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Aldehydes in Lake and Sea Waters

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The vertical distribution of aldehydes in Lake Kizaki during summer stagnation is described. Aldehydes are found only in the hypolimnion, not in the upper aerobic water layers. The highest aldehyde content in three series of vertical samples is 0.11 mg./l. in terms of formaldehyde equivalents. It was shown by laboratory experiments that formaldehyde is rapidly decomposed in aerobic lake water, but very slowly in anaerobic lake water. In sea waters, aldehydes are not found in the surface water layer, and no systematic variation is noticed in the verticall distribution.

The decomposition of organic substances to carbon dioxide is an important process in the carbon cycle in natural waters. In order to investigate this process thoroughly, it is first necessary to elucidate the distribution of the organic substances produced and preserved in a water body and its deposits. In this connection we have previously reported on carbohydrates and organic acids in lake waters.[1,2]

In the present paper some results will be given on aldehydes in lake and sea waters and in an interstitial water of a lake mud.

Results and Discussion

Lake Waters and Interstitial Water of Lake Mud.—Three series of the vertical distribution of aldehydes in Lake Kizaki during summer stagnation are given in Table I. Aldehydes are found only in water layers below a depth of 20 m., not in the upper aerobic water layers. The highest aldehyde content is 0.11 mg./l. in terms of formaldehyde equivalents; this is observed in anaerobic water layers near the bottom. The aldehyde content in an interstitial water of the bottom mud is 0.044 mg./l. in terms of formaldehyde equivalents (Table II).

In order to make it clear why aldehydes are found only in the hypolimnion, the decomposition rates of formaldehyde under aerobic or anaerobic conditions at 20°C and 8°C in lake water were assertained.*[1] The anaerobic conditions at 8°C refer approximately to the conditions at a depth of 25 m. in the lake. The results are shown in Fig. 1. As is shown in Fig. 1-A, under aerobic conditions at 20°C, 50 μg./l. of formaldehyde is completely decomposed in 30 hr., but under anaerobic conditions at 8°C, 50 μg./l. of formaldehyde invariably remains for 3 days, and then is gradually decomposed and so completely lost over the next 3 days. Even at 20°C the lifetime of formaldehyde under anaerobic conditions is twice that under aerobic conditions. It is clearly demonstrated that formaldehyde is decomposed through microbiological processes by the fact that no decrease in formaldehyde is observed in sterilized lake water*[2] over an 8 day period. From these experimental results it may be concluded that aldehydes can not be found in aerobic water layers because of their rapid decomposition rate, while in anaerobic hypolimnion their slow rate of decomposition allows them to be preserved in a detectable concentration. Thus

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1) K. Sugawara and E. Kamata, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **86**, 1275 (1965).

2) E. Kamata, ibid., **87**, 244 (1966).

*[1] Surface water from Lake Kizaki was used for these experiments.

*[2] The water was intermittently heated in a boiling water bath 8 times for 30 min. a day.

TABLE I. THE VERTICAL DISTRIBUTION OF ALDEHYDES IN LAKE KIZAKI

Depth m.	Temp. °C	O_2 ml./l.	pH	Fe^{2+} mg./l.	HCHO mg./l.
		Aug. 7, 1961			
0	25.9	7.3	7.0		<0.01
5	19.5	12.5	9.5		<0.01
10	10.5	6.8	6.5		<0.01
15	8.2	5.8	6.5		<0.01
20	7.7	5.6	6.3		<0.01
25	7.1	3.2	6.1		0.01
26	—	—	—		0.01
28	—	0.4	—		0.01
28.5	—	—	—		0.02
29 (bottom)	7.0	—	—		0.02
		Nov. 2, 1961			
0	15.1	6.54	6.9		<0.01
5	15.0	6.41	6.8		<0.01
10	13.6	5.35	6.5		<0.01
15	8.6	2.93	6.3		<0.01
20	7.7	1.57	6.3		<0.01
25	7.1	0.00	6.3	0.8	0.02
28	7.05	0.00	6.6	5.6	0.07
28.5 (bottom)	—	0.00	6.5	8.4	0.11
		Oct. 30, 1962			
0	13.0	6.82	7.0		<0.01
5	13.7	6.71	7.0		<0.01
10	13.8	5.80	6.8		<0.01
15	13.7	1.85	6.3		<0.01
20	8.70	0.17	6.2		<0.01
25	6.60	0.10	6.4	0.5	0.01
27.5	—	0.00	6.2	5.4	0.02
28.5 (bottom)	6.53	0.00	6.6	6.0	0.01

