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The sea-surface microlayer: phytoneuston productivity and effects of atmospheric particulate matter

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Abstract

The sea-surface microlayer, the upper 50 μm of the ocean surface, provides a habitat for an important biota (the neuston), an interface for exchange of gases between the atmosphere and oceans and a site for deposition of anthropogenic metals and other materials from the atmosphere. Several recent studies have suggested that biochemical processes, including photosynthesis, in the microlayer are inhibited relative to the bulk seawater. We compared the biomass, species composition and productivity of phytoneuston to that of phytoplankton in Sequim Bay, Washington State, USA. Mean enrichment ratios (microlayer:bulk water concentrations) for bacteria, microalgae, chlorophyll pigments and photosynthesis (estimated gross) were 2 444, 380, 12 and 40, respectively. Compared to the bulk water, the microlayer had a unique assemblage of microalgae with a higher concentration of chlorophyll *c*. When exposed to high light intensities (summer) or metal-rich urban atmospheric particulate matter, radiocarbon-measured photosynthesis was lower in phytoneuston than in phytoplankton. Deposition of atmospheric particulate matter at rates similar to those occurring in urban coastal areas resulted in a significant ($P < 0.01$) reduction in radiocarbon-measured photosynthesis in the sea-surface microlayer. These apparent decreases in photosynthesis are believed to result from the extracellular release of ^{14}C as glycolate or other soluble compounds and may not reflect a true decrease in gross primary productivity in the microlayer. Further measurements of the degree of extracellular carbon release will be necessary to quantify gross photosynthetic rates in the microlayer.

Introduction

The sea-surface microlayer (upper 50 μm or less) covers 71% of the Earth's surface, and biological and chemical processes in the microlayer could affect the exchange of gases as well as anthropogenic materials between the atmosphere and oceans (MacIntyre, 1974; Wangersky, 1976). Of the 5 billion metric tons of carbon released to the atmosphere annually from the burning of fossil fuel, about 1 billion metric tons diffuse across the air-sea interface into the dissolved CO_2 pool of surface ocean water (Smith, 1981). In addition, a major portion of metals (Settle and Patterson, 1982) and hydrocarbons (Hunter and Liss, 1977; Atlas and Giam, 1981) released from the combustion of fossil fuels deposits on the sea surface.

Neuston (microorganisms which inhabit the aquatic microlayer) could affect the exchange rates of gases and materials at the interface. Any negative impact on the health or physiology of neuston, then, could have important implications for the global cycling of materials (Hardy, 1982).

Previous comparisons of phytoneuston and phytoplankton differ in their results. Many reports indicate an enrichment of biological activity in the microlayer with, for example, phytoneuston (microalgae) densities 10 to 10 000 times greater than phytoplankton densities only a few centimeters below (Harvey, 1966; Bursa, 1968; Maynard, 1968; Hardy, 1973; Manzi *et al.*, 1977; Wandschneider, 1979; Nesterova, 1980; Hardy and Valett, 1981). Several studies of chlorophyll pigments in the microlayer compared to the bulk water have found high surface enrichments at least in natural slick areas (Nishizawa, 1971; Harvey and Burzell, 1972; Hardy, 1973; Gallagher, 1975). Likewise, studies of photosynthetic productivity indicate that the microlayer is about ten times as productive as the subsurface water (Hardy, 1973; Gallagher, 1975).

Other studies have found depletions or only occasional enrichments in the microlayer biota. For example, Taguchi and Nakajima (1971) reported enrichments of chlorophyll pigments in only 9 of 22 samples and Daumas *et al.* (1976) found a drum-collected sample from a clean area depleted while a polluted area was enriched. Also, several reports

suggest that neuston are stressed in some way and not as physiologically active as plankton (Marumo *et al.,* 1971; Dietz *et al.,* 1976). Depletions in microlayer chlorophyll *a* (Albright, 1980; Carlson, 1982) and photosynthetic carbon fixation (Albright, 1980) compared to bulk water have been attributed to inhibitory factors such as high light intensities in the sea-surface microlayer.

