



Review

Isotope analysis for marine environmental studies

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ABSTRACT

Nuclear techniques and isotopes can be efficiently exploited for studying pollution processes of different origin and their connected mechanisms of diffusion. The IAEA Environment Laboratories through its Marine laboratories is since almost fifty years applying these methodologies for environment assessment to sustain member states in a sustainable development of their environment.

This review does not pretend to report in an exhaustive manner on the effectiveness of the use of isotope for environmental studies, but it provides a short summary of the application of isotope analysis as tools to track the source and the levels of chemical and biological contamination. Emphasis is placed, in particular, on the use of isotope analysis for the determination and the tracking of organic pollutants.

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1. Introduction

The greatest natural resource on the Planet, the World Ocean is both the origin of most life forms and the source of survival for hundreds of millions of people. Pollution of the oceans was an essential problem of the 20th century that was associated with the rapid industrialization and unplanned occupation of coastal

zones. It continues to be a concern in the 21st century. The most serious environmental problems encountered in coastal zones are presented by runoff of agricultural nutrients, heavy metals, persistent organic pollutants such as pesticides, and harmful algal toxins. Oil spills from ships and tankers continually present a serious threat to birds, marine life and beaches. Also, many pesticides that are banned in most industrialized countries remain in use today, their trans-boundary pathway of dispersion affecting marine ecosystems the world over. In addition to these problems, ocean dumping of radioactive waste has occurred in the past, and might occur again, with authorised discharges of radioactive substances from nuclear

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facilities into rivers and coastal areas contributing to the contamination of the marine environment.

A trans-boundary issue, marine pollution is often caused by inland economic activities, which lead to ecological changes in the marine environment. Examples include the use of chemicals in agriculture, atmospheric emissions from factories and automobiles, sewage discharges into lakes and rivers promoting the occurrence of harmful algal blooms (HABs), and many other phenomena taking place hundreds or thousands of kilometres away from the seashore. Sooner or later, these activities affect the ecology of estuaries, bays, coastal waters, and sometimes entire seas, consequently having an impact on the economy related to maritime activities.

In order to ensure the sustainable use of marine ecosystems it is necessary to measure critical contaminants individually and to obtain reliable data on their source, levels, dynamics and fate. Isotope analysis provides a unique source of information for identifying nuclear and non-nuclear contaminants and tracing their pathways in the environment, as well as for investigating their biological effects. This review provides a short summary of the application of isotope analysis to track the source and the levels of contamination, emphasising the use of stable isotope analysis for the determination and the tracking of organic pollutants.

2. Tracking contaminants in the marine environment through the application of isotopic tracers

Determining pollution sources is one of the biggest issues in evaluating the incidence and severity of contaminants in the marine environment. For the past 50 years, the impact of human activity has aggravated environmental conditions in marine ecosystems. In effect, a wide range of waste and discharge emerging from industries and activities undertaken at the local, sub-regional and regional levels combine in the world's ocean currents, resulting in a global distribution of contaminants. To curb these phenomena it is imperative for countries to apply environmental regulation that considers socioeconomic development on par with environmental protection at local and global scales. However, effective environmental regulation can only be accomplished if contaminant distributions are clearly linked to known processes or sources. Stable carbon isotope analysis can help track sources of organic pollutants. The stable isotopic composition of a contaminant in the environment is the end result of a composite sequence of events. Chemicals produced from distinct sources by essentially different processes are expected to exhibit specific isotopic compositions that can be used to identify sources.

One of the most significant advances in analytical chemistry in the past few years has been the development of individual compound-specific stable isotope analysis (CSIA). This technique, which is based on gas chromatography/isotope ratio mass spectrometry (GC/IRMS) allows for the measurement of the carbon isotopic signature of individual compounds within a complex mixture. CSIA of carbon is being used to uniquely identify naturally occurring pollutants, such as polycyclic aromatic hydrocarbons (PAHs), chlorinated solvents, polychlorinated biphenyls (PCBs) and crude oils and refined hydrocarbon products. GC/IRMS can be also used to measure the nitrogen and hydrogen isotopic composition of individual compounds. The ability to monitor more than one isotopic composition greatly improves the ability to identify the sources and processes controlling contaminant behaviour in the environment. While GC/IRMS systems are not yet available to measure the chlorine isotopic composition of individual chlorinated contaminants, chlorine isotope analysis is a useful technique for studying the sources and fate of common chlorinated contaminants. Molecular level radiocarbon (^{14}C) analysis of compounds is

also used to determine which compounds are either natural products or derived from industrial synthesis.

