Free Ammonia, Albuminoid Nitrogen, and Organic Nitrogen in the Waters of the Pacific Ocean off the Coasts of Washington and Vancouver Island.

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Introduction.

Results of the free ammonia, albuminoid and organic nitrogen determinations for the waters of the Puget Sound area during the summers of 1931 and 1932 were presented in a previous paper (3). It was pointed out that, first, the free ammonia was present in quantities bordering on the lower limit of sensitivity of the Wattenberg method; second, the organic nitrogen content decreased with depth; and, third, the albuminoid nitrogen/organic nitrogen ratios averaged 0.47 with the smallest ratios occurring at the greatest depths. In order to determine if these same relationships persist in the far deeper waters of the ocean, additional data have since been secured for the waters of the Pacific Ocean off the Washington coast.

Methods.

Except for free ammonia, the same analytical methods were employed as in the earlier work. The W i t t i n g - B u c h (2) method for determining free ammonia was substituted for W a t t e n b e r g's (8) as an extensive investigation (10) has shown that the former promises great accuracy and sensitivity and yet involves none of the difficulties encountered in the latter. W i t t i n g's procedure as originally recommended was followed, although T r e a d w e l l's Nessler reagent was substituted for R a b e n's. This important modification eliminates the non-sensitive range always found when determining small quantities of ammonia in sea water with the latter reagent.
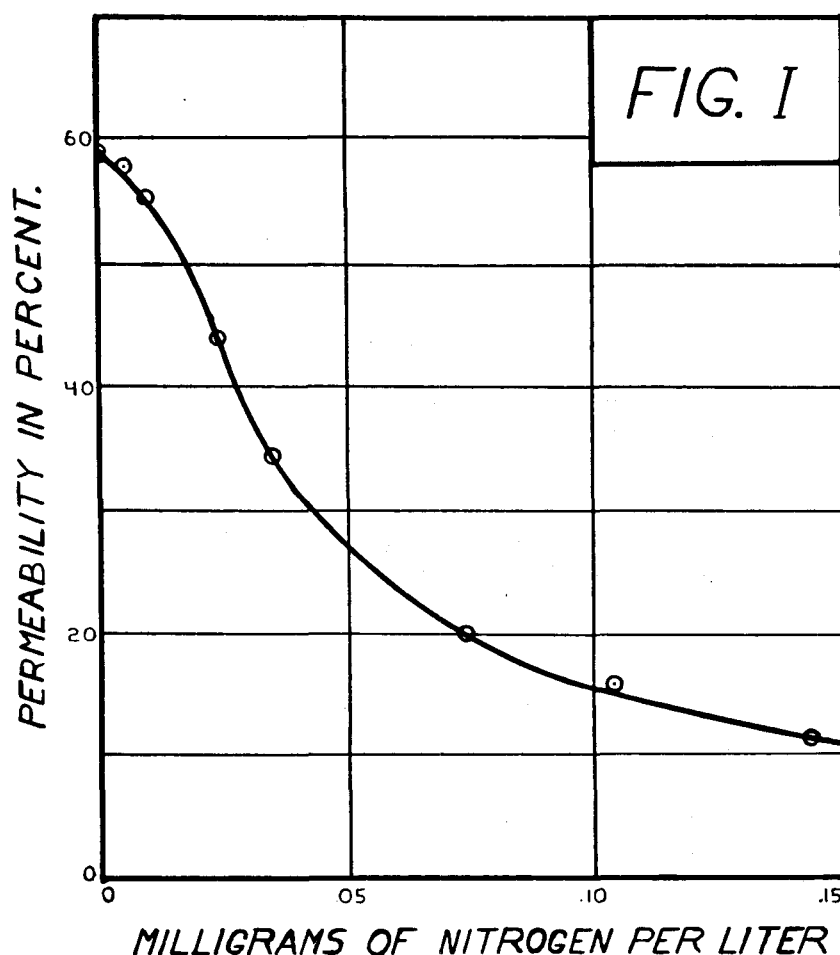
Fig. I.
Permeability of sea water (Cl = 17.0 — 20.0 °/oo) containing known
quantities of ammonia.

Reagents for the Witting-Buch Ammonia Determinations.

