The seasonal variation in the nutrient chemistry of the surface microlayer of Galway Bay, Ireland



Phosphorus Nitrogen Silicon Microlayer Galway Bay

Phosphore Azote Silice Microcouche Baie de Galway

Wm. Berry Lyons ^a, M. J. S. Pybus, J. Coyne Department of Oceanography, University College, Galway, Ireland. ^a Present address: Department of Earth Sciences, University of New Hampshire, Durham, N. H. 03824 U.S.A.

Received 12/8/79, in revised form 8/10/79, accepted 10/11/79.

ABSTRACT

Enrichments of various nutrient chemicals (C-N-P-Si) in the surface microlayer of the ocean have been demonstrated by various workers yet these studies have not dealt with possible temporal changes in microlayer chemistry. We have collected surface microlayer samples and bulk water samples 50 cm below the surface over a 20 month period at three regular stations in Galway Bay, Ireland. Phosphate enrichments coincided with spring phytoplankton blooms while reactive silicate and nitrate enrichments were associated with high chlorophyll a values in the sub-surface water. The data suggest that in Galway Bay, the largest nutrient enrichments in the surface microlayer are caused by biological activity.

Oceanol. Acta, 1980, 3, 2, 151-155.

RÉSUMÉ

Variations saisonnières des sels nutritifs présents dans le film superficiel (Baie de Galway, Irlande)

L'enrichissement de la couche ultrasuperficielle du milieu marin en sels nutritifs (C-N-P-Si) a été mise en évidence dans plusieurs travaux scientifiques, mais ces études n'ont pas lié ces changements à des modifications possibles dans la chimie du film de surface. Dans trois stations de la baie de Galway, nous avons collecté des échantillons du film superficiel et de la couche d'eau située à 50 cm au-dessous de la surface pendant une période de 20 mois. L'enrichissement en phosphate coïncide avec la floraison de printemps du phytoplancton alors que l'enrichissement en nitrate et en silicate « réactif » est associée à des valeurs élevées de chlorophylle a dans l'eau prélevée à 50 cm. Les résultats obtenus dans la baie de Galway permettent de penser que les enrichissements les plus forts observés dans ce film superficiel sont le résultat de l'activité biologique.

Oceanol. Acta, 1980, 3, 2, 151-155.

INTRODUCTION

Only recently has the chemistry of the surface microlayer (top 150 μ m) of the world's oceans been given much attention (MacIntyre, 1974). Little is known about this boundary between air and sea, and the interactions and processes involved in its development and composition are poorly understood (Duce *et al.*, 1972*b*). The knowledge of these interactions and processes should help to discern the importance of the boundary in the

geochemical cycling of elements and the effects of aerosol pollutants on the oceanic system.

The most frequently observed chemical phenomenon of the air-sea interface is the chemical enrichment of organic compounds and biologically active elements (Garrett, 1967; Williams, 1967; Duce *et al.*, 1972*a*, Wade, Quinn, 1975). The observed enrichments in the surface microlayer compared to the bulk water below could be caused by a number of proposed mechanisms, such as: 1) the aerosol input of continental materials, both weathering products (Prospero, Carlson, 1972) and anthropogenically introduced pollutants (Patterson, Settle, 1973; Daumas *et al.*, 1976), 2) rain, and 3) physical and chemical flotation processes involving particulates (Wallace *et al.*, 1972) and bubble scavenging (Baylor *et al.*, 1962).

The work of Goering and Menzel (1965), Goering and Wallen (1967), Williams (1967), and Barker and Zeitlin (1972) has established that soluble and particulate phosphorus and nitrogen compounds are enriched at the ocean's surface relative to the bulk water below. These studies of nutrient microlayer chemistry have not dealt with the possible temporal changes in microlayer enrichments caused by seasonal variations in seawater chemistry or biological productivity. The study of seasonal changes in the concentrations of nutrients in the surface microlayer provides insight into the mechanisms involved in the development and maintenance of the microlayer itself. The present study attempts to elucidate the effects of seasonal changes in productivity on the enrichment of nutrient chemicals in the microlayer of a temperate, unpolluted estuary.

