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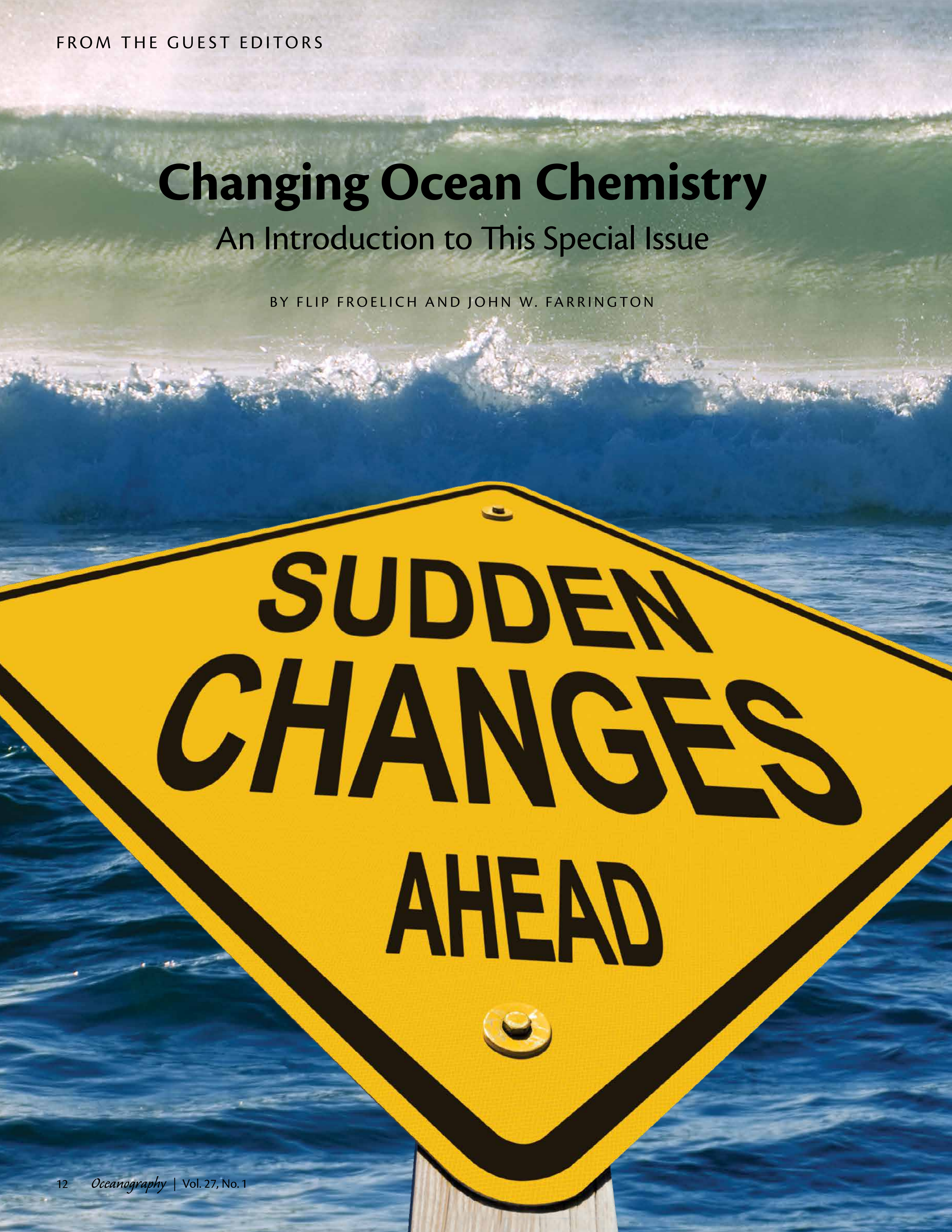
FROM THE GUEST EDITORS

Changing Ocean Chemistry

An Introduction to This Special Issue

BY FLIP FROELICH AND JOHN W. FARRINGTON



The modern industrialized and urbanized world, dubbed the "Anthropocene" by Paul Crutzen (2006), includes the past 250 years of multiple human impacts. Nobel Prize winner and atmospheric chemist Crutzen states:

> *During the past 3 centuries human population increased tenfold to 6,000 million, growing by a factor of four during the past century alone. More than half of all accessible fresh water is used by mankind. Fisheries remove more than 25% of the primary production of the oceans in the upwelling regions and 35% in the temperature continental shelf regions. 30–50% of the world's land surface has been transformed by human action. Coastal wetlands have lost 50% of the world's mangroves. More nitrogen is now fixed synthetically and applied as fertilizers in agriculture than fixed naturally in all terrestrial ecosystems. Many of the world's rivers have been dammed or diverted.*

And, of course, burning of fossil fuels has increased the carbon dioxide concentration of Earth's atmosphere by over 40%. Almost a quarter of the CO_2 we have burned escaped from the atmosphere into the ocean, causing ocean acidification. Over 80% of the heat added to Earth's surface in the past 50 years resides in the upper 1,000 m of the ocean, not in the atmosphere.

The quantification of secular change in marine environments presents difficult challenges for ocean chemists because anthropogenic change is often embedded in the fabric of natural change. Traditional methods (see the cover) of extracting water samples from the surface and interior of the ocean with specially fabricated and super clean bottles arranged in rows on a titanium rosette and hung from a Kevlar hydrographic "wire" produces a vertical array of data at different points on the surface of the ocean every day or so (*Eulerian oceanography*). For most of the ultra trace inorganic elements and natural and synthetic anthropogenic organic molecules and micro-plastics and particles, there is still no alternative to recovering the physical samples and doing the lab analyses, although some progress has been made with in situ samplers by employing sorbents to preconcentrate analytes. Thus, to develop time series of tracers in the sea requires ships costing upwards of $50,000 per day to repeatedly occupy the same stations and transects in order to string together multiple snapshots. An alternative hydrographic approach—reoccupying the same station every month for decades—produces well-resolved time series. But again, ascribing changes to anthropogenic causes vs. natural variability is difficult unless the length of the time series exceeds the time domain of natural variability, and the latter is seldom known in any detail (e.g., North Atlantic Oscillation vs. climate warming). True change over time periods of fewer than many decades is difficult to perceive, much less to ascribe cause and effect. Sustaining long time series at even a few remote ocean stations is not only costly but requires continuity in equipment and personnel that has become intergenerational. A third and future method for monitoring ocean chemical change is the promise of mounting chemical sensors on self-reporting ocean floats and gliders (*Lagrangian oceanography*), devices that the physical oceanography community has been deploying in the ocean by the thousands for decades. It will take time to develop and calibrate the chemical sensors and to map the chemistry of the ocean in order to quantify important changes of the present and future. Pioneering efforts have already demonstrated the path forward, but much more needs to be accomplished. A fourth way to look at ocean change is to search the geological record for periods of abrupt natural change like the last deglaciation (when CO_2 increased by over 50%) and for periods of extremely warm climates like the Eocene (50 million years ago) or cold climates like the last glaciation. Such paleogeochemical time series might reveal how the planet's natural feedbacks will try to reset the human-made changes in our future.

SPECIAL ISSUE ARTICLES

In this issue, we look at different time scales of ocean chemical change. In the first section of the special issue (*Past Records: Paleocene to Holocene*), the first two articles set the stage for natural change and extreme warmth based on the paleo records of ocean CO_2, carbonate, and O_2 as the planet emerged from the last glacial period 20,000 years ago (~ 5°C cooler, CO_2 ~ 190 ppm) to the warmest part of the Holocene about 10,00 years ago (CO_2 ~ 280 ppm) (*Yu et al.; Jaccard et al.*). These records are not perfect analogs for the impending Anthropocene changes in ocean warming, acidification, and deoxygenation, but they do contain parallels that these authors explore for future change. The third article in this section (**Froelich and Misra**) delves into the reasons the Paleocene-Eocene hothouse that occurred about 60–50 million years ago had very high CO_2 (perhaps over 1,000 ppm) in a world without any permanent ice on the poles. Again, the analogs to the Anthropocene are tenuous. Even if humankind were to burn all the fossil carbon on Earth's surface within the next 300 years and push CO_2 near 1,000 ppm, it would still take several thousands of years for the ice caps to melt and for sea level to rise 100 m. However, we should learn as much as we can about these past extreme climates in order to understand details of cause and effect.

