

## Chemistry of the sea-surface microlayer 3. studies on the nutrient chemistry of the northern Arabian Sea

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**Abstract** - Sea-surface microlayer (SML) and sub-surface layer (SSL) were sampled at 99 stations covering five transects from coastal to offshore regions during the cruises of *O.R.V. Sagar Kanya* and *R.V. Gaveshani* in the Northern Arabian Sea.

Nutrients showed enrichment in the surface microlayer compared to those in sub-surface water and there was a decreasing trend in the enrichment factor from nearshore to offshore. The nutrient concentrations were correlated with Chlorophyll values at 1 m depth. Relatively high enrichment factors, in (SML) in coastal waters could be attributed to the influence of freshwater carrying considerable quantities of nutrients into the sea either from land runoff or from the industrial and domestic wastewater discharges. The interrelationships and the possible mechanisms causing the accumulation of nutrients at sea surface are discussed.

### INTRODUCTION

The sea surface microlayer has been known to contain enriched levels of many chemical parameters relative to sub-surface waters (NORKRANS, 1979 and 1980; FEHON and OLIVER, 1979). These wastes are spread over the surface layers depending upon the circulation and movements of water. Other factors which contribute to the increase in the concentration of the chemical substances in the sea surface microlayer (SML) are aerosol input of continental materials, weathering products, anthropogenically introduced pollutants, rain, physical and chemical floatation processes involving particulates and bubble scavenging (DUCE *et al.*, 1972; WADE and QUINN, 1975; PELLENBERG, 1981; SINGBAL and NARVEKAR, 1988). Since the accumulation of many chemical substances in SML is very prominent, it serves as a potential site of enrichment for different pollutants.

Since there is a total lack of information from Indian waters on the chemistry of SML, the present investigation has been undertaken to study the nutrient chemistry of sea surface microlayer and sub-surface layers in the coastal and offshore waters of the Northern Arabian Sea to elucidate the variations of enrichment of nutrients in the SML and also temporal and seasonal variations in enrichment levels.

### METHODS

Samples of the surface microlayer and sub-surface layers (1m below the surface) were collected from 99 stations during various cruises on board *O.R.V. Sagar Kanya* and *R.V. Gaveshani* from the Northern Arabian Sea waters (Fig. 1) using the microlayer sampler fabricated and tested in the Laboratory (SINGBAL and NARVEKAR, 1988).

The surface microlayer samples were collected by lowering the sampler from the bow of ship which was directed to move slowly on a straight path through waters which meet the selected station. The sampler was placed into the water with the screen in a horizontal position parallel to the sea surface. It was allowed to drain for brief period of 5 seconds before collecting in a pre-cleaned 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. Sub-surface water samples from a depth of 1m were collected using a Niskin bottle simultaneously with the SML sampler for comparison with the later.

