

## CHEMISTRY OF THE SEA SURFACE MICROLAYER 1. FABRICATION AND TESTING OF THE SAMPLER

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### ABSTRACT

A screen sampler fabricated to study the sea surface microlayer (SML) has been described. The screen sampler was tested in the Mandovi estuary and adjacent waters. Physico-chemical parameters of the subsurface waters from a depth of 25 cm was also studied for comparison with that of the SML.

Key-words: Surface microlayer, sampler, nutrient elements, metals, Mandovi estuary.

The properties of SML differ considerably from those of the associated subsurface waters (Goering and Menzel, 1965; Williams, 1967). SML serves as a potential site of enrichment of various kinds of substances. Chemical analyses of SML had shown accumulation of a large number of organic compounds (Garrett, 1967; Nishizawa, 1971; Seba and Corcoran, 1969), trace metals (Piotrowicz, Ray, Hoffson and Duce, 1972), nutrient elements (Harvey, 1966) as well as microorganisms (Blanchard and Syzdek, 1970). Although enrichment of chemical properties at SML was known for many years, the study of SML acquired special attention only recently. Monitoring the changes in nutrient distribution in the SML is important since it might serve as an indicator of primary productivity. Distribution of phosphorus, nitrogen and silicon in SML was studied only by a few workers (Goering and Menzel, 1965; Williams, 1967 and Nishizawa, 1971).

The proper sampling of SML entails many difficulties. A variety of techniques (Van Vleet and Williams, 1980) capable of sampling surface layer to varying thickness ranging from 0.01 to 400  $\mu\text{m}$  had been published. To begin with a commonly used screen sampler (Garrett, 1965) was re-designed to suit for collection of samples for analysis of nutrients and metals. The sampler was fabricated at N.I.O. and the working of the sampler was tested in the Mandovi estuary and adjacent waters.

***Fabrication and operation of the SML sampler:*** A polyethylene screen of mesh size 25 was tightly mounted in between two plexiglass frames of outer dimensions 88 cm  $\times$  88 cm and inner dimension 80 cm  $\times$  80 cm. The screen was tightened with the help of PVC nuts and bolts (Fig.1). The assembly was suspended on nylon strings as shown. The sampler was operated in the upcurrent direction from a fibre glass unpainted row boat. To collect SML samples the sampler was introduced vertically into the water and

retrieved parallel to the surface water. It was allowed to drain for a brief period of 5 seconds before collecting in a precleaned polyethylene bottle. The sample was drained along one of the corners of the sampler till most of the adhering water was drawn. This procedure was repeated several times to collect a sufficient volume of sample.

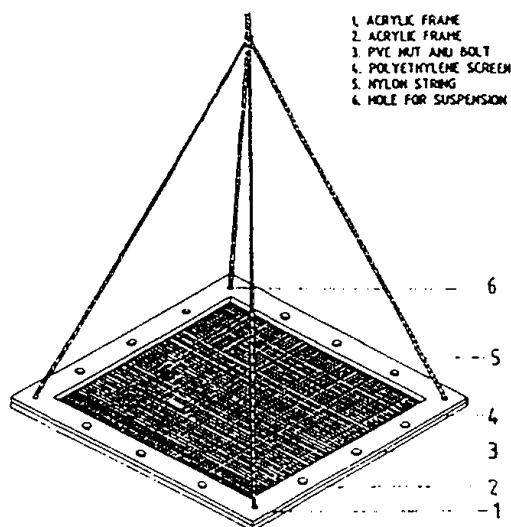


Fig.1. Screen sampler for sea surface microlayer collection.

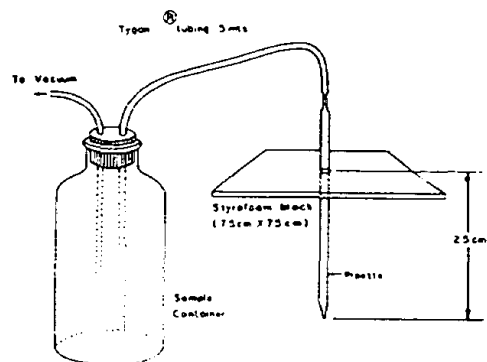


Fig.2. Subsurface water collection assembly.

