

## STUDIES ON FOAM\*

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### ABSTRACT

Under light wind conditions, long lines of surface slicks and patches of foam appear quite commonly in the Vellar Estuary. The foam is of a very stable type, and persists normally for from several minutes to a few hours and collect in large masses along the shores in the lower part of the estuary.

Microscopic examination of freshly collected foam revealed the presence of a considerable amount of phytoplankton (chiefly species belonging to the genera *Coscinodiscus* and *Trichodesmium*) and detrital material in addition to fine silt particles.

The foam samples were chemically analysed for the anions like Nitrate, Phosphate and Silicate and cations such as Iron, Copper and Manganese. The foam seems to be very rich in these constituents, the concentration being a hundred fold more than those of sea water (except reactive silicate). The range of variation in the concentration of the above constituents is as follows:

	Range $\mu\text{g/gm}$ dried foam		
Nitrate	1345.0	to	3430.0
Phosphate	550.0	to	615.0
Silicate (cold reactive)	146.0	to	233.0
Iron	18206.0	to	37967.0
Copper	5272.0	to	9887.0
Manganese	420.0	to	678.0

Further, the chemical composition as well as water content of the foam samples collected during different periods vary considerably.

### INTRODUCTION

SURFACE slicks appear in coastal waters and estuaries when light wind prevails. In estuaries, with the beginning of high tide, slicks extend into the river and form glossy patches in parallel with the shore line. If the light wind persists and blows at an angle less than  $50^\circ$  to the slick line, the bubbles found commonly in the slicks slowly drift towards the shore where they accumulate into huge foam masses are usually left behind in the shore or sometimes drift back into the water.

Dietz and LaFond (1950) and LaFond and Bhavanarayana (1959) have observed surface slicks in many coastal waters and suggested that the formation of slick typically marked by foam is due to organic material which spreads into a monomolecular layer. Due to convergence, such layers will appear as patches in light wind conditions or in the form of evenly spaced streaks when the wind speed increases. Bubbles produced in these slicks due to the wind and wave action aggregate into very stable foam masses. Oils released from dead and decaying

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organisms may also play a major part in the bubble formation (Woodcock, 1948, 1955). Analysis of surface films show that oleic acid released by phytoplankton, is abundant in slicks (Garrett, 1965). Baylor *et al.* (1962) have shown that artificial air bubbles rising through sea water adsorb phosphates. Along with phosphates, particulate food materials are also adsorbed into bubbles (Sutcliffe *et al.*, 1963, Baylor and Sutcliffe, 1963). This will indicate that foam consists of considerable amount of adsorbed inorganic and organic materials. The present attempt relates to a study of the composition of the foam - mainly to study the cations such as iron, manganese and copper and the anions, nitrate, phosphate and silicate.

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#### MATERIAL AND METHODS

The foam bubbles aggregate into large and small masses, near the shoreline. If the shore line is slightly curved inwards the foam will remain floating freely in the water. Otherwise it will be washed ashore by the action of wind. For the present study the freely floating foam alone was collected to avoid any contamination by the shore material. The foam was transported to the laboratory in plastic buckets, without adding any antifoaming agent and was compressed with a glass plate. The compressed foam was passed through a coarse bolting cloth to expel air and larger plant materials such as grass and leaves. After 2 hours of settling the foam was again passed through coarse bolting cloth and the liquid foam by now was devoid of any air bubbles. This liquid foam was very turbid due to adsorbed mud. After measuring the volume and weight of the liquid foam it was dried in an oven at 70°C to remove water. The dried foam was weighed, ground in a glass mortar and sieved through a fine mesh bolting cloth (100 mesh). The powdered foam was stored in plastic containers. The samples of foam collected at different dates from different regions of the estuary are indicated in Table 1.

*Analysis:* For the estimation of total iron, copper, manganese and phosphate, 50 mg of powdered foam was digested with 5 ml of 1:1 nitric acid and 2 ml of perchloric acid (70%) in a sand bath. Digestion was continued until solid material just began to separate. The digested sample was dissolved in 10 ml of diluted hydrochloric acid (4%) and kept overnight at room temperature. The solution was then centrifuged and the clear supernatant fluid was analysed for iron, copper, manganese and phosphate by the following spectrophotometric methods.

