

Nuclear and isotopic techniques for investigating marine pollution

A survey of selected applications that scientists are using to identify, trace, and investigate contamination of the oceans

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The oceans are a vast mixing pot for the elements and compounds found on the Earth's crust, whether naturally formed or as a result of human activities. The "pot" is stirred about once every 1.6 thousand years — only about four times since human history was recorded but at the speed of a blender on the geological time scale. Its constituents are therefore characterized by major components which do not appear to change their relative concentration with time, and by a much smaller fraction (less than 0.1% of the dissolved salts) in disequilibrium as a result of their participation in basic life processes, their introduction by humans as contaminants, or their geochemical reactivity.

Marine scientists are often faced with huge practical challenges in order to measure individual trace components within this mixture and to obtain data on their dynamics. The information is essential for understanding marine fertility and for investigating the transport, fate, and effects of marine contaminants. Nuclear and isotopic techniques are currently providing a unique source of information for identifying some non-nuclear contaminants and tracing their pathways in the environment and, potentially, for investigating their biological effects. This article surveys some major achievements in this field and looks at the scope for future development.

Oceanographic tracers

Seawater is a solution of largely uniform composition which varies in concentration (salinity) from place to place. Most of our knowledge of ocean circulation is thus based

upon relatively simple physical measurements of salinity and temperature and the measurement of currents by current meters, drifting buoys, or calculations based on density gradients and geostrophy. These methods have provided good estimates of the horizontal transport of water masses but are inaccurate on the vertical scale. A quantitative knowledge of vertical mixing is vital if we are to understand the ocean's capacity for assimilating contaminants (introduced from terrestrial sources or as a result of dumping), and as a receptor for "greenhouse gases" (thus providing the ultimate control mechanism for global warming).

Much of our current knowledge of large-scale oceanic mixing processes comes from measurements of natural series radionuclides — such as cosmogenic carbon-14 which was used to "date" the deep waters of the oceans — or by observing radio-geochemical disequilibria between primordial uranium and thorium series decay products. The introduction of "man-made" radionuclides into the marine environment has provided a particularly valuable tool for studying pollution transport, since they were introduced over a short period of time (as in the case of atmospheric weapons testing, which was effectively suspended after 1963) or as a point source in the case of nuclear power or reprocessing facilities. The literature on this topic is voluminous and a single example will be used to illustrate the impact of this work.

Perhaps the most noble of all the anthropogenic radiochemical tracers of oceanic mixing was tritium, which was produced in large quantities during nuclear weapons tests and introduced to the oceans's surface, particularly in northern latitudes, as tritiated water (HTO). "Was" is used since tritium, with an 11.3 year half-life, has now decayed away to levels which can only be detected by sophisticated mass spectrometric measurements of its daughter, helium-3. The IAEA, particularly the Isotope

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Hydrology Section, made good use of the period when tritium was relatively easy to measure. Apart from original work in the field, the Agency brought together specialists from all over the world and edited a number of key publications. The work generated valuable data which show that in the 25 year period since tritium was first introduced into the ocean in large amounts, the plume of tritiated water can be seen to have flowed over the sill of the Denmark straight and penetrated 5 kilometers into the abyss. (*See graph, next page.*) This was far faster than the rate predicted by physical oceanographers and demonstrates that water soluble airborne contaminants produced by modern industries (e.g., PCBs, DDT, CFCs) could already have penetrated the deep ocean.

Now that tritium is no longer convenient as an ocean-scale tracer, the search is continuing for other longer-lived radionuclides which reflect mixing processes. Suitable candidates are krypton-81 (half life 2.1×10^5 years), which is an inert but not very soluble fission product that may reflect air-sea exchange; neptunium-237, mainly introduced as a waste product of nuclear fuel or reprocessing plants but with a very long half-life (2.1×10^6 years); and iodine-129, a fairly conservative fission product with a half life of about 10^7 years.

The problem with using these potential tracers is their low concentration and weak radioactivity. This makes conventional counting virtually impossible. For example, to measure neptunium-237 in contaminated seawater, the samples are typically 10 tons in size and, after concentration and chemical separation, samples are "counted" for two weeks! The IAEA's Marine Environment Laboratory (IAEA-MEL) in Monaco is currently investigating new "non-nuclear" techniques for measuring some of these tracers using inductively coupled plasma mass spectrometry (ICP-MS). This search may eventually provide oceanographers with new tools to track the pathway and dispersion of contaminants, whether nuclear or non-nuclear, and to model the ocean's capacity for assimilating them.