Metals, primarily of atmospheric and anthropogenic origin (Patterson and Settle, 1974; Duce *et al.,* 1976; Dehairs *et al.,* 1982), frequently occur in high concentrations in sea-surface microlayers relative to the bulk seawater (Dehairs *et al.,* 1982; Hardy *et al.,* in press, a, b). We suggested that biologically active metals might inhibit the photosynthetic productivity of phytoneuston (Hardy and Crecelius, 1981). Others have suggested that anthropogenic contaminants, collecting at the air-sea interface, could lead to a decrease in worldwide productivity beginning with a supression of the photosynthetic activity of phytoneuston (Mileikovskii, 1981).

We conducted microcosm and field studies to test the hypothesis that the sea-surface microlayer is typically depleted in species, chlorophyll pigments and photosynthetic productivity compared to the subsurface water. In addition, we examined sea-surface deposition of urban atmospheric particulate matter as a potential inhibitor of photosynthesis in natural phytoneuston and phytoplankton populations.

Materials and methods

Bacterial density

Densities of bacterioneuston and bacterioplankton present during the photosynthetic experiments were determined. Samples were collected from the microlayer (upper 20 μm) using the polycarbonate filter technique (Sewell *et al.,* 1981) and from 10 cm depth in the water through a syringe. Acridine orange was added to the samples and stained individuals were enumerated by epifluorescence microscopy (Watson *et al.,* 1977).

Species abundance of microalgae

Samples were collected from the microlayer (upper 50 μm) by the glass plate technique (Hardy *et al.,* in press, b) and from the bulk water (20 cm depth) by subsurface opening of 250 ml polyethylene bottles. Samples were preserved in Lugol's iodine solution, concentrated by settling and enumerated at 400× magnification by the Ütermohl technique to a 10% confidence level for the total counts (Venrick, 1978). Our purpose was to obtain an estimate of total abundance and numbers within major taxonomic groups; consequently, no attempt was made at detailed species identifications. In all samples, occasional dead cells were found. These were rare, and only visibly viable (chloroplast-containing) cells were enumerated.

Chlorophyll pigments

Samples were collected from Sequim Bay (Washington State, USA) near the laboratory in July. To derive mean values for the entire bay, a random sampling method was employed. The bay was divided into 250 numbered quadrats and the 7 stations to be sampled in the middle of each quadrat were drawn from a random number generator. Samples for chlorophyll were also collected during the photosynthetic experiment of 21 July 1983. Samples were collected from the microlayer (upper 50 μm) with a glass plate sampler (Hardy *et al.,* in press, b) and from the subsurface water (0.5 m depth) by subsurface opening of 2-liter polyethylene bottles. Samples were filtered, frozen at −70 °C, later extracted with a tissue grinder in 90% acetone and then analyzed for pigments using the spectrophotometric equations of Strickland and Parsons (1972).

Photosynthetic productivity

Photosynthetic rates of phytoneuston and phytoplankton and the effects of atmospheric particulate matter (APM) were determined by both incubator and *in situ* experiments. Seawater was collected at outgoing to slack tide near the entrance to Sequim Bay. In six experiments conducted between January and May, 1983, water was collected in 1-liter polyethylene beakers. Duplicate treated beakers were placed in an incubator at ambient seawater temperature either in the light (85 μE m^{-2} s^{-1} cool-white fluorescent) or in the dark. In the July experiment, seawater was collected in 7.6-liter clear polycarbonate tanks (Cambro® Co.) modified to contain a drain near the bottom. Tanks, with lids on, were lowered below the surface, the lids were removed and the tanks were raised slowly to the surface (with the drain open) to trap the surface microlayer and 6 liters of subsurface water. The drains were closed and duplicate tanks without lids were placed in an outdoor sea table, cooled with flowing ambient-temperature seawater and exposed to natural daylight (mean 1 230 μE m^{-2} s^{-1}). Dark tanks or beakers were placed in an incubator at the same temperature. $NaH^{14}CO_3$ (0.1 to 0.5 ml; 200 to 1 000 μCi l^{-1} of seawater) was added below the water surface of all experimental tanks. Salinity was measured with a refractometer and light energy, in the photosynthetically active wavelength range (400 to 700 nm), with a Li-Cor Inc.® photometer (LI-185A, with 190-S probe).