Treadwell's Nessler Reagent: Dissolve 115 grams of mercuric iodide
and 80 grams of potassium iodide in enough water to make 500 ml.
Add 500 ml. of 6N sodium hydroxide. Two ml. of this reagent are
used for every 100 ml. of solution being tested. *Barium Chloride
Solution:* Dissolve 200 grams of barium chloride dihydrate per liter.
Free of ammonia by partial evaporation and then dilute to original
volume with ammonia-free distilled water. *Sodium Hydroxide-
Sodium Bicarbonate Solution:* Dissolve 200 grams of sodium hydroxide
and 69 grams of sodium bicarbonate per liter. Free of ammonia as in
the barium chloride solution.

Procedure.

To 250 ml. of the sample in a 300 ml. bottle are added in succession 10 ml. of barium chloride and 20 ml. of sodium hydroxide-sodium bicarbonate solutions. With chlorinities less than 17 $^o/_{oo}$ smaller quantities of reagents are recommended (Cl = less than 11.0$^o/_{oo}$, 5 ml. BaCl$_2$; Cl = 11.0 — 13.9 $^o/_{oo}$, 6.5 ml. BaCl$_2$; Cl = 14.0 — 16.9 $^o/_{oo}$ 8.0 ml. BaCl$_2$, with twice as much NaOH—NaHCO$_3$ in each case). This eliminates the formation of turbid solutions upon nesslerization which is believed to be due to excess of reagents.

The samples reported in this paper were treated with reagents as soon as taken and the analyses completed in the shore laboratory. The time intervening between sampling and nesslerization was kept at a minimum to prevent the formation of ammonia from decaying plankton, though at least three days standing has been found necessary to insure complete precipitation of the magnesium hydroxide. The clear supernatant liquid was siphoned from the precipitate and an aliquot part nesslerized. One half-hour later, the permeability of the sea water was compared with that of untreated distilled water, employing the Zeiss-Pulfrich photometer. The ammonia content of the sample was then obtained from this reading by use of a standard curve. With this method an accuracy of $\pm$ 0.001 mg. of ammonia nitrogen per liter was obtained in the range from 0.000 to 0.050 mg.

Standard Curve.

The permeabilities of nesslerized solutions, prepared from ammonia-free sea water and known quantities of ammonium chloride solution were determined, and from these values a standard curve was constructed. In the preparation of the ammonia-free water the removal of the ammonia by boiling after the precipitation with BaCl$_2$ and NaOH—NaHCO$_3$ gave the better results as turbidities did not then follow nesslerization. In the range 17.0—20.0 $^o/_{oo}$, no correction for chlorinity was found necessary as the various standard curves coincided within the limits of experimental error. Figure I is a typical curve for this range.

Location of Stations.

During the summer of 1933 ocean samples[1]) were collected during two cruises of the M. S. "Catalyst", the University of Washington research boat. On one cruise, July 6—8, samples were collected at Stations 31, 34, 39, and 41. The first station was a hundred miles west of Vancouver Island. It was well past the continental shelf, which is approximately twenty-five miles wide in this region. Station 34 was five miles from Vancouver Island on shallow fishing banks. The second inshore station No. 39 was five miles W.S.W. of Tatoosh

