

## Dissolved organic copper compounds in seawater

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**Abstract:** The concentrations of copper organic compounds dissolved in sea water in the western North Pacific, Indian and Southern Ocean were determined from the collection of XAD-2 resin followed by atomic absorption spectrophotometry. The average concentration of total copper dissolved in surface water is  $0.5 \mu\text{g l}^{-1}$  for the western North Pacific,  $0.7 \mu\text{g l}^{-1}$  for the Indian Ocean and  $1.3 \mu\text{g l}^{-1}$  for the Southern Ocean, respectively; 60 to 90 % of this copper is organically bound. Most of the copper organic compounds are involved in neutral or basic organic compounds with a molecular size ranging from  $2 \times 10^3$  to  $2 \times 10^4$ . The intimate correlation between the organically bound copper and the combined amino acids adsorbed on the XAD-2 resin indicate that the organic ligand to the copper organic compounds might be polymer organic matter. The composition of the amino of the metal organic compounds suggests that few species of amino acids are concerned with metal complexation. These amino acids are not free but in a combined states, in polypeptides or polynucleotides accompanied with carbohydrates.

**Key words:** copper, seawater, metal-organic compounds, molecular size

### INTRODUCTION

Since the first report of BUGLIO *et al.* (1961), who used ultra-filtration and dialysis techniques, many researchers have tried to find evidence for the existence of organically-associated copper dissolved in sea water (ALEXANDER & CORCORAN 1967; SLOWEY & HOOD 1966; WILLIAMS 1969; BUCHAN 1967; FOATER & MORRIS 1971; SUGAI & HEALY 1978; SUGIMURA *et al.* 1978, 1980; HASLE & ABDULLAH 1981; MIHES & QUINN 1981; BATLEY & FLORENCE 1976; KREMLING *et al.* 1981, 1983; HIROSE *et al.* 1982; VAN DEN GERG 1984, SUNDA & HUNTSMAN 1991, 1992).

The source and nature of this organically associated copper remain unresolved, but there is increasing evidence that an appreciable amount of dissolved copper is originally involved in organic compounds as a dissolved form, and that the organically bound copper is not a secondary artifact of

the analytical procedure (KREMLING *et al.* 1981, 1983; SUGIMURA *et al.* 1984; HIROSE *et al.* 1982, MOFFETT *et al.* 1990).

In contrast, recently much smaller amounts of copper in sea water compared with those of previous work (cf: BREWER 1975) have been found. This copper has been reported as "total", after using careful sampling, acidified storage and simple APDC/DDTC or dithizone extraction (BENDER & GAGNER 1976; BOYLE & EDMOND 1975; BOYLE *et al.* 1977, 1979; BRULAND *et al.* 1978; BRULAND 1980; MOORE & BURTON 1976; MOORE 1978; MUROZUMI *et al.* 1980). Based on the result, they claimed that the high concentration of copper in the previous works might have been derived from a procedural contaminant.

However, careful examination of the procedure, and an equilibrium calculation, indicate that the chemical species determined by APDC or DDTC extraction are ionic or only weakly bound copper with stability constant less than  $10^{10}$ , not  $10^{30}$  as

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given by KEMP-NIELSEN (1972). This mistake was caused by an erroneous use of  $10^{28.8}$  for the stability constant of DDTC-Cu as instead of the true value of  $10^{8.8}$  in the "Stability Constant Table" (1979). Therefore, there is presently wide misunderstanding of copper species determined by DDTC chelate.

HIROSE *et al.* (1982) reported that the stability constant of naturally occurring copper organic complexes is  $10^1$  to  $10^3$  fold higher than that of the EDTA-Cu complex. This result indicates that the dominant species of copper in sea water is organically bound and only a small portion of the copper is present as inorganic ions, compounds or complexes. In this connection, the electrochemical study revealed that about 10% of copper in sea water is in inorganic ion form at pH 8 (SUNDA & HUNTSMAN 1992). The calculated amount of inorganic portion of copper is in quite good agreement with that of the recent paper on the chemical species of copper (SAAGER *et al.* 1992). HIROSE & SUGIMURA (1983) presented a comprehensive model which can be applied universally for inorganic and organic sea water systems, and pointed out that the "oceanographically consistent value" represents only the inorganic portion of metals dissolved in sea water. For a better understanding of the present marine environment, it is important to know much more about the chemical speciation of trace metals in sea water.

In this report, I give the results of a study on the concentration and chemical form of copper dissolved in sea water in a wide area of ocean from surface to the deep, along with the results on the molecular nature of copper organic compounds in sea water.

#### SAMPLES AND METHOD OF ANALYSIS

Water was collected using a Niskin non-metallic sampler during cruises in the western North Pacific, Indian and Southern Ocean on board the *M. S. Ryofu-maru* (Japan Meteorological Agency), *Kofu-maru* (Hakodate Marine Observatory), *Seifu-maru* (Maizuru Marine Observatory), *Chofu-maru* (Nagasaki Marine Observatory) and *Umitaka-maru* (Tokyo University of Fisheries). The surface water was collected at the bow of the ship before arrival at each station.

Immediately after sampling, 20 liters of the water was placed in a pre-cleaned low density polyethylene bottle and it was pumped through an inline  $0.45 \mu\text{m}$  pore size filter (Nuclepore). The water in the filtration system was allowed to contact only with glass, the filter, and teflon, and there was no exposure to the ambient air.

**Organically associated copper:** Fifteen liters of the filtrate were used for the determination of copper-organic compounds by means of XAD-2 adsorption

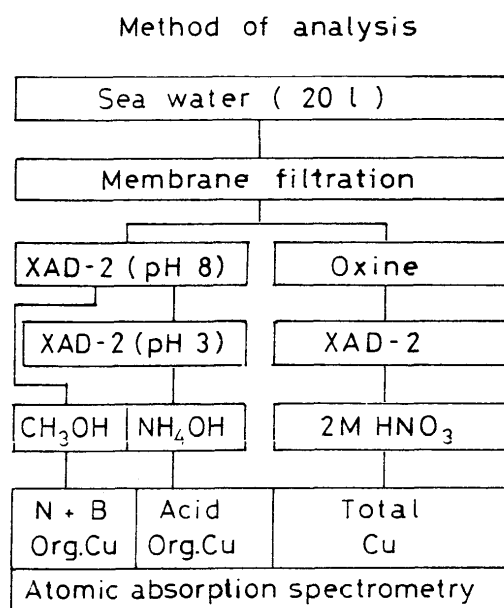


Fig. 1 A schematic diagram of the analytical methods for total and organic copper compounds in seawater.