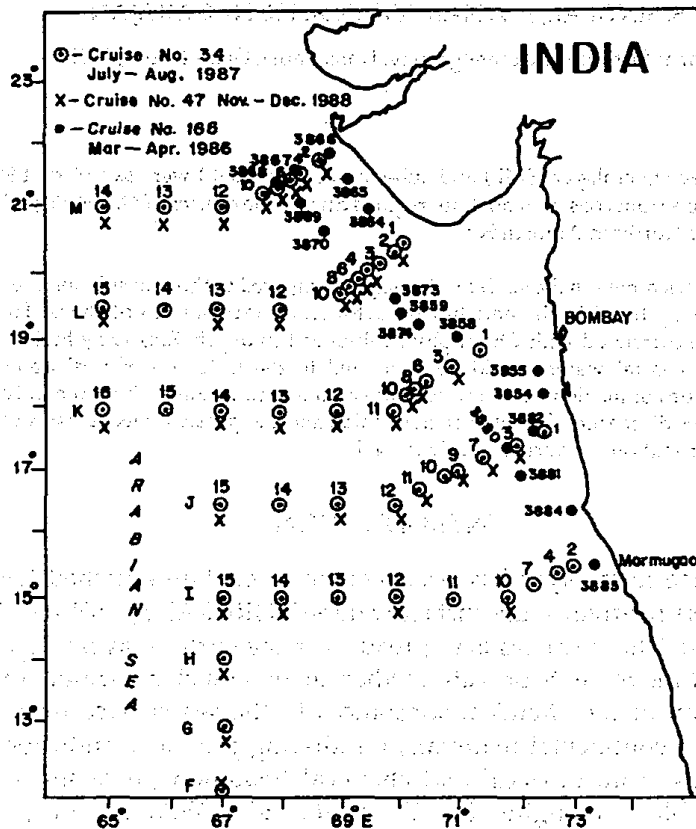


Fig. 1. Sampling locations in the northern Arabian Sea during ORV *Sagar Kanya* and RV *Gatveshani* cruises.

The chemical parameters analysed in SML and sub-surface layer (SSL) using standard method of analysis, (GRASSHOFF *et al.*, 1983) were phosphate, inorganic nitrogen compounds and silicate.

The enrichment factors (EF) were calculated for different chemical parameters following the relation used by PIOTROWICZ *et al.* (1972).

$$\text{Enrichment Factor (EF)} = \frac{\text{Concentration in SML}}{\text{Concentration in SSL}} - 1$$

## RESULTS

Table 1,2 and 3 present concentrations of nutrients in SML and SSL and also the enrichment factors of these nutrients in SML relative to SSL in water samples collected from coastal and offshore waters during different seasons.

In general, all the parameters showed enrichment in SML though its magnitude varied from season to season and parameter to parameter. The overall enrichment

Table 1. Nutrient data for surface microlayer, subsurface layer and enrichment factors in the Arabian Sea (pre-monsoon season)

Stns	NH <sub>4</sub> <sup>+</sup> -N μmol l <sup>-1</sup>			NO <sub>3</sub> <sup>-</sup> -N μmol l <sup>-1</sup>			NO <sub>2</sub> <sup>-</sup> -N μmol l <sup>-1</sup>			PO <sub>4</sub> <sup>-</sup> -P μmol l <sup>-1</sup>			SiO <sub>4</sub> <sup>-4</sup> -Si μmol l <sup>-1</sup>		
	SML	SSL	EF	SML	SSL	EF	SML	SSL	EF	SML	SSL	EF	SML	SSL	EF
3856	3.64	3.54	0.03	0.37	0.05	6.40	0.14	0.02	6.00	0.10	0.02	4.00	0.95	0.83	0.14
3867	4.23	2.98	0.41	0.62	0.08	6.75	0.08	0.05	0.57	0.59	0.57	0.03	1.69	1.27	0.32
3868	3.18	3.38	-0.06	0.13	-	-	0.06	0.01	2.28	0.48	0.34	0.40	1.73	1.34	0.29
3865	6.47	3.98	0.62	0.62	0.11	4.64	0.09	0.01	3.71	0.11	0.02	4.50	1.58	1.04	0.51
3869	3.23	4.28	-0.25	0.14	-	-	0.03	0.00	-	0.19	0.32	-0.40	1.81	1.13	0.59
3864	4.08	3.09	0.32	0.44	0.14	2.14	0.08	0.03	2.33	0.36	0.09	2.77	1.21	0.88	0.37
3870	9.56	3.93	1.43	0.07	-	-	0.05	0.00	-	0.44	0.44	0.00	1.32	1.00	0.32
3873	4.13	7.46	-0.45	0.08	0.07	0.14	0.04	0.01	1.28	0.35	0.45	-0.22	1.09	0.67	0.61
3859	8.96	3.98	1.25	1.00	0.16	5.25	0.09	0.00	-	0.09	0.34	-0.72	2.62	1.38	0.90
3874	4.97	5.52	-0.10	0.29	0.07	3.14	0.03	0.01	1.79	0.44	0.26	0.70	2.24	1.88	0.18
3858	5.98	4.93	0.21	1.14	0.09	11.67	0.16	0.03	3.75	0.35	0.10	2.30	1.64	1.44	0.14
3855	7.12	5.62	0.27	1.42	0.19	6.47	0.13	0.06	1.35	0.57	0.21	1.64	3.35	2.84	0.18
3854	3.59	6.18	-0.42	2.50	0.17	14.71	0.10	0.04	1.31	0.63	0.27	1.32	-	-	-
3882	16.33	9.21	0.77	0.52	0.26	1.00	0.08	0.03	1.50	0.13	0.06	1.00	-	-	-
3880	11.45	48.10	-0.77	0.52	0.18	1.89	0.06	0.02	1.20	0.19	0.08	1.25	2.34	2.03	0.15
3881	16.58	5.57	1.97	0.31	0.11	1.82	0.07	0.02	2.37	0.11	0.17	-0.32	2.03	1.70	0.19
3884	9.21	12.35	-0.26	0.10	0.13	-0.23	0.09	0.03	2.00	0.22	0.19	0.16	0.36	0.13	1.66
3885	11.10	8.01	0.38	0.26	0.04	5.50	0.09	0.06	0.50	0.55	0.48	0.13	0.69	0.45	0.50

