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INORGANIC SUSPENDED MATTER IN SEA WATER

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ABSTRACT

The suspended matter in sea water has been separated with membrane filters (down to 0.1 μ A.P.D.); the inorganic fraction, determined by ignition, has been partly analysed. The methods used are briefly described. An appreciable quantity of finely divided claylike material was found, and it is suggested that, by adsorption of organic matter from the water, this may support the bacterial flora. Samples taken regularly from the English Channel show a seasonal variation, the quantity found being greatest in winter and ranging from 0.16 to 1.20 mg/l, the mean being 0.6 mg/l. The analyses showed approximately 43 $^{0}/_{0}$ SiO₂, 13 $^{0}/_{0}$ Fe₂O₃, and 13 $^{0}/_{0}$ Al₃O₃. Silicon in suspension generally exceeded that in solution.

At three deep water stations in the eastern Atlantic, rather smaller quantities of suspended matter (0.05–1.00 mg/l) compared to the Channel were found. Some of the figures may be high owing to precipitation of calcium carbonate during storage. In the upper waters silicon in suspension exceeded that in solution, but below c. 100 m the reverse was the case. The amount of iron in suspension resembled that found by direct analysis. Some results for aluminium in suspension show quantities around 37 μ g Al/l in the English Channel and around 12 μ g in the eastern Atlantic.

INTRODUCTION

Suspended matter in sea water has been studied by optical methods and by filtration, direct determination and analysis. Jerlov (1950, 1951, 1953, 1955), who has used the Tyndall effect to measure particle distribution in several areas of the ocean, has shown that it may be used to characterise water masses. Kullenberg (1953), using Jerlov's light-scatter data, has estimated the oceanic concentration of suspended matter as being not more than 0.056 mg/l. Tsujita (1953a, 1953b, 1955), using ordinary and electron microscopes, reported qualitative and descriptive studies.

Pettersson (1943) used glass-frit filters and measured dried organic and inorganic material in Gullmar Fjord. Krey (1950a, 1950b, 1952) used paper and membrane filters to determine total dried material in northern European waters. Armstrong and Atkins (1950) determined the inorganic part of the suspended matter retained by fine filter paper and reported some partial analyses for surface water samples taken 20 miles offshore from Plymouth.

Fox, et al. (1952) used absorptive filters to determine organic matter (calculated from carbon and nitrogen determinations) in northeastern Pacific waters. Goldberg, et al. (1952), using membrane filters, measured total and inorganic suspended matter in water from the same area. Atkins, et al. (1954) used membrane filters, measured the albedo of the discoloured filters as an index of suspended matter and reported the results of microscopic examinations. Jones and Wills (1956) also used membrane filters and found a linear relationship between the concentration of suspended matter and the attenuation coefficient for light, measured with a specified instrument.

The work described below was undertaken in 1951 and 1952 to find the quantities of suspended inorganic material in subsurface waters in the English Channel and in deeper waters of the Atlantic.

ACKNOWLEDGMENTS

I am indebted to the late Dr. W. R. G. Atkins, C.B.E., and to Dr. H. W. Harvey, F.R.S., for encouragement and discussion; also I wish to express my appreciation and thanks for the help and facilities given by the Director and Staff of the National Institute of Oceanography, Wormley, Godalming, Surrey, for collecting and filtering samples aboard R.R.S. DISCOVERY II.

APPARATUS AND UNITS

Collecting Gear-Wooden bucket (later polyethylene was used), Nansen-Pettersson bottle, or Ekman reversing hydrographic bottle.

Sample Bottles-5 gallon carboys, Winchester bottles (2.71) or Pyrex Erlenmeyer flasks (2.21). These containers were reserved for this work and kept dust-free.

Filtration Apparatus-"Stefi" filter with glass-frit disc, used as described by Cole and Jones (1949) except that the supporting filter paper was omitted.

