CONTINUOUS WATER SAMPLING AND WATER ANALYSIS IN ESTUARIES

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ABSTRACT

Salinity, temperature, light transmission, oxygen saturation, pH, $\underline{p}CO_2$, chlorophyll *a* fluorescence, and the concentrations of nitrate, nitrite, dissolved silica, orthophosphate, and ammonia are continuously measured with a system designed primarily for estuarine studies. Near-surface water (2-m depth) is sampled continuously while the vessel is underway; on station, water to depths of 100 m is sampled with a submersible pump. The system is comprised of commercially available instruments, equipment, and components, and of specialized items designed and fabricated by the authors. Data are read from digital displays, analog strip-chart recorders, and a teletype printout, and can be logged in disc storage for subsequent plotting.

Data records made in San Francisco Bay illustrate physical, biological, and chemical estuarine processes, such as mixing and phytoplankton net production. The system resolves large- and small-scale events, which contributes to its reliability and usefulness.

INTRODUCTION

The range of environments encompassed by estuaries (river to ocean) places additional demands on water-sampling equipment and analytical instrumentation and methods that were originally intended for oceanographic use. Water-sampling equipment must be capable of operating to depths of 100m, but suitable for river depths of as little as 4 m. An instrument must operate over wider ranges of salinity, temperature, and the parameter of interest than are commonly found in ocean waters. Similarly, the quantitative effects of environmental variables on analytical methods must be known and the methods must be accurate for both seawater and freshwater.

Turbulent mixing induced by winds, tides, and river inflow creates large variations in chemical and physical parameters over relatively short distances. Salinity can vary 10^{o}/oo over as little as 2 m of depth, and surface-salinity differences across rip lines can be greater than 5^{o}/oo (Schemel 1975). The sampling method is critically important. For example, high tidal-current speeds require a vessel to be anchored for vertical sampling and the water quality can vary significantly over the period of time required for the casts. As a consequence, data obtained from a STD (salinity-temperature-depth) cast may not correlate well with chemical analyses of samples obtained from a bottle cast.

Our approach to water sampling and analysis in estuaries is largely the consequence of the resources which we have available, our experience with other methods, and our understanding of the complex nature of estuaries. The system and methods discussed here have been progressively improved over several years. Equipment, instruments, and sensors were purchased when possible (Table 1), but a large fraction of the system was designed and fabricated by our machine and electronics shops. Details of these specialized items are described by Schemel and Dedini (1979), Dedini and Schemel (1980), and Leap and Dedini (1982).

METHODS

A most important feature of the system is that water is sampled with pumps and salinity and chemical parameters are measured on the vessel. Secondly, all instrumentation and analytical methods are modified, where necessary, to enable continuous measurement of the pumped-sample stream. This approach offers important advantages which are discussed below.

Water-Pumping Equipment

Horizontal profiles of parameters are made by sampling water from a through-hull fitting near the bow of the vessel with a flexible-impeller centrifugal pump (Fig.1). The pump is located near the hull fitting (to minimize suction effects) about 2 m below the water line. This pump delivers over 100 L min^{-1} to the laboratory. Excess flow is discharged overboard to minimize the flushing time (approx. 30 seconds) of the tubing. Water temperature is measured at the hull fitting by a thermistor probe.

Table 1. Manufacturers of Instruments and Equipment[1]

Item	Model	Manufacturer
Centrifugal pump	6400	Jabsco Products, Costa Mesa, Calif.
Submersible pump	4CM2	Berkeley Pump Co., Berkeley, Calif.
pH meters	801, 801A	Orion Research Inc., Cambridge, Mass.
pH combination electrodes	476050	Corning Instruments, Medfield, Mass.
Six channel analog recorders	260	Gould, Inc. Cleveland, Ohio
Fluorometer and nephelometer	10-000R	Turner Designs, Palo Alto, Calif.
AutoAnalyzer system	II	Technicon Corp., Tarrytown, N. Y.
Advanced calculator and accessories	700B	Wang Laboratories, Inc., Tewksbury, Mass.
Salinity-temperature meter	350	W. Petersen (Consultant), Palo Alto, Calif.
Photometer sensor	411	Hydroproducts, San Diego, Calif.
Termistor elements	44018	Yellow Springs Instruments, Yellow Springs, Ohio
Oxygen probe	5400	Yellow Springs Instruments, Yellow Springs, Ohio
Infrared analyzer	215A	Beckman Instruments, Fullerton, Calif.
Laboratory salinometer	RS7-B	Beckman Instruments, Fullerton, Calif.
Depth transducer	PG143-161	Gentran Inc., Sunnyvale, Calif.

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[1] The mention of brand names is for identification purposes and does not constitute endorsement by the U. S. Geological Survey.

