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OFF OREGON

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An intensive chemical investigation, that includes the determinations of salinity, oxygen, nutrients, pH, alkalinity, and total carbon dioxide of the Columbia River plume off the Oregon coast in July 1967 shows the following unique features:

1. Along the axis of the river plume both the salinity minimum and temperature maximum occur. The location of these extrema at zero, ten, twenty meters depths differ considerably, suggesting different patterns of water flow at different depths.
2. Throughout the plume region, at salinities less than 32.5‰, the plume water is supersaturated with respect to dissolved oxygen, and a subsurface oxygen maximum exists at the depths of 30-50 meters.
3. The relationship between apparent oxygen production by marine organisms and nutrient concentrations shows biological production

of dissolved oxygen is a definite cause for the oxygen supersaturation in the plume region.

4. The plume area off Oregon is a source of oxygen transfer from the ocean into the atmosphere.

Chemical Features of the Columbia
River Plume off Oregon

by

Milton Charles Cissell

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CHEMICAL FEATURES OF THE COLUMBIA RIVER PLUME OFF OREGON

I. INTRODUCTION

The Columbia River empties into the northeastern Pacific Ocean at a latitude of $46^{\circ}26'$ north along a nearly north-south coastline. The 1967 annual discharge was 2.3×10^{14} liters (Park, Osterberg and Forster, 1969). The flow of the Columbia River varies seasonally with a maximum in early summer and a secondary maximum in January.

The Columbia River is the largest single contributor of fresh water to the coastal environment between southeastern Alaska and southern California. During the early summer when river discharge is the highest and coastal runoff is the lowest, the Columbia River may make up to 95 percent of the total fresh water added to the northeastern Pacific Ocean. In winter when river discharge is not generally maximum and coastal runoff is high, the Columbia River may contribute some 65 percent of the total fresh water input into this region (Budinger, Coachman and Barnes, 1964).

The current system off the Washington and Oregon coasts consists principally of the poorly defined California Current. This southward moving current is produced by the divergence of the West Wind Drift Current as it approaches the North American continent

at a latitude of 45° north. The divergence takes place well offshore, with the northern branch feeding the gyre in the Gulf of Alaska thus its name the Alaskan Current. The southern branch gives rise to the California Current. In winter a secondary current is observed near the coast which moves to the north. This is the Davidson Current.

Tibby (1957) and Rosenberg (1962) have analyzed the area off the Oregon and Washington coasts for water mass characterization. Rosenberg found the presence of four different water masses contributing to the overall makeup of the area.

The chemical composition of the Columbia River system has been tabulated by Livingston (1963). Livingston's table gives the major species of cations and anions. Park, Osterberg and Forster (1969) prepared the chemical budgets of the river, which consist of alkalinity, total carbon dioxide, phosphate, nitrate and silicate, for 1966 and 1967. The rivers in the Columbia River system appear to be mainly dilute calcium bicarbonate waters.

The chemical composition of the Columbia River discharge varies seasonally. Park, Osterberg and Forster (1969) show the seasonal fluctuation in certain chemical and physical parameters throughout the year 1967. The maximum in temperature occurs in late summer with a minimum in winter and spring. Maxima in the phosphate, silicate and nitrate concentrations occur in early spring and decline to a minimum level in late summer.

Prior to 1961, little was known about the chemistry of the Columbia River plume formed off Washington and Oregon. . Anderson, Barnes, Budinger, Love and McManus (1961) give a bibliographic review of the chemical literature and cruise data available prior to 1961.

Stefánsson and Richards (1963) give the first general description in the plume area on a seasonal basis. For the winter season the concentration of nutrients in the plume could be predicted from salinity-nutrient relationships when biological activity was low. Stefánsson and Richards (1963) discuss the physical and biological process important in determining the observed chemical distributions in the plume area. Park (1967) discusses the nutrient relationships and distributions plus the preformed nutrients for waters off Oregon.

The exchange rates of oxygen across the sea surface off Oregon, away from the river plume, has been determined by Pytkowicz (1964). According to him the subsurface oxygen maximum formed in summer is due to the warming of the surface layer with a loss of oxygen above the level of maximum production.

In order to discuss the difference between river water, open ocean water and upwelled water, a determination of the Columbia River plume boundary is necessary. Budinger, Coachman and Barnes (1964) use a plot of salinity versus logarithm of depth.

They find that 32.5‰ is a good approximation of the plume boundary. Park (1966a) employs specific alkalinity to determine the Columbia River plume boundary. He concludes that the plume water possesses a salinity of less than 32.5‰.

Anderson (1964) discusses the distribution of chlorophyll a and phytoplankton productivity off the Washington and Oregon coasts. Plume water, in general, contains more phytoplankton and has a higher rate of photosynthesis than ambient waters. Hobson (1966) discusses the influence of fresh water runoff on the standing crop of marine phytoplankton. Plume water possesses higher concentrations of diatoms than does the ambient water.

A major source contributing artificial radionuclides to the ocean off Oregon is the nuclear facilities at Hanford, Washington, which is located along the major stream of the Columbia River. Radioactive waste induced by the nuclear reactor operations provide convenient radioactive tracers to identify the existence of the river effluent off Oregon. Osterberg, Cutshall and Cronin (1965) use chromium-51 as a radioactive tracer of Columbia River water at sea. Undoubtedly other radioactive elements could be used for the same purpose. In addition, in the event there exists appreciable thermal pollution in the river water by the reactor operation, temperature also may become an additional water tracer in the river plume.

The purpose of this thesis is to investigate:

1. The precise chemical makeup of the river plume by multi-component studies including such parameters as pH, alkalinity, and total carbon dioxide. This will establish the chemical reference for summer 1967, which in turn will be used for future oceanic pollution studies.
2. The relationship between the 1967 river water chemical studies (Park, Osterberg and Forster, 1969) and the offshore chemical system.
3. The availability of various physical-chemical tracers for the Columbia River effluent in the ocean.
4. The in situ biological alteration of the Columbia River plume on the chemical makeup.

II. OBSERVATIONS

The physical and chemical cruise 6707A to study the Columbia River plume formed off the Washington, Oregon, and northern California coasts was conducted by the R/V YAQUINA of Oregon State University from July 5 to July 15, 1967. The cruise track and positions of the hydrographic stations are shown in Figure 1. Station numbers given on the east-west line off Newport, Oregon, refer to the distance in nautical miles from the coast. All other station numbers refer to the particular spots sampled on this cruise.

Seventy-four hydrographic casts were taken of which 52 casts were 200 meters or less while 9 casts were over 1200 meters deep.

Water samples were measured at sea for salinity, temperature, oxygen, phosphate, silicate, pH, alkalinity and total carbon dioxide. Samples were collected, frozen and analyzed for nitrate ashore. Salinity was determined by an inductive salinometer manufactured by Industria Manufacturing Engineers Pty. Ltd., Sydney, Australia (Brown and Hamon, 1961). "A Manual of Sea Water Analysis" by Strickland and Parsons (1965) was followed for oxygen, phosphate, and alkalinity determinations.

Silicate concentration was measured by an automated analysis given by Armstrong, Stearns and Strickland (1967) using the Technicon Autoanalyzer[®] (Hager, 1969). The only modification of

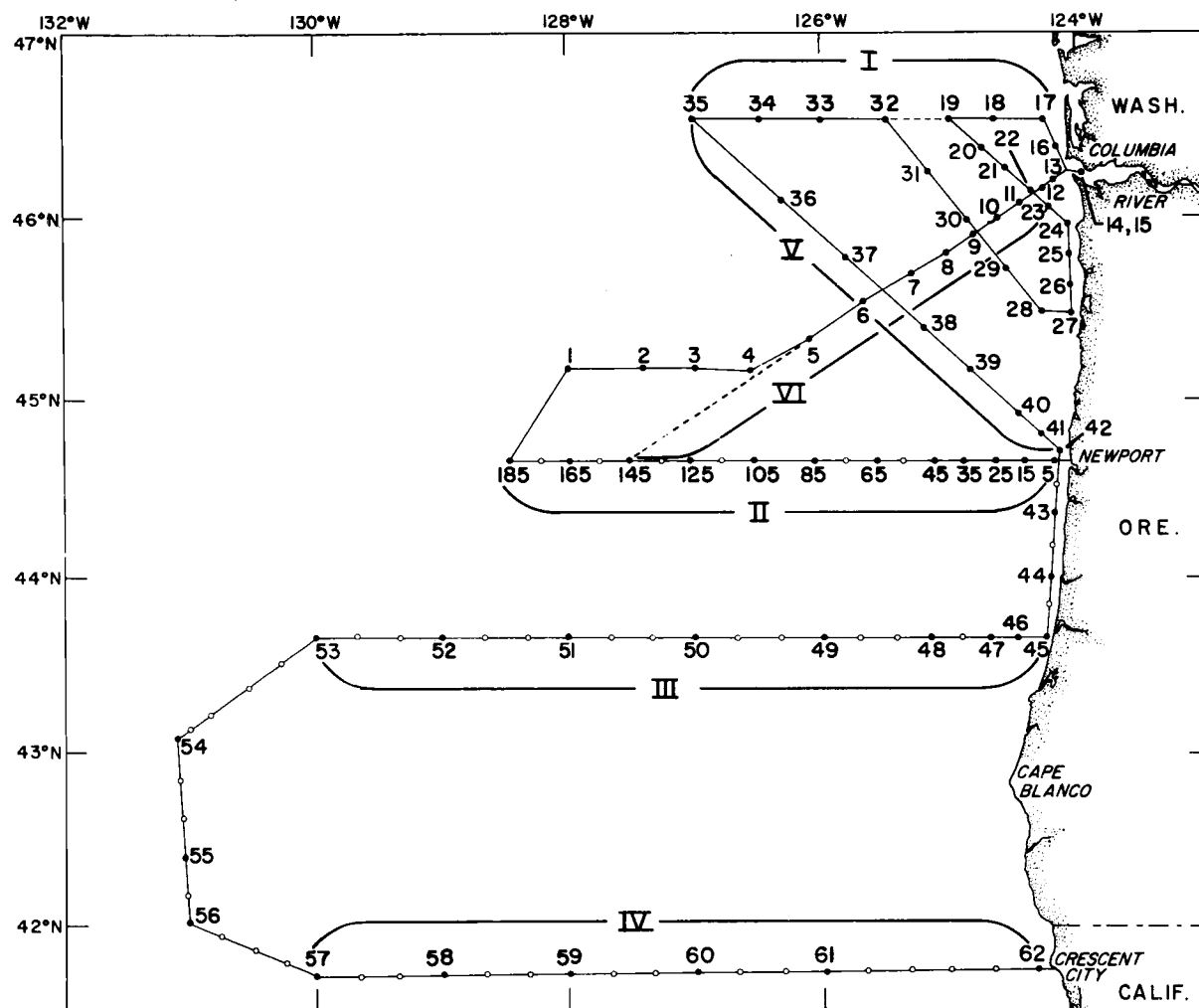


Figure 1. The cruise track and positions of the hydrographic stations of the R/V YAQUINA 6707A, July 5-15, 1967. Transects I-IV are along the east-west line. Transect V is approximately perpendicular to axis of Columbia River plume, while transect VI follows closely to the plume axis.

the procedure was the introduction of a third sampling tube (0.1 ml/min) to allow samples up to 250 μ M to be measured. Analytical precision was about $\pm 1\%$ (Hager, Gordon and Park, 1968).

pH was determined by a glass-electrode technique described by Park (1966b). A Beckman pH meter, Model 7600, expanded scale, was used to measure the pH values.

Total carbon dioxide was measured by a gas chromatographic technique (Park, 1965). Samples were usually run within several hours after collecting.

III. RESULTS

Salinity

Surface salinity pattern (Figure 2) shows the following two features. Fresh water originating from the Columbia River is found, in general, to the direction southwest from the river mouth. It is shown by the low salinity isopleths. However, near the coast the summer coastal upwelling introduces high salinity water to the surface.

At 10 meters depth the same trends, the low salinity water in the plume and the saline water in the upwelling region, are observable distinctly. At 20 meters depth, we observe an evidence of the low salinity Columbia River water offshore, of less than 32.0‰. However, at 50 meters depth we can barely detect the influence of the river plume as shown by the scanty existence of low salinity water having salinity less than 32.5‰. At 100 meters depth, there exists no trace of river water.

Throughout all these depths, the influence of the summer coastal upwelling is evident.