2.1. Hydrocarbons and oils

Hydrocarbons and oil products are a group of pollutants that have complex and diverse composition and which cause various impacts on living organisms – from physical and physicochemical damage to carcinogenic effects. Hydrocarbons can be synthesized by living organisms (biogenic origin), produced during the degradation of the organic matter (diagenetic origin), formed during incomplete organic matter combustion (pyrolytic origin) and introduced in the modern environment via natural and anthropogenic release of fossil fuel combustibles (petrogenic origin). The estimated average annual amount of oil entering the marine environment from ships and other sea-based activities, based on data from 1988 to 1997 is 1,245,200 tonnes/year [1]. It is important to distinguish and evaluate the relative importance of those different sources that contribute to the contamination of a particular environment. Until recently, source apportionment studies of hydrocarbons in the environment mostly relied on molecular fingerprint recognition. Nevertheless, processes affecting hydrocarbons in the marine environment (evaporation, dissolution, photooxidation, biodegradation, etc.) might alter the initial hydrocarbon molecular profiles due to the preferential compound losses or degradation, increasing the chances of ambiguity in using molecular profiles in source identification.

Petroleum genesis induces a wide range of isotopic signals, which in general differ significantly from the isotopic compositions of unpolluted marine ecosystems. The complex isotopic fractionation patterns induced by physical and biological processes result in characteristic $^{13}\text{C}/^{12}\text{C}$ ratios that can be used to classify crude oils, petroleum products and tars. While most emphasis has been placed on the use of bulk carbon isotopes for source and correlation purposes, a number of forensic applications include other stable isotopes. Sulphur, nitrogen and deuterium isotopic abundances also reflect source and geological histories of formation, which contain 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. While bulk measurements provide useful information, the compound specific isotope analysis of individual components within a specific type of oil represents a unique signature of its origin and maturation [2].

In conjunction with the existing tools of biomarkers, GC-IRMS has been used for forensic identification of gasoline and crude oil spills. For example, it allows correlating hydrocarbons spilled in aquatic environments with their suspected source(s) based on comparison of the isotopic composition of individual hydrocarbons. Differences in the isotope composition of individual compounds within a gasoline or crude oil sample are immediately apparent and reflect their different origins. In this regard, although weathering can result in a remarkable loss of volatile hydrocarbons, $\delta^{13}\text{C}$ values of non-volatile and semi-volatile compounds are unaffected by weathering and their isotopic profiles can be used to identify and trace the source of an oil spill.

After the Erika spill,¹ bulk and individual compound isotopic analyses on oil residues sampled along the Atlantic Coast of France allowed the unambiguous differentiation of samples related to the Erika oil spill from those due to other tar ball incidents [3]. CSIA of carbon was also recently used in conjunction with non-nuclear fingerprinting techniques to investigate the sources of the oil slicks

¹ The Maltese tanker “Erika” broke in two parts close to the Atlantic coast of France on December 12, 1999. It is believed about 10,000 tonnes of oil spilled into the sea.



Fig. 1. The red line shows the route taken by the oil carrier Prestige, from the time it started leaking oil on 13/11/2002 until it sank in 19/11/2002. The dark smudges indicate the oil spill detected by satellite remote sensing. Data compiled with nuclear techniques complemented with satellite imagery can be instrumental in identifying pollution sources (adapted from UNEP-WCMC, 2002). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

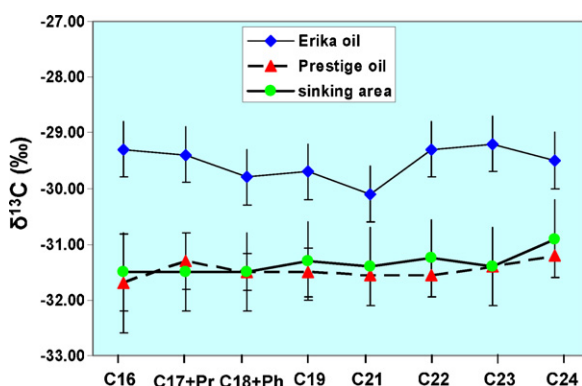


Fig. 2. Comparison of the carbon isotopic signatures of the fuel oil found above the Prestige wreck in October 2006 with the one originally carried by the tanker in 2002 and that from the Erika [3]. The variation in $\delta^{13}\text{C}$ is reported for the different hydrocarbons (C_n where n is the number of carbon atoms in n -alkanes; Pr, pristane, Ph, phytane) [4].

sampled in the vicinities of the wreck more than four years after the Prestige² accident (Fig. 1). The isotopic data was used to ascertain that the oil from the slicks matched the oil originally carried by the Prestige tank (Fig. 2) [4].

