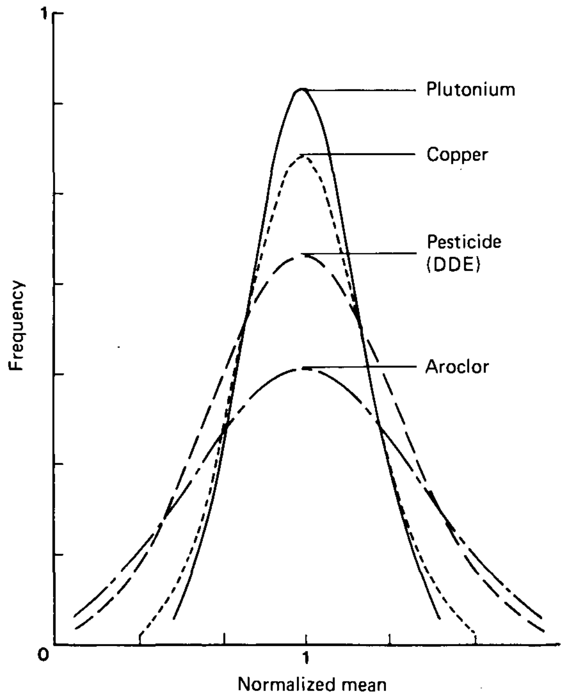
Precision of data

But, how precise are the analytical data? Results obtained from exercises on mussels (for trace metals and chlorinated hydrocarbons) and algae (for plutonium) are, at first glance, somewhat surprising. *(See accompanying graph.)* Copper, for example, can be measured rather precisely (the coefficient of variation, a measure of data spread, is typically 25-35%). In contrast, Aroclor, a PCB mixture (PCBs are highly toxic chlorinated hydrocarbons used in electrical transformers) can only be measured with very poor precision (coefficient of variation about 70-85%). Analytical precision for radionuclide measurements is surprisingly good, especially considering the difficulty in measuring alpha emitters such as plutonium (239 and 240) at low environmental concentrations. This probably reflects the highly specialized nature of the 45 laboratories contributing data on radionuclides (staff members of many of these labs received training at ILMR). On the other hand, the poor precision of data on pesticides (DDE is given as an example) and PCBs seriously limits our ability to make environmental assessments of these critical contaminants and calls for concerted international action in the future.

Regional activities

Not all of ILMR's work is conducted on a worldwide scale. In collaboration with UNEP's Regional Seas Programme, ILMR has, since 1983, organized special intercalibration exercises in non-nuclear contaminants for the Mediterranean Sea area (MEDPOL), the Gulf area (ROPME), the West and Central Africa area (WACAF), the East Asian Seas and, more recently, in

Relative precision of data



The curves illustrate the spread of data (as normalized distributions) obtained from exercises on mussels (for trace metals and chlorinated hydrocarbons) and algae (for plutonium).

South America for the Permanent Commission for the South Pacific (CPPS). The work was greatly facilitated by the creation, in 1986, of a new section of ILMR denominated the Marine Environmental Studies Laboratory (MESL) which conducts ILMR's work on non-nuclear contaminants in collaboration with other agencies. MESL's co-operative work with UNEP and IOC provides comprehensive support for quality assurance for the regions. Together with UNEP, IOC, the Food and Agriculture Organization (FAO), World Health Organization (WHO), and World Meteorological Organization (WMO), the laboratory tests and edits an extensive series of "reference methods for marine pollution studies". They provide a set of reliable techniques and guidelines for sampling the marine environment, measuring a wide range of chemical and microbiological contaminants, evaluating the biological effects of contaminants, and organizing a quality control programme. The laboratory also participates in international expert groups which seek to rationalize the availability of reliable methodologies and standard reference materials.

Encouraging participation

Intercalibration exercises provide information about data quality in labs which return data sets, but what about the labs which do not send their data or are classified as "outliers"? Unfortunately, the number of scientists submitting data is often only about 50% of those who originally agreed to participate in a given exercise. The reasons for this are many — technical reasons such as equipment failures, staff shortages, etc. or a feeling that the lab may not be "up to standard". This latter reason is unfortunate since the exercises are entirely confidential.

Recently, with help from UNEP, MESL has been trying to address the problem of non-participation as part of the comprehensive support programme. Laboratories selected for support are visited by MESL staff to assess the particular problems they may face. They then send one or more staff members to one of MESL's training courses. Following this initial period of training, a specialist staff member of MESL accompanied by MESL's electronic engineer visit the Member State lab to participate in a routine monitoring exercise (the electronic engineer services their equipment and gives advice on proper calibration and preventive maintenance). Most importantly, the MESL specialist shows the staff at the laboratory how to make and calibrate internal reference materials (IRM) for future quality control purposes and keeps in touch with the laboratory when he returns to Monaco. Quality control using internal reference materials is the most effective way of assuring day-to-day precision and accuracy. The IRM is measured following every 10 unknown samples and the results are plotted on a quality control chart. At a glance, it is possible to see when the data quality is inadequate (warning and control limits are set on the chart) and the analyses are halted until the problem is resolved. Laboratories following this procedure should always do well in intercalibration exercises.

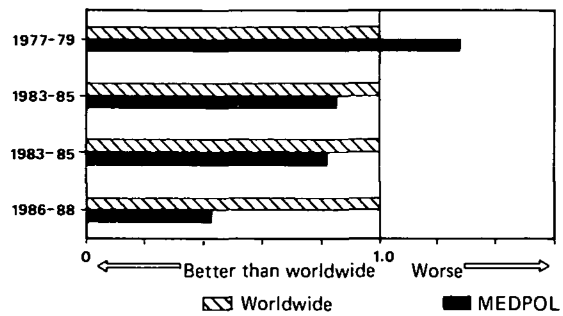
Data quality assurance

ILMR, and more recently MESL, have paid particular attention to the laboratories in the Mediterranean region over the last 10 years. Based on the results of the intercalibration exercises, the comprehensive approach to quality assurance is working. *(See accompanying graph.)*

The first exercise (before UNEP's MEDPOL programme began) showed that the Mediterranean labs lagged behind the world average. As the programme advanced, the data quality improved dramatically. With good quality data, the Mediterranean monitoring programme now makes a meaningful contribution to the environmental protection and development of the region.

The need for concerted action on data quality assurance is one in which the IAEA will have an important role to play in the future largely thanks to its unique experience in this field and its established reputation. In the coming years, pressure on the resources of the marine environment will continue to increase as demands for food, energy, raw materials, transport, and recreation grow, and as mankind continues to use the oceans for intentional disposal of waste. The coastal zone is where this environmental stress will be particularly acute. By providing a flexible mechanism for technical support, adjusted to real environmental problems, the UN agencies are endeavouring to keep marine environmental scientists well armed to face these challenges, not alone, but as part of a global team with a common aim.

Trace metal data quality (marine biota), Mediterranean Sea Area (MEDPOL) and Global intercalibration



Note: Pooled coefficient of variation (for cadmium, copper, mercury, manganese, lead). Normalized to 1 for the worldwide exercise.

Results are shown for statistically-pooled coefficients of variation (a measure of precision) for four intercalibration exercises on homogenized lyophilized biota, distributed worldwide and regionally. Since 1977, the data quality has improved dramatically.