**Collection of subsurface water samples:** Subsurface water samples from a depth of 25 cm were collected simultaneously along with the SML samples for comparison with the latter. The collection assembly (Fig.2) consisted of a styrofoam block, measuring 75 cm x 75 cm x 10 cm through which a pipette was inserted. The tip of the pipette projected exactly 25 cm from the lower surface of styrofoam block and a tygon<sup>(R)</sup> tubing (internal diameter 0.6 cm) was attached to the upper end of the pipette. The assembly was floated on the water surface and sample was sucked through the tube directly into a container of hard polyethylene.

Five SML and subsurface sample pairs were collected from a station in the Mandovi estuary and subsequently analysed at the shore laboratory. Samples were analysed for nutrients following standard analytical procedures (Grasshoff, Ehrhardt and Kremling, 1983). Salinity was measured on board using a Beckman RS 5-3 portable salinometer and counterchecked in the laboratory on Autosal 8400 salinometer. Iron, zinc, copper and nickel were determined in a Hilger Watt Atomspek (Atomic Absorption Spectrophotometer) following standard procedure (Brewer, Spencer and Smith, 1969).

To calculate the thickness of the SML, the sampler was dipped 22 times and the total volume of sample measured. The area covered by the screen material was calculated from the thickness of the screen wires (0.1 mm) and its mesh size (25 wires/inch). The effective area of collection

Table I – Variation of some physico-chemical properties of sea surface microlayer samples (SML) and subsurface water (SSW) collected from Station A from Mandovi estuary on 12.3.1985 during high tide.

Time (hrs.)	Sample	Air temp. °C	Water temp. °C	S% <sub>o</sub>	PO <sub>4</sub> -P	NH <sub>4</sub> -N	(µg-atl <sup>-1</sup> )			(µg <sup>-1</sup> )			
							NO <sub>2</sub> -N	NO <sub>3</sub> -N	SiO <sub>4</sub> -Si	Fe	Zn	Cu	Ni
1100	SML	34.5	-	26.17	0.50	6.93	0.46	2.26	30.50	39	3.5	0.80	0.60
	SSW	29.90	29.90	25.62	0.26 (0.92)	0.61 (10.36)	0.34 (0.35)	1.72 (0.31)	29.30 (0.04)	17 (1.29)	0.3 (10.66)	0.80 (0.00)	0.40 (0.50)
1200	SML	37.0	-	27.87	0.44	5.17	0.46	2.46	25.60	34	16.8	1.0	0.30
	SSW	30.90	30.90	27.44	0.43 (0.02)	0.37 (12.97)	0.34 (0.35)	2.02 (0.22)	24.50 (0.04)	20 (0.70)	4.8 (2.50)	0.5 (1.00)	0.40 (-0.25)
1300	SML	35.2	-	29.72	0.97	3.05	0.54	2.96	19.80	20	59	1.1	0.50
	SSW	31.00	31.00	29.03	0.70 (0.31)	0.99 (2.08)	0.39 (0.38)	2.41 (0.23)	21.40 (-0.07)	11 (0.82)	25 (1.36)	0.4 (1.75)	0.30 (0.67)
1400	SML	33.5	-	31.11	0.94	2.01	0.45	2.73	15.40	15	15.50	0.50	0.40
	SSW	30.80	30.80	30.37	0.94 (0.00)	0.60 (2.35)	0.45 (0.00)	2.37 (0.15)	14.30 (0.08)	33 (-0.55)	4.80 (1.81)	0.50 (0.00)	0.40 (0.00)
1500	SML	34.0	-	31.81	0.90	1.40	0.45	2.77	14.10	18	6.00	0.50	0.60
	SSW	31.10	31.10	31.19	0.79 (0.54)	0.81 (0.73)	0.40 (0.13)	2.64 (0.05)	12.90 (0.09)	35 (-0.49)	4.6 (0.30)	0.30 (0.67)	0.60 (0.00)

Figures in brackets are Enrichment Factors (EF).