The measurement of hydrogen isotope ratios in specific petroleum hydrocarbons is also a powerful technique to identify the source of the contaminant since the hydrogen isotope ratios of crude oil hydrocarbons show a wide compositional variation and are conserved during aerobic biodegradation. In the future, both hydrogen and carbon isotopic data should be considered when tracing contamination sources and monitoring biodegradation.

In addition to the stable isotopes, radiocarbon (¹⁴C) measurements can potentially provide information on oil contamination. Petroleum-derived organic matter is ¹⁴C free, on the other hand total marine organic matter is labelled with ¹⁴C originating from both ¹⁴C produced naturally in the atmosphere by cosmic radiation and in nuclear weapons explosions. Therefore, the absence of the ¹⁴C signal in contaminants derived from fossil-fuel (as the complete decay during the oil's geological formation) provides a useful quantitative indication of the contribution of petroleum carbon to the total marine organic matter.

2.1.1. Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are a widespread class of organic contaminants that enter the marine environment mostly due to atmospheric deposition and oil spills. They can be formed during incomplete combustion processes (pyrolytic origin) of organic matter (e.g. coal, oil, wood), and are also major constituents of crude oil (petrogenic origin). They might also derive from the biological and physicochemical alteration of organic matter, which occurs in sediments after deposition (diagenetic origin). As some PAHs exhibit mutagenic and carcinogenic properties, the knowledge of their sources is of key importance due to their ecotoxicological nature, which present long-term health effects on nearshore marine systems, affecting ecological processes, public health and social and commercial use of marine resources. In this context, molecular stable carbon isotopic composition of PAHs by GC/IRMS is a powerful tool for use in conjunction with molecular fingerprint examination for studying the sources and environmental fate of hydrocarbons in the modern environment. For instance, atmospheric contaminants from combustion source materials such as soot from biomass, natural gas, coal burning and vehicle exhausts might be tracked to source materials because of the isotope signals of the PAH products [5,6].

Other studies on carbon isotopic analysis of PAHs in sediment samples near a former gas-manufacturing plant in Illinois indicated that the hydrocarbons were not the same as the tarry soil samples recovered from the gas plant [7]. The dominant signatures identified in the surface sediments came from a mixture of PAH sources such as coal tars and carburetted water gas tars. Source apportionment might be complex because the range of $\delta^{13}\text{C}$ values of PAHs originating from different combustion processes such as diesel, coal, gasoline, and wood burning smoke might overlap each another. However, it has been shown that distinct isotopic signatures are produced by primary petroleum and combustion-related PAH sources, as well as between the combustion of C_4 plants using the C_4 photosynthetic pathway, termite nests or biogenic natural gas. On the other hand, radiocarbon dating of individual PAHs using off-line gas chromatography/accelerator mass spectrometry (GC/AMS) is emerging as a promising tool to apportion fossil and contemporary or biogenic sources of compounds in marine samples [8,9].

2.2. Halogenated organic compounds

Most of the halogenated organic compounds belong to the category of persistent organic pollutants, which have a tendency to bioaccumulate along the food chain, causing toxic and mutagenic effects. A few studies have reported the ¹³C compound specific isotope analysis (CSIA) of commercial polychlorinated biphenyl (PCB) and polychlorinated naphthalene mixtures (PCN) such as Aroclors, Kanechlors, Phenoclors, etc. to establish baseline data for future identification of these anthropogenic contaminants [10]. Recent studies have also detected some bipyrrolic halogenated organic compounds worldwide and accumulating in the marine food webs [11]. To date, it has been difficult to determine whether these compounds are natural products or derived from industrial synthesis. Radiocarbon ¹⁴C is a tracer used to distinguish between natural or synthetic compounds. In this context, radiocarbon analysis may be used as a tool to establish the origin of halogenated organic compounds since all recent natural products have modern or contemporary ¹⁴C levels. In contrast, synthetic goods derived from petrochemical products contain no measurable ¹⁴C.

² On November 13, 2002, the tanker "Prestige" vessel broke in two at 240 km off NW Spain and sank at more than 3000 m depth with about 58,000 tonnes of heavy fuel oil and leaking from several cracks in the structure.

³ C_4 designates the photosynthetic pathway of the plants that fix carbon to produce a four-carbon molecules, in contrast to the majority of plants that produce C_3 molecules.

