Using Isotopes to Understand the Oceans and Climate Change

A. Introduction

1. The ocean plays a critical role in modulating the earth's climate. Recent human influence has caused the ocean to absorb additional heat and CO2, because of the increase in atmospheric CO2. The oceans absorb CO2 through physical as well as biological processes. Over the last 50 years radionuclides from both natural and anthropogenic sources have served as sensitive and increasingly indispensable tracers of ocean processes that are important in regulating climate change. Marine scientists have also applied various isotopic techniques to understand the sources, pathways, dynamics, and fate of carbon, as well as pollutants and particles that enter the oceans from land or atmosphere. For example, radiocarbon (14C) and tritium (3H) have been used to determine sources, ages, and pathways of great ocean currents and water masses; carbon-13 (13C), nitrogen-15 (15N), and phosphorus-32 (32P) have served to map ocean productivity and to track the transfer of CO2 to seawater, marine biota, and organic compounds.

2. This annex focuses on the diagnostic value of natural and anthropogenic isotopes to track ocean circulation and cycling of carbon, and to verify global ocean models which underpin future climate predictions and impacts.

B. Ocean Circulation

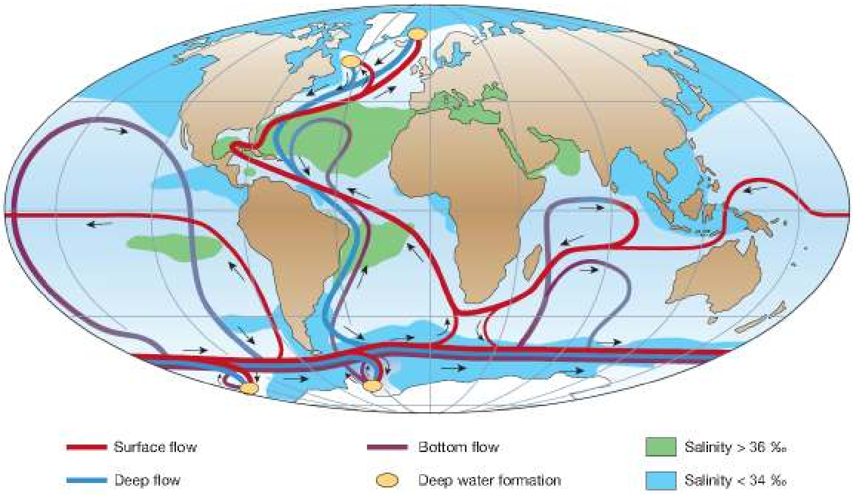

FIG. 1. The major global ocean currents that make up the ocean's thermohaline circulation, which is driven by winds and differences in salinity and temperature due to exchange of heat and freshwater. Source: after Rahmstorf (2002)

3. The major circulation patterns of the global ocean are shown in Figure 1. Large-scale currents are driven by winds as well as seawater density differences arising from changes in salinity and temperature. Cold and dense surface waters in the North Atlantic and Antarctic sink to depths up to

4000 m and travel as submarine currents into the Atlantic, Indian, and Pacific Oceans (blue and purple). This loop is completed as the effects of winds and the exchange of heat and freshwater drive warm surface currents (red) back to the Atlantic Ocean.

4. Radiocarbon measurements indicate that ages of deep waters increase from about 100 years for the North Atlantic to about 2000 years in the North Pacific. This ‘slow’ circulation regime nevertheless moves and mixes 900,000 Gigatons of water per year, equivalent to 30 times the global river flow. This ‘ocean conveyor belt’ also transports many Gigatons of carbon and nutrients which are vital for life. Enormous quantities of heat are also redistributed. For example, in the North Atlantic, the northward flowing warm surface currents, including the Gulf Stream, provide heat to northwest Europe of more than one Petawatt, which is equivalent to the energy output from more than one million 1-GW nuclear power plants.