Articles in the second section (*Anthropocene: The Future, So Far…*) deal with aspects of recent past and future ocean chemical change. **Anderson et al.** describe the current GEOTRACES program, a major international effort designed to gather global snapshots of ocean tracer concentrations and isotopes, building on the GEOSECS program that began more than 40 years ago. **Grand et al.** provide a synthesis of the past decade of their US CLIVAR-CO_2 Repeat Hydrography Program, designed to detect changes in dust deposition. They collect multiple snapshots of dissolved Fe and Al in the upper 1,000 m along selected transects. Dust Fe is a critical limiting component for open ocean primary production in regions with high nutrients but no iron, so understanding the changing climate impacts of dust delivery to the sea is critical to evaluating the ocean's carbon response to terrestrial change (**Duce**).

One of the most important toxic metal time series in the ocean concerns Pb, an element added to gasoline as tetraethyl-Pb until it was phased out and finally banned in 1996 in the United States. **Boyle et al.** describe the ultratrace Pb concentration and isotope data collected over the last four decades that show initial Pb increases from industrial processes and gasoline, followed by decreases. Well-documented Pb and Pb-isotope data for Bermuda coral show a tenfold increase in anthropogenic Pb after 1880 in Atlantic surface waters downwind of North America. Lead then started decreasing in the late 1970s as anthropogenic sources were controlled. Mercury has recently been conquered analytically in the ocean. **Lamborg et al.** describe new Hg data that suggest anthropogenic atmospheric sources of Hg to the ocean, for example, global atmospheric dispersion from coal-fired power plant emissions, has not yet penetrated most of the global ocean. Only in the North Atlantic downwind of North America does there appear to be an anthropogenic signal. This parallels the pattern of Pb contamination in the North Atlantic, which is not now at toxic levels in the ocean. Hg, on the other hand, is known to be concentrated as methylated-Hg at the top of the marine food chain (e.g., tuna) and presents a neurotoxin risk when large fish are ingested by humans, regardless of whether the ultimate source is natural or anthropogenic. Lamborg et al. expect Hg contamination of the surface ocean to increase in the future.

A recent traumatic event, the March 2011 Tohoku-Oki earthquake and tsunami that swept ashore on northeastern Honshu and destroyed the nuclear power plants at Fukushima Dai-ichi, resulted in very large, abrupt atmospheric and oceanic releases of Cs-134 and Cs-137 radioisotopes. **Buesseler** tracks the North Pacific ocean dispersal of this fallout and compares the magnitude of its release and fate to the natural radioactive background in the sea, to long-term releases of radioisotopes from stable nuclear power plants, to releases from the 1960s atmospheric bomb tests, and to releases from Chernobyl.

Based on syntheses of measured change over the past few decades, **Doney et al.** predict future changes in the ocean: increased warming, decreasing biological production, subsurface deoxygenation, acidification (lower pH), greater calcite and aragonite shell solubility, and decreasing CO_2 uptake.

> *Global warming should be called ocean warming, as more than 80% of the added heat resides in the ocean.*

They make a strong case that these ocean changes are proceeding at rates faster than the most abrupt global changes in the geological record, casting doubt on paradigms and models that would use past change and past extreme environments as predictors of the future. There is a growing data set documenting that increasing pCO_2 in the surface ocean has measurably decreased pH. **Pilson** works through the homogenous equilibrium calculations to predict decreases in surface ocean pH and plankton carbonate shell solubility as CO_2 continues to increase. These ocean acidification calculations are laid over the Keeling curve of past atmospheric CO_2 increases since 1978.

