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The Growing Human Footprint on Coastal and Open-Ocean Biogeochemistry

Scott C. Doney

Climate change, rising atmospheric carbon dioxide, excess nutrient inputs, and pollution in its many forms are fundamentally altering the chemistry of the ocean, often on a global scale and, in some cases, at rates greatly exceeding those in the historical and recent geological record. Major observed trends include a shift in the acid-base chemistry of seawater, reduced subsurface oxygen both in near-shore coastal water and in the open ocean, rising coastal nitrogen levels, and widespread increase in mercury and persistent organic pollutants. Most of these perturbations, tied either directly or indirectly to human fossil fuel combustion, fertilizer use, and industrial activity, are projected to grow in coming decades, resulting in increasing negative impacts on ocean biota and marine resources.

The ocean plays a pivotal role in the global biogeochemical cycles of carbon, nitrogen, phosphorus, silicon, and a variety of other biologically active elements and chemical compounds (1, 2). Human fossil-fuel combustion, agriculture, and climate change have a growing influence on ocean chemistry, both regionally in coastal waters and globally in the open ocean (3–5) (Fig. 1). Some of the largest anthropogenic impacts are on inorganic carbon (6), nutrients (4, 7), and dissolved oxygen (8, 9), which are linked through and affect biological productivity. Seawater chemistry is also altered, some times quite strongly, by the industrial production, transport, and environmental release of a host of persistent organic chemicals (10) and trace metals, in particular mercury (11), lead (12), and perhaps iron (13).

Marine biogeochemical dynamics is increasingly relevant to discussions of ecosystem health, climate impacts and mitigation strategies, and planetary sustainability. Human-driven chemical perturbations overlay substantial natural biogeochemical cycling and variability. Key scientific challenges involve the detection and attribution of decadal and longer trends in ocean chemistry as well as more definitive assessments of the resulting implications for ocean life and marine resources.

The biogeochemical state of the sea reflects both cycling and transformations within the ocean, much of which are governed by biological dynamics, and fluxes across the ocean boundaries with the land, atmosphere, and sea floor (2, 14). For most chemical species, seawater concentrations are governed more by kinetics—the rates of net formation and transport processes—than by chemical equilibrium with particles and sedi-

ments. Clear exceptions are dissolved gases such as carbon dioxide (CO_2) and oxygen (O_2), which are driven to solubility equilibrium with the partial pressure of gases in the atmosphere in the surface ocean by air-sea gas exchange.

Phytoplankton in the ocean surface plays a crucial biogeochemical role, converting CO_2 and nutrients into particulate organic and inorganic matter via photosynthesis and releasing O_2 in the process. The rate of marine primary production is governed by temperature, light (strongly influenced by surface turbulent mixing depths), and limiting nutrients, most notably nitrogen, phos-

phorus, iron, and silicon for some plankton. Some fraction of the biologically produced particulate matter subsequently sinks into the subsurface ocean and is consumed by microbes and macrofauna, releasing CO_2 and nutrients and consuming subsurface O_2 . Export production thus maintains strong vertical gradients in biogeochemical tracers over the water column.

The global biologically driven export flux of $\sim 10 \text{ Pg of C year}^{-1}$ must be balanced by a supply of “new” nutrients brought up from below by ocean circulation, input by rivers, or deposited from the atmosphere. With sufficient iron and phosphorus, some diazotrophic microbes can produce “new” nitrogen in situ through nitrogen fixation that converts inert nitrogen gas into biological reactive nitrogen. Marine microbes produce and consume a number of trace gases that can influence climate, for example CO_2 , nitrous oxide (N_2O), methane (CH_4), and dimethylsulfide (DMS).