STUDY SITE AND METHODS

Surface microlayer samples were collected monthly over a 20 month period during 1973-1974 at three regular stations in Galway Bay, Ireland (Fig.). Occasionally during this period, all three stations were not able to be sampled due to inclement weather. The three stations are designated as North Sound, South Sound and Inner Bay. The two Sound stations were selected since they are the major water exchange routes between the oceanic water to the west and the Bay water to the east. During high fresh water flow from the River Corrib and the surrounding smaller streams in Co. Galway, lower salinities are recorded in the surface water of the North Sound compared to that of the South Sound. The Inner Bay station was chosen because this area is more estuarine in character than the other two stations.



Sampling locations (•) in Galway Bay, Ireland.

Our microlayer sampling procedure is designed after that of Harvey and Burzell (1972). A clean 4 mm thick glass plate that has been pre-washed in concentrated HCl and rinsed in distilled water is vertically lowered and slowly withdrawn from the water surface. The water and associated hydrophobic surface film are then removed from the plate into a polyethylene sampling bottle using a neoprene rubber windshield wiper blade.

Prior to sampling, the wiper blade and collection container are cleaned and pre-rinsed in seawater. During the collection operations the glass plate is held by hand with a clean polyethylene glove. Hatcher and Parker (1974) have recently shown through laboratory experimentation that this sampling technique is more efficient for certain organic compounds than the more frequently used screen technique developed by Garrett (1965).

Collections were made and completed on the leeward side of the ship immediately after the vessel had come on station. Approximately 150 ml of the surface microlayer was generally obtained in a sampling interval of about 8 minutes.

The subsurface samples were collected at a depth of 50 to 100 cm using 1.3 l polyethylene NIO bottles. Upon collection, both samples were filtered through a prerinsed 9 cm Whatman GF/C fiber filter and immediately placed in a freezer at dry ice temperatures. The shipboard filtering and freezing were undertaken to ensure that particulate material was removed from the sample and that bacterial and container adsorption effects were kept to a minimum.

Laboratory experiments were conducted to determine the effect of our sampling technique on possible sample contamination. Estuarine water which had previously been analyzed for PO_4^{3-} , NO_3^{-} , NO_2^{-} and SiO_2 was subjected to the sampling procedure outlined above. This water was then analyzed for the above mentioned constituents. Within the precision of the techniques, no increase was observed in any of these nutrients.

At most of the stations where microlayer samples were collected, samples for chlorophyll *a* determinations were also taken. These samples were collected at a depth of 5 m using 3 1 PVC Van Dorn type bottles, filtered through Millipore 47 mm HA filters and stored according to the procedure of Stickland and Parsons (1968).

The nutrient samples were transferred in the frozen state from the vessel to the laboratory, where they were maintained in a deep freezer until the time of analysis. In most cases, the time between sampling and analysis was not more than two weeks. The samples were thawed and immediately analyzed for phosphate (Murphy and Riley, 1962) and nitrate (Wood *et al.*, 1967), using ammonium chloride instead of EDTA as recommended by Strickland and Parsons (1968). Nitrite was also determined using the technique of Bendschneider and Robinson (1952). Reactive silicate was determined 24 hours after thawing (Burton *et al.*, 1970) using the method of Mullin and Riley (1955). Chlorophyll *a* was determined according to Strickland and Parsons (1968).

Separate glassware was used with each analytical technique. Between analyses the glassware was stored

Table 1

Precision of analysis reported as a coefficient of variation.

PO4	SiO ₂	NO,
$\begin{array}{c} 0.32 \ \mu M .1^{-1} \pm 0.06 \\ 0.64 \ \mu M .1^{-1} \pm 0.03 \\ 1.29 \ \mu M .1^{-1} \pm 0.03 \end{array}$	$10.7 \ \mu M.1^{-1} \pm 0.2 \\ 1.1 \ \mu M.1^{-1} \pm 0.1 \\ -$	1.1 μM.1 ⁻¹ ± 0.1 - -

filled with distilled water. The precision of the various nutrient analyses reported as coefficients of variation are tabulated in Table 1.

Table	2
North	Sound.