Membranes-"Gradocol" membranes of 4 cm diameter, made by the method of Elford (1931), were supplied by The Wright-Fleming Institute, St. Mary Hospital, London. The average pore diameter (A.P.D.) of each batch was given; for all except the preliminary experiments it was between 0.47 and 0.51 μ or 0.09 and 0.12 μ . Spectrophotometer-The "Unicam" S.P. 500 instrument was used

with slit widths of 0.05 and 0.03 mm at 390 and 465 m μ respectively.

Units-Inorganic suspended matter is reported in mg/l, silica as mg SiO₂/l, iron as μg Fe/l, aluminium as μg Al/l.

EXPERIMENTAL

PRELIMINARY EXPERIMENTS

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These were intended to determine whether membrane filtration of 21 of water and semimicro analysis would give results comparable to the paper filtration with 201 quantities used in previous work (Armstrong and Atkins, 1950); also, they were intended to test the reproducibility of the methods.

In the first experiment, six surface samples were taken with the usual precautions, using a wooden bucket. Two were in carboys (251), two in glass bottles (21), and two in conical pyrex flasks (21). The carboy samples were filtered on paper, the residue being washed with 5 % ammonium nitrate solution instead of distilled water and acetone as formerly. By this means an effort was made to avoid the disruption of plant cells and peptisation of fine material which may occur with distilled water. The 21 samples, filtered successively on membranes of 1.0 and 0.2μ A.P.D., were washed with ammonium nitrate. All residues were ignited at 500° C and weighed in platinum. Before proceeding with the usual analysis of the paper-filtered samples, chloride was determined by titration with mercurous nitrate, the residue being then evaporated and ignited to volatilise the reagents so that the analysis would proceed by standard methods. The ash of the material on the membranes was fused with sodium carbonate, dissolved in water, and neutralised with hydrochloric acid, after which silicon was determined colorimetrically on an aliquot portion. Another portion was used for colorimetric determination of iron, using 1:1 bipyridyl. A second experiment was done with papers and membranes, using water taken from a depth of 10 m by suction into carboys through a hose, for comparison with water from the same depth taken with a Nansen-Pettersson bottle. A surface sample was also taken as well as duplicate samples at 50 m.

Results of these experiments, given in Table I, show quite good agreement between the carboy and 21 samples as well as fair reproducibility. The amounts of salt found show that the washing is reasonably effective, since some chloride is to be expected from the contents of plant cells or small animals. In three of the analyses the quantity of inorganic matter retained by each size membrane was determined; 6, 5, and 10 % of the totals were caught on the 0.2 μ membrane. This is an appreciable fraction, and for the work which followed, average pore diameters of 0.5 and 0.1 μ were chosen as the finest which could conveniently be used; with these, filtering rates were roughly 30 min and 4–8 hours for 21 samples for the respective sizes. The method of filtration was standardised

Date and Depth (m)	Volume (l)	Filters	Inorganic Suspended Matter (mg/l)	SiO2 (°/0)	Fe ₂ O ₃ (°/0)	Salt (from chloride) (%)	
1951							
26 Februa	ury						
0	25.7	Paper	0.82	38	12	8	
0	25.8	Paper	0.85	36	14	3	
0	2.72	1.00 1	0.73	47	14	_	
0	2.72	1.09μ and	0.83	42	10		
0	2.28	0.21μ	1.20	42	11	_	
0	2.22	memorane	0.79	44	14	_	
28 March							
10	25.4	Paper	0.85	35	8		
10	25.7	Paper	0.82	55	9	e diman	
10	2.31)	1.00	0.87	44	7		
10	2.22	1.09μ and	0.82	40	12		
50	2.20	0.21μ	0.98	40	6	10 10 10 10 10	
50	2.22	membrane	0.92	41	9		

TABLE I. SUSPENDED MATTER IN SEA WATER; COMPARISON OF ANALYSES

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from 24 April 1951, with some exceptions mentioned below, but the methods of analysis continued to change somewhat as more convenient techniques evolved. Since the methods are all conventional they are described only briefly.