Ocean upwelling and mixing bring water with elevated CO_2 and nutrients to the surface and replenish subsurface O_2 , with ventilation time scales of years to a few decades in the main thermocline (upper 1 km of the water column) and many centuries for deep waters. Natural ocean-atmosphere climate modes (e.g., El Niño–Southern Oscillation and Pacific Decadal Oscillation) generate substantial interannual to interdecadal variability in ocean biogeochemistry. The major external source terms to the ocean are typically river inputs and atmospheric deposition of dust,

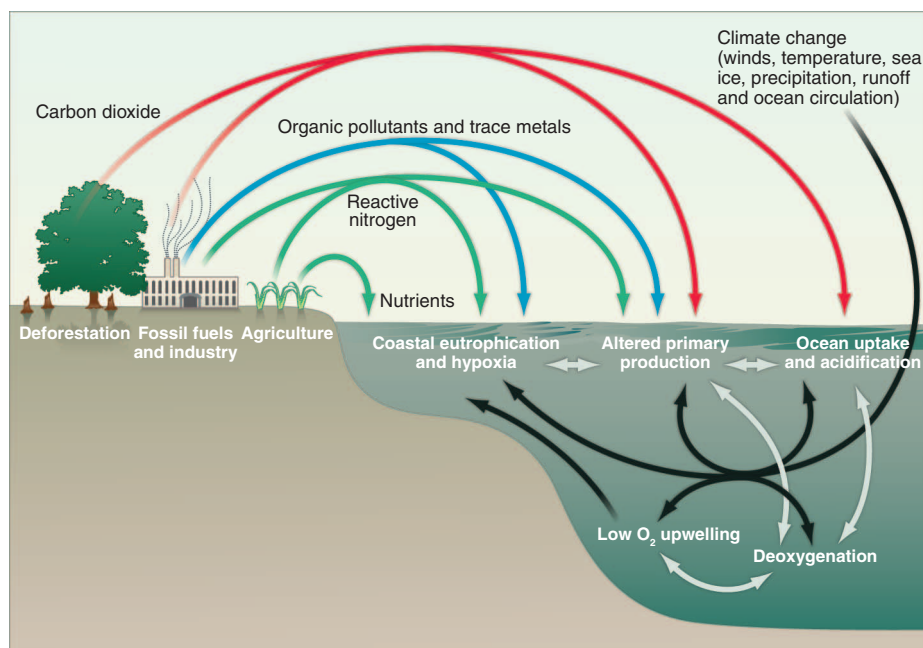


Fig. 1. Schematic of human impacts on ocean biogeochemistry either directly via fluxes of material into the ocean (colored arrows) or indirectly via climate change and altered ocean circulation (black arrows). The gray arrows denote the interconnections among ocean biogeochemical dynamics. Note that many ocean processes are affected by multiple stressors, and the synergistic effects of human perturbations is a key area for further research.

aerosols, and precipitation. These source terms are balanced mostly by losses to the seafloor via the burial of the small fraction (<1% of organic matter) of sinking particulate matter that is not destroyed either in the water column or in surface sediments.

Human Drivers on Biogeochemical Cycles and Ocean Climate

For most of history, it was inconceivable that humankind could directly influence ocean chemistry other than in local and inconsequential manners. That changed after the industrial revolution with the development of modern energy systems, chemical industries, and agriculture that process ever-growing volumes of material, some of which are released either advertently or inadvertently into the environment and eventually reach the ocean. For example, because of human fossil-fuel combustion, deforestation, and land-use change (3), global mean atmospheric carbon dioxide (CO_2) has grown by almost 40% from about 280 parts per million (ppm) in the preindustrial era to nearly 388 ppm by 2010 (15). The invention of the Haber-Bosch process, which converts N_2 gas into fixed nitrogen for agricultural fertilizer, has had an even greater proportional impact on the global nitrogen cycle, approximately equaling the annual production of reactive nitrogen from natural sources (4). Comparable amplifications of a factor of 2 to 3 have occurred in the emissions of reactive phosphorus (16) and mercury (17) to the atmosphere and hydrosphere.