RESULTS AND DISCUSSION

The results of the microlayer and subsurface samples from the three Galway Bay stations are presented in Table 2-4. The enrichment in the microlayer (E_s) is defined according to Piotrowicz *et al.*, (1972) as:

$$E_{s} = \left[\frac{[X] \text{ microlayer}}{[X] 0.5 \text{ m}}\right] - 1,$$

where [X] is the concentration of the respective nutrient at the depth indicated.

Date	PO₄ (μM.1⁻¹) Micro	PO₄ (μM.1 ⁻ ') 0.5 m	E,	SiO ₂ (µM.1 ⁻¹) Micro	SiO ₂ (µM.1 ⁻¹) 0.5 m	E _s	NO3 (µM.1 ⁻¹) Micro	NO, (μM.1 ⁻¹) 0.5 m	E _s	NO ₂ (μM.1 ⁻¹) Micro	NO₂ (μM.1 ') `0.5 m	E,	Chlorc " <i>a</i> " (µg/l)
10.3.73	1.19	1.00	0.2	8.1	7.6	0.1			_	_		_	_
15.5.73	0.41	0.29	0.4	1.8	1.2	0.5	0.6	0.4	0.0	< 0.1	< 0.1	0.0	1.23
15.6.73	0.41	0.32	0.3	3.1	3.1	0.0	0.3	0.1	0.0	< 0.1	< 0.1	0.0	1.32
14.8.73	0.58	0.32	0.8	2.6	2.4	0.1	0.2	< 0.1	0.0	0.3	0.2	0.0	1.28
12.9.73	0.74	0.67	0.1	2.9	3.5	-0.2	2.0	0.8	1.5	0.3	0.3	0.0	1.10
17.10.73	0.83	0.41	1.0	4.0	3.0	0.3	2.3	1.8	0.3	0.6	0.4	0.0	1.23
13.3.74	0.77	0.41	0.9	4.9	3.4	0.4	9.0	7.2	0.2	0.7	0.3	1.3	2.84
10.4.74	0.61	0.51	0.2	4.4	2.8	0.6	4.2	4.2	0.0	0.4	0.2	0.0	2.82
10.5.74	1.03	0.22	3.6	1.1	0.7	0.6	0.3	< 0.1	0.0	0.1	0.1	0.0	3.97
18.7.74	0.22	0.16	0.4	0.9	1.1	-0.2	< 0.1	< 0.1	0.0	< 0.1	< 0.1	0.0	1.22
18.9.74	0.35	0.51	-0.3	2.3	2.5	-0.1	0.8	0.7	0.0	0.2	0.2	, 0.0	1.39
15.10.74	0.77	0.54	0.4	4.8	4.0	0.2	1.6	3.2	-0.5	0.4	0.4	0.0	1.68

Table 3

South Sound.

Date	PO₄ (μM .1⁻¹) Micro	PO, (μΜ.1) 0.5 m	E _s	SiO ₂ (µM.1 ⁻¹) Micro	SiO, (µM,1 ⁻¹) 0.5 m	E _s	NO ₃ (μΜ.1 ¹) Micro	NO₃ (μM.1⁻') 0.5 m	E _s	NO ₂ (μΜ.1 ⁻¹) Micro	NO ₂ (µM.1 ⁻¹) 0.5 m	E _s	Chloro " <i>a</i> " (µg/l)
9.3.73	0.90	0.51	0.8	8.9	8.8	0.0	_	-	-	_	_	_	-
13.4.73	0.54	0.12	3.5	1.6	0.7	1.3	1.3	0.1	12.0		_	-	2.05
18.5.73	0.58	0.22	1.6	0.9	0.8	0.1	0.4	0.3	0.0	0.1	< 0.1	0.0	1.14
16.6.73	0.54	0.32	0.7	3.0	2.1	0.4	0.3	0.1	0.0	0.2	< 0.1	0.0	1.29
18.7.73	0.48	0.29	0.7	2.0	1.6	0.2	0.3	< 0.1	0.0	0.1	< 0.1	0.0	1.35
15.8.73	0.64	0.35	0.8	2.1	1.6	0.3	0.1	< 0.1	0.0	0.1	< 0.1	0.0	0.76
13.9.73	0.41	0.35	0.2	2.0	2.0	0.0	0.3	0.2	0.0	0.2	0.1	0.0	-
16.10.73	0.67	0.48	0.4	4.2	3.5	0.2	3.2	2.3	0.4	0.6	0.3	1.0	0.96
24.11.73	0.58	0.70	-0.2	5.1	4.8	0.1	5.7	6.0	0.0	0.4	0.3	0.0	1.11
9.4.74	0.83	0.64	0.3	4.9	4.1	0.2	8.6	7.6	0.1	0.3	0.3	0.0	1.39
20.6.74	0.41	0.32	0.3	2.1	2.7	-0.2	< 0.1	< 0.1	0.0	< 0.1	< 0.1	0.0	0.74
19.7.74	0.35	0.25	0.4	0.9	1.3	-0.3	0.1	< 0.1	0.0	< 0.1	< 0.1	0.0	1.67
17.10.74	0.96	0.70	0.4	5.4	3.8	0.4	2.6	2.3	0.1	2.3	0.5	3,6	1.21