(SUGIMURA & SUZUKI 1980, 1983), and the 5 liter remainder was used for the analysis of total dissolved copper by using Oxine-XAD-2 (SUGIMURA & SUZUKI 1983). A schematic diagram of the analytical methods is shown in Fig. 1. Copper organic compounds were separated from the seawater by passing the sample through two successive sets of XAD-2 resin columns (25 mm dia. and 15 cm long) at the pH (8) of natural sea water and at pH 3. The species absorbed on the 1st column were named "neutral and basic" copper organic compounds and those on the 2nd column were termed acidic copper organic compounds. Elution of the compounds from the resin was done on each 200 ml of eluate, methyl alcohol for the 1st column and dilute  $\text{NH}_4\text{OH}$  (pH 10) for the 2nd column.

The eluate was evaporated to dryness on a hot plate and the residue was dissolved in 0.2 M  $\text{HNO}_3$ . The concentration of copper in the solution was determined by atomic absorption spectro-photometry.

**Total copper dissolved:** For the determination of total copper, 20 ml each of conc.  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  were added to the solution and the mixture was boiled for one hour on a hot plate. After neutralization of the solution with dilute  $\text{NH}_4\text{OH}$ , 5 ml of 1% oxine solution was added and the mixture was passed through the XAD-2 resin column (25 mm dia. 20 cm long) at a flow rate of 4 ml per minute. The resin was washed with deionized water, and elution of the metal oxinate complex was done using 200 ml of 2M  $\text{HNO}_3$ . The eluate was evaporated until dry on a hot plate, and the residue was dissolved in 0.2M  $\text{HNO}_3$ . An aliquot of the solution was assayed for atomic absorption spectro-photometry of copper.

The blank value of the whole procedure was  $10 \mu\text{g l}^{-1}$ , which was carried out using XAD-2 resin, methyl alcohol, dilute  $\text{NH}_4\text{OH}$  and other reagents. Every procedure was carried out under HEPA filtered air and using precleaned glass, plastic wear and chemicals.

**Organic analysis:** The total and free amino acid concentrations were determined by fluorometry (SUGIMURA & SUZUKI 1983). Determination of proteins was carried out by fluorometry using hypochlorite-thiamine reagent (KINOSHITA *et al.* 1976). Individual amino acids were determined on an automatic amino acid analyzer (JEOL, JLC-200A) after acid hydrolysis and Cu-chellex resin preconcentration (SIEGEL & DEGENS 1966). Organic nitrogen was determined by high temperature catalytic oxidation method for liquid samples using a Sumigraph Model N-200 analyzer (SUZUKI *et al.* 1985).

## RESULTS AND DISCUSSIONS

Prior to the presentation of the results, it is important to clarify the meaning of inorganic and organic systems, as the dissolved metal species vary widely their size and chemical nature. Therefore, to obtain a meaningful result from a chemical analysis of sea water, information on the physical and chemical nature of dissolved species is required prior to a decision about the analytical procedure.

The XAD-2 adsorption method is one of the methods that separates inorganic and organic metal species by using van der Waals force of hydrophobic compounds dissolved in sea water (SUGIMURA & SUZUKI 1984). Another approach is gel-filtration, in which the separation of dissolved metal species is done by their molecular size. For gel-filtration, Sephadex gels (G-10,15,25,50,75,100) were used in glass columns (15 mm dia. 30 cm long). The voidance effluent from each gel-column was collected and subjected to the analysis. For the fraction with molecular sizes larger than 700 daltons, most compounds are observed to have sizes of  $5 \times 10^3$  to  $3 \times 10^4$ .

It is noted that the "reactive" Cu that is extractable as APDC/DDTC complex is involved with the fraction smaller than 700 daltons, and the remainder does not react with the reagent but is quantitatively adsorbed on the XAD-2 resin.

The amount of Cu adsorbed on the XAD-2 resin at pH 8 and 3 is the same as that of Cu involved in the macromolecular fraction. Therefore, it can be concluded that the dissolved copper species adsorbed on the XAD-2 resin in the two solutions with different pHs are organically bound, originated in sea water, and were not formed as a secondary product on the resin during the analytical procedure.

### Comparison with other methods

Since the report of BOYLE & EDMOND (1975) and others, the concept of a lower concentration of copper in sea water compared with that of previous works has been widely accepted and is regarded as an "oceanographically consistent value" at present. However, in their work, no attention was given to the chemical species determined by DDTC/APDC extraction. Acidified preservation of a water sample at ambient temperature is not relevant to the decomposition of organically bound metals in sea water, but provides information only on favored conditions for the preservation of organic matter against microbial decomposition. In this connection, BERNHARD (1975) indicates that the dissociation and association of metal-chelate in sea water is reversible against the variation of pH of the solution.

As stated before, species of APDC/DDTC extractable copper is in inorganic or only weakly bound organic complexes at the selected analytical conditions.

A comparison was made of the concentration of copper in sea water using different methods: DDTC-extraction, APDC-extraction, oxine-XAD-2, method and chelating resin.

As shown in Table 1, without oxidative treatment of the organic matter in sea water, the result of oxine-XAD-2 is much higher than those of the others. After oxidative treatment, every result shows the same value. Furthermore, after pretreatment with XAD-2 resin, which means the removal of metal organic species from the solution, the result of the oxine-XAD-2 method is the same as that of the others.

Therefore, there is every reason to believe that the result of oxine-XAD-2 represents the "total" concentration of copper and that the results of other studies are concerned only with the inorganic or labile organic species of copper in sea water.

