

AN ABSTRACT OF THE THESIS OF

KENT WILLIAM KANTZ for the MASTER OF SCIENCE

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CHEMISTRY AND HYDROGRAPHY OF OREGON COASTAL WATERS

AND THE WILLAMETTE AND COLUMBIA RIVERS;

MARCH AND JUNE, 1971

Abstract approved: Redacted for Privacy
Robert L. Smith

An inexpensive method for calibrating an infrared analyzer to measure varying ranges of carbon dioxide partial pressures (PCO_2) is described.

A discussion is made of the hydrographic (temperature, salinity, and sigma-t) and chemical (dissolved oxygen, AOU, PCO_2 , pH, and nutrients) variables that were observed along the Newport hydrographic line in March and June 1971. A winter storm in late March led to an inshore feature of doming isolines. Indications of early seasonal upwelling and photosynthesis were also observed. June conditions were characterized by a deteriorated upwelling regime and an inshore phytoplankton bloom. The Columbia River plume was also driven abnormally close (65 kilometers) to shore by southwesterly winds.

Chemical variables as observed in the Columbia and Willamette Rivers in June, 1971 are compared to data from a study made in December, 1968. A large gradient in P_{CO_2} and temperature is observed in the Willamette River approximately 3.5 kilometers upstream from the confluence in June, but not in December. This observation is related to the seasonal flow patterns of the two rivers. Chemical variables in the Columbia River are influenced by seasonal phytoplankton activity, but oxidation of organic matter is the predominating factor in the Willamette River. P_{CO_2} values calculated from pH and alkalinity measurements agreed to ± 5 percent with directly measured P_{CO_2} values in the Columbia River.

Chemistry and Hydrography of Oregon Coastal Waters
and the Willamette and Columbia Rivers;
March and June, 1971

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CHEMISTRY AND HYDROGRAPHY OF OREGON COASTAL WATERS
AND THE WILLAMETTE AND COLUMBIA RIVERS;

MARCH AND JUNE, 1971

I. INTRODUCTION

The waters off the Oregon coast are no doubt one of the most highly studied open ocean areas in the world. Several oceanographic groups, especially those located at the University of Washington and Oregon State University, devote a large portion of their energies investigating the Northeast Pacific Ocean.

Two features make the waters off Oregon especially fascinating to the oceanographer. One is the phenomenon known as coastal upwelling. The other is the Columbia River, the largest river on the Pacific Coast of North America, and its influence on the oceanic waters.

By monitoring such common hydrographic parameters as temperature and salinity, investigators have made detailed studies of these features (e.g., Smith, Pattullo and Lane, 1966; Cissell, 1969). The oceanographer also finds that several chemical parameters lend themselves well to this study. Such variables as dissolved oxygen, nutrient (i.e., phosphate, nitrate and silicate) concentrations, pH and P_{CO_2} (partial pressure of CO_2) are all very useful in discussing the varying impact of these two factors on oceanographic

conditions (Frolander and Park, 1963; Park, 1968; Hager, 1969; Ball, 1970).

The purpose of this study was to investigate the late winter and the late spring conditions in 1971 that existed along the Newport hydrographic line. Seasonal fluctuations in upwelling, location of the Columbia River plume, and primary biological activity should manifest themselves in a comparison study of these two seasons. Data was collected on two cruises aboard the R/V YAQUINA. The late winter cruise (Y7103E) was from March 28 to March 31 and the late spring cruise (Y7106B) from June 12 to June 16. The first day of the spring cruise, which departed from Portland, Oregon, was spent enroute to the Pacific Ocean via the Willamette and Columbia Rivers. A discussion is made of observed river conditions and how they compared to a similar study made in December, 1968.

In addition to the normal analyses done at sea (i. e., temperature, salinity, pH, alkalinity, dissolved oxygen and nutrients), direct measurement of PCO_2 was made using a specially developed system (Gordon and Park, 1972). Due to the complexity of this PCO_2 monitoring system and its rather unique features, a separate section on this analysis is included.

II. ANALYSES

A. P_{CO_2} Measurements

The methodology for measuring air and seawater carbon dioxide concentrations with an infrared analyzer was introduced by Takahashi (1961).

The present system (Gordon and Park, 1972) in use at our laboratory measures seawater P_{CO_2} by equilibrating a closed volume of circulating air with a continuous stream of seawater being pumped through the equilibrator (Figure 1). After passing through a Drierite[®] column to remove water vapor, the air stream travels through the sample cell of an infrared analyzer. The output from the analyzer is then monitored by one channel of a two-pen recorder. Continuous surface sampling is done through a seacock two meters below the ship's water line. Depths to 100 meters can be sampled by lowering a submersible pump attached to the hydrowire. Atmospheric P_{CO_2} is measured by pumping air from an inlet located at mast height (approximately eight meters above sea level) on the bow of the ship. Water vapor is again removed before the air passes through the infrared analyzer.

A gas programmer allows any one of four possible gases (either of two reference gases, atmospheric air or equilibrator air) to pass through the analyzer. The sequence of gases can be manually

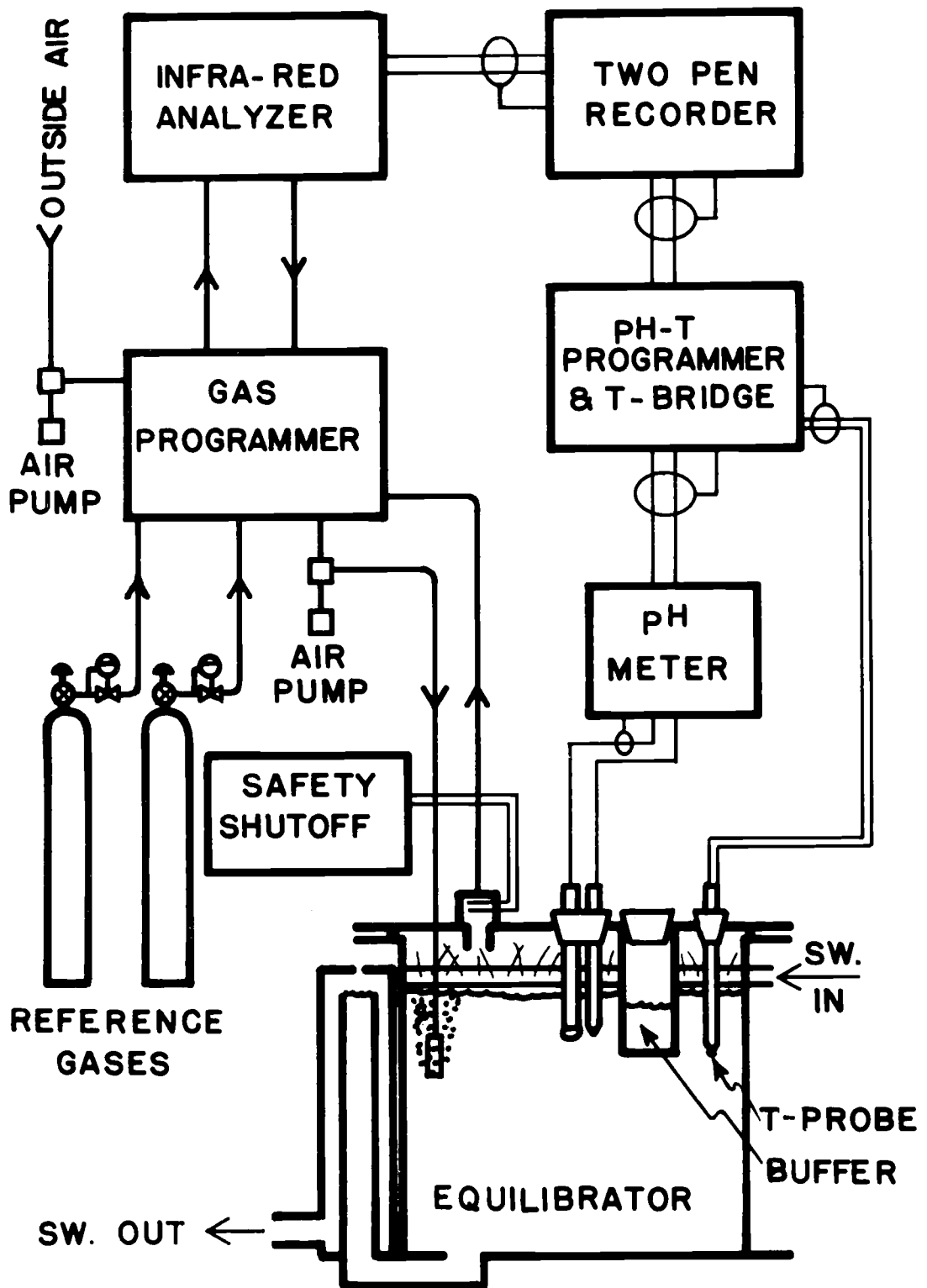


Figure 1. Block diagram of PCO_2 system. (From Gordon and Park, 1972)

selected or automatically timed.

B. Equilibrator pH Monitor and Thermistor Probe

Continuous pH readings from the equilibrator are made with a Leeds & Northrup Model 7405 pH Indicator. A glass and a reference electrode are fitted into a two-hole rubber stopper which is then inserted through the top of the equilibrator and into the seawater (Figure 1). The Indicator is standardized with a precision buffer (± 0.005 pH units) every 4 to 8 hours. The accuracy of this method is estimated to be ± 0.02 pH units (Gordon and Park, 1972).

A thermistor probe is also inserted through the top of the equilibrator and allows continuous monitoring of equilibrator temperatures with estimated accuracy of $\pm 0.05^\circ\text{C}$ (Gordon and Park, 1972).

The outputs of the pH Indicator and thermistor probe are alternately recorded by the other channel of the two-pen recorder.

C. Other Chemical Data

A sampling valve on the seawater manifold which supplies the equilibrator allows for the discrete sampling for dissolved oxygen, nutrient, pH, alkalinity, and salinity determinations.

Salinities were determined using a Hytech Salinometer, Model 6220. The modified Winkler method (Strickland and Parsons, 1968) was used for dissolved oxygen determinations. An Orion Model 801

digital pH meter and a glass-reference electrode pair were used for pH determinations. Alkalinities were run using a modified Anderson and Robinson technique (Wyatt et al., 1971). Nutrient analyses were made using the Technicon AutoAnalyzer[®] as described by Atlas et al. (1971).

Depending upon the quantity of water needed for each analysis, either a 4-liter Niskin or a standard NIO bottle was used to collect a water sample. A certain number (n in Table 1) of discrete samples were then drawn from this bottle and analyzed for one of these variables. The mean values and a precision estimate of ± 2 standard deviations ($\pm 2 s$) are reported in Table 1 for the various analyses. The precision estimates include errors introduced by both the sampling procedure and the analytical technique.

D. Calibration of the Infrared Analyzer

Two types of calibrations will be described. An absolute calibration of the analyzer allows comparison of our data with those of other workers in the field. The nonlinearity of the analyzer is determined in a separate calibration procedure. The scheme described does not require a large number of precisely known calibration gases and is therefore relatively inexpensive.

The absolute calibration of the infrared analyzer is accomplished by using a pair of reference gases. The CO_2 concentrations of these

Table 1. Results of experiment to measure analytical precisions.

<u>Cruise</u>	<u>Y7103E</u>		<u>Y7106B</u>	
	<u>mean \pm 2 s</u>	<u>n</u>	<u>mean \pm 2 s</u>	<u>n</u>
Salinity (‰)			34.516 \pm 0.005	7
Oxygen (ml/l)			0.70 \pm 0.25	8
			0.91 \pm 0.17	8
pH			8.257 \pm 0.007	5
Phosphate (μ M)	1.74 \pm 0.06	5	2.70 \pm 0.03	2
	3.03 \pm 0.03	5	3.12 \pm 0.03	10
Silicate (μ M)	9.13 \pm 0.38	4	6.50 \pm 0.20	2
	60.58 \pm 0.89	5	87.45 \pm 0.62	2
Nitrate and Nitrite (μ M)	7.02 \pm 0.29	10	5.31 \pm 0.34	2
	38.07 \pm 0.60	5	42.23 \pm 0.89	10
PCO ₂ *			258.0 \pm 8 (Sea PCO ₂)	
			316.8 \pm 8 (Air PCO ₂)	

* Accuracy, not precision, estimate. See Appendix II.

gases (tanks of compressed nitrogen and carbon dioxide) are obtained by comparison with gases analyzed at Scripps Institution of Oceanography (referred to as SIO gases) or to secondary reference gases analyzed at OSU. To check results, and internal consistency, each tank is analyzed several times using various sets of reference gases as standards.

Zero concentration gas (i. e. 0 ppm of CO_2) is checked for CO_2 contamination by first passing the gas directly through the infrared analyzer. The reading is compared to that made by passing the gas through a column of Lithasorb[®] (CO_2 absorbant) prior to its entry into the analyzer. A summary of recent calibration data is found in Table 2. (See Gordon and Park (1972) for previous calibrations.)

The methodology for estimating the nonlinear part of the response of a non-dispersive infrared gas analyzer is described in detail by Gordon and Park (1972). However, an additional problem was encountered in this work. A new cell assembly had to be installed in the analyzer prior to the March, 1971 cruise. Whereas the manufacturer (i. e., the Mine Safety Appliance Company) had supplied calibration curves (for two specified gas concentration ranges) with the original unit, the purchaser must evaluate the new nonlinearity introduced when the cell assembly is replaced. The procedure used for evaluating the new response is outlined in Figure 2 and can be described as follows:

Table 2. Recent gas calibrations.

OSU Number	Cylinder Number	Nominal Concentration (ppm)	Accepted Concentration* (ppm ± avg. dev. ppm)	Standards Employed	Average of Recent Analyses (ppm ± avg. dev. ppm)	Number of Recent Analyses	Present Accepted Conc. (if different from Column 4)	
2	41825 M	610	655.0 ± 0.4	OSU	654.0 ± 0.3	1		
3	37606 M	320	310.9 ± 0.3	SIO	318.3 ± 0.9	5		
5	33422 M	360	363.8 ± 0.1	SIO	363.9 ± 1.3	4		
7	7279 NCG	228	219.0 ± 1.0	OSU	218.9 ± 3.0	3		
8	13235 AIRCO	352	352.3 ± 0.1	SIO	350.8 ± 1.0	4		
14	13183T M	332	327.5--Analyzed at SIO		326.1 ± 0.5	6		
16	30485 M	215	208.5 ± 0.4	OSU	208.4 ± 3.0	2		
17	19498 M	390	387.4 ± 0.8	OSU	387.2 ± 0.2	2		
19	37644 M	600	605.4 ± 0.8	OSU	605.7 ± 1.6	4		
20	535520 M	0	≤ 0.2 (taken as 0)--Absorption of any CO ₂ with Lithasorb®					
22**	84225 M	620	532.2 ± 0.3	OSU	535.6 ± 1.5	3	534.7 ± 2.0 (Avg. of 4 analyses)	
24	6775T M	365	365.0--Analyzed at SIO		367.1 ± 0.7	5		
25	2420369 M	0	≤ 0.2 (taken as 0)--Absorption of any CO ₂ with Lithasorb®					
26	3748P M	280	308.3--Analyzed at SIO		306.5 ± 1.3	4		
27	2382T M	600			637.9 ± 3.1	4	637.9 ± 3.1	
28	49346 M	600			636.3 ± 4.2	4	636.3 ± 4.2	
29**	2232008 M	0	≤ 0.1 (taken as 0)--Absorption of any CO ₂ with Lithasorb®					

* All values except tanks #14, #20, #24, #25, #26, #27, #28, #29 are from Gordon (1972).

** Gases used on cruises Y7103E and Y7106B.

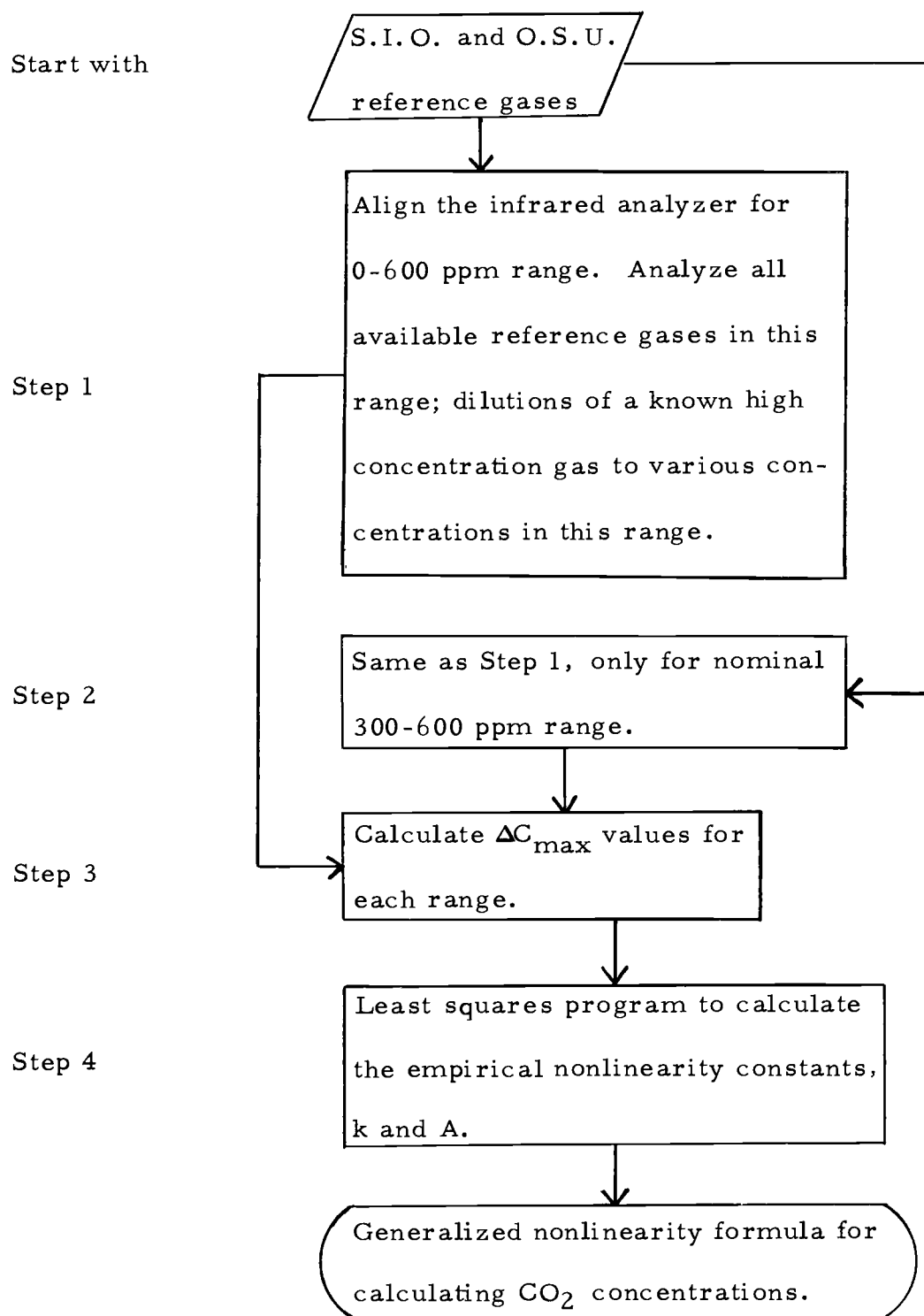


Figure 2. Procedure used for determining the nonlinearity of the infrared analyzer.