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MILLIGRAMS OF NITROGEN PER LITER
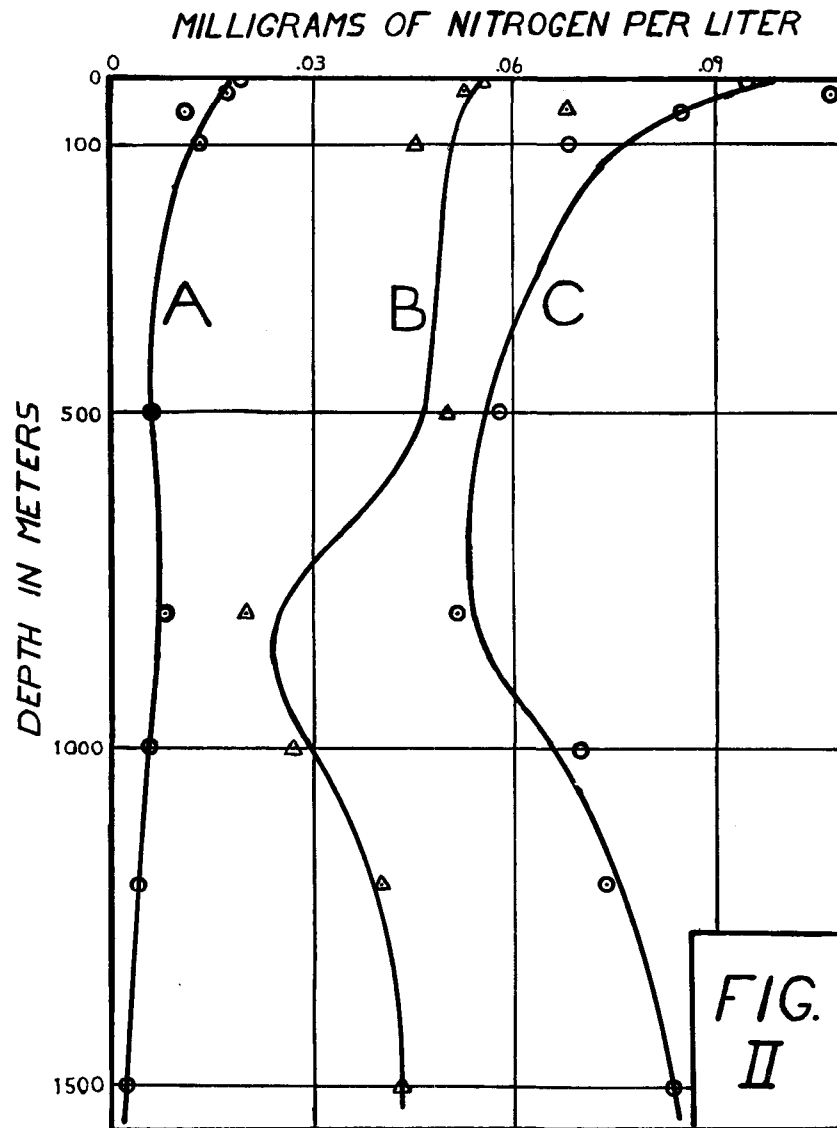
Fig. II.
Average free ammonia (Curve A), albuminoid nitrogen (curve B), and organic nitrogen (curve C) of the Pacific Ocean off the coast of the State of Washington and Vancouver Island.

Island in the submarine valley extending from the Juan de Fuca Strait across the continental shelf. Station No. 41 was located about twenty-five miles inside the Strait. During another cruise of the "Catalyst", July 22—24, samples were collected at Stations 59, 60, 62. The first

Table I.

Station No. 31   49°20'N   127°59'W   July 4, 1933

Depth (Meters)	NH₃-N	Alb. N	Org. N	Ratio: $\frac{\text{Alb. N}}{\text{Org. N}}$	NO₃-N	NO₂-N
		(Milligrams N per liter)				
0	0.045	0.05	0.07	0.72	0.01	0.0000
25	.028	.06	.09	.67	.00	.0000
50	.030	.04	.06	.67	.13	.0070
100	.022	.07	.07	1.00	.32	.0000
500	.020	.04	.05	0.80	.69	.0000
1000	.018	.01	.07	.14	.66	.0000
2000	.000	.02	.07	.29	.81	.0000

Station No. 59   49°22'N   129°29'W   July 22, 1933

Depth (Meters)	NH₃-N	Alb. N	Org. N	Ratio: $\frac{\text{Alb. N}}{\text{Org. N}}$	NO₃-N	NO₂-N
		(Milligrams N per liter)				
0	0.012	0.09	0.12	0.75	0.21	0.0000
25	.026	.05	.11	.45	.02	.0000
50	.012	.09	.09	1.00	.09	.0050
100	.005	.05	.07	0.71	.20	.0030
300	.004				.48	.0000
500	.005	.04	.06	.67	.69	.0000
700	.001				.72	.0000
800	.023	.02	.06	.33	.72	.0000
900	.001				.93	.0000
1000	.001	.02	.06	.33	.79	.0000
1100	.005				.86	.0000
1200	.013	.02	.05	.40	.88	.0000
1500	.000	.04	.10	.40	.75	.0000
2000	.050				.72	.0000

two were two hundred miles and the third one hundred miles off shore. For greater convenience of discussion the stations have been grouped so that the results of the four deep stations are recorded in Tables I and II, while those of the inshore stations are shown in Tables III and IV. The results given in Tables I and II are presented graphically in Figure II.

Discussion of Results.

Free Ammonia.

Comparatively little ammonia was found in the samples taken at the four deep stations. Of the thirty-nine samples analyzed twenty-three contained 0.005 mg. or less, while only three contained more than 0.030 mg. ammonia nitrogen.