METHODS

Collection of Samples. All obvious methods of avoiding contamination of samples by dust and dirt were used. In dry weather the deck of the ship was hosed down for some distance all round the sampling position.

Filtration. This was done within three days of collection of samples with the important exceptions noted below. The whole volume taken was used. Carboy samples were filtered on paper and the residue was analysed as described by Armstrong and Atkins (1950). The 2l samples were filtered first through a 0.5μ membrane. When all the water had passed through, three or four successive portions of about 100 ml were used in succession to wash out the sample bottle, the inside of which was freed of adhering material by cleaning with a rubber tipped rod. The filtered water was returned to the bottle. The membrane, washed with three 20 ml portions of 5 % w/v ammonium nitrate solution (neutralised with ammonia to phenol red and filtered through $0.1 \,\mu$ membrane), was set aside on filter paper, spotted with glycerol (50 $^{\circ}/_{0}$ v/v) and kept under cover until ignited. The water was refiltered through a 0.1 μ membrane, which was treated similarly. The volume of water was then measured and recorded.

Ignition. This was in platinum crucibles for 30 min at 500° C. The spotting with glycerol kept the membranes moist and prevented flaring and *dusting*. Weights were recorded to the nearest 10^{-5} g and were corrected for the blank on the membrane and glycerol and for the average loss of platinum on ignition.

Silicon. Silicon was found by loss on treatment with hydro-fluoric acid.

Iron. The residue from the silicon determination was fused with potassium bisulphate; the melt was dissolved in hydrochloric acid $(10 \, ^0/_0 \, \text{v/v})$ and made to a known volume. Iron was determined colorimetrically with thiol-acetic acid until August 1951, when the following method, which also determined aluminium, was adopted.

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Iron and Aluminium. After extraction of the bisulphate melt, as before, the solution was neutralised to phenolphthalein with ammonia and buffered to pH 5, after which iron and aluminium were extracted as the oxinates by shaking with a chloroform solution of 8-quinolinol $(1 \ 0/_0 \ w/v)$. The absorbencies of the extract were measured at 390 and 465 m μ to determine iron and aluminium. Blanks were carried through all stages. The method is almost interferencefree for iron, but a number of elements can interfere with the aluminium determination. There was no reason to suppose, however, that interference would amount to more than about $1 \ 0/_0$ of the ash.

Calcium. This was done on one set of samples only, after the oxine extraction, by precipitation as oxalate and ignition to carbonate. Since the samples had by then had considerable handling and since weights of less than 1 mg CaCO_3 were found, no great accuracy is claimed.

RESULTS

Samples were taken monthly at the International Hydrographic St. E1, 20 m offshore in the English Channel, from 26 February 1951 to 11 March 1952. The inorganic suspended matter and its included silicon as SiO_2 are shown in Fig. 1.

Some samples taken from R.R.S. DISCOVERY II in deep water were also examined (Table II). Some of the deeper samples were composite ones from adjacent depths, as is shown. Samples from Sts. 2918 and 2927 were filtered on the ship within three days of collection, but those from St. 2929 were done at the Plymouth Laboratory 11–18 days after sampling. It was found necessary to use the double filtration (0.5 followed by $0.1 \,\mu$ membrane) only for samples down to 100 m; time was saved and extra manipulation avoided by filtering the cleaner samples from deep water on a $0.1 \,\mu$ membrane only. In these samples the suspended matter was just visible on the membrane as a faint greyish-brown stain.