Urban APM (NBS Standard 1648) contains high levels of potentially toxic metals, especially Pb (Hardy and Crecelius, 1981). Between 0 (control) and 256 μg m^{-2} of APM was sprinkled onto the water surface of each container. The APM dust dispersed within 1 to 2 min to form an almost uniform layer on the water surface.

After 4 h incubation (10.00 to 14.00 hrs), we collected samples of microlayer and subsurface water. Microlayer samples were collected on 47 mm diam 0.45 μm polycarbonate filters (Unipore®, Bio Rad Laboratories). The

filters were floated on the surface for 1 min and then lifted off with forceps (Kjelleberg *et al.*, 1979; Van Vleet and Williams, 1980; Sewell *et al.*, 1981; Syzdek, 1982). The quantity of sample removed from the microlayer was determined gravimetrically and indicated a volume of $32.6 \pm 7.6\ \mu l$ (SD) or a sample depth of $20\ \mu m$. The samples were placed, sample side up, on a filter holder and rinsed at less than 1 atm vacuum with 100 ml of clean prefiltered seawater. For collection of subsurface water, 50 ml samples were taken by syringe, filtered onto polycarbonate filters (as above) and rinsed. Filters were fumed over concentrated HCl to remove inorganic carbon (Lean and Burnison, 1979) and counted by liquid scintillation. Counts were corrected for background and efficiency (external standards ratio) and converted to mg carbon using appropriate pH, salinity and carbonate alkalinity (Strickland and Parsons, 1972).

Results

Ambient seawater and incubation temperatures ranged from 8.3 °C in January to 13.0 °C in July. Salinity was 30‰ from January to 4 May, and 31‰ on 24 May and 21 July. Daylight conditions from January through 4 May were mostly cloudy before and on the day of sample collection, with light energy (similar to the incubator) of 85 $\mu E\ m^{-2}\ s^{-1}$ or less. The week previous to and on the day of 24 May and 21 July experiments, the weather was clear with bright sun.

On the average over the sampling seasons, concentrations of bacteria, microalgae, total chlorophyll pigments and rates of photosynthetic carbon fixation were all highly enriched in the surface microlayer compared to the bulk seawater (Fig. 1).

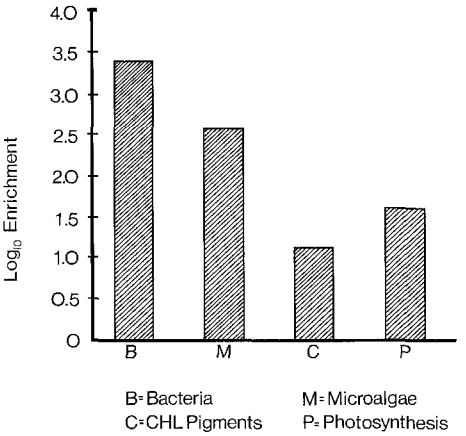

Fig. 1. Mean biological enrichments over the 5 sampling months (microlayer concentration divided by bulk water concentration)

Bacteria

Bacteria were abundant in both the microlayer and subsurface water during the photosynthetic experiments (Table 1). Densities of total bacterioneuston were significantly greater than those of bacterioplankton. Ratios of neuston to plankton density (N:P) were 133 in February, 23 to 34 in April through May, and reached over 12 000 in July when a dense, visible, surface-slick was present.

Microalgae

We found major differences in abundance and taxonomic composition between the phytoneuston and phytoplankton (Table 2). Phytoneuston were consistently more abundant than phytoplankton. Ratios of density (N:P) for total individuals were 4 to 9 in April and May and reached over 1 500 in July. Some taxa (*Cocconeis* sp., *Cylindrotheca* sp., small pennate diatoms, *Tropidoneis* sp., *Cyclotrichium* sp., *Cryptomonas* sp., small microflagellates and *Ebria tripartita*) occurred preferentially as part of the neuston community. Other taxa (*Chaetoceros* sp., *Skeletonema* sp. and *Amphidinium* sp.) were typically or exclusively planktonic (Table 2).