Coastal Stations

levels of nutrients were higher during the pre-monsoon season compared to the other seasons (Table 4).

Table 2. Nitrite, phosphate, silicate and chlorophyll distribution in surface microlayer, sub-surface layer and enrichment factors in the Arabian Sea (SW monsoon season).

Stns	NO <sub>2</sub> <sup>-</sup> -N μmol l <sup>-1</sup>			PO <sub>4</sub> <sup>3-</sup> -P μmol l <sup>-1</sup>			SiO <sub>4</sub> <sup>4-</sup> -Si μmol l <sup>-1</sup>		Chl-a mg m <sup>-3</sup>	
	SML	SSL	EF	SML	SSL	EF	SML	SSL	EF	SSL
<b>Coastal and offshore waters</b>										
M2	0.02	0.00	-	0.50	0.39	0.28	0.68	1.02	-0.33	0.16
M4	0.05	0.00	-	0.36	0.36	0.00	0.61	0.70	-0.13	0.09
M8	0.01	0.00	-	0.52	0.46	0.13	0.65	0.74	-0.12	0.13
L1	0.42	0.41	0.02	0.61	0.54	0.13	3.15	3.28	0.17	0.19
L3	0.11	0.10	0.10	0.35	0.40	-0.13	1.96	1.57	0.25	0.22
L6	0.04	0.02	1.00	0.24	0.28	-0.14	2.80	1.96	0.43	0.10
L10	0.08	0.02	3.00	0.37	0.53	-0.30	1.30	1.06	0.23	0.10
L13	0.06	0.02	2.00	0.55	0.39	0.41	0.84	0.65	0.29	0.16
L14	0.10	0.00	-	0.33	0.30	0.10	0.57	0.24	1.38	0.12
K1	0.02	0.00	-	0.07	0.29	-0.76	0.84	0.81	0.04	-
K3	0.06	0.07	-0.14	0.33	0.55	-0.40	2.36	2.45	-0.04	0.24
K6	0.00	0.00	-	0.14	0.28	-0.50	0.42	0.41	0.02	0.22
K11	0.05	0.03	0.67	0.19	0.31	-0.39	0.38	0.27	0.41	0.12
K12	0.10	0.01	9.00	0.39	0.32	0.22	0.17	0.98	-0.83	0.10
K13	0.06	0.01	4.00	0.48	0.93	-0.48	1.11	0.45	1.47	0.13
K15	0.01	0.00	-	0.34	0.27	0.26	0.34	0.25	0.36	0.22
K16	0.11	0.00	-	0.19	0.36	-0.47	0.41	0.00	-	0.27
J1	0.13	0.00	-	0.00	0.51	-1.00	3.94	4.64	-0.15	0.25
J3	0.02	0.00	-	0.21	0.31	-0.32	1.04	0.98	0.06	0.27
J7	0.04	0.00	-	0.35	0.30	0.17	1.60	1.40	0.14	0.22
J10	0.02	0.00	-	0.33	0.22	0.45	1.47	1.28	0.15	0.10
J12	0.04	0.00	-	0.27	0.28	-0.04	0.08	0.17	-0.53	0.15
J13	0.13	0.13	0.00	0.12	0.25	-0.52	0.50	0.31	0.61	0.12
J14	0.13	0.08	0.63	0.31	0.33	-0.06	0.90	0.73	0.23	0.18
I2	0.01	0.00	-	0.53	0.54	-0.02	9.11	9.52	-0.04	-
I4	0.00	0.00	-	-0.49	0.49	0.06	7.13	7.01	0.02	-
I7	0.00	0.00	-	0.40	0.75	-0.47	7.36	2.23	2.30	-
I10	0.03	0.02	0.50	0.16	0.18	-0.11	0.51	0.54	-0.60	0.13
I11	0.06	0.02	2.00	0.28	0.38	-0.26	1.08	0.92	0.17	0.10
I12	0.06	0.03	1.00	0.13	0.25	-0.48	0.81	0.70	0.16	0.12
I13	0.03	0.00	-	0.31	0.33	-0.06	0.27	0.10	1.70	0.12