Investigating contaminants

The introduction of a radiolabelled tracer into a controlled experimental system permits the marine scientist to investigate the interaction of individual contaminants with other environmental components. Such experiments have to be set up carefully so that the introduced radioisotope has the same chemical speciation as the component being studied and does not itself

alter the geochemical equilibrium of the study system.

This approach has been employed at IAEA-MEL and many other institutions worldwide since the 1960s for investigating the partition of trace metals between sediments and seawater and the biological uptake of metals. As a result of this work, a compilation of sediment/sea water partition coefficients and biological concentration factors was published in 1985 for a wide range of elements, both radioactive and non-radioactive. The importance of studying

Studies of ocean pollution often include the use of nuclear and isotopic techniques. (Credit: Kurt Adams, UNEP-SELECT)



such interactions is not an academic matter. The adsorption of metals onto particles suspended in seawater and their subsequent deposition on the floor of the sea, is the principle mechanism of self-purification of the ocean. It maintains the concentration of many toxic metals in the sea below levels which would otherwise damage the integrity of the marine ecosystem or cause detrimental consequences to the human population consuming fish or shellfish. A quantitative knowledge of the sea's capacity to assimilate contaminants allows scientifically based levels to be set for discharging effluents to the marine environment from coastal sources.

Current investigations using labelled compounds follow three general approaches, each with considerable future scope for development:

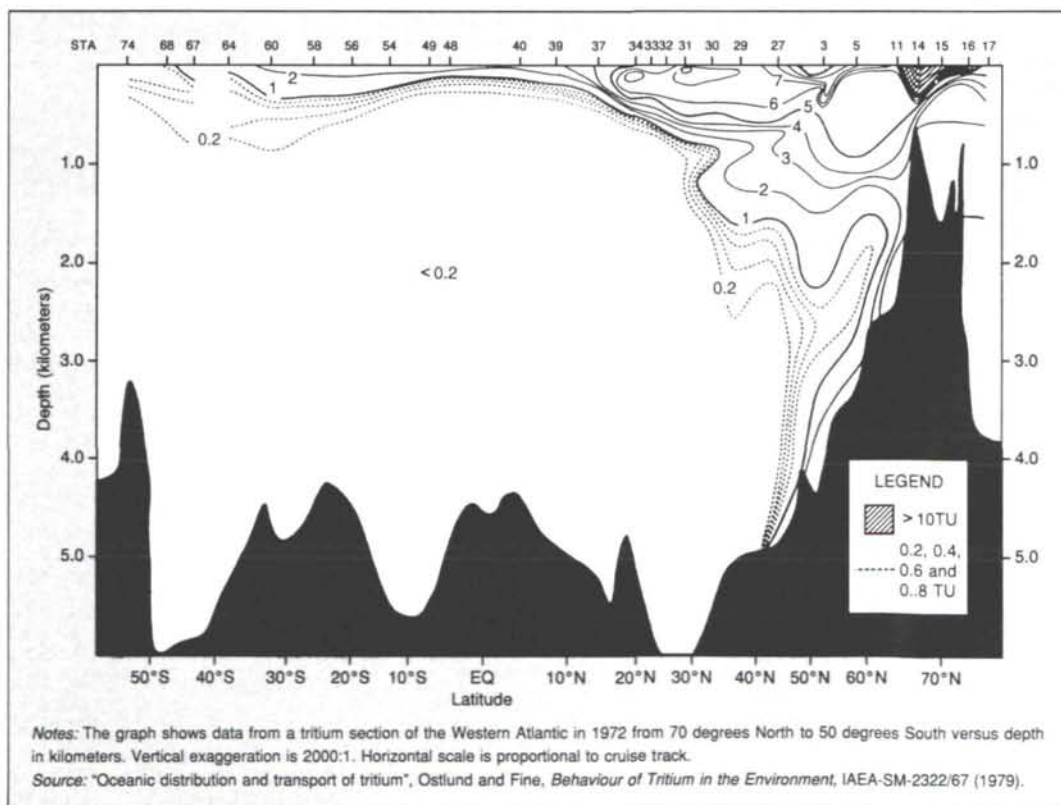
● **Continuation of laboratory experiments on inorganic contaminants using controlled microcosms (sediment/water, water/animals, water/sediment/animals).** Much work remains to be done to understand the mechanisms and dynamics of metal accumulation by marine plants and animals, particularly their ability to remobilize and bioaccumulate metals transported to the sea floor by adsorption onto sinking particles or as a result of waste disposal (dumping). IAEA-MEL has pioneered many of these studies resulting in over 100 scientific publications. The Agency's research contract programme has also supported the further