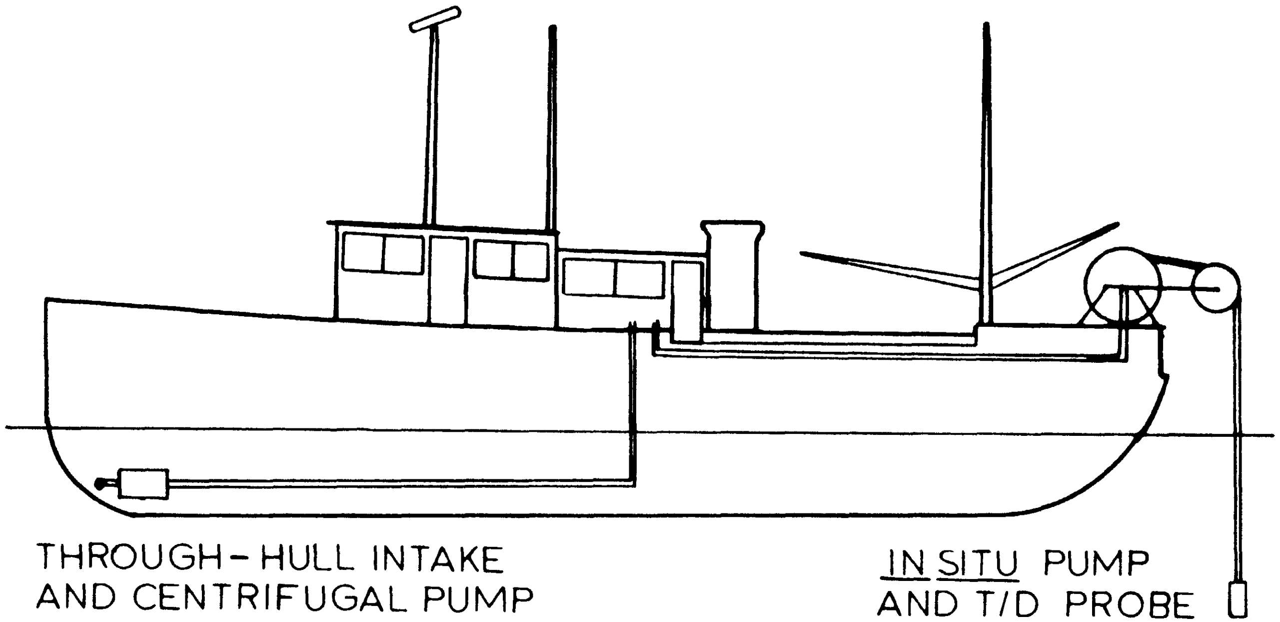

Figure 1. Bow-intake and *in situ* water-pumping systems.

The *in situ* pumping system for vertical sampling consists of a temperature- and depth-measuring (T/D) probe attached to a submersible well pump, 100 m of 1-in. (ID) polyethylene tubing with electrical conductors, and an electrically-driven winch assembly. This pump delivers about 30 L min^{-1} and has a relatively long flushing time (2 min) because of the tubing length.

Continuous Physical and Chemical Measurements

All continuous measurements except *in situ* temperature and pump depth are made on the vessel (Table 2; Fig.2). Water from either pump can be selected at a manifold and distributed to the instruments. In addition, water is routinely collected at this point for several discrete analyses. Some of these are required for calibration of the continuous measurements.

Salinity is perhaps the most important variable in estuaries because it is a measure of the dilution of ocean water by river water. Distributions of many chemical parameters are determined by dilution alone. The required precision is less than that necessary in the ocean ($\pm 0.1^{o}/oo$ is sufficient), but the range must extend from less than $0.1^{o}/oo$ to ocean values. We were unable to obtain a suitable salinometer specifically designed for continuous-flow operation. Therefore, a salinometer with a pyrex-glass cell placed through the sensing head was developed. Salinity is verified by discrete samples taken over the range of salinity in the estuary and analyzed with a laboratory salinometer. Results

Table 2. Continuous and Discrete Measurements

Continuous Measurements	Reference
Salinity	Schemel and Dedini (1979).
Temperature	Schemel and Dedini (1979).
Depth	Schemel and Dedini (1979).
Light transmissivity	None (photometry).
Oxygen saturation	Clark et al. (1953).
pCO_2	Gordon and Park (1972).
pH	Bates (1964).
Chlorophyll a fluorescence	Lorenzen (1966).
Turbidity	None (nephelometry).
Dissolved silica	Technicon Corp. (1976).
Orthophosphate	Atlas et al. (1971).
Nitrate plus nitrite	Technicon Corp. (1973).
Nitrite	Technicon Corp. (1973).
Ammonia	Solorzano (1969).

Discrete Measurements	Reference
pH	Bates (1964).
Alkalinity	Edmond (1970).
CO_2	None (infrared analysis).
Particulate organic carbon	Menzel and Vaccaro (1964).
Suspended particulate matter	None (gravimetric).
Chlorophyll a	Strickland and Parsons (1972).
Dissolved oxygen	Carpenter (1969).