Chlorophyll pigments

In July, the microlayer enrichment of photosynthetic pigments differed according to the pigment type. Throughout Sequim Bay, chlorophyll *a* concentrations in the microlayer compared to the bulk water were enriched at some stations and depleted at others. A similar pattern for chlorophyll *a* has been reported elsewhere (Carlson, 1982). Considering the mean and variance over all seven stations sampled in Sequim Bay on 11 July, there was no significant difference between chlorophyll *a* concentrations in the microlayer (upper $50\ \mu m$) and bulk water (30 cm) depth (Table 3). Chlorophylls *b* and *c*, on the other hand,

Table 1. Total number of bacteria per ml in neuston and in plankton of Sequim Bay, Washington State, USA, in 1983. Values are means ($\pm$ SD)

Sample	25 February	6 April	4 May	24 May	21 July
Bacterioneuston (N) (microlayer)	4.60×10^8 (4.83×10^8)	1.41×10^7 (0.69×10^7)	1.96×10^7 (5.00×10^6)	2.58×10^7 (6.46×10^6)	30.5×10^9 (6.7×10^9)
Bacterioplankton (P) (bulk water)	3.45×10^6 (2.77×10^6)	4.67×10^5 (3.51×10^5)	8.6×10^5 (1.8×10^5)	7.7×10^5 (1.8×10^5)	2.46×10^6 (4.5×10^5)
Ratio N:P	133	30	23	34	12.3×10^3

Table 2. Abundance of microalgae (individuals ml^{-1}) in neuston and plankton of Sequim Bay, Washington State, USA

Taxon	6 April 1983		4 May 1983		24 May 1983		21 July 1983	
	Neuston	Plankton	Neuston	Plankton	Neuston	Plankton	Neuston	Plankton
Centric diatoms								
Chaetoceros sp.	0.00	0.00	0.00	0.00	0.00	260.00	0.00	2 700.00
Coscinodiscus sp.	0.00	0.00	0.00	30.00	0.00	0.00	0.00	0.00
Leptocylindrus sp.	0.00	0.00	100.00	79.00	0.00	15.00	0.00	0.00
Rhizosolenia spp.	23.00	0.00	0.00	3.00	1 990.00	182.00	0.00	0.00
Skeletonema sp.	0.00	0.00	0.00	0.00	0.00	130.00	0.00	0.00
Melosira sp.	0.00	0.00	100.00	0.00	100.00	0.00	0.00	0.00
Pennate diatoms								
Cocconeis sp.	0.00	0.00	40.00	3.00	300.00	0.00	7 576.00	0.00
Cylindrotheca sp.	13.00	5.00	100.00	30.00	50.00	33.00	8 250.00	20.00
Navicula sp.	0.00	0.00	0.00	41.00	0.00	0.00	0.00	59.00
Nitzschia sp.	0.00	0.00	540.00	330.00	400.00	200.00	0.00	0.00
Small pennates	81.00	29.00	610.00	20.00	2 180.00	28.00	39 904.00	60.00
Tropidoneis sp.	0.00	0.00	0.00	0.00	50.00	0.00	82 500.00	0.00
Ciliates								
Cyclotrichium sp.	6.40	5.80	20.00	0.00	50.00	10.00	0.00	0.00
Dinoflagellates								
Amphidinum sp.	0.00	14.85	0.00	0.00	0.00	0.00	0.00	0.00
Dinophysis sp.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	20.00
Gymnodinium sp.	0.00	0.00	0.00	3.00	0.00	0.00	0.00	0.00
Peridinium sp.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	20.00
Unidentified spp.	89.00	14.00	20.00	3.00	0.00	0.00	31.00	0.00
Euglenoids								
Eutreptiella marina	6.40	1.70	50.00	0.00	0.00	2.60	0.00	0.00
Microflagellates								
Cryptomonas sp.	170.00	67.00	100.00	30.00	400.00	150.00	0.00	19.70
Unidentified spp.	174.00	8.40	6 070.00	290.00	1 850.00	270.00	4 260 000.00	59.00
Silicoflagellates								
Dictyocha sp.	0.00	0.00	0.00	0.00	0.00	2.60	0.00	0.00
Ebria tripartita	0.00	7.30	100.00	0.00	1 850.00	5.10	96 000.00	0.00
Total	562.80	153.05	7 750.00	862.00	9 220.00	1 319.30	4 494 230.01	2 957.70
Ratio neuston:plankton	3.7		9.0		7.0		1 519	