development of work on the physical chemistry of seawater/sediment interactions in national institutions. This has led to a much better understanding of the thermodynamics and kinetics of adsorption processes and permits the development of more accurate models to describe and predict the dispersion of contaminant metals (including radionuclides) under real environmental conditions.

● **Development of tracer techniques for organic compounds.** The use of labelled organic compounds in experiments designed along the lines described above has been widely explored in the marine environment only in recent years. In addition to providing an opportunity for studying the interaction of these compounds with biotic and abiotic components of the environment, well-designed experiments can investigate the degradation of the compounds themselves. (See related article in this edition on applications of these techniques for pesticide studies.) The future key to wider success for this approach will be in the realm of preparatory organic chemistry of labelled analogues of the many hundreds of organic contaminants posing a potential threat to the marine and coastal environments.

● **Tracer release experiments in the marine environment.** For monitoring dispersion of toxic materials from deep underwater effluent outfalls (pipelines from which waste is discharged into

Tritium in the Western Atlantic Ocean in 1972



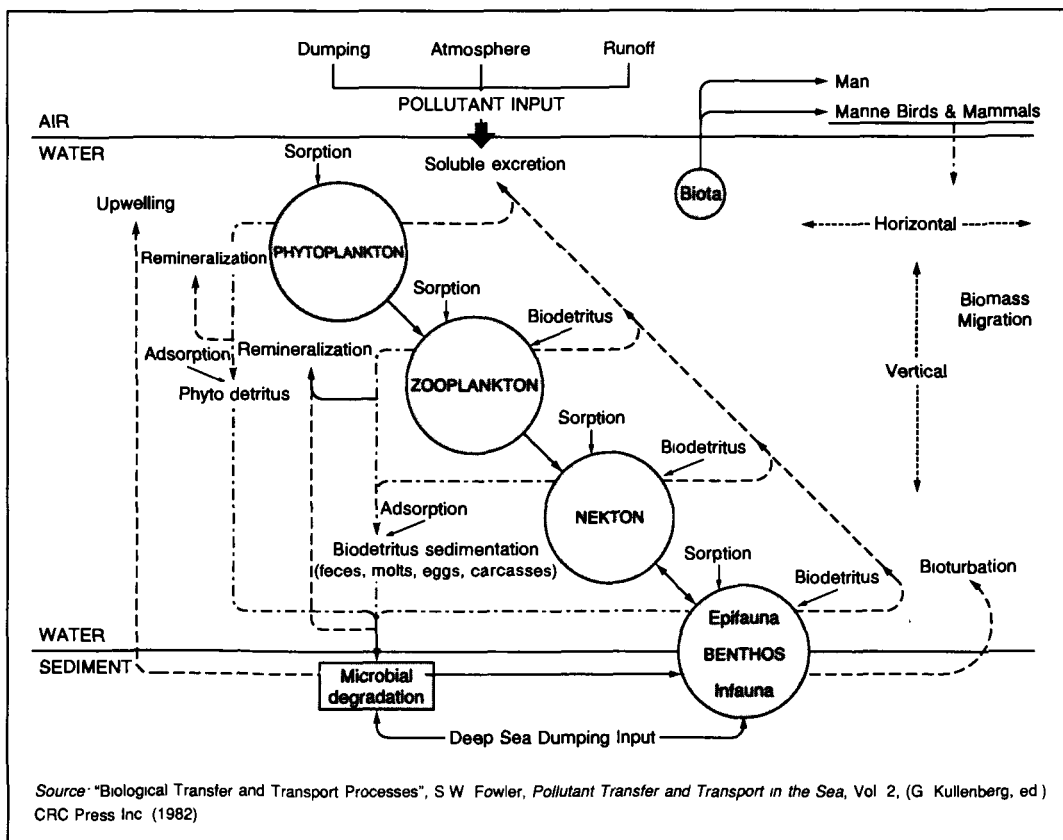
the ocean), it is necessary to conduct field surveys with as many measurements as possible over a short period of time. Unfortunately, the chemical measurement of most contaminants is laborious and time-consuming and it is convenient to add an easily measured tracer to the effluent itself.