Indirect human effects on ocean chemistry can also occur, mainly through climate change. According to the most recent synthesis by the Intergovernmental Panel on Climate Change, warming of the climate system since the mid-20th century is unequivocal and is very likely caused by the increase in anthropogenic greenhouse gas concentrations (CO_2 , N_2O , CH_4 , and chlorofluorocarbons) (18). Documented physical changes relevant to ocean biogeochemistry include upper-ocean warming, altered precipitation patterns and river runoff rates, and sea-ice retreat in the Arctic and the West Antarctic Peninsula. Reduced stratospheric ozone over Antarctica appears to be causing a major shift in atmospheric pressure (more positive Southern Annular Mode conditions), which strengthens and displaces poleward the westerly winds in the Southern Ocean and which also may be increasing ocean vertical upwelling (19). Future

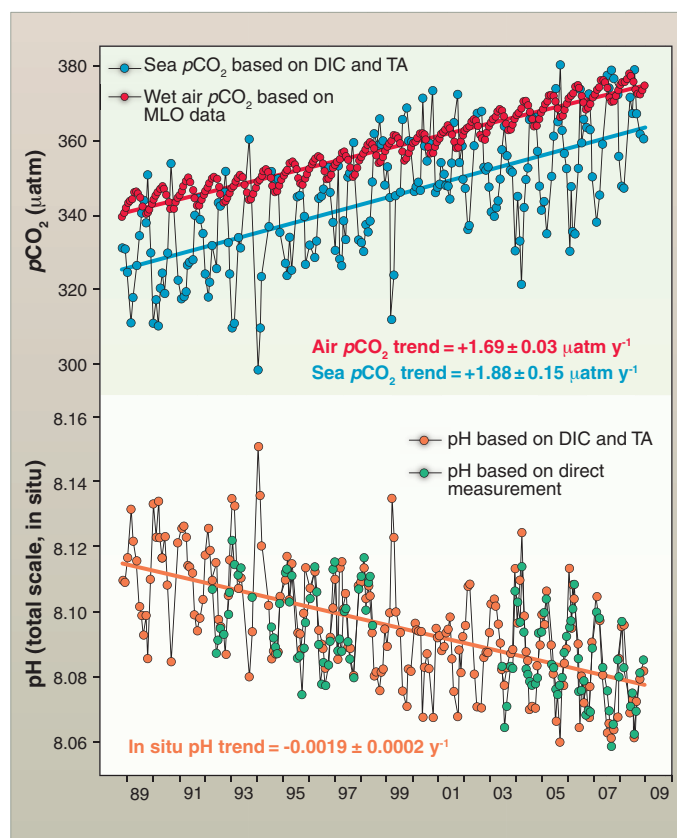


Fig. 2. Time series of (top) atmospheric CO_2 and surface ocean pCO_2 and (bottom) surface ocean pH at the atmospheric Mauna Loa Observatory (MLO) on the island of Hawai'i and Station ALOHA in the subtropical North Pacific north of Hawai'i, 1988–2008. [Adapted from (26)]

climate projections indicate continuation, and in many cases acceleration, of these trends as well as other changes such as more intense tropical storms, an ice-free summer in the Arctic, and a very likely reduction in the strength of the Atlantic deepwater formation.

Ocean Uptake of Anthropogenic CO_2

Rising atmospheric CO_2 causes a net air-to-sea flux of excess CO_2 that dissolves in surface seawater as inorganic carbon through well-known physical-chemical reactions. The global uptake rate is governed primarily by atmospheric CO_2 concentrations and the rate of ocean circulation that exchanges surface waters equilibrated with elevated CO_2 levels with subsurface waters. The distribution, global inventory, and decadal trend in anthropogenic CO_2 are well characterized from ship-based observations (6, 20) and models (3). Based on a recent synthesis, in 2008 fossil-fuel combustion released $8.7 \pm 0.5 \text{ Pg of C year}^{-1}$ to the atmosphere primarily as CO_2 , contributing to an ocean uptake of $2.3 \pm 0.4 \text{ Pg of C year}^{-1}$ (3). Cumulative ocean carbon uptake since the beginning of the industrial age is equivalent to about 25 to 30% of total human CO_2 emissions (6).