Except for occasional samples most of the ammonia occurred in the upper 100 meters of water, as is clearly indicated by Figure II, (curve A) while below this layer but little ammonia was found. The average for the surface waters of the four deep stations was 0.020 mg. ammonia nitrogen, while at 1500 meters it was only 0.002 mg. This

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Table II.

Station No. 60   48°24′30″N   128°01′W   July 23, 1933

Depth (Meters)	NH₃-N	Alb. N (Milligrams N per liter)	Org. N	Ratio: $\frac{Alb.\ N}{Org.\ N}$	NO₃-N	NO₂-N
0	0.013	0.03	0.10	0.30	0.00	0.0000
25	.005	.05	.12	.42	.00	.0000
50	.002	.05	.10	.50	.10	.0080
100	.023	.04	.07	.29	.52	.0000
500	.001	.04	.06	.67	.70	.0000
800	.000	.02	.04	.50	.52	.0000
1000	.004	.05	.06	.83	.72	.0000
1200	.000	.03	.07	.43	.74	.0000
1500	.004	.02	.08	.25	.90	.0000

Station No. 62   47°50′N   125°43′W   July 24, 1933

Depth (Meters)	NH₃-N	Alb. N (Milligrams N per liter)	Org. N	Ratio: $\frac{Alb.\ N}{Org.\ N}$	NO₃-N	NO₂-N
0	0.008	0.05	0.09	0.56	0.00	0.0000
25	.010	.05	.11	.45	.00	.0000
50	.000	.09	.09	1.00	.08	.0050
100	.003	.02	.06	0.33	.42	.0000
500	.000	.08	.06	.?	.82	.0000
800	.000	.02	.06	.33	.81	.0000
1000	.000	.03	.09	.33	1.10	.0000
1200	.005	.07	.10	.70	0.79	.0000
1500	.003	.02	.06	.33	.69	.0000

Table III.

Station No. 34   49°01′15″N   125°46′45″W   July 6, 1933

Depth (Meters)	NH₃-N	Alb. N (Milligrams N per liter)	Org. N	Ratio: $\frac{Alb.\ N}{Org.\ N}$	NO₃-N	NO₂-N
0	0.053	0.07	0.17	0.41	0.07	0.0025
10	.048	.07	.17	.41	.26	.0037
25	.038	.08	.11	.72	.41	.0060

Station No. 39   48°19′N   124°55′W

Depth (Meters)	NH₃-N	Alb. N (Milligrams N per liter)	Org. N	Ratio: $\frac{Alb.\ N}{Org.\ N}$	NO₃-N	NO₂-N
0	0.031	0.02	0.11	0.18	0.36	0.0038
25	.020	.03	.07	.43	.43	.0033
50	.012	.09	.09	1.0	.48	.0026
100	.004	.10	.08	.?	.48	.0021
200	.015	.06	.07	.85	.52	.0029
300	.077	.00	.03	.00	—	.0006

Table IV.

Station No. 41   48°21′N   124°11′30″W   July 8, 1933

Depth (Meters)	NH$_3$-N	Alb. N	Org. N	Ratio: $\frac{Alb. N}{Org. N}$	NO$_3$-N	NO$_2$-N
		(Milligrams N per liter)				
0	0.014	0.07	0.09	0.78	0.33	0.0039
25	.012	.08	.09	.89	.31	.0040
50	.008	.06	.10	.60	.40	.0030
100	.000	.05	.07	.71	.50	.0011
175	.001	.07	.07	1.0	.53	.0011

Note: The nitrate and nitrite data in the above tables were obtained by T. G. Thompson and co-workers.

Table V.

Average Albuminoid Nitrogen/Organic Nitrogen Ratios at Various Depths.

Depth	Ratio	Depth	Ratio
0	0.58	800	0.39
25	0.50	1000	0.41
50	0.79	1200	0.51
100	0.58	1500	0.32
500	0.78	2000	0.29

vertical distribution of ammonia agrees with the findings of other investigators (4) (9). Wattenberg (9) attributed the larger quantities of ammonia in the surface waters to the decomposition of dead plankton in the upper, plankton-rich layer while more rapid nitrification prevents the accumulation of ammonia at lower depths.