Step 1. The infrared analyzer was aligned using tank #20 as zero gas (i.e., the gas used to set the analyzer output near zero) and tank #28 as span gas (i.e., the gas used to set the analyzer near 100% output). All reference gases in this range were then analyzed (see Table 1 for a list of all gases available for the nonlinearity determination). In addition, several dilutions of tank #22 were made. (Gordon and Park (1972) present details of the dilution procedure.)

Step 2. The analyzer was realigned using tank #3 as zero gas and tank #28 as span gas. All reference gases in this range were analyzed and several dilutions were made.

Step 3. The concentrations of the reference gases were known. The concentrations of the various dilution runs could be easily calculated (as outlined in Gordon and Park, 1972). From the recorder chart readings and the concentrations of the zero and span gases, a "linear concentration" can be calculated. For example, if gas X was analyzed against a zero gas with concentration of 0 ppm and a span gas with concentration of 600 ppm and the recorder readings were zero for the zero gas, 1000 for the span gas and 500 for gas X, then the "linear concentration" of X would be 300 ppm. In this way a nonlinearity correction (ΔC_x) could be calculated for each gas (i.e., $\Delta C_x = C_{\text{linear}} - C_{\text{known}}$).

Using a Wang Programmable Calculator, a parabola for each concentration range was fitted by the method of least squares through

points generated by plotting these nonlinearity correction vs. respective recorder chart readings. The maximum nonlinearity (ΔC_{\max}) is defined as the maximum departure of the analyzer response from linearity and occurs at mid-scale (i. e., the mean of the recorder readings of the zero and span gas). Therefore the ΔC_{\max} for each range could be determined from the parabolic plots.

Step 4. Gordon and Park (1972) have shown that the nonlinearity is itself a nonlinear, increasing function of the range which may be expressed as:

$$\Delta C_{\max} = kR^A \quad (1)$$

where k and A equal the empirical constants that describe the maximum mid-range nonlinearity of the analyzer and R equals the range (i. e., the difference between the CO₂ concentrations of the span and zero reference gases). It follows from Equation 1 that the nonlinearity is a function of the range only and that the nonlinearity is zero at zero range. Using this information and ΔC_{\max} values from Step 3, a least squares power curve was fitted by using the Wang Programmable Calculator. This program calculates coefficients fitting data points to $y = ax^b$. Applied to Equation 1, y would be a ΔC_{\max} value and x the corresponding range (R), while a and b refer to the desired constants k and A, respectively.

End Result. Previous to the present work, the Fortran IV computer

program used for P_{CO_2} data reduction had constant values for k and A (i. e., those values determined by Gordon and Park (1972) for the original unit). The program has been modified so that different values for k and A can be read into the program. This facilitates data reduction, when major components of the infrared analyzer such as the cell assembly have been changed.

The nonlinearity determination was made during September, 1971. When the derived constants, k and A , were used in the reduction of reference gas calibrations made in April, the results deviated from accepted concentration values by 2 to 3 percent. However, calibrations run immediately after the nonlinearity determinations were within 0.5 percent agreement. Apparently the nonlinearity of the system had changed between April and September. The reason for this change is not clear, however changes in the optical alignment of the infrared analyzer sometimes occur in transit from ship to laboratory and back. Another possible contributing source of changing nonlinearity was an excessively worn recorder slide wire, which was not discovered until after the cruises.

It was decided that the best method available for reducing the cruise data would be to calculate a ΔC_{\max} value using gas calibration data from April, 1971 (Appendix I). Since the same gas concentration range was used for both the April calibrations and the 1971 cruises, the ΔC_{\max} should be the same in all three cases (assuming that the

nonlinearity remained constant). Final air P_{CO_2} values for both cruises (see Chapters III and IV) agreed, within accuracy limits, to values reported by other workers (Bolin and Keeling, 1963). This supported the validity of the ΔC_{max} value used in reducing the cruise P_{CO_2} data.

E. P_{CO_2} Data Reduction and Units

Corrections for pressure and humidity effects have to be made to the observed carbon dioxide concentrations as measured in the infrared analyzer sample cell. An illustration of how these corrections enter into the calculation of final P_{CO_2} values and an accuracy estimate of the P_{CO_2} values are presented in Appendix II. All data was reduced using a CDC 3300 computer. A complete description of the programs can be found in Gordon and Park (1972).

The standard gas concentrations are given as ppm (by volume) CO_2 in dry nitrogen. Streams of sample gas (i.e., equilibrator and mast air) are directly compared to these standard gases. After corrections for pressure variations in the instrument and the humidity effects, the final P_{CO_2} values are reported as volume mixing ratios, expressed in ppm. Assuming that Dalton's Law is obeyed, this ratio will numerically equal the partial pressure of CO_2 at one atmosphere total pressure. The values are calculated relative to an undried atmosphere (i.e., water vapor is included in the total atmospheric pressure) and at equilibrator, not in-situ, temperature.

III. OCEANOGRAPHIC CONDITIONS AND CHEMICAL VARIABLES ALONG THE NEWPORT HYDROGRAPHIC LINE FOR MARCH, 1971

A. Previous Studies off the Oregon Coast During Winter

Stefánsson and Richards (1964) made a detailed study of the seasonal variation of several chemical and physical parameters (e.g., dissolved oxygen, nutrient concentrations and density) off the Washington and Oregon coasts. The two physical factors that seem to influence these parameters most heavily in the upper 100 meters are the Columbia River plume and meteorological conditions. In winter, Columbia River discharge is usually minimal (Barnes et al., 1972). The meteorological conditions are normally ruled by low pressure centers which result in southerly winds and high precipitation along the coast. Thus, the Columbia River plume is driven north of its mouth during the winter season. Winter storms result in a relatively deep (70-75 meters) wind-mixed surface layer. Ball (1970) observed this phenomenon in the vertical distributions of temperature, salinity and sigma-t along the Newport hydrographic line for the winter months of 1968. The permanent pycnocline resided in a horizontal field at approximately 75-90 meters depth. Low salinities (30.0 to 32.0‰) and temperatures ($< 10^{\circ}\text{C}$) resulting from surface dilution by high coastal runoff caused a nearshore density stratification. The distribution of phosphate, nitrate and silicate also agreed with this

picture. Nearly uniform concentrations were observed in the upper 80 meters in waters seaward of NH-20. (Conversions from station location in nautical miles to kilometers offshore is presented in Table 3.) Waters near the coast were higher in nutrients indicating the influence of coastal runoff.

Table 3. Conversions for station locations (nautical miles) to kilometers offshore.

<u>Station Location</u> <u>(nautical miles)</u>	<u>Kilometers</u> <u>Offshore</u>
NH-1	2
NH-5	9
NH-10	19
NH-15	28
NH-20	37
NH-25	46
NH-35	65
NH-45	83
NH-55	102
NH-65	120
NH-70	130
NH-75	157

Dissolved gases in the wind mixed layer are usually near equilibrium with the atmosphere during the winter. Stormy winter weather results in a broken, turbulent sea surface which is ideal for air-sea gas exchange. Benson (1965) has discussed the role of bubble entrainment in gas exchange at the sea surface during periods of turbulent surface conditions. Extensive information on PCO_2 distribution in the surface waters is lacking. Data from a January 1970

cruise (Gordon, 1973) indicate near equilibrium conditions existed between the atmosphere (P_{CO_2} values ranging from 318.8 to 321.6 ppm) and the surface waters (P_{CO_2} values ranging from 305.4 to 324.0 ppm).

A noticeable feature for certain vertical sections taken during the winter off the Oregon coast is a peaking or doming of sigma-t isolines in the nearshore regime in waters above 100 meters (Wyatt, 1972).

B. Results

The main objective of this cruise was to do a chemical survey of the Newport hydrographic line during the late winter, pre-upwelling season. Directly measured P_{CO_2} data had never been collected during this season in this region. (Gordon and Park (1972) present a list of all cruises on which P_{CO_2} data has been collected by OSU's chemical oceanography group.)

A severe storm hit the Pacific Northwest about March 26 (Schwerdt, 1971). Sustained 42 knot winds, with gusts to 62 knots, were reported in Portland, Oregon. Figure 3 indicates that the southerly wind components, as observed in Newport, Oregon, varied from approximately 16 to 20 knots for the period March 26-29. Ships at sea were reporting seas of 16 feet with swells of 20 feet. The storm subsided during the next few days and the cruise departed

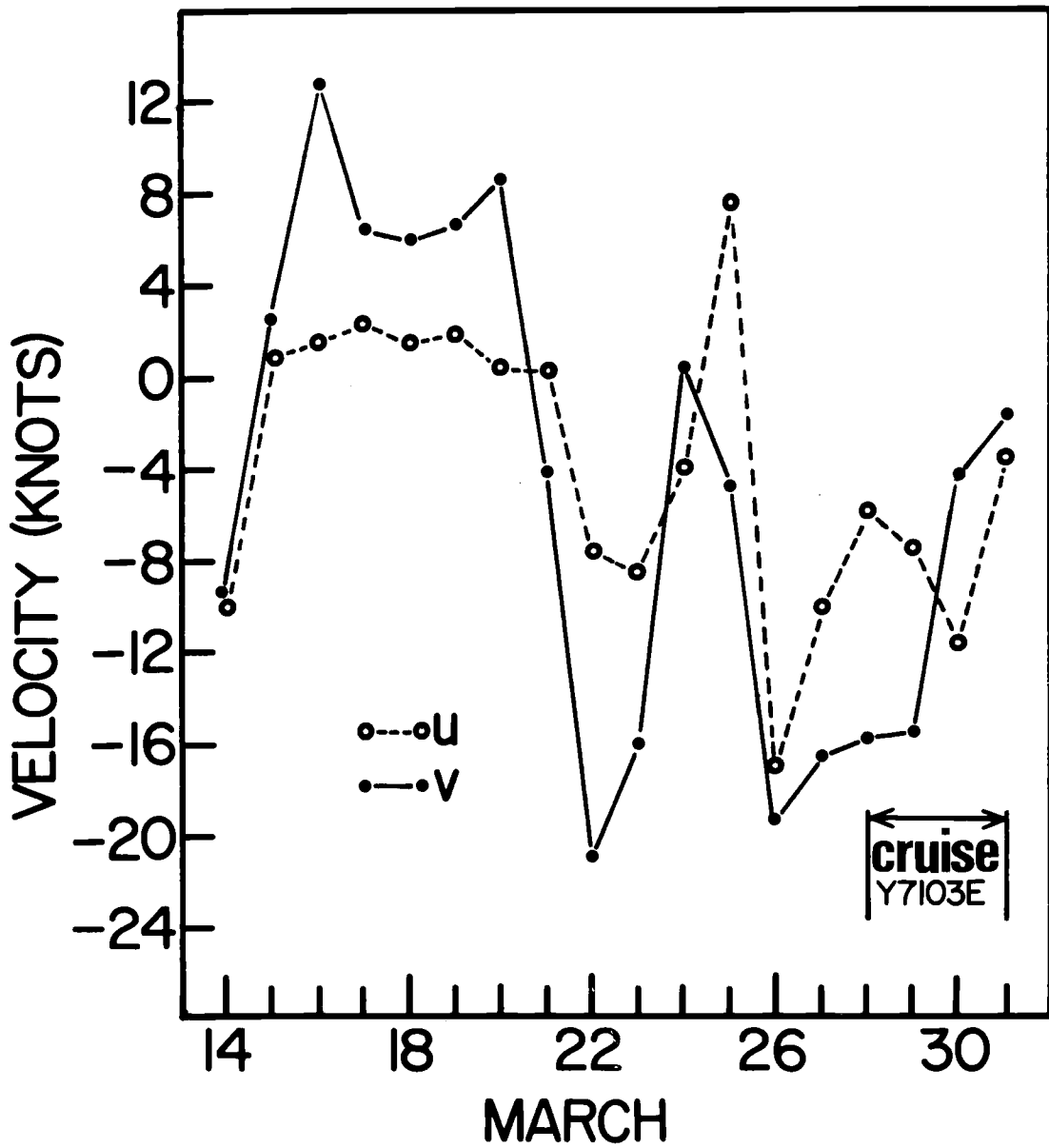


Figure 3. Daily component wind averages, March 1971. u is the east-west component with positive values indicating wind from the east and v is the north-south component with positive values indicating wind from the north. (Observations made at the south jetty in Newport, Oregon)

March 28.

The distribution of various physical and chemical parameters along the Newport hydrographic line appear in Figures 4-9. Sampling locations and depths are indicated by small dots in these figures.

Temperature

The temperature distribution (Figure 4a) is characterized by nearly vertical isotherms to 90 meters. Bands of progressively warmer water appear as one moves shoreward from NH-45. An area of relatively cold water is found ranging from NH-45 to NH-70 and warmer temperatures occur west of NH-70. The doming of isotherms, which is observed below 50 meters at NH-25, will be discussed later.

Salinity

Inshore isohalines are nearly vertical (Figure 4b). A pool of low salinity ($< 32.4\text{‰}$) surface water is centered around NH-25. Water of less than 32.2‰ occurs inshore of NH-5. The permanent halocline is located at about 100 meters depth at NH-65 and rises shoreward. Doming is again observed at NH-25.

P_{CO_2}

The vertical distribution of P_{CO_2} is presented in Figure 5a. Two features, similar to those seen in the oxygen distribution

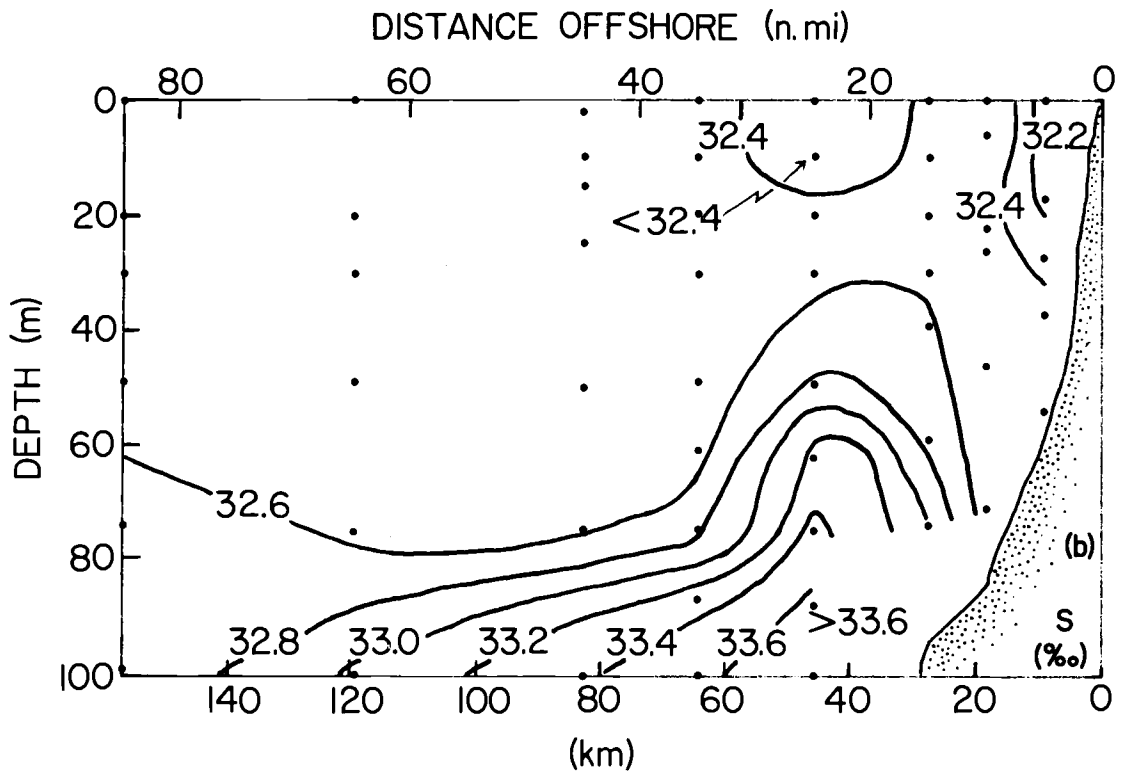
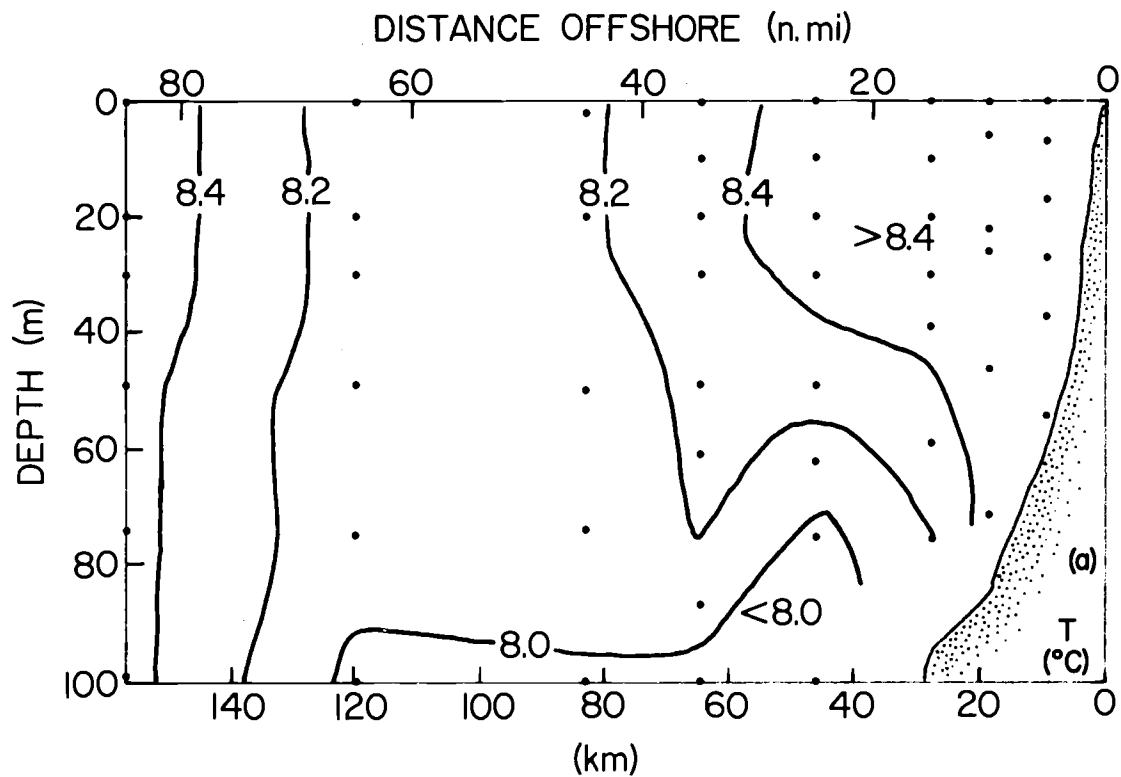


Figure 4. Vertical distribution of (a) temperature and (b) salinity along the Newport hydrographic line, March 1971.

