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SEASONAL VARIATION IN THE CONCENTRATION OF COPPER IN THE SURFACE WATERS OF SAN JUAN CHANNEL, WASHINGTON¹

By

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ABSTRACT

The concentration of copper in the surface water of San Juan Channel in the State of Washington was determined over a period of 17 months. The average concentration in all samples analyzed was $0.023 \mu\text{g-at/L}$. A definite seasonal trend was indicated with an autumn minimum of $0.016 \mu\text{g-at/L}$ and a summer maximum of $0.028 \mu\text{g-at/L}$. The copper content varied inversely with the values obtained for density, phosphates and silicates. On several occasions during early summer, abnormally high values of $0.060 \mu\text{g-at/L}$ were obtained at times of lower low tide, low salinity, high water temperature and when there were no meteorological disturbances. Presumably these abnormal values result from reactions that take place in areas where anaerobic conditions cause precipitation of copper sulfide, which is then oxidized to soluble copper sulfate under favorable climatic conditions. By the process of leaching and drainage such waters, because of their low densities, become surface water in the adjacent areas.

INTRODUCTION

In a recent paper, Chow and Thompson (1952) outlined a method for the determination of copper in sea water, summarized results of

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previous investigations, and gave data on a number of analyses. The present investigation was undertaken to study the seasonal variation in the concentration of copper in the surface waters of San Juan Channel near the Friday Harbor Laboratories, University of Washington, to ascertain possible correlation between the concentration of copper and other minor constituents of sea water, to observe the extent of changes in the concentration of copper during a tidal cycle, and to note variations at different depths.

METHODS OF ANALYSIS

The standardized oceanographic procedures employed in this study are outlined as follows:

Temperature: Obtained with Richter type reversing thermometers, which were graduated to 0.05° C. Readings were made to 0.01° C.

Chlorinity: Determined by the Knudsen method, the silver nitrate solution being standardized against the standard sea water of the Copenhagen Hydrographic Laboratories.

Dissolved Oxygen: Determined by the modified Winkler method (Thompson and Robinson, 1939).

Inorganic Phosphates: Determined by the refined Deniges molybdenum blue method (Robinson and Thompson, 1948a). In order to compensate for the salt effect, phosphate-free synthetic sea water was used in the preparation of comparison standards. Analyses were made as soon as samples had reached room temperature.

Silicates: Determined by the silico-molybdate colorimetric method, using potassium chromate solution buffered with borax as permanent standards (Robinson and Thompson, 1948b).

Copper: Ascertained by the diethyldithiocarbamate method (Chow and Thompson, 1952). To prevent contamination from sampling devices, all surface samples were collected in Pyrex glass bottles and the samples were immediately transferred to polyethylene containers. Only stainless steel wire was utilized when depth samples were secured with the ZoBell bacteria sampling bottle (ZoBell, 1941). Each value given for copper was the average of three determinations.

RESULTS

The monthly average oceanographic data for the surface waters of San Juan Channel are given in Table I and Fig. 1. The mean temperature for the year was 9.04° C, with a range from 6.57° to 13.10° C. The range for monthly average temperatures varied from 6.79° C in January 1952 to 11.23° and 10.63° in August 1951 and 1952 respectively.

TABLE I. MONTHLY AVERAGE CONCENTRATION OF COPPER AND VARIOUS OCEANOGRAPHIC DATA FOR THE SURFACE WATERS OF SAN JUAN CHANNEL NEAR FRIDAY HARBOR, WASHINGTON, DURING 1951 TO 1953.

