A SEA OF CHANGE:

Monitoring the Oceans' Carbon Cycle

By David M. Karl and Christopher D. Winn

The Earth undergoes major processes of change that are reckoned in scales of decades to millennia (*1*). Most of these changes result from natural causes. During the past century, however, human activities have contributed directly to what is now considered an inevitable, detrimental change in the global environment (*2*). Although the proximate cause of this change appears to be the atmospheric accumulation of so-called "greenhouse" gases (CO_2, H_2O, NO_2, CH_4, chlorofluorocarbons) as a direct consequence of urbanization and industrialization, the ultimate cause clearly is overpopulation of our planet.

Because of their ability to store and transport large amounts of heat and to serve as a potential sink for anthropogenic CO_2, the world's oceans may play an important role in modulating global climate. Unfortunately, the rates of these fundamental processes are not well known (*3, 4*); consequently, predicting global environmental change currently is not possible. Long-term records of relevant biogeochemical parameters are essential for documenting ecosystem changes and for differentiating natural ecosystem variability from changes induced by human activities. However, long-term studies generally have been discouraged, especially in academic institutions, because of the relatively high costs involved and negative attitudes about "environmental monitoring." Consequently, time-series data are rare. Most of the time-series data currently available are based on retrospective studies such as ice core or sediment core analyses.

> "Long-term records of relevant biogeochemical parameters are essential for documenting ecosystem changes"

In 1986, the International Council of Scientific Unions (ICSU) established the International Geosphere–Biosphere Programme (IGBP): A Study of Global Change. As described by executive director and secretariat Thomas Rosswall, "IGBP will be a worldwide research effort, unprecedented in its comprehensive interdisciplinary scope, to address the functioning of the Earth system and to understand how this system is changing. The body of information generated by the IGBP will form the scientific underpinning for predictions relating to future causes and effects of global change" (*2*).

The major oceanic component of IGBP is the Joint Global Ocean Flux Study (JGOFS), established in 1987 as a core project of IGBP under the auspices of the Scientific Committee for Ocean Research (SCOR). JGOFS research will focus on the oceanic carbon cycle and its sensitivity to change, and on the regulation of the atmosphere–ocean CO_2 balance (*5, 6*). The U.S. component of JGOFS consists of five specific program elements:

- process studies designed to capture key regular events;
- time-series observations of long duration at strategic sites;
- a global survey of important oceanic properties;
- a vigorous modeling effort to assimilate results, create knowledge, and generate testable hypotheses; and
- development of an accessible, composite biogeochemical data base (*7*).

Of these program elements, the time-series studies will be crucial for assessing the baseline or mean state of oceanic ecosystems and the natural variability therein. The

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studies are prerequisites for the design of any program to measure human activity-induced global environmental change (*8, 9*).

In 1988, two U.S.–JGOFS time-series stations were established: one in the North Atlantic Ocean near Bermuda (*10*) and the other in the North Pacific Ocean near Hawaii. This article will focus on the Hawaii Ocean Time-series (HOT) program.

The oceanic carbon cycle

The ocean and atmosphere systems are closely coupled, and the flux of carbon across the air–sea interface is substantial on a global scale. It is generally believed that the oceans have removed a significant portion of anthropogenic CO_2 added to the atmosphere; however, the absolute partitioning between the ocean and terrestrial spheres is not well documented (*4*).

The cycling of carbon within the ocean is controlled by a set of reversible oxidation–reduction reactions that involve dissolved inorganic carbon (DIC) and organic matter, in which marine biota serve as the critical catalysts. Principal pathways for the production and decomposition of organic matter involve prokaryote and eukaryote oxygenic photoautotrophy and aerobic bacterial respiration, respectively (*11*). The determination of the rates and mechanisms of the removal of DIC from the ocean surface by biological processes, the export of biogenic carbon (as organic and carbonate particles) to the ocean's interior, and the sites of remineralization and burial of biogenic carbon all are important to the JGOFS program (*6*). The continuous downward flux of biogenic materials, termed the "biological pump" (*12*), is a central component of all contemporary studies of biogeochemical cycling in the ocean, and therefore, of all studies of global environmental change. Recent estimates indicate that the oceanic biological pump can remove ~ 7.4 gigatons (1 gigaton = 10^{15} g) of C per year from the oceans (*13*). This value is approximately 10–20% of global primary production, and is roughly equivalent to the annual input of CO_2 to the atmosphere by fossil fuel burning.