### Concentration of copper in ocean water

The results of determination of total and organically bound copper dissolved in surface sea water from the western North Pacific to the Southern Ocean are shown in Table 2.

### Surface distribution

(A) Western North Pacific: The surface concentration of copper organic compounds ranged from  $0.18$  to  $0.77 \mu\text{g l}^{-1}$  with an average value of  $0.17$  to  $0.49 \mu\text{g l}^{-1}$ . As shown in Fig. 2, the surface concentration of copper organic compounds along  $137^\circ\text{E}$  is relatively low in subtropical waters. The concentration of total copper ranged from  $0.3$  to  $0.9 \mu\text{g l}^{-1}$  with an average value of  $0.5$  to  $0.3 \mu\text{g l}^{-1}$ . The ratio of organic to total copper ranges from  $0.6$  to  $1.0 \mu\text{g l}^{-1}$  and the major part of the copper organic compounds are neutral and

Table 1 Comparison of analytical methods to determine "total" copper concentration dissolved in sea water.

Pretreatment	I	II	III	IV
Direct	0.49	0.05	0.05	0.06
After XAD	0.05	0.05	0.05	0.05
After oxidation	0.50	0.50	0.50	0.50

Method: I, XAD-Oxine  
 III, DDTC-CHCl<sub>3</sub>

II, APDC-MIBK  
 IV, Chelex-100

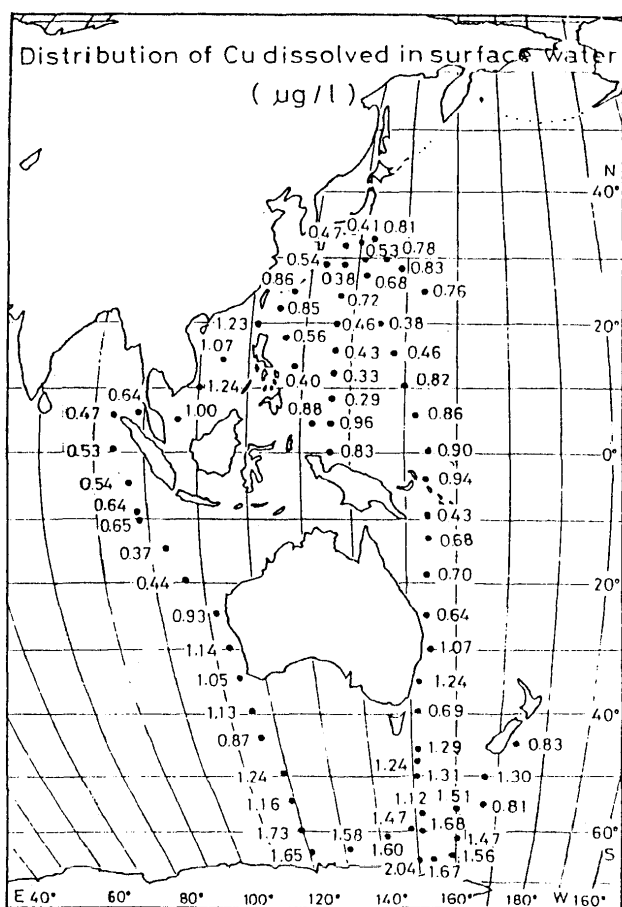


Fig. 2 Distribution of dissolved copper concentrations in the surface oceanic water.

basic organic compounds. The concentration of the neutral and basic organic fraction ranged from 0.28 to 0.69  $\mu\text{g l}^{-1}$ , with an average of 0.17 to 0.42  $\mu\text{g l}^{-1}$  and the average concentration of the acidic organic fraction was 0.07  $\mu\text{g l}^{-1}$ .

(B) Indian Ocean: The total concentration of copper in Indian Ocean water ranged from 0.37 to 1.05  $\mu\text{g l}^{-1}$ . The higher concentration is observed

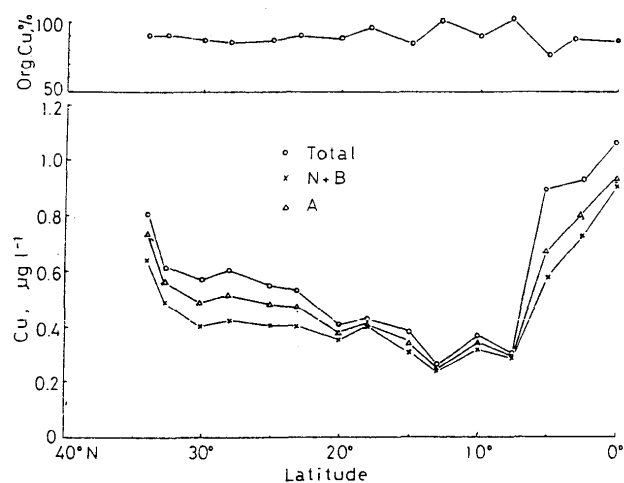


Fig. 3 Latitudinal distribution of total and organic copper compounds in surface water.

in the water along the west coast of the Australian continent. With respect to the copper organic species, the concentration of the neutral and basic organic species ranged from 0.20 to 0.55  $\mu\text{g l}^{-1}$  and that of acidic species ranged from 0.03 to 0.09  $\mu\text{g l}^{-1}$ .

(C) Southern Ocean: The water south of 40°S contained a high concentration of copper ranging from 0.69 to 2.04  $\mu\text{g l}^{-1}$ , whereas the concentration of organically bound copper is nearly the same as that in other waters north of the Antarctic Convergence.

In the Antarctic water, both total and organic copper increased up to 2.04  $\mu\text{g l}^{-1}$  and 1.24  $\mu\text{g l}^{-1}$ , respectively. It should be noted that most of the organically bound copper is involved in the neutral and basic organic fractions.

(D) Okhotsk Sea: The concentration of total copper is on the same order of magnitude as seen in the western North Pacific, but the concentration of organically bound copper is much lower than that of other areas of the ocean. The low concentration of copper organic compounds in this area is mainly due to the low concentration of neutral and basic copper organic compounds in water of the Okhotsk Sea.