Samples collected in the Strait of Juan de Fuca (Table IV) likewise showed but little ammonia. It will be noted that these values are not essentially different from those of the deep stations where this water has but recently had its origin (7). Both the shallow inshore ocean stations (Table III) contained considerably larger quantities of ammonia. In the submarine valley the ammonia had a minimum value at 100 meters with much larger quantities at surface and bottom. From an examination of the ammonia data reported it will be observed that the samples with exceptionally high ammonia content were, for the most part, from the waters near the bottom. The waters impregnating the bottom muds have been shown (1) (5) to be especially rich in free ammonia which, in turn, diffuses and enriches the supernatant water. This action might easily account for the greater concentration of ammonia in all three samples at Station 34, though the decrease in ammonia content with depth would result from the usual effects of ammonia formation in the surface waters and vigorous nitrification in the lower depths.

Albuminoid and Organic Nitrogen.

Due to the greatly diminished biological activity in the open ocean the albuminoid and organic nitrogen were present in even smaller quantities than in the inland waters of this region. The average content of albuminoid nitrogen for the four deep stations was 0.04 mg. per liter, and of organic nitrogen 0.08 mg. compared with an average of 0.10 and 0.21 mg. respectively for the inland waters.

Figure II (Curves B and C) gives the vertical distributions found for albuminoid and organic nitrogen. The albuminoid nitrogen was practically constant down to 500 meters, showed a minimum at 800 meters and then increased with depth to an amount slightly less than the surface value. The organic nitrogen decreased rapidly with depth to 100 meters, also had a minimum value at 800 meters, then increased again until at the bottom the surface value was almost equalled.

The lesser quantities of albuminoid and organic nitrogen below the photosynthetic zone and above eight hundred meters may be attributed to the decreasing quantity of plankton. The minimum values found at eight hundred to one thousand meters may be unquestionably correlated with similar minimum values for oxygen reported by T h o m p s o n, T h o m a s and B a r n e s (7). From a study of various data, particularly temperature, oxygen, chlorinity and carbon dioxide, for the waters of the Bering Sea, Gulf of Alaska and off the coast of Washington, T h o m p s o n and his co-workers believe that it is possible this layer of water has come as a subsurface current from the stagnant bottom waters of the Gulf of Alaska. Whatever the origin of this layer may have been, there must be a close relationship between the amount of oxygen and the amount of decomposition that has taken place since somewhen and somewhere the dissolved oxygen present in the water has been utilized in the decomposition of organic material.

The average albuminoid/organic nitrogen ratios for the various depths have been calculated and listed in Table V. As in the deepest waters of the Puget Sound region, the lower depths have the lowest ratios. The average ratio of all the samples above eight hundred meters is 0.57 while those samples at eight hundred meters or below yield an average ratio of 0.40. The abrupt change in this ratio beginning at eight hundred meters indicates that the nitrogeneous material below this depth is of a more stable character. The long absence from a region of biological activity has given an opportunity for the decomposition of the less stable material.

The only reports of the albuminoid nitrogen content of deep waters, as far at the authors are aware, are those of N a t t e r e r on the Mediterranean Sea and R a b e n on the North and adjacent seas as reported by B r a n d t (8). The average for all samples analyzed by N a t t e r e r was 0.103 mg. per liter, the lowest average for any one trip being 0.041 mg. and the highest 0.139 mg. per liter. R a b e n obtained an average of 0.126 mg. per liter in the North Sea and practically the same quantity in the waters west of the Thomsen Ridge near the Orkney Islands. To these values of R a b e n and N a t t e r e r,

however, should be added a part of the free ammonia reported by them (0.040 and 0.047 mg. per liter respectively) since it is now known that when free ammonia is determined by distillation a portion of the albuminoid nitrogen is liberated as ammonia on boiling. These values are, therefore, approximately three times as large as those reported in this paper. The scarcity of plankton in the Pacific Ocean would naturally result in low values inasmuch as albuminoid nitrogen is closely related to the plankton content.

Summary.

1. The quantity and distribution of ammonia in the Pacific Ocean off the Washington coast corresponds to that found in other oceans.

2. The amount of albuminoid and organic nitrogen is less than that found in the inland waters of this region.

3. Other investigators have reported much larger values for albuminoid nitrogen in the Mediterranean and North Seas.

4. The vertical distributions of albuminoid and organic nitrogen show minima at eight hundred to one thousand meters with greater values at surface and bottom.

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