As the particles sink through the mesopelagic zone (200–2000 m depth), more than 90% of the exported organic matter is recycled to DIC through the combined activities of bacteria and metazoans. These intermediate-depth waters thus can be viewed a "biological filter," at least with respect to the transport of particulate organic matter. Consequently, less than 1% of the organic carbon initially produced near the ocean surface ever enters the deep sea, and only a small fraction of that amount is preserved permanently in abyssal sediments. Despite the importance of the biological pump and biological filter, we lack a detailed understanding of the structure, mechanisms, and rates of these processes. The HOT program is designed, in part, to provide a comprehensive and quantitative description of the organic carbon cycle in the upper kilometer of the North Pacific Ocean.

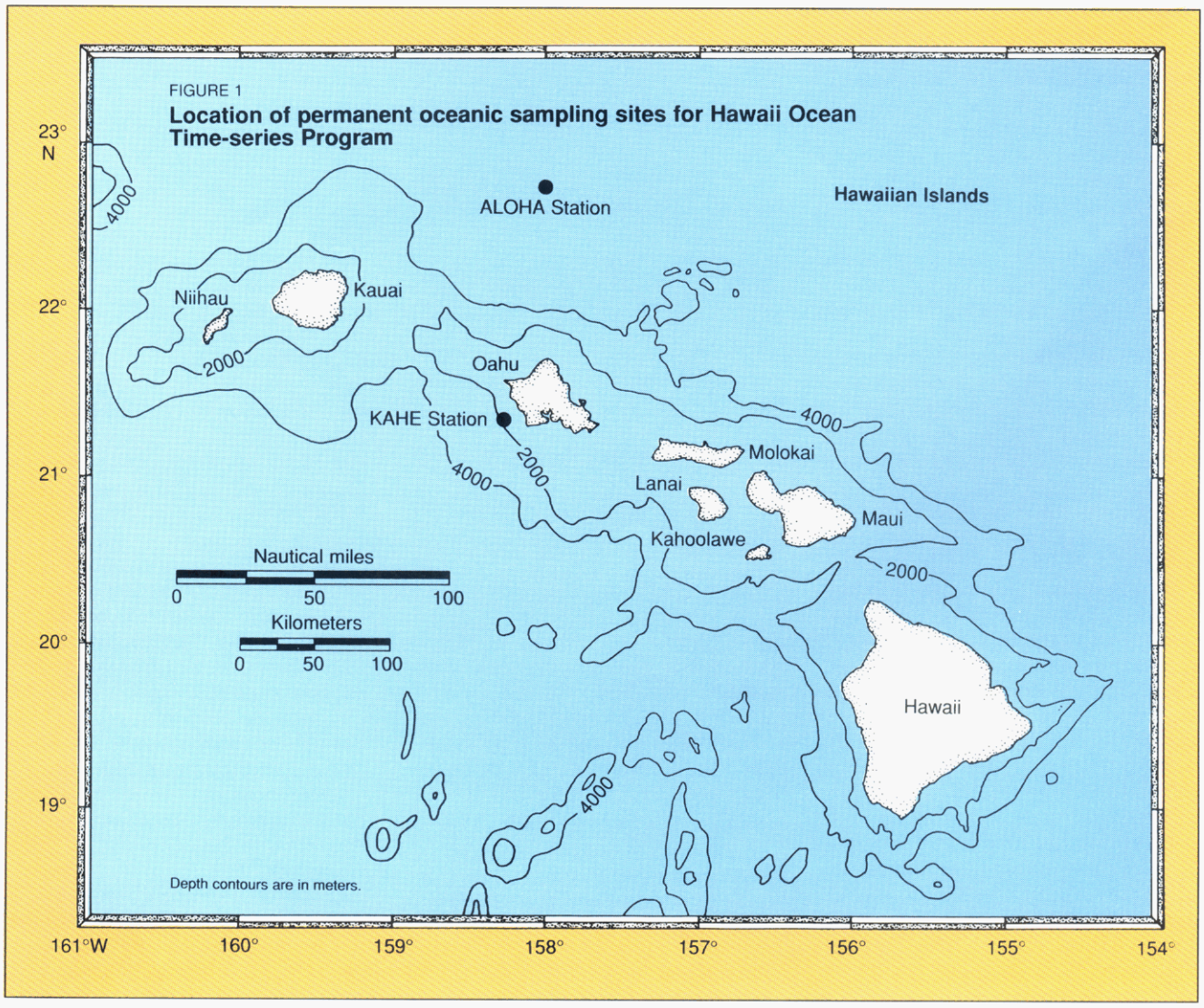


FIGURE 1
Location of permanent oceanic sampling sites for Hawaii Ocean Time-series Program

TABLE 1
Summary of Hawaii Ocean Time-series Program measurements

Parameter	Depth range (m)	Analytical procedure
Continuous profiles		
Depth (pressure)	0–4800	Pressure transducer on SeaBird CTD[a]-rosette package
Temperature	0–4800	Thermistor on SeaBird CTD-rosette package
Salinity (conductivity)	0–4800	Conductivity sensor on SeaBird CTD-rosette package
Dissolved oxygen	0–4800	Beckman polarographic sensor on SeaBird CTD-rosette package
Fluorescence	0–1000	Sea-Tech fluorometer on SeaBird CTD-rosette package
PAR[b] and natural fluorescence	0– 150	Biospherical Instruments, PNF-300
Discrete water bottle samples		
Dissolved oxygen	0–4800	Winkler titration
Dissolved inorganic carbon	0–4800	Coulometry
Dissolved nitrate and nitrite (low level)	0– 200	Chemiluminescence