Climate change is expected to decrease ocean uptake of anthropogenic CO_2 because of lower CO_2 solubility in warmer waters and slower physical transport into the ocean interior due to increased vertical stratification and reduced deepwater formation (21). In contrast, stronger Southern Ocean winds and ocean upwelling may increase future uptake of anthropogenic CO_2 (22). Changes in ocean circulation also alter the upward transport of subsurface water enriched in nutrients and dissolved inorganic carbon, and these biogeochemical feedbacks tend to partially offset climate effects on anthropogenic CO_2 uptake. In model estimates for the contemporary Southern Ocean for example, enhanced efflux of natural CO_2 due to stronger winds and upwelling more than compensates for increased anthropogenic CO_2 uptake, leading to a net reduction in global ocean uptake (19, 23). Recent observations of the air-sea difference in the partial pressure of carbon dioxide (pCO_2), the driving force for air-sea CO_2 exchange, indicate a weakening of oceanic uptake in a number of regions, although there remains some debate about whether this signal should be attributed primarily to climate change or decadal climate variability (3, 24).

Ocean Acidification

Ocean uptake of anthropogenic CO_2 also alters ocean chemistry, leading to more acidic conditions (lower pH) and lower chemical saturation states (Ω) for calcium carbonate (CaCO_3) minerals used by many plants, animals, and microorganisms to make shells and skeletons (25). Seawater acid-base chemistry is buffered largely by the inorganic carbon system, and CO_2 acts as a weak acid in seawater. Processes that add CO_2 , like air-to-sea gas flux or bacterial respiration of organic matter, increase the concentration of hydrogen ions (H^+) and thus decrease pH ($\text{pH} = -\log_{10}[\text{H}^+]$).

Critically for many organisms, the addition of CO_2 reduces carbonate ion (CO_3^{2-}) concentration through the reaction $\text{H}^+ + \text{CO}_3^{2-} \rightarrow \text{HCO}_3^-$, even though the total amount of dissolved inorganic carbon (DIC) goes up ($\text{DIC} = [\text{CO}_2] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$). Declining CO_3^{2-} in turn lowers CaCO_3 saturation state, $\Omega = [\text{Ca}^{2+}][\text{CO}_3^{2-}]/K_{\text{sp}}$, where K_{sp} is the thermodynamic solubility product that varies with temperature, pressure, and mineral form. Ocean surface waters are currently supersaturated ($\Omega > 1$) for the two major forms used by marine organisms, aragonite (corals and many

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mollusks) and calcite (coccolithophores, foraminifera, and some mollusks). Because of pressure effects and higher metabolic CO_2 from organic matter respiration, Ω decreases with depth, often becoming undersaturated ($\Omega < 1$), at which point unprotected shells and skeletons begin to dissolve.

Ocean acidification is documented clearly from ocean time-series and survey measurements over the past two decades (Fig. 2) (26, 27). From preindustrial levels, contemporary surface ocean pH has dropped on average by about 0.1 pH units (a 26% increase in $[\text{H}^+]$), and additional declines of 0.2 and 0.3 pH units will occur over the 21st century unless human CO_2 emissions are curtailed substantially (28). Surface ocean CaCO_3 saturation states are declining everywhere, and polar surface waters will become undersaturated for aragonite when atmospheric CO_2 reaches 400 to 450 ppm for the Arctic and 550 to 600 ppm for the Antarctic (29). Subsurface waters will also be affected but more slowly, governed by ocean circulation, with the fastest rates in the main thermocline and high latitudes where cold surface waters sink into the ocean interior. Many coastal waters naturally have low pH, a factor amplified by acid rain (30) and nutrient eutrophication (see below).

The rates of change in global ocean pH and Ω are unprecedented, a factor of 30 to 100 times faster than temporal changes in the recent geological past, and the perturbations will last many centuries to millennia. The geological record does contain past ocean acidification events, the most recent associated with the Paleocene-Eocene Thermal Maximum 55.8 million years ago. But these events may have occurred gradually enough and under different enough background conditions for ocean chemistry and biology that there is no good paleo-analog for the current situation (31).