2.3. Perchlorate

The widespread introduction of synthetic and agricultural perchlorate (ClO_4^-) into the environment has contaminated numerous municipal water supplies – in the marine environment, contamination by this compound presents an unequivocal problem. Various potential sources of ClO_4^- are present, including agriculture (past or present), fireworks manufacture and use, military bases including missile storage and launch facilities, road-flare runoff, and lawn fertilizer, among others. Stable isotope ratio measurements of chlorine and oxygen have been applied for discrimination of different ClO_4^- sources in the environment. More recently, the characteristic ^{36}Cl and ^{37}Cl isotopic abundances found in the three principal sources of ClO_4^- present in the environment allowed these sources to be distinguished from each other. These results may have immediate forensic applications in delineating the sources of ClO_4^- in water supplies and foodstuffs, and they may provide important constraints for determining the natural production mechanism of ClO_4^- [12].

3. Stable isotopes to study bioremediation

In situ bioremediation has emerged as one of the most important alternatives to mitigate the damage caused by marine oil spills and other hydrocarbons. However, it is imperative that biotransformation processes are accurately understood and quantified. Quantification of intrinsic biodegradation may also reduce site remediation costs where engineered remediation is instituted. For that, the natural abundance of stable isotopes of essential elements involved in the biodegradation processes (carbon, hydrogen and oxygen) are used to monitor the occurrence of in situ biodegradation, the pathways of degradation and the rates and extent of biodegradation of fuel or chlorinated hydrocarbons. Monitoring of in situ biotransformation using stable isotopes may be achieved by the analysis of isotopic compositions (i) of the products of degradation, (ii) the residual fractions of the contaminant, and (iii) dissolved inorganic carbon of the water, because isotopic fractionation results in preferable degradation of chemical bonds with lighter compared to heavier isotopes⁴ [13]. Carbon dioxide produced by organic matter oxidation, inorganic carbon dissolution, or contaminant hydrocarbon degradation has characteristic ^{13}C isotope ratios. Their ^{13}C values are useful tools for the assessment of in situ biodegradation in complex environments. Furthermore, the oxygen isotopic compositions of molecular oxygen, nitrate, and sulphate in complex systems are affected primarily by microbial processes, and isotopic fractionation during microbial respiration produces a significant change in the $\delta^{18}\text{O}$ of the residual molecules. The combination of the isotopic compositions of CO_2 and O_2 help to distinguish between aerobic and anaerobic production of CO_2 and for quantifying microbial respiration rates [14].

In general, quantitatively differentiating the effects of biotransformations from physical processes on contaminants is challenging. However, CSIA allows for the rapid determination of carbon and hydrogen isotopic signatures of organic compounds over the course of biodegradation by measuring the two stable isotopes of carbon and of hydrogen. CSIA is used as an indicator parameter to assess the in situ biodegradation of the chlorinated solvents and fuel oxygenates, e.g. methyl *tert*-butyl ether. In comparison with the carbon isotopes, the hydrocarbon isotopes display large variation in the deuterium isotope values. Indeed, the hydro-

gen isotope ratio of the light petroleum hydrocarbons can also be used to monitor in situ bioremediation of crude oil contamination.

4. Stable isotopes to track bio-magnification of contaminants

Many persistent organic pollutants (POPs) present in the aquatic environment tend to accumulate in aquatic organisms due to their hydrophobicity. The widespread and persistent nature of these chemicals has been linked to various environmental effects, including pollution of water, sediments, and of the aquatic food chain. The health effects posed by exposure to these chemicals include disturbances ranging from disorders of the nervous or immune system, to increases in the risk of certain cancers. In the last two decades, the study of biomagnification⁵ profiles of POPs including PCBs, PAHs, organotins and trace elements through aquatic food webs has been facilitated through stable isotope ratio analysis of bioelements, such as carbon and nitrogen. In general, the stable nitrogen isotope ratio $\delta^{15}\text{N}$ increases by 3–4‰ per trophic level in a food chain. Thus, the value of $\delta^{15}\text{N}$ is suitable for determining the trophic position of each organism in a food web. The stable carbon isotope ratio, $\delta^{13}\text{C}$, is enriched slightly by about 1‰ per trophic level, enabling its use in identifying primary carbon sources in a food web [15].

5. The use of isotope labelling to study the fate of contaminants

Understanding contaminant input routes, transport mechanisms and environmental conditions provides the basis for determining the fate of contaminants. This enables us to explain and anticipate contaminant impacts on environmental biodiversity and human health. Data on the environmental fate of contaminants are required in order to determine the potential of a pollutant to reach coastal waters, including information on its hydrolysis, photolysis and aquatic metabolism. The introduction of a labelled tracer into a controlled experimental system permits the investigation of the interaction of individual contaminants with biotic and abiotic components of the environment. Classically, carbon-14 labelled xenobiotics⁶ are applied to study the fate of organic compounds in laboratory mesocosms.⁷ The radioactivity of the label is used to trace the mineralization ($^{14}\text{CO}_2$), the portion of extractable material and to quantify the part of the label incorporated within the sediment-bound residues or accumulated into the organisms. Compared with the ^{14}C technique, the ^{13}C labelling method allows for direct structural assignments of the compounds by mass spectrometry, easy handling and can be performed in the field.