Among the nitrogenous compounds, high levels of ammonia were encountered in SML (3.18 to 16.58 μmol l<sup>-1</sup>) compared to other nutrients. However, the overall enrichment of nitrate was higher than nitrite and ammonia (Table 4).

Phosphate showed variable behaviour of enrichment and depletion but the magnitude was higher in pre-monsoon and post-monsoon seasons (Table 4).

Concentrations of silicate in SML and in SSL did not change very much and the enrichment factor was almost always less than 1.

## DISCUSSION

This study reveals that the concentrations of various nutrients are higher at the SML than the SSL and the concentrations as well as enrichment factors at the SML are higher in coastal waters (Table 1). The higher concentration of nutrients may be due to anthropogenic inputs and/or aeolian transport (JUNGE, 1963). Similar observations regarding concentrations of surface ammonia have been correlated with rainfall at Bermuda (KENNETH and REMSEN, 1985). Tables 1,2 and 3 show that ammonia, nitrite and nitrate in SML have higher concentrations than those in the SSL at almost

Table 3. Phosphate and silicate distribution in surface microlayer, sub-surface layer and enrichment factors in the Arabian Sea (Post-monsoon season).

Stn.	PO <sub>4</sub> <sup>3-</sup> -P			SiO <sub>4</sub> <sup>4-</sup> -Si		
	μmol l <sup>-1</sup>			μmol l <sup>-1</sup>		
	SML	SSL	EF	SML	SSL	EF
<b>Coastal and offshore waters</b>						
M2	0.40	0.95	-0.58	5.05	4.56	0.11
M4	0.34	0.25	0.36	0.30	0.00	-
M6	0.35	0.30	0.17	2.10	4.19	-0.50
M8	-	0.33	-	2.30	4.06	-0.43
M10	0.51	0.33	0.55	1.85	1.20	0.50
M12	0.77	0.23	3.22	1.33	2.04	-0.35
M13	0.45	0.16	1.81	1.64	1.15	0.43
M14	3.99	0.35	10.40	1.79	0.92	0.75
L2	0.76	0.65	0.17	7.20	8.34	-0.14
L4	0.90	0.38	1.37	4.29	3.98	0.08
L6	0.18	0.24	-0.25	4.61	4.31	0.07
L8	0.51	0.22	1.32	3.93	3.30	0.19
L10	1.05	0.39	1.69	3.75	4.18	-0.10
L12	0.44	0.35	0.26	1.96	1.73	0.13
L13	0.74	0.55	0.35	1.57	1.48	0.06
L15	0.28	0.96	-0.71	0.03	0.20	-0.85
K3	0.41	0.24	0.71	1.15	1.03	0.12
K8	0.64	0.53	0.21	1.12	0.84	0.33
K10	1.04	0.40	1.60	1.05	0.67	0.57
K11	0.97	0.30	1.23	1.09	0.74	0.47
K12	0.61	0.30	1.03	1.01	0.66	0.53
K13	0.59	0.46	0.28	1.82	1.48	0.23
K14	0.49	0.25	0.96	1.25	1.52	-0.18
K16	0.73	0.54	0.35	0.71	0.55	0.29
J3	0.17	0.26	-0.35	1.26	0.98	0.29
J7	0.93	0.68	0.22	1.25	0.98	0.28
J9	0.18	0.40	-0.55	1.00	1.38	-0.28
J11	0.08	0.09	-0.11	1.57	1.09	0.44
J12	0.55	0.46	0.20	0.92	0.72	0.28
J13	0.28	0.12	1.33	2.04	1.91	0.07
J15	0.38	0.28	0.36	1.77	1.47	0.20
I10	0.35	0.04	7.75	1.23	0.93	0.32
I12	0.68	0.11	5.18	1.16	0.87	0.33
I14	0.61	0.52	0.17	0.90	0.90	0.00
I15	0.25	0.37	-0.32	2.57	0.98	1.62