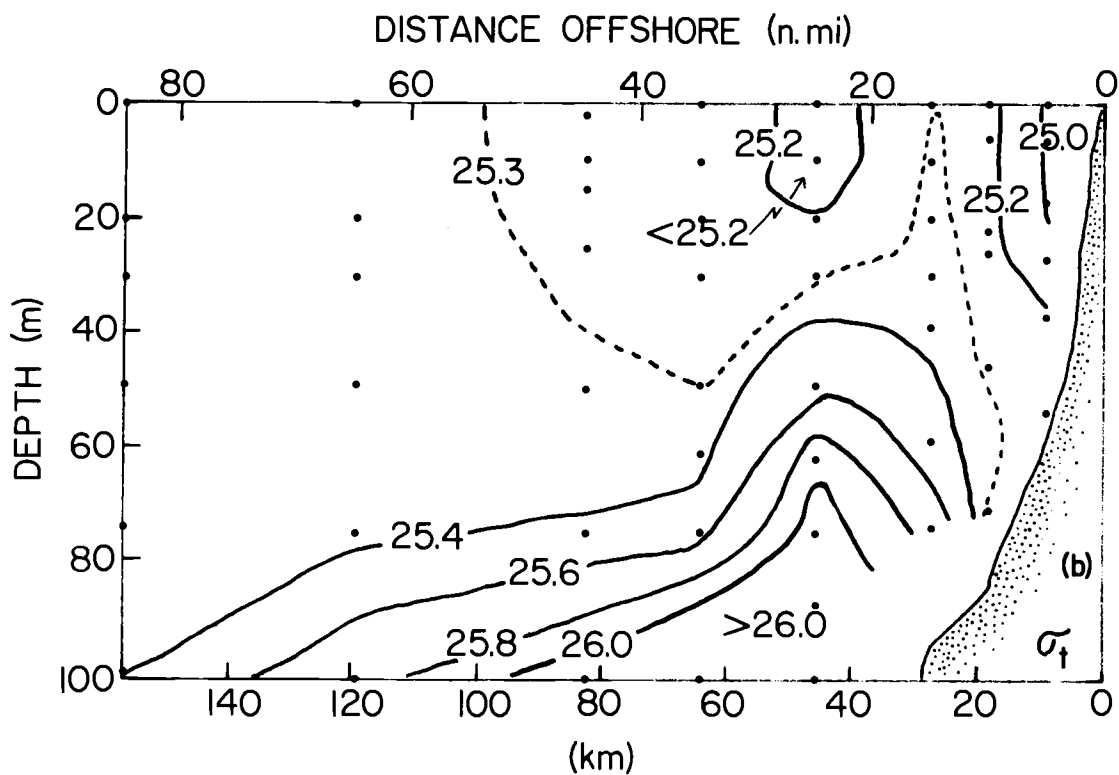
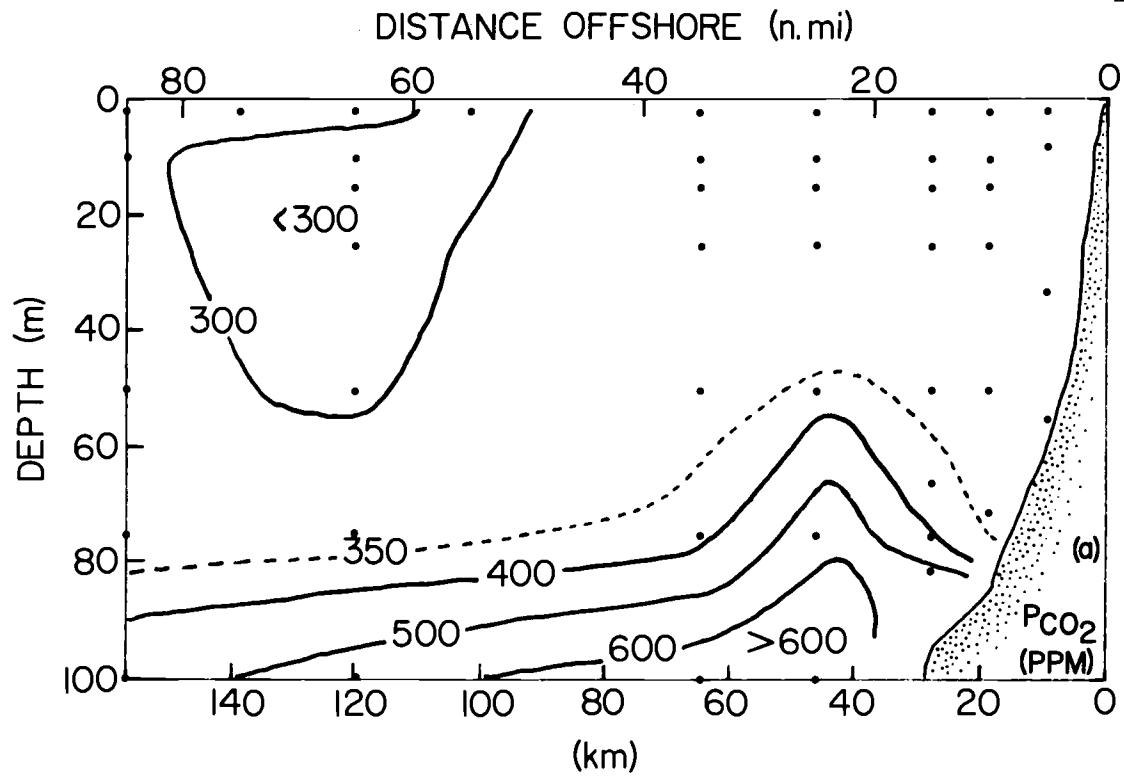


Figure 5. Vertical distribution of (a) P_{CO_2} and (b) σ_t along the Newport hydrographic line, March 1971.

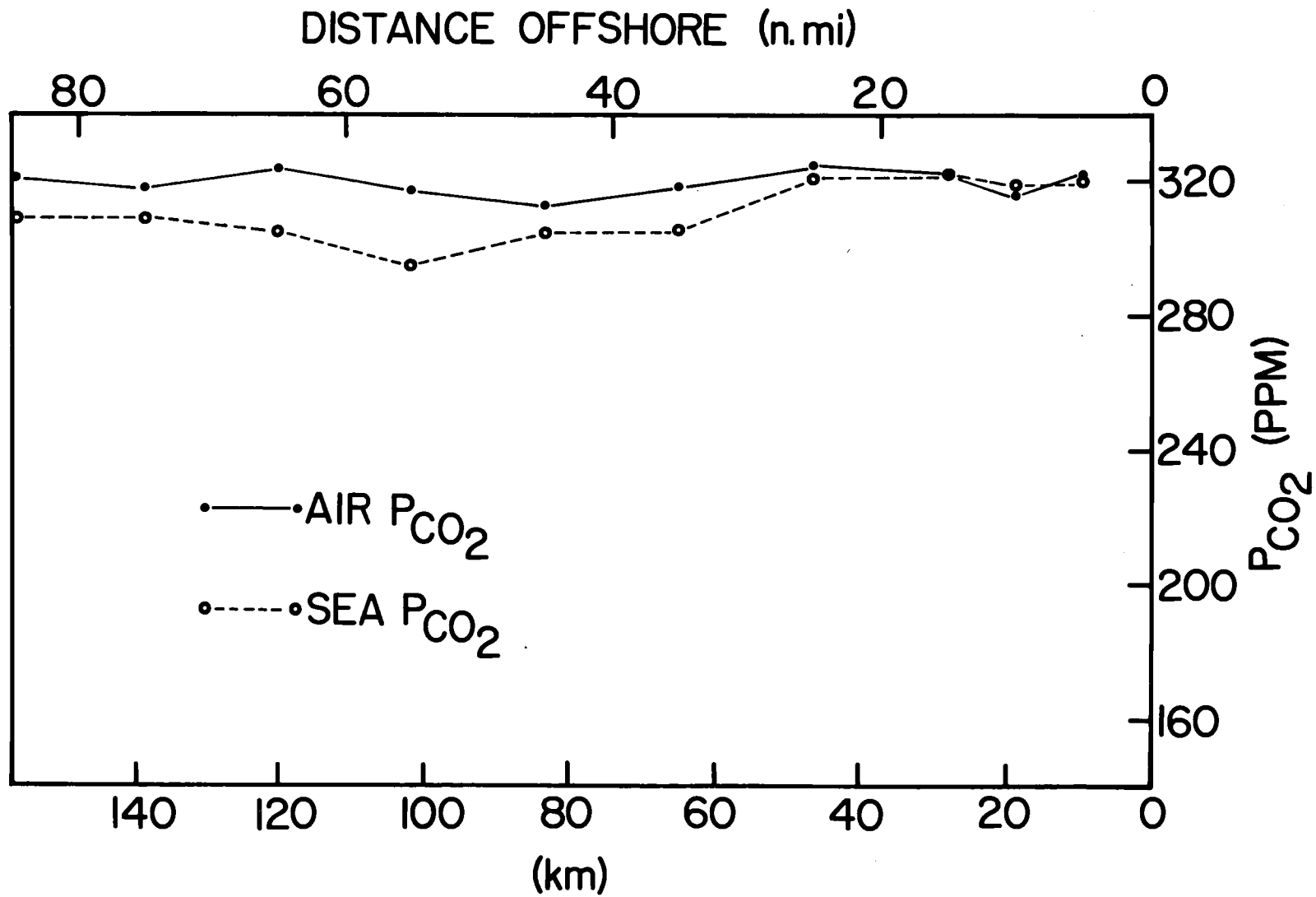


Figure 6. Air-sea surface P_{CO_2} gradient along the Newport hydrographic line, March 1971.

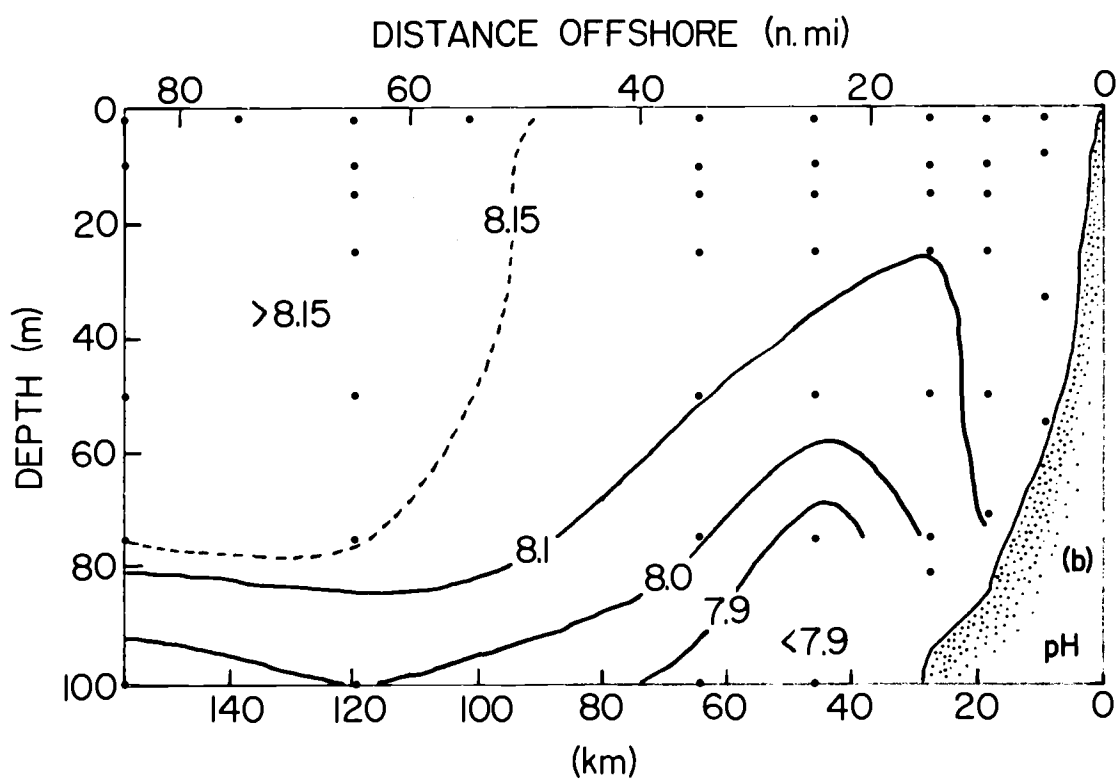
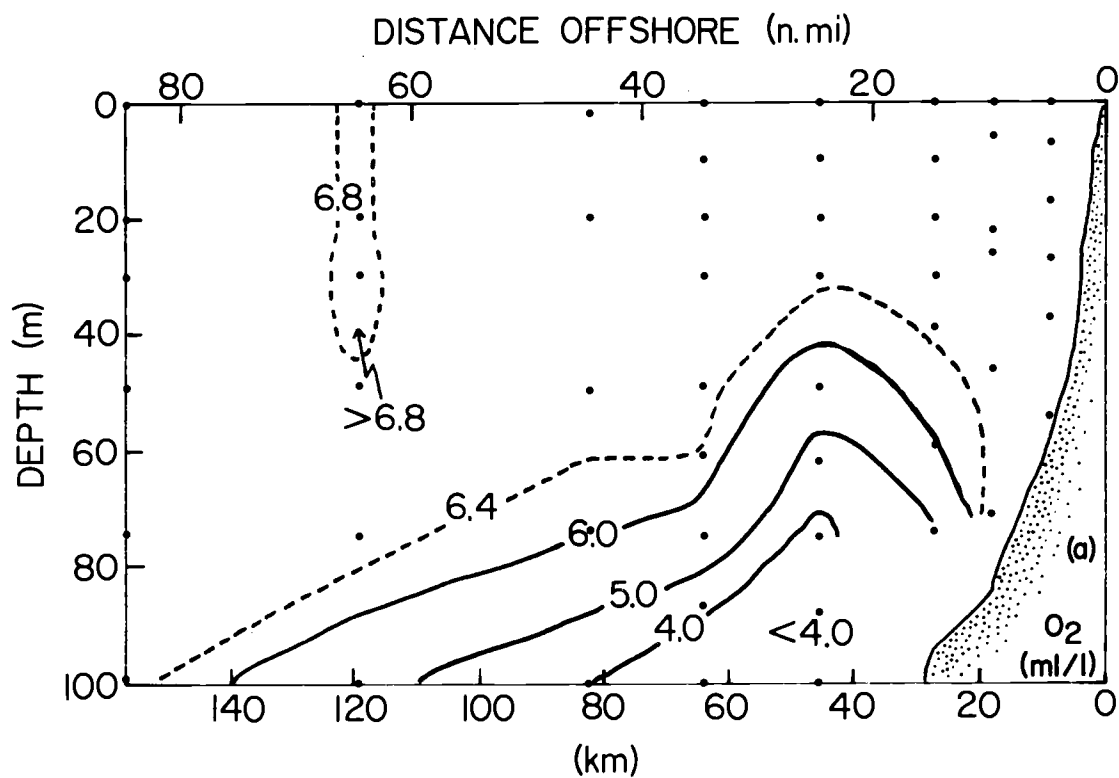


Figure 7. Vertical distribution of (a) oxygen and (b) pH along the Newport hydrographic line, March 1971.