6. Stable isotopes to study eutrophication

The rise in the human population in coastal watersheds and changes in land use has led to increases in the delivery of nutrients in aquatic environments. The resulting eutrophication of coastal waters has many adverse effects in the marine environment, through disturbance of ecological balances and fisheries, and through interference with recreational activities and quality of life. Eutrophication – nutrient enrichment leading to elevated

⁴ The stability of a chemical bond depends on the isotopic composition. Bonds between lighter isotopes (e.g. ^{12}C – ^2H) are more readily broken than bonds between heavier isotopes (e.g. ^{13}C – ^2H).

⁵ Biomagnification is the increase in concentration of a substance that occurs in a food chain as a consequence of persistence, food chain energetic and low rate of internal degradation of the substance.

⁶ Chemical found in an organism, but not normally produced or expected to be present in it.

⁷ A mesocosm refers to “an experimental system that simulates real-life conditions as closely as possible, whilst allowing the manipulation of environmental factors”.

production of particulate organic matter – is one of the profound impacts caused on coastal ecosystems by human activity. Increased nutrients loading can lead to blooms of toxic red tides including enhanced primary production, changes in community structure, increases in sedimentation and oxygen consumption, oxygen depletion in the bottom water and sometimes the death of benthic animals and fish. These adverse effects have prompted the search for suitable indicators of eutrophication to assess water quality of aquatic ecosystems [16]. Stable nitrogen isotope ratios ($^{15}\text{N}/^{14}\text{N}$; i.e. $\delta^{15}\text{N}$) have been widely used as indicators of anthropogenic eutrophication in aquatic ecosystems. Sewage water typically has a high nitrogen stable isotope ratio ($\delta^{15}\text{N}$) due to denitrification during the treatments. Applications of nitrogenous fertilizer to agricultural farmlands lead also to an enhancement of soil de-nitrification and increase the $\delta^{15}\text{N}$ in groundwater. In contrast, the $\delta^{15}\text{N}$ of nitrogen derived from atmospheric deposition and nitrification fixation by bacteria are much lower. Groundwater and sedimentary organic matter with an elevated $\delta^{15}\text{N}$ appears to act as an indicator of the level of anthropogenic nitrogen loads to coastal waters, and the $\delta^{15}\text{N}$ delivered to the coastal waters are transferred to the food chain. Nitrogen isotope ratios of marine producers may be used to identify incipient eutrophication in coastal waters.

The dual isotope analysis of nitrate (NO_3^-) in water ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) is used to further differentiate sources of nitrate when $\delta^{15}\text{N}$ ranges overlap. For example, $\delta^{18}\text{O}$ can be used to separate NO_3^- fertilizer from soil nitrogen and ammonia (NH_4) in fertilizer and rain. Additionally, both the $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of the residual nitrate increase systematically as a result of denitrification. Other isotopes, e.g. sulphate oxygen and sulphur isotopes in river water might also enable the discrimination between natural (geological, sea water, geothermal and volcanic) and anthropogenic sources such as fertilizers. Employment of more than one isotopic proxy will allow for a more accurate identification of the nutrient sources available to primary producers.

The analysis of proxy records preserved in sediments often provide the only way to reconstruct environmental change in areas impacted by eutrophication and to establish pre-impact baselines. Stable carbon isotope ratios in microfossils provide a tool for reconstructing historical environments, in particular organic carbon delivery to sediments. Increased organic matter inputs typically lead to a decrease in ^{13}C in the carbonate shells with a concomitant ^{13}C increase in the organic matter. Furthermore, the main indicators of enhanced primary production linked to eutrophication is phytoplankton. Their remains, and the specific chemical markers derived from them (e.g. lipid biomarkers) [17], can be used to track changes in plankton communities in response to eutrophication. Moreover, since eutrophication leads to raised ^{13}C values due to increased marine phytoplankton production, the compound specific carbon isotope analysis of lipid biomarkers reflect the strength of the eutrophication.

7. Use of radioisotopes for the detection of toxins in harmful algae blooms (HABs)

One of the most worrisome manifestations of HABs is that certain algal species produce toxins that can accumulate in seafood products (predominantly shellfish and fish) and then pose a risk to human consumers. Fig. 3 shows a map of the regions affected by the phenomena of HABs and the increase of HABs events worldwide.