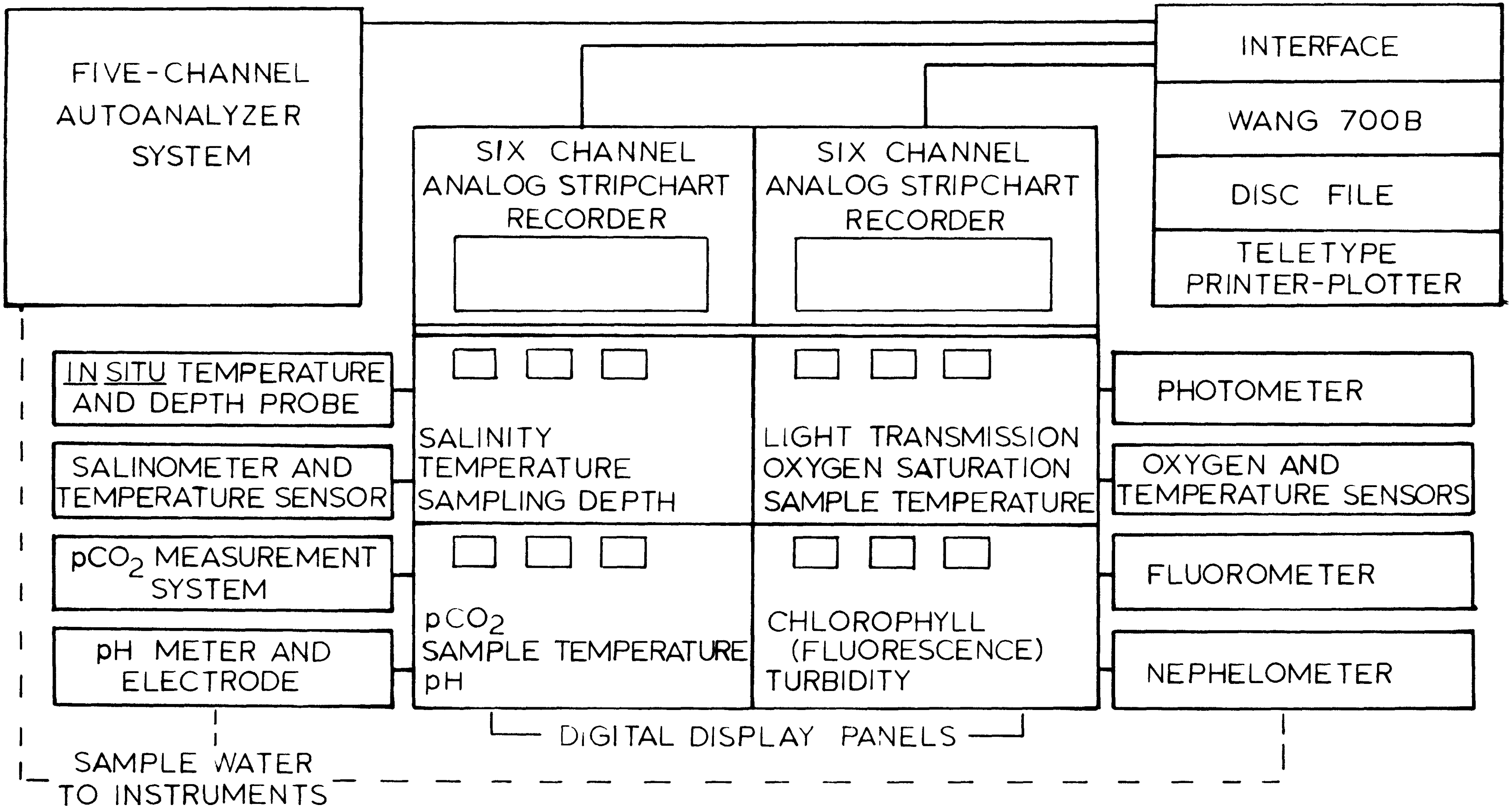

Figure 2. Block diagram showing continuous-measurement instruments and data acquisition system.

typically agree within ±0.05^{o}/oo.

All temperature measurements are made with thermistor probes. Measurement circuitry is located near each probe. Circuitry is routinely calibrated at the ice point and near 20^{o}C.

Dissolved oxygen is measured with a polarographic probe. When the probe is polarized, the resulting current is proportional to the partial pressure of oxygen in the sample. A thermistor varies amplifier gain to compensate for membrane diffusivity changes. Data are recorded as percent oxygen saturation. Sensitivity adjustment is made in air (100 percent) and in sodium sulfite solution (0 percent). Calibration is established by relating probe values to discrete analyses (Winkler titration). Results usually agree within 5 percent of the probe value.

Two carbonate-system parameters, partial pressure of CO_2 ($\underline{p}CO_2$) and pH, are continuously measured. The $\underline{p}CO_2$ is estimated by equilibrating a circulating volume of air with the flow of sample water and measuring the $\underline{p}CO_2$ of the dried air with an infrared analyzer (Fig.3). The infrared analyzer is standardized with CO_2 in artificial air (nitrogen plus oxygen) mixtures. Standards are automatically introduced at regular intervals by the gas controller. Partial pressures are expressed as parts per million (ppm) by volume of dry air, which is numerically equivalent to partial pressure at a total pressure of one atmosphere.