**IRON :** dipyrldyl method (Lewis and Goldberg, 1954).

**MANGANESE :** Pot. periodate oxidation method (Snell and Snell, 1959).

**COPPER :** Sodium diethyl dithiocarbamate method (Chow and Thompson, 1952).

**PHOSPHATE :** Murphy and Riley (1962) as modified by Strickland and Parsons (1968).

For the estimation of soluble, reactive nitrate, phosphate and silicate, 500 mg of powdered foam sample was shaken with 100 ml of distilled water in a mechanical shaker for 1 hour and filtered through Whatman No. 41 filter paper. The filtrate was diluted suitably with distilled water and the soluble nitrate, phosphate and silicate were estimated in aliquots of the filtrate according to the methods outlined

in Strickland and Parsons (1968) and the concentration of each one is expressed in mg/g or  $\mu$ g/g dried foam.

### RESULTS

Microscopic examination of the foam revealed the presence of many groups of diatoms and algal detritus. The dominant diatoms were *Concinodiscus* sp., but other diatoms were not identifiable because of the deterioration. In foam samples Nos. 7 and 8, the blue green alga, *Trichodesmium erythraeum* was abundant. Living *Trichodesmium* was found in large numbers in foam sample No. 8. Apart from the plant material, a small amount of animal remains such as eggs and cuticular exo-skeleton of *Halobates*, exo-skeleton of red bugs and dipterans were also present. However, bulk of the organic matter was found to be constituted by detritus. More than 70% of the solid foam consists of very fine mud particle. Only very small amount of exo-skeletons of crustaceans in decaying condition were seen.

The measurement of actual volume of the foam was very difficult. The size of the bubbles varied widely and the foam mass was always altered to a considerable degree by wind and temperature. However, it was found that approximately 50 litres of foam, after condensation, gave 1 litre of liquid. The 'half life' of the foam (LaFond and Bhavanarayana, 1959) seem to vary with the amount of organic substances like oil and mud particles present. If the mud particles were greater then the 'half life' appeared to be between 3 and 4 hours. If the mud particles were less, then the 'half life' was found to be 6 and 8 hours. This indicates the remarkable stability of this type of foam. However, in the field due wind and temperature, the foam left on the shore was devoid of bubbles and formed a brown layer over the sand within 2 hours.

TABLE 1. Details of place and date of collection, volume and weight of foam

Foam No.	Place of collection	Date of collection	Volume of liquid foam in ml	Volume of water in ml	Weight of dried foam in gm	Ash% or dried foam
2	Between Biological Station and Jetty	Jan. 1969	500	490	15.0	74-75
3	Biological Station	Jan. 1969	500	490	13.7	69-76
4	Jetty	Jan. 1969	500	477	29.6	70-71
6	Between Biological Station and Jetty	Jan. 1969	1000	975	33.9	75-76.8
7	Near mouth	Feb. 1969	2250	2160	78.8	67-70.2
8	Salt pan	Mar. 1969	1100	1050	63.0	65-70

The weight of the dried foam (Table 1) was dependent upon the quantity of particulate material adsorbed to it rather than to the volume of liquid foam. For example, 1 litre of liquid foam of sample No. 8 yielded 63 gms of dried foam whereas in another sample (Foam-7) 2.25 litres of liquid foam yielded only 79 gms of dried foam.

#### Iron

Iron was found to be the most abundant cation present in the foam. It ranged from 22 mg to 44 mg/g of dried foam (Table 2). In foam samples 2, 3, 4, 6 and 7 the concentration of iron was less than 30 mg/g whereas in foam 8 it was 44 mg/g.

*Copper*

The concentration of copper in the foam samples analysed ranged from 4 to 14 mg/g (Table 2). In foam samples 2, 3, 4 and 6 the copper concentration was found to be between 4 and 5 mg/g. In sample 7 as much as 7 mg/g of copper was present, while foam sample 8 had twice as much.