Date	Temp. (°C)	Chlorinity (‰)	Dissolved Oxygen		Phosphate-P (μg-at/L)	Silicate-Si (μg-at/L)	Copper (μg-at/L)	
			σ_t	(mg-at/L)				(% Sat'n)
1951								
August	11.23	16.52	22.75	0.413	72.4	1.70	27	0.028 (7)*
September	10.61	16.92	23.42	0.383	66.6	1.90	33	0.022 (29)
October	9.74	17.11	23.83	0.364	63.8	2.15	37	0.019 (8)
November	8.76	17.01	23.84	0.427	71.0	2.20	40	0.016 (7)
December	8.00	16.92	23.81	0.498	83.7	2.10	40	0.018 (7)
1952								
January	6.79	16.97	24.06	0.537	88.0	2.10	40	0.017 (6)
February	6.90	16.81	23.82	0.553	90.6	2.10	40	0.018 (6)
March	7.12	16.89	23.90	0.543	89.4	1.90	38	0.021 (7)
April	7.71	16.93	23.88	0.530	88.6	1.90	35	0.021 (7)
May	8.71	16.78	23.53	0.494	84.4	1.90	34	0.022 (7)
June	9.51	16.48	22.96	0.444	75.6	1.75	34	0.025 (8)
July	10.43	16.27	22.54	0.461	79.5	1.65	34	0.028 (11)
August	10.63	16.65	23.05	0.382	66.1	1.70	35	0.028 (8)
1953								
June	9.89	16.62	23.09	0.456	77.5	1.70	38	0.028 (7)
July	10.81	16.22	22.56	0.440	76.0	1.70	39	0.032 (27)
August	10.83	16.51	22.80	0.387	66.0	1.90	41	0.025 (22)
September	10.87	16.54	22.84	0.375	65.3	1.90	44	0.020 (9)

*Figure in parentheses after value for copper designates number of different samples.

