FINAL REPORT

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A Field Study Of Surface Nutrient Enrichment In The California Current

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INTRODUCTION

Haury et al. (1994) and Haury & Shulenberger (1998) used historic oceanographic survey data to describe the general features of surface enrichment of inorganic nutrients in the North Pacific Ocean, with emphasis on the California Current. Survey data from all other oceans contain similar evidence of surface nutrient enrichments (Haury et al., 1994). Haury & Shulenberger (1998) also reviewed and evaluated the possible causes for surface nutrient enrichment.

The objective of the research carried out under this ONR grant was to study in greater detail the vertical, horizontal, and temporal structure of surface nutrient enrichment in a limited part of the California Current off Southern California. Analysis of these high-resolution data indicates what we once thought was a single unique characteristic of some vertical profiles of nutrients is two separate features, one in the mixed layer, one in the thermocline. We propose new hypotheses to characterize the vertical structure of surface nutrient enrichment and to explain the formation of the mixed layer feature.

A NEW HYPOTHESIS: SURFACE NUTRIENT ENRICHMENT AND SUBSURFACE NUTRIENT REDUCTION

Vertical profiles of silicate, phosphate, nitrate and nitrite at nearshore, midcurrent, and offshore stations in the California Current (Fig.1) reveal (Figs. 2, 3, and 4) that "surface enrichment" is, in fact, two separate features. By referencing nutrient concentration differences in the mixed layer, if present, and in the shallow pycnocline to the concentration at the base of the mixed layer (or surface, if no mixed layer), it is clear there are consistent differences in profile characteristics. These differences suggest two separate phenomena: 1) In a mixed layer, nutrients can increase from at or above the pycnocline to the surface, so that a physically isotropic surface layer displays surface nutrient enrichment (SNE); 2) Beneath the mixed layer in the shallow pycnocline, nutrients often decrease dramatically before increasing to values greater than in the mixed layer; thus appearing as subsurface nutrient reduction (SNR). In the base of the mixed layer, there is often an "isonutrient" layer between the two features. When a mixed layer is not present, subsurface nutrient reduction occurs, similar to that in the pycnocline below a mixed layer (Fig. 3). The occurrence of SNE and SNR are independent of each other, as would be expected for chemical features occurring in vertically separated depth strata that differ in physical and biological properties and dynamics.

FIELDWORK

The data were collected as a part of the California Cooperative Oceanic Fisheries Investigations (CalCOFI) program on cruise 9610RR (10 October - 2 November 1996), the first scientific cruise of RV Roger Revelle.¹. The survey pattern and types of sampling at each station are shown in Fig. 1. The standard CalCOFI techniques used and the data obtained are presented in SIO (1998). These techniques and observations were augmented to provide greater resolution in the time, concentration, and spatial structure of surface nutrient enrichment.

1) At all stations, four additional CTD/rosette samples were taken in the upper 100 m of the routine 500 m casts to increase the resolution of the near-surface structure of SNE. One extra sample was a replicate surface bottle.

2) On three Line 90 stations, separate casts were taken to resolve the vertical structure of nutrients in the mixed layer and top of the thermocline by sampling 24 depths in the upper 125 m.

3) On some stations of Line 93 and all stations of Line 90, a "high-resolution" automated analyzer (HRAA) with enhanced low levels of detection supplemented the standard CalCOFI nutrient measurements (see below and Table 1).

4) At Station 93.50, we followed a drifting buoy drogued at 15 m for 24 hr while taking 24-bottle CTD casts in the upper 125 m at 4 hr intervals. At

¹ ONR funded several other investigations complementary to the routine CalCOFI work on this cruise: e.g., Collier, Goericke, Mitchell

Station 90.120, a fixed geographic position was occupied for 24 hr with similar sampling.

The high-resolution automated nutrient analyzer (HRAA) used the standard CalCOFI equipment and methods (SIO, 1998), but the chemistry and optical paths were set up for greater sensitivity at low nutrient concentrations. HRAA data used in most analyses were rounded to consistent values separated by the precision of the technique (Table 1).