Table 3. Chlorophyll pigments (mg m^{-3}) in the microlayer (neuston) and bulk seawater (plankton) of Sequim Bay

		Chl *a*	Chl *b*	Chl *c*	Total chl	Phaeo-pigment
July 11	Neuston	23±28	6±16	61±20	94±41	21±23
(7 stations throughout bay)	Plankton	13±10	0	8± 3	21±13	1± 1
$n = 7$	Enrichment[a]	–	+	+	+	–
July 21	Neuston	1 213±24	5±8	556±166	1 775±150	177±54
(experiment)	Plankton	7± 1	0	10± 2	17± 3	0
$n = 2$	Enrichment[a]	+	–	+	+	+

[a] Significantly elevated in the microlayer compared to subsurface water ($P<0.05$); Student's *t*-test

were highly enriched in the microlayer compared to the bulk water, resulting in an average total chlorophyll concentration 4.5 times greater in the microlayer than in the bulk water. Phaeopigments, chlorophyll degradation products, were generally higher in the microlayer at the seven stations (11 July), but their enrichment was not significant, due to the variability between sampling stations.

During the photosynthetic experiment of 21 July, the concentration of total active pigments was 100 times greater in the microlayer than in the bulk water; phaeo-

pigments were high in the neuston, but absent in the plankton (Table 3). Samples for the experiment were from a thick, visible, surface-slick. Such natural slicks cover much of the area of the bay during mid-to-late summer.

Photosynthetic productivity

The difference between carbon fixation in the light and the dark normally yields a rate of particulate carbon fixation believed to be somewhere between gross and net photosynthesis (Harris, 1978; Peterson, 1980). We found that radiocarbon-measured photosynthetic rates were much greater in the microlayer than in the bulk water during the winter and spring. From January to early May, phytoneuston productivity (light minus dark values) without additions of APM was between 8 and 227 mg C m^{-3} h^{-1} compared to rates of 0.25 to 6.5 mg m^{-3} h^{-1} in the bulk phytoplankton (Table 4). Productivity of the phytoplankton was low in winter, increased during the typical spring bloom (Chester *et al.*, 1979), and then decreased in mid-summer (21 July). In contrast, particulate carbon fixation (light minus dark) in the phytoneuston was highest during the winter and early spring (21 January–4 May), but decreased to negative rates during summer (Table 4). The negative summer values in the phytoneuston result from low rates of carbon fixation in the light compared to the dark. However, when carbon fixation in the light only is compared, that in the neuston was about 14 times greater than that in the plankton even in summer.

Photosynthetic efficiency (μg C h^{-1} $cell^{-1}$) ranged between 2 and 8 for the phytoplankton, but in the phytoneuston decreased from 15 in April to 0.05 in July, probably reflecting increasing photoinhibition in the surface layer (Fig. 2). Also, on 21 July, photosynthesis per unit chlorophyll in phytoneuston was only 34% of that in phytoplankton.