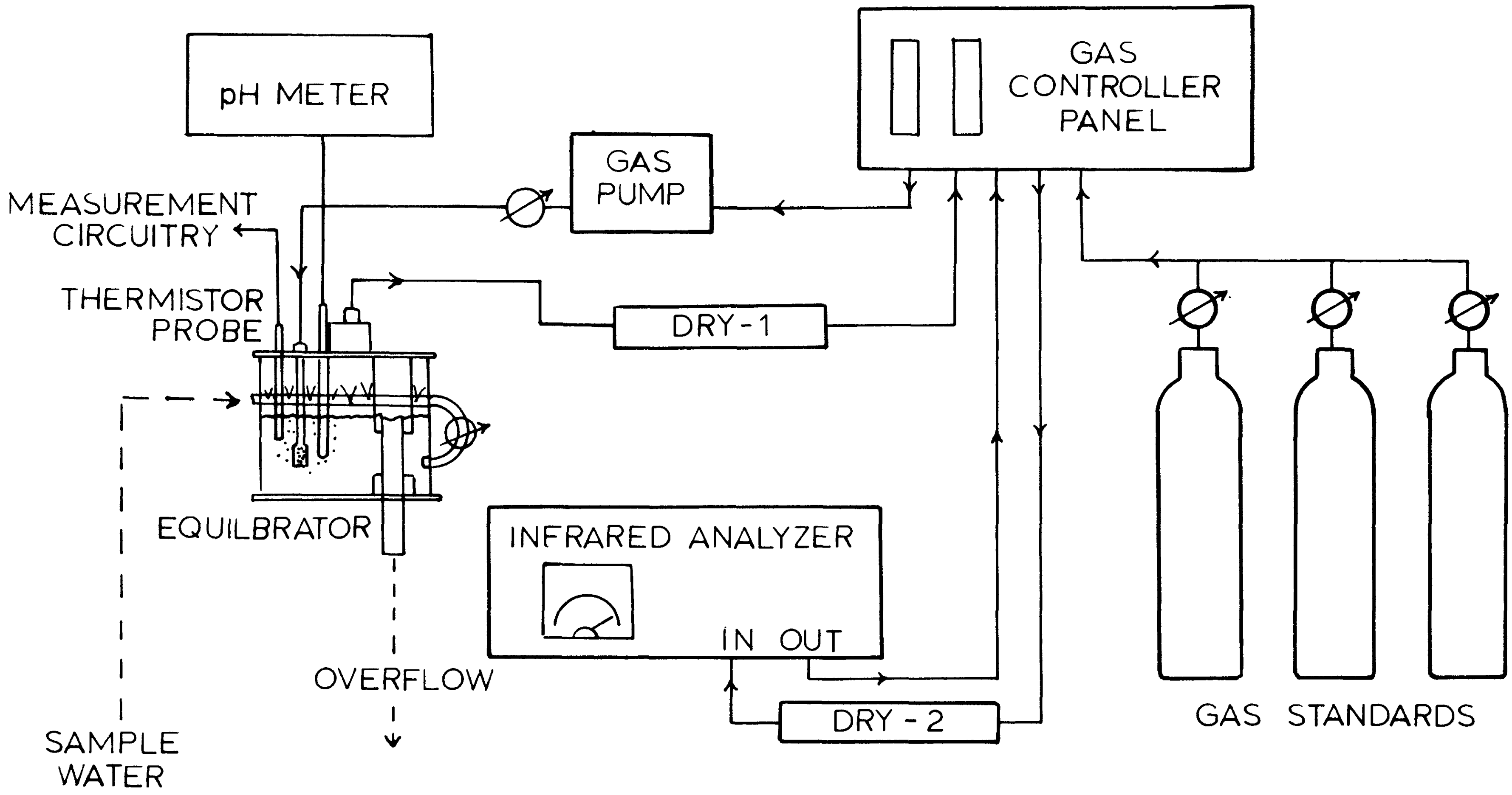

Figure 3. The $\underline{p}CO_2$ and pH measurement equipment and instrumentation.

Temperature and pH are measured in the equilibration chamber. Because pH and $\underline{p}CO_2$ are temperature-dependent variables, *in situ* values must be calculated from measured values and the difference between the sample and *in situ* temperatures. Continuous pH measurements are made electrometrically with a combination electrode. Continuous pH values are compared to discrete measurements for calibration. Continuous pH usually agrees with discrete pH within ±0.025pH.

The concentration of *in vivo* chlorophyll *a*, that in living organisms, is estimated with a fluorometer. The fluorometer is calibrated with discrete spectrophotometric (trichromatic) analyses.

Two optical methods evaluate the relative abundance of light absorbing and scattering constituents (turbidity) in the water. Light transmission over a 10-cm path length is measured with a photometer in a flow-sample cell. The nephelometer is more sensitive and has a wider measurement range than the photometer.

Relative turbidity data are routinely correlated with discrete suspended particle mass measurements and are useful in comparing differences in incident light penetration.

The concentrations of five phytoplankton nutrients, dissolved (reactive) silica, orthophosphate, nitrate, nitrite, and ammonia, are continuously measured. Sample water is continuously filtered through a 0.1um (pore size) filter before analysis. Raw data are corrected for ionic-strength and refractive-index dependencies. Calibrations are made with mixed standards prepared in artificial river water and sea water. Continuous measurements are routinely verified by discrete sample analyses.

Data Acquisition

All continuous measurements are recorded on analog stripcharts. These records help identify instrument malfunctions and allow the operators to note spurious data. Data can be interpreted as they are being collected, to anticipate more effectively the locations for collection of discrete samples.

Continuous-measurement signals, except those for the nutrients, are displayed on digital meters for convenient manual data logging. Signals are also interfaced to a Model 700B calculator, which computes mean values each minute, based on 50 samplings of each channel. Mean values are printed on a teletype and logged in flexible-disc storage. A parameter in disc storage can be recalled and regressed against any other parameter for data editing and interpretation.

MEASUREMENTS IN SAN FRANCISCO BAY

A typical sampling cruise in San Francisco Bay consists of vertical samplings at selected stations and depths and continuous horizontal sampling between these stations (Fig.4). Examples of results from cruises in South Bay (20 March 1978) and in North Bay (30 March 1977) show covariations related to phytoplankton net production and turbulent mixing, and thus illustrate the capabilities of the system.