DEFINITIONS

Surface Nutrient Enrichment (SNE)

The occurrence of SNE was based on the scoring method described in Haury & Shulenberger (1998). Briefly, for SNE to be present, a surface nutrient concentration $([N]_0; Fig. 5)$ had to exceed a deeper value in the mixed layer by an amount greater than the measurement precision for that nutrient; presence was given a value (flag) of 3. If the difference equaled the precision, then two or more subsurface depths had to be less than the surface value to be scored present. If only one subsurface value was lower at the precision limit, then the cast was scored as trace (flag of 2). If no subsurface value was less than the surface sample, enrichment was absent (flag of 1). The strength of the enrichment (SNE[N]; Fig. 5) is the difference between the surface value and the mixed layer minimum value; the thickness of the enriched layer (ZSNE[N]; Fig. 5) is the depth to the shallowest minimum value.

SNE could be due to chance occurrences of values within the mixed layer that are lower than the surface value—if so there should also be a similar number of values larger than the surface value. In all the data, there are 15 nutrient values in the mixed layer higher than the surface value (3 exceeded analytical precision). In contrast, there are 106 mixed layer minima (i.e., values less than the surface value): 74 exceeded analytical precision. We conclude that SNE is a real feature of the mixed layer and is not due to random variability.

Subsurface Nutrient Reduction (SNR)

The same criteria and similar terms for SNE were used to define SNR, except the nutrient concentration at the base of the mixed layer was used as the reference for SNR strength (SNR[N], Fig. 5).

Physical Structure

A mixed layer was defined as surface waters with density changes over depth of less than 0.005 sigma theta units. The base of the mixed layer (mixed layer depth, or MLD) was determined by the first density increase of greater than 0.005 sigma theta. When no mixed layer was present by this definition, we assumed that a subsurface minimum is a SNR.

ANALYSES

The assumptions upon which most parametric statistics are based were almost never satisfied by our data. Nonparametric statistics proved too insensitive because of weak "signal strength" and the relatively infrequent occurrence of surface nutrient enrichment. We therefore relied on multivariate techniques (such as multiple factor ANOVA) as indicators of effects and trends, but not statistical significance.

Analysis of SNE & SNR used descriptors (Fig. 5) derived from the high-resolution and standard autoanalyzer. Tests for the presence or absence of SNE and SNR, done for silicate, phosphate and nitrate only (nitrite too infrequent), were based on the flag values assigned to profiles. We used mixed layer depth, wind speed, time of day, and cloud cover as measures of the physical conditions and processes expected to determine presenceabsence.

RESULTS

Table 2 presents the percent of stations at which surface nutrient enrichment occurred without distinction to SNE or SNR; these data are presented for comparison with the frequency of occurrence of surface nutrient enrichment in the historical CalCOFI (1984-1995) data presented by Haury & Shulenberger (1998). It is clear from the table that the HRAA method detects many more profiles with surface enrichment; this is especially true for nitrate and nitrite.

Table 3 presents the frequency of occurrence (percent of stations) of SNE and SNR based on the standard and high-resolution analyses. Again, the HRAA technique reveals that SNE and SNR are much more common phenomena than suggested by the standard methods.

The data collected was insufficient to provide other than an indication of the effect of location (frequency as a function of line or station). Similar to the relationships found by Haury & Shulenberger (1998) from the historical CalCOFI data, frequency of occurrence in the 9610 data increased with distance from shore. No relationship was apparent by line (Haury & Shulenberger found enrichment, except for nitrite, more frequent in the southern lines).

Silicate and phosphate showed a linear increase in frequency of occurrence of SNE with increasing wind speed; there was little or no effect on nitrate. Frequency of occurrence for all three nutrients increased with increasing mixed layer depth (MLD) only between 0 and 10 m. There was no effect when MLD's were deeper than 10 m. Cloud cover had no effect.

The frequency of silicate and nitrate SNR increased with increasing wind speed; the effect on phosphate was inconsistent. The effect of mixed layer depth on the frequency of occurrence of SNR was opposite that on SNE—frequency decreased with MLD increasing from 0 to about 20 m, then the frequency leveled. Cloud cover had no effect

The thickness of SNE (i.e., the depth from surface to the minimum value in the mixed layer) increased with increasing mixed layer depth to a maximum at around 30 to 40 m MLD, then decreased (Fig. 6A). The increase in thickness with a deeper MLD is understandable since the deeper the mixed layer, the thicker the potential SNE; this

probably says nothing about causality. The decrease beyond 40 m MLD is curious, however. Using wind speed as the factor (Fig. 6B) and mixed layer depth as covariate, wind speed had little affect on the thickness of any SNE nutrient; silicate and phosphate enrichments were slightly thicker at wind speeds greater than about 25 kts. But since MLD is highly correlated with wind speed and would be expected to be thicker with stronger winds, the association appears to be between SNE thickness and wind speed.