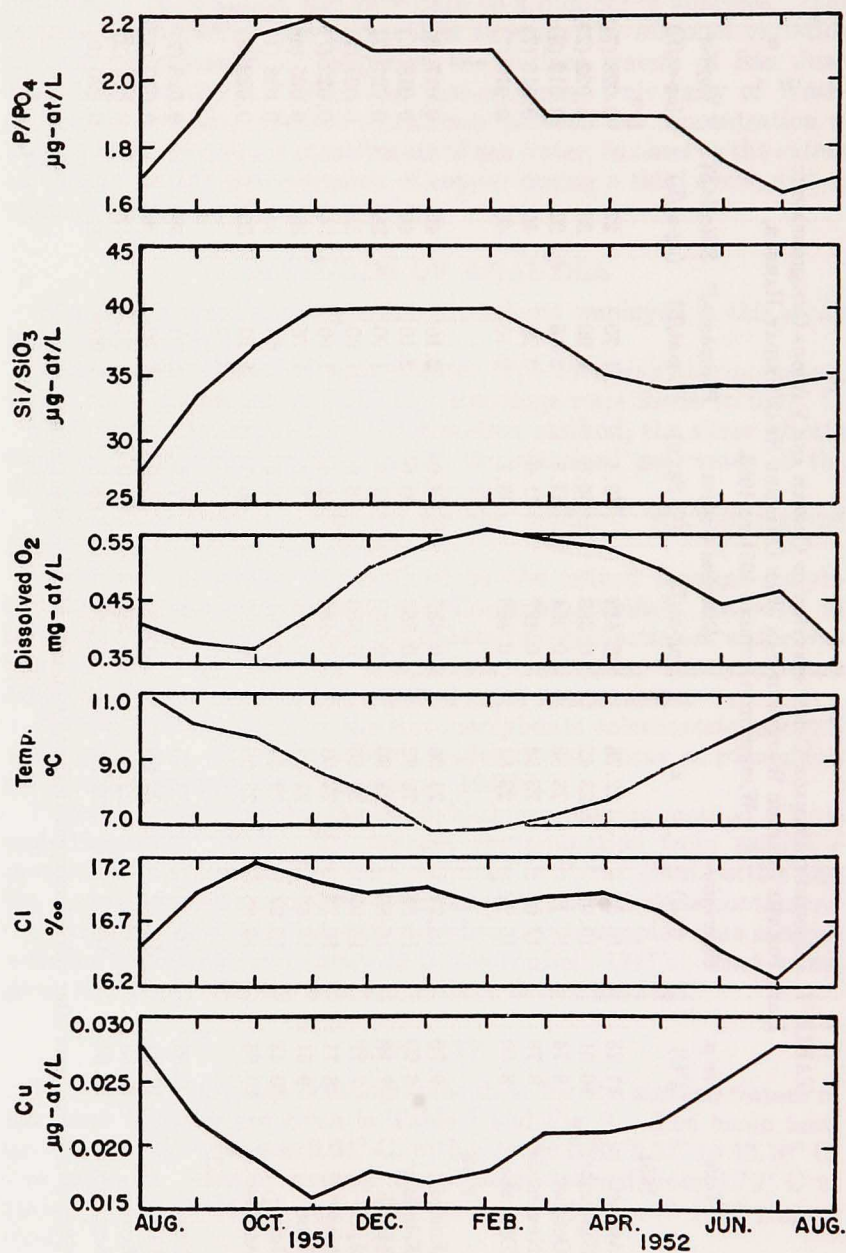


Figure 1. Seasonal variation of copper concentration and various oceanographic data for the surface waters of San Juan Channel, Washington.

The maximum chlorinity, 17.21 ‰ Cl (31.09 ‰ S), was observed in October, the minimum, 15.00 ‰ Cl (27.11 ‰ S), in mid-July. This minimum salinity occurred with the maximum temperature of 13.5° C.

The highest values for dissolved oxygen were obtained during the winter months, after which gradual decreases occurred until the lowest values were reached in October.

With the first bloom of diatoms in February, the concentrations of organic phosphates and silicates decreased and continued to decrease until the lowest values were reached in July. The highest concentrations, associated with the highest salinities of the year, were attained in November.

The monthly average copper concentration of the surface waters showed a definite seasonal trend with an autumn minimum and a summer maximum. In other words, the concentration of copper varied inversely with those of phosphates and silicates. Increase in copper content became evident in March and continued until July, when the highest values were noted. From August to November the copper concentrations decreased until minimum values were obtained. From November to March the copper content remained rather constant.

On various occasions during the summer months, abnormally high values for copper were sometimes encountered in surface water samples, particularly in those taken at times of slack tide and zero wind. Values as high as 0.060 µg-at/L were noted on several occasions. Fluctuations in the copper concentration between individual samples appeared to be greatest during the summer months and occurred in waters of low salinities and high temperatures at times of lower low tides when there was no meteorological disturbance.

A station in San Juan Channel was occupied to ascertain the vertical distribution of copper in water by using the ZoBell sampling equipment. These data are shown in Table II. Several other vertical stations had been occupied prior to the use of the ZoBell sampler, but the data were considered unreliable because of probable contamination of the samples. The authors have found that any equipment made of bronze, brass, or copper alloys which has been coated, plated, or painted with protective substances is unreliable for taking samples on which copper is to be determined. Furthermore, they observed that care must also be exercised in securing surface samples free of contamination from a ship, especially if copper paint has been used on the hull.

The chemical composition of the inshore waters varies not only with the season but to a lesser extent with the tide. Observations made

TABLE II. VERTICAL DISTRIBUTION OF COPPER IN THE WATERS OF
SAN JUAN CHANNEL, WASHINGTON, JULY 25, 1952.
LAT. 48° 36.4' N; LONG. 123° 04.4' W.

Depth (m)	Temp. (°C)	Chlorinity (‰)	δ_t	Copper ($\mu\text{g-at/L}$)
0	10.4	16.76	23.22	0.020
10	10.4	16.76	23.22	0.020
20	10.3	16.77	23.25	0.021
40	10.1	16.78	23.30	0.022
70	10.1	16.91	23.50	0.022
100	10.0	16.92	23.52	0.020
120	9.7	16.95	23.60	—
140	9.6	16.96	23.64	—

during a tidal cycle showed a range of 0.013 to 0.018 $\mu\text{g-at/L}$ for surface waters. Higher values were obtained on the ebbing tide.

For comparison, surface sea water samples were collected in the Pacific Ocean from 60 to 500 miles beyond the Washington coast as well as at the entrance of the Strait of Juan de Fuca. The results are given in Table III. The waters of several lakes in Washington—three in Seattle in King County, two in Snohomish County, and two on San Juan Island in San Juan County—were analyzed for the copper content; the results are given in Table IV.