On the basis of laboratory experiments and limited surveys across ocean chemistry gradients, ocean acidification will likely reduce shell and skeleton growth by many marine calcifying species including corals and mollusks (25). Ocean acidification also may reduce the tolerance of some species to thermal stress. Some studies suggest a threshold of about 550 ppm atmospheric CO_2 where coral reefs would begin to erode rather than grow because of acidification and surface ocean warming; this would negatively affect diverse reef-dependent taxa (32). Polar ecosystems also may be particularly susceptible when surface waters become undersaturated for aragonite, the mineral form used by many mollusks.

Some organisms may benefit in a high- CO_2 world, in particular photosynthetic organisms that are currently limited by the amount of dissolved CO_2 in seawater. In laboratory experiments with elevated CO_2 , higher photosynthesis rates are found for certain phytoplankton species, seagrasses, and macroalgae, and enhanced nitrogen-fixation rates are found for some cyanobacteria. Indirect impacts on noncalcifying organisms and marine ecosystems as a whole are possible but more difficult to characterize from present understanding.

Climate Change and Trends in Biological Productivity

Primary production by upper-ocean phytoplankton forms the base of the marine food web and drives ocean biogeochemistry through the export flux of organic matter and calcareous and siliceous biominerals from planktonic shells. Satellite observations indicate a strong negative relationship, at interannual time scales, between productivity and warming in the tropics and subtropics, most likely because of reduced nutrient supply from increased vertical stratification (33). Numerical models project declining low-latitude marine primary production in response to 21st-

century climate warming (34). The situation is less clear in temperate and polar waters, although there is a tendency in models for increased production because of warming, reduced vertical mixing, and reduced sea-ice cover. The climate signal in primary production may be difficult to distinguish from natural variability for many decades (35).

Changes in atmospheric nutrient deposition also can alter productivity but mostly on regional scales near industrial and agricultural sources. Present anthropogenic reactive nitrogen deposition to the surface ocean ($54 \pm 23 \text{ Tg of N year}^{-1}$) (Fig. 3) supports an export production of $\sim 0.3 \text{ Pg of C year}^{-1}$ ($\sim 3\%$ of global total) while producing an additional $\sim 1.6 \text{ Tg year}^{-1}$ of N_2O (7). In much of the North Pacific, equatorial Pacific, and Southern Ocean, phytoplankton are limited by iron, but most of the atmospheric iron deposition is in the form of mineral dust that is not readily bioavailable. Anthropogenic combustion sources and increased cloud-water acidity are increasing soluble iron input to the ocean (13, 36). Models suggest that anthropogenic iron deposition could have a greater positive impact on productivity than anthropogenic nitrogen and also enhance nitrogen fixation, but direct observations are lacking (37).

Coastal Hypoxia and Open-Ocean Deoxygenation

Low subsurface O_2 , termed hypoxia, occurs naturally in open-ocean and coastal environments from a combination of weak ventilation and/or strong organic matter degradation (8, 9). Dissolved O_2 gas is essential for aerobic respiration, and low O_2 levels negatively affect the physiology of higher animals, leading to so-called "dead-zones" where many macrofauna are absent. Thresholds for hypoxia vary by organism but are $\sim 60 \mu\text{mol of O}_2 \text{ kg}^{-1}$ or about 30% of surface saturation. Under suboxic conditions ($< 5 \mu\text{mol kg}^{-1}$), microbes begin to use nitrate (NO_3)