In the past, widespread use has been made of highly fluorescent tracers, such as Rhodamine, but these are carcinogenic and break down relatively slowly. An alternative is to release short-lived gamma-emitting radionuclides and follow their distribution by underwater gamma spectrometry deployed from a small vessel or even a helicopter. This approach is now in wide use by the French Commission of Atomic Energy (CEA) for studying the efficiency of sewage outfalls in the Mediterranean. The CEA system employs gold-198 (half-life 2.7 days) as a tracer. The anionic gold in solution converts irreversibly to metallic gold in contact with solid material and thus labels the solid effluent particles irrespective of their size. The technique enables the particles to be traced in the water column and, within a one week period, at their point of deposition on the sea floor. (See figure.) Similar systems are currently being investigated by the IAEA using sand grains labelled by iridium-192 (half-life 74 days).

Bio-geochemical research and pollution studies

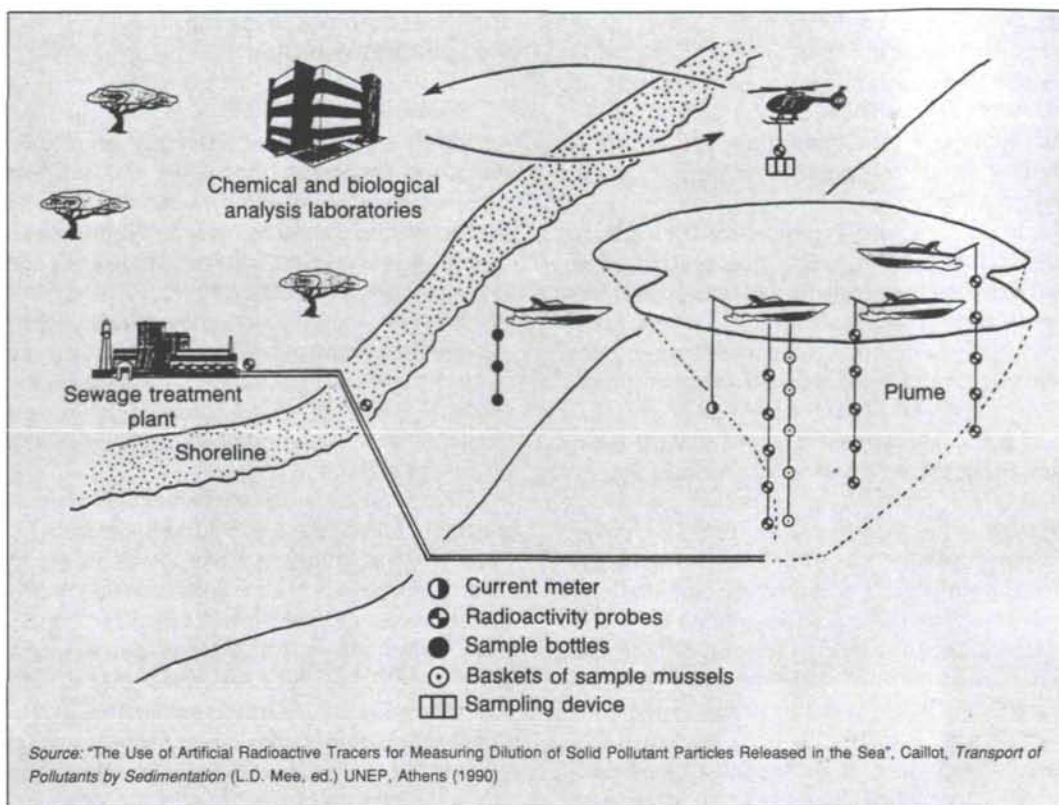
Stable isotopes of the same element have inherently small physical differences in atomic/molecular properties. Frequently this leads to preferential selection of one isotope relative to another during natural environmental processes. These fractionations (especially between isotopes of the elements hydrogen, carbon, nitrogen, oxygen, and sulphur) can provide a powerful tool to investigate physical, chemical, and biological processes in nature. This provides the essential bio-geochemical information for understanding the environmental behaviour and cycling of pollutants.