TABLE IV. CONCENTRATION OF COPPER IN SEVERAL FRESH WATER LAKES
NEAR SEATTLE AND ON SAN JUAN ISLAND, WASHINGTON

Location	Copper, $\mu\text{g-at/L}$
Lake Washington, Seattle, King County	0.065
Lake Union, Seattle, King County	0.070
Salmon Bay, Seattle, King County	0.075
Hall Lake, Snohomish County	0.080
Chase Lake, Snohomish County	0.085
Echo Lake, San Juan Island	0.090
Sportsman Lake, San Juan Island	0.105

DISCUSSION

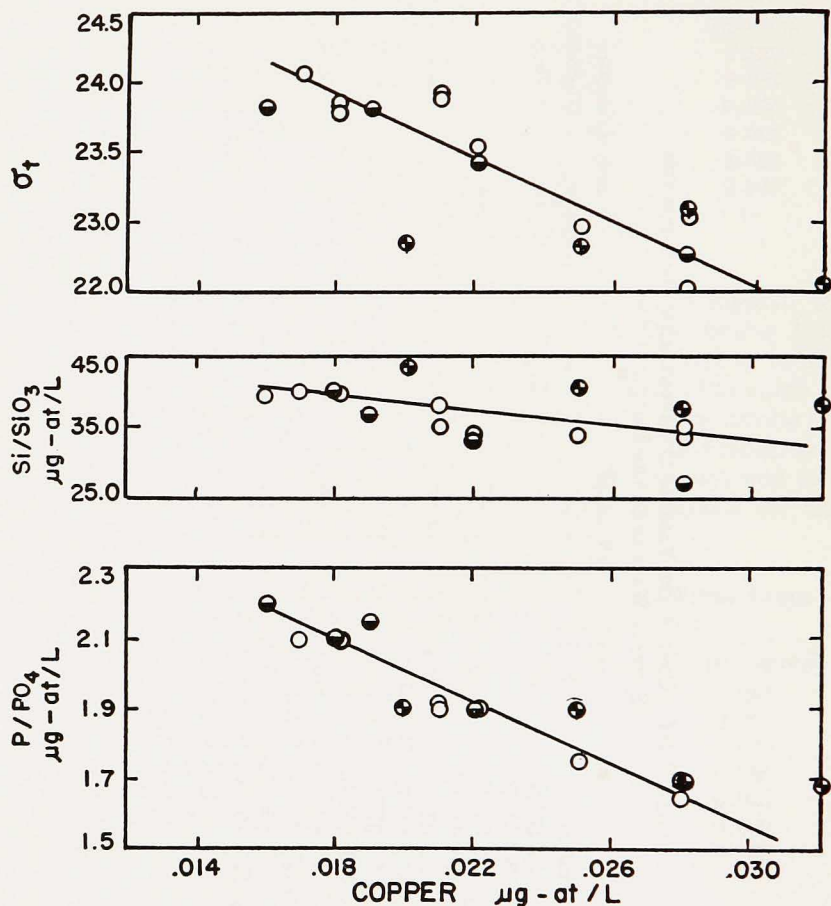
The copper concentration in 200 samples of surface water collected in San Juan Channel ranged from 0.012 to 0.060 $\mu\text{g-at/L}$, with an average of 0.023. The data demonstrate a definite seasonal trend, with a summer monthly maximum of 0.028 $\mu\text{g-at/L}$ and an autumn minimum of 0.016 $\mu\text{g-at/L}$. The concentration of phosphates and silicates, determined simultaneously with the copper, showed summer minima and winter maxima and thus varied inversely as the copper. The