Temperature

Surface temperature distribution (Figure 3) shows higher temperature, greater than 16°C, in the Columbia River plume and

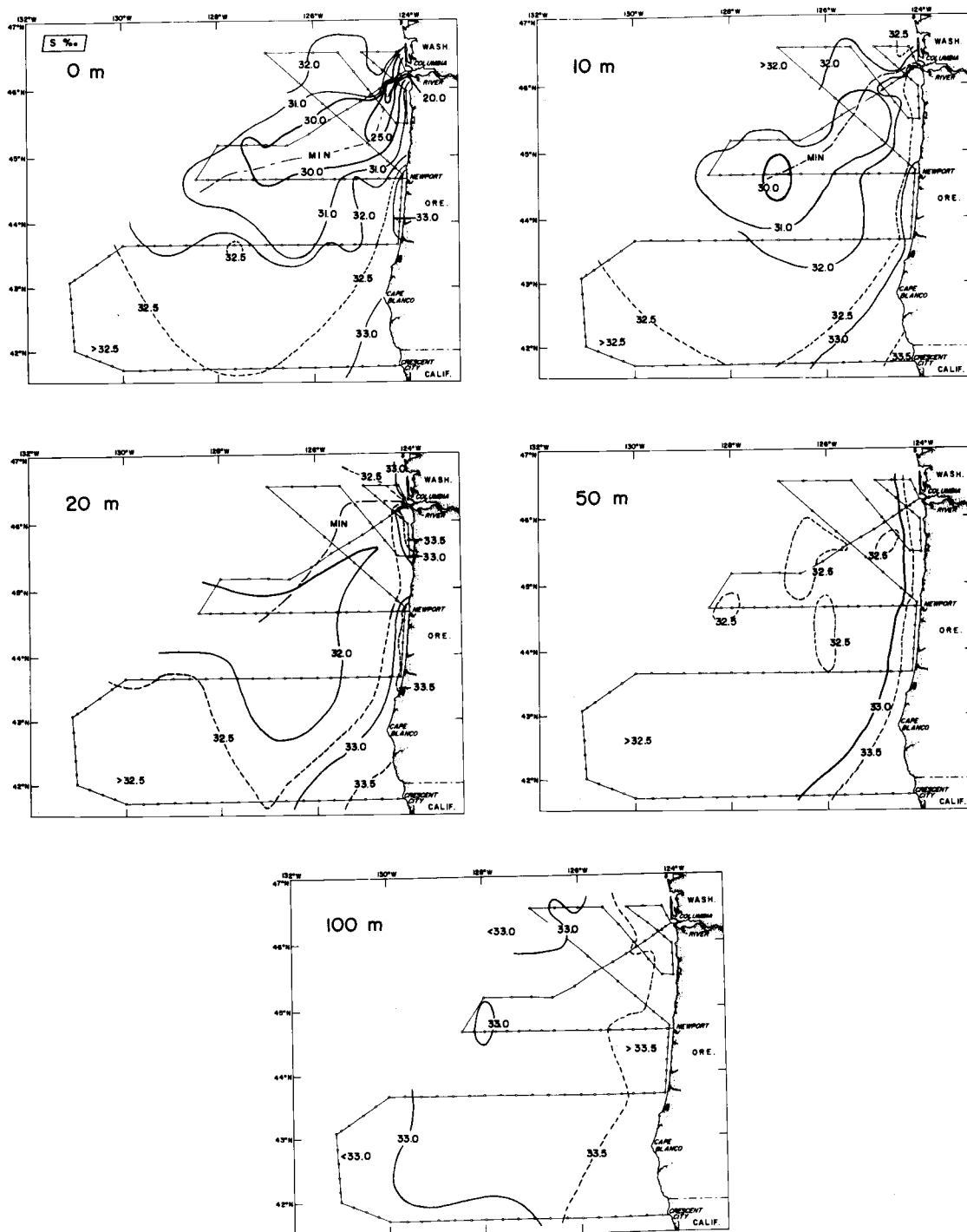


Figure 2. Salinity distributions in the Columbia River plume; surface, 10m, 20m, 50 m, and 100 m. Salinity minimum is shown by broken line.

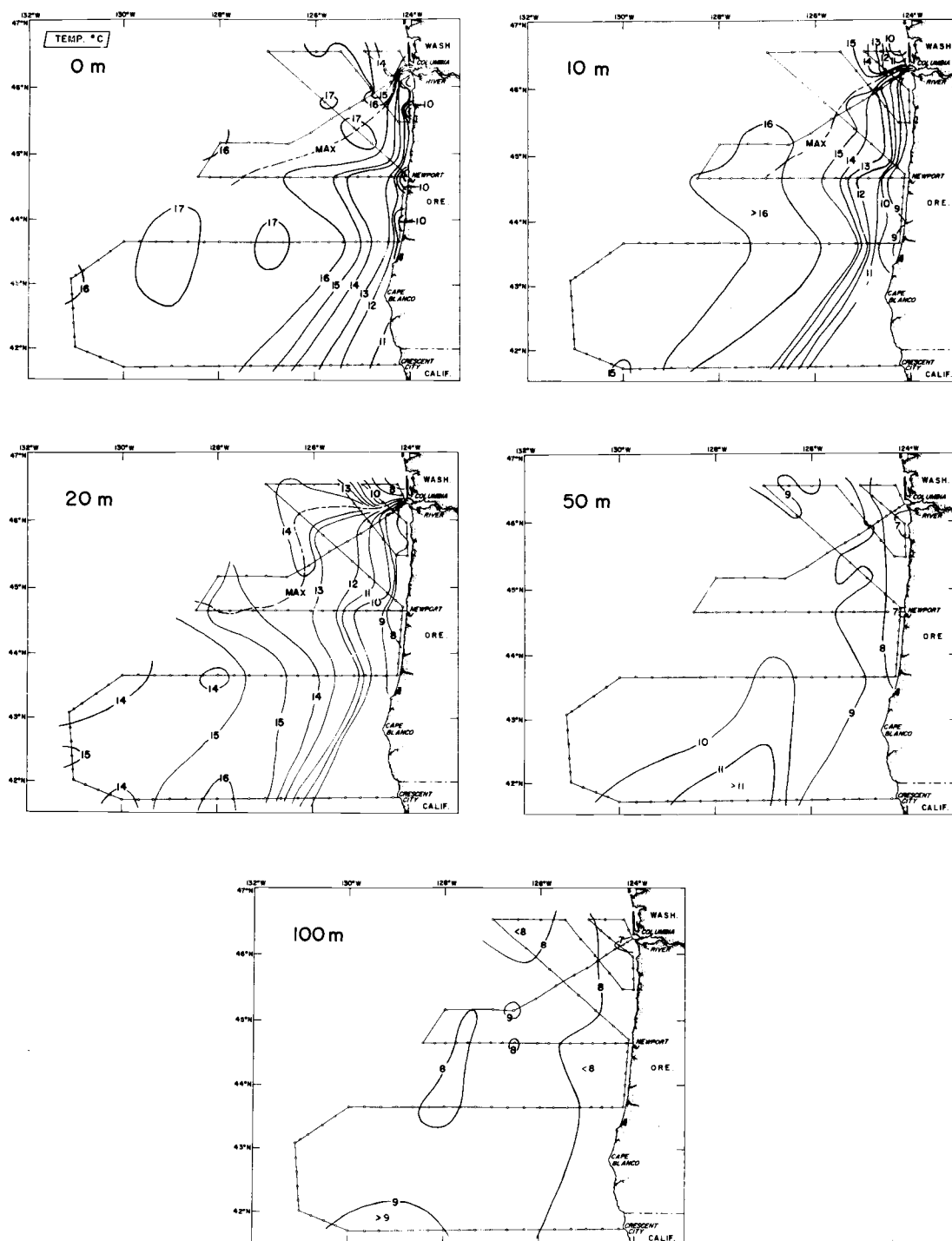


Figure 3. Temperature ($^{\circ}\text{C}$) distribution in the Columbia River plume; surface, 10 m, 20 m, 50 m and 100 m. Temperature maximum is shown by broken line.

lower temperature, less than 12°C , in the coastal upwelling region. Near the river mouth the temperature maximum follows the major direction of the axis of plume (Figure 3).

Below 50 meters, only the influence of coastal upwelling is observable. At 50 meters depth the 9°C line shows it and at 100 meters the 8°C line indicates it.

Oxygen

Oxygen distributions are complex (Figure 4). At the sea surface, one can divide the oxygen distribution into three areas: near the coast, 30 kilometers offshore, and farther offshore. Near the coast we find patchy low oxygen areas. Thirty kilometers offshore, between the Columbia River mouth and Cape Blanco, we observe the maximum oxygen value ranging from 7 to 10 ml/liter. Farther offshore oxygen concentration is essentially featureless with a typical value of 6 ml/liter. In general, between 10 and 50 meters the oxygen concentration increases with depth except in the upwelling region.

At 100 meters depth, the coastal upwelling region possesses an oxygen value of less than 3 ml/liter.

Phosphate

Phosphate distribution is also complex (Figure 5). At the sea

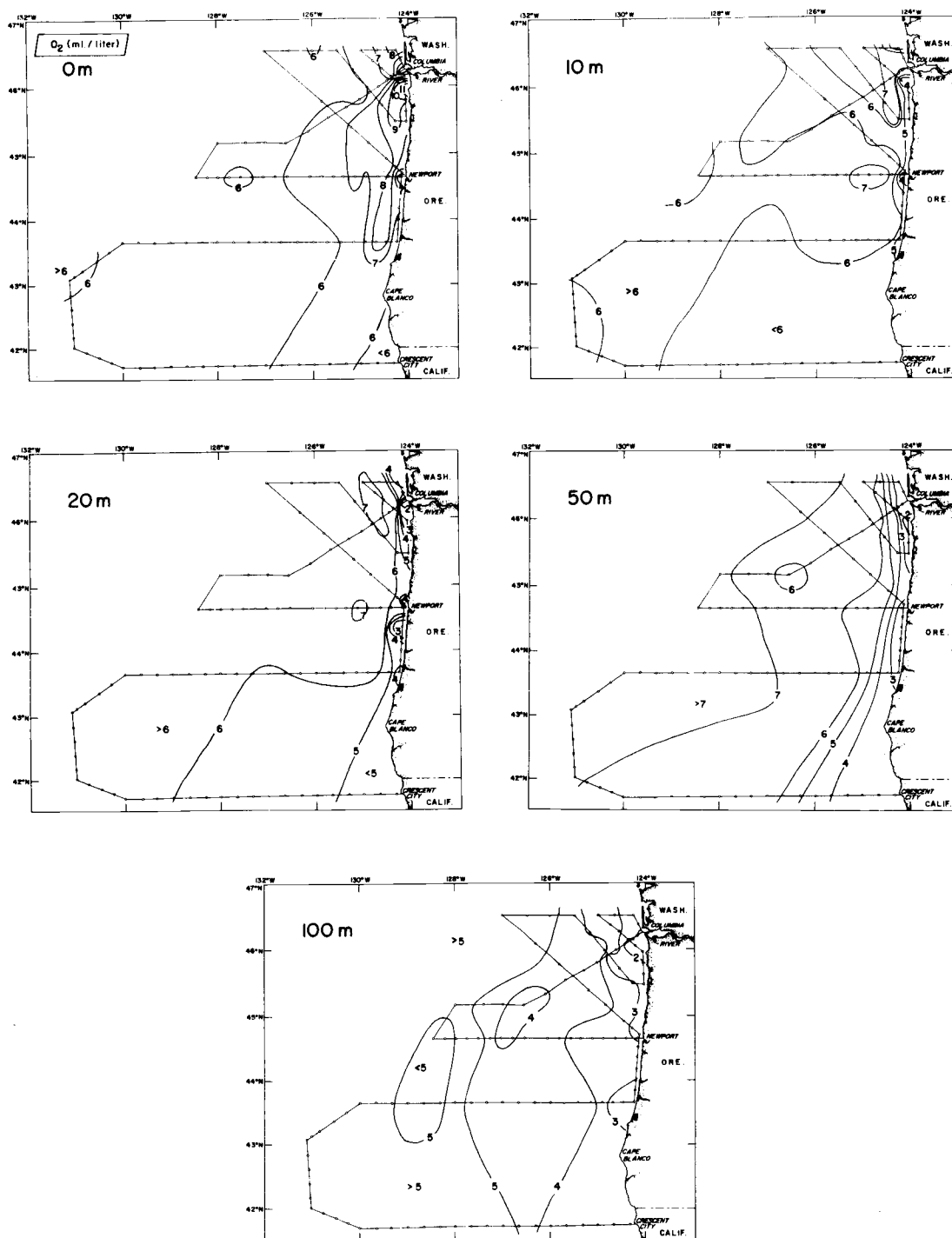


Figure 4. Oxygen distribution (ml/liter) in the Columbia River plume; surface, 10 m, 20 m, 50 m and 100 m.