The heterogeneity within and among toxin classes makes toxin detection and quantification challenging. Different species of algae – examples are shown in Fig. 4 – produce different types of toxins. Numerous approaches to toxin detection have been developed, generally categorised as whole animal (in vivo) bioassay, in vitro bioassays, and quantitative instrumental analysis. One useful tech-

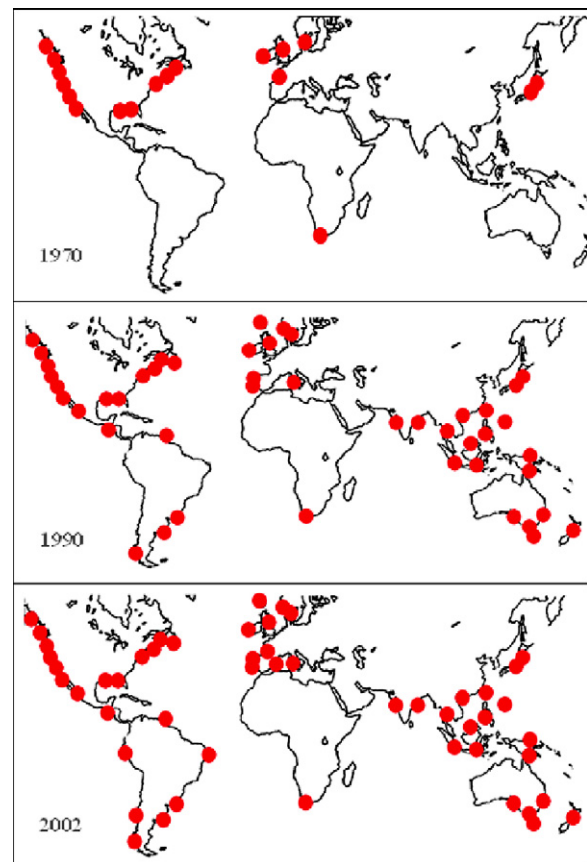


Fig. 3. Harmful algal blooms (HABs) events (sites indicated with red dots) – a growing concern worldwide – produce toxins that accumulate in marine species rendering them unfit for human consumption (adapted from IOC-UNESCO website <http://ioc-unesco.org/hab/>). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

nique of analysis employs radioisotopes – the receptor binding assay (RBA). The RBA is a technique based on the function, or pharmaceutical activity of the toxins – i.e., the highly specific interaction of a toxin with a biological receptor. For example, the saxitoxins (STXs) are toxic because they bind to and block sodium channels in certain types of human tissues, disrupting muscle function and leading to paralysis and death. The sodium channel is the logical receptor to be used in a receptor binding assay for STXs. RBAs have been developed for toxins that affect the sodium channel (PSP, NSP and CFP toxins) [18,19] and glutamate receptor (ASP toxins) [18,20]. The binding of toxin molecules containing a radionuclide such as Tritium (^3H) to the receptor sites is then determined by a liquid scintillator counter. Like the animal bioassay, the RBA provides an estimate of the total toxicity potency of the seafood sample

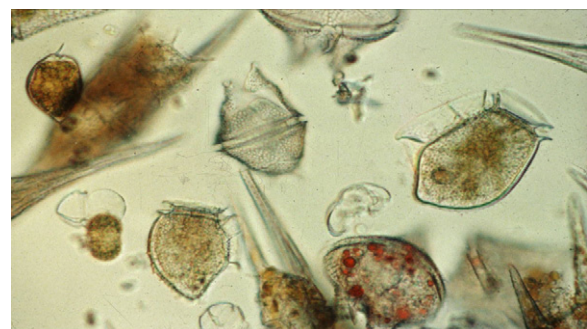


Fig. 4. Example of harmful microalgae.

tested. In addition, it allows a large sample throughput during HABs events.

The ability of the receptor binding assay to detect very low levels of toxins in seawater and in seafood makes this alternative method appropriate for an early warning which facilitates the management of HABs in terms of human health impact and decision making for fisheries closure.