There was no apparent relationship between the strength of any SNE nutrient and wind speed (Fig. 7A). Silicate SNE strength increased with depth when mixed layers were deeper than 25m; nitrate strength tended to be weaker with thicker mixed layers (Fig. 7B).

The strength of silicate and phosphate SNR increased with increasing wind speed, but not nitrate, excluding wind speeds of zero which had high strengths for silicate and phosphate (Fig. 8A). Interestingly, MLD had no noticeable effect on SNR strength of any nutrient (Fig. 8B).

The effects time of day on surface enrichment (the general phenomenon) and on SNE and SNR were analyzed first by using all cast data and then the two 24 hr station data separately. The analysis for diel effects on the general phenomenon was done because Haury & Shulenberger (1998) found in the historical data a weak relationship between strength and time of day.

Time of day, considered either by two-hour intervals or partitioning into day-night casts, had no effect on the frequency of occurrence of surface enrichment (without regard to SNE and SNR) using the standard nutrient analyses. However, while not statistically significant, the HRAA data showed surface enrichment of all three nutrients, especially nitrate, more frequent at night. Reanalysis for diel effects on SNE and SNR showed that for both HRAA and standard analyses, SNE was more frequent at night and SNR was more frequent during the day.

Standard and HRAA analyzed casts agreed that the general phenomenon of surface enrichment was stronger during the day than during the night except for the HRAA analysis of phosphate, which indicates phosphate enrichment is stronger at night.

For SNE, HRAA and standard analyses agreed that silicate and nitrate enrichments are stronger during the day, phosphate stronger at night. For SNR, both analyses agreed

that all nutrients had greater reductions during the day except for HRAA phosphate, where there was no significant difference (nights tended to be slightly stronger than day).

Chi square tests of association between SNE and SNR, based on the number of mutual co-occurrences of enrichment, showed no significant relationship for any nutrient. This supports our hypothesis that surface nutrient enrichments are actually two separate, probably independent, phenomena.

Vertical sections of properties along CalCOFI lines show (e.g., Fig. 9) that SNR can be a large-scale advective feature. The intense spatial coverage from 24 hr stations demonstrate, however, that some SNR's cross isopycnals, evidence that subsurface reductions are not all advective features (Fig. 10). In this figure, the silicate-density relationships of the SNR found in casts 107 and 108 are unlike those at any surrounding stations. Cast 109 nutrient properties in the SNR are identical to the surface waters found in Cast 6 at the adjacent station—if this cast is the source water, a subduction of 25 m in 20 km must have occurred; temperature and salinity defining the density in both casts are similar. The properties on casts 110 and 111 are similar to cast 105 (Station 93.40, 40 km away), also implying subduction along isopycnals produced this portion of the SNR.

CONCLUSIONS

The high-resolution observations of the structure of surface nutrient enrichment made on CalCOFI cruise 9610 demonstrate that our interpretation of enrichment in the historical data was too simple. The feature is not only much more common than standard techniques suggested, but it is also actually two separate phenomena that probably have distinctly different causes and effects.

Formation mechanisms

Haury & Shulenberger (1998) listed (their Table 5) and discussed the following potential mechanisms for the formation and maintenance of the general phenomenon of surface nutrient enrichment:

- 1) Atmospheric deposition (dust and rain)
- 2) Bubbles
- 3) Vertical circulations
 - a) Langmuir circulation
 - b) Diurnal convection
- 4) Dissolution of silica
- 5) Horizontal advection
- 6) Supply and demand
 - a) Uptake and regeneration rates
 - b) Photoinhibition
 - c) Photochemistry
- 7) Vertical migrations
 - a) Zooplankton and micronekton
 - b) Phytoplankton

They concluded "an imbalance between nutrient consumption and regeneration by euphotic zone plankton is the most important factor in producing of surface nutrient" enrichment. The recognition of two different features making up surface nutrient enrichment made possible by high-resolution vertical nutrient data requires a reevaluation of the mechanisms.