Table 4

Inner Bay.

Date	PO₄ (μM.1 ⁻¹) Micro	PO ₄ (μM.1 ⁻¹) 0.5 m	E _s	SiO ₂ (µM.1 ⁻¹) micro	SiO ₂ (µM.1 ⁻¹) 0.5 m	E _s	NO₃ (µM . l⁻¹) Micro	NO ₃ (μM.1 ⁻¹) 0.5 m	E _s	NO ₂ (µM.1 ⁻¹) Micro	NO ₂ (µM.1 ⁻¹) 0.5 m	E,	Chloro " <i>a</i> " (µg/l)
11.3.73	_	_		8.7	8.3	0.0	-	_	-	_	_	_	_
14.4.73	0.35	0.06	4.8	0.9	0.7	0.3	_	-	-	 ,	_	-	_
16.5.73	0.41	0.12	2.4	2.3	0.4	4.8	0.7	0.1	6.0	0.1	< 0.1	0.0	1.26
26.7.73	0.51	0.35	0.4	1.6	1.5	0.0	0.1	< 0.1	0.0	< 0.1	< 0.1	0.0	-
16.8.73	0.77	0.45	1.2	1.5	1.5	0.0	< 0.1	< 0.1	0.0	0.2	< 0.1	0.0	1.84
16.10.73	0.83	0.45	0.8	3.5	3,1	0.1	2.5	1.8	0.4	0.8	0.6	0.0	-
24.11.73	1.35	0.90	0.5	8.0	7.6	0.0	7.1	7.6	- 0.1	0.9	0.6	0.0	-
19.2.74	1.90	1.09	0.7	6.0	10.1	-0.4	19.4	17.3	0.1	0.6	0.3	0.0	0.56
20.6.74	0.45	0.22	1.0	2.3	2.3	0.0	1.1	0.1	10.0	< 0.1	< 0.1	0.0	0.63
20.7.74	0.48	0.12	3.0	0.9	0.8	0.0	0.2	0.1	0.0	< 0.1	< 0.1	0.0	1.44
22.8.74	0.74	0.19	2.9	1.9	1.5	0.3	0.7	0.2	2.5	< 0.1	< 0.1	0.0	1.08
16.10.74	0.77	0.29	1.7	6.3	5.0	0.3	2.9	1.6	0.8	0.8	0.2	3.0	1.04

Phosphate was enriched in the microlayer relative to the water 50 cm below in all but two samples. In 1973 the largest enrichments were observed in the April and May samples from the South Sound and Inner Bay stations. In the following year the maximum phosphate enrichment occurred in the North Sound in the May sample. These enrichments coincide with the spring phytoplankton bloom in Galway Bay in each year.

Reactive silicate enrichments were all below $E_s = 0.4$ except in April of 1973 for the South Sound, the Inner Bay in May of 1973 and the North Sound in May of 1973 and April and May of 1974. All these were associated with high chlorophyll *a* values in the subsurface water.