Dissolved nitrate and nitrite (standard)	0–4800	Autoanalyzer
Dissolved phosphorus (low level)	0– 200	Magnesium-induced coprecipitation, spectrophotometry
Dissolved phosphorus (standard)	0–4800	Autoanalyzer
Dissolved silica	0–4800	Autoanalyzer
Dissolved organic carbon	0–1000	High-temperature oxidation, infrared detection
Dissolved organic nitrogen	0–1000	UV digestion, autoanalyzer
Dissolved organic phosphorus	0–1000	UV digestion, autoanalyzer
Particulate carbon and nitrogen	0–1000	High-temperature combustion, gas chromatography
Particulate phosphorus	0–1000	High-temperature ashing, spectrophotometer
Pigments, chlorophyll *a*	0– 200	High-pressure liquid chromatography and fluorometry
Primary production	0– 200	"Clean" ^{14}C in situ incubations
Adenosine triphosphate	0–1000	Boiling buffer extraction, firefly bioluminescence
Bacteria and cyanobacteria	0–1000	Epifluorescence microscopy
Lipopolysaccharide	0–1000	*Limulus* amoebocyte lysate assay
Sediment traps		
Total mass	150, 300, 500	Filtration and gravimetric analysis
Particulate carbon and nitrogen	150, 300, 500	High-temperature combustion, gas chromatography
Particulate phosphorus	150, 300, 500	High-temperature ashing, spectrophotometry
Identification	150, 300, 500	Brightfield[c] and epifluorescence microscopy
Calcium carbonate	150, 300, 500	Weight loss on acidification of total mass
Biogenic silica	150, 300, 500	Sample digestion, spectrophotometry

[a] Seabird is manufacturer; CTD = conductivity-temperature-depth.
[b] Photosynthetically available radiance.
[c] Visible or white light microscopy.
Note: The mention of any manufacturer or brand of any equipment or instrument does not constitute an endorsement by the authors, *ES&T*, or the American Chemical Society.