Surface Nutrient Enrichment (SNE)

We continue to support SNE formation dependent on an imbalance between supply and demand. The finding that its frequency of occurrence and thickness varies directly with wind speed/mixed layer depth prompts the following hypothesis: Enrichment of nutrients in surface water forms when the wind stirs and subsequent mixing redistributes thin layers of regenerated nutrients within the mixed layer. We suggest that in a mixed (not mixing) layer during low wind conditions, thin layers of intense biological activity form. In these layers, inorganic nutrients are regenerated and their concentration exceeds that of the surrounding layers. The thin, higher nutrient waters are almost never sampled by bottles and when they are, the small nutrient differences are disregarded as noise or measurement error. When the wind begins to blow and mix the mixed layer downward, the thin layers are disturbed and the high nutrients are redistributed from the surface to the depth of mixing.

Subsurface Nutrient Reduction

We again suggest nutrient regeneration exceeding uptake is the most likely mechanism forming some nutrient reductions in the top of the pycnocline. A significant fraction of the observed reductions, however, appear to be due to horizontal advection/subduction of low nutrient surface water underneath adjacent lower density and nutrient water.

Our results demonstrate that assumptions (modeling or otherwise) of (1) uniform distribution of nutrients in the mixed layer and (2) monotonically increasing nutrients from the base of the mixed layer downward; are almost always wrong. The devil is in the details, and biological/physical models will never be correct until they incorporate and predict the variability in vertical distributions evidenced by sensitive and highly resolved vertical profiles throughout the euphotic zone.

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SIO (1991) Physical, chemical and biological data, CalCOFI Cruises 9003 and 9004. SIO Ref. 91-4, 96 pp.

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	Standard CalCOFI	HRAA CalCOFI 9610
PO ₄	W 0-4 P 0.01	0 – 1.5 0.003
SiO₃	W 0-90 P 0.1	0-22.5 0.02
NO ₃	W 0-50 P 0.1	0 - 12 0.02
NO ₂	W 0-1.5 P 0.01	0 – 0.75 0.005

Table 1. Range (W) and precision (P) of standard and "high-resolution (HRAA) autoanalyzers used during CalCOFI cruise 9610 (in μ M). Standard CalCOFI values taken from SIO (1991).

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Table 2. Percent frequency of occurrence of surface nutrient enrichment on CalCOFI 9610 (Fig. 1) by standard and high resolution automated analyzer techniques. Number of profiles in parentheses. Surface enrichment does not distinguish SNE and SNR so comparison can be made with the historical CalCOFI data (1984-1995; Haury & Shulenberger 1998) given below the 9610 data.

	Silicate	Phosphate	Nitrate	Nitrite
Present	38 (33)	30 (26)	7 (6)	1 (1)
Trace	11 (9)	16 (14)	6 (5)	1 (1)
Absent	51 (44)	54 (46)	87 (75)	98 (84)
Total	100 (86)	100 (86)	100 (86)	100 (86)

CalCOFI 9610 Standard Analysis

Present	78 (25)	63 (20)	$\begin{array}{c} 35 & (11) \\ 13 & (4) \\ 52 & (16) \end{array}$	9 (3)
Trace	6 (2)	13 (4)		0 (0)
Absent	16 (5)	24 (8)		91 (29)
Total	100 (32)	100 (32)	100 (31)	100 (32)

Present	51	(1697)	28	(905)	8	(269)	2	(66)
Trace Absent	15 34	(495) (1135)	20 52	(680) (1733)	80	(388) (2669)	5 93	(3088)
Total	100	(3327)	100	(3318)	100	(3326)	100	(3326)

1984-1995 CalCOFI Data

Table 3. Percent frequency of occurrence of surface nutrient enrichment (SNE) and subsurface nutrient reduction (SNR) on CalCOFI 9610 by standard and high resolution automated analyzer techniques. Number of profiles in parentheses. Category labeled as "Undefined" indicates the number of profiles with no detectable mixed layer, thus SNE is undefined (see text).