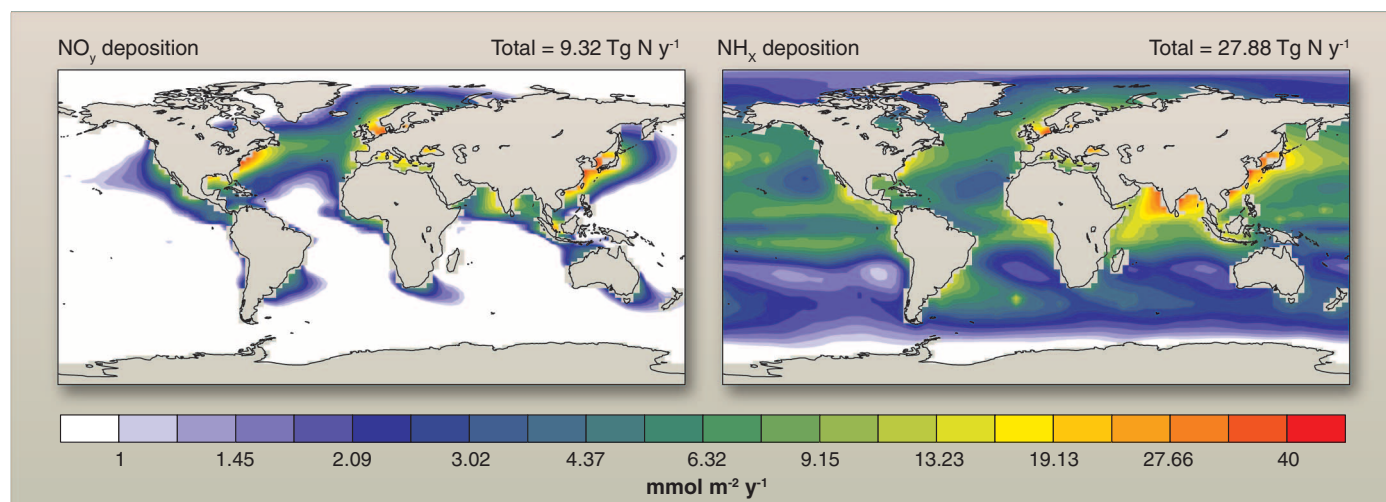


Fig. 3. Model estimated deposition fluxes of anthropogenic reactive nitrogen ($\text{mol N m}^{-2} \text{ year}^{-1}$) to the ocean surface for oxidized forms (NO_y), primarily from fossil fuel combustion sources, and reduced forms (NH_x) primarily from agricultural sources. [Adapted from (30)]

rather than O_2 as a terminal electron acceptor for organic matter respiration (denitrification), resulting in reactive nitrogen loss and N_2O production. Toxic hydrogen sulfide (H_2S) production occurs under anoxic (no O_2) conditions. The organic matter respiration that generates hypoxia also elevates CO_2 , thus leading to coupled deoxygenation and ocean acidification in a future warmer, high- CO_2 world. The synergistic effects of these multiple stressors may magnify the negative physiological and microbial responses beyond the impacts expected for each perturbation considered in isolation (38, 39).

Fertilizer runoff and nitrogen deposition from fossil fuels are driving an expansion in the duration, intensity, and extent of coastal hypoxia, leading to marine habitat degradation and, in extreme cases, extensive fish and invertebrate mortality (8, 40, 41). About half the global riverine nitrogen input (50 to 80 Tg of N year⁻¹) is anthropogenic in origin (4, 42), and anthropogenic nitrogen deposition is concentrated in coastal waters downwind of industrial and intensive agricultural regions (30). The result is coastal eutrophication and enhanced organic matter production, export, and subsurface decomposition that consumes O_2 . Nutrient eutrophication is also associated with increased frequency of harmful algal blooms (43).

Worldwide there are now more than 400 coastal hypoxic systems covering an area > 245,000 km² (40). Population growth and further coastal urbanization will only exacerbate coastal hypoxia without careful land and ocean management. Accelerated hypoxia may also result from climate warming and regional increases in precipitation and runoff that increase water-column vertical stratification; on the other hand, more intense tropical storms could disrupt stratification and increase O_2 ventilation (8).

