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Yoshimi SUZUKI[1]

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 $\mu g\,l^{-1}$ for the western North Pacific, 0.7 $\mu g\,l^{-1}$ for the Indian Ocean and 1.3 $\mu g\,l^{-1}$ for the Southern Ocean, respectivly; 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 2×10^3 to 2×10^4. 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; MIIIES & 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 & EDOMOND 1975; BOYLE *et al.* 1977, 1979; BRULAND *et al.* 1978; BRULAMD 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 from 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 "oceano-graphically 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 Obervatory), Seifu-maru (Maizuru Marine Obeservatory), 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 precleaned low density polyethylene bottle and it was pumped through an inline 0.45 μm 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
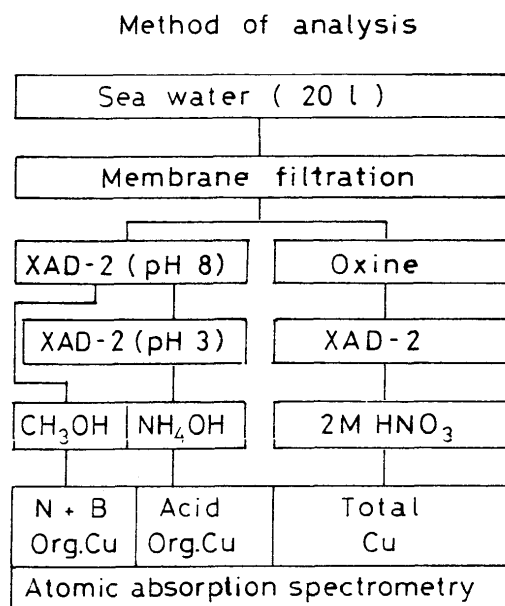
Method of analysis

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 NH₄ 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 HNO₃. 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. HNO₃ and H₂O₂ were added to the solution and the mixture was boiled for one hour on a hot plate. After neutralization of the solution with dilute NH₄OH, 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 HNO₃. The eluate was evaporated until dry on a hot plate, and the residue was dissolved in 0.2M HNO₃. An aliquot of the solution was assayed for atomic absorption spectrophotometry of copper.

The blank value of the whole procedure was 10 μg l^{-1}, which was carried out using XAD-2 resin, methyl alcohol, dilute NH_4OH 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-chelex 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 derWaals force of hydrophobic compounds dissolved in sea water (SUGIMURA & SUZUKI 1984). Another approch 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 5×10^3 to 3×10^4.

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 decompotion. 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 tretment, 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 μg l^{-1} with an average value of 0.17 to 0.49 μg l^{-1}. As shown in Fig. 2, the surface concentration of copper organic compounds along 137°E is relatively low in subtropical waters. The concentration of total copper ranged from 0.3 to 0.9 μg l^{-1} with an average value of 0.5 to 0.3 μg l^{-1}. The ratio of organic to total copper ranges from 0.6 to 1.0 μg 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   II. APDC-MIBK
         III. DDTC-CHCl₃   IV. Chelex-100

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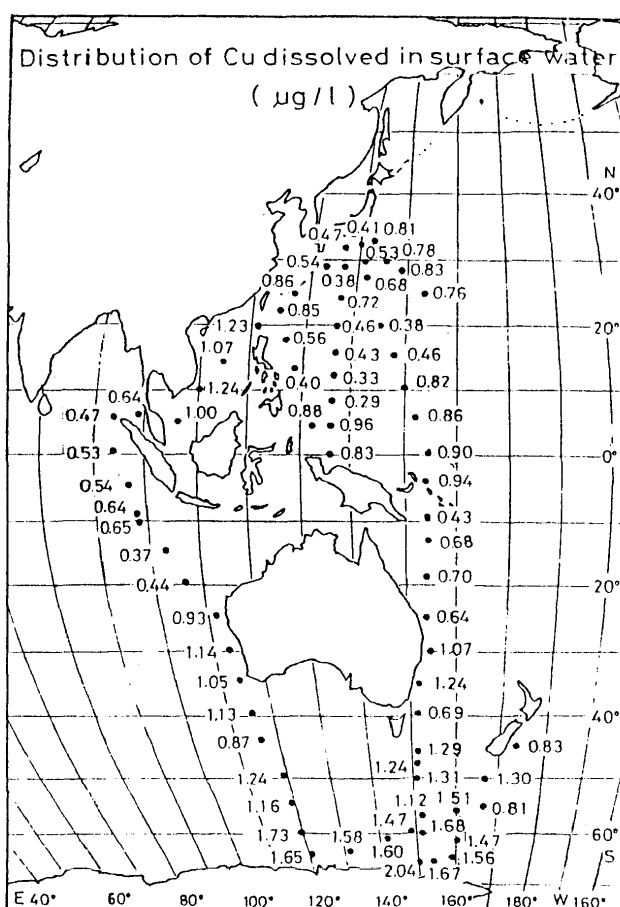

Fig. 2 Distribution of dissolved copper concentrations in the surface oceanic water.

basic organic compounds. The concentration of the neutral and basic organic fraction ranged from 0.28 to 0.69 μg l⁻¹, with an average of 0.17 to 0.42 μg l⁻¹ and the average concentration of the acidic organic fraction was 0.07 μg l⁻¹.