SURFACE NUTRIENT ENRICHMENT (SNE)

ſ	Silicate	Phosphate	Nitrate	Nitrite
Present Trace Absent Undefined	$ \begin{array}{c} 11 & (6) \\ 6 & (3) \\ 83 & (43) \\ (2) \end{array} $	27 (14) 4 (2) 69 (36) (2)	6 (3) 6 (3) 88 (46) (2)	0 (0) 0 (0) 100 (52) (2)
Total	100 (54)	100 (54)	100 (54)	100 (54)

Standard CalCOFI Analysis

High Resolution Analysis

Present	71 (20)	65 (18) 21 (6)	32 (9) 29 (8)	7 (2) 25 (7)
Absent	18 (5)	14 (4)	39 (11)	68 (19)
Undefined	(4)	(4)	(3)	(4)
Total	100 (32)	100 (32)	100 (31)	100 (32)

SUBSURFACE NUTRIENT REDUCTION (SNR)

Standard CalCOFI Analysis

	Silicate	Phosphate	Nitrate	Nitrite
Present Trace Absent	11 (6) 6 (3) 83 (45)	13 (7) 6 (3) 81 (44)	0 (0) 4 (2) 96 (52)	2 (1) 0 (0) 98 (53)
Total	100 (54)	100 (54)	100 (54)	100 (54)

High Resolution Analysis

Present	56 (18)	35 (11)	13 (4)	3 (1)
Trace	6 (2)	9 (3)	16 (5)	13 (4)
Absent	38 (12)	56 (18)	71 (22)	84 (26)
Total	100 (32)	100 (32)	100 (31)	100 (31)

FIGURES

- Figure 1. Survey grid of California Cooperative Fisheries Investigations cruise 9610. Line numbers indicated at the offshore stations only. Sampling done at each station indicated by symbols denoted in legend: HRAA stations are those where nutrient analyses were done by high resolution automated autoanalyzer.
- Figure 2. Profiles illustrating surface nutrient enrichment and subsurface nutrient reduction at nearshore (A), mid current (B), and offshore (C&D) stations.

Figure 3. Profiles of subsurface nutrient reduction in profiles where there was no mixed layer.

- Figure 4. A) Nutrient profiles from Station 93.50, Cast 113, comparing raw and rounded highresolution (HRAA) data to the standard autoanalyzer data. B) Nutrient profiles from Station 90.57 (Cast 140) comparing raw and rounded HRAA data. Note in Fig A) the monotonic decline in silicate to 13 m (7 depths) and nitrate to 32 m (10 depths except 12 and 14 m) that is obscured by precision considerations
- Figure 5. Schematic diagrams of SNE and SNR showing the descriptors used to quantify profile characteristics for analyses. See text for details.
- Figure 6. A) Thickness of the surface nutrient enrichment (SNE) of silicate, phosphate and nitrate with mixed layer depth (MLD) as factor and wind speed as covariate; B) wind speed as factor and mixed layer depth as covariate. Thickness plotted as the means and least significant differences obtained from the multifactor ANOVA. (1 kt = 0.51 m/sec)
- Figure 7. A) Strength of the surface nutrient enrichment (SNE) of silicate, phosphate and nitrate with wind speed as factor and mixed layer depth (MLD) as covariate; B) mixed layer depth as factor and wind speed as covariate. Strength plotted as means and least significant differences obtained from the multifactor ANOVA. (1 kt = 0.51 m/sec)
- Figure 8. A) Strength of the subsurface nutrient reduction (SNR) of silicate, phosphate and nitrate with wind speed as factor and mixed layer depth (MLD) as covariate; B) mixed layer depth as factor and wind speed as covariate. Strength plotted as means and least significant differences obtained from the multifactor ANOVA. (1 kt = 0.51 m/sec)
- Figure 9. Vertical section of phosphate concentration along Line 93. The phosphate SNR between stations 90 and 120 follows isopycnals, indicating this feature is caused by advection of low phosphate waters from farther offshore. The minimum (a SNR) at stations 50-60, however, lies across isopycnals, an indication of in situ processes. (See also Fig. 10).
- Figure 10. Vertical section of density and silicate from the seven casts taken over 24 hrs while following a drifter at Station 93.50. The strong silicate SNR appears to be a complex structure resulting from both in situ (Casts 108-110, cross isopycnal SNR) and advective (Casts 110-112, SNR follows isopycnals) processes



Figure 1



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Figure 2



Figure 3



Figure 4A

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Figure 4B



Figure 5







Figure 6A







Figure 6B

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Figure 7A

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