B.1. Natural isotopes in the Oceans

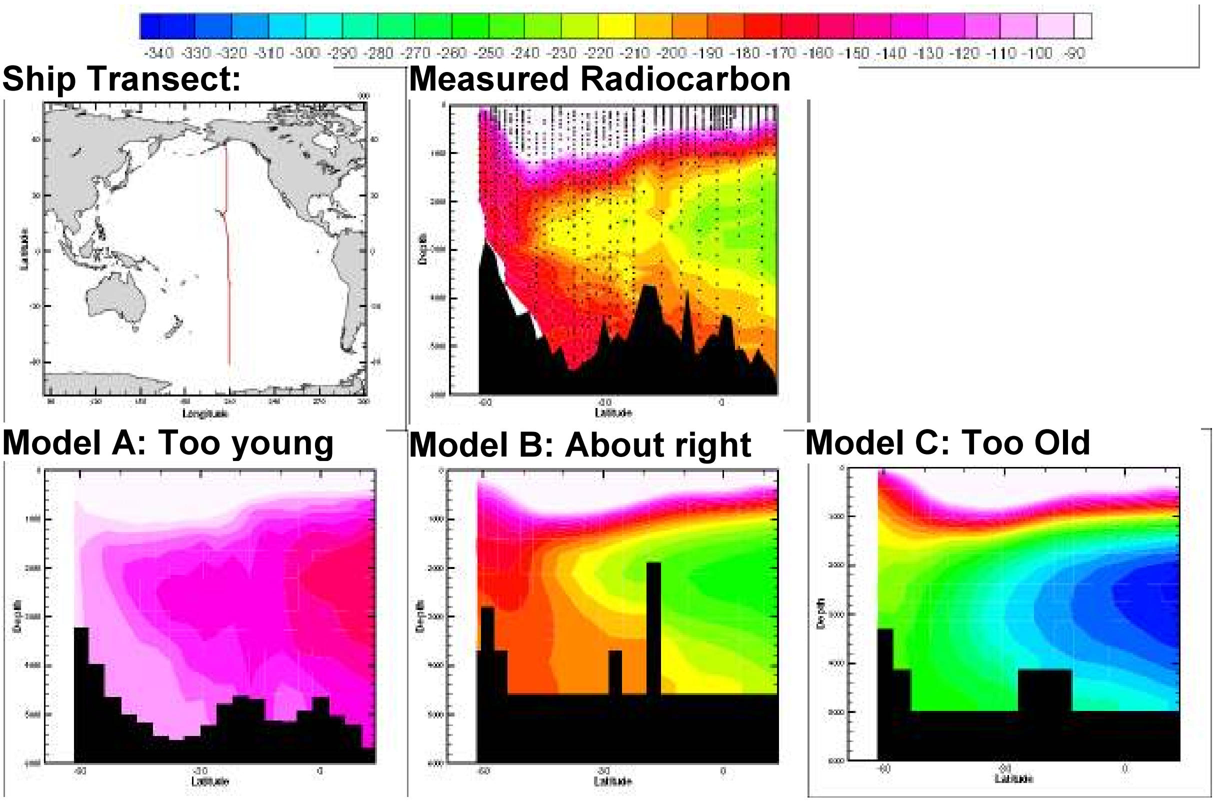

FIG. 2. Comparison of observed vs. modelled $\Delta^{14}C$ along the World Ocean Circulation Experiment (WOCE) ship track P16 in the central Pacific. The top left slide shows this north-to-south sampling line down the middle of the Pacific Ocean. Just to the right, is the corresponding latitude-depth section of $\Delta^{14}C$ data from the Antarctic to the Alaska. In the bottom row are three ocean circulation model simulations: model A is too young, model B is about right, and model C is too old relative to the Pacific $\Delta^{14}C$ data.

B.1.1. Natural Radiocarbon

5. Oceanic measurements of 14C include both a natural component and a nuclear-era (anthropogenic or bomb) component. Natural 14C is produced in the atmosphere by cosmic ray interactions to produce 14CO2 gas, much of which is then absorbed by the ocean. Naturally produced 14C is useful to evaluate circulation and ventilation of ocean waters below 1000 metres, where there is little contamination by weapons origin 14C. Naturally produced 14C is particularly useful because it

exhibits horizontal and vertical gradients in the deep ocean due to a combination of its radioactive decay (half life of 5730 years) and the slow mixing and ventilation of deep-ocean waters (100 to 1000 years). Thus natural 14C provides a means to clock deep-ocean circulation, unlike tracers such as temperature and salinity. This enables scientists not only to derive the sources and ages of deep water masses but also to check the accuracy of global ocean circulation models. For instance, Fig. 2 shows a comparison of observed and modelled natural 14C along a north-to-south ship transect located in the centre of the Pacific Ocean.