Table 4. Ranges of variations of enrichment factor of chemical parameters during different seasons.

Season	NH <sub>4</sub> <sup>+</sup> -N μmol l <sup>-1</sup>	NO <sub>3</sub> <sup>-</sup> -N μmol l <sup>-1</sup>	NO <sub>2</sub> <sup>-</sup> -N μmol l <sup>-1</sup>	PO <sub>4</sub> <sup>3-</sup> -P μmol l <sup>-1</sup>	SiO <sub>4</sub> <sup>4-</sup> -Si μmol l <sup>-1</sup>
<b>Coastal waters</b>					
Premonsoon	-0.77-1.97	-0.23-14.71	0.50-6.00	-0.72-4.50	0.14-0.90
<b>Coastal and offshore waters</b>					
Monsoon	-	-	-0.14-9.00	-1.00-0.45	-0.83-2.30
Post monsoon	-	-	-	0.71-10.40	-0.85-1.62

all the stations. This can be attributed to (i) quick oxidation of  $\text{NH}_4^+\text{-N}$  to  $\text{NO}_2^-\text{-N}$  by bacterial nitrification in the microlayer (GOERING and MENZEL, 1965) (ii) The photolysis of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  in the microlayer (KENNETH *et al.*, 1985) (iii) biological activity, (WILLIAM, 1967). Among nitrogenous compounds the greatest enrichment factors were observed for nitrite and nitrate, the maximum values being 9.0 and 9.8 respectively.

The concentrations of phosphate are higher in SML than the SSL. However, the enrichment factor is found to be higher near the stations close to the shore (Table 1). This may be accounted for by the increased concentrations of phosphate in nearshore waters due to the industrial and domestic discharges. The rising of gas bubbles up to the surface and their bursting could also enrich the SML (BAYLOR *et al.*, 1962; WILLIAMS, 1967 and GOERING and WALLEN, 1967).

The concentration of silicate in SML is not much higher than that in the SSL. The enrichment levels are comparatively higher in nearshore stations due to the influence of fresh waters carrying considerable quantities of silicate into the sea.

From Table 2, it is observed that chlorophyll *a* values were higher corresponding to lower nutrient concentrations. Nutrient chemistry of the surface microlayer may be a valuable indicator of phytoplankton growth. DAUMAS (1974) and PIOTROWICZ *et al.* (1972) observed that SML is partly controlled by biological activity.

*Acknowledgements*- The authors express their sincere thanks to Dr. B.N. DESAI, Director, NIO, for his encouragement to carry out this investigation. Thanks are due to Dr. R. SEN GUPTA for going through the manuscript and making valuable suggestions.

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