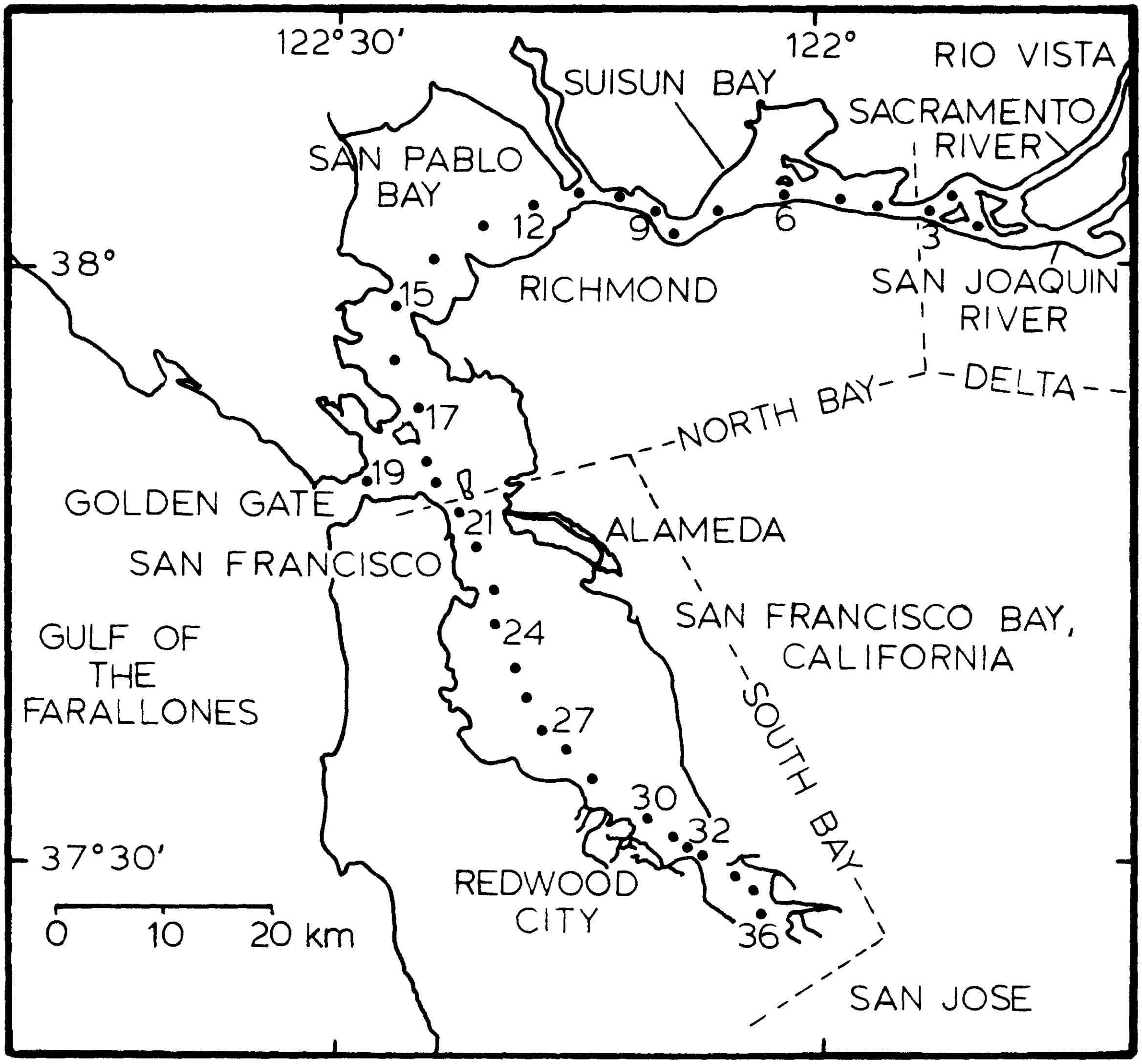

Figure 4. Sampling-station locations in San Francisco Bay.

South Bay

During March 1978, the effects of net production by phytoplankton were observed in near-surface water at Station 25 (Fig.5). The $\underline{p}CO_2$ was depleted to below the atmospheric level (approx.320 ppm), and chlorophyll a concentrations were increased. Only small variations in salinity were observed. Utilization of CO_2 during photosynthesis removes carbonic acid, lowering $\underline{p}CO_2$and increasing the pH. Oxygen is produced by photosynthesis.

The two patches of water with increased chlorophyll a concentrations correlate well with increases in pH and oxygen saturation and with decreases in pCO_2. The seaward patch is approximately 1 km wide and was traversed in about 5 minutes. The more diffuse variations in pH and $\underline{p}CO_2$ are presumably due to the flushing time of the equilibration chamber, which requires 1 to 2 minutes to resolve step changes, such as are observed across rip lines in the Bay.