(E) East China Sea: The concentration of total copper is high in the water off the river mouth of the Yangtze River and it decreases gradually with distance from the river mouth. Since the concentration of organically bound copper is nearly constant in these waters, it seems that the decrease of total copper is mainly due to the dilution and removal of inorganic or labile copper species from the surface water.

(F) Japan Sea: The concentration of copper dissolved in surface water in the central part of the Japan Sea ranges from 0.20 to 0.30  $\mu\text{g l}^{-1}$  and



(Table 2 continued)

Location	Water temp. (°C)	Salinity	Total	Organic		Location	Water temp. (°C)	Salinity	Total	Organic	
				N <sub>B</sub>	A					N <sub>B</sub>	A
(Dec., 1977)											
24°60' N	26.9	34.64	0.86	0.47	0.08	27°35' N	20.8	34.94	0.56	0.45	0.08
126°57' E						130°10' E					
20°00' N	28.0	34.51	1.23	0.56	0.05	27°54' N	21.6	34.97	0.52	0.40	0.08
121°45' E						130°10' E					
14°21' N	28.3	34.64	1.07	0.70	0.08	28°11' N	21.9	34.90	0.49	0.33	0.08
114°31' E						129°45' E					
09°56' N	28.4	35.69	1.24	0.48	0.04	28°41' N	20.8	34.94	0.50	0.42	0.08
110°00' E						130°53' E					
04°54' N	27.8	33.24	1.00	0.51	0.05	29°08' N	20.6	34.95	0.59	0.41	0.08
106°31' E						132°15' E					
04°25' N	29.2	34.32	0.94	0.50	0.08	29°29' N	20.9	34.90	0.61	0.44	0.08
153°23' E						133°28' E					
00°04' N	29.2	34.36	0.90	0.44	0.07	30°00' N	21.1	34.90	0.57	0.40	0.06
154°24' E						132°55' E					
05°18' N	28.5	34.36	0.86	0.40	0.08	30°25' N	21.3	34.89	0.53	0.42	0.05
151°55' E						132°23' E					
10°16' N	27.7	34.56	0.82	0.38	0.08	30°46' N	21.5	34.88	0.62	0.42	0.11
149°55' E						132°00' E					
15°21' N	27.0	34.76	0.46	0.27	0.05	31°00' N	20.1	34.84	0.71	0.51	0.13
147°28' E						131°43' E					
20°09' N	25.1	35.15	0.38	0.20	0.05	31°10' N	19.0	34.83	0.72	0.48	0.10
145°43' E						131°30' E					
39°58' N	19.9	35.68	0.69	0.37	0.05	(April, 1981)					
151°17' E						34°43' N	17.2		0.63	0.47	0.08
34°57' N	23.8	35.49	1.24	0.74	0.07	139°56' E					
151°09' E						33°04' N	17.8		0.57	0.41	0.07
30°00' N	26.7	35.41	1.07	0.49	0.05	142°15' E					
153°32' E						31°38' N	18.2		0.43	0.30	0.07
25°03' N	26.7	35.35	0.64	0.35	0.05	144°21' E					
153°32' E						28°45' N	21.4		0.37	0.30	0.07
18°30' N	28.0	35.26	0.70	0.40	0.05	148°19' E					
154°42' E						27°11' N	21.2		0.36	0.28	0.06
12°59' N	28.6	35.06	0.68	0.32	0.07	150°17' E					
154°46' E						25°44' N	21.4		0.45	0.32	0.07
09°59' N	28.6	34.57	0.42	0.17	0.04	152°09' E					
154°17' E						30°04' N	19.1		0.53	0.37	0.07
(Jan., 1981)						146°43' E			0.47	0.35	0.08
30°01' N	19.3	34.95	0.55	0.40	0.05	31°36' N	18.8				
137°01' E						143°19' E					
25°00' N	21.8	34.900	0.56	0.41	0.07	32°39' N	21.4		0.52	0.33	0.08
137°00' E						140°52' E					
20°01' N	24.5	34.95	0.39	0.31	0.05	(Sept., 1981)					
136°59' E						34°40' N	25.4		0.59	0.40	0.05
15°00' N	26.5	34.53	0.35	0.30	0.05	139°46' E					
137°00' E						34°18' N	24.4		0.47	0.31	0.07
10°01' N	28.2	35.74	0.37	0.30	0.05	139°52' E					
137°01' E						33°55' N	27.4		0.52	0.34	0.07
05°01' N	27.6	34.09	0.84	0.53	0.08	139°57' E					
137°01' E						33°29' N	27.3		0.36	0.25	0.05
00°00' N	28.9	34.32	0.96	0.84	0.09	140°04' E					
137°00' E						33°08' N	27.1		0.32	0.26	0.06
18°44' N	25.2	34.53	0.42	0.30	0.07	139°45' E					
152°13' E						34°47' N	26.7		0.44	0.29	0.07
21°19' N	24.0	34.84	0.50	0.42	0.05	141°03' E					
130°45' E						35°26' N	26.8		0.47	0.32	0.07
23°04' N	23.5	34.70	0.47	0.37	0.05	141°49' E					
129°33' E						35°50' N	24.5		0.52	0.31	0.07
15°10' N	21.5	34.83	0.53	0.43	0.08	141°41' E					
128°10' E						36°07' N	21.3		0.53	0.33	0.05
24°23' N	22.2	35.03	0.61	0.44	0.08	141°25' E					
128°03' E						(Dec., 1981)					
23°01' N	22.0	34.99	0.42	0.35	0.06	33°00' N	21.1	34.49	0.64	0.27	0.08
128°24' E						137°00' E					
21°45' N	22.7	34.99	0.47	0.34	0.09	32°30' N	22.8	34.57	0.50	0.30	0.07
128°47' E						137°01' E					
20°57' N	23.7	34.95	0.45	0.39	0.07	32°00' N	22.1	34.50	0.42	0.22	0.06
128°00' E						137°01' E					
22°03' N	23.5	34.86	0.48	0.39	0.08	31°00' N	22.3	34.78	0.78	0.34	0.07
129°24' E						136°59' E					
23°39' N	22.6	34.99	0.51	0.41	0.08	30°00' N	22.7	34.65	0.62	0.36	0.07
130°01' E						136°59' E					
24°50' N	21.5	34.98	0.50	0.39	0.08	29°00' N	22.2	34.71	0.54	0.41	0.08
130°34' E						137°00' E					
15°56' N	20.2	34.98	0.52	0.40	0.07	28°00' N	22.3	34.74	0.62	0.39	0.07
131°04' E						137°00' E					
26°39' N	21.0	34.93	0.51	0.41	0.08	25°41' N	24.5	34.71	0.62	0.41	0.08
131°30' E						135°57' E					
27°19' N	20.6	34.94	0.48	0.42	0.07	32°57' N	21.9	34.48	0.52	0.37	0.06
131°04' E						133°35' E					
						32°24' N	22.4	34.82	0.66	0.33	0.06
						133°53' E					