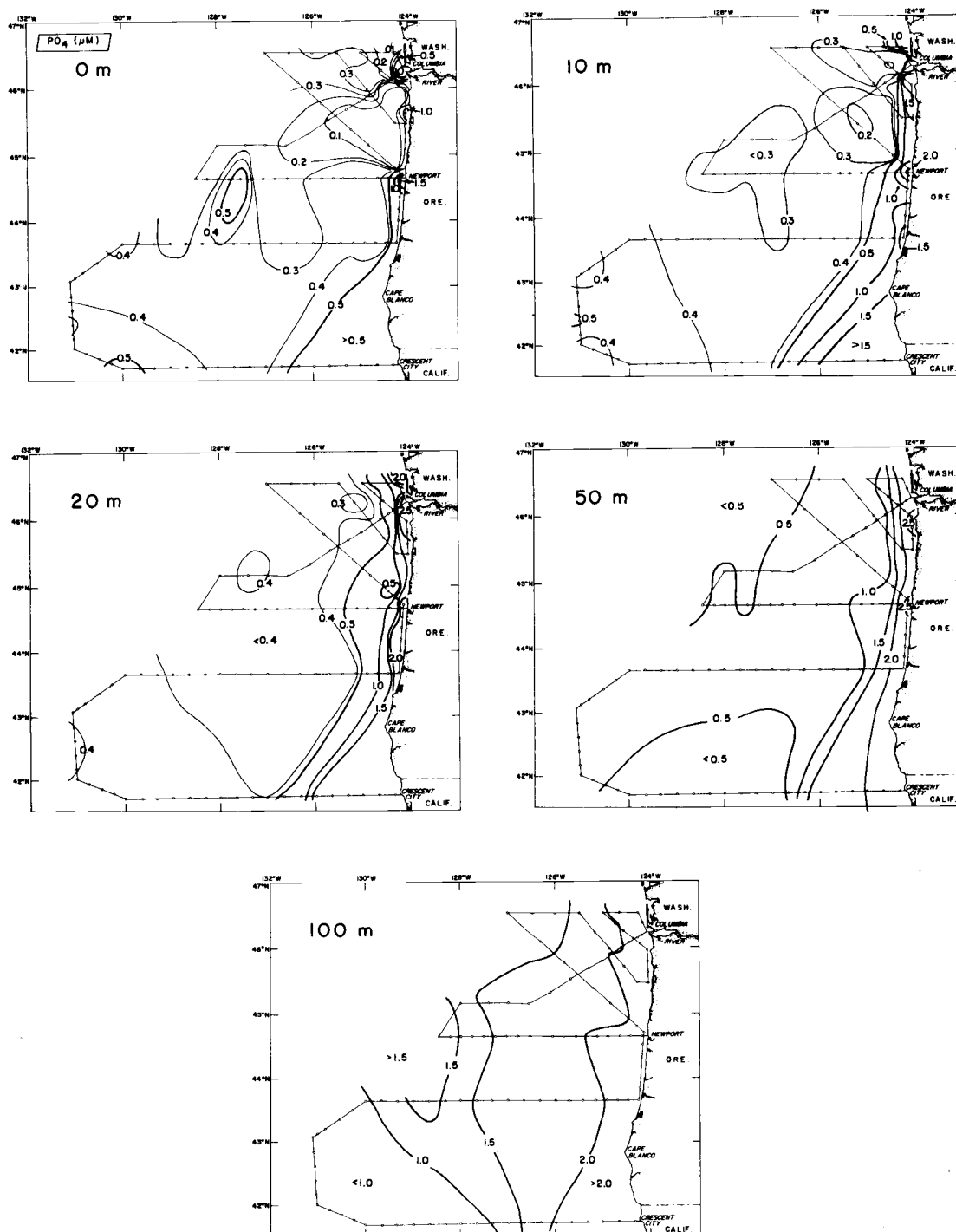


Figure 5. Phosphate distribution (μM) in the Columbia River plume; surface, 10 m, 20 m, 50 m and 100 m.

surface very low phosphate content was observed in the river plume, as low as $0.1 \mu\text{M}$. In the upwelling region its concentration goes up to as much as $1.5 \mu\text{M}$. The 10-meter phosphate distribution is essentially the same as that observed at the sea surface. Below 20 meters, phosphate concentration increases near the coast. This is due to the coastal upwelling.

Surface distribution of nitrate, silicate, pH, alkalinity and total carbon dioxide

Surface silicate, alkalinity and carbon dioxide distributions (Figure 6) display their similarities with the surface salinity distribution (Figure 2). These three distributions essentially reflect the contribution of river water chemical composition. The surface pH distribution (Figure 6), however, resembles that of the oxygen distribution (Figure 4); the area which has high pH, greater than 8.4, corresponds to the oxygen concentration of greater than 7.0 ml/liter.

Over a wide region off Oregon, except near the river mouth and the upwelling region, the surface nitrate concentration (Figure 6) shows essentially zero concentration.

Vertical distribution

In order to show the vertical distribution of all the measured

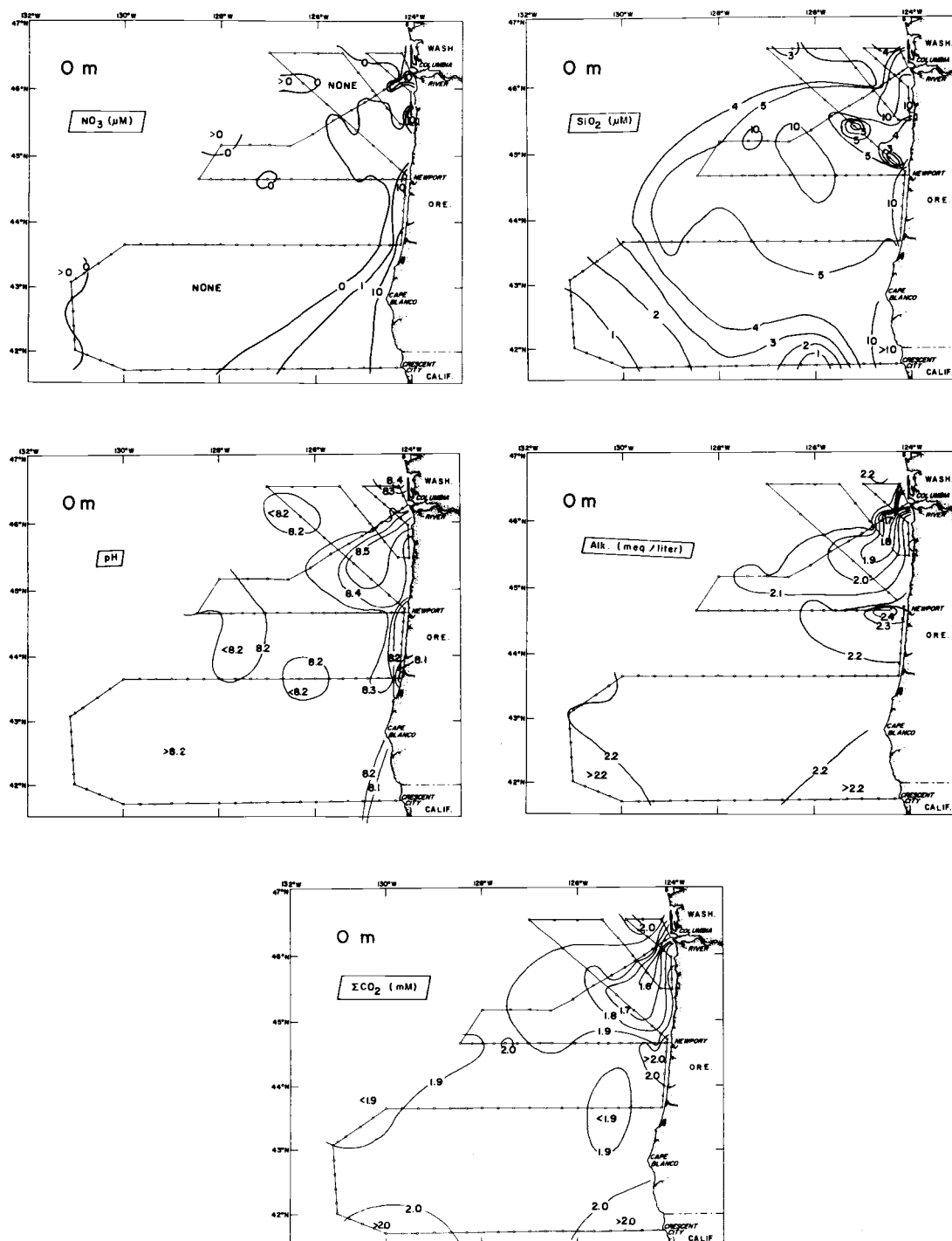


Figure 6. Surface distributions of nitrate (μM), silicate (μM), pH, alkalinity (meq/liter), and total carbon dioxide (mM).

parameters clearly, six transects were selected in and near the river plume. The location of these transects are shown in Figure 1. They consist of four east-west lines (Transects I-IV) (Figures 7-10), one transect perpendicular to the axis of the river flow (Figure 11) and the last transect being close to parallel to the axis (Figure 12). All of these vertical distributions distinctly show the influence of coastal upwelling by the upward trend of their isopleths as we approach the coast (Figures 7-12).

The vertical distribution of salinity of these transects shows the depth and width of the river plume. In general, the depth of the plume is confined within the upper 50 meters as exemplified by the isohaline of 32.5‰ (Figures 7-12). The width of the plume varies from one transect to another.

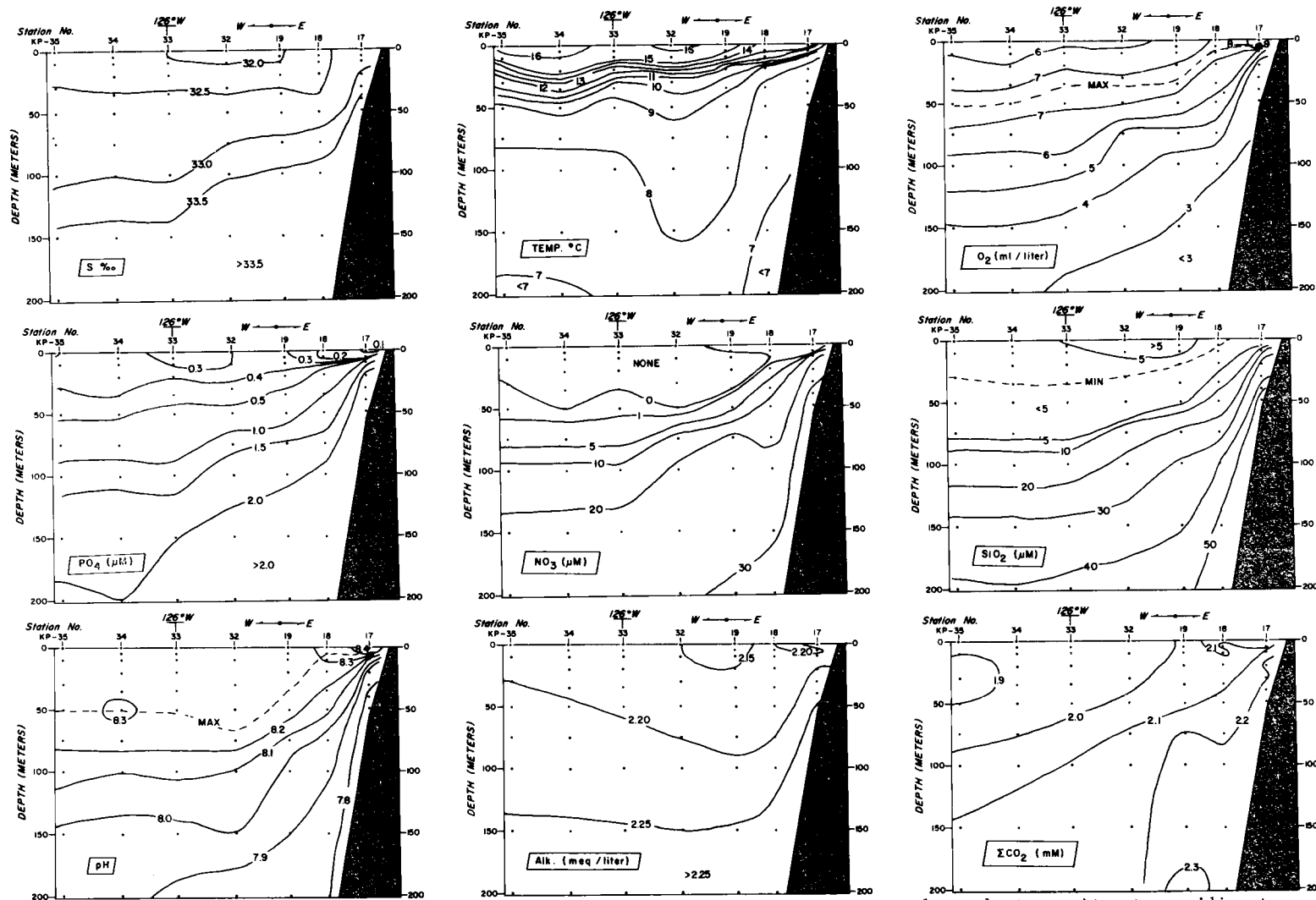


Figure 7. Vertical distributions of salinity, temperature, oxygen, phosphate, nitrate, silicate, pH, alkalinity and total carbon dioxide along transect I.