Combined measurements of natural samples for their carbon-13/carbon-12 and nitrogen-15/nitrogen-14 abundances have proven useful to identify sources of marine organic matter, nutritional sources for marine food webs, and trophic relationships among marine organisms. Research at IAEA-MEL has elucidated uptake mechanisms and inter-relationships between planktonic communities which form the basis of the marine food web. Other research involving the Laboratory has provided insight into the allochthonous and autochthonous inputs which feed into marine ecosystems and the trophic relationships therein.



Marine pollutant transfer and transport by biological processes

Principle of field experiments to study the efficiency of sewage pipelines to the ocean



A potentially important area of pollution research which is likely to develop in future years relates to the fact that fertilizer nitrogen is reduced in the heavy isotope. This offers a useful method to differentiate fertilizer inputs in studies on eutrophication (or the unusual increase in the fertilization of the sea). Eutrophication has been recognized as a most serious source of perturbation of the marine environment caused by human activities. Since it is impossible to chemically distinguish between "natural" and "man-made" nutrients, the isotopic technique offers a unique possibility of assessing the significance of land-based sources of nutrients and eventually controlling them.

Dating of sediment cores

It is only during the last century that man has significantly polluted his environment. This coincides with industrialization, advances in technology, and the use of fossil fuels. With many pollutants — such as heavy metals and hydrophobic organics — in aquatic environments, these elements/compounds are bound to particulate material. Deposited sediments, therefore, represent a repository and once buried within the sediments these pollutants are frequently trapped and stabilized (especially under anoxic conditions).

Under these circumstances, it is possible to take a sediment core and to estimate the sedimentation rate by using suitable geochronological techniques. Lead-210 (derived from the natural uranium-238 decay series with a half-life of 22.4 years) has proven to be the most widely used nuclide in geochronological studies to investigate pollution histories. The lead's activity can be analyzed throughout the sediment core so that sections represent 22.4 year time intervals. Layers can then be analyzed for relevant pollutants whose flux and deposition over time can be determined.

Confirmation of dating can be achieved by monitoring artificial nuclides associated with weapons testing (usually caesium-137 has been selected). These elements/isotopes peak at around 1963. Although bioturbation within sediments can mix materials within cores, the approach described has been successfully used to assess input histories of trace metals, pesticides, polychlorinated biphenyls, saturated hydrocarbons (oil), and polycyclic aromatic hydrocarbons (PAH).

An example of the historical record of lead and PAH pollution from fossil fuel combustion has been obtained from a dated sediment core from a United Kingdom estuary. (See graph, next page.) It demonstrates the dramatic increase in release of these contaminants during the last decades.

Isotopic techniques to "fingerprint" oils

Petroleum genesis induces a wide range of isotopic signals which, in general, differ significantly from the isotopic compositions of the natural modern marine environment. Stable carbon isotope ratios have been valuable in the exploration for petroleum and in the understanding of formation processes.

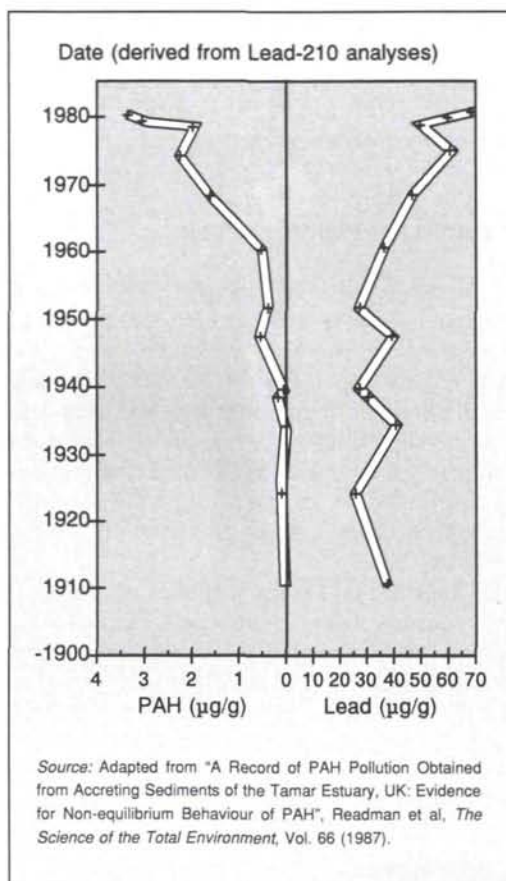
Although present in oils at lesser quantities than carbon, sulphur and nitrogen isotopic abundances have also been shown to reflect source and geological histories of formation. Thus they also afford oil-field specific ratios. The characteristic isotopic ratios of these elements can be exploited to "fingerprint" oils spilled into the environment in order to determine the source or sources. Studies have demonstrated that the isotopic compositions are comparatively resistant to change during weathering of the oil in the marine environment.