(Table 2 continued)

Location	Water temp. (°C)	Salinity	Total	Organic	
				N, B	A
(µg l <sup>-1</sup> )					
38°25' N	2.2		0.48	0.12	0.19
145°21' E					
35°39' N	11.7		0.43	0.20	0.11
145°48' E					
30°10' N	18.1		0.54	0.41	0.06
147°08' E					
(Jan., 1984)					
33°59' N	17.0	34.78	0.61	0.42	0.08
137°00' E					
31°56' N	20.7	34.87	0.54	0.40	0.08
137°00' E					
30°00' N	19.6	34.77	0.56	0.38	0.08
136°59' E					
27°01' N	20.6	34.82	0.54	0.38	0.08
137°02' E					
24°59' N	23.5	34.96	0.36	0.26	0.05
137°00' E					
20°00' N	25.7	34.84	0.29	0.20	0.05
136°59' E					
16°57' N	26.4	34.78	0.28	0.20	0.05
137°00' E					
14°58' N	28.1	34.64	0.26	0.19	0.05
136°58' E					
09°59' N	28.1	34.30	0.29	0.20	0.05
136°57' E					
08°02' N	28.6	34.14	0.42	0.27	0.08
137°00' E					
05°00' N	28.7	34.19	0.50	0.36	0.08
136°56' E					
03°00' N	28.2	34.38	0.73	0.46	0.08
137°00' E					
00°02' N	29.7	33.91	0.77	0.30	0.14
136°58' E					
31°03' N	20.2	34.90	0.43	0.34	0.07
131°50' E					
30°52' N	20.2	34.89	0.50	0.42	0.08
132°06' E					
33°29' N	17.1	34.83	0.56	0.44	0.08
141°30' E					
34°12' N	17.2	34.83	0.58	0.46	0.08
140°54' E					
38°05' N	26.8	34.00	0.32	0.15	0.05
136°13' E					
38°50' N	26.2	34.02	0.24	0.05	0.05
135°39' E					
39°58' N	25.3	33.74	0.28	0.10	0.05
134°47' E					
41°00' N	24.4	33.87	0.23	0.10	0.05
134°01' E					
41°00' N	23.5	33.73	0.26	0.12	0.05
135°40' E					
40°11' N	25.3	34.05	0.29	0.10	0.10
136°15' E					
39°20' N	25.5	33.78	0.27	0.12	0.08
136°50' E					
38°32' N	26.5	34.30	0.28	0.10	0.05
137°26' E					
37°40' N	27.1	34.18	0.22	0.12	0.05
138°00' E					
(July, 1982)					
35°29' N	22.3	34.38	0.26	0.12	0.06
131°30' E					
36°00' N	22.1	34.37	0.28	0.12	0.06
139°59' E					
36°51' N	20.9	34.57	0.30	0.08	0.08
130°42' E					
38°30' N	21.3	34.28	0.34	0.20	0.08
130°30' E					
37°58' N	21.0	34.31	0.32	0.18	0.08
131°00' E					
36°20' N	23.0	34.48	0.26	0.14	0.06
132°28' E					
36°17' N	23.3	34.49	0.28	0.14	0.06
134°07' E					
37°22' N	22.2	34.49	0.28	0.12	0.05
133°16' E					
38°11' N	23.6	34.27	0.28	0.18	0.06
132°38' E					
39°24' N	22.4	34.46	0.30	0.20	0.06
133°23' E					

Location	Water temp. (°C)	Salinity	Total	Organic	
				N, B	A
(µg l <sup>-1</sup> )					
(Oct., 1977)					
45°31' N	12.1	33.05	0.63	0.10	0.02
144°02' E					
45°32' N	12.0	33.14	0.51	0.12	0.04
147°00' E					
86°45' N	11.5	32.59	0.70	0.14	0.04
149°00' E					
46°46' N	11.3	32.94	0.76	0.10	0.04
145°59' E					
46°45' N	9.0	32.14	0.60	----	0.05
144°31' E					
48°01' N	10.3	32.45	0.67	0.09	0.02
149°01' E					
48°40' N	8.6	32.60	0.99	0.12	0.02
152°40' E					
50°01' N	9.2	32.29	1.01	0.16	0.03
151°00' E					
50°01' N	9.5	31.51	0.46	0.10	0.02
149°03' E					
50°45' N	7.3	30.81	0.67	0.14	0.02
145°40' E					
50°45' N	8.3	31.80	0.71	0.20	0.04
147°15' E					
48°00' N	8.5	32.48	0.71	0.11	0.04
149°59' E					
46°57' N	8.1	32.69	0.47	0.12	0.02
151°03' E					
45°00' N	6.8	32.70	0.76	0.14	0.02
153°00' E					
(Oct., 1978)					
45°31' N	6.8	30.63	0.64	0.12	0.04
143°00' E					
45°30' N	10.2	33.02	0.50	0.08	0.02
147°00' E					
46°29' N	7.4	32.36	0.68	0.09	0.04
148°59' E					
48°00' N	6.4	32.29	0.57	0.14	0.07
146°03' E					
48°01' N	8.0	32.74	0.89	0.10	0.03
148°01' E					
48°01' N	6.6	32.45	0.64	0.17	0.07
151°59' E					
50°02' N	6.6	32.45	0.92	0.11	0.03
153°02' E					
50°00' N	5.1	31.46	0.65	0.16	0.09
145°00' E					
47°00' N	4.0	33.04	0.90	0.15	0.03
151°00' E					
45°00' N	6.8	32.80	0.75	0.09	0.02
153°02' E					
44°20' N	7.4	32.73	0.67	0.10	0.04
151°32' E					
(July, 1980)					
44°51' N	13.7	31.93	0.48	0.24	0.07
144°58' E					
45°02' N	10.9	32.51	0.52	0.17	0.08
146°01' E					
45°58' N	11.6	32.17	0.44	0.16	0.07
147°58' E					
46°25' N	11.3	32.25	0.43	0.20	0.08
148°56' E					
46°45' N	10.5	32.09	0.37	0.19	0.09
149°49' E					
46°55' N	7.9	32.28	0.42	0.17	0.08
149°57' E					
47°20' N	3.6	32.59	0.39	0.18	0.07
150°20' E					
46°54' N	2.5	33.19	0.40	0.23	0.08
151°10' E					