Bates et al. dig deep into the global ocean carbon cycle, using CO_2 and

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acidification data to synthesize surface ocean dissolved inorganic carbon (DIC), pCO_2, alkalinity, and pH from the seven longest ocean time series stations. When plotted on the same time and concentration scales, all clearly show multidecadal increases in DIC and pCO_2 and decreases in pH and aragonite saturation that are significant and clearly global. Surface ocean carbon chemistry is clearly changing. Vertical particulate fluxes of organic material caught in traps at long time series moorings do not yet show distinct multidecadal change because of high natural biological variability. However, based on the 35-year Oceanic Flux Program time series data collected near Bermuda, ***Conte and Weber*** argue that the connection between upper ocean processes and deep particle fluxes is beginning to show how basin-scale climatic forcing affects particle fluxes. From another long time series, ***Scranton et al.*** describe changes in nutrient, oxygen, and CO_2 hydrography and vertical particulate fluxes of organic matter that have been monitored in the anoxic Cariaco Basin since 1996. Increasing concentrations of deep nutrients, long-term shoaling of the oxicline, and thinning of the suboxic region in the water column between the bottom of the oxic layer and the top of the sulfide layer are consistent with decreasing ventilation rates and reduction in deep water densities.

Brewer and Hofmann report on methods to improve descriptions of the ocean oxygen field to help quantify the effects on marine animals of physiological stress induced by hypoxic waters. They make a plea for reporting these oxygen limits in a more rigorous manner so that physiological stresses due to deoxygenation caused by ocean warming can be better predicted. ***Emerson and Bushinsky*** discuss this decrease in oxygen in the very few subsurface locations of the open ocean that have 50 years of accurate O_2 data. They argue that continuous global mapping of this change in O_2 and in annual net community production and carbon export will be required to verify the geographical patterns predicted by global climate models. One cost-effective method for obtaining global coverage will be development of oxygen sensors affixed to floats, gliders, and moorings that are already in wide use by the ocean physics community to monitor changes in ocean circulation.

Eutrophication in nearshore environments with strong vertical stratification due to freshwater outflows can develop bottom water deoxygenation leading to hypoxia and collapse of benthic ecosystems, sometimes called "dead zones." ***Rabalais et al.*** review the worldwide increase in size and number of these human-caused hypoxic zones due to increased nutrient loading of rivers and coastal zones from upstream fertilization and release of sewage. Long-term observations of change in open-ocean and coastal-zone oxygen are often accompanied by changes in nutrients such as nitrogen. ***Fulweiler and Heiss*** explore changes in sediment nitrogen fixation over the past decade in Narragansett Bay and use them to show how human-made nutrient loading has affected the bay over the past 40 years. They suggest that the coastal ocean nitrogen cycle responds quickly to changes in organic matter supply, implying the possibility of fast and significant future changes in the global marine nitrogen cycle.

Human impacts on ocean chemistry extend beyond the coastal zone and effects on nutrients, carbon, and oxygen. ***Farrington and Takada*** review the status of "organic chemicals of environmental concern," both natural "human-accelerated" organics (e.g., polycyclic aromatic hydrocarbons [PAHs] that are by-products of fossil fuel burning and petroleum inputs) and human synthesized xenobiotics (for example, DDT and PCBs). Knowledge of the biogeochemical cycles of these compounds needs to expand beyond the advances made in coastal and continental shelf ecosystems to a better understanding of the open ocean/deep ocean. This will enable better identification of emerging organic contaminants of long-term concern that result from continuing innovations and uses of organic chemicals in industrial processes, pharmaceuticals, and personal care products. Efficacious input to policy and management decisions can result from these efforts. PCBs and several other organochlorines are banned by international accords. Floating weathered crude oil in the form of tar balls is an example of a contaminant in the sea that, similar to Pb, has decreased significantly over the past several decades due to successful controls on indiscriminate oil tanker ballast water releases. (***Peters and Siuda***).

And finally, this issue would not have been possible without the dozens of colleagues who assisted in quickly reviewing and editing these papers on very short deadlines. We thank Ellen Kappel and her crew of magicians at *Oceanography* for guiding us through the trials and tribulations of editorship and Don Rice at the US National Science Foundation for funding this special issue.

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