TABLE III. COPPER AND VARIOUS OCEANOGRAPHIC DATA FOR THE SURFACE WATERS OF THE PACIFIC OCEAN

<i>Date</i>	<i>Location</i>	<i>Temp.</i>	<i>Chlorinity</i>	σ_t	<i>Dissolved Oxygen</i>		<i>Copper</i>
		(°C)	(‰)		(mg-at/L)	(% Sat'n)	(μ g-at/L)
Aug. 19, 1952	Lat. 48° 30' N	10.86	17.38	24.02	0.435	76.5	0.018
	Long. 124° 44' W						
Aug. 19, 1952	Lat. 48° 31' N	—	17.97	—	0.545	—	0.020
	Long. 126° 47' W						
Aug. 20, 1952	Lat. 48° 33' N	15.69	17.99	23.92	—	—	0.016
	Long. 130° 04' W						
Aug. 23, 1952	Lat. 47° 37' N	14.93	18.05	24.17	0.540	103.3	0.018
	Long. 136° 15' W						
Aug. 25, 1952	Lat. 46° 52' N	14.91	18.00	24.10	0.525	100.4	0.020
	Long. 128° 27' W						
Aug. 29, 1952	Lat. 46° 45' N	13.76	17.82	24.09	—	—	0.016
	Long. 125° 40' W						

inverse relationship of copper to phosphates, silicates and density of the waters is shown in Fig. 2.

Atkins (1953), in studies of copper concentration for the waters of the English Channel, obtained a maximum of $0.39 \mu\text{g-at/L}$ during the



LEGEND

- MONTHLY AVERAGE 1951
- MONTHLY AVERAGE 1952
- MONTHLY AVERAGE 1953

Figure 2. Concentration of copper related to values of phosphates, silicates and density of the surface waters of San Juan Channel, Washington.

winter months and a minimum of $0.024 \mu\text{g-at/L}$ during the autumn. His minimum value agrees well with our over-all average, but his maxima are much greater than those obtained for the waters of San Juan Channel. The seasonal trend of copper for the English Channel is just the reverse of that observed by us.

The results obtained by Morita (1950, 1953) for copper concentrations in waters of Tokyo Bay and Ise Bay, Japan, are closer in agreement with our data. He found a higher concentration, $0.038 \mu\text{g-at/L}$, near shore and attributed this to land drainage. The concentration of copper decreased as the open ocean was approached until values of $0.012 \mu\text{g-at/L}$ were obtained for the surface waters of the Kuroshio.

The highest observed concentrations of copper in San Juan Channel were found in waters of low salinity during the summer months and at times of lower low tide. The low salinity waters of the region investigated resulted from flood waters of the Fraser River in Canada, which is by far the largest river of the region. The river discharges into the Strait of Georgia, where marked salinity and temperature gradients are noted, particularly during and immediately after flood stages. Favorable winds and tidal currents carry some of the warm and diluted water of the upper strata into San Juan Channel during July and August (Phifer and Thompson, 1937).

Results of several spot checkings of the Fraser River, in unpublished data of the British Columbia Research Council of Canada (Wright, 1952), show that some of the upstream tributaries of the river contained copper in concentrations four times higher than the saline waters of the San Juan Islands area. The relatively greater concentration of copper indicated for the Fraser River may account to a partial degree for the increasing copper in the surface waters of San Juan Channel during the summer.

The data given in Tables I and III indicate that the waters of San Juan Channel have approximately the same copper concentration as those of the Pacific Ocean during a major portion of the year. The copper content given in Table IV for a few lakes in Washington and that quoted for the Fraser River are considerably higher than the copper content of the open ocean waters. From these observations it might appear logical to conclude that the relatively high copper concentrations in the San Juan Channel waters (see Table I) are the result of land drainage. This is undoubtedly true to a certain extent, but it cannot explain the abnormally high individual values of copper obtained occasionally during the early summer months.

Observations of a similar nature have been reported for the Mississippi River estuary (Riley, 1937) and for Long Island Sound (Prytherch, 1934; Galtsoff, 1943). The high values given for Long

Island Sound may be attributed in part to the discharge into the Sound of considerable industrial waste carried by rivers which pass through many cities engaged in the manufacture of brass and copper products.

The high values noted for San Juan Channel on several occasions during the summer months can hardly be attributed to river discharge or to industrial pollution. It is therefore postulated that hydrogen sulfide, produced in certain regions of the area where there are extensive mud flats or where marked anaerobic conditions exist, reacts with the soluble copper in the sea water to precipitate copper sulfide which thus accumulates in the muds. Furthermore, copper contained in decaying organisms is likewise precipitated. The low tides of the region in the summer months occur during the daylight hours, the heat of the sun partially dries the mud flats, and the increased temperature favors the oxidation of the insoluble copper sulfide to the readily soluble copper sulfate. The drainage waters from these mud flats, warmer than the adjacent water, will have a high copper concentration, and, because of the lower density, will tend to float as surface water. It is also postulated that precipitation of copper as copper sulfide is favored during the colder months of the year when the oxygen content of the bottom waters is less than that during the summer months and when conditions for oxidation in the mud flats are less favorable for oxidation.