When the analyses for SiO_2 , Fe_2O_3 and Al_2O_3 had been completed, it was obvious that a large part of the suspended matter at St. 2929 was unaccounted for, therefore these samples were then analysed for calcium. The quantities found made up most of the deficiency. Because these samples had been stored longer than the others, it was thought possible that at least part of the calcium found had been precipitated after collection of the samples, as in one case

TABLE II. INORGANIC FRACTION OF SUSPENDED MATTER IN SEA WATER, EASTERN ATLANTIC, 1952

Concentration						Composition							
Station, Date and Location	Depth (m)	Inorg. Suspend. Matter (mg/l)	Silicon (µg SiO ₂)	Iron (µg/l)	Alum- inium (µg/l)	$SiO_{s} + Fe_{s}O_{s} + Al_{2}O_{s}$ (mg/l)	solved Silicon (µg/l SiO ₃)	SiO ₂ (*/•)	Fe ₂ O ₃ (°/•)	Al ₂ O ₃ (°/ ₆)	CaCO. (°/•)	Total (°/ ₀)	Si: Al (atoms)
2918	0	0.11	50	7	6	0.08	50	50	10	11	-	71	15
3 June 1952	20	0.21	150	6	8	0.17	70	70	4	7		81	34
49°02' N 15°19' W	100	0.63	430	17	23	0.50	310	68	4	7		79	33
Sounding 4720 m	960	0.88	280	43	49	0.45	780	33	7	11	-	51	10
	1820	0.27	60	23	14	0.18	840	23	12	10	-	45	8
	2620	0.33	80	15	16	0.14	1680	25	7	9	-	41	9
	3730	0.14	50	23	10	0.10	2700	35	26	12	-	73	7
2927	0	0.21	50	66	6	0.17	60	25	45	6	_	76	14
8 June 1952	20	0.36	-	26	13		70	-	10	7	-	-	-
43°23' N 19°23' W	100	0.17	-	19	4		220	-	16	5		-	-
Sounding 6000 m	960	0.12	50	5	6	0.07	720	46	6	9	-	61	17
	1420	0.11	70	8	8	0.09	840	61	10	14	-	85	15
	2400a	0.06	80	-	4		1140	80	-	14	-	-	-
	3000b	0.15	100	6	2	0.12	1800	70	6	2	_	78	12
	4100c	0.05	40	6	2	0.05	2500	78	19	9	-	106	30
	5200d	0.09	70	25	7	0.12	2700	80	40	15		135	18
	5880	0.17	70	17	12	0.12	2700	40	15	13	-	68	10
2929	0	0.54	350	22	14	0.42	60	66	6	5	18	95	44
10 June 1952	20	0.61	110	26	13	0.24	60	30	6	4	27	67	46
44°30' N 15°26' W	100	0.76	80	18	8	0.12	210	11	3	2	60	76	19
Sounding 5500 m	980	1.00	80	16	14	0.13	720	8	2	3	60	73	9
	1840	0.15	60	9	12	0.09	840	39	9	15	53	116	9
	3000e	0.30	60	7	9	0.08	1980	19	3	6	36	64	11
	36 00 <i>f</i>	0.50	70	13	9	0.11	2400	14	4	4	47	69	12
	5310	0.57	90	33	17	0.16	2800	15	8	6	50	79	8
NOTES: Equal volu	mes from	a) 2180 2380 2580	m b) 5	2770 m 2890 3120 3350	c) 3580 1 3980 4300 4460	m d)4 5 5	750 m 050 380 580	e) 2180 m 3010 3210	f) 34 36 38	150 m 150 150			

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observed before (Armstrong and Atkins, 1950: 140) when an unusually high calcium content of 70 $^{0}/_{0}$ was found in a sample which had been kept overlong. For best comparison, the sums of the other constituents (silica, ferric oxide, and alumina) have been tabulated separately where possible. Also recorded are the relevant concentrations of dissolved silica (as determined by reaction with molybdate) and silicon aluminium ratios.



Figure 1. Suspended matter and silicon (solid portion of histogram) in mg/l at International Hydrographic Station E1 (50°02' N, 4°22' W) February 1951 to March 1952; filtered on 0.5 and 0.1 μ A.P.D. membranes excepting February and March 1951, when 1.0 and 0.2 μ A.P.D. were used.