B.1.2. Helium-3

6. As opposed to the relatively homogeneous sea-surface input of 14C, helium-3 (3He) in the ocean is injected along deep ocean ridges. These deep-ocean hydrothermal sources provide a unique marker of deep-ocean circulation, and in particular the direction and dispersion of deep currents (see Figure 3). It was recently found that oceanographic circulation patterns deduced from 3He data contradicted the classic model of deep-ocean circulation. It became obvious to many that the unique features of 3He could shed much light on the mysteries of deep-ocean circulation. However, our insight remains limited by the spatial variability and unknown intensity of 3He sources along ocean ridges. Consequently, oceanographers are starting to use 14C-calibrated circulation models to back-calculate the source location and inputs of 3He needed to account for the world-wide database of 3He measurements. Applying a similar "inverse modeling" strategy to other data, such as to measurements of a contaminant in the deep-ocean, could perhaps be useful in identifying its source, such as near old radioactive dump sites in the north-eastern Atlantic.

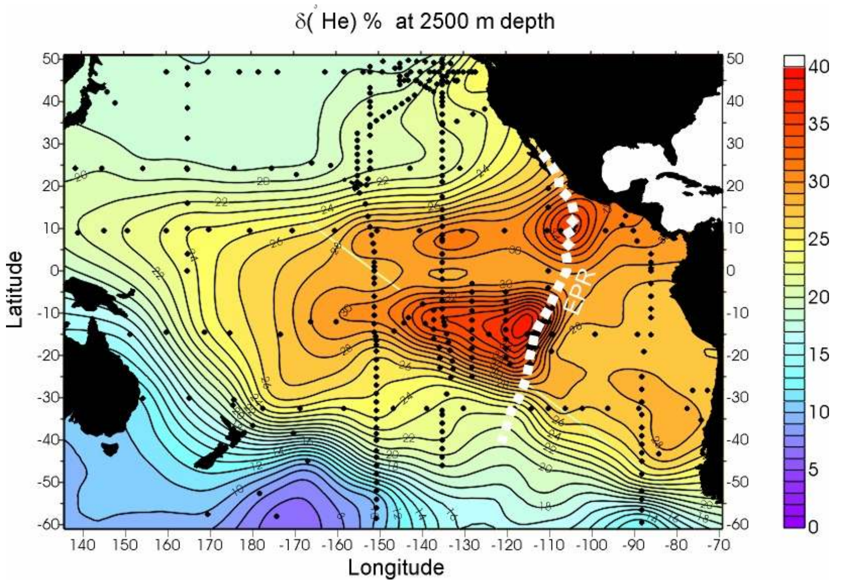

FIG. 3 Map of δ^3He at a depth of 2500 m in the Pacific. Two helium plumes extend westward from the ridge axis of the East Pacific Rise (EPR) Credit: John Lupton NOAA/PMEL

B.1.3. Uranium and Thorium Decay Series

7. Natural radioactivity in seawater is primarily derived from the three primordial radioactive parents, uranium-238 (238U), uranium-235 (235U) and thorium-232 (232Th), which yield over 22

radioactive daughter products with widely different half-lives and reactivities. Along each of these three natural radioactive decay pathways, soluble species, such as uranium, often decay to particle reactive species, such as thorium; one also finds the opposite tendency of a particle reactive species decaying to a soluble species. These discrepancies in particle reactivity lead to 'secular disequilibrium' and dramatically different distributions in the water column. Oceanographers have exploited these particle-scavenged 'clocks' to derive information on sources and fluxes of marine and terrestrial particles, carbon, and gases as well as on inputs and stirring rates of the present and past ocean.

8. The oceanic dispersion and sedimentation of mineral and biogenic particles and the reactivities of these particles with dissolved chemicals help regulate the long-term fate of carbon and related elements, including oxygen and nutrients. Consequently, it is expected that uranium and thorium derived rates of particle dynamics will increasingly underpin future ocean climate models, particularly for simulation of large-scale erosion, carbon-sequestration, and biological changes under future greenhouse scenarios.

B.2. Anthropogenic Isotopes in the Ocean

B.2.1. Weapons testing-derived

9. The world-wide fallout of anthropogenic radionuclides from atmospheric testing of nuclear weapons peaked in the early 1960s and has since dispersed and been diluted in the marine environment. Although resulting inputs of 3H, 14C, strontium-90 (90Sr), caesium-137 (137Cs), and plutonium (Pu) isotopes can still be detected 50 years later throughout much of the marine ecosystem, the radiological dose to humans from seafood consumption is typically one hundredth that resulting from naturally occurring radionuclides. Marine scientists have exploited this global-scale, pulse-like input along with the different behaviours of these radioisotopes to trace and clock both small-scale near-shore and large-scale oceanic process including circulation, sedimentation, and biological productivity.