North Bay

The record obtained during March 1977 is more complex and illustrates the effects of mixing and net production (Fig.6). Near-surface water from Station 16 to Station 15 decreased in salinity and $\underline{p}CO_2$, while temperature, chlorophyll a, pH, and oxygen saturation increased. Chlorophyll a patches correlate with the oxygen saturation record, and short-term chlorophyll a variations are highly correlative (inversely) with salinity. The vertical profile at Station 15 shows that chlorophyll a and oxygen are more concentrated in

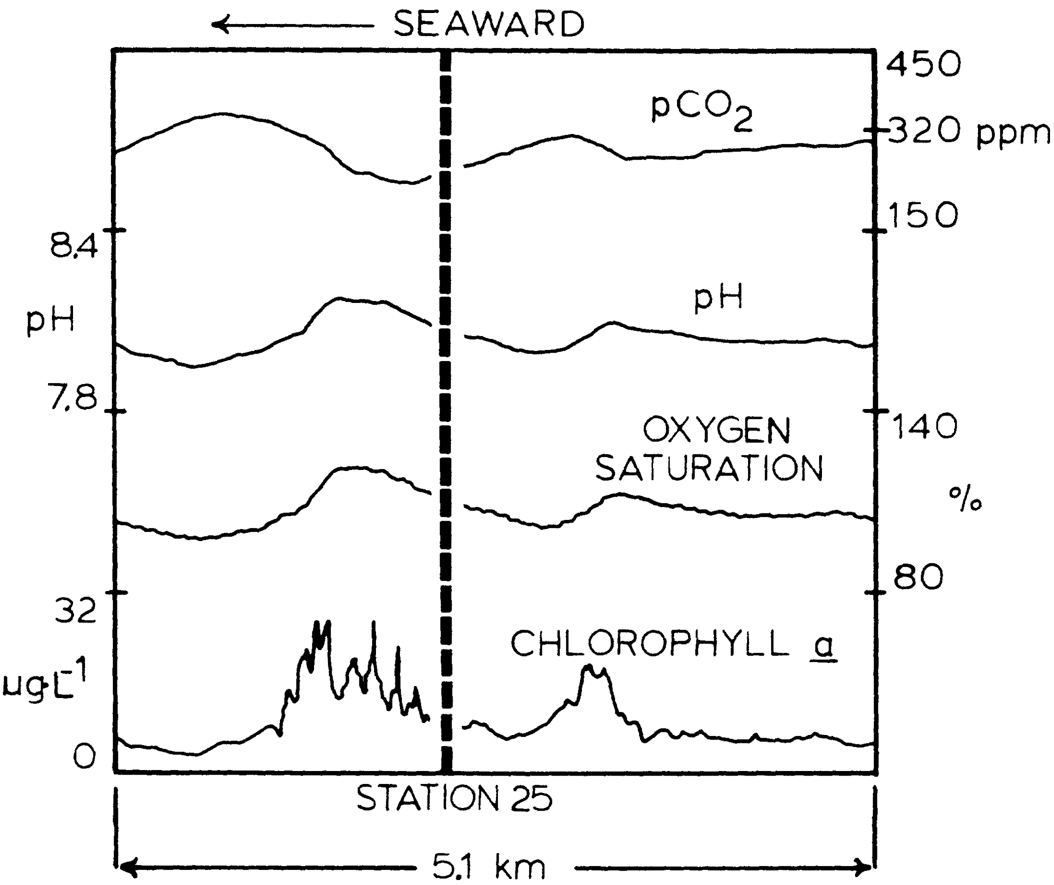

Figure 5. Near-surface chlorophyll *a*- pH, *p*CO$_2$, and oxygen saturation near Station 26 in South Bay (20 March 1978).