Stable isotope ratios were recently used by IAEA-MEL in conjunction with non-nuclear fingerprinting techniques (including fluorescence spectrophotometry, capillary gas chromatography-flame ionization detection, and capillary gas chromatography-mass spectrometry) to investigate the extent of contamination of the Gulf marine environment following the massive spillage of petroleum during the Gulf War. (See related article in this edition.)

In addition to the stable isotopes, carbon-14 measurements can potentially provide information on oil contamination. Petroleum-derived organic matter contributes a zero carbon-14 signal to the specific activity of modern marine organic carbon (which is 261 mBq/g) or to the carbon activity of current terrestrial matter (271 mBq/g), which thus is still around 20% higher than the purely natural baseline specific activity because of the recent influence of nuclear weapons testing. The coastal marine organic reservoir is relatively depleted in carbon-14 through a combination of factors. However, the zero carbon-14 signal from petroleum contamination (because of complete decay during the oil's geological formation) should provide a useful quantitative indication of the contribution of petroleum carbon to the total organic matter of the marine organic pool.

Labelling techniques in "molecular biology"

While the presence of many contaminants in the environment can be quantified using chemical analytical techniques, the question that al-



Distribution of lead and polycyclic aromatic hydrocarbons in a sediment core in the United Kingdom

ways arises is, "Are the levels sufficient to cause detrimental biological effects?"

In recent years much effort has been focused on the evaluation of relationships between contaminant exposure and observed biological effects in marine organisms. Measures of sub-acute exposure have included investigations of cytological changes, induction of enzymes, and quantification of chromosomal aberrations. Recently attention has been directed towards "genotoxic" compounds. These refer to pollutants which act by damaging the DNA, thereby providing the opportunity for induction of cancer. Such compounds include PAH and polychlorinated biphenyls (PCBs), both of which are classes of ubiquitous environmental pollutants.

In chemical carcinogenesis, chemical modification of the DNA is believed to be the critical initial step. This frequently involves binding of the organic pollutant (or its "active" metabolite) to the DNA. Ultra sensitive techniques are required to detect low levels of carcinogen-DNA binding. Phosphorus-32 post-labelling methods developed for base composition and sequencing analyses of nucleic acids have proven particularly successful to investigate carcinogen-DNA adducts. The technique has proven effective to determine adducts arising

from low-level environmental exposure. Scientists have demonstrated that in some marine organisms the adducts persist for months, thus affording information on the exposure history of organisms to chemical carcinogens.

Neutron activation analysis

Neutron activation analysis (NAA) is one of the most sensitive and accurate techniques for trace metal measurement in solid matrices. It is thus readily applicable for the study of many trace metals in marine matrices. Activation of major components of the sea salt itself limits its utility in seawater analysis; however, this is easily facilitated by chemical separation of the analyte trace metals (by co-precipitation) prior to analysis.

Unfortunately, many institutes do not have ready access to the rather costly facilities required for instrumental NAA. Nevertheless, its power as a reference technique is well employed by the intercomparison exercises of IAEA's Analytical Quality Control Service. The participation of more than 20 institutions applying NAA helps to assure an accurate calibration of

IAEA's reference materials used by hundreds of analysts worldwide. In this manner, the benefits of nuclear techniques are transferred to the many institutions which do not have the technical or financial resources to apply them on a routine basis.

An ongoing challenge

The few examples selected for this brief review serve to illustrate the major role that nuclear techniques have already played in marine pollution studies (as with oceanography in general) and the important role which they should play in the future.

The IAEA, and particularly its Marine Environment Laboratory in Monaco, have worked for over 30 years in the development and furtherance of applied nuclear techniques for studying the marine environment. This work will never be complete. The challenges facing human society are continuously increasing, requiring the continual development of new and better approaches to assessing, predicting, and minimizing the impact of human development on the natural environment. □

Collecting marine organisms off the coast of Monaco. (Credit: IAEA-MEL)