Expanding coastal hypoxia is also induced in some regions by reorganization in ocean-atmosphere physics. Off the Oregon-Washington coast, increased wind-driven upwelling is linked to the first appearance of hypoxia, and even anoxia, on the inner shelf after 5 decades of hypoxia-free conditions (44). Further south in the California Current System, the depth of the hypoxic surface has shoaled along the coast by up to 90 m (45). The same physical phenomenon, along with the penetration of fossil-fuel CO_2 into off-shore source waters, are introducing waters corrosive to aragonite ($\Omega < 1$) onto the continental shelf (46). There is conflicting evi-

dence on how coastal upwelling may respond to climate change, and impacts may vary regionally (47).

Extensive deoxygenation is also occurring in the open ocean, most notably in the thermocline of the North Pacific and tropical oceans (9, 48) (Fig. 4). A portion of the observed oxygen change likely reflects decadal variability in ocean circulation, but similar to ocean CO_2 distinct secular trends are apparent at some long-term time series stations (49). Models project further reductions of 1 to 7% in the global oxygen inventory and expansions of open-ocean oxygen minimum zones over the 21st century from

water concentrations. Such pollutants are passed up the food chain and are most concentrated in marine organisms at the higher trophic levels including predatory fish, marine mammals, and seabirds.

Key factors in determining overall biological impacts for a particular pollutant are source magnitudes and locations, physical and biological transport pathways, toxicity, and persistence in the environment. Pollutants exhibit elevated levels near local point sources and in coastal and open-ocean waters because of atmospheric deposition downwind of industrial regions (e.g., western Pacific near East Asia and North Atlantic near

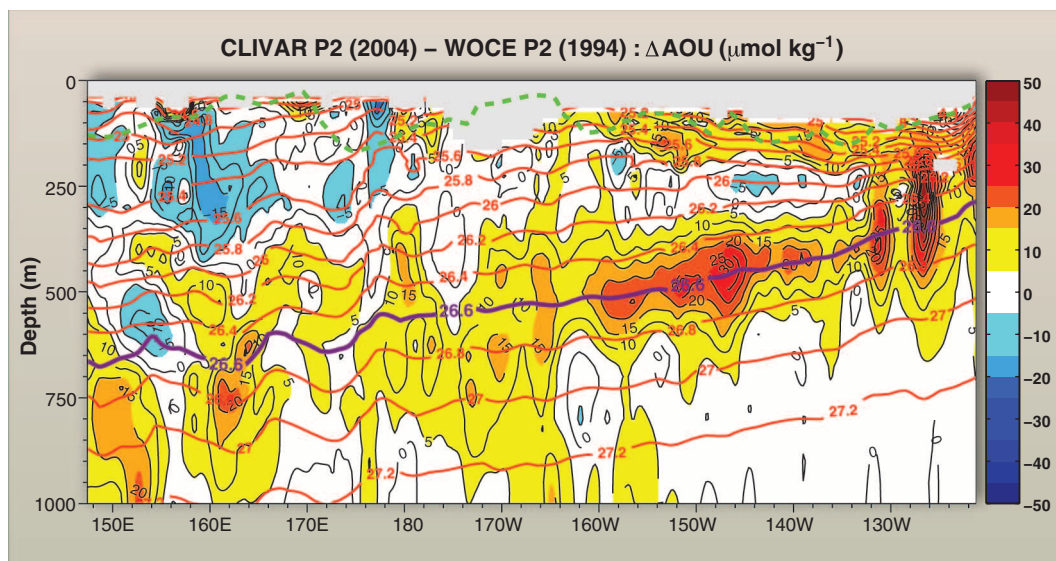


Fig. 4. Decadal change in subsurface O_2 from 1994 to 2004 along 30°N in the North Pacific with positive values indicating an increase in apparent oxygen utilization (AOU) and a decline in O_2 ($\mu\text{mol kg}^{-1}$); contour plot is overlaid by mixed-layer depths (green line) and potential density surfaces (pink) (48). The large AOU increase on the 26.6 potential density anomaly surface (purple line) is a combination of a decadal-time-scale ventilation cycle in the North Pacific and a smaller deoxygenation trend estimated to be about $5 \mu\text{mol kg}^{-1} \text{decade}^{-1}$ (48, 49). CLIVAR, Climate Variability and Predictability Program; WOCE, World Ocean Circulation Experiment.

decreased solubility in warmer waters and slower ventilation rates (50).