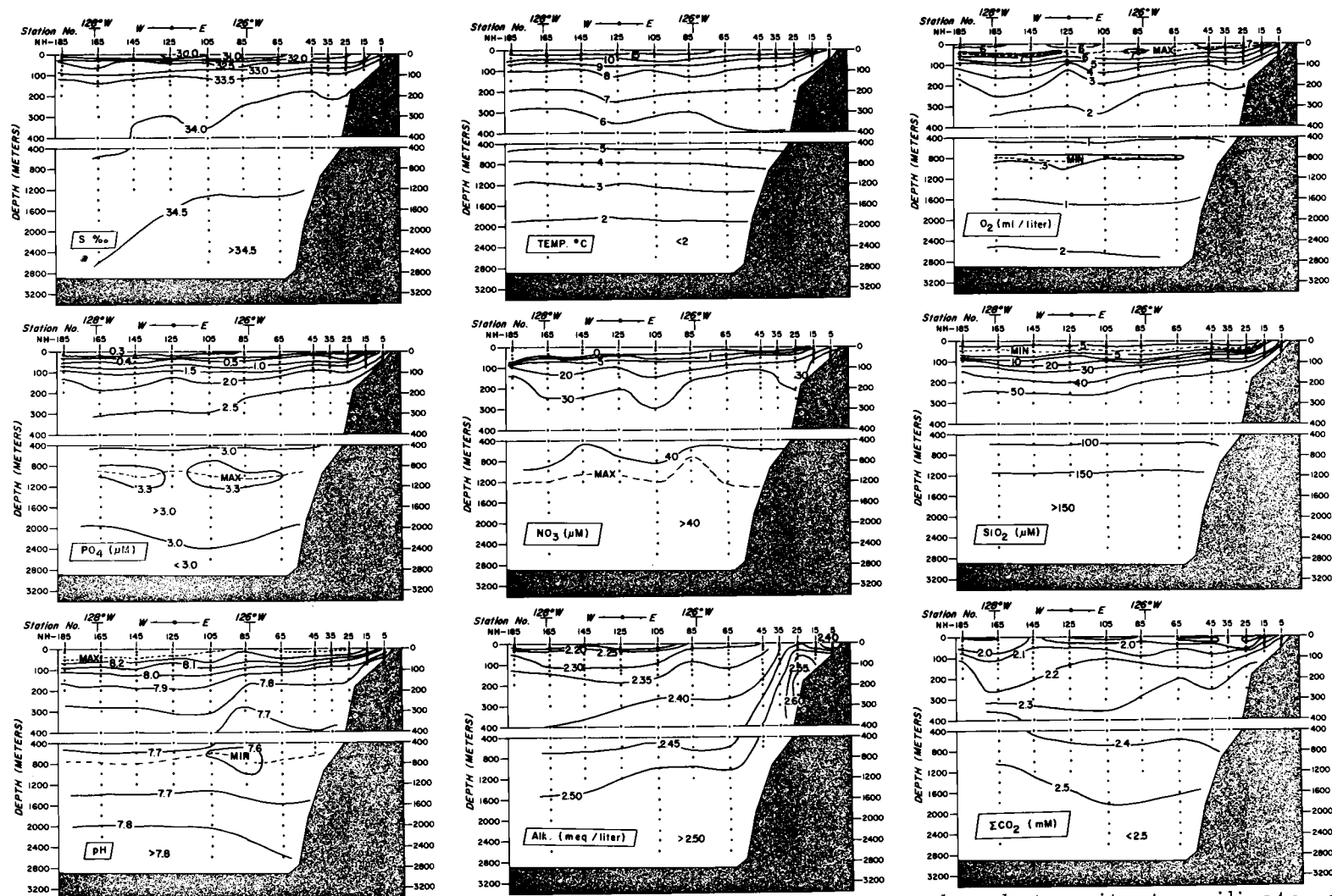


Figure 8. Vertical distributions of salinity, temperature, oxygen, phosphate, nitrate, silicate, pH, alkalinity and total carbon dioxide along transect II.

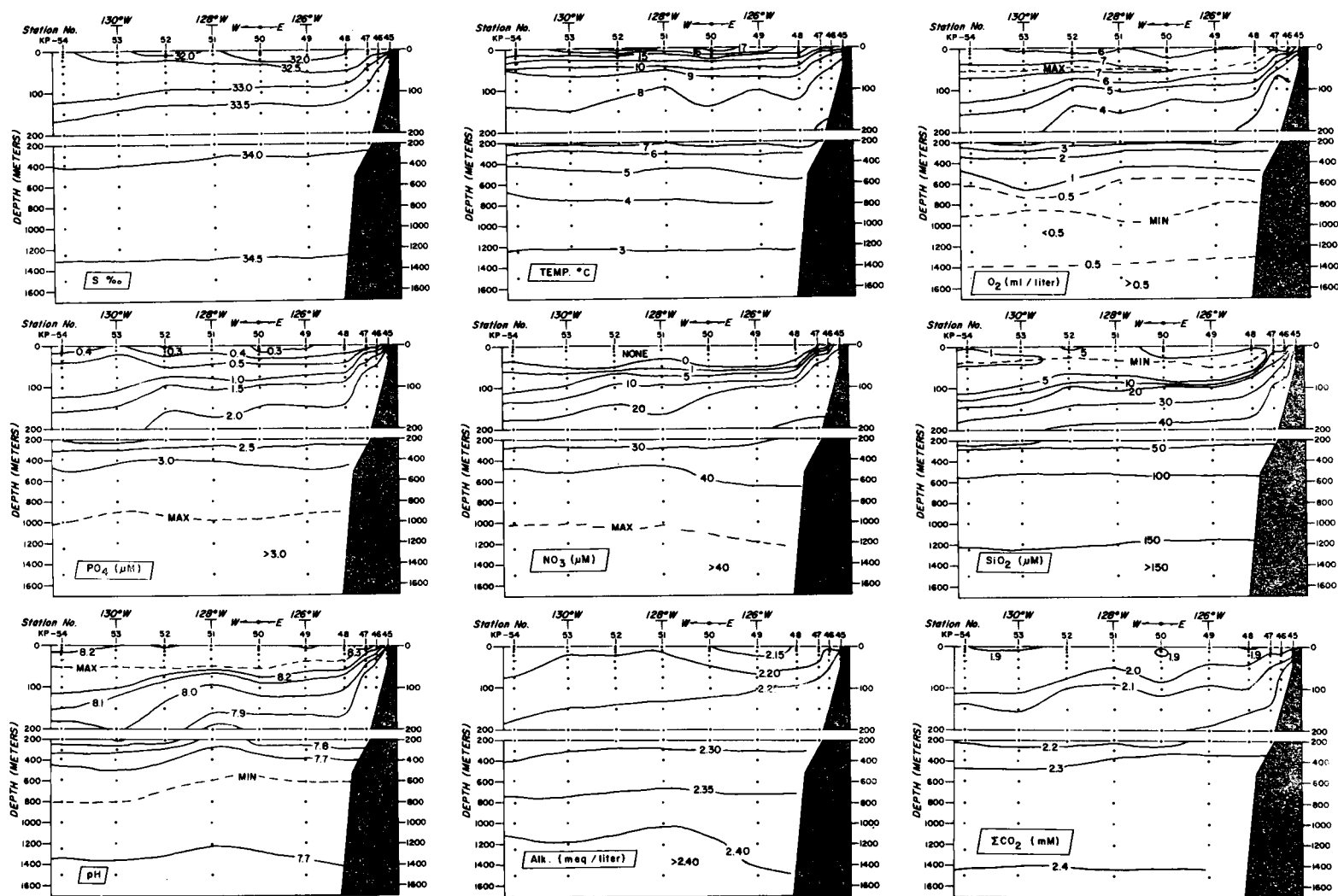


Figure 9. Vertical distributions of salinity, temperature, oxygen, phosphate, nitrate, silicate, pH, alkalinity and total carbon dioxide along transect III.

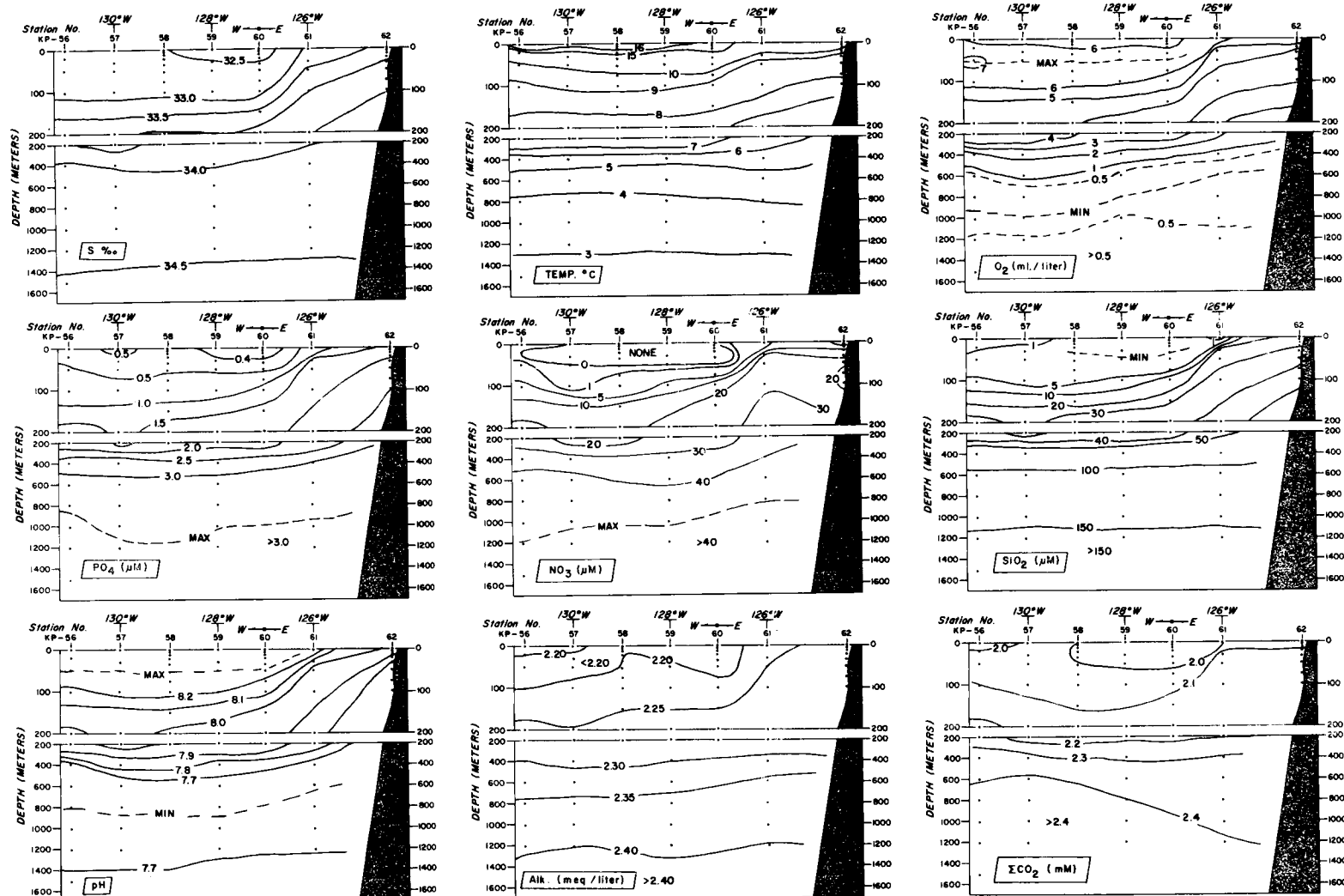


Figure 10. Vertical distributions of salinity, temperature, oxygen, phosphate, nitrate, silicate, pH, alkalinity and total carbon dioxide along transect IV.