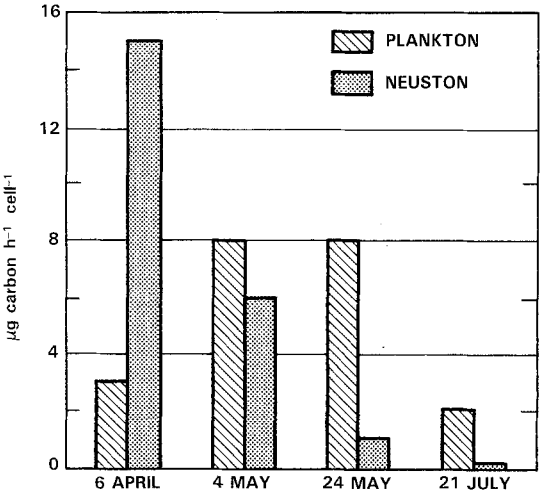

Fig. 2. Photosynthetic efficiency in the sea-surface microlayer

In January, we also measured the increase in dissolved carbon possibly released by photorespiration. Over a period of 7 h of light, followed by 17 h of dark there was 46 mg C m^{-3} h^{-1} more dissolved carbon (activity passing through a 0.45 μm membrane filter) released during the light/dark cycle than in the continuous dark exposure.

Our data (Table 4) indicate that addition of atmospheric particulate matter rich in metals inhibited photosynthesis in the neuston as measured by light minus dark radiocarbon uptake. Photosynthesis as a percentage of the control (no APM addition) decreased exponentially with increasing APM deposition rates (Fig. 3). APM additions as low as 1 mg m^{-2} h^{-1} resulted in a significant ($P < 0.01$)

Table 4. Influence of atmospheric particulate matter (APM) on photosynthetic productivity (mg C m^{-3} h^{-1} ± SD), *N*: no. of replicates for each condition

Date	APM (mg m^{-2} h^{-1})	*N*	Neuston (N)				Plankton (P)			Ratio N:P
			Light	Dark	Light minus dark	% change from control	Light	Dark	Light minus dark	
21 Jan	0	4	455 ± 249	228 ± 84	227 ± 148	–[a]	1.89 ± 0.38	0.30 ± 0.29	1.6	143
	3	3	209 ± 251	225 ± 187	−16 ± 103	−116 ± 31	2.98 ± 0.95	0.33 ± 0.31	2.7	0
	16	4	104 ± 62	231 ± 213	−128 ± 133	−134 ± 49	2.52 ± 0.35	0.41 ± 0.24	2.1	0
25 Feb	0	4	15.0 ± 1.0	7.0 ± 1.2	8.0 ± 0.6	–[a]	0.27 ± 0.06	0.02 ± 0.00	0.25	27
	0.5	4	10.5 ± 1.0	4.4 ± 0.5	6.1 ± 0.5	−21 ± 8	0.32 ± 0.08	0.03 ± 0.01	0.29	21
	1.7	3	15.4 ± 2.7	9.2 ± 4.5	6.2 ± 1.9	−22 ± 27	0.30 ± 0.08	0.04 ± 0.01	0.26	23
6 April	0	4	18.9 ± 2.5	10.6 ± 3.7	8.3 ± 2.2	–[a]	0.45 ± 0.19	0.05 ± 0.02	0.4	20
4 May	0	4	62.0 ± 5.1	18.9 ± 6.9	43.1 ± 2.0	–[a]	6.73 ± 5.79	0.20 ± 0.11	6.5	7
	16	4	81.1 ± 45.0	114.5 ± 58.1	−33 ± 30	−180 ± 73	9.79 ± 5.84	0.31 ± 0.14	9.5	0
	64	4	65.0 ± 27.0	105 ± 83	−40 ± 59	−201 ± 150	11.73 ± 0.68	0.33 ± 0.09	11.4	0
24 May	0	3	59 ± 12	140 ± 12	−81 ± 1	–[a]	10.35 ± 5.14	0.27 ± 0.11	10.1	1[b]
21 July	0	5	177 ± 53	236 ± 50	−59 ± 16	–[a]	6.14 ± 0.25	0.18 ± 0.04	5.96	34[b]

[a] Control value, i.e., no added APM
[b] Estimate based on 60% extracellular ^{14}C release from photoinhibition