The Global Spread of Industrial Pollutants

Point sources of pollution from industrial discharges and oil spills are often highly visible and destructive to the local and regional marine environment (51). Perhaps less well known is the global spread of industrial pollutants into what otherwise would appear to be pristine environments. Elevated oceanic levels of persistent organic pollutants (10) and methyl mercury, a highly toxic organic form (11), raise serious concerns for marine ecosystem health and, potentially, human health through the consumption of contaminated seafood. Many organic and organo-metallic compounds bioaccumulate in the fatty tissues of marine organisms at levels orders of magnitude higher than ambient sea-

North America and Western Europe) (17, 52) (Fig. 3). However, they are also distributed globally, found in even the most remote marine locations, transported through the atmosphere (i.e., black carbon); by ocean currents; and in some cases by migrating animals (53).

Elemental mercury (Hg^0), the main chemical form in the ocean, is transformed into the more toxic methyl mercury form by microbes, particularly in reduced environments such as coastal sediments and perhaps oxygen minimum zones (11). Although mercury distributions are poorly characterized from direct seawater measurements, time histories reconstructed from numerical models (17) and biological samples (e.g., seabird feathers) indicate increasing trends over the 20th century (11). It is encouraging that, after the phaseout of leaded gasoline in

North America that began in the mid-1970s, the high levels of anthropogenic lead observed in the North Atlantic declined sharply and are now comparable to those occurring at the beginning of the 20th century (12).

Some persistent organic pollutants are synthetic and did not exist in nature before industrial manufacture. Production for some organic pollutants peaked in developed nations in the mid- to late 20th century but is continuing to grow in the developing world. Commonly measured synthetic contaminants include pesticides like DDT, polychlorinated biphenyls, and brominated flame retardants such as polybrominated diphenyl ethers. However, there are many more organic compounds synthesized and used that presumably exist in the ocean but that have not been detected (54).

Human activities have also increased levels of naturally occurring compounds such as polycyclic aromatic hydrocarbons, which have sources from petroleum spills and natural oil seeps as well as, primarily, incomplete combustion from wildfires, biomass burning, and fossil fuels (55). In a study on the Gulf of Maine downwind of the Northeast United States, another combustion product, black carbon, contributed up to 20% of the total particulate organic carbon in seawater and about half of the “molecularly uncharacterized” fraction (56). Environmental samples often contain organic compounds similar in chemical structure to known pollutants but which may be biosynthesized natural products; compound-specific radiocarbon analysis is emerging as a powerful tool for distinguishing between natural and industrial sources (10).

Future Research Directions

A deeper understanding of human impacts on ocean biogeochemistry is essential if the scientific community is to provide appropriate and timely information to the public and decision-makers on pressing environmental questions. Although some progress has been made on a nascent ocean observing system for CO₂ (57), the marine environment remains woefully undersampled for most compounds. The oceanographic community needs to develop a coordinated observational plan that takes better advantage of in situ autonomous sensors and observation platforms (58). Monitoring efforts should be paired with laboratory and field process studies to better elucidate the biological effects of changing chemistry at organism, population, and ecosystem levels.

In particular, more detailed biochemical, system biology, and genomic studies are required to explain mechanistically the responses of cells and organism to external perturbations, supplementing what have often been to date more phenomenological findings. Genomic and physiological research should be embedded in large-scale ecological and biogeochemical spatial

surveys and time series to facilitate scaling to ecosystems (59). Further work is needed across scales exploring possible synergistic effects among multiple stressors and to assess the potential for biological acclimation and adaptation to human perturbations over decadal to centennial time scales. Lastly, targeted research is needed on the impacts on marine resources and fisheries, potential adaptation strategies, and the consequences for human social and economic systems (60).

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