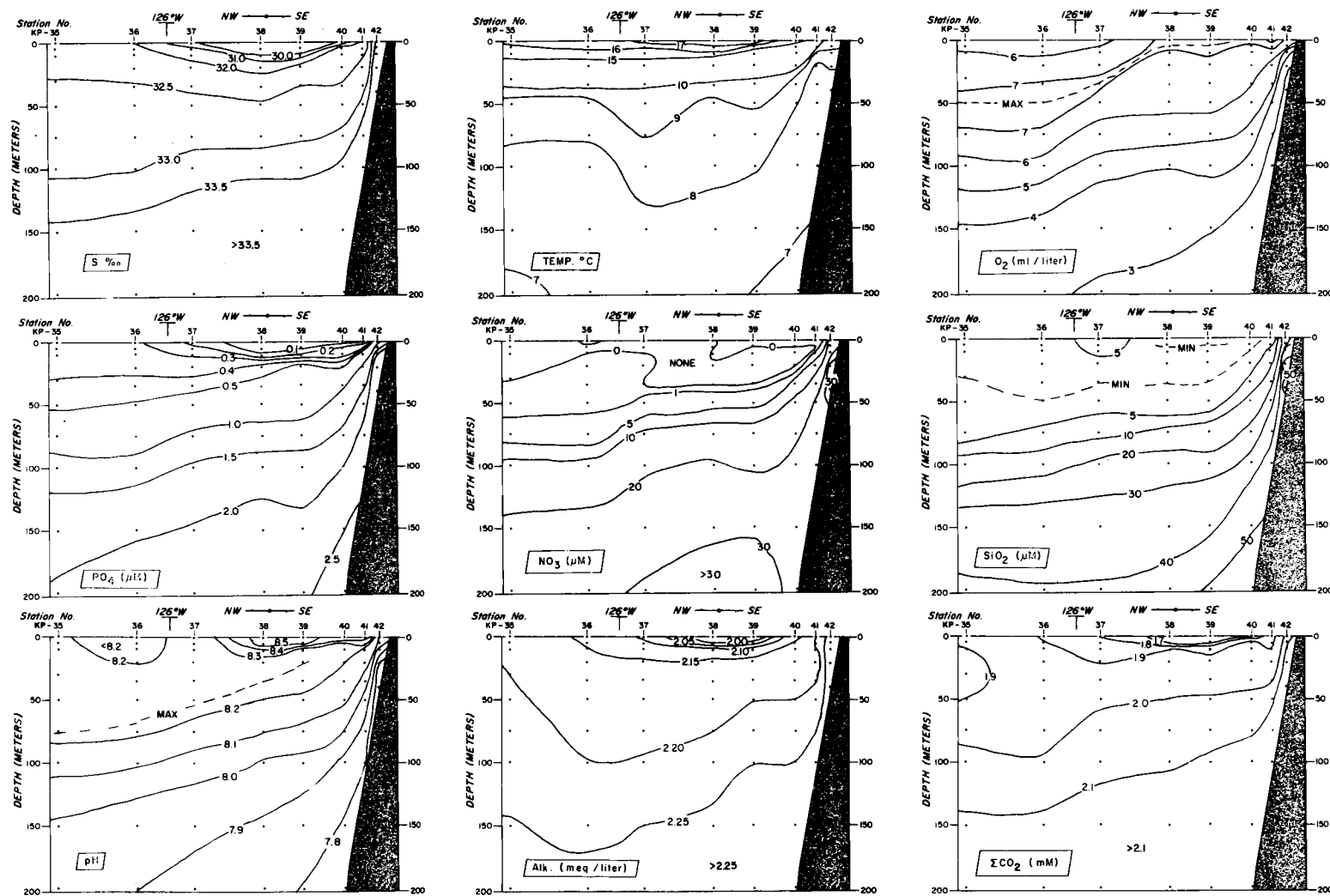


Figure 11. Vertical distributions of salinity, temperature, oxygen, phosphate, nitrate, silicate, pH, alkalinity and total carbon dioxide along transect V.

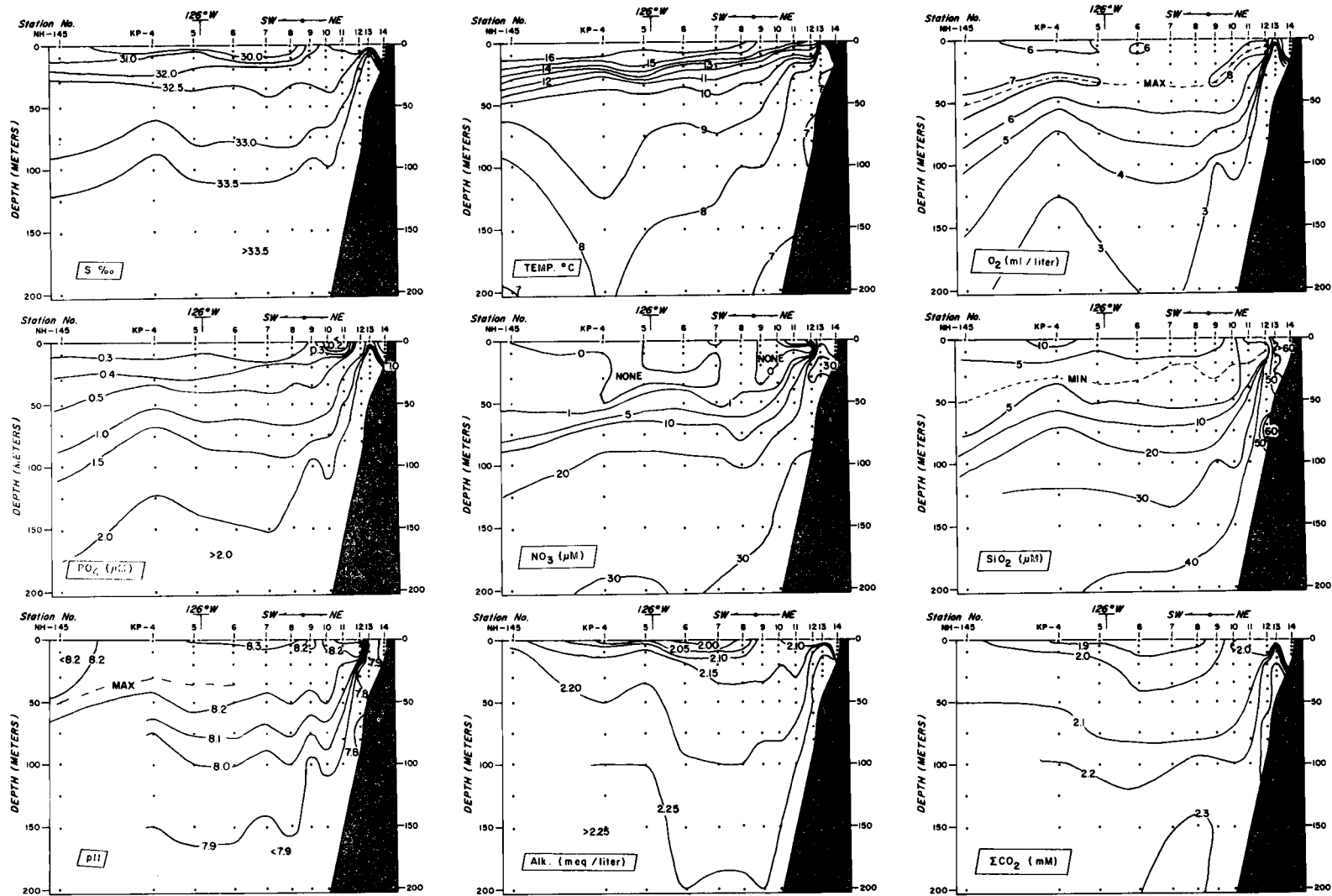


Figure 12. Vertical distributions of salinity, temperature, oxygen, phosphate, nitrate, silicate, pH, alkalinity and total carbon dioxide along transect VI.

IV. DISCUSSION

Salinity and temperature

An effective way to determine the influence of the Columbia River water off Oregon is by the examination of salinity. Budinger, Coachman and Barnes (1964) suggested that a salinity value of 32.5‰ is a good index salinity for ascertaining the horizontal and vertical extent of the river effluent. Temperature also becomes an effective way to monitor the axis of the river plume. It is based on the fact that river water temperature differs considerably from surface seawater temperature. According to Park, Osterberg and Forster (1969), the river temperature ranged from 7.0°C in February to 21.4°C in August in 1967 (Figure 13). Off the Oregon coast outside of the river plume the annual temperature range is between 9°C and 17°C. Therefore the plume water, the mixture of river and seawater, would have different temperatures from that of sea surface temperature.

In July 1967, an average river temperature was 19.0°C (Park, Osterberg and Forster, 1969) while the sea surface temperature outside the plume was about 16.0°C; therefore, one should observe the maximum temperature along the major axis of flow. Indeed, the cruise data substantiates this hypothesis (Figures 2 and 3). Both the salinity minimum and temperature maximum, shown by broken lines

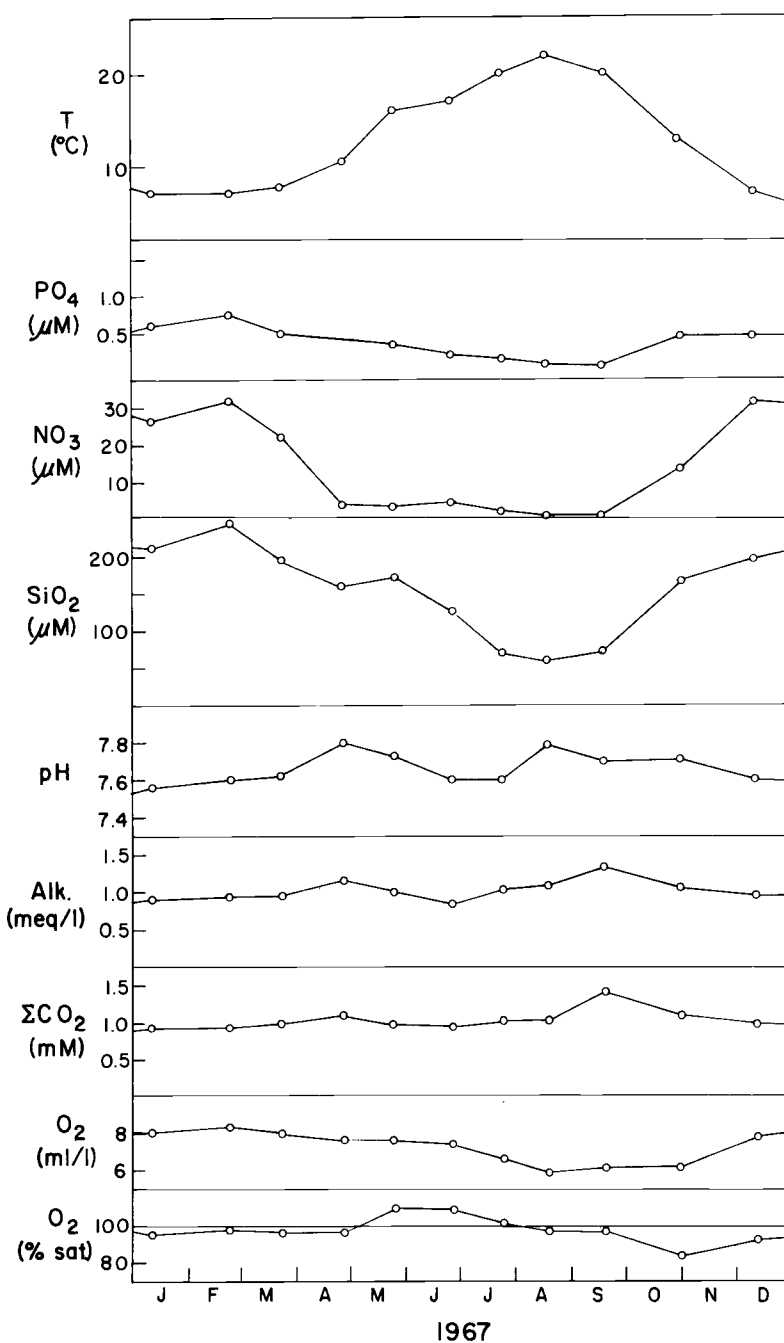


Figure 13. Seasonal distribution of temperature and chemical parameters in the Astoria estuary at zero salinity for 1967 (Park, Osterberg and Forster, 1969).

in the upper 20 meters in Figures 2 and 3, agree very well. Here, at the sea surface we notice the salinity minimum and temperature maximum go southward initially and turn west later. At 10 meters depth the location of these minimum and maximum is different from that at the sea surface. The intensity of initial southward direction for the extrema decreases and they occupy more westerly positions than at the sea surface.

At 20 meters depth the location of these extrema deviates farther westward than at shallower depths. Although not shown, the ship's thermograph clearly pinpoints the lowest surface salinity area by its recorded temperature maximum. I, therefore, advocate the use of continuous sea surface temperature monitoring to determine the major flow of the Columbia River effluent off Oregon.

Since the river plume possesses low salinity and high temperature, its sigma-t is often lower than 20; while at salinity of 32.8‰ and temperature of 16° C, its sigma-t is 24. Therefore, the plume water rides over the normal surface seawater off Oregon. Because of the strong vertical pycnocline within the river plume, the normal seawater lying under the plume is covered by the plume water and effectively insulated from the atmosphere. Any in situ production of organic matter in the seawater under the plume water would accumulate the chemical changes and only diffusion would reduce its accumulation. Many chemical extrema (oxygen maximum, silicate

minimum, pH maximum), therefore, should be found immediately below the influence of the plume during the photosynthesis period.

The in situ organic production will be examined later.

Alkalinity and total carbon dioxide

From the study of Park, Osterberg and Forster (1969) we find that both alkalinity and carbon dioxide in river water have very small seasonal variance (Figure 13) with an average value of 1.0 meq/liter and 1.0 mM for alkalinity and total carbon dioxide, respectively. Therefore, these two parameters can be utilized as the river effluent tracers in the ocean, provided that they do not undergo appreciable in situ changes. Since alkalinity is influenced very little by marine organisms, it has been used by Park (1966a, 1968a) as water tracer in the Columbia River plume. Based on his method, the specific alkalinity (alkalinity/chlorinity) distribution was plotted near the river mouth (Figure 14). The surface distribution of specific alkalinity resembles the salinity distribution and it is over 0.150 near the river mouth while away from the plume it is reduced to 0.123.