TABLE 2. The composition of foam. The values are expressed in mg or  $\mu\text{g}$  per 1 g of dried foam

Foam No.	Iron mg	Copper mg	Manganese mg	Total Phosphate mg p	Soluble Nitrate $\mu\text{g N}$	Soluble Silicate $\mu\text{g Si}$	Soluble Phosphate $\mu\text{g P}$
2	30.87	4.239	0.442	0.618	149	146	4.0
3	27.85	4.020	0.616	0.719	142	159	6.9
4	28.16	4.623	0.627	0.674	131	178	14.5
6	28.69	4.723	0.611	0.724	136	222	24.1
7	22.63	6.997	0.434	0.911	100	185	18.2
8	44.08	14.463	0.849	1.207	89	233	23.5

*Manganese*

The amount of manganese present in the different foam samples ranged from 0.4 mg/g to 0.85 mg/g (Table 2). In samples 3, 4 and 6 it was a little over 0.6 mg/g. Foam samples 2 and 7 showed 0.4 mg/g of Mn while foam sample 8 showed, as in the case of copper and iron, very high concentration of manganese (0.85 mg/g)

*Phosphate*

The total phosphate content was seen to vary from 0.6 mg/g to 0.72 mg/g in foam samples 2, 3, 4 and 6 (Table 2). In sample 8 the total phosphorus was more than 1.2 mg/g.

However, the soluble reactive phosphate concentration was very low in the foam. Apparently there seems to be no relationship between the total phosphorus and soluble phosphorus. In foam samples 2 and 3, the soluble phosphorus was less than 10  $\mu\text{g/g}$  in concentration, while in other foam samples, more than 15  $\mu\text{g/g}$  of soluble phosphate was observed. In samples 6 and 8 the soluble, reactive phosphorus was slightly more than 23  $\mu\text{g/g}$ .

*Silicate*

The soluble reactive silicate content ranged from 140  $\mu\text{g/g}$  to 190  $\mu\text{g/g}$  in foam samples 2, 3, 4 and 7 (Table 2). Like soluble reactive phosphate, the soluble reactive silicon concentration was also high in foam samples 6 and 8 (more than 220  $\mu\text{g/g}$ ). The low silicon content of the samples and the fact that about 70% of the foam is mud indicates that perhaps it may be present in non-reactive or polymeric form.

*Nitrite*

The soluble nitrite content ranged from 100 to 150  $\mu\text{g/g}$  in all the foam samples except in sample 8 where it was only 89  $\mu\text{g/g}$ . Sample 8 shows high concentrations of  $\text{PO}_4$ ,  $\text{SiO}_2$ ,  $\text{NO}_3$ , but not nitrite. This may, in all probability be due to the nitrogen occurring in organically bound form.

## DISCUSSION

Slicks contain a large amount of organic aggregates. The surface of slicks is composed of a monomolecular layer of organic matter and Dietz and LaFond (1950) suggested that this monomolecular layer is formed by the lipid material derived from either phytoplankton or zooplankton. It is well known that many groups of diatoms and algae contain oil droplets which will be released on death and decay. This oil will ultimately reach the surface water owing to its low density and spread out as a monomolecular layer due to its polarity. Garrett (1965) has observed that the slick is formed mainly by lipid materials such as oleic acid. Studies on dissolved organic matter suggests that it shall exist in the form of aggregated masses, rather than detrital fragments (Riley, 1963; Riley *et al.*, 1964, 1965; Johannes, 1967; Kane, 1967). About 27% of the dried solid material in the foaming slick has been found to be organic matter (Ewing, 1950). Baylor *et al.* (1962) have observed air bubbled through sea-water will remove inorganic phosphates from water. Further studies show that the phosphate is adsorbed to the bubbles and later bound to large organic molecules (Sutcliffe *et al.*, 1963). They have also observed higher concentrations of phosphate in Windrows (Slicks) than in water outside the slick. Vijayaraghavan and Paul Pandian (1967) have shown that the nitrate and phosphate content of slick water is 2 to 10 times more than that of the adjacent sea-water.

It is therefore, obvious that bubbles and aggregates of bubbles in the form of foam can adsorb a considerable amount of organic matter. Along with the organic matter mud particles also adhere to the bubbles. In shallow estuaries (where the depth is not more than 3 to 4 m) one can expect a substantial displacement of mud from the bottom to the surface during high tide and light wind. In the narrow Vellar Estuary, the bubbles aggregate into foam masses and drift towards the shore.

It is clear from the data presented, that cations are highly concentrated in foam. If the volume of water in the liquid foam is taken to represent the sea-water, then 1 gm of dried foam is approximately equivalent to about 40 ml of seawater. This will mean that as much as 750 mg of iron is present in one litre of liquid foam. When compared to the concentration of iron in sea water, it would be 75,000 times more concentrated in foam. Similarly, the other cations, copper and manganese, are also highly concentrated in foam (Table 2).