(6336 cm<sup>2</sup>) was obtained after subtracting the area covered by the screen material from the total frame area of 6400 cm<sup>2</sup>. Dividing the sample volume collected per dip by the effective area of collection gives the thickness of the SML. The calculated thickness varied from 197 to 229 μm, with an average of 212 μm. This value is slightly higher than the reported values (60-150 μm) for the thickness of the SML using different types of screen samplers (Garrett, 1965; Piotrowicz, Ray, Hoffman and Duce, 1972; Duce, Quinn, Olney, Piotrowicz, Ray and Wade, 1972; Barker and Zeitlin, 1972; Harvey and Burzell, 1972).

The results of chemical analyses are presented in Table I. The enrichment factors for different parameters were calculated according to Piotrowicz, Ray, Hoffman and Duce (1972).

$$\text{Enrichment Factor (EF)} = \frac{\text{Conc. in SML}}{\text{Conc. in subsurface water from 25 cm depth}} - 1$$

Salinity of SML and subsurface water samples did not differ significantly. In three out of five sample pairs, phosphate showed enrichment in SML. The phosphate enrichment factors ranged from 0.00 to 0.92. Chapman and Liss (1981) did not observe phosphate enrichment in the coastal waters whereas, Williams (1967) has reported an EF of 2.5. Lyons, Pybus, Coyne (1980) in their study in Galway Bay, Ireland, noticed that phosphate enrichment in the microlayer was related to phytoplankton bloom. Nitrite enrichment ranged from 0.00 to 0.38 but nitrate enrichment varied between 0.05 to 0.31. Ammonia showed very high enrichment and factors ranged from 0.73 to 12.97. Both nitrate and ammonia showed a decreasing trend in their enrichment in SML at higher salinity. An EF of 0.6 can be calculated for nitrite from the reported values of Chapman and Liss (1981). Williams (1967) and Nishizawa (1971) on the other hand found lack of nitrite enrichment in their samples. The EF for ammonia found by us are in some cases higher than those reported by Nishizawa (1971) (EF = 3.6) but still lower than those reported by Williams (1967) (EF = 19.7). High ammonia concentrations in the SML were also reported by Goering and Manzel (1965). The enrichment of silicates was insignificant in all SML samples. Baier and Goupil (1973) however observed a major silica component associated with diatom remnants in the natural slicks collected off south east coast of U.S.A. Lyons, Pybus, Coyne (1980) attributed the increased enrichment of dissolved silicate to the high phytoplankton content in the subsurface water and breakdown and dissolution of diatom remnants that have been transported to the surface through some unspecified mechanism.

Among the trace metal studies for their enrichment in SML, zinc showed enrichment to a greater extent (EF = 0.30 to 10.66) which decreased at higher salinities. Iron showed a similar trend with low enrichment factors ranging from -0.49 to 1.29. High enrichment of upto 19 have been reported for zinc by Pattenden, Cambray, Playford (1981) and a range of 0.0 to 1.7 for EF of iron has been quoted by Piotrowicz, Ray, Hoffman and Duce (1972). Duce, Quinn, Olney, Piotrowicz, Ray and Wade (1972) however reported high enrichment factor of upto 28 from iron. Piotrowicz, Ray, Hoffman, Duce (1972) and Duce, Quinn, Olney, Piotrowicz, Ray and Wade (1972) reported no iron enrichment in the inorganic phase and suggested a process of chelation by surface active organic ligands in SML.

In our studies Cu and Ni showed enrichment factors ranging 0.0 to 1.75 and -0.17 to 0.67 respectively. These ranges are similar to the ranges 0.0 to 1.7 and 0.0 to 0.3 for Cu and Ni respectively reported by Piotrowicz, Ray, Hoffman and Duce (1972) in the chloroform extractable organic phase. These authors did not notice any enrichment for Cu and Ni in the inorganic phase. Duce, Quinn, Olney, Piotrowicz, Ray and Wade (1972) however, reported EF upto 35 for Cu and upto 49 for Ni which are considerably higher than our observations and those of Piotrowicz, Ray, Hoffman and Duce (1972).

The observed salinity range from 25.62 to 31.81 is too narrow to conclude that high salinity caused the EF to fall as observed for Fe, Zn, ammonia, nitrite and nitrate. All samples were collected during the high tide, therefore it appears that the EF for the properties, generally decreased downstream along the estuary. Further studies on microlayer samples collected over a wide salinity range may throw more light on the salinity dependence of EF of the properties.

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