Surface microlayer enrichments of nitrate were less frequent than those of phosphate and less systematic than those of reactive silicate. Albeit, the largest enrichment of any of the nutrients studied was that of nitrate in the April 1973 sample from the South Sound. This too was associated with one of the highest chlorophyll *a* values recorded $(2.05 \ \mu g.l^{-1})$.

Baylor *et al.* (1962) suggested that the enrichment of phosphate in the surface microlayer of the ocean could be due to the adsorption of phosphate on rising gas bubbles. Goering and Wallen (1967) found that a difference in sea states from Beaufort 2 to 4 was unable to affect significantly the vertical distribution of phosphate. They, in turn, ruled out a wind induced bubbling transport mechanism for phosphate enrichment in the surface microlayer. Our observations of sea state (Beaufort 1-5) show no relationship with the enrichments found in the microlayer.

It has been proposed by Daumas (1974) that the changes in nutrient chemistry of the surface microlayer may be a valuable indicator of phytoplankton growth, while Piotrowicz *et al.* (1972) have concluded that the concentrations of various trace metals in the surface microlayer are, in part, controlled by biological activity. From our results it appears that enrichment of the microlayer is associated with phytoplankton growth. If wind speed is important in maintaining nutrient enrichments in the microlayer of Galway Bay, it seems to be a secondary effect.

Baier and Goupil (1973) indicate that the natural sea slicks sampled off the southeast coast of the U.S.A. include a major silica component that is associated with diatom remnants. They suggest that these natural forming surface slicks have their origin in plankton blooms. In this study on the occasions when enrichment of reactive silicate in the microlayer was observed, chlorophyll a values were high and surface water

silicate concentrations were decreasing. It would appear that during periods when diatoms are removing large quantities of reactive silicate from the photic zone, the enrichment of reactive silicate in the microlayer is the largest. This adds credence to the argument that the enrichment of nutrients in the microlayer is related to phytoplankton activity. The increased enrichment of dissolved silicate in the microlayer in the spring may be due to the breakdown and dissolution of diatom remanants that have been transported to the surface by some unspecified mechanism.

Nitrate enrichments in the microlayer were also related to periods of high phytoplankton concentration. Enrichment also apparently occurred at times during the summer months, however at this time the concentrations of both nitrate and nitrite were approaching the limits of detection of the methods used and these results may therefore be misleading. The nitrite concentrations in the surface microlayer were always greater than those 50 cm below. This suggests three possible mechanisms: 1) the oxidation of NH_3^- to NO_2^- by bacterial nitrification in the microlayer (Goering, Menzel, 1965), 2) the reduction of NO_3^- to NO_2^- by nitrate reducing bacteria in the microlayer (Goering, Menzel, 1965), or 3) the photolysis of NO_3^- to NO_2^- in the microlayer (Zafiriou, 1974). Unfortunately, our data do not allow us to suggest which mechanism might be most responsible.

The data from this study suggest that in Galway Bay nutrient chemical enrichment in the surface microlayer is directly related to biological activity. Maximum enrichments occur at times of maximum phytoplankton growth.

Acknowledgments

We would like to deeply thank our UCG colleagues, T. Furey, A. Hensey, F. I. O'Brien and P. de Bhaldraithe for their help in obtaining the samples. We acknowledge Prof. B. McK. Bary for his encouragement and support of this research. The senior author is deeply indebted to all those who made his stay in Ireland so dear. Drs. T. C. Loder and H. E. Gaudette reviewed the original manuscript. This is UNH CREAM contribution No. 33.

REFERENCES

Baier R. E., Goupil D. W., 1973. Collection and identification of sea surface films with special attention to natural slicks and foams, *Abstracts, Bull. Union. Oceanogr. Fr.*, A-1, August.

Barker D. R., Zeitlin H., 1972. Metal ion concentrations in seasurface microlayer and size-separated atmospheric aerosol samples in Hawaii, J. Geophys. Res., 77, 5076-5086.

Baylor E. R., Sutcliffe W. H., Hirschfeld D. S., 1962. Absorption of phosphates on to bubbles, *Deep-Sea Res.*, 9, 120-124.