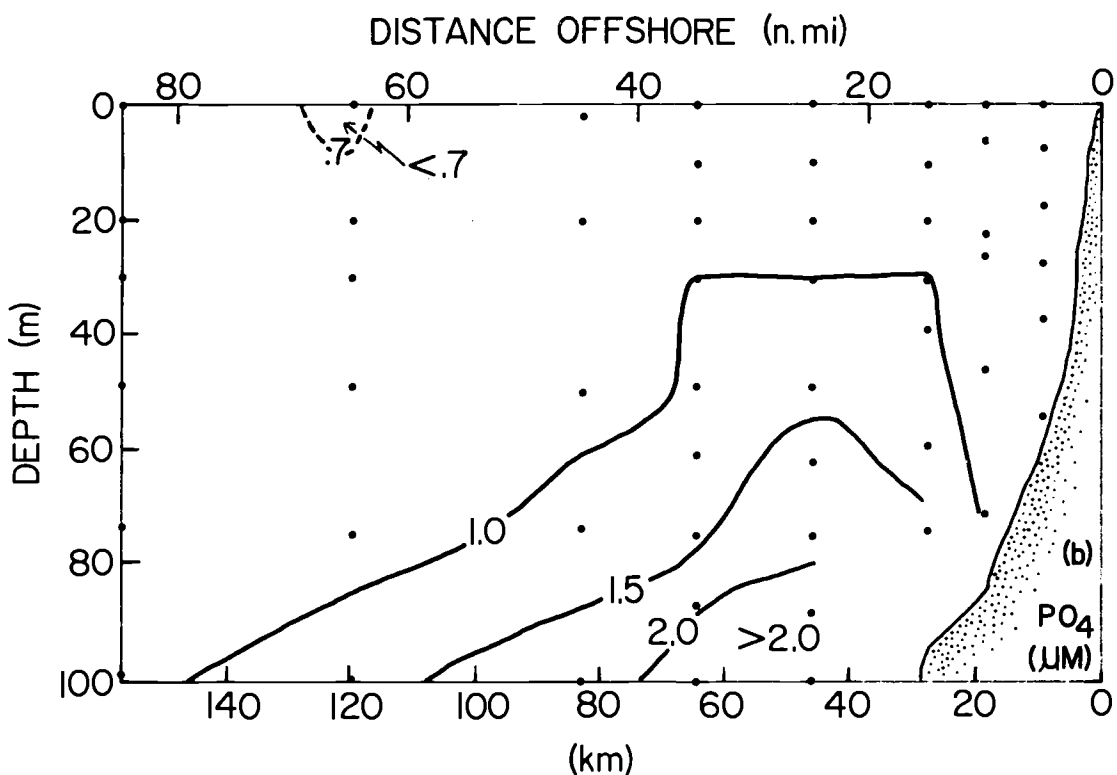
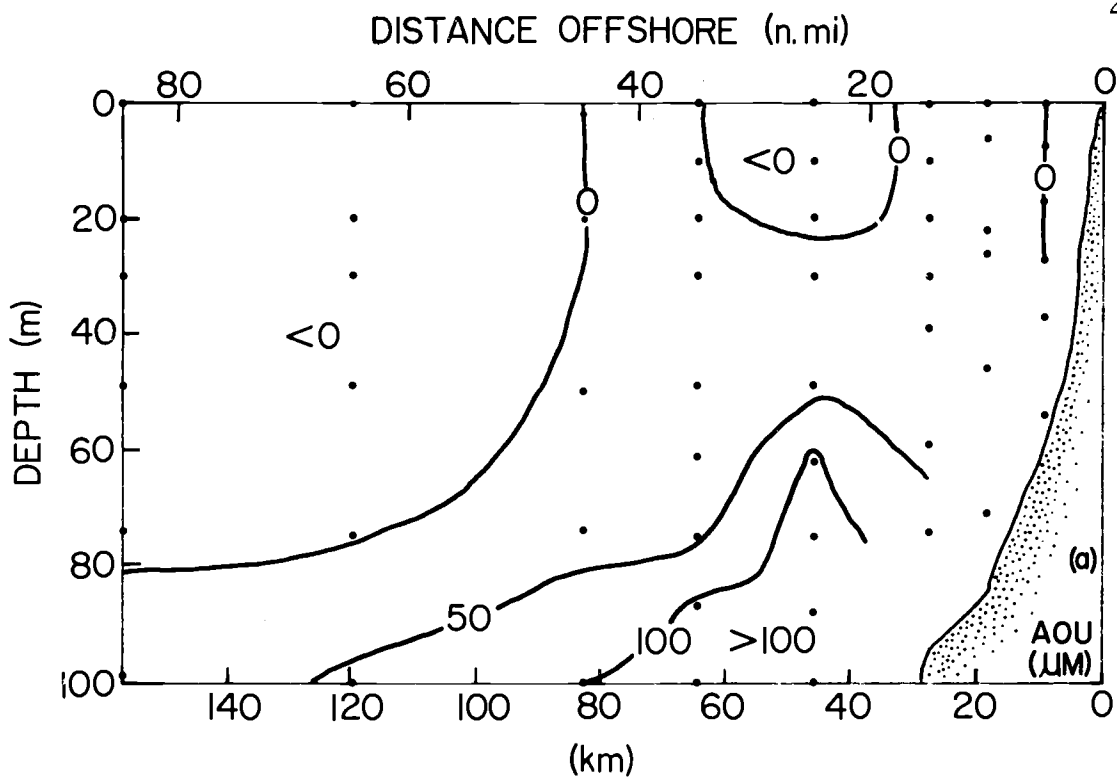


Figure 8. Vertical distribution of (a) AOU and (b) phosphate along the Newport hydrographic line, March 1971.

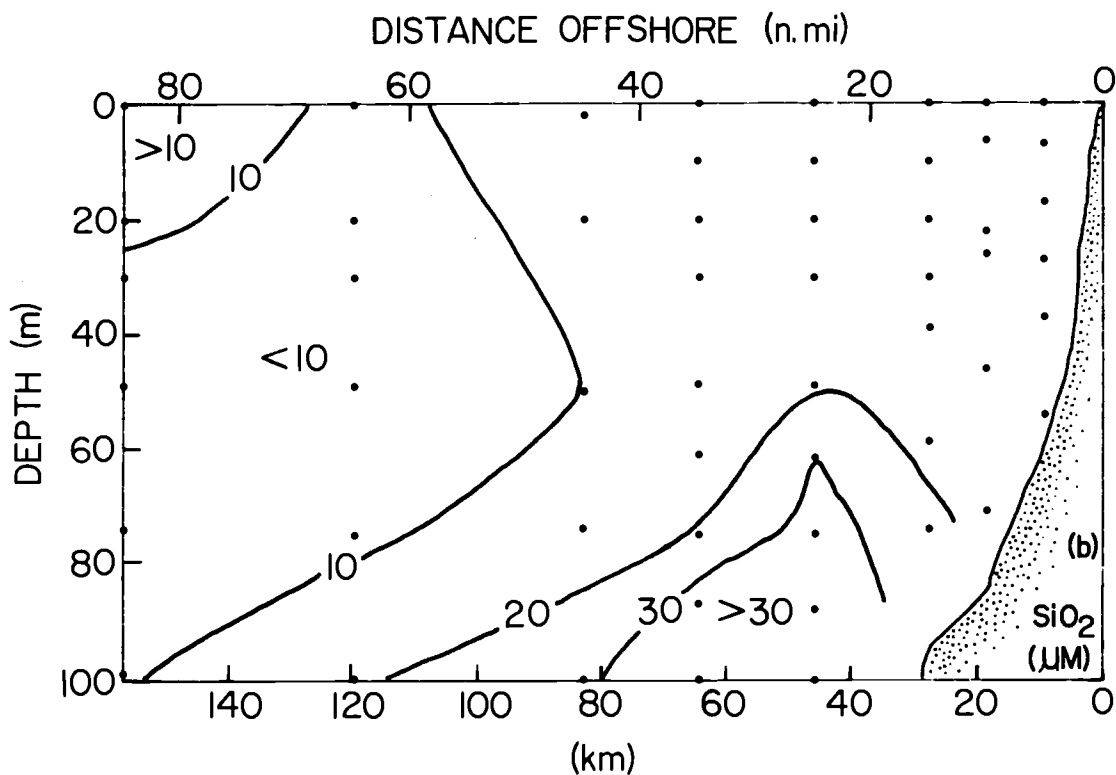
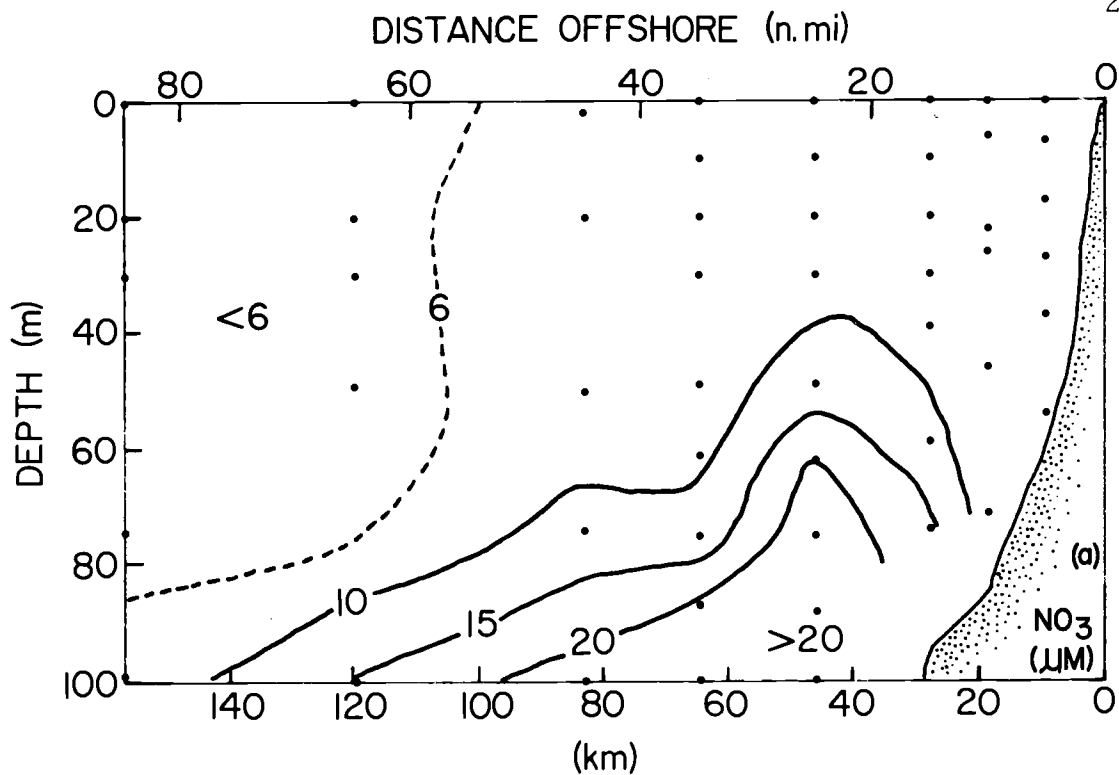


Figure 9. Vertical distribution of (a) nitrate and (b) silicate along the Newport hydrographic line, March 1971.

(Figure 7a), are again prominent here; i.e., the doming of isolines in the nearshore region and relatively low P_{CO_2} values correlating with relatively high oxygen concentrations in the nearsurface waters around NH-65. A comparison of surface seawater P_{CO_2} and atmospheric P_{CO_2} is made in Figure 6. Nearshore surface waters are close to equilibrium but those farther offshore than NH-25 appear to be slightly undersaturated (i.e., air $P_{CO_2} >$ sea P_{CO_2}). Air P_{CO_2} values varied slightly around 320 ppm (the standard deviation of 11 measurements made along the Newport hydrographic line was 3.5 ppm).

Sigma-t

A trend of vertical isopycnals is observed in the nearshore region (Figure 5b). This feature and the presence of the doming phenomenon are the most prominent features of the density distribution. The permanent pycnocline coincides with the permanent halocline, a normal occurrence off the Oregon coast.

Oxygen

No nearsurface oxygen maximum was observed (Figure 7a). The highest concentrations occurred in the nearsurface waters around NH-65 in the pool of relatively cold water described in the temperature section.

pH

The vertical distribution of pH is presented in Figure 7b. The measurements from the equilibrator pH monitor were used for this plot. This means that a direct comparison can be made of the P_{CO_2} and pH values, as both were determined at equilibrator temperatures. The main features of this section are doming isolines in the near-shore region and relatively high pH values (>8.15) in the surface waters around NH-65.

AOU

Apparent oxygen utilization (AOU) is defined as: $AOU = O_2' - O_2$, where O_2' is the solubility of oxygen at the in-situ temperature and salinity and O_2 is the measured oxygen concentration (Redfield et al., 1963). The general picture is nearly saturated conditions (Figure 8a) except in the area of doming isolines (i.e., in and below the pycnocline). Maximum saturation (percent saturation = $O_2/O_2' \times 100$) values of approximately 102 percent were found in the near surface waters at NH-25 and NH-65. The lower boundary of the mixed layer is delineated by the appearance of increasingly positive AOU isolines and coincides with the permanent pycnocline.

Nutrients

Nutrient sections (Figures 8b, 9a, 9b) reflect the general trends shown by the other chemical parameters. The doming is observed in all sections. A minimum in nutrients is observed near the surface around NH-65.

C. Discussion and Conclusions

Dilution of surface seawater by coastal runoff resulted in the nearly vertical trends of isotherms and isohalines in the nearshore region. Vertical mixing of cold deep water and warmer surface water probably resulted in the low temperature zone centered around NH-55. Such isolated regions of warm or cool water are often observed off the Oregon coast (Wyatt, 1972).

The doming of isolines at NH-25 presents a more complex oceanographic feature. Average daily wind components as recorded in Newport, Oregon, for the last half of March, 1971, are presented in Figure 3. Northerly wind components varying from approximately 3 to 13 knots were observed for the period March 15-20. Southerly components ranging from approximately 2 to 21 knots dominated the last part of the month. This particular sequence of winds could have caused the doming in the following way. When the winds had a component from the north in the middle of March, early seasonal coastal

upwelling was initiated (Smith, 1968). Upwelling is usually associated with the onset of northerly winds and continues through the summer and into the fall. Surface waters move offshore and are replaced by subsurface waters, which are lower in temperature, oxygen, and pH and higher in salinity, nutrients and P_{CO_2} . This explains the shoaling of isolines shoreward, as was observed in the vertical sections. Mooers (1970) has observed downwarping of isopycnals beneath the inshore edge of the seasonal pycnocline. This event was related to the decay phase of coastal upwelling. If the winds shifted to a southerly direction (as occurred after March 20), upwelling would cease and surface waters would be driven onshore. This one-sided convergence of water resulted in a coastal phenomenon (i.e., downwelling) where inshore waters pile up at the coast and downwarping of isopycnals occurred (Wooster and Reid, 1963). The doming could therefore be explained by a reversal of wind velocities. In the middle of March upwelling was initiated and isolines began to rise shoreward. When the winds reversed later in the month, downwelling caused a downwarping of these isolines at their inshore extremes.

The response time (defined here as the time lag occurring between the initial perturbation of the system, i.e., a change in wind direction, and the subsequent modification of the frontal layer, i.e., the pycnocline) of these waters has been estimated by various authors. O'Brien and Hurlburt (1972), Hurlburt and Thompson (1972), and

Atlas (1973) observed modifications of the frontal layer due to variations in the wind on a time scale of a few days.

These estimates were for positive perturbations (i.e., response times leading to observable upwelling conditions). Response times for negative perturbations (i.e., those leading to a decay in upwelling) are probably of similar magnitude. A maximum response time of eight days was observed for the decay conditions (i.e., doming) that existed on March 28 (the winds changed direction March 21, see Figure 3).

An unusually large drop in surface P_{CO_2} occurred between NH-25 and NH-35. Values shoreward of NH-25 were apparently in equilibration with the observed atmospheric P_{CO_2} value of 320 ppm. However, surface values seaward of NH-25 were consistently 15 to 25 ppm below this atmospheric value. Table 4 divides the offshore

Table 4. Comparison of predicted ΔP_{CO_2} (due to temperature changes) and observed ΔP_{CO_2} values in surface waters along the Newport hydrographic line, March, 1971.

<u>Zone</u>	<u>Representa- tive T° C</u>	<u>Representa- tive P_{CO_2}</u>	<u>Obs. ΔT</u>	<u>Predicted* ΔP_{CO_2}</u>	<u>Obs. ΔP_{CO_2}</u>
NH-5 to NH-25	8.50	320 ppm			
			0.15	1.8	16
NH-25 to NH-45	8.35	304 ppm			
			0.25	3.3	14
NH-45 to NH-65	8.10	290 ppm			

* Using $dP_{CO_2}/dT = 13 \text{ ppm}/^\circ\text{C}$; at constant T, S, CA, and ΣCO_2 (Gordon, 1973).

area into three zones, each with a representative temperature and P_{CO_2} value. The observed changes in P_{CO_2} are larger than those predicted solely by temperature changes in the surface waters (changes due to the salinity gradient are small and therefore disregarded). A change in barometric pressure will result in a proportional change in atmospheric P_{CO_2} (if the concentration of CO_2 remains constant). A 978-mb area of low pressure (Schwerdt, 1971) was reported off the Oregon coast during the aforementioned storm, whereas during the March cruise (March 28-31) the pressure varied slightly around a high of 1025 mb. Therefore the predicted atmospheric P_{CO_2} during the storm would be $(978/1025) \times 320 \text{ ppm} = 305 \text{ ppm}$. As indicated in Figure 6, sea surface P_{CO_2} values west of NH-35 varied slightly around such a value of 305 ppm.

Apparently the surface waters had equilibrated during the storm with an atmosphere where the P_{CO_2} was approximately 305 ppm. After the storm, the barometric pressure rose and the atmospheric P_{CO_2} returned to the expected value of 320 ppm (Bolin and Keeling (1963) discuss average atmospheric P_{CO_2} values). The surface waters did not re-equilibrate with the atmosphere, as evidenced by the P_{CO_2} values of surface waters west of NH-35. The higher surface P_{CO_2} values found inshore (which appeared to be in equilibrium with the atmosphere) most likely resulted from diffusion of CO_2 from the doming region of high P_{CO_2} (Figure 5a) into the inshore surface

waters.

Gordon et al. (1971) observed the influence of patchy phytoplankton activity on the PCO_2 distribution in the Subarctic Pacific Ocean. Decreasing PCO_2 values, even in the early spring (i. e., March and April), were related to biological activity. Low PCO_2 values (minimum of 288.4 ppm at 10 meters depth) and high oxygen saturations (up to 102 percent) in the nearsurface waters around NH-65 indicated that a local phytoplankton bloom had altered the chemistry of these waters. Photosynthesis would also deplete nutrient concentrations in the region. The lowest concentrations of all three nutrients (Figures 8b, 9a, 9b) were observed in these waters around NH-65 and therefore corroborated this hypothesis of an early season phytoplankton bloom.

IV. OCEANOGRAPHIC CONDITIONS AND CHEMICAL VARIABLES ALONG THE NEWPORT HYDROGRAPHIC LINE FOR JUNE, 1971

A. Previous Studies off the Oregon Coast During Spring

As mentioned in Chapter IIIC, a change in winds from southerlies to northerlies usually occurs in the spring. These winds initiate upwelling; the extent is dependent upon the duration and velocity of the northerly winds. Upwelling is set up in about one week (Mooers et al., 1972). The permanent pycnocline (approximated by the 25.5 sigma-t surface) intersects the surface forming a near-stationary, inclined frontal layer off the coast. Examples of such occurrences are given by Mooers (1970).

Park et al. (1962) used hydrogen ion, dissolved oxygen and inorganic phosphate concentrations as indicators of coastal upwelling. Vertical sections along the Newport hydrographic line (for August, 1961) present a pattern of shoreward rising isolines which break the surface in a band extending from just offshore to approximately 40 kilometers offshore.