HOT site selection

The central portion of the North Pacific Ocean is the largest uniform body of water on our planet; delimited from 15° N to 35° N latitude and 135° E to 135° W longitude, it occupies approximately 20×10^6 km^2 of the Earth's surface. In October 1988, a permanent site, referred to as Station ALOHA (A Long-term Oligotrophic Habitat Assessment), was established about 100 km north of Oahu, HI, at 22° 45′ N, 158° 00′ W (Figure 1). Station ALOHA is in deep water (4750 m), 50 km upwind of the steep topography associated with the Hawaiian Ridge, and is relatively free of biogeochemical effects of the Hawaiian Islands. For these reasons, Station ALOHA is considered to be a valid benchmark for the study of oligotrophic oceanic processes. Station KAHE, a coastal site located off Kahe Point at the 1500-m isobath, also is routinely occupied as part of our field program.

The primary study area is characterized by warm (>24 °C) surface waters with low nitrate concentrations (<10 nM), shallow but seasonally variable mixed layers (40–100 m depth), low standing stocks of living organisms, and a persistent deep water maximum in chlorophyll concentration at approximately 100 m (*14*). As with most complex oceanic phenomena that have been investigated to date, we expect that time-series measurements of individual components of the carbon cycle will contain a substantial amount of random or "white" noise [i.e., constant variance per unit frequency (*15–17*)]. The separation of signal from noise obviously is fundamentally important to the HOT program. Variability in time and space will need to be assessed because it will be impossible to define ecosystem variability and variations rigorously without knowledge of local-scale (10–100 km) heterogeneity. Although the variability in the rates of key biogeochemical processes in the oligotrophic North Pacific Ocean on annual time scales was expected to be small relative to other marine ecosystems that are dominated by strong seasonal cycles, we already have observed considerable variability (factors of 3- to 7-fold) in key biogeochemical processes, such as rates of primary production and particle flux, during our first three years of investigation.

Core parameters

Ideally, the suite of time-series parameters should collectively provide the data base necessary for calibration and validation of existing biogeochemical models, including

local meteorology; upper ocean physics; and rates of organic particle production, export, and remineralization (Table 1). Because the magnitude of most long-enduring changes in oceanic properties is likely to be small relative to natural variability, it is essential that each measurement be made at the highest level of precision and accuracy. Therefore, well-structured quality control and assurance and interlaboratory comparison and calibration programs are crucial. Although it is straightforward to estimate analytical precision, accuracy is problematic because of a scarcity of certified reference materials for many of the desired analytes and rate processes. This becomes increasingly important as global data sets are established that comprise the collective contributions of many individual laboratories.

Our specific cruise objectives, sampling strategies, and analytical protocols are described in detail elsewhere (*14, 18*), and will be summarized here only briefly. Currently, data are collected at approximately monthly intervals during five-day research cruises; station time at ALOHA typically is 72 h. During this time, we deploy and recover a free-drifting, satellite-tracked sediment trap mooring with individual collectors positioned at depths of 150, 300, and 500 m. We also conduct a 12-h in situ primary productivity experiment using a separate radio-tracked buoy and collect discrete water samples to depths of 4700 m for specific chemical and biochemical determinations (Table 1).

During each HOT cruise, a "burst" of consecutive profiles of water temperature and conductivity from the surface to 1000 m also is made over a 36-h period to span the local inertial period (~ 31 h) and three semidiurnal tidal cycles. This sampling strategy is designed so that the high-frequency signals can be averaged to prevent these components from "aliasing" the lower frequency signals that are of greater interest to our program (*14*). During a given 36-h period, vertical displacements of isotherms and associated biogeochemical gradients in excess of 30 m typically are observed in the upper portion of the water column. This regular, periodic movement of isotherms may have important implications for primary production and particle flux by displacing light-limited, nutrient-saturated algae into the lighted portion of the water column; these effects are not routinely included in oceanic productivity models.

To understand oceanic variability more fully and to quantify secular changes, it will be necessary to collect data at each time-series station for at least a decade, and probably longer. For example, current models suggest that the magnitude of the oceanic sink for CO_2 is 2 gigatons $year^{-1}$ (*19*), a "predicted" increase of approximately 1 mmol C m^{-3} $year^{-1}$ for surface waters. This annual increase in DIC is equivalent to the current analytical precision (0.05–0.10%) in the measurement of DIC; this again emphasizes the importance of maintaining an accurate, high-precision time-series data base. Moreover, the natural annual variability in DIC concentrations at Station ALOHA exceeds this "predicted" annual increase by at least an order of magnitude. Similarly, it has been demonstrated that the seasonal variability in mixed-layer pCO_2 near Bermuda is greater than the secular pCO_2 increase measured for the 24-year period 1957–1981 (*20*). Clearly, the unambiguous demonstration of a long-term increase in surface ocean DIC or pCO_2 will require at least a decade of careful measurement.