In first approximation the total carbon dioxide can be treated exactly the same way as the surface specific alkalinity was plotted to trace the river plume. The use of total carbon dioxide is, of course, less preferred, for it is affected by biological activities

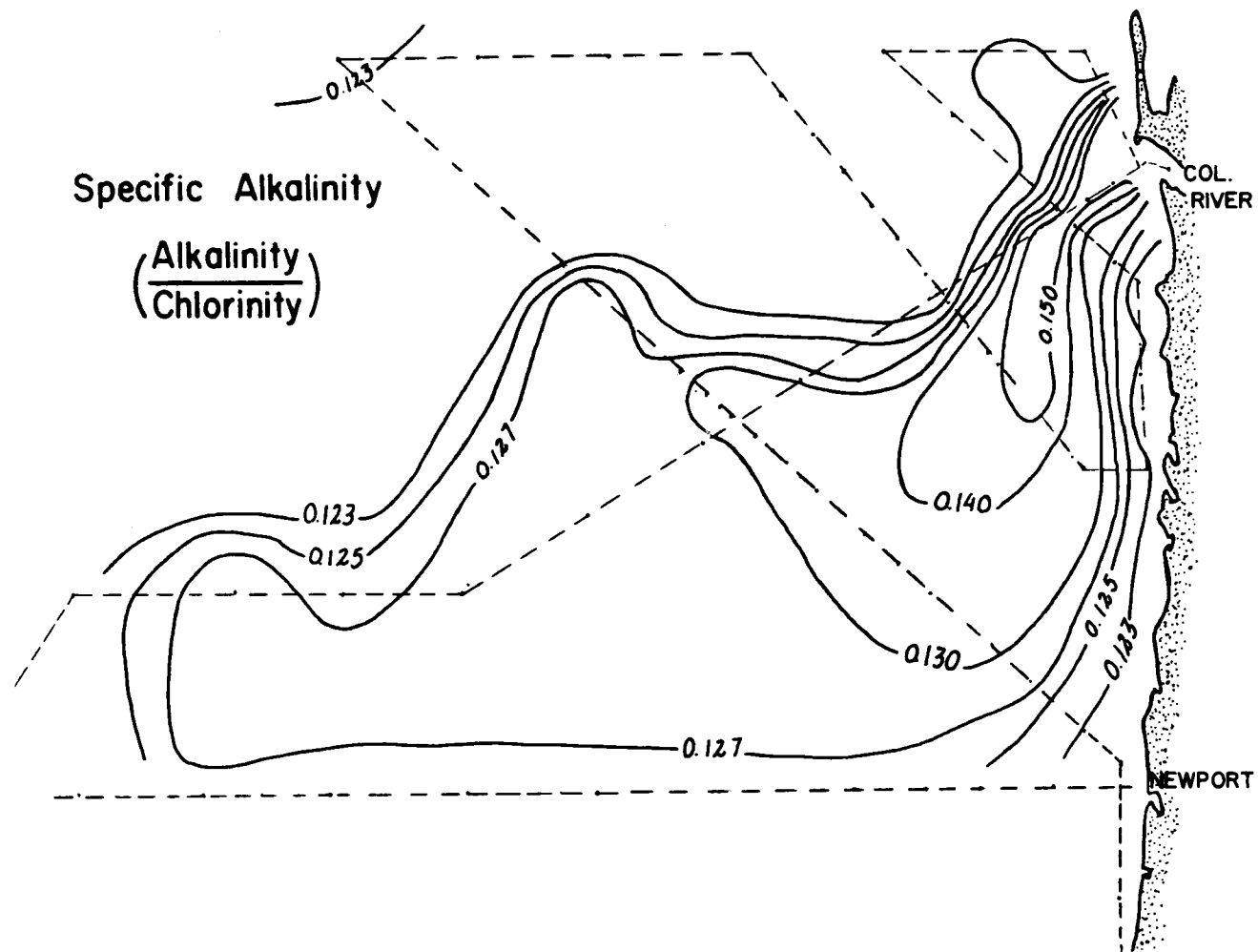


Figure 14. Surface specific alkalinity (alkalinity/chlorinity) distribution in the Columbia River plume, July 1967.

by as much as 0.2 mM.

Oxygen and pH

There are striking resemblances between oxygen and pH both horizontally and vertically. Where high oxygen content, over 7.0 ml/liter is found (Figure 14), also high pH, over 8.4, is found (Figure 6). When examining the vertical distribution of both oxygen and pH, the near surface maximum in both oxygen and pH is consistently found immediately below the influence of the river plume. Its depth is generally 50 meters. The oxygen minimum zone (800-900 meters) coincides with the pH minimum (Figures 7-12).

Park (1968b) discusses the basic relationship between the oxygen and pH distribution in the oceans. His analysis indicates that there exists a linear relationship between AOU (Apparent Oxygen Utilization) and pH in the normal oceanic pH range between 7.5 and 8.3. AOU is defined as 100 percent oxygen saturation minus oxygen concentration measured.

With respect to the formation of near surface oxygen maximum there are two major ways to produce it. The first way is the degassing of oxygen from the surface layer into the atmosphere by the increase in surface temperature from winter to summer. The second way is by the biological production of oxygen in the seawater immediately beneath the plume. In this case, the first mechanism,

the degassing of oxygen, does not apply directly, for the surface water is influenced strongly by the river effluent. The maximum formed by physical force is therefore primarily due to covering of low oxygenated plume water over the normal seawater. However, the oxygen concentration at the oxygen maximum zone, near 50 meters depth, increases from winter to summer off Oregon (not shown). This net increase has to come from photosynthesis.

To illustrate the in situ oxygen production, the vertical distribution of percent oxygen saturation is employed along the transect VI (Figure 15). Here, away from the upwelling region, dissolved oxygen is supersaturated from the sea surface to 50 meters deep. At the oxygen maximum zone the percent oxygen saturation is as much as 114 percent (Figure 15). At the same depth pH is as high as 8.29 while nitrate concentration goes down to essentially zero. Since in situ temperature increase should lower in situ pH, the high oxygen saturation with high pH does not come from the in situ temperature increase. The active agent to increase the in situ pH is photosynthesis. Depletion of nitrate also supports the mechanism in the formation of subsurface maximum from biological production.

Nutrients

The most striking features of the nutrient data are the

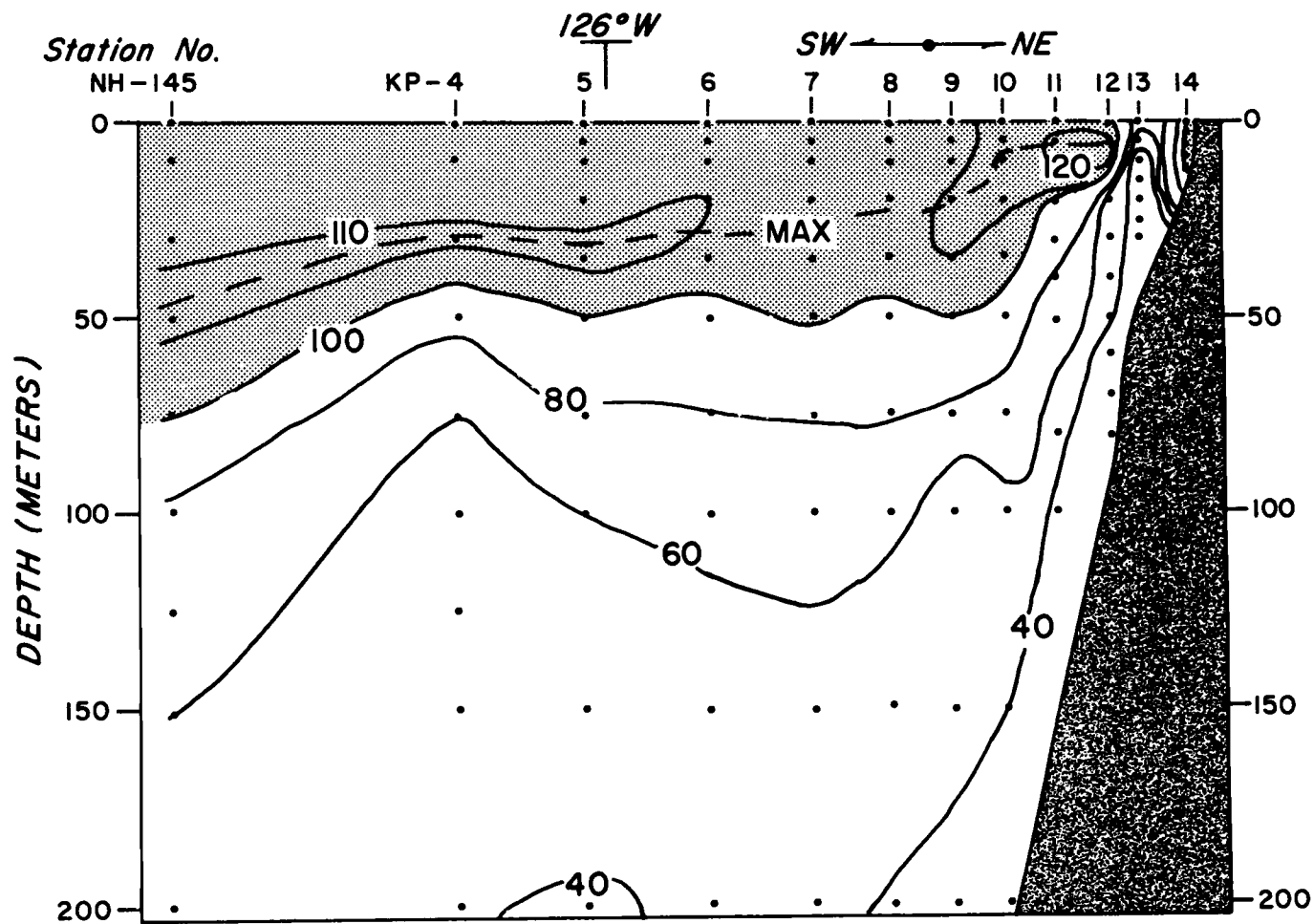


Figure 15. Percent saturation of oxygen along transect VI in the Columbia River plume. Percent oxygen maximum is shown by broken line.

widespread subsurface silicate minimum at slightly above 50 meters depth and the nonexistence of nitrate in a zone in the upper 50 meters. The cause of their unique distributions appears to be biological.

The nutrient concentration in the river water for July 1967 was $0.15 \mu\text{M}$ for phosphate, $3 \mu\text{M}$ for nitrate and $92 \mu\text{M}$ for silicate (Park, Osterberg and Forster, 1969). The cruise 6707A data near the river mouth (KP-14) agree with the river water data: it was $0.17 \mu\text{M}$ for phosphate, $2.3 \mu\text{M}$ for nitrate and $97 \mu\text{M}$ for silicate at the surface.

According to Stefánsson and Richards (1963), the waters of the Columbia River plume consist primarily of two component mixtures of Columbia River water and of surface seawater, but they may contain variable fractions of entrenched and intermixed deep water. Our cruise data indicate the possible mixing of river water with the upwelled water as shown by the vertical distribution of salinity at station KP-13 (Figure 12). At this station the upwelled water having salinity of 33.7‰ exists at the depth of 10 meters while at the surface its salinity was 15.9‰ . However, from the water budgetary point of view the fraction of upwelled water in the plume water does not appear large. Therefore, in first approximation the nutrient distribution in the river plume should be determined by the mixing ratio of surface seawater and river water provided we do not consider any biological uptake.

In theory, if one has a representative nutrient reference for the surface seawater one can calculate the nutrient concentration of the plume water. However, such a calculation is difficult for the surface water which undergoes chemical changes due to spring phytoplankton bloom. In their nutrient studies, Stefánsson and Richards (1963) used winter nutrient data as reference surface seawater data. Their values were $1\ \mu\text{M}$ for phosphate, $6\ \mu\text{M}$ for nitrate and $9\ \mu\text{M}$ for silicate. If we use their nutrient reference data, we would expect higher phosphate and nitrate concentrations for the plume water than for the river water data given by Park, Osterberg and Forster (1969) and lower concentrations for silicate. In reality the reference nutrient data given by Stefánsson and Richards cannot be accepted because of the possible spring phytoplankton bloom occurring in the surface water before it mixed with the river water. Furthermore, the surface nutrient distribution may not be the same from one year to another.

If the mean nutrient data in the upper 10 meters at station KP-35 is assumed as a reference surface seawater, one finds the nutrient concentrations of $0.32\ \mu\text{M}$ for phosphate, $0.0\ \mu\text{M}$ for nitrate and $2.6\ \mu\text{M}$ for silicate. The station KP-35 is located at the outermost of transect I and slightly north of the river mouth; therefore, it should have the least influence of the river water, yet it is not too far from the river mouth (Figure 7). Based on our own

reference nutrient data, the expected nutrient concentration for the plume water can be expressed by the following equations.

$$(\text{PO}_4)_{\text{plume}} = 0.15 + 0.0053S(\text{‰}) \quad (1)$$

$$(\text{NO}_3^-)_{\text{plume}} = 3.0 - 0.093S(\text{‰}) \quad (2)$$

$$(\text{SiO}_2)_{\text{plume}} = 92 - 2.9S(\text{‰}) \quad (3)$$

The observed salinity-nutrient relationships (Figure 16) do not agree satisfactorily with the above equations. The majority of phosphate data are lower than the expected values. Nitrate values are very low, less than 1 μM , for the entire plume water samples. For silicate approximately two-thirds of the samples agree with the expected values but the remaining samples are low.