Weapons Radiocarbon

10. A much used tracer of ocean circulation is the 14C that is derived from atmospheric weapons tests, which increased atmospheric 14C up to nearly twice its natural level before it declined again after 1963 due to implementation of test ban treaties. Bomb and natural 14C are distinguished in the ocean by comparisons with other chemical and isotopic markers. Oceanographers have been able to use the weapons test 14C signal, which has penetrated the upper 1000 metres of the ocean, to validate surface circulation fields simulated by ocean models. General patterns between models and data are similar, with lows in equatorial and high latitude regions and highs in the subtropics. The differences evident between models and data for some regions (e.g., western boundary currents, North Pacific) call for better and finer scale models in these areas. Bomb 14C also serves as a marker of recent carbon inputs including the concurrent invasion of anthropogenic CO2, which originates mainly from combustion of fossil fuels.

Weapons Tritium

11. Like 14C, tritium is produced naturally in the upper atmosphere and brought to the earth's surface as rain and snow. In addition, weapons testing injected large quantities of tritium into the atmosphere. Bomb tritium levels overwhelm natural levels throughout the upper 1000 m of the ocean. Thus bomb tritium has been used not only to track shallow water masses but also to date them by exploiting tritium's 12.3-year half-life. Tritium measurements have provided the clearest demonstration yet of the decadal-scale progress of cold sub-polar waters sinking into the deep North Atlantic. Tritium releases from nuclear power plants have also been used to clock dispersion in coastal shelf seas.

Other tracers

12. Other anthropogenic, bomb-produced tracers (including 90Sr, 137Cs and plutonium isotopes) have not been measured as systematically throughout the world's ocean. However, their unique marine chemical properties are starting to be exploited by some ocean modellers in attempts to evaluate and improve simulations of the movement and fate of sediments, nutrients, and pollutants at both regional and global scales.

C. Ocean uptake of CO2 and its Impacts

C.1. Global Carbon Cycle

13. The present day reservoirs and flows of natural and anthropogenic carbon are summarised in Figure 4. Time series measurements of atmospheric CO2 have revealed an exponential increase from 280 parts per million (ppm) to 380 ppm since industrialisation began in 19th century. Carbon dioxide is the primary greenhouse gas after water vapour that regulates the global heat balance on earth. The ocean absorbs CO2 through physical as well as biological processes, namely through photosynthesis by microalgae (phytoplankton), ingestion of phytoplankton by microscopic animals (zooplankton), and eventual settling of that carbon into the abyss. The infiltration of anthropogenic CO2 into the ocean, which is due to physical processes, has been tracked by ocean measurements of carbon isotopes (12C, 13C, and 14C). These isotopic data indicate that the ocean is currently absorbing about 2 Gigatons per year of anthropogenic CO2, which is about one third of the total annual anthropogenic CO2 emissions from fossil fuel burning and deforestation.

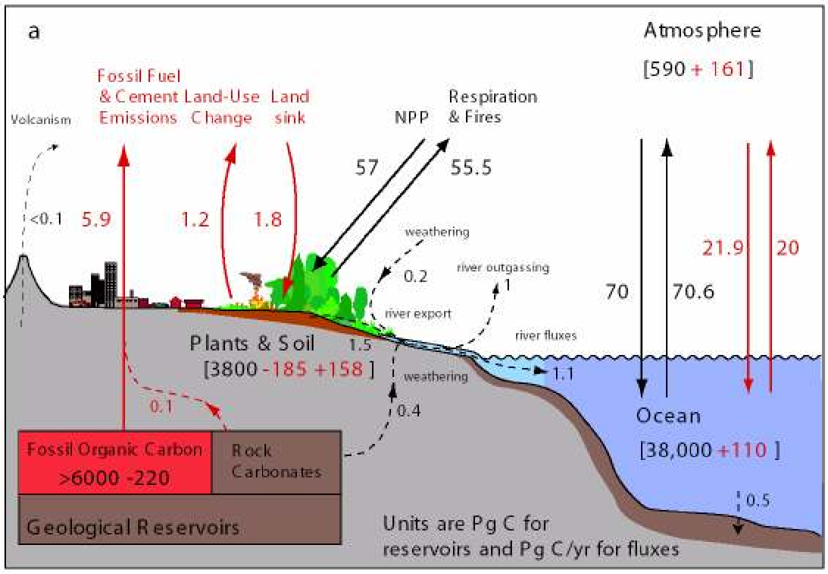

FIG. 4. Illustration of the carbon cycle's major reservoirs and the fluxes between them, including both the natural (black) and anthropogenic components (red). Anthropogenic components are averages for the 1980's and 1990's. Source: (Units are in Gigatons C for reservoirs and in Gigatons C per year for fluxes) Sabine et al. 2004. Emissions of CO2 from cement production amount to about 10% of the fossil fuel CO2 emissions. NPP is net primary production due to terrestrial plant photosynthesis.