A time series study over a several day period (in June, 1970) along the Depoe Bay hydrographic line indicated a clear trend of steepening P_{CO_2} isolines as upwelling intensified over the time interval (Gordon, 1972). The approximate position of the inclined frontal layer could be located by observing where the largest surface

gradient in P_{CO_2} occurred. On June 17, 1970, surface P_{CO_2} data indicated that the front was located between NH-3 ($P_{CO_2} = 336.4$ ppm) and NH-5 ($P_{CO_2} = 199.3$ ppm). On June 21, the front could be located between NH-5 ($P_{CO_2} = 581.5$ ppm) and NH-7 ($P_{CO_2} = 262.8$ ppm). Inshore surface P_{CO_2} values (ranging from 336.4 to 847.1 ppm) indicated the influence of upwelling in these waters. P_{CO_2} measurements (values ranging from 182.0 to 338.1 ppm) seaward of the frontal layer were mostly less than air P_{CO_2} values (average value = 316.5 ± 1.5 ppm for 13 measurements).

The northerly winds also drive the Columbia River plume in a southwesterly direction away from the river's mouth (i. e., Astoria, Oregon). Cissell (1969) has used several parameters (e. g., salinity, temperature, dissolved oxygen and nutrients) as tracers to determine the location of the plume off the Oregon coast. He concluded that the major flow could be located by observing the surface temperature maximum and salinity minimum. In July, 1967, the plume's axis intersected the Newport hydrographic line approximately 230 kilometers offshore (Cissell, 1969). Ball (1970) observed a salinity minimum ($< 30\text{‰}$) approximately 160 kilometers offshore in July 1968.

Pytkowicz (1964) observed a near surface oxygen maximum off the Oregon coast during the summer. This is a well-discussed and often observed phenomenon (Cissell, 1969; Ball, 1970; Stefánsson and Richards, 1964). Pytkowicz attributed the maximum to a loss of

oxygen from the waters above the seasonal thermocline to the atmosphere. Stefánsson and Richards (1964) contended that the offshore sinking of recently upwelled water which has been enriched in oxygen by photosynthesis is the chief contributor to the maximum.

The importance of biological activity (i. e., photosynthesis) and the resultant impact on the nutrient and oxygen concentrations is discussed by Redfield et al. (1963), Stefánsson and Richards (1964), and Park (1967).

B. Results

The main purpose of this cruise was to do a chemical survey of the Newport hydrographic line during the late spring upwelling season. The ship departed Portland, Oregon on June 12 and a chemical survey of the Willamette and Columbia Rivers was made enroute to the ocean.

The meteorological events preceding and occurring during this cruise (June 12-16) were influencing factors on the oceanographic conditions. Figure 10 presents the average daily wind components for a 19-day period preceding and including the June cruise. For the entire period May 29 to June 16 the east-west component was directed onshore. For the period May 29 to June 4 the north-south component was directed to the south. The winds had a component directed to the north for a total of seven days during the period June 5-13.

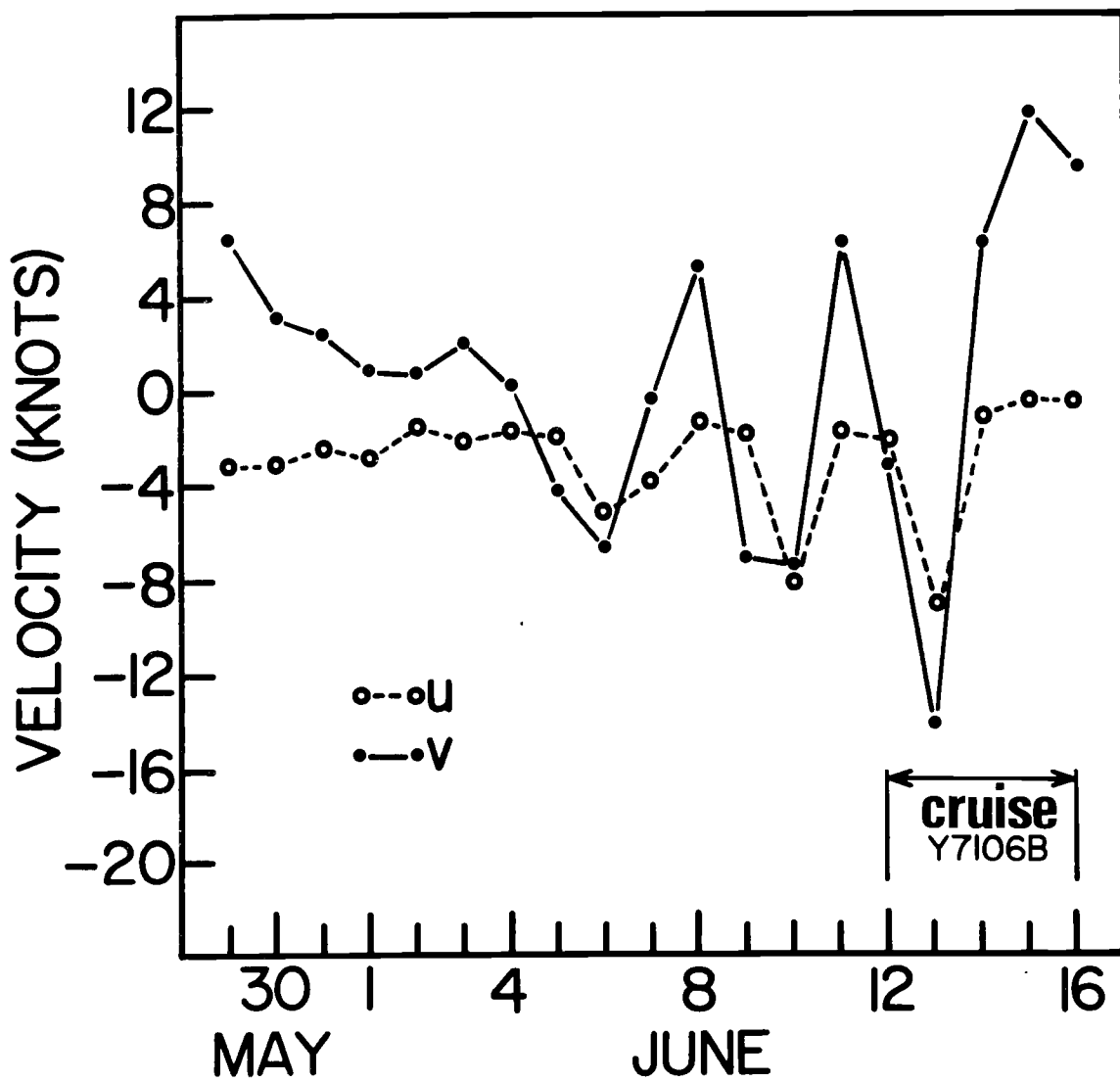


Figure 10. Daily component wind averages, May and June 1971.
 (See Figure 3 for explanation of u and v)

The distribution of various physical and chemical parameters along the Newport hydrographic line are presented in Figures 11-16.

Temperature

The shoreward inclination of the 8°, 9° and 10°C isotherms (Figure 11a) are typical of an upwelling environment. However, these isotherms level out and run approximately horizontal shoreward of NH-15. The warmest water is found at the surface in a band ranging from around NH-35 to NH-65.

Salinity

Nearly horizontal isohalines (Figure 11b) predominate in the upper 20 meters. Shoreward inclination is illustrated only by those isolines in waters deeper than 20 meters between NH-5 and NH-25. A pool of relatively low (< 32‰) salinity water is observed ranging from shore to NH-65 with the minimum (27.22‰) at NH-35.

P_{CO₂}

The vertical distribution of P_{CO₂} (Figure 12a) is analogous to the oxygen distribution (Figure 14a). The sloping P_{CO₂} isolines (e.g., the 400, 500, . . . , 1000 ppm surfaces) coincide with the permanent pycnocline. None of these isolines intersect the sea surface. The inshore regime (shoreward of NH-5) is predominated by low (< 200

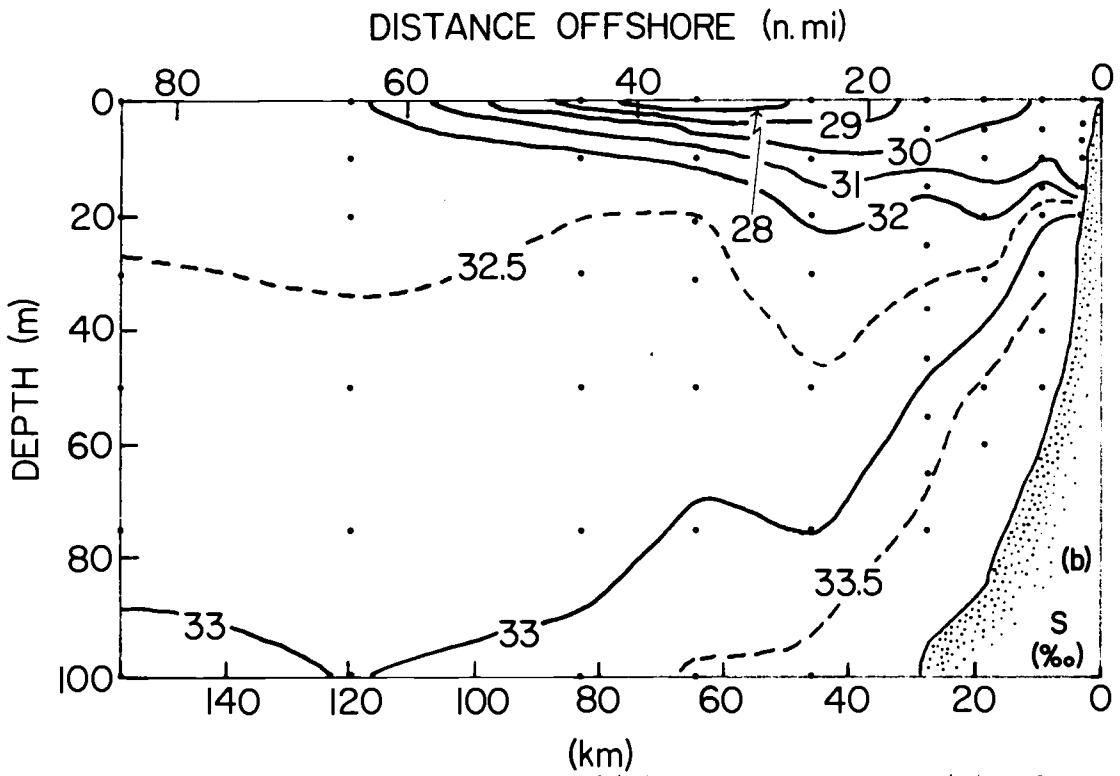
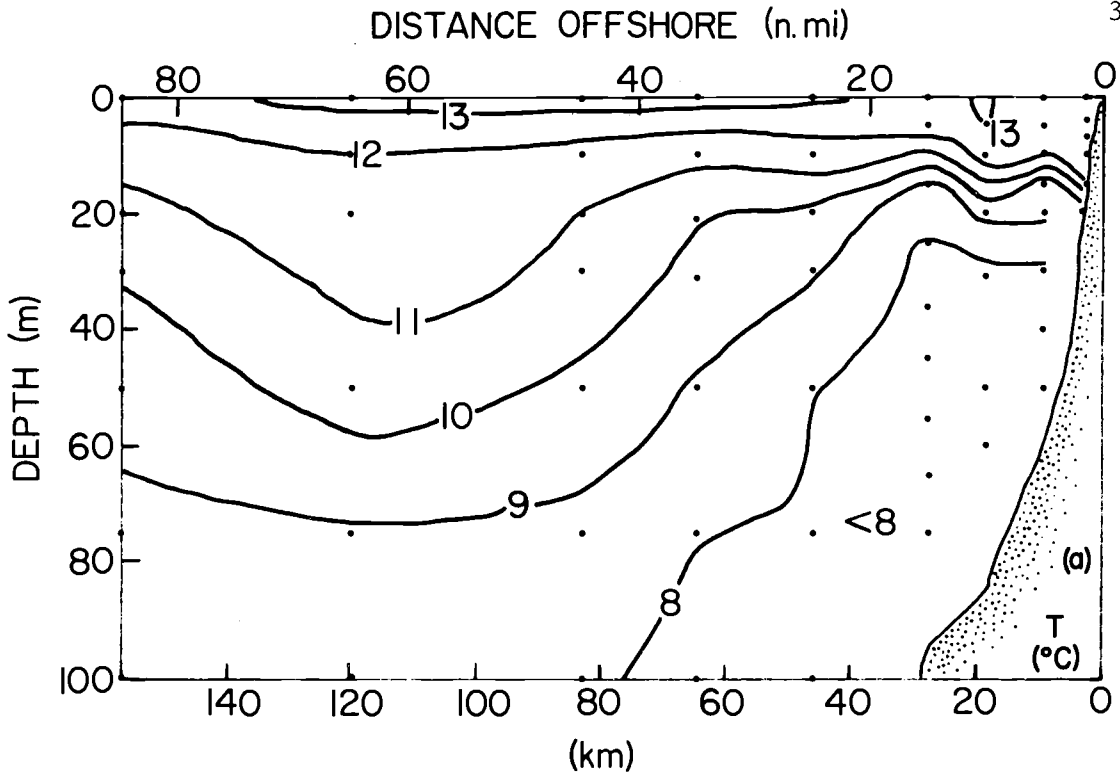


Figure 11. Vertical distribution of (a) temperature and (b) salinity along the Newport hydrographic line, June 1971.

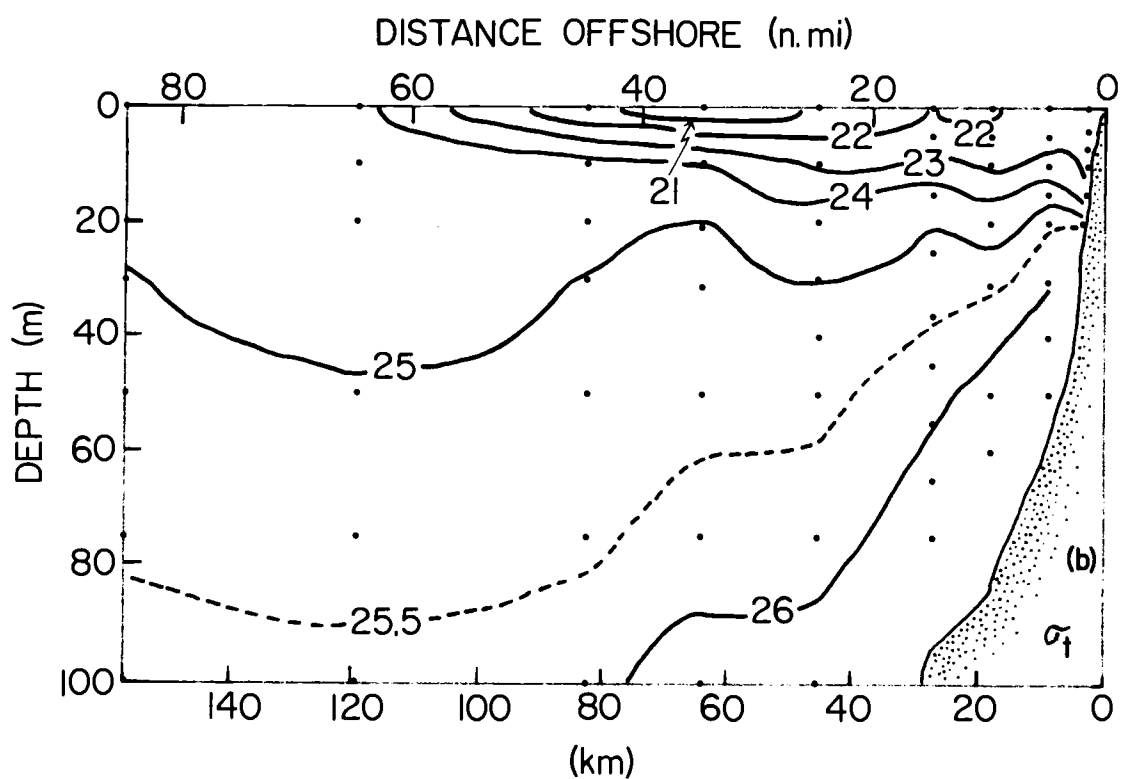
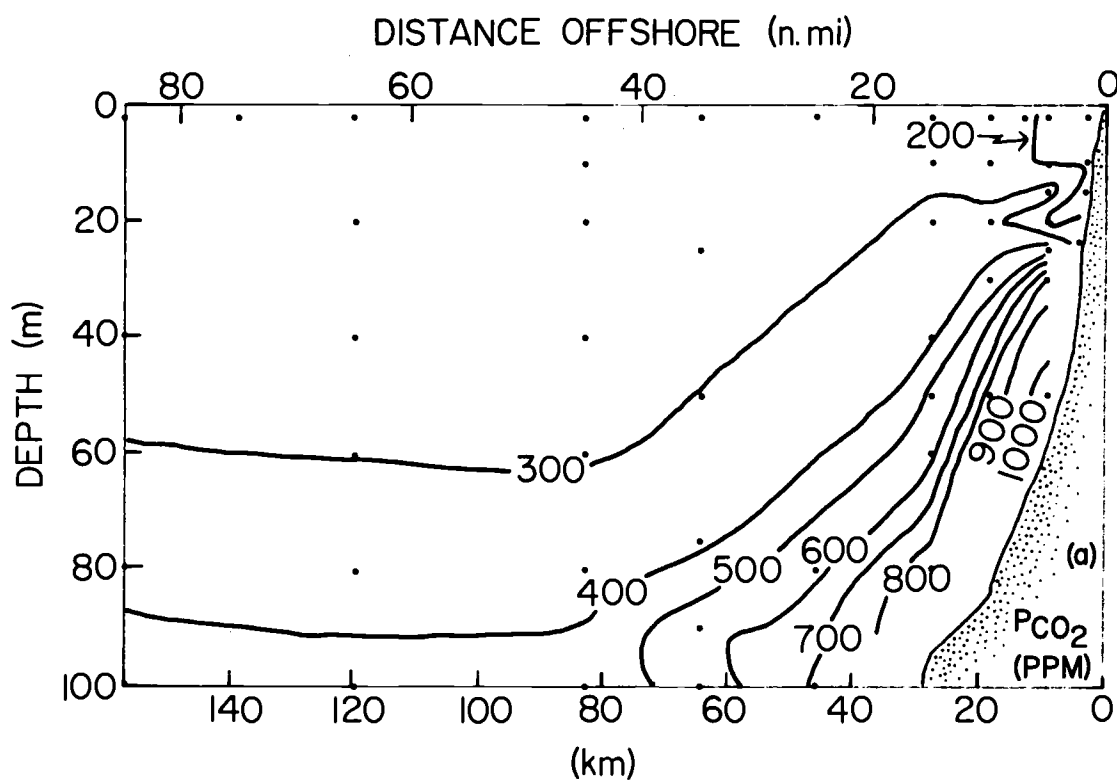


Figure 12. Vertical distribution of (a) PCO_2 and (b) σ_t along the Newport hydrographic line, June 1971.