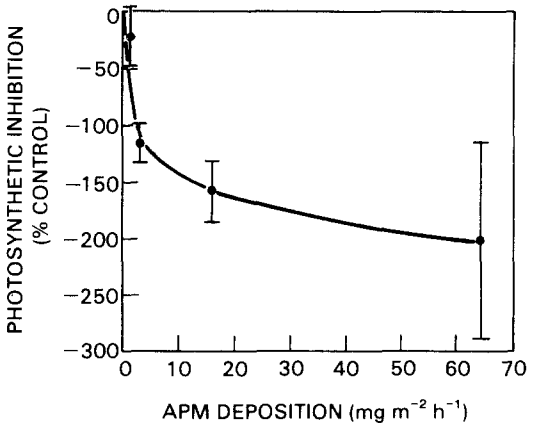

Fig. 3. Inhibition (percentage change from control) of radiocarbon-measured primary productivity in the sea-surface microlayer (upper 20 μm) with increasing additions of metal-rich atmospheric particulate matter (APM)

reduction in the light minus dark photosynthetic rate of phytoneuston.

Discussion and conclusions

Our results support those of Albright (1980) and Carlson (1982) and indicate no consistent enrichment of chlorophyll *a* in the microlayer. However, we find that concentrations of total active chlorophylls (chlorophylls $a+b+c$), on the average, are 12 times greater in the microlayer than in the bulk water. Unpublished studies by us confirm that such microlayer pigment enrichments are typical in Puget Sound. Chlorophylls *b* and *c* are believed to transfer energy to chlorophyll *a*, especially under conditions of high light intensity (Jeffrey, 1980) typical of the surface microlayer. The higher concentrations of accessory pigments in the microlayer probably reflect the abundance of cryptomonads and diatoms at the surface. Because of high variability in concentrations between field stations (July 11), we found no significant difference in phaeopigment concentrations, although enrichment of these pigments in the microlayer was strongly suggested (Table 3). High phaeopigment concentrations in the microlayer could result from: (1) photo-oxidation of chlorophyll under high surface light intensities, (2) a higher grazing rate and pigment digestion by zooneuston compared to zooplankton, or (3) simply collection of less active or dead phytoplankton at the surface. The last possibility seems unlikely since we found a unique species composition and no apparent increase in the percentage of dead cells in the phytoneuston compared to the phytoplankton. Thus, our results do not support the hypothesis that the microlayer is typically depleted in chlorophyll pigments compared to the subsurface water.

We found that during the summer, or in winter and spring when exposed to levels of urban atmospheric particulate matter >2 mg m^{-2} h^{-1}, carbon fixation rates of neuston appeared lower in the light than in the dark (Table 4). Ultraviolet radiation can reduce carbon-14 measured photosynthesis in surface waters (Lorenzen, 1979; Smith and Baker, 1980; Worrest *et al.*, 1980, 1981). However, the ^{14}C technique underestimates total photosynthesis in proportion to the release of ^{14}C-labelled soluble products of photosynthesis from cells. Such apparent photoinhibition is a common occurrence in *in situ* ^{14}C experiments, especially in the presence of high levels of ultraviolet irradiance (Harris, 1980), when marine diatoms are exposed to elevated levels of lead (Rivkin, 1979) or during nutrient depletion (Harris, 1978). Thus, subtraction of dark ^{14}C fixation from light ^{14}C fixation can lead to serious underestimates of primary production (Legendre *et al.*, 1983).