14. Furthermore, ocean carbon isotope measurements have revealed regional differences in the ocean's CO2 storage capacity. Similarities between the infiltration of anthropogenic CO2 into the ocean and corresponding anthropogenic changes in 14C/12C and 13C/12C make these isotopes particularly appropriate for evaluating and improving numerical models designed to quantify past, present, and future ocean carbon uptake.

C.2. Acidification of the Ocean

15. The ocean's vast capacity to absorb CO2 is largely due to its natural abundance of carbonate ion, an antacid that neutralizes CO2 as it enters the surface ocean from the atmosphere. As atmospheric CO2 levels continue to increase, present-day ocean carbonate ion concentrations are being lowered along with seawater pH due to a process known as ocean acidification. Over the last 20 years, reductions in ocean pH have been documented by direct measurements in the Atlantic and Pacific Oceans. Surface ocean pH has declined by 0.1 unit since the onset of the industrial revolution; most of that change occurring over the last 30 years. By the end of this century, surface ocean pH will drop by another 0.3 to 0.4 units, which represents a 100 to 150% increase in hydrogen ion concentration. The amount of man-made anthropogenic CO2 that is going into the ocean, currently 4 kg per person per day, is already suspected to be affecting marine life. During the 21st century, corals and other calcifying organisms may suffer a great decline. As carbonate ion concentrations drop, calcifying organisms have more trouble forming their essential skeletal or shell material out of calcium carbonate. Eventually calcification rates, which are often measured by addition of the radiotracer calcium-45, could slow to the point where they are outpaced by erosion and organisms would simply fade away. Corals provide fish habitat and breeding grounds, defence against storms and erosion, and underpin a multi-billion dollar tourism industry. Ocean acidification will have pervasive impacts on marine organisms, food webs, and toxicity of pollutants, such as heavy metals. Marine radioecological studies conducted under high CO2 scenarios will help unravel some of the long-term effects of ocean acidification.

D. Biological Cycling of Carbon

D.1. Tracking carbon export and burial in deep sediments

16. Phytoplankton assimilate inorganic carbon dissolved in the surrounding seawater and transform it into organic carbon within their cells, leading to a decrease in CO2 concentration, which promotes further transfer of CO2 from the atmosphere to the surface ocean. Phytoplankton lie at the base of the food chain and are grazed by marine zooplankton. These tiny surface-dwelling animals ingest phytoplanktonic carbon for energy, while packaging their carbon waste into faecal material that is excreted and settles into the deep ocean. Thus carbon is pumped from the atmosphere through the surface ocean and into the deep ocean as organic carbon. This transfer is facilitated because ingested or dying plankton also contribute dense silica (diatoms) or calcium carbonate material from their tiny shells, which helps to send particles further into the abyss. Once the organic carbon and calcium carbonate particles reach the ocean interior they remain isolated from the atmosphere for centuries. A small portion even becomes incorporated into marine sediments. This vertical carbon-transport process, termed the "biological pump", naturally keeps atmospheric CO2 levels lower by concentrating carbon in the deep ocean.

17. Two complementary approaches have been used to quantify the flux of carbon and sinking particles in the oceans. Firstly, in order to capture particles as they fall from the surface to the deep ocean, large conical or cylindrical traps have been deployed. These sediment traps (Figure 5) are either set adrift to float for a few days at a constant density level or they are fixed to moorings at a variety of depths for up to two years. Beyond simply assessing particle and carbon fluxes, the Agency has further used sediment traps to evaluate associated fluxes of radionuclides, both of anthropogenic and natural origin

18. Secondly, information has been gathered based on abundances of natural radionuclides in seawater. Oceanographers have exploited the deficit of the seawater activity of the daughter thorium-234 (234Th), which is particle reactive, relative to that of its parent 238U, which is soluble. In upper waters, where particles are produced, thorium adsorbs onto freshly produced particles and thereby leaves the system as these particles settle. The resulting deficit in 234Th along with its half-life of 24 days, much shorter than its parent, is used to assess its removal from the productive upper ocean. The carbon flux is estimated by converting the 234Th flux and the particulate organic carbon to 234Th ratios as measured in large particles collected in the field with either in-situ pumps or sediment traps.