(Table 2 continued)

Location	Water temp.	Salinity	Total	Organic	
				N.B	A
( $\mu\text{g l}^{-1}$ )					
31°55' N 129°20' E	27.1	34.22	0.67	0.50	0.08
31°55' N 127°47' E	27.0	34.05	0.41	0.33	0.08
31°55' N 126°12' E	26.6	31.72	1.75	0.17	0.33
31°28' N 125°03' E	24.1	31.25	1.70	0.20	0.38
31°00' N 125°16' E	27.8	27.12	4.24	0.34	0.60
31°01' N 126°25' E	27.1	31.80	1.72	0.24	0.30
30°58' N 128°44' E	28.2	34.20	0.44	0.14	0.06
31°01' N 129°55' E	28.9	34.21	0.46	0.20	0.08
30°05' N 128°55' E	30.0	33.07	0.84	0.27	0.18
29°20' N 129°55' E	30.0	34.02	0.50	0.26	0.08
28°48' N 128°48' E	29.9	34.45	0.52	0.28	0.08
29°24' N 127°54' E	29.4	34.21	0.59	0.25	0.08
30°00' N 127°02' E	29.4	30.42	2.86	0.28	0.41
30°00' N 125°45' E	28.7	29.62	3.24	0.24	0.46
30°01' N 124°30' E	28.7	33.20	0.94	0.28	0.22
29°18' N 125°34' E	28.6	33.53	0.83	0.24	0.20
28°44' N 126°26' E	29.5	33.11	0.92	0.28	0.24
28°07' N 127°12' E	28.8	34.34	0.64	0.24	0.08
27°30' N 128°14' E	29.2	34.47	0.46	0.18	0.08
27°00' N 126°30' E	29.4	34.52	0.48	0.20	0.08
28°00' N 125°00' E	28.8	33.44	0.78	0.24	0.20
29°15' N 123°45' E	27.8	33.80	0.65	0.24	0.18
27°51' N 123°01' E	28.6	33.74	0.68	0.20	0.22
27°00' N 124°00' E	28.8	33.73	0.70	0.22	0.22
26°21' N 125°00' E	28.5	34.29	0.43	0.18	0.08
25°41' N 126°01' E	29.9	34.51	0.38	0.20	0.08
(Aug. 1978)					
29°59' N 124°30' E	27.9	30.71	3.86	0.31	0.38
29°37' N 125°08' E	28.4	30.82	3.22	0.26	0.28
29°18' N 125°33' E	29.6	30.87	3.78	0.26	0.36
29°00' N 126°00' E	30.2	32.72	2.50	0.18	0.30
28°15' N 126°55' E	29.7	34.33	0.55	0.20	0.08
27°48' N 127°48' E	28.4	34.58	0.48	0.24	0.10
28°48' N 128°48' E	29.0	34.54	0.46	0.22	0.10
29°25' N 127°37' E	29.9	34.28	0.50	0.30	0.10
29°59' N 127°00' E	30.2	32.58	1.04	0.24	0.12
30°00' N 125°45' E	29.2	30.32	2.98	0.26	0.34
29°31' N 128°18' E	29.3	31.91	2.38	0.24	0.28
28°59' N 123°31' E	28.7	34.14	0.50	0.22	0.10
28°42' N 124°00' E	28.9	34.19	0.48	0.20	0.10
27°59' N 125°00' E	29.2	31.97	2.44	0.28	0.28

Location	Water temp. (°C)	Salinity	Total	Organic	
				N.B	A
( $\mu\text{g l}^{-1}$ )					
27°20' N 126°00' E	28.9	34.20	0.46	0.24	0.10
26°40' N 126°59' E	29.2	34.53	0.48	0.22	0.10
29°39' N 130°05' E	28.5	34.49	0.48	0.24	0.10
30°59' N 129°56' E	27.8	34.20	0.42	0.22	0.08
31°00' N 128°11' E	27.5	34.35	0.48	0.24	0.10
31°00' N 124°40' E	26.1	33.85	0.80	0.28	0.14
31°57' N 124°42' E	26.0	32.34	1.30	0.28	0.26
31°54' N 126°15' E	26.0	32.84	1.44	0.30	0.28
31°56' N 127°47' E	27.6	34.10	0.46	0.22	0.10
31°54' N 129°20' E	27.6	34.31	0.44	0.20	0.10

the value is a little lower than those of other areas of the ocean. The low concentration of organically bound copper, which is less than 20% of the total, may be a characteristic of the water of the Japan Sea water. As seen in Table 2 and Fig. 3, in the open part of the ocean, more than 80% of the total copper dissolved in the surface water is in organically bound forms, of which most are involved in neutral and basic organic compounds.