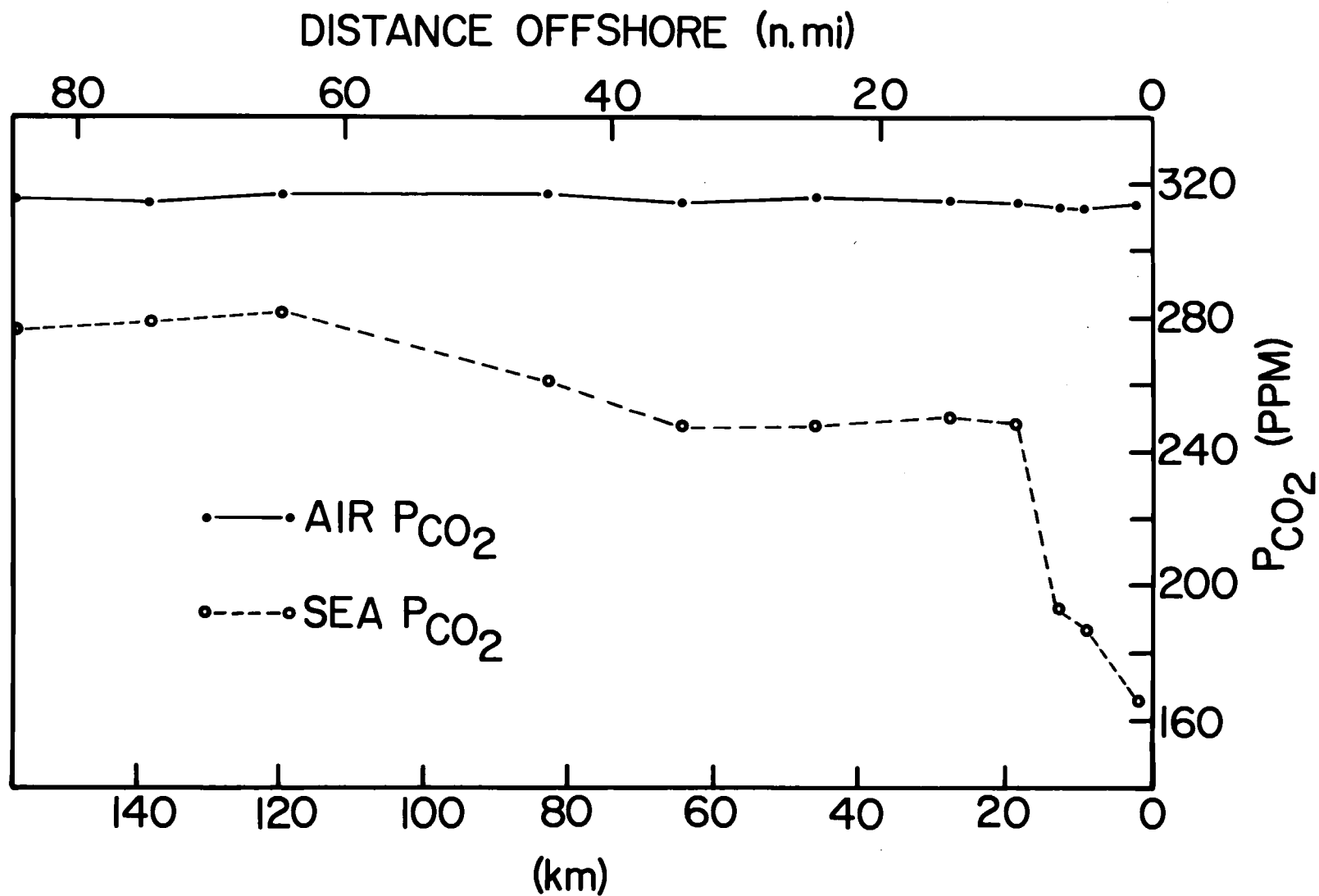


Figure 13. Air-sea surface P_{CO_2} gradient along the Newport hydrographic line, June 1971.

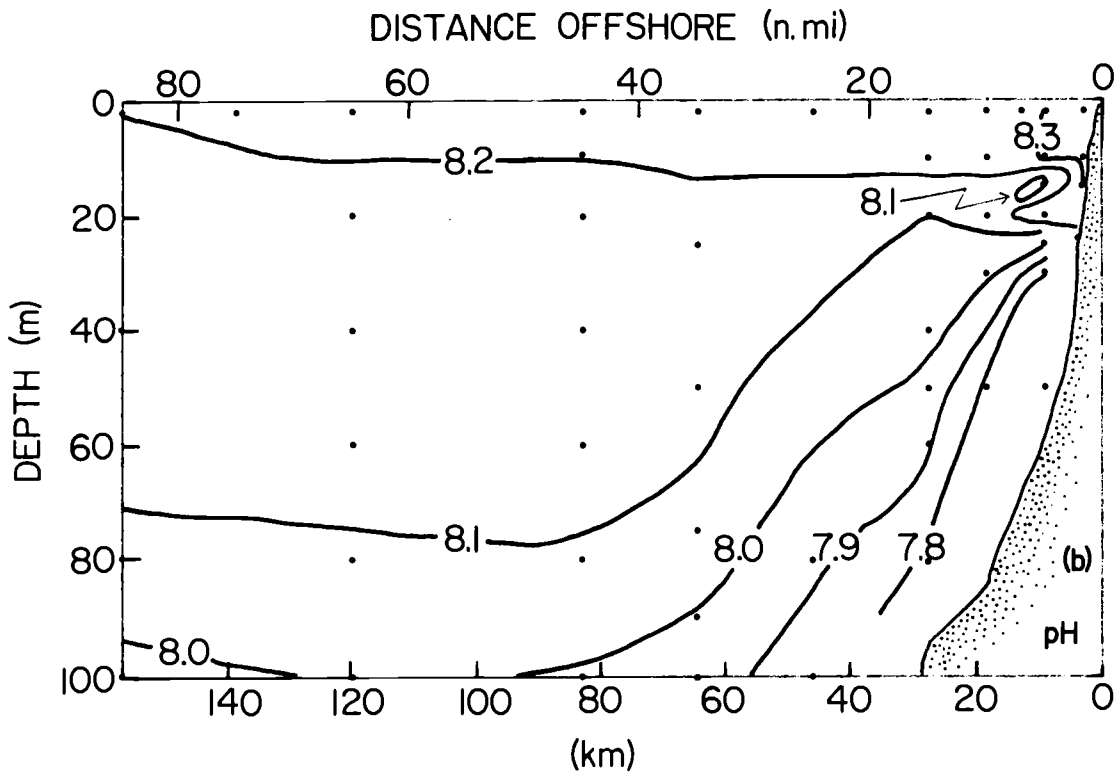
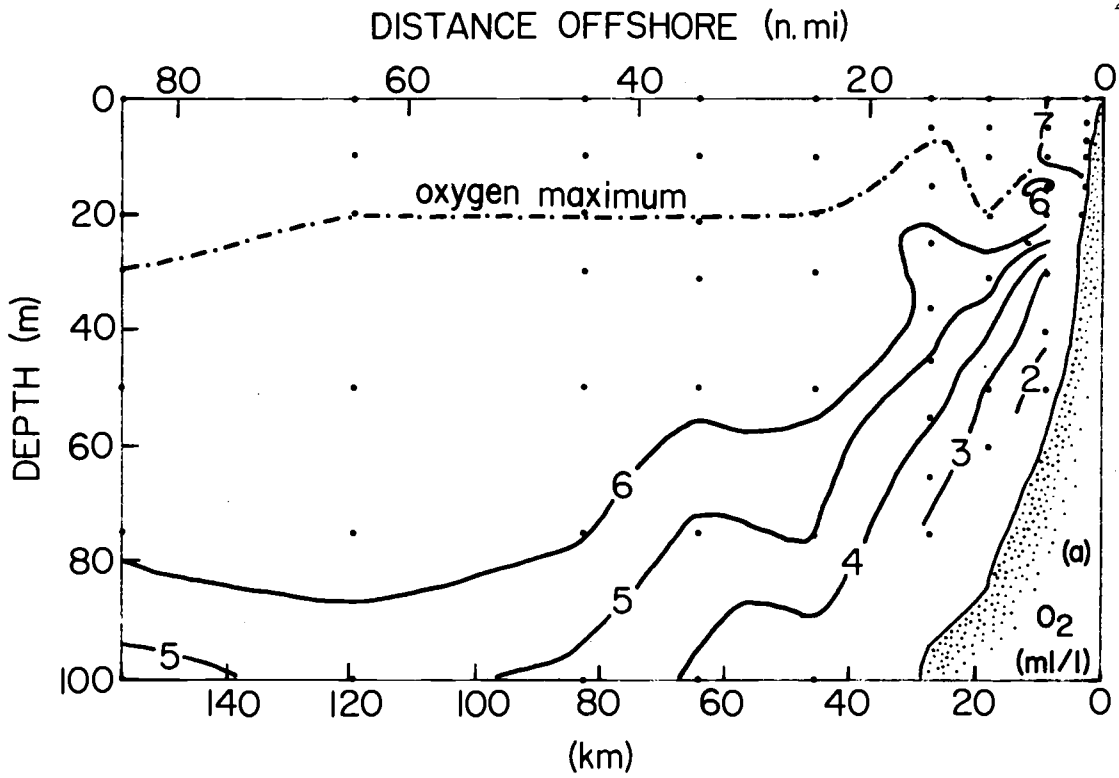


Figure 14. Vertical distribution of (a) oxygen and (b) pH along the Newport hydrographic line, June 1971.

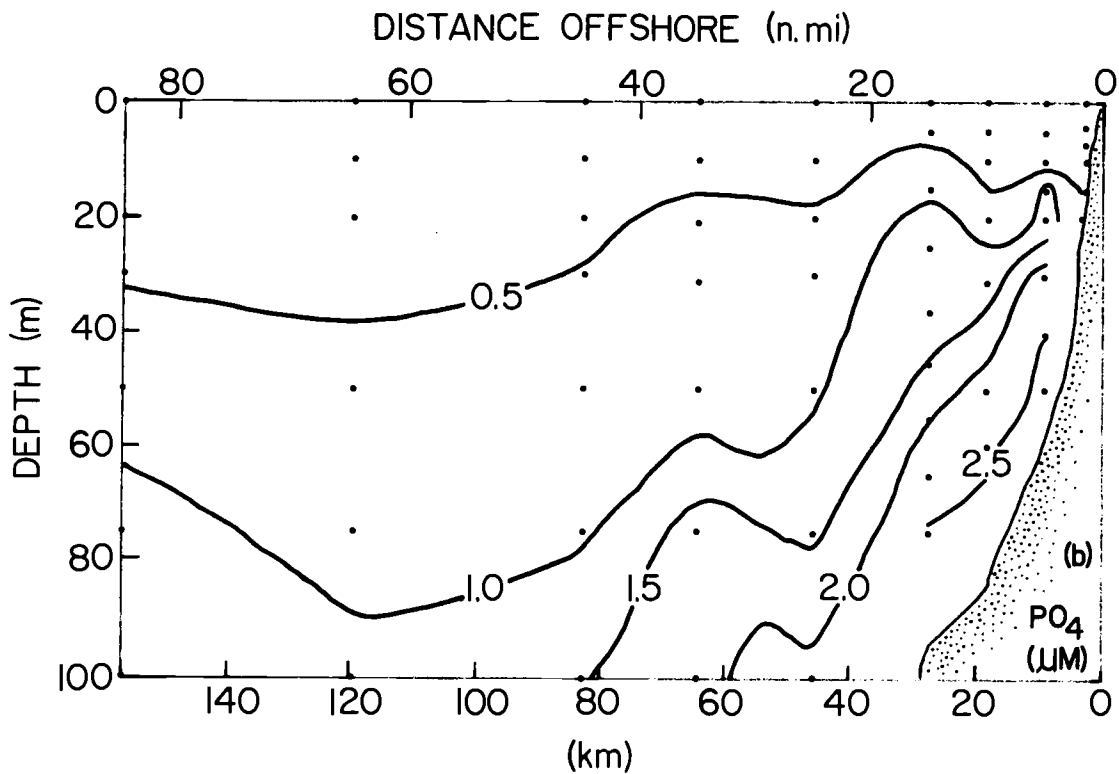
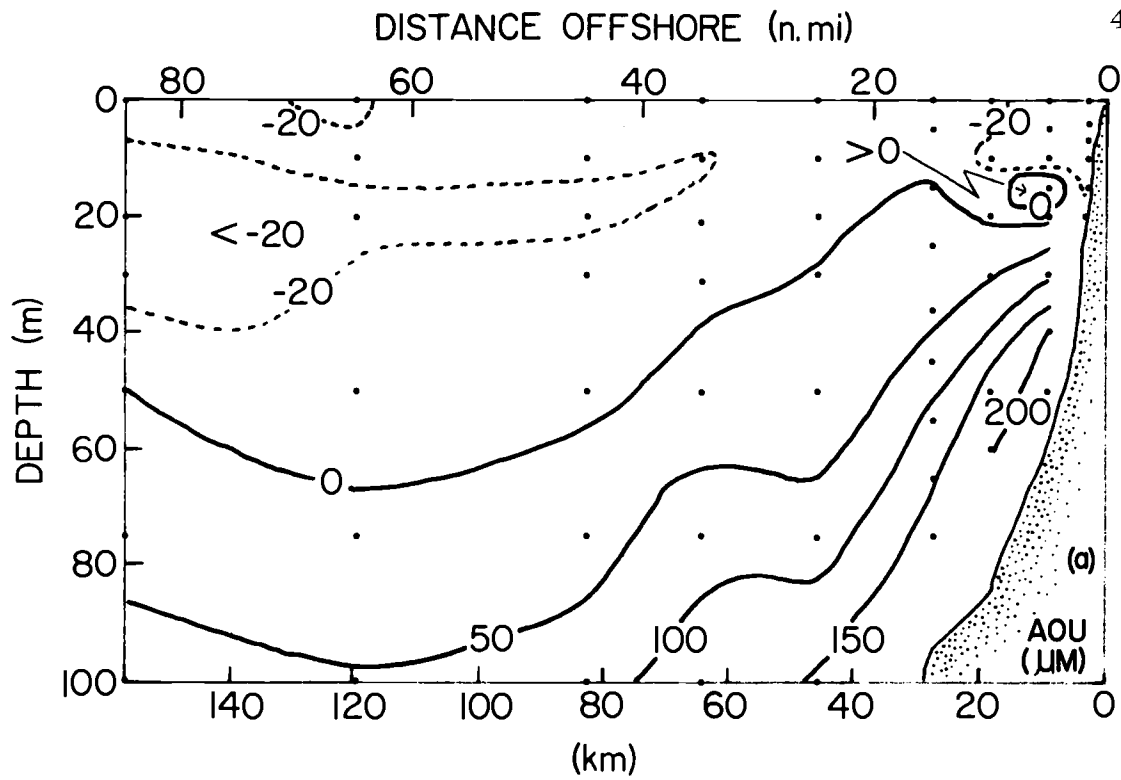


Figure 15. Vertical distribution of (a) AOU and (b) phosphate along the Newport hydrographic line, June 1971.

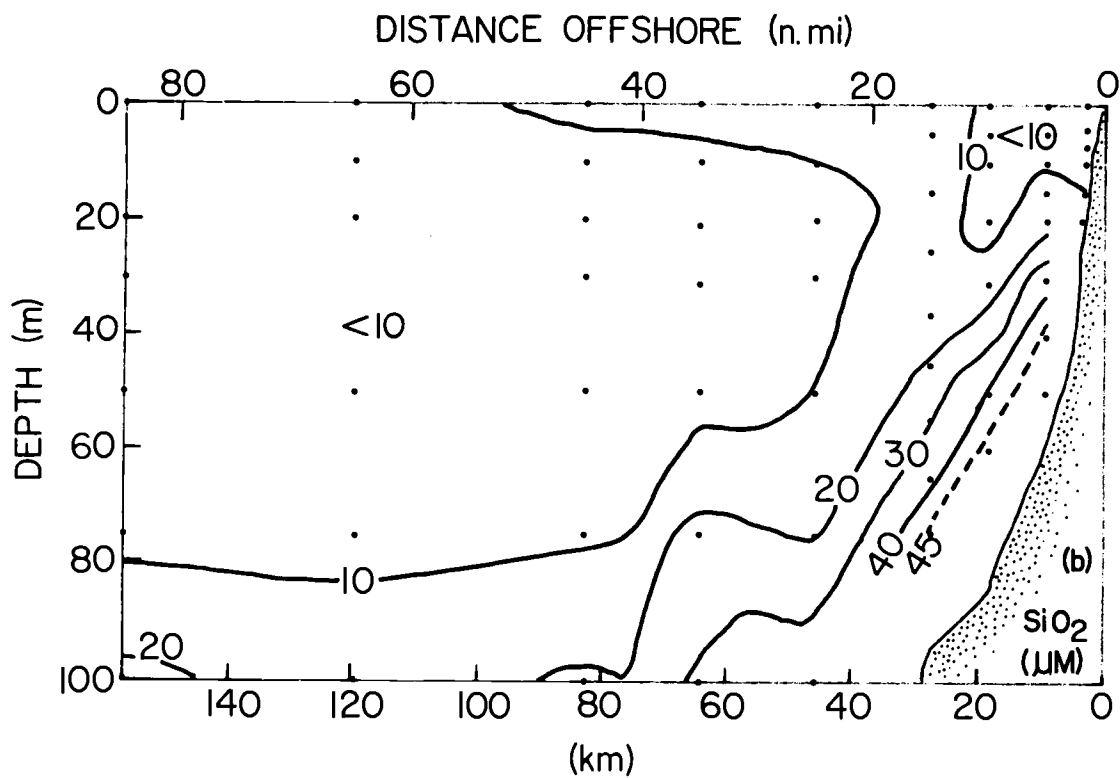
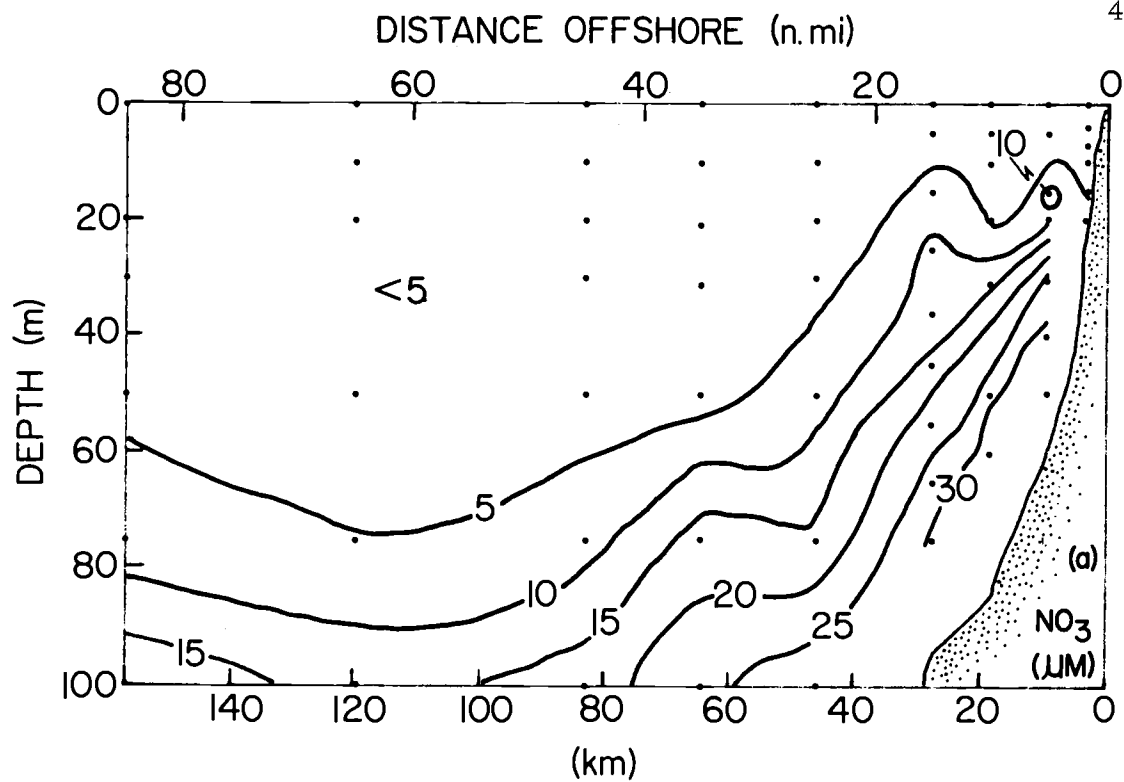