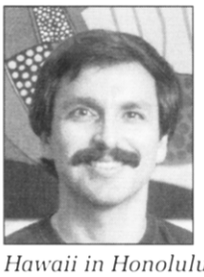
Finally, JGOFS time-series sites also are expected to provide calibration data for remotely sensed observations (e.g., from satellites and moored instruments), deep-water laboratories for the development and testing of novel techniques and instruments, and sites for educational activities and intercomparison experiments. In the future, additional JGOFS time-series sites will be established to document regional ecosystem variability and variations in other representative oceanic provinces. For this purpose, high-latitude stations, especially in the Southern Hemisphere, will be essential for a complete understanding of the sensitivity of the oceanic carbon cycle to global environmental change.

Prospectus

Long-term, time-series studies are ideally suited to the study of slow or subtle processes, rare or irregularly spaced events, and complex phenomena (*21*), all of which are fundamental to our understanding of biogeochemical cycles in the world ocean. The HOT program already has begun to furnish a time-series data set on oligotrophic ecosystem variability, a rich source of testable hypotheses. During the initial stages of what we hope will become a long-term study, it is essential to reevaluate the experimental design to ensure that the data being collected are the most relevant to JGOFS objectives. Preliminary results from our measurements at Station ALOHA indicate variability in biogeochemical processes at frequencies ranging from hours to months. Consequently, a strategy that calls for denser sampling ultimately may be required to resolve adequately the stochastic changes that appear to control oligotrophic ecosystem dynamics.

In the near future, we will establish the capability of making continuous measurements of sea-surface meteorology, upper ocean physics, dissolved gas concentrations, ocean optics, and particle flux from bottom-moored platforms. We also anticipate enlisting the unique capabilities of an instrumented, autonomous underwater vehicle to help resolve spatial and temporal variability in physical and biogeochemical processes. Finally, the deployment of a semipermanent (3- to 6-month duration) staffed research platform at Station ALOHA, which could be serviced by helicopter or high-speed surface craft, would greatly improve our ability to document and interpret variability in biogeochemical rate processes that are not amenable to remote sensing.

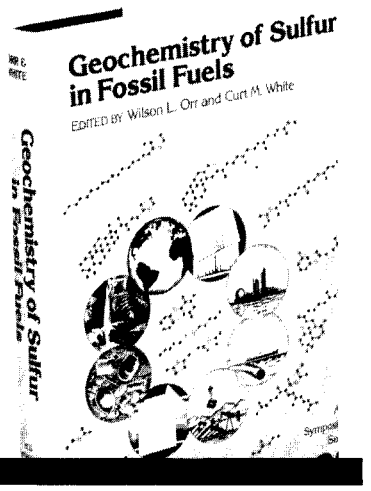
A longer term goal of oceanic time-series studies will be to establish the capability of obtaining systematic global measurements of key biogeochemical parameters in a manner analogous to the World Weather Watch program for atmo-



David M. Karl is chairman of the Biological Oceanography Research Division and professor of oceanography, School of Ocean and Earth Science and Technology, at the University of Hawaii in Honolulu.



Christopher D. Winn is assistant research oceanographer, School of Ocean and Earth Science and Technology, University of Hawaii.



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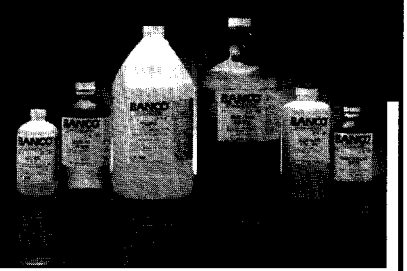
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spheric processes (*22, 23*). The emergence of a coordinated and comprehensive global ocean observation network would provide numerous opportunities for ocean climate prediction and for basic research in oceanography.

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