#### Vertical distribution

The results of determination of copper concentration with depth are shown in Table 3. Among 17 series of determinations, 7 are in the western North Pacific, 2 in the East China Sea, 2 in the Okhotsk Sea, 1 in the Japan Sea, 1 in the Indian Ocean and 4 in the Southern Ocean. As seen in the table, except one or two stations, the total concentration of copper is nearly constant with depth, whereas the concentration of organically bound copper is highest in intermediate water.

An example of the vertical distribution, from the surface to very close to the bottom, of copper in the western North Pacific is shown in Fig. 4(a and b), together with the distributions of salinity, water temperature, dissolved oxygen, reactive nutrients, amino acids, protein, organic nitrogen and carbon. As seen in the Fig. 4(a and b), the vertical distribution of total copper shows three maxima: surface, near the salinity minimum and very close to the bottom, and nearly constant values for other depths. The highest value was observed in the water very close to the bottom, as high as 1.5  $\mu\text{g l}^{-1}$ .

The concentration of organically bound copper decreased gradually from the surface to 5,000 m depth, with a small maximum near the bottom of the seasonal thermocline, and the concentration increased from 5,000 m to the bottom.

The causes of the decrease from the surface to

Table 3 Concentrations of total and organic copper compounds in the vertical water samples

Depth (m)	Water temp. (°C)	Salinity	Total ( $\mu\text{g l}^{-1}$ )	Organic	
				N,B	A
<b>(May, 1977) (29°53'N, 146°49'E, depth=6030m)</b>					
0	22.4	34.77	0.81	0.67	0.05
96	17.7	34.74	0.55	0.42	0.05
240	16.6	34.72	0.57	0.48	0.05
481	12.2	34.41	0.65	0.35	0.06
723	5.2	34.07	0.66	0.33	0.06
977	3.9	34.22	0.60	0.29	0.11
1465	2.6	34.46	0.54	0.30	0.11
1963	2.1	34.56	0.67	0.35	0.09
2953	1.6	34.64	0.65	0.43	0.06
4114	1.5	34.67	0.79	0.49	0.82
5110	1.5	34.67	0.89	0.48	0.32
<b>(Jan., 1978) (04°00'N, 134°34'E, depth=4820m)</b>					
0	28.1	34.42	0.88	0.63	0.08
100	23.9	34.96	1.14	0.74	0.12
196	11.7	34.51	0.63	0.40	0.06
525	6.8	34.55	0.67	0.48	0.07
634	6.3	34.54	0.91	0.59	0.13
1075	4.2	34.57	0.57	0.29	0.07
1336	3.3	34.59	0.50	0.80	0.06
1808	2.4	34.63	0.53	0.31	0.05
2460	1.8	34.66	0.61	0.24	0.06
3211	1.6	34.67	0.78	0.44	0.09
4471	1.5	34.68	0.96	0.46	0.18
<b>(May, 1978) (29°55'N, 146°49'E, depth=6100m)</b>					
0	18.9	34.80	0.78	0.60	0.05
203	16.9	34.74	0.53	0.40	0.04
478	12.2	34.44	0.81	0.33	0.06
678	5.8	34.01	0.90	0.39	0.08
987	3.8	34.27	0.64	0.29	0.10
1487	2.6	34.50	0.70	0.31	0.06
1990	2.0	34.59	0.65	0.30	0.08
2990	1.6	34.66	0.80	0.38	0.07
3573	1.5	34.68	0.78	0.45	0.08
4936	1.5	34.70	0.81	0.68	0.11
<b>(Jan., 1979) (13°00'N, 131°48'E, depth=5202m)</b>					
0	27.2	34.61	0.25	0.20	0.02
87	27.2	34.63	0.18	0.14	0.02
194	20.1	34.07	0.28	0.22	0.02
526	7.1	34.55	0.44	0.40	0.02
736	5.5	34.55	0.48	0.31	0.12
1094	4.0	34.62	0.57	0.16	0.20
1410	3.1	34.66	0.63	0.17	0.20
1653	2.7	34.68	0.72	0.18	0.27
2360	1.9	34.73	0.84	0.17	0.31
3111	1.6	34.73	1.23	0.43	0.29
3926	1.6	34.76	1.47	0.51	0.33
4368	1.6	34.76	1.62	0.49	0.40
<b>(Mar., 1979) (29°53'N, 147°05'E, depth=6,160m)</b>					
0	18.4	34.91	0.82	0.62	0.04
89	18.4	34.87	0.54	0.40	0.05
199	16.7	34.76	0.60	0.42	0.07
298	15.4	34.64	0.57	0.41	0.05
505	11.2	34.37	0.74	0.33	0.07
786	6.2	34.06	0.96	0.27	0.12
972	4.1	34.23	0.63	0.30	0.12
1488	2.7	34.50	0.67	0.32	0.09
2011	2.0	34.60	0.65	0.29	0.10
3041	1.7	34.63	0.62	0.41	0.09
3995	1.6	34.67	0.78	0.45	0.09
4971	1.5	34.68	0.82	0.60	0.10
<b>(Apr., 1979) (39°09'N, 143°46'E, depth=4,650m)</b>					
0	16.9	34.80	0.67	0.19	0.04
90	16.1	34.75	0.70	0.12	0.07
190	13.7	34.57	0.84	0.09	0.05
292	10.8	34.35	0.93	0.10	0.03