FIG. 5 Sediment trap (left) used to catch marine particles (right) that settle from the surface to the deep ocean.

E. Climate change records

E.1. Diagnosing past isotope signatures

19. Global climate change research has come to rely on radio- and stable-isotope analyses made on natural archives including marine sediments, ice cores, and corals. Stable isotopes are powerful tools because they offer records of past environmental conditions, including temperature, salinity, and pH as well as humidity, biodiversity, and circulation.

20. For example, oxygen isotope records (18O/16O) locked up in the carbonate shells of marine microfossils called foraminifera, or in long-lived corals have been widely used to estimate past temperature, salinity, and circulation regimes, such as the intensity and frequency of past El Niño/Southern Oscillation events as well as related glacial-interglacial changes. Stable carbon isotope records (13C/12C) in foraminifera provide constraints on ocean circulation patterns, oceanic nutrient levels, as well as atmospheric CO2 concentrations. Nitrogen isotopic ratios (15N/14N) have been used as a recorder of changes in the productivity and nutrient levels in seawater.

21. Recently, the advent of the highly sensitive accelerator mass spectrometry (AMS) technique to determine 14C ages on sub-milligram quantities of carbon, e.g., extracted from corals, foraminifera microfossils, marine organic matter, and small volumes of seawater has led to a revolution in our understanding in many process-based aspects of marine science. The demand for AMS analyses of 14C in marine samples has made it a ubiquitous research tool that is now provided as a commercial service in numerous marine laboratories worldwide.

E.2. Radio-dating marine records

22. Measurements of isotopes in annual bands from corals has provided sensitive tropical time series of past ocean salinity, temperature, and pH. Seasonal and interannual variations in these isotopic signatures within these annual growth bands have provided reconstructions of El Niño fluctuations over the last 50 years.

E.3. Unravelling Carbon Cycles with Compound-specific Isotope Analysis

23. Marine isotope chemists have succeeded in miniaturizing and merging conventional carbon isotope techniques into gas chromatography-isotope ratio mass spectrometry (GC-IR-MS) making it possible to analyse carbon isotope ratios in less than a millionth of a gram of organic compound. This will enable scientists, for the first time, to simultaneously identify the sources, pathways and fate of thousands of organic compounds and pollutants found in the marine environment.

24. For example, microscopic phytoplankton, account for most of living carbon in the ocean, but leave no visual trace following death and burial in sediments. However, they leave molecular fingerprints containing climate-diagnostic isotopes (13C, 15N, 18O). These molecular fossils can now be analysed using GC-IR-MS of sediment extracts. For example, scientists have demonstrated that 13C in alkenone compounds, which are one class of algal compounds out of many that are preserved in sediments, can be used to reconstruct ecosystem structure and temperature in dated marine sediments covering last 300 million years.

25. Other GC-IR-MS applications include distinguishing terrestrial versus marine inputs of methane plant biomass, and hydrocarbons, and pollutant versus natural origins for many toxic chlorinated organic compounds which accumulate in marine life.

F. Conclusions

26. This review illustrates a large number of radioactive and stable isotopes that are now being used to trace ocean processes that are important in regulating climate and ocean carbon uptake as well as in evaluating and improving ocean models. New trends in nuclear analytical technologies, as mentioned

below, will further enable marine scientists to address key societal and environmental issues such as climate change and ocean acidification.

New Technologies

27. There is a strong trend towards smaller bench-top analysers and nanoscale technologies, resulting in affordable and portable nuclear and isotopic tools.

Regional Marine Models

28. There is increasing demand by marine environmental managers for regionally validated marine ecosystems models dealing with erosion, climate risks, blooms and accidental pollution. The numerous natural radiotracers being discovered in coastal marine environments are likely to provide critical insight as these models are evaluated and improved as needed for good sustainable management

Increasing access and international links

29. Ocean and climate studies are by their nature, international and open networks. As such, they provide affordable ways for more Member States to participate and influence the direction of international programmes.

30. Environmental and anthropogenic isotopes have proven to be sensitive and uniquely informative benchmarks of past and future global environmental change. With instrumental miniaturisation and declining costs, there will be further growth in using marine isotopic techniques to better diagnose the state of the oceans.

Recommended Further Reading:

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