The primary cause of the low nutrient concentrations in the plume water is photosynthesis, for the percent saturation of oxygen in the plume is always greater than 100 percent (Figure 15) and the apparent oxygen production (AOP) is as much as 2 ml/liter (Figure 16). AOP is defined as the measured oxygen concentration minus 100 percent oxygen saturation.

Gas-nutrient relationship

The basic relationship between AOU and nutrients off Oregon has been discussed by Park (1967). Our cruise data concur with his

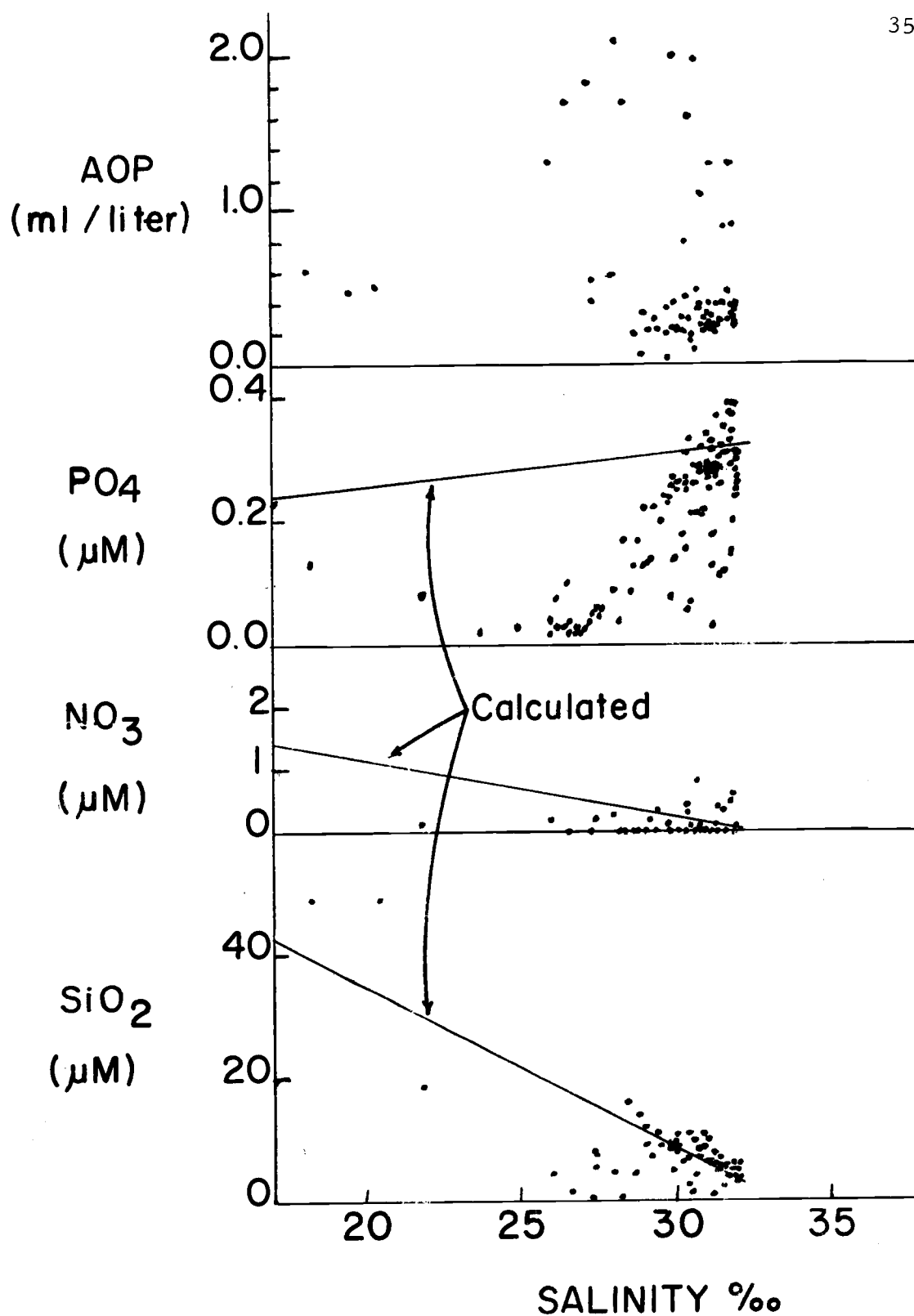


Figure 16. The salinity-nutrient and salinity-AOP relationships in the Columbia River plume July 1967. Solid lines are calculated from the river and sea surface nutrient away from the plume area.

findings (Figure 17) with AOU: ΔN : ΔP of 3.09 ml/liter: 16 μM : 1 μM . Our seawater samples came from below the Columbia River plume, deeper than 50 meters, and from upwelled seawater samples.

For AOU-silicate relationship, our data also agree with that of Park (1967). Within the silicate concentration of 40 μM the AOU: ΔSi ratio of 3.09 ml/liter: 23 μM follows (Figure 17). Since our cruise data agrees with that of Park's (1967), the preformed phosphate and nitrate distributions should be the same as the values calculated by Park. They are approximately 1.1 μM and 8 μM for preformed phosphate and preformed nitrate respectively from the depths immediately below the plume, at 50 meters and down to the sea floor.

The oxygen-nutrient relationship within the plume is complex. Here two major processes that alter oxygen concentrations are the air-sea oxygen exchange and in situ oxygen production by photosynthesis. Therefore, apparent oxygen production (AOP) we calculated is a net result of both processes. If AOP is primarily due to the biological oxygen production rather than the heating of seawater, then one should observe the inverse relationship between the AOP values and nutrient concentrations we observed. In first approximation one observes it (Figure 18). In the salinity range of 25-30‰ the rate of decrease of phosphate is approximately 1 μM per 2 ml of AOP. This phosphate uptake is much greater than the

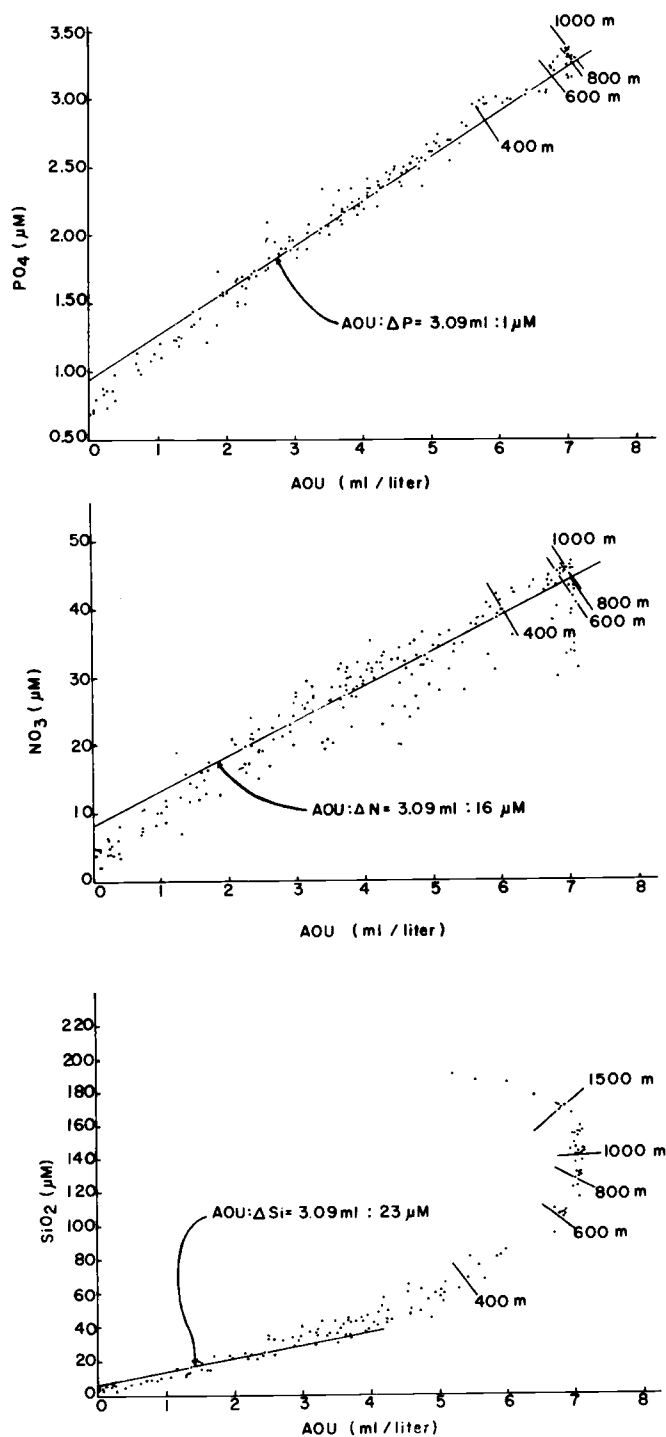


Figure 17. AOU-nutrient relationships. The straight lines are from the biochemical oxidation model of Richards (1965) and from Park (1967).

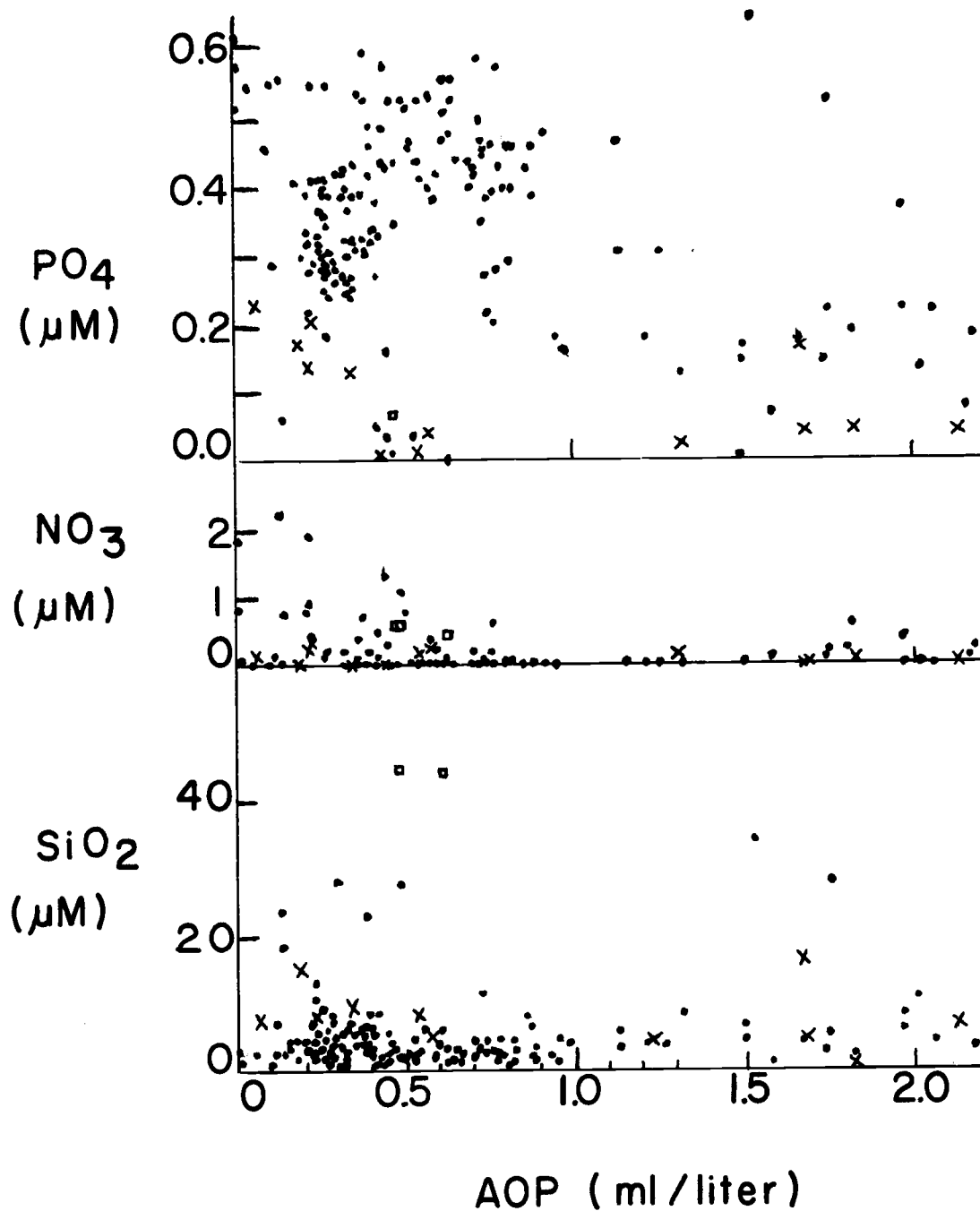


Figure 18. AOP-nutrient relationships in the Columbia River plume, July 1967. Symbols represent the following ranges: •, over 30‰; x, between 25-30‰; Δ, between 20-25‰; ◻, below 20‰.

assimilation ratio of 3.09 ml/liter: 1 μ M between AOP and Δ P.