495	6.4	34.07	1.24	0.07	0.42
736	4.4	34.19	1.47	0.06	0.56
955	3.6	34.30	1.59	0.05	0.47
1418	2.6	34.50	2.03	0.07	0.49
1919	2.0	34.58	1.73	0.14	0.80
2884	1.6	34.65	1.64	0.17	0.48
3512	1.5	34.67	1.70	0.29	0.52
4420	1.5	34.68	1.65	0.37	0.59
<b>(Apr., 1980) (30°00'N, 147°02'E, depth=6,211m)</b>					
0	19.2	34.77	0.78	0.56	0.06
108	17.6	34.83	0.83	0.37	0.07
208	16.9	34.73	0.81	0.28	0.06
282	15.8	34.66	0.53	0.51	0.07
471	11.0	34.39	0.71	0.41	0.05
770	5.2	34.07	0.90	0.27	0.13
1227	3.1	34.38	0.84	0.23	0.14
1942	1.8	34.61	0.58	0.14	0.09
2529	1.7	34.62	0.56	0.14	0.09
2795	1.6	34.68	0.57	0.18	0.09
3260	1.6	34.66	0.56	0.16	0.10
3724	1.5	34.67	0.54	0.16	0.00
4195	1.5	34.67	0.56	0.14	0.09
5016	1.5	34.67	0.57	0.14	0.09
5214	1.5	34.68	0.58	0.26	0.08
<b>(continued)</b>					
5508	1.5	34.69	0.64	0.42	0.32
6021	1.6	34.69	1.04	0.52	0.52
6211	1.6	34.69	1.22	0.61	0.61
<b>(Jan., 1981) (18°44'N, 132°23'E, depth=5760m)</b>					
0	25.2	34.58	0.42	0.30	0.30
89	24.9	34.71	0.48	0.48	0.41
259	18.1	34.87	0.56	0.23	0.23
518	8.4	34.21	0.53	0.18	0.18
658	5.6	34.21	0.54	0.17	0.17
886	4.2	34.43	0.58	0.18	0.18
1365	2.9	34.57	0.50	0.15	0.15
1889	2.1	34.62	0.47	0.18	0.18
2574	1.8	34.66	0.48	0.17	0.17
3415	1.6	34.68	0.44	0.17	0.17
4309	1.6	34.68	0.42	0.16	0.16
5264	1.8	34.69	0.45	0.17	0.17
<b>(Apr., 1981) (23°36'N, 151°08'E, depth=6100m)</b>					
0	22.3	35.06	0.37	0.31	0.31
100	19.3	34.83	0.52	0.23	0.23
193	17.2	34.85	0.48	0.12	0.12
289	15.7	34.69	0.48	0.12	0.12
476	11.2	34.33	0.51	0.13	0.13
715	5.7	34.06	0.57	0.19	0.19
780	5.7	34.10	0.49	0.15	0.15
1104	3.5	34.35	0.48	0.14	0.14
1483	2.5	34.52	0.49	0.14	0.14
2341	1.7	34.63	0.43	0.14	0.14
3932	1.5	34.68	0.41	0.13	0.13
4892	1.5	34.68	0.45	0.10	0.10
5382	1.5	34.69	0.44	0.11	0.11
5875	1.6	34.69	0.43	0.11	0.11
<b>(Mar., 1982) (30°15'N, 146°51'E, depth=6210m)</b>					
0	18.4	34.87	0.67	0.48	0.48
92	18.0	34.80	0.58	0.39	0.39
248	16.3	34.61	0.56	0.28	0.28
488	12.4	34.44	0.68	0.27	0.27
716	5.4	34.10	0.66	0.28	0.28
978	4.0	34.21	0.66	0.28	0.28
2010	2.0	34.61	0.59	0.26	0.26
3045	1.7	34.59	0.60	0.36	0.36
4010	1.6	34.67	0.70	0.42	0.42
4980	1.5	34.68	0.72	0.48	0.48
<b>(Jan., 1983) (03°52'N, 135°03'E, depth=4840m)</b>					
0	27.9	34.90	0.82	0.86	0.86
81	23.6	34.75	0.66	0.48	0.48
177	17.3	34.75	0.60	0.46	0.46
299	8.2	34.44	0.58	0.44	0.44
749	5.6	34.54	0.78	0.46	0.46
1244	3.7	34.58	0.54	0.30	0.30
1741	2.5	34.62	0.50	0.26	0.26
2240	1.9	34.67	0.52	0.26	0.26
2527	1.8	34.68	0.50	0.26	0.26
3555	1.5	34.69	0.54	0.27	0.27
4542	1.5	34.70	0.58	0.28	0.28
4839	1.6	34.70	0.62	0.34	0.34
<b>(Mar., 1983) (38°51'N, 145°29'E, depth=5320m)</b>					
0	2.6	33.204	0.42	0.10	0.10
100	3.5	33.30	0.44	0.12	0.12
200	3.4	33.28	0.52	0.10	0.10
300	3.1	33.55	0.48	0.12	0.12
500	3.0	33.95	0.50	0.18	0.18
750	3.1	34.14	0.54	0.20	0.20
1000	2.3	34.35	0.58	0.24	0.24
1500	1.7	34.51	0.68	0.17	0.17
2000	1.6	34.51	0.72	0.17	0.17
3000	1.7	34.58	0.74	0.12	0.12
4000	1.6	34.54	0.68	0.12	0.12
5140	1.6	34.64	0.68	0.10	0.10
<b>(May, 1983) (36°59'N, 144°02'E) (depth=6000m)</b>					
0	12.4	34.69	0.42	0.18	0.18
48	5.4	34.69	0.44	0.30	0.30
98	3.3	34.69	0.52	0.24	0.24
240	3.9	34.69	0.48	0.32	0.32
480	3.5	34.69	0.56	0.24	0.24
720	3.0	34.69	0.54	0.20	0.20
960	2.7	34.69	0.58	0.17	0.17
1100	2.0	34.69	0.50	0.17	0.17
2000	1.8	34.69	0.52	0.12	0.12
2500	1.7	34.69	0.56	0.12	0.12
<b>(Jan., 1984) (23°59'N, 128°18'E, depth=2450m)</b>					
0	21.3	34.84	0.58	0.40	0.40
22	21.3	34.85	0.54	0.37	0.37
49	21.4	34.85	0.49	0.38	0.38
102	21.3	34.85	0.52	0.38	0.38
155	20.1	34.82	0.47	0.27	0.27
207	18.0	34.81	0.50	0.24	0.24
269	16.7	34.75	0.49	0.24	0.24
323	15.6	34.67	0.48	0.20	0.20
539	10.0	34.29	0.53	0.20	0.20
819	5.0	34.28	0.61	0.16	0.16
1206	3.1	34.46	0.57	0.16	0.16
1779	2.2	34.58	0.52	0.16	0.16