TABLE II. THE ALDEHYDE CONTENT IN AN INTERSTITIAL WATER OF THE BOTTOM MUD FROM LAKE KIZAKI

Date of sampling: Sept. 21, 1963.
Water content: 78 g./100 g. of fresh mud.
Fe^{2+}: 20 mg./l.
Aldehydes as HCHO: 0.044 mg./l.

aldehydes liberated from organic matters are decomposed to carbon dioxide and can be found in anaerobic hypolimnion as a result of dynamic equilibrium, production-decomposition.

Sea Water.—Sea waters were obtained during the cruise of the Ryofu Maru belonging to the Japan Meteorological Agency made as the JEDS-4 (The Fourth Japanese Deep Sea Expedition). After being frozen, the samples were transported to our laboratory. Table III gives three series of the vertical distribution of aldehydes down to a depth of about 4000 m. The degree of the aldehyde content is expressed by a + sign. A +unit is approximately equivalent to 0.01 mg./l. in terms of formaldehyde equivalents. Aldehydes are not found in the surface water layer. This is caused by the higher temperature and the aerobic conditions. No systematic variation in aldehydes is

TABLE III. THE VERTICAL DISTRIBUTION OF ALDEHYDES IN SEA WATERS

Depth m.	Temp.* °C	Cl* o/oo	O_2* ml./l.	Aldehyde
St. JEDS-4-E_{4-1}(Ry 1508) 38°01′N, 146°00′E Jun. 20, 1961				
0	18.3	19.05	5.50	0
50	13.61	19.10	5.11	++++
100	10.09	18.96	4.66	+++
197	7.19	18.79	5.23	+++
395	4.28	18.74	3.43	++++
593	4.05	18.91	1.60	+++
791	3.46	18.99	1.13	+++
988	2.94	19.03	0.94	++++
1483	2.30	19.10	1.15	+
2188	1.78	19.16	2.12	+++
2733	1.62	19.19	2.65	++
3278	1.52	19.19	3.08	+
St. JEDS-4-E_5 (Ry 1510) 38°00′N, 146°57′E Jun. 22, 1961				
0	18.7	19.04	5.40	0
20	16.72	19.04	5.95	0
50	12.96	19.08	5.27	+++
100	9.76	18.93	4.72	+
199	6.72	18.79	5.07	0
398	4.39	18.79	2.91	0
596	3.94	18.94	1.46	+++
787	3.28	19.00	1.04	+
989	2.91	19.03	0.97	++
1474	2.29	19.10	1.15	+++
1990	1.89	19.14	1.83	0
2488	1.67	19.18	2.52	++
2988	1.54	19.19	2.96	+++
3409	1.51	19.20	3.31	0
3907	1.41	—	—	+
St. JEDS-4-E_6 (Ry 1511) 38°01′N, 148°00′E Jun. 23—24, 1961				
0	18.9	19.06	5.30	0
50	14.60	19.05	5.72	+++
100	10.78	18.97	4.81	+++
391	4.69	18.81	2.77	+++
588	4.09	18.92	1.55	+++
783	3.41	18.98	1.11	+++
980	2.98	19.04	0.99	+++
1226	2.50	19.08	0.96	++
1472	2.28	19.12	1.16	+++
2143	1.81	19.16	2.05	++
2643	1.62	19.19	2.71	++
3140	1.53	19.19	3.01	++
3235	1.52	19.19	3.09	+
3735	1.48	19.19	3.27	0
4108	1.49	19.20	3.29	+++

* J. Masuzawa and H. Akamatu, *Oceanogr. Magazine* (Tokyo), **13**, 122 (1962).