If the observed AOP: Δ P ratio of 2 ml/liter: 1 μ M is the net result of the air-sea exchange as well as the oxygen production having the assimilation ratio of AOP: Δ P of 3.09 ml/liter: 1 μ M, then 1 μ M uptake of phosphate should produce 3.09 ml/liter of oxygen; however, our estimation shows only 2 ml/liter of AOP. Therefore, it may be possible that 1 ml/liter of oxygen produced could have escaped into the atmosphere from the ocean. However, not enough data are available to substantiate the possibility of this air-sea exchange. Furthermore, nitrate uptake we observed does not correlate with the normal assimilation ratio. Therefore, it is conceivable that the assimilation ratio we have here could be quite different from the typical oceanic assimilation ratio of AOP: Δ N: Δ P of 3.09 ml/liter: 16 μ M: 1 μ M.

The AOP-nitrate relationship shows a decreasing trend of nitrate concentration with the increase in AOP. This observation is consistent with the mechanism of nitrate uptake by marine organisms during their photosynthesis. Throughout the plume zone nitrate concentration never exceeds 1 μ M/liter. Furthermore, one does not detect the presence of nitrate in the major portion of the river plume. Therefore, it appears nitrate is a limiting nutrient for the phytoplankton growth. However, whether or not nitrate is the limiting nutrient has to wait for the analysis of ammonia distribution,

for ammonia is preferred to nitrate by phytoplankton as their nutrient source.

Silicate concentration appears to decrease with the increase in AOP (Figure 18). However, our data show substantial scatter. Between the salinity 25-30‰ the rate of decrease in silicate appears to be about $30 \mu\text{M}/3 \text{ ml}$ of AOP. This assimilation ratio is not too far from the initial dissimilation ratio of AOU: ΔSi of 3.09 ml/liter: $23 \mu\text{M}$ (Park, 1967).

Boundary of the Columbia River plume

The establishment of proper boundary for the Columbia River plume off Oregon is important in describing the various processes that take place within the plume. Budinger, Coachman and Barnes (1964) employ plots of salinity versus the logarithm of depth to determine the boundary. They find a salinity range of 32.4 to 32.7‰ being the boundary zone that separates from the plume zone to open seawater. For the sake of simplicity they suggest that the isohaline of 32.5‰ represents the plume boundary.

The vertical distribution of salinity from several stations of cruise 6707A was plotted by the method of Budinger, Coachman and Barnes (1964) (Figure 19). The salinity range we observed at the salinity convergence at 30-40 meters depth was 32.3 to 32.6‰ with the majority of the curves closer to the 32.5‰ isohaline. The

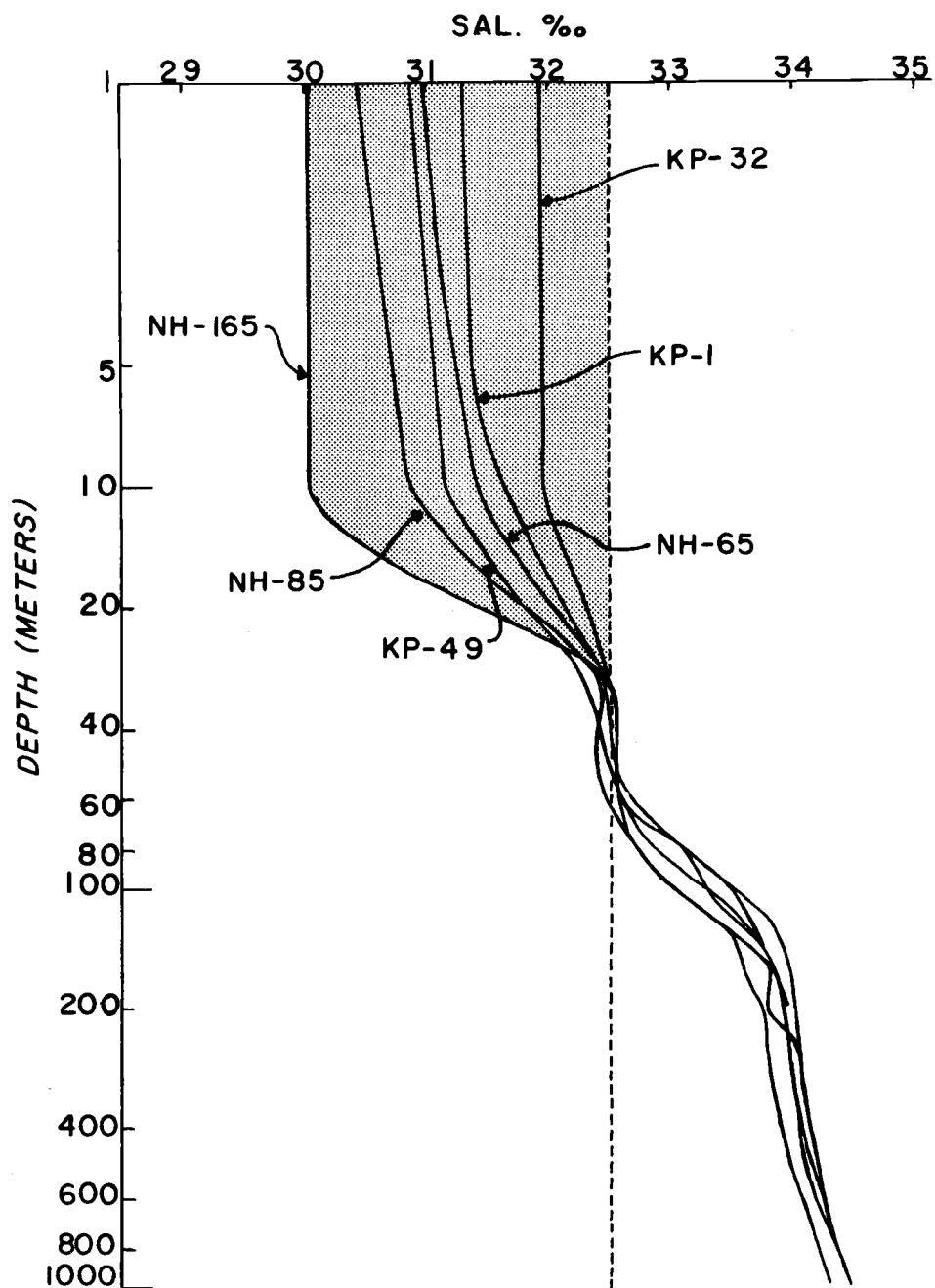


Figure 19. Vertical distribution of salinities in the Columbia River plume area at selected stations. Notice that salinity lines converge at 30 meters depth.

32.5‰ isohaline, therefore, can be chosen to represent the boundary of the Columbia River plume for our cruise.

Sugiura (personal communication) employed a plot using salinity and alkalinity as the variables in determining the boundary of the plume. He concluded that the 32.8‰ isohaline may be taken as the plume boundary. His conclusion is not far away from the boundary salinity of 32.5‰ estimated by Budinger, Coachman and Barnes (1964). This discrepancy between the two methods may be due to the scatter in the alkalinity data.

In reality, the use of the isohaline of 32.5‰ to distinguish the plume water from the normal seawater is not always applicable. For example, during the 17-month period, July 1963 to November 1964, surface waters 150-200 kilometers west of Newport, Oregon, had salinities of less than 32.5‰ (Park, 1968a). Therefore, other means for distinguishing plume water from low salinity surface waters should be found. The Hanford originated radionuclides (Osterberg, Cutshall and Cronin, 1965) as well as the use of the unique chemical composition of the Columbia River water itself should be potentially useful for making this distinction. Further scrutinization on the chemical composition of the Columbia River system is needed.

BIBLIOGRAPHY

- Anderson, G. C. 1964. The seasonal and geographic distribution of primary production off the Washington and Oregon coasts. *Limnology and Oceanography* 9: 284-302.
- Anderson, G. C., C. A. Barnes, T. F. Budinger, C. M. Love and D. A. McManus. 1961. The Columbia River discharge area of the northeast Pacific Ocean, a literature survey. Seattle, University of Washington, Dept. of Oceanography. 99 p.
- Armstrong, F. A. J., C. R. Stearns and J. D. H. Strickland. 1967. The measurement of upwelling and subsequent biological processes by means of the Technicon Autoanalyzer® and associated equipment. *Deep-Sea Research* 14: 381-389.
- Barstow, D., W. Gilbert and B. Wyatt. 1969. Hydrographic data from Oregon waters, 1967. Corvallis, Oregon State University, Dept. of Oceanography. 77 p. (Data Report no. 35)
- Brown, N. L. and B. V. Hamon. 1961. An inductive salinometer. *Deep-Sea Research* 8: 65-75.
- Budinger, T. F., L. K. Coachman and C. A. Barnes. 1964. Columbia River effluent in the northeast Pacific Ocean, 1961, 1962: Selected aspects of physical oceanography. Seattle, University of Washington, Dept. of Oceanography. 78 p. (Technical Report no. 99)
- Hager, S. W. 1969. Processes determining silicate concentrations in the northeastern Pacific Ocean. Master's thesis. Corvallis, Oregon State University. 57 numb. leaves.
- Hager, S. W., L. I. Gordon and P. K. Park. 1968. A practical manual for use of the Technicon Analyzer® in seawater nutrient analyses. Corvallis, Oregon State University, Dept. of Oceanography. 31 p. (Final report to the Bureau of Commercial Fisheries on Contract 14-17-0001-1759. Ref. 68-33)
- Hobson, L. A. 1966. Some influences of the Columbia River effluent on marine phytoplankton during January 1961. *Limnology and Oceanography* 11: 223-234.

- Livingston, D. A. 1963. Composition of rivers and lakes. 6th ed. Washington, D. C. 64 p. (U. S. Geological Survey. Professional Paper 440-G)
- Mullin, J. B. and J. P. Riley. 1955. The colorimetric determination of silicate with special reference to sea and natural waters. *Analytica Chimica Acta* 2: 162-170.
- Osterberg, C. L., N. Cutshall and J. Cronin. 1965. Chromium-51 as a radioactive tracer of Columbia River water at sea. *Science* 150: 1585.
- Park, K. 1965. Gas chromatographic determination of dissolved oxygen, nitrogen, and total carbon dioxide in sea water. *Journal of the Oceanographical Society of Japan* 21(1): 28-29.
- Park, K. 1966a. Columbia River plume identification by specific alkalinity. *Limnology and Oceanography* 11: 118-120.
- Park, K. 1966b. Surface pH of the northeastern Pacific Ocean. *The Journal of the Oceanological Society of Korea* 1(1-2): 1-6.
- Park, K. 1967. Nutrient regeneration and preformed nutrients off Oregon. *Limnology and Oceanography* 12: 353-357.
- Park, K. 1968a. Alkalinity and pH off the coast of Oregon. *Deep-Sea Research* 15: 171-183.
- Park, P. K. 1968b. The processes contributing to the vertical distribution of apparent pH in the northeastern Pacific Ocean. *The Journal of the Oceanological Society of Korea* 3(1): 1-7.
- Park, P. K., C. L. Osterberg and W. O. Forster. 1969. Chemical budget of the Columbia River. In: *Bioenvironmental studies of the Columbia River estuary and adjacent ocean region*. Washington, D. C., U. S. Atomic Energy Commission. (In press)
- Pytkowicz, R. M. 1964. Oxygen exchange rates of the Oregon coast. *Deep-Sea Research* 11: 381-389.
- Richards, F. A. 1965. Anoxic basins and fjords. In: *Chemical oceanography*, ed. by J. P. Riley and G. Skirrow. Vol. I. London, Academic. p. 611-645.

- Rosenberg, D. H. 1962. Characteristics and distribution of water masses off the Oregon coast. Master's thesis. Corvallis, Oregon State University. 45 numb. leaves.
- Stefánsson, U. and F. A. Richards. 1963. Processes contributing to the nutrient distribution off the Columbia River and Strait of Juan de Fuca. *Limnology and Oceanography* 8: 394-410.
- Stefánsson, U. and F. A. Richards. 1964. Distributions of dissolved oxygen density and nutrients off the Washington and Oregon coasts. *Deep-Sea Research* 11: 355-380.
- Strickland, J. D. H. and T. R. Parsons. 1965. A manual of sea water analyses. Rev. ed. Ottawa. 185 p. (Fisheries Research Board of Canada. Bulletin no. 125)
- Tibby, R. B. 1957. The water masses off the west coast of North America. *Journal of Marine Research* 43: 112-121.