8. Long-lived radionuclides and isotope ratios measurements

With the advent of advanced mass spectrometric (MS) techniques, long-lived radionuclides determination has become more accurate and fast compared to radiometric methods. The advantages with MS techniques are the outstanding capacity to determine precise and accurate isotopic abundances and isotopic ratios. Isotope ratio measurements have been applied increasingly for investigating the fine isotope variations in the nature, age dating of geological samples, provenance determination of environmental contamination, nuclear material accounting and pollution control, and for biological studies with tracer experiments. Applied to marine ecosystems, the technique assists in determining and tracking sources of contamination. Moreover, mechanisms of transport of contaminants as well as their accumulation/desorption from sediments can be followed. Sources of environmental contamination can be identified by an isotopic abundance and/or an isotopic ratio analysis which serves as a kind of “fingerprint” of the contamination. Chemicals produced from distinct sources by essentially different processes are expected to exhibit specific isotopic compositions that can be used to identify pollution sources. Once the different source terms (e.g., anthropogenic or natural geogenic) are identified, the isotopic ratios can be used to quantify the contribution of each source by source apportionment. Recent developments in mass spectrometry with the developments of better performing magnetic sectors and their coupling to electrostatic sectors have brought a new dimension to this field. In addition to its simple and robust sample introduction, high sample throughput, and high mass resolution, the flat-topped peaks generated by this technique provide for accurate and precise determination of isotope ratios. These features, in combination with the ability of the inductively coupled plasma source to ionize nearly all elements in the periodic table, have resulted in an increased use of inductively coupled plasma-mass spectrometry (ICP-MS) for such measurements in various sample matrices.

Although not only single-collector, but also multi-collector sector field ICP-MS has provided to be very useful in isotopic studies, the introduction of multi-collector sector field ICP-MS seems to become even more important for determination of natural isotopic variations in the element of interest. The enhanced precision of isotope ratio measurements makes possible to tackle these demanding applications, but it is imperative to realise that to obtain meaningful results very strict prerequisites must be fulfilled with regard to sample preparation, avoidance of cross-contamination and correction for mass discrimination.

Moreover mass spectrometric technique can be coupled with chemical separation on-line methods such as liquid chromatography, allowing a fast throughput of samples avoiding manual radiochemical separations. Fig. 5 shows the simultaneous separation and determination of actinides and lanthanides in marine sediment by ICP-MS on-line coupled to a chromatographic system.

The ability to measure isotope ratios allows also the use of isotope dilution as a calibration strategy in ICP-MS, along with the more common approaches of external calibration and the standard additions. An isotope ratio is far more robust than a signal intensity, which makes isotope dilution mass spectrometry (IDMS)

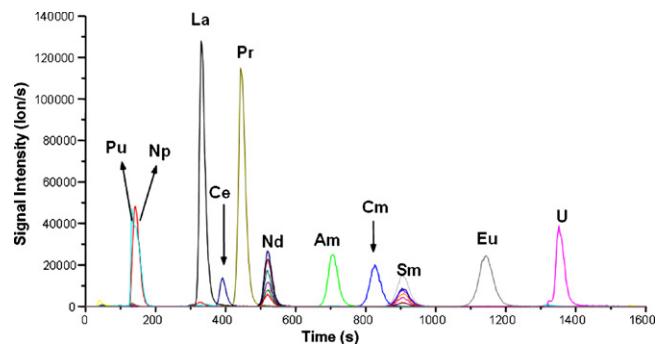


Fig. 5. Simultaneous chromatographic separation and on-line mass spectrometric determination of lanthanides and actinides in a marine sediment sample. This is instrumental in determining isotope ratios that are important in identifying and tracking sources of contamination (M. Betti, ITU Summer School 2003 on “Actinide Science and Applications”; EU Joint Research Centre - ITU, Karlsruhe).

a very reliable approach. When carried out with the utmost care and control of all factors affecting the final uncertainty, IDMS provides highly accurate and precise results and therefore is the best calibration strategy for certification measurements in the production cycle of various certified reference materials. Its use is also advisable when the sample pre-treatment includes a trace/matrix separation step, for which quantitative recovery is not guaranteed.

9. Radiometric dating/radio-chronology

Historical records of organic and inorganic pollution combined with isotopic fingerprinting of contaminant sources are a powerful argumentative tool to link the evolution of contaminants with socioeconomic decisions. This is illustrated in a combined investigation examined whether pollution in the marine sediment environment was responsible for a ten-year decrease in lobster catch in Batabano Bay (Cuba) [21,22]. The first conclusion derived from the dating and pollution measurements of this study is that in general pollution levels in the Batabano Bay are very low and have not significantly changed during the period of interest, except for some local hotspots. The study demonstrates that in order to reconstruct changes in pollution over time environmental archives (i.e. marine sediments, corals) are helpful as they store information on the pollution during the geological past. A record of pollution is obtained by combining age-dating with the measurements of the pollutant of interest.

A basic concept of environmental pollutant and climate change studies is to find environmental archives that could be characterised and dated. This is important in order to show the impact of events and discharges in the past. Sediments are usually acting as sinks of material and could be used to study environmental records. In undisturbed sediment newly formed material lay on top of the older forming such an archive where the sediments can be dated and also with the possibility to characterise the pollutants and their changes over time. Several dating techniques exist for such recordings. Most of these dating techniques are based on the radioactive decay rates of the different radionuclides present in the system. In Table 1 the most common dating techniques are presented.