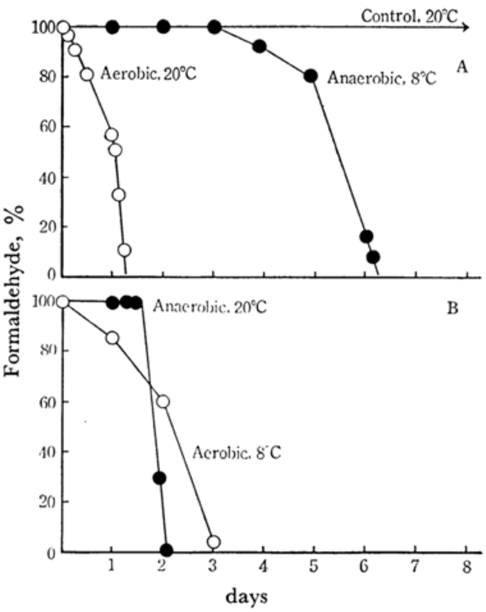

Fig. 1. Decomposition of formaldehyde in lake water under the aerobic or anaerobic condition. The concentration of formaldehyde added, 50 μg./l.

noticed. The lower temperature of the water layers below the surface layer should explain the preservation of a detectable amount of aldehydes.

Experimental

Reagents.—*A Standard Solution of Formaldehyde.*—A stock solution of formaldehyde is standardized by the dimedone method.[3] The aliquot of the stock solution is then used as the standard solution (1 μg./ml.).

3-*Methyl*-2-*benzothiazolone Hydrazone Hydrochloride (MBTH) Reagents.*—1) 0.4% aqueous solution. 2) 0.4% (1+1000) hydrochloric acid solution.

1% *Ferric Chloride Solution.*

Saturated Sodium Chloride Solution.

Crystals of Anhydrous Sodium Sulfate.

Organic Solvents.—1) Acetone. 2) A mixed solvent, (1+1) acetone-chloroform.

Apparatus.—Coleman model 14 spectrophotometer. Tokyo Photo-electric Laboratory filter photometer, model 7A (for field work). Sharp TE-10 automatically temperature-controlled water bath.

Procedure 1 (for lake water).—To 10 ml. of a test solution 2 ml. of a 0.4% MBTH aqueous solution is added. After the mixture has stood for 20 min., 0.5 ml. of 1% ferric chloride solution is added. After an additional 10 min., 12.5 ml. of acetone is added. The absorbance is read at the wavelength of 670 mμ within 30 min.

Procedure 2*3 (for the interstitial water and sea water).—To 9 ml. of a test solution 1 ml. of a saturated sodium chloride solution is added; then 2 ml. of a 0.4% MBTH (1+1000) hydrochloric acid solution is added. After the mixture has stood for 20 min., 0.5 ml. of 1% ferric chloride solution is added. After an additional 10 min., the mixture is transferred into a separatory funnel with 12 ml. of a (1+1) acetone-chloroform solvent and shaken twenty times. The extract is poured into a 10 ml. measuring flask, and the flask is filled up to the mark with the solvent. Then the extract is quickly dehydrated in a stoppered test tube with 6 g. of anhydrous sodium sulfate. The suspended particles in the extract are filtered off through dry filter paper. The absorbance is read at the wavelength of 670 mμ. The color is stable for at least two hours.

For the determination of aldehydes in sea water, 10 ml. of a test solution is used without the addition of the sodium chloride solution.

The Separation of the Interstitial Water from Lake Mud.—A lump of frozen lake mud (~200 g.) is melted and filtered through a Millipore Filter (type HA) under a nitrogen atmosphere.

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[*3] A modified procedure[4] of the original method by Sawicki et al.[5]

[3] J. H. Yoe and L. C. Reid, *Ind. Eng. Chem.*, *Anal. Ed.*, **13**, 238 (1941).

[4] E. Kamata, This Bulletin, **38**, 2005 (1965).

[5] E. Sawicki, T. R. Hauser, T. W. Stanley and W. Elbert, *Anal. Chem.*, **33**, 93 (1961).