Figure 16. Vertical distribution of (a) nitrate and (b) silicate along the Newport hydrographic line, June 1971.

ppm) P_{CO_2} values. An isolated area of high (> 300 ppm) P_{CO_2} is centered at NH-5 at 15 meters depth. The sea surface is undersaturated with P_{CO_2} compared to the atmosphere (Figure 13). The degree of undersaturation increases as one moves shoreward from NH-65, with the most dramatic increase occurring between NH-5 and NH-1. The mean air P_{CO_2} value for 11 measurements was 315.0 ± 1.5 ppm.

Sigma-t

The same trends that occurred in the salinity section are also observed here. The inclination of the permanent pycnocline (i.e., 26 sigma-t surface) and the nearly horizontal seasonal pycnocline (i.e., 25 sigma-t surface) are the main features in this distribution (Figure 12b). Note the downwarping of the 23 and 24 sigma-t surfaces near the coast which results in a large density gradient in these waters.

Oxygen

A near surface oxygen maximum is indicated by dashed lines in Figure 14a. The maximum rises toward the surface as it approaches shore. After rising to less than 10 meters depth at NH-15, it sinks to 20 meters at NH-10 and again rises to approximately 10 meters at NH-5. The inclination of the isolines in the region of the permanent pycnocline is again a prominent feature. A localized oxygen minimum

is observed at 15 meters depth at NH-5.

pH

The pH section (Figure 14b) is characterized by the same features that were observed in the PCO_2 distribution. The sloping pH isolines (e.g., 7.8, 7.9, 8.0, 8.1) coincide with the inclined pycnocline. The highest pH values (>8.3) are found inshore. The anomalous area at NH-5 at 15 meters depth is again observed; here by relatively low (<8.1) pH values.

AOU

The AOU section (Figure 15a) indicates various areas of supersaturated water. The most highly saturated area (with AOU values ranging from -14 to $-48 \mu\text{M}$) lies inshore near the coast. A small pool centered near NH-65 has a minimal AOU value of $-22 \mu\text{M}$ and a tongue of supersaturated water intrudes the offshore area at approximately 20 meters. An isolated area centered at NH-5 at 15 meters depth has anomalously high ($29 \mu\text{M}$) AOU values.

Nutrients

All three nutrients (Figures 15b, 16a, 16b) present essentially the same features. The sloping isolines are prominent. The lowest silicate concentrations ($<10 \mu\text{M}$) are observed inshore; likewise for

nitrate ($< 0.5 \mu\text{M}$) and phosphate ($< 0.3 \mu\text{M}$) All nutrients show anomalously high concentrations around NH-5 at 15 meters depth. An area of relative high (10 to 20 μM) concentration silicate is observed in the surface waters ranging from approximately NH-10 to NH-50.

C. Discussion and Conclusions

Apparently upwelling had been initiated in late May when northerly winds were prevalent. The north-south wind component started to vary around June 4 and led to the decay of upwelling conditions that were observed on the June cruise.

Northerly winds would drive the Columbia River plume south, while the onshore wind component would drive the plume shoreward. Any coastal runoff would also be held inshore by these persistent onshore winds. The salinity minimum ($< 28\text{‰}$) observed near NH-35 must have arisen from these conditions. The surface temperature maximum (13.39°C) and surface silicate maximum ($20 \mu\text{M}$) located at NH-35 are also indicative of Columbia River plume water (Cissell, 1969).

The remnants of upwelling can be seen in the inshore waters. Higher salinities ($> 30\text{‰}$) and lower temperature ($< 12.7^\circ\text{C}$) could result in part from mixing of cold, salty upwelled water with the warmer, fresher surface seawater. These inshore waters have undergone in-situ warming at the surface, so temperatures predicted by

simple two-point mixing would not be observed (Figure 17).

Low PCO_2 values (< 200 ppm), negative AOU values (< -20 μM) and low nitrate and phosphate concentrations (< 0.03 μM) in the inshore waters are indicative of extensive primary production, or a "bloom." This bloom could have originated when upwelling was supplying high nutrient concentrations to these waters. After upwelling conditions subsided nutrients were no longer resupplied and the observed inshore conditions resulted.

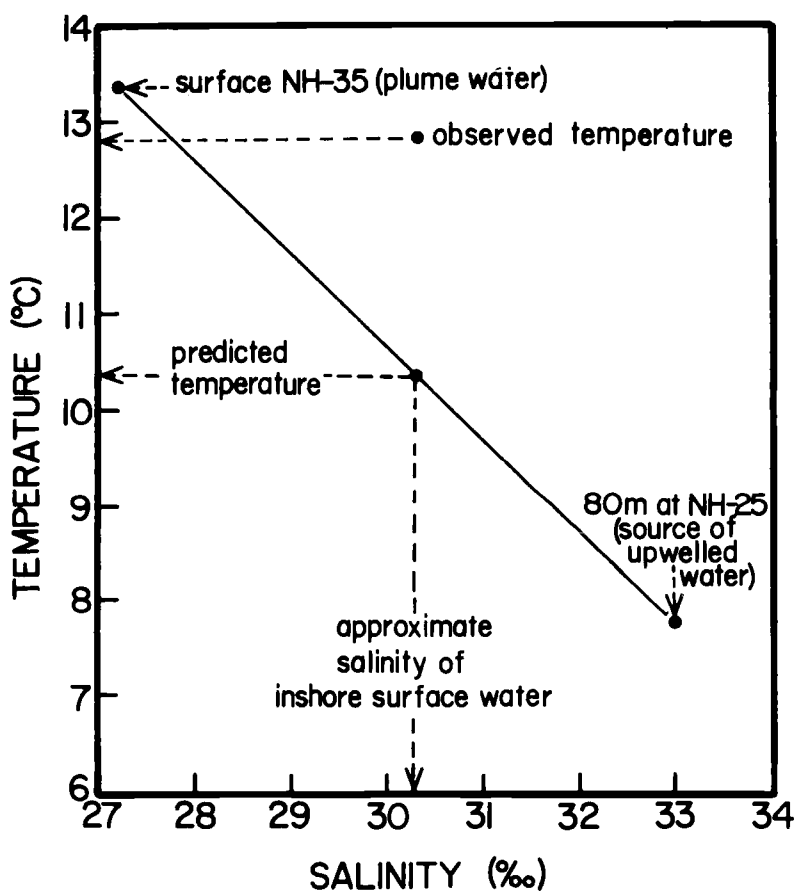


Figure 17. Mixing diagram of Columbia River plume water and upwelled water, June 1971.

An isolated pocket of water having a comparatively high AOU value is located at NH-5 at 15 meters depth. This peculiarity appeared in each vertical section as a result of one data point (i. e., sampling from 15 meters depth at NH-5). Since the feature was observed on both the P_{CO_2} cast (Figures 12a and 14b) and the hydrocast (e. g., Figures 14a, 15, 16), it is no doubt a real feature occurring at this location. However a definitive discussion of the chemistry and water movement in this area would require more closely spaced samples at the inshore stations with additional sampling at NH-3 and NH-7. Since such data is lacking, only suggestive comments, such as the following, can be made about conditions in this area:

1. The area lies in a zone of an intense density gradient, as shown in Figure 12b. Organic matter from the productive area just above sank into this region where it was entrapped due to the stability of the water column and extensive, rapid oxidation took place.
2. The intrusions of the 200 and 300 ppm P_{CO_2} isolines into regions of higher P_{CO_2} (Figure 12a) may indicate an offshore sinking of surface waters which have been modified by photosynthesis (i. e., increased oxygen concentration, decreased CO_2 and nutrient concentrations).
3. The meteorological conditions were fluctuating in such a way that the particular circumstances observed here were only transient and a time series study would have been necessary for an

understanding of the active inshore processes.

The near surface oxygen maximum would most likely result from degassing of the surface waters (Pytkowicz, 1964). The rising and falling of the maximum around NH-15 may be an exaggerated artifact resulting from the uncertainty in the exact location of the maximum at the inshore stations. However, if the oxygen-rich, inshore waters did sink as they moved offshore (Stefánsson and Richards, 1964), the maximum should also sink. The offshore movement would be along isentropic (approximately constant density) surfaces. The 23, 24 and 25 sigma-t surfaces have some rising and sinking trends that correlate with the rising and sinking of the oxygen maximum. Intrusion of low concentration nutrient water is also observed in this region (NH-5 to NH-15). Which of these two factors, degassing or offshore movement of oxygen-rich water, is the main contributor to the oxygen maximum is not known.

An area of oxygen supersaturation (approximately 108 percent) was observed in the surface waters around NH-65. Photosynthesis would lead to such an increase in oxygen saturation, but should also deplete nutrient concentrations. Nitrate and phosphate concentrations at NH-65, 0.6 and 0.4 μM respectively, were higher than at NH-35, both 0.2 μM . However the oxygen saturation (approximately 102 percent) indicated little or no photosynthetic activity at NH-35. Obviously, no correlation among photosynthesis, oxygen production

and nutrient consumption in these two regions can be made from only the data collected on this cruise. A time series study to observe the changing nutrient and oxygen concentrations at each location would have been most valuable here.

V. COMPARISON OF SPRING AND WINTER CONDITIONS IN THE WILLAMETTE AND COLUMBIA RIVERS

The June, 1971 cruise departed Portland, Oregon and various chemical parameters (Table 5) were monitored enroute to the Pacific Ocean (Figure 18).

A comparison of the data collected in June, 1971 with data collected in December, 1968 (Park et al., 1969) is presented in Table 6. These months are at opposite extremes of both the Columbia and Willamette Rivers' annual flow cycle. Barnes et al. (1972) report that, for a 15 year mean, maximum discharge for the Columbia occurred in June and near minimal discharge occurred in December. In contrast, data collected over a 33-year period (Coles, 1961) indicated that maximum discharge in the Willamette River occurred during the winter months (notably December, January and February) while minimal flow occurred in late summer (notably July, August and September).

The influence of biological activity (i. e., photosynthesis) should be maximal around June and minimal around December. Park et al. (1972) studied the effects of biological alteration in the Columbia River. They observed approximately 100 percent oxygen saturations and increased nutrient concentrations in the Astoria estuary during the winter months of 1966 and 1967. Oxygen saturations in December,

Table 5. Chemical data collected in the Columbia and Willamette Rivers, June 1971.

<u>Stn</u>	<u>T(°C)</u>	Sea <u>PCO₂</u> <u>(ppm)</u>	Air <u>PCO₂</u> <u>(ppm)</u>	<u>pH</u>	Alk <u>(meq/l)</u>	Oxy <u>(ml/l)</u>	AOU <u>(μM)</u>	Phos <u>(μM)</u>	Nit <u>(μM)</u>	Silc <u>(μM)</u>
WR1	14.67	1343.5								
WR2	14.53	1490.5	340.1	7.24	0.38	6.50	30	1.2	15.6	83*
WR3	14.67	1456.0								
WR4	13.32	420.8								
WR5	13.29	449.8								
WR6**	13.28	427.1	339.0	7.94***	0.75	8.82	-69	0.8	5.0	140
CR1	13.31	387.2								
CR2	13.32	415.2								
CR3	13.38	452.6	315.3	7.96	0.78	8.94	-74	0.8	5.1	139
CR4	13.32	485.1								
CR5	13.43	520.0	310.6	7.79***		8.73	-66	0.8	5.7	128
CR6	13.50	552.4								
CR7	13.26	537.1		7.90	1.04	8.69	-61	0.9	5.4	132
CR8	13.07	568.7	315.0	7.88	0.86	8.53	-53	0.8	5.1	132
CR9	13.58	643.2	314.5	7.81	0.70	8.09	-37	0.8	6.0	
CR10	13.86	500.1	315.5	7.94	0.95	7.80	-30	1.8	5.8	145

* from 10 m depth

** confluence of Willamette and Columbia Rivers

*** value from discrete, not equilibrator, sample

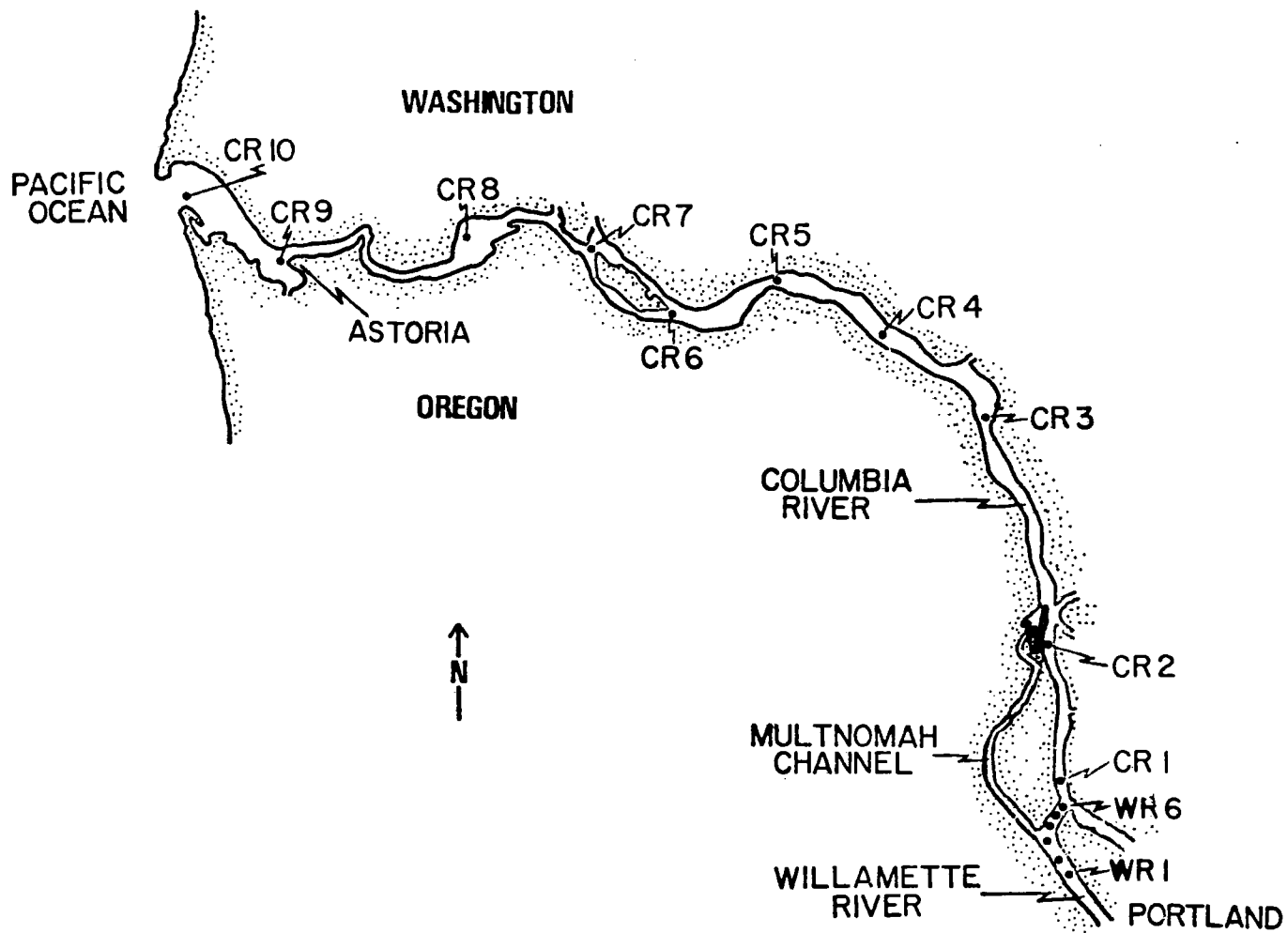


Figure 18. Station locations in the Willamette and Columbia Rivers, June 1971.

Table 6. Comparison of winter and spring conditions in the Willamette and Columbia Rivers.