Another interesting point to note is the low concentration of soluble phosphorus and high concentration of total phosphorus in foam. Sutcliffe *et al.* (1963) have found that air bubbles passed through sea water adsorb phosphates and that major portions of the adsorbed phosphorus exist in the form of insoluble fraction. They have further recorded that the total phosphorus in the spray droplets is very high and suggested that during the formation of particles, considerable amounts of soluble phosphorus is adsorbed, bound or changed in such a way as to mask or prevent the test of soluble phosphorus. This view is firmly supported by the results of the investigations in foam material in the present study.

Like soluble phosphorus, the soluble silicon content also is very low even though mud particles are present in the foam. Recently Burton *et al.* (1970) have pointed out that silicon can occur in a polymeric form which will not react with reagents of silicon estimation. Probably this may apply also in the present case since only low silicon values were obtained for the foam samples.

The high concentration of cations in foam sample 8 may be due to the presence of large amounts of living *Trichodesmium* cells.

## REFERENCES

- BAYLOR, E. R., W. H. SUTCLIFFEE AND D. S. HIRSCHFELD 1962. Adsorption of phosphates onto bubbles. *Deep Sea Res.*, 9: 120-124.
- AND W. H. SUTCLIFFEE 1963. Dissolved organic matter in sea-water as a source of particulate food. *Limnol. Oceanog.*, 8: 369-371.
- BURTON, J. D., T. M. LEATHERLAND AND P. S. LISS 1970. The reactivity of dissolved silicon in some natural waters. *Ibid.*, 15: 473-476.
- CHOW, T. J. AND T. G. THOMPSON 1952. The determination and distribution of copper in sea-water. Part I. The spectrophotometric determination of copper in sea water. *J. Mar. Res.*, 11: 124-138.
- DIEZ, R. S. AND E. C. LAFOND 1950. Natural slicks on the ocean. *Ibid.*, 9: 69-76.
- EWING, G. 1950. Slicks, surface films and internal waves. *Ibid.*, 9: 161-187.
- GARRETT, W. D. 1965. Collection of slick-forming materials from the Sea surface. *Limnol. Oceanog.*, 10: 602-605.
- JOHANNES, R. E. 1967. Ecology of organic aggregates in the vicinity of a coral reef. *Ibid.* 12: 189-195.
- KANE, J. E. 1967. Organic aggregates in surface waters of the Ligurian Sea. *Ibid.*, 12: 286-294.
- LAFOND, E. C. AND P. V. BHAVANARAYANA 1959. Foam on the sea. *J. mar. biol. Ass. India*, 1: 228-232.
- LEWIS, G. J. AND E. D. GOLDBERG 1954. Iron in marine waters. *J. mar. Res.*, 13: 183-197.
- MURPHY, J. AND J. P. RILEY 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta.*, 27: 31-36.
- RILEY, G. A. 1963. Organic aggregates in seawater and the dynamics of their formation and utilization. *Limnol. Oceanog.*, 8: 372-381.
- P. J. WANGERSKY AND D. VAN HEMERT 1964. Organic aggregates in tropical and subtropical surface waters of the North Atlantic Ocean. *Ibid.*, 9: 546-550.
- D. VAN HEMERT AND P. J. WANGERSKY 1965. Organic aggregates in surface and deep waters of the Sargasso Sea. *Ibid.*, 10: 354-363.
- SNELL, F. D. AND C. T. SNELL 1959. Colorimetric methods of analysis. Vol. II A. Van Nostrand-Inc. New York, 793 p.
- STRICLAND, J. D. H. AND T. R. PARSONS 1968. A practical handbook of seawater analysis. *Fish. Res. Bd. Can. Bull.*, 167: 1-311.
- SUTCLIFFEE, W. H., E. R. BAYLOR AND D. W. MENZEL 1963. Sea surface chemistry and Langmuir circulation. *Deep Sea Res.*, 10: 233-243.
- VIJAYARAGHAVAN, S. R. AND AL. PAUL PANDIAN 1967. The concentration of inorganic phosphate and nitrate in the slicks in the inshore waters at Porto Novo. *Proc. Symp. Ind. Ocean. NISI-INCOR*.
- WOODCOCK, A. H. 1948. Note concerning human respiratory irritation associated with high concentration of plankton and mass mortality of marine organisms. *J. mar. Res.*, 7: 56-62.
- 1965. Bursting bubbles and air pollution. *Sewage and Industrial wastes*, 27: 1189-1192.