Three kinds of radionuclides are normally used for age-dating of marine archives: anthropogenic, cosmogenic and natural radionuclides. In order to use these radionuclides, the initial concentration must be known together with the production and losses in the system. Anthropogenic radionuclides can be used as tracers for sedimentation, oceanographic and geochemical processes. The anthropogenic radionuclides are often easy to measure; they have a unique signature and a well-defined source term and act like nuclear fingerprints for processes in time and space and can for that

Table 1
The most common applications for radiometric dating/radio-chronology.

Dating technique	Application and range	Principles	Further reading
Anthropogenic radionuclides (e.g. ^{137}Cs , plutonium isotopes)	Sediments, past ~50 years	Time of release of anthropogenic radionuclides from e.g. nuclear facilities sets a time marker in environmental archives	[23]
^{210}Pb	Sediments, <150 years	The decrease of ^{210}Pb in sediments is a function of time	[24]
^{14}C	Organic material, <50,000	Decay of ^{14}C in organisms.	http://www.radiocarbon.org/ [25] http://www.c14dating.com/
Luminescence dating	Dating of minerals in e.g. sediments, <400,000 years	Minerals (feldspar, quartz) “store” information on the absorbed dose they have received over time. This “memory” can be recorded and can be translated in age information	http://www.nclr.risoe.dk/ http://crustal.usgs.gov/laboratories/luminescence_dating/technique.html
Uranium series ($^{230}\text{Th}/^{234}\text{U}$, $^{234}\text{U}/^{238}\text{U}$) dating	Sediments, corals, <1.5 mill years	Disequilibrium between daughter and parent leading to either a deficiency or an excess of the daughter nuclides which can be measured as a function of time	http://www.onafarawayday.com/Radiogenic/index.htm [24]

reason also be used in radiometric dating. Anthropogenic enriched radionuclides have only been present in our environment in a very short/recent geological-time scale. The first significant appearance of anthropogenic radionuclides – e.g. ^{137}Cs and plutonium isotopes – in the environment was a result of atmospheric nuclear bomb tests, which peaked in 1963. Thus, the first appearance of ^{137}Cs in sediments can be used as a time marker. Cosmic radiation interacts with our atmosphere and forms so called cosmogenic radionuclides such as ^{14}C and ^{10}Be by particle reaction. It is assumed that this production has been fairly constant over time. These radionuclides are scavenged from the atmosphere to the surface of the earth mainly by rain and the distribution pattern and fluxes are well known. Carbon combines with O_2 and is incorporated into living organisms. When the organism dies, the ^{14}C concentration (in relation to ^{12}C) in the dead organism will be a function of time and can consequently be used in radio-chronology. For minerals ^{14}C cannot be used as it is not incorporated in the matrix. For such material the uranium-, and thorium-decay series and primordial radionuclides (e.g. potassium/argon ($^{40}\text{K}/^{40}\text{Ar}$) decay system) are applied for age determination. These radionuclides have similar half lives as the age of our solar system and are mostly used in long geological timescale. A special case of, and frequently used radionuclide in dating of sediments, is the natural radionuclide ^{210}Pb in the ^{238}U decay chain. This technique is based on that the daughter radionuclide ^{222}Rn in the ^{238}U decay chain is a noble gas and some fraction of the Radon will diffuse in to the atmosphere where it decays to particle reactive daughter nuclides. These daughters will rapidly decay to ^{210}Pb which has a longer half life (about 22 years) than the intermediate radionuclides. These aerosol particles, with the ^{210}Pb , are then scavenging down, and if they have been integrated in the aquatic environment, further down to the sediments. It is assumed that the annual flux of ^{210}Pb is constant, leading to that the concentration of ^{210}Pb in the sediment will be a function of time enabling dating of the sediments. This dating technique is frequently applied for dating of recent (<150 years) sediments. In addition, one technique called luminescence dating can be used for mineral material. Not based on the measurements on any decay rate, rather, this technique uses the accumulated absorbed dose for ionizing radiation received from its surrounding environment. Table 1 summarises the most common applications and give few references where more extensive reference lists can be found on each of these techniques.

10. Conclusion

The unique diagnostic power of isotope studies can help to understand the threats to the marine environment. Most major pollution problems facing the marine environment can only be investigated using nuclear and isotopic techniques, which offer the diagnostic and dynamic information needed to identify the source of contamination, its history of accumulation, its environmental pathways and its impact on the environment. Such information is needed to make cost effective mitigation decisions.

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