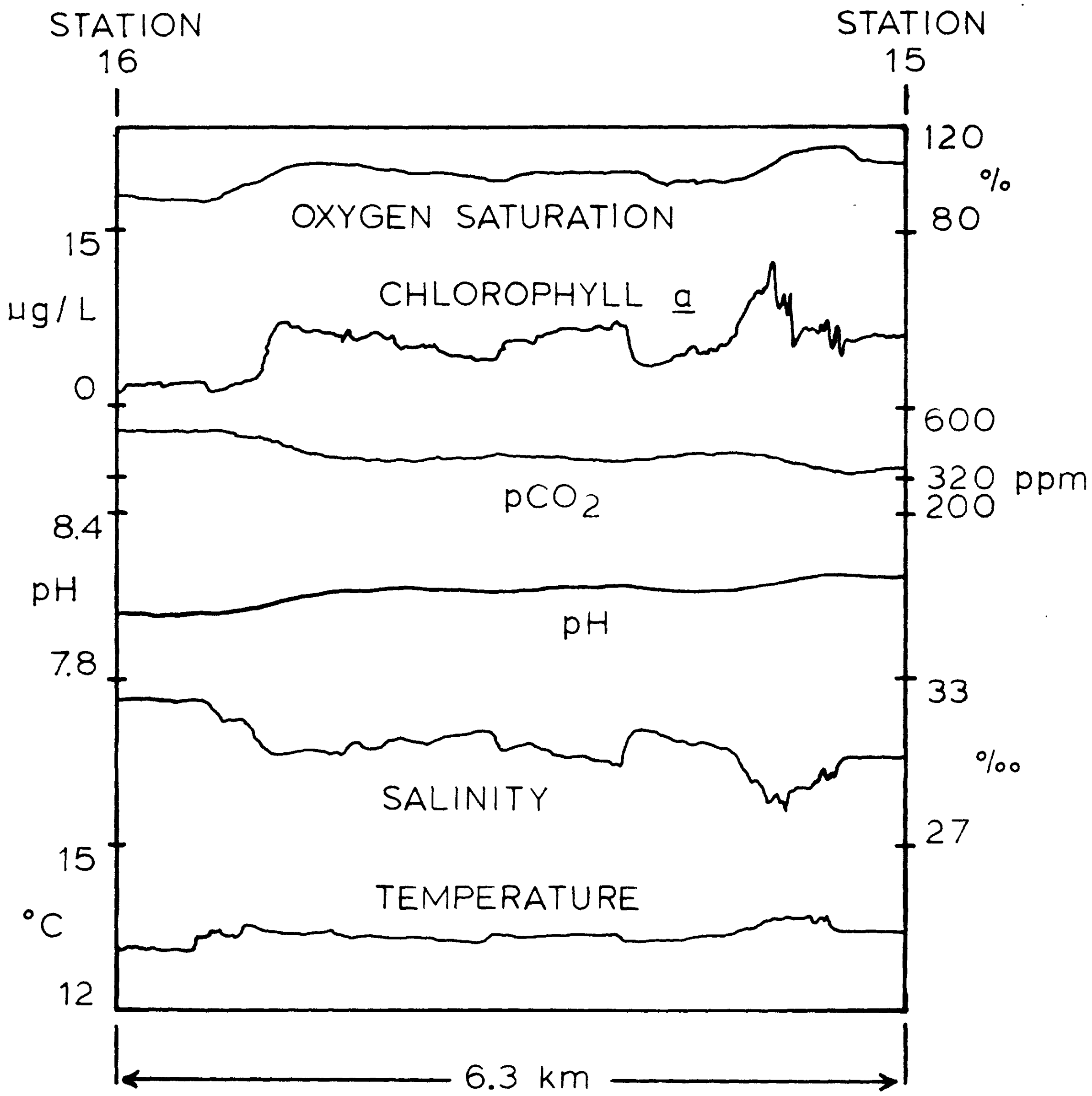

Figure 6. Near-surface salinity, temperature, chlorophyll a pH, pCO_2, and oxygen saturation between Station 16 and Station 15 in North Bay (30 March 1977).

near-surface waters (surface to 5 m) than in deeper waters (Fig.7). The $\underline{p}CO_2$ is depleted to near the atmospheric level in the near-surface waters, and $\underline{p}CO_2$ and salinity increase with depth. Thus, variations in the near-surface record are possibly the result of vertical mixing as well as of lateral variations in salinity and in the abundance and productivity of phytoplankton.

On a larger scale, lateral variations in chlorophyll a and $\underline{p}CO_2$ were major features observed at that time (Fig.8). Increased chlorophyll a concentrations were located in the seaward part of the estuary, where $\underline{p}CO_2$ was depleted below what would be expected by mixing river water and ocean water (conservative mixing).

DISCUSSION

Continuous measurements are advantageous for estuary studies. Large and small-scale features are resolved, which increase our understanding of active processes. Covariations are typical under certain conditions; experienced operators use these to evaluate system operation and identify malfunctions. Spurious data can be recognized, which is often not possible with discrete analyses.

Calibration procedures can be more rigorous than is possible with in situ probes, and calibrations can be made as frequently as necessary. Nurtient concentrations and $\underline{p}CO_2$, for example, are not readily adaptable to in situ measurement. Our sampling methods enable continuous measurement of these, with confidence that they relate directly to other