DISCUSSION

General. The large proportion of calcium (returned as carbonate) in the samples from DISCOVERY St. 2929, which had been stored during warm weather for longer than usual, casts some doubt on the validity of the figures for total inorganic suspended matter and on their representation of conditions in the sea. Some precipitation may have taken place in all samples after collection. Rise of temperature and release of pressure may cause sea water samples to become supersaturated with respect to calcium carbonate, and the particulate matter would probably provide many nuclei for crystallisation.

This possible artifact may have been partly controlled, since most of the samples were filtered shortly after collection. Inspection of the analyses shows that generally the effect could not have been great, since calcium carbonate could rarely exceed 50 $^{\circ}/_{0}$ of the suspended matter even if it accounted for all the deficiency in the analyses.

Means of some of the data are given for convenience. It should be stressed that these are not true means since the sampling is biassed and since surface samples carry more weight than they should.

Total Inorganic Suspended Matter. For the English Channel, quantities of 0.16 to 1.20 mg/l (mean of all determinations 0.61) were found. Fig. 1 shows the seasonal variation, more being found during winter months than during other seasons. This effect is not likely to have been influenced by calcium precipitation following collection of samples, which is more probable in summer. It is simply explained as being the result of increased land drainage and turbulent mixing of bottom deposits in winter. There is an occasional tendency for the quantity of suspended matter to be higher at the surface than at subsurface depths.

At the deep water stations, concentrations varied from 0.05 to 1.00 mg/l, but the highest figures at St. 2929 were certainly due to high calcium content and may be put down to the prolonged storage. This effect may also be suspected at 960, 1820, and 2620 m at St. 2918.

 $SiO_2 + Fe_2O_3 + Al_2O_3$. This sum has been entered in Table II where possible. Apparently it shows more regularity than the total suspended matter.

Silicon. At St. E1, concentrations of 54 to $520 \ \mu g \ SiO_2/l$ were found. The seasonal variation is seen in Fig. 1; the decrease in summer goes with an increased diatom population. Except for one occasion, the silica in suspension exceeded that in solution, the latter ranging from 26 to $190 \ \mu g \ SiO_2/l$ [means for the whole water column (Armstrong, 1954)]. On 22 August 1951, silica in suspension at 5 and 10 m was $50 \ \mu g \ SiO_2/l$ whilst dissolved silica was about twice this value.

It is possible that resolution of suspended silica (much of which must be in diatoms) is rapid at times during the summer months.

At the deep water stations, suspended silica is not in excess except at or near the surface, but even in deep water it amounts to $2-10^{\circ}/_{0}$ of that in solution.

Iron. At the English Channel station there is a tendency for iron concentrations to be greater in winter than in summer, with higher values at the surface. The concentrations varied from 10 to 145 μ g Fe/l, the mean being about 50 μ g Fe/l. These results are in agreement with those of direct determinations for this station in 1955 and 1956 when there was an unbiassed mean of 35 μ g Fe/l for two years (Armstrong, 1957).

At the deep water stations the range was 5-66 μ g Fe; these values are comparable with those found directly for deep water stations in the Bay of Biscay (Armstrong, 1957).

Aluminium. From August 1951 to March 1952 the range was 8-107 (mean 37) μ g Al/l. In deep water the range was 2-49 (mean 12) μ g Al/l. These values may be compared with an estimated concentration for the open Pacific of about 30 μ g Al/l (Arrhenius, 1954).

Silicon: aluminium Ratios. The atomic ratios for the deep water stations vary from 8 to 46 and show a great excess of silicon compared with ratios for any of the common clay minerals.

CONCLUSIONS

It has been shown that an appreciable quantity of finely divided suspended matter exists both in offshore waters in the English Channel and in the open ocean. Because of its claylike nature, it is likely to be strongly absorbent, both of inorganic and organic substances in the water, and it may well be the chief support of 1958]

the rather sparse bacterial flora in sea water. Its relatively large silica content may influence the silicon cycle and the growth of diatoms, at least in upper waters.

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