To partially demonstrate the correctness of these assumptions, East Sound, a body of water that extends into the southern side of Orcas Island in the San Juan Archipelago, was selected because there is practically no drainage from the adjacent land during the summer months and no industrial pollution. It is 11 km in length and has an average width of 2 km. As the central portion of the Sound is approached, the width is constricted for a short distance to 1 km; the head of the Sound widens to 3 km. There is no threshold or shallow ridge at the entrance to the Sound. The depth throughout is rather uniform from 25 to 30 m. As the head of the Sound is approached, shoaling occurs so that extensive mud flats lie exposed at low tides, but otherwise the shores are rather rocky and steep. The tidal range is about 2 m, but there is little tidal turbulence except in the constricted portion of the Sound. The waters are characterized by an unusually rich diatom growth in the spring and early summer months. Interchange with outside water is comparatively slow. The bottom, largely mud, is rich in organic matter. From the region of constricted width to the head of the Sound, the muds from the bottom contain quantities of hydrogen sulfide which can be detected only in the waters secured within the first few centimeters from the bottom.

Preliminary studies showed that the concentration of copper in the surface waters tended to increase toward the head of the Sound, as is indicated in the summary of data taken during the months of two summers on six different occasions.

Location	No. of Samples	Average	Minimum and Maximum
		Cu Values ($\mu\text{g-at/L}$)	Cu Values ($\mu\text{g-at/L}$)
Area beyond East Sound	6	0.027	0.018-0.041
Entrance to East Sound	5	.038	.021-0.060
Constricted part of East Sound	9	.034	.024- .065
Head of East Sound, various parts	14	.046	.024- .132

In order to ascertain the amount of copper in the sediments, short core samples were secured in polyethylene tubes inserted in the core samplers. The water immediately above the sediment in the tubes was analyzed for copper and also for soluble inorganic phosphates. The top portions of the sediments in the cores were analyzed for copper with the following results:

Location	—Analysis of Water—		Analysis of Sediments
	PO_4/P $\mu\text{g-at/L}$	Cu $\mu\text{g-at/L}$	Cu $\mu\text{g-at/kg}$
Area beyond East Sound	2.2	0.17	382
Entrance to East Sound	2.2	.33	457
Constricted Part of Sound	1.8	.26	502
Head of East Sound (5 different samples)	5.4	.34	590

A hole was dug in the mud flat at the head of the Sound, and analysis of the water from it showed 0.86 $\mu\text{g-at/L}$ Cu and 8.0 $\mu\text{g-at/L}$ inorganic phosphate-phosphorus. The waters in several tide pools showed an average of 0.050 $\mu\text{g-at/L}$ Cu while the concentration of copper in the sea water 3 meters from the shore was 0.042 $\mu\text{g-at/L}$. All of these results indicate potentialities for the enrichment of surface waters with copper and phosphates that result from reactions in the intertidal area. The degree of this enrichment may be greater for copper than for phosphates, because, if it is assumed that 1 liter of drainage water from a mud flat containing 0.86 $\mu\text{g-at/L}$ Cu and 8.00 $\mu\text{g-at}$ $\text{PO}_4/\text{P/L}$ mixes with 100 liters of adjacent sea water containing 0.024 $\mu\text{g-at/L}$ Cu and 1.0 $\mu\text{g-at}$ $\text{PO}_4/\text{P/L}$, the copper concentration in the resulting mixture would have an increase of well over 30% while the phosphates would increase less than 10%.

Thus it seems possible that the occasionally high copper encountered in the surface waters of San Juan Channel may be due not only to river discharge but to conditions that occur in shoals of the area, as exemplified by the conditions demonstrated for East Sound.

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