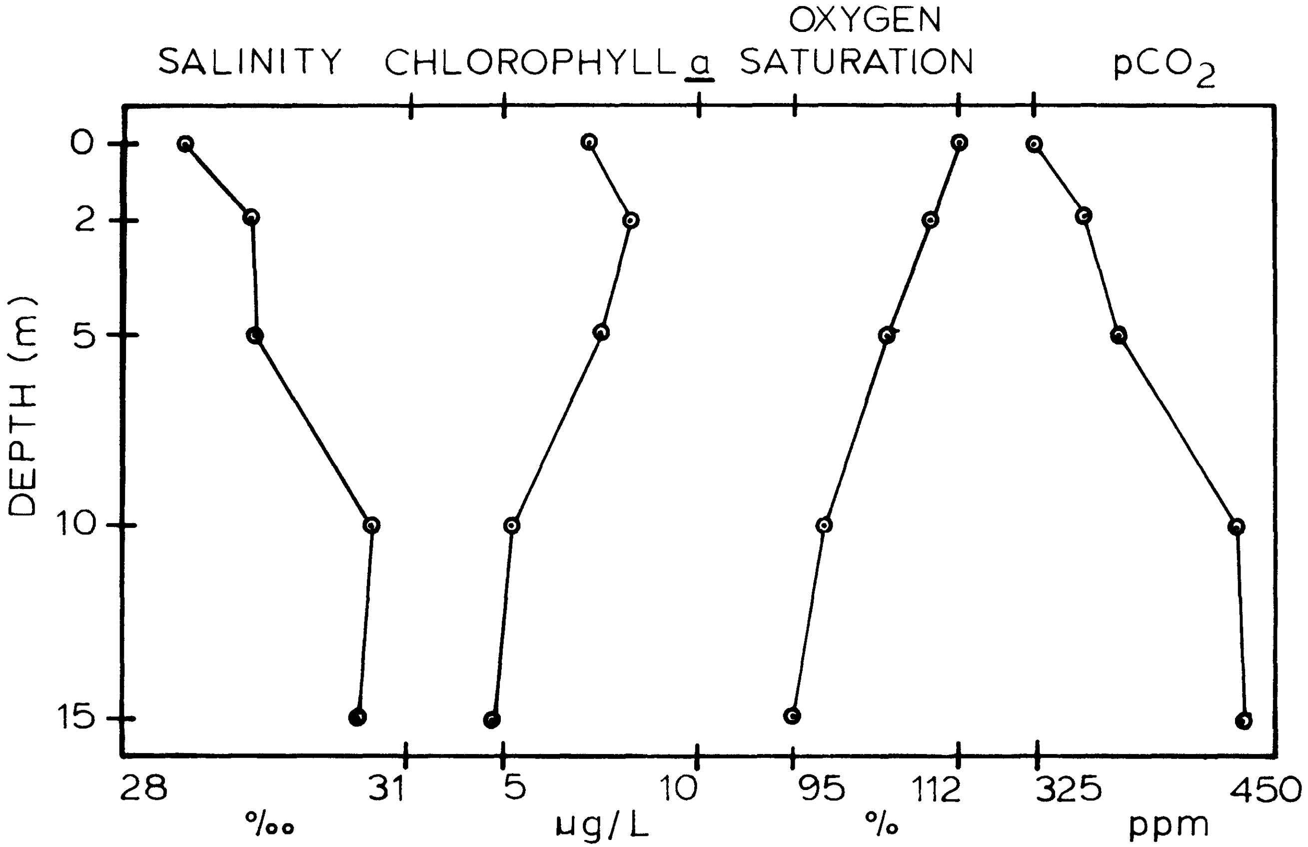

Figure 7. Vertical distribution of salinity, chlorophyll *a* pH, and $\underline{p}CO_2$ at Station 15 in North Bay (30 March 1977).

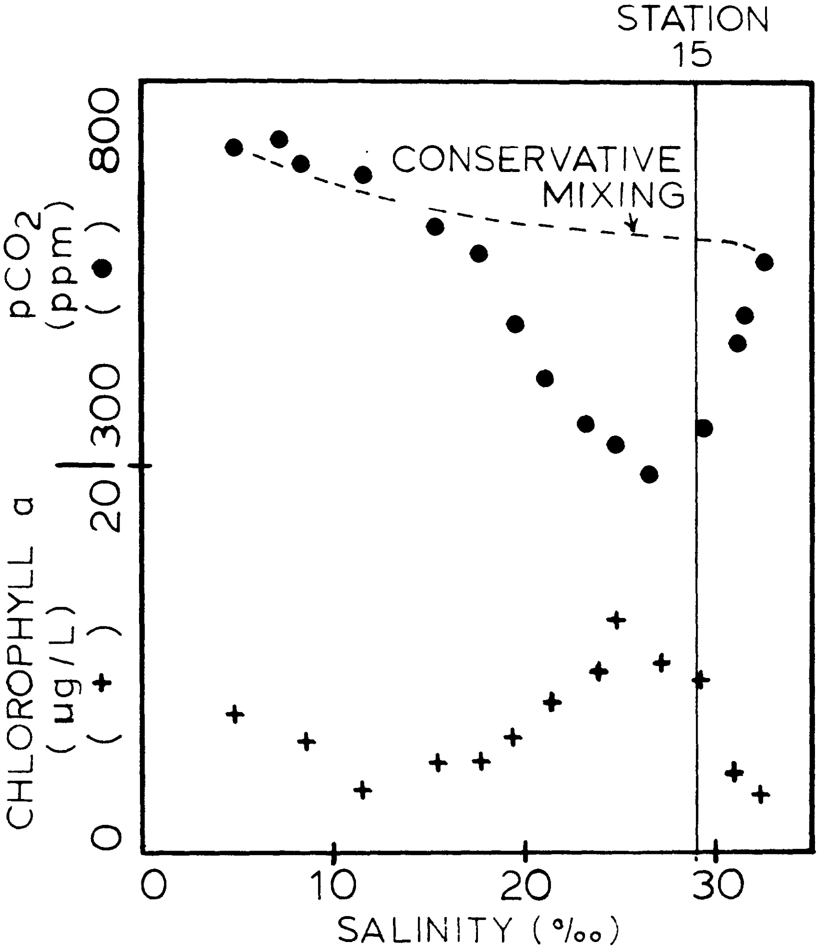

Figure 8. Distribution of near surface chlorophyll *a* and $\underline{p}CO_2$ in North Bay (30 March 1977).

measurements. Discrete samples are taken at the water manifold to calibrate or check the calibration of instruments. In the latter case they constitute an independent data set. These are normally taken on vertical profiles, when the pump is lowered to a specified depth and samples are taken when all continuous measurement readings are stable.

Calculations can be made with some measurements as a cross-check. For example, when salinity, temperature, and two of the four carbonate-system parameters are known, the other two may be calculated (Skirrow 1975). Suspect data are deleted if calculated values fall outside the error incurred in the calculation.

The continuous-sampling and multiparameter-measurement system has proved to be useful in studies of San Francisco Bay, the Potomac River, and other estuaries. The equipment and instruments are mechanically and electronically reliable and the analytical methods are appropriate for estuarine waters.

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