Bendschneider R. K., Robinson R. J., 1952. A new spectrophotometric determination of nitrite in seawater, J. Mar. Res., 11, 87-96.

Burton J. D., Leatherland T. M., Liss P. S., 1970. The reactivity of dissolved silicon in some natural waters, *Limnol. Oceanogr.*, 15, 473-476.

Daumas R. A., 1974. Influence de la température et du développement planctonique sur le mécanisme d'accumulation de la matière organique à la surface de la mer, *Mar. Biol.*, **26**, 111-116.

Daumas R. A., Laborde P. L., Marty J. C., Saliot A., 1976. Influence of sampling method on the chemical composition of water surface film, *Limnol. Oceanogr.*, **21**, **2**, 319-326.

Duce R. A., Quinn J. G., Olney C. E., Piotrowicz S. R., Ray B. J., Wade T. L., 1972 a. Enrichment of heavy metals and organic compounds in the surface microlayer of Narragansett Bay, R. I., *Science*, 197, 161-163.

Duce R. A., Stumm W., Prospero J. M., 1972 b. Working symposium on sea-air chemistry: Summary and recommendations, J. Geophys. Res., 77, 5059-5061.

Garrett W. D., 1965. Collection of slick-forming materials from the sea surface, *Limnol. Oceanogr.*, 10, 602-605.

Garrett W. D., 1967. The organic chemical composition of the ocean surface, *Deep-Sea Res.*, 14, 221-227.

Goering J. J., Menzel D. W., 1965. The nutrient chemistry of the sea surface, *Deep-Sea Res.*, 12, 839-843.

Goering J. J., Wallen D., 1967. The vertical distribution of phosphate and nitrite in the upper one-half meter of the southeast Pacific, *Deep-Sea Res.*, 14, 29-33.

Harvey G. W., Burzell L. A., 1972. A simple microlayer method for small samples, *Limnol. Oceanogr.*, 17, 156-157.

Hatcher R. F., Parker B. C., 1974. Laboratory comparisons of four surface microlayer samplers, *Limnol. Oceanogr.*, 19, 162-165.

MacIntyre F., 1974. Chemical fractionation and the sea-surface microlayer processes, in *The Sea*, volume 5, edited by E. D. Goldberg, Wiley-Interscience. New York, 245-300.

Mullin J. B., Riley J. P., 1955. The colorimetric determination of silicate with special reference to sea and natural waters, *Anal. Chim. Acta*, 12, 162-176.

Murphy J., Riley J. P., 1962. A modified single solution for the determination of phosphate in natural waters, *Anal. Chem. Acta*, 27, 31-36.

Patterson C., Settle D., 1973. Contributions of industrial lead via aerosols to the occans, *Abstracts, Bull. Union Oceanogr. Fr.*, D-6, August.

Prospero J. M., Carlson T. N., 1972. Vertical and aeral distribution of Saharan dust over the western equatorial North Atlantic Ocean, J. Geophys. Res., 77, 5255-5256.

Piotrowicz S. R., Ray B. J., Hoffman G. L., Duce R. A., 1972. Trace metal enrichment in the sea-surface microlayer, J. Geophys. Res., 77, 5243-5254.

Strickland J. D. H., Parsons T. R., 1968. A Practical Handbook of Seawater Analysis, Fisheries Research Board of Canada Bulletin 167, Ottawa, 311 p.

Wade T. L., Quinn J. G., 1975. Hydrocarbons in the Sargasso Sea Surface microlayer, Mar. Pollut. Bull., 6, 54-57.

Wallace G. T. Jr., Loeb G. I., Wilson D. F., 1972. On the flotation of particulates in seawater by rising bubbles, J. Geophys. Res. 77, 5293-5301.

Williams P. M., 1967. Sea surface chemistry: organic carbon and the organic and inorganic nitrogen and phosphorus in surface films and subsurface waters, *Deep-Sea Res.*, 14, 791-800.

Wood E. D., Armstrong F. A. J., Richards F. A., 1967. Determination of nitrate in seawater by cadmium-copper reduction to nitrite, J. Mar. Biol. Assoc. U. K., 47, 23-31.

.

156