	Willamette		Columbia	
	<u>Dec. 1968*</u>	<u>June 1971[#]</u>	<u>Dec. 1968</u>	<u>June 1971</u>
PCO ₂ (ppm)	1200	1427	541 to 981	387 to 643
pH	7.12	7.24	7.54 to 7.99	7.79 to 7.96
T(°C)	7.40	14.60	7.03 to 7.65	13.07 to 13.86
Alk (meq/l)	0.38	0.38	0.70 to 1.09	0.70 to 1.04

* Dec. 1968 data from Park et al. (1969)

[#] Average of stations WR1-WR3

1968 ranged from 91 to 105 percent for various locations in the Columbia River sampled between Portland and Astoria, Oregon (Gordon, 1972). This was contrasted to the supersaturated waters (110 to 115 percent) and decreased nutrient concentrations observed by Park et al. (1972) in the summer months. They also observed a maximum nitrate/phosphate ratio of 67 in December, 1967 and a minimum ratio of 1 in June, 1966.

The conditions observed in June, 1971 corroborated the results of these earlier investigations. A sudden drop in temperature ($\Delta T = 1.35^\circ \text{C}$) and PCO₂ ($\Delta \text{PCO}_2 = 1035 \text{ ppm}$) occurred between stations WR3 (Multnomah Channel) and WR4 (~ 1.5 kilometers farther down-river). Even though WR4 is ~ 3.5 kilometers upstream from the rivers' confluence, the water has the prominent characteristics of

the Columbia River. These conditions contrast those observed by Park et al. (1969) in December, 1968. They observed high (>1000 ppm) P_{CO_2} and low (7.1) pH values for all sampled locations in the Willamette River, including the confluence. Coupling of a high Columbia discharge with a low Willamette flow, as occurred in June, resulted in the intrusion of Columbia River water approximately 3.5 kilometers upstream from the confluence into the Willamette River. In December, opposite flow patterns occurred and the Columbia River had no influence on water in the Willamette River.

P_{CO_2} values in the Columbia River were approximately 150 to 250 ppm lower in June than in December even though the river was approximately $6^\circ C$ warmer in June. Oxygen saturations ran as high as 120 percent. The nitrate/phosphate ratio was 7, which is not as low as the June, 1966 value, but is considerably less than the normal marine assimilation ratio of 16 (Richards, 1965). These conditions illustrate the biological impact on the river during the late spring season.

The Willamette River did not show the influence of biological production. The winter (December, 1968) P_{CO_2} value (at $7.4^\circ C$) was 1200 ppm and the oxygen saturation was 105 percent. If these waters warmed to $14.6^\circ C$ (i. e., June temperature), the ΔP_{CO_2} would be approximately 300 ppm ($dP_{CO_2}/dT = 45$ ppm/ $^\circ C$ at constant T, S, CA and ΣCO_2 with $P_{CO_2} = 1200$ ppm; Gordon, 1973) The June P_{CO_2}

value of 1427 ppm could be explained by the warming of waters between winter and spring. An oxygen saturation of only 90 percent (AOU = 30 μM) also indicated that primary biological production was not in dominant control of the river chemistry. The outfall of waste discharge into the river controls the water quality (more than two-thirds of all Oregon residents live within the drainage area of the Willamette Basin). The oxidation of organic waste will deplete the dissolved oxygen in the water while increasing the concentration of both molecular CO_2 and nutrients. The effects of organic oxidation are especially prevalent in the summer months when low river flow rates are inadequate to handle large waste load discharges. Gleeson (1972) has written an excellent review of the once extensive pollution occurring along the Willamette River and recent measures to solve this problem.

Atmospheric P_{CO_2} values varied from a high of 343.5 ppm at the St. John's Bridge (station WR1) in Portland to approximate values of 315.0 ppm at the Columbia River estuary (stations CR9 and CR10) near Astoria, Oregon. The CO_2 pressure measured in both rivers was considerably above that of the atmosphere. The Willamette River was oversaturated by approximately 1100 ppm (Sea P_{CO_2} - Air P_{CO_2}) while the Columbia River was approximately 175 ppm oversaturated. The higher degree of oversaturation in the Willamette River is most likely related to the higher population density, and resultant organic pollution, that exists in the Willamette River basin as compared with

the Columbia River basin.

Figure 19 presents the relationship between observed and calculated PCO_2 values for selected points (i.e., those where sufficient data was available to do the calculation) in the Columbia River.

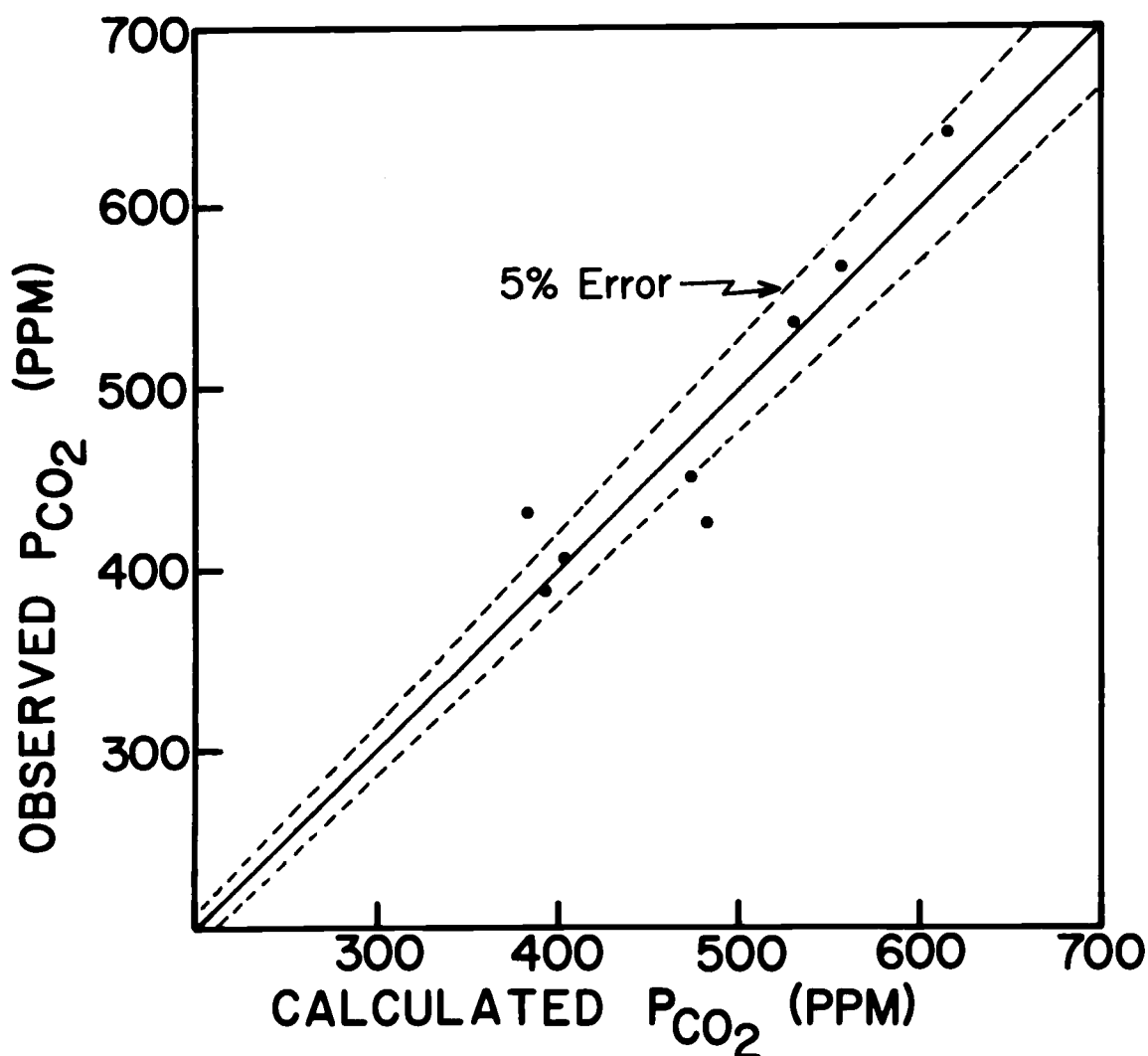


Figure 19. Observed PCO_2 vs. calculated PCO_2 in the Columbia River, June 1971. Dashed lines indicate relative discrepancy $[(\text{observed}-\text{calculated})/\text{observed}]$ limits of ± 5 percent. (Alkalinities range from 0.70 to 0.77 meq/l; see text.)

The calculated P_{CO_2} values were derived from Equation 2 (Skirrow, 1965),

$$P_{CO_2} = CA \cdot \frac{a_H}{K_1' \cdot \alpha_s \cdot [1 + 2K_2'/a_H]} \quad (2)$$

where CA is the carbonate alkalinity, a_H is the hydrogen ion activity as measured by a pH meter, α_s is the solubility coefficient of carbon dioxide, and K_1' and K_2' are respectively Lyman's (1956) first and second dissociation constants of carbonic acid. This equation is derived from Henry's law ($C_{CO_2} = P_{CO_2} \cdot \alpha_s$) and the equations for the first and second dissociations of carbonic acid.

The total alkalinity of the Columbia River varied from 0.70 to 1.04 meq/l. No systematic trend could be observed in the alkalinity changes as stations progressed downriver (e.g., see Table 5). Possible point sources (e.g., industries, river barges or towns) could have been adding effluent containing hydroxide, ammonia or organic bases that resulted in a localized alkalinity increase. The computer program used to solve Equation 2 assumes that carbonate alkalinity equals total alkalinity at zero salinity. If the total alkalinity is in fact higher than the carbonate alkalinity, P_{CO_2} values as calculated by Equation 2 will be higher than the observed values. For this reason suspiciously high alkalinity values were replaced by a value of 0.74 meq/l (average of three lowest values) to do the P_{CO_2} calculations.

When the alkalinity correction is made, the relative discrepancy $[(\text{observed } P_{\text{CO}_2} - \text{calculated } P_{\text{CO}_2})/\text{observed } P_{\text{CO}_2}]$ between calculated and observed P_{CO_2} values is approximately within ± 5 percent. The comparison of calculated vs. observed P_{CO_2} values made for the June, 1971 study corroborates the conclusion of Park et al. (1969) that if reliable values of pH and alkalinity (or total CO_2) are available, P_{CO_2} values can be calculated with a precision of ± 5 percent. Alkalinity and pH measurements do not require the rather complex technology involved in the direct measurement of P_{CO_2} by an infrared analyzer. The monitoring of these two variables (along with temperature and salinity) is therefore a much simpler and often adequate method for obtaining P_{CO_2} values. However, no simple measurement of the atmospheric P_{CO_2} can be made using these two parameters.

VI. SUMMARY

The dominating influence of meteorological conditions was evident in both the March and June, 1971 cruises. The uniform winter conditions of an entirely well-mixed surface layer of at least 100 meters depth were not observed. Early seasonal upwelling, followed by a severe storm which led to a decay of upwelling conditions, had created an inshore situation of doming isolines. Indication of an isolated phytoplankton bloom was also observed. Such phenomena as upwelling and phytoplankton activity are normally associated with the spring and summer seasons. However, conditions such as those observed here indicate that sporadic appearances of these events may occur even in the winter months and lead to modifications in both the hydrology and chemistry of the near surface waters.

Upwelling was a prominent factor in June. Its influence was clearly shown by comparing the chemical parameters of subsurface inshore waters as observed in June vs. those observed in March. P_{CO_2} values ranging up to 1000 ppm (vs. 300 ppm in March), AOU values of approximately 200 μM (vs. 50 μM in March) and consistently higher nutrient concentrations in June epitomize the alteration of these waters by upwelling. The importance of phytoplankton activity in the modification of the various chemical parameters (e.g., P_{CO_2} values < 200 ppm, AOU values < -20 μM , phosphate and nitrate concentrations

$< 0.03 \mu\text{M}$) was observed in the surface waters just off the coast. The often observed feature of a well-defined frontal layer intersecting the sea surface, which usually accompanies periods of intense upwelling, was not observed. Winds from the southwest led to some deterioration in the coastal upwelling regime and drove the Columbia River plume unusually close to shore (a surface salinity minimum of 28‰ was observed approximately 65 kilometers offshore). The result was that waters normally influenced predominately by upwelling were now being affected by Columbia River water.

The Columbia River is influenced by seasonal biological activity. Photosynthesis results in supersaturated waters (i. e., oxygen saturations up to 120 percent) and a lowering of P_{CO_2} values (at least 250 ppm lower in spring than winter). The Willamette River (between Portland Harbor and its mouth) is heavily influenced by the varying flow rates of both the Willamette and Columbia River. In the late spring, the Columbia River flow is high and the Willamette flow is low. In June, 1971 a sharp gradient in P_{CO_2} was observed approximately 3.5 kilometers upstream in the Willamette, indicating the intrusion of Columbia River water. No such gradient was observed in the winter (December, 1968) when the rivers' flow maxima are reversed. In-situ oxidation of organic effluents led to a high oversaturation (1100 ppm) of P_{CO_2} in the Willamette River. However, an oxygen saturation in Portland Harbor of approximately 90 percent in

June, 1971 vs. nearly 0 percent in 1950 (Gleeson, 1972) indicated that pollution levels have dropped tremendously in the last 20 years.

P_{CO_2} values calculated from pH and alkalinity measurements agreed to within ± 5 percent with measured P_{CO_2} values in the Columbia River.

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APPENDICES

APPENDIX I

Calculation of ΔC_{\max}

The ΔC_{\max} value used for P_{CO_2} data reduction in this study was calculated from gas calibration runs made on April 12, 1971.

Tanks #2, #19 and #24 were compared against tank #25 (zero gas) and tank #22 (span gas). This was the same range (i.e., $C_S - C_Z$) that was used on both 1971 cruises.

If the concentrations of all calibration gases (Table 1) are well-known, a reliable value for ΔC_{\max} can be calculated by using the following equation (Gordon and Park, 1972):

$$\Delta C_{\max} = \Delta C_x / \left[1 - \left(\frac{R_x - R_m}{R_s - R_m} \right)^2 \right]$$

where ΔC_x = nonlinear correction to gas concentration (i.e.,

$$\Delta C_x = C_{\text{linear}} - C_{\text{actual}})$$

R_x = recorder reading of analyzed gas "x"

R_s = recorder reading of span gas

$R_m = (R_s + R_z)/2$; (R_z = recorder reading of zero gas)

Results of these calibrations are summarized as follows:

<u>Tank #</u>	<u>Number of Comparisons</u>	<u>ΔC_{\max}</u>
2	7	45.53
19	8	48.43
24	12	49.09

Average of these results: $\Delta C_{\max} = 47.68 \pm 3.78$ (± 2 s).

APPENDIX II

Sample Calculation and Accuracy Estimate of P_{CO_2}

A sample calculation, using data collected at NH-45 during the June, 1971 cruise is presented to show how raw data is used in calculating final P_{CO_2} values. An error limit is estimated for each variable and a minimum and maximum value for P_{CO_2} is calculated.

Equations are from Gordon and Park (1972).

$$SEA P_{CO_2} = C_x \left(\frac{P + \Delta P_{ref}}{P + \Delta P_{eq}} \right) \left(\frac{P - P_{sv}(T) \cdot (1 - 0.000537 \cdot S)}{P} \right)$$

where $C_x = CO_2$ concentration as measured in the IRA sample cell.

Limits: See below.

P = Barometric pressure as measured by a temperature compensated aneroid barometer. Limits: 1025.4 to 1027.4 mb.

ΔP_{eq} = Difference in pressure between the atmosphere and the sample cell of the IRA when the equilibrator air is flowing through the analyzer. Measurement is by a water filled manometer connected to the outlet of the cell.

Limits: -29.1 to -29.6 mb. (Negative values indicate that the pressure in the IRA sample cell is less than the ambient atmospheric pressure.)

ΔP_{ref} = Same as ΔP_{eq} except that reference gas or atmospheric air is flowing through the IRA. Limits: 2.2 to 2.6 mb.

$P_{\text{sv}}(T)$ = Saturation vapor pressure of pure water at temperature $T(^{\circ}\text{C})$. Limits: 15.17 to 15.37 mb. (Dependent only upon equilibrator temperature. Limits: 13.2 to 13.4 $^{\circ}\text{C}$.)

S = Salinity of seawater. Limits: 28.417 to 28.427‰.

C_x is calculated from the following:

$$C_x = C_z + \frac{C_s - C_z}{R_s - R_z} (R_x - R_z) - \Delta C_{\text{max}} \left[1 - \left(\frac{R_x - R_m}{R_s - R_m} \right)^2 \right]$$

where C_z = Concentration of zero reference gas. Limits 0 to 0.2 ppm.

C_s = Concentration of span reference gas. Limits: 530.9 to 538.5 ppm. (This limit encompasses the 95 percent confidence interval derived from the standard deviation of four analyses.)

R_z = Recorder chart reading for C_z . Limits: 9 to 11.

R_s = Recorder chart reading for C_s . Limits: 886 to 888.

R_x = Recorder chart reading for C_x . Limits: 503 to 505.

$R_m = \frac{R_z + R_x}{2}$. Limits: 448 to 450.

ΔC_{max} = Maximum nonlinearity of the IRA for the particular span range being used. Limits: 43.0 to 52.4. (This limit

encompasses the 95 percent confidence interval derived from the standard deviation of three measurements, which are listed in Appendix I.)

Results: Limits for C_x : 246.2 to 262.5 ppm.

Limits for Sea P_{CO_2} : 250.0 to 266.8 ppm.

(Accepted value as calculated by computer = 258.0 ppm.)

Conclusion: Accuracy for Sea P_{CO_2} value approximated to be ± 8 ppm. Most of this uncertainty results from the wide error limits on reference gas concentrations.

The same analysis can be made for Air P_{CO_2} . Again using data from NH-45 during the June, 1971 cruise:

$$\text{Air } P_{CO_2} = C_x [P - AH] / P$$

where C_x = Same meaning and errors as described for Sea P_{CO_2} .

Limits: 312.3 to 328.8 ppm.

P = Same as described above.

AH = Absolute humidity; dependent only upon the wet and dry bulb temperatures. Limits: 11.77 to 12.01 mb.

Results: Limits for Air P_{CO_2} : 308.6 to 325.2 ppm.

(Accepted value as calculated by computer = 316.8 ppm.)

Conclusion: Accuracy for Air P_{CO_2} is also approximated to be ± 8 ppm.