Rapid formation of glycolate and other soluble organics appears to occur when cells are metabolically stressed (Sharp, 1977) and increases with increasing photoinhibition (Fogg, 1966). These compounds are released as soluble extracellular products or metabolized by the glycolate pathway to CO_2 (photorespiration). The percentage of ^{14}C released in this way increases with light intensity and can exceed 90% of the total fixed carbon in the presence of very high light intensities (Watt, 1966). Even in our January experiment, we found a significantly higher release of dissolved ^{14}C in the light over that in the dark. Light-saturated rates of photosynthesis often occur in phytoplankton above about 100 μE m^{-2} s^{-1} (Harris, 1978). At the natural light intensity of our July experiment (1 230 μE m^{-2} s^{-1}), photoinhibition probably exceeds 60% (Harris, 1980). Applying a 60% correction to our neuston rates in the light, light minus dark carbon fixation on 24 May becomes: 59 mg m^{-3} h^{-1} [in light] $\times$ 2.5 [correction factor for photoinhibition] $-$ 140 mg^{-3} h^{-1} [in dark] $=$ 7.5 mg m^{-3} h^{-1}, a value slightly less than that of the plankton. Similarly, on 21 July, productivity would be 34 times greater in the neuston than in the plankton. Such corrections provide, at best, only an estimate of the actual productivity. Future studies on neuston productivity should include measurements of extracellular carbon release and/or a correction using the inhibitor 3-(3,4-dichlorophenyl)-1,1-dimethyl urea (DCMU) to replace the dark bottle (Legendre *et al.*, 1983).

Albright (1980) found that the photosynthetic activity of phytoneuston in coastal British Columbia was inhibited compared to the plankton. However, data for light-dark bottles only were reported. Thus, identification of possible photorespiration or extracellular release of carbon is not possible. In addition, Albright's samples were preserved in formalin which can cause marked losses of ^{14}C from the particulate fraction (Peterson, 1980), especially from delicate flagellates which often dominate neuston populations. Our results suggest that photoinhibition, higher metal levels in the microlayer, or some other form of stress probably leads to release of significant quantities of labelled extracellular products. This can lead to erroneously low estimates of productivity in phytoneuston using the ^{14}C radiocarbon technique. Indeed, our data, corrected for extracellular carbon release, indicate that the productivity per unit volume without atmospheric particle addi-

tions is 10 to 100 times greater in the phytoneuston than in the phytoplankton, an enrichment which agrees with that measured previously by the oxygen-production technique (Gallagher, 1975).

APM is highly enriched in metals, such as Pb (Hardy and Crecelius, 1981), which are potentially toxic to marine phytoplankton (Rivkin, 1979). Sea surface deposition of Pb over northern hemisphere ocean areas alone amounts to about 31 000 metric tons annually (Servant, 1982), of which 40 to 60% may solubilize in seawater (Hardy and Crecelius, 1981). We reported previously (Hardy and Crecelius, 1981) that deposition rates of APM greater than 850 mg m^{-2} d^{-1} could inhibit phytoplankton productivity. Natural deposition levels do not normally reach this level, but we suggested that because APM metals have long residence times and remain at high concentrations in the sea-surface microlayer (Hardy *et al.,* in press, a), they might inhibit phytoneuston productivity.

Our previous data (Hardy *et al.,* in press, a) indicate that during a 4 h exposure of the microlayer to atmospheric particulate matter (APM) most of the lead remains in the microlayer. Therefore, in the present study, deposition of 16 mg m^{-2} h^{-1} (Table 4) would represent a total Pb concentration in the microlayer of 22 mg l^{-1} and a soluble Pb concentration in the microlayer of about 4.3 μg l^{-1} (Hardy *et al.,* in press, a). Rivkin (1979) has shown that soluble Pb between 1 and 10 μg l^{-1} decreases net photosynthetic production by increasing the excretion of labelled organics to between 27 and 61% of the total carbon fixed by photosynthesis.

Our results indicate that APM depositions greater than about 1 mg m^{-2} h^{-1} (157 μg Pb m^{-2} d^{-1}) inhibit primary productivity at the sea surface when light minus dark particulate ^{14}C values are used. This probably results from an increased release of ^{14}C-labelled extracellular products when the microalgae are exposed to high levels of lead (Rivkin, 1979). Natural deposition rates in coastal areas often reach 40 mg APM m^{-2} d^{-1} or 150 μg Pb m^{-2} d^{-1} (Hodge *et al.,* 1978; Rohbock *et al.,* 1981). Such levels would be expected to reduce particulate carbon fixation in the sea-surface microlayer.

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