(B) Indian Ocean: The total concentration of copper in Indian Ocean water ranged from 0.37 to 1.05 μg l⁻¹. The higher concentration is observed

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 μg l⁻¹ and that of acidic species ranged from 0.03 to 0.09 μg l⁻¹.

(C) Southern Ocean: The water south of 40°S contained a high concentration of copper ranging from 0.69 to 2.04 μg 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 μg l⁻¹ and 1.24 μg 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 μg l⁻¹ and

Table 2 Concentrations of total and organic copper compounds in surface water.

Location	Water temp. (°C)	Salinity	Total	Organic (µg l⁻¹) N.B	A
(May,1977)					
33°40' N 141°21' E	20.2	34.99	0.75	0.58	0.06
30°48' N 145°41' E	19.5	34.93	0.77	0.64	0.05
29°53' N 146°49' E	21.4	34.77	0.81	0.67	0.05
28°02' N 149°17' E	22.7	35.25	0.83	0.69	0.08
25°06' N 152°59' E	24.7	35.30	0.76	0.59	0.07
(Jan,1978)					
24°01' N 137°00' E	24.7	35.06	0.72	0.52	0.07
21°52' N 124°58' E	24.4	35.07	0.85	0.71	0.05
20°01' N 137°00' E	23.9	34.83	0.46	0.33	0.06
17°25' N 127°18' E	26.4	34.98	0.56	0.40	0.06
16°00' N 137°00' E	27.4	34.80	0.43	0.30	0.08
12°33' N 129°51' E	27.4	34.70	0.40	0.31	0.06
12°00' N 137°00' E	27.4	34.65	0.33	0.20	0.07
08°00' N 137°00' E	28.1	34.43	0.29	0.13	0.05
04°00' N 137°01' E	27.9	34.50	0.96	0.57	0.08
04°00' N 134°33' E	28.1	34.42	0.88	0.63	0.08
03°03' S 137°02' E	28.6	34.18	0.83	0.68	0.09
(May,1978)					
32°44'N 143°10' E	20.3	34.89	0.81	0.53	0.07
31°58' N 137°18' E	19.5	34.63	0.47	0.21	0.12
31°21' N 151°39' E	19.5	34.80	0.41	0.20	0.11
30°24' N 141°16' E	21.2	34.78	0.53	0.40	0.05
29°53' N 137°11' E	21.2	34.95	0.38	0.29	0.06
29°33' N 133°29' E	21.5	34.81	0.54	0.42	0.07
(Sept.,1978)					
34°33' N 139°50' E	27.7	34.43	0.96	0.73	0.08
32°27' N 140°27' E	27.9	34.70	0.41	0.24	0.10
30°46' N 141°07' E	28.1	34.65	0.54	0.44	0.07
27°34' N 141°58' E	28.2	34.87	0.68	0.48	0.06
(Jan.,1979)					
34°00' N 137°01' E	16.8	34.72	0.81	0.64	0.09
32°41' N 136°59' E	18.7	34.76	0.62	0.48	0.08
31°01' N 151°43' E	18.5	34.72	0.73	0.51	0.09
30°23' N 132°28' E	21.1	34.91	0.57	0.43	0.08
29°59' N 137°07' E	21.0	34.82	0.57	0.40	0.09
29°29' N 133°30' E	20.3	34.87	0.74	0.42	0.09
28°12' N 129°45' E	21.0	34.86	0.97	0.50	0.08
28°00' N 137°00' E	23.1	34.84	0.61	0.42	0.09
27°40' N 123°00' E	19.1	34.69	0.96	0.48	0.17
27°40' N 125°32' E	23.5	34.70	1.47	0.96	0.24
27°34' N 130°36' E	21.5	34.89	0.78	0.62	0.05
27°00' N 131°31' E	22.0	34.87	0.69	0.54	0.05
26°40' N 127°00' E	23.1	34.72	1.21	0.49	0.10
26°40' N 124°30' E	20.7	34.70	1.08	0.50	0.12
25°37' N 125°59' E	23.4	34.69	0.94	0.47	0.09
25°04' N 127°51' E	22.2	34.93	0.56	0.44	0.05
22°59' N 137°00' E	24.0	34.88	0.70	0.40	0.07
22°56' N 128°45' E	23.9	34.91	0.49	0.37	0.05
20°34' N 129°28' E	24.0	34.94	0.50	0.41	0.05
20°00' N 137°00' E	26.0	34.87	0.40	0.35	0.05
18°00' N 136°59' E	26.5	34.68	0.42	0.40	0.02
15°01' N 137°01' E	27.1	34.67	0.38	0.31	0.02
12°38' N 132°00' E	27.4	34.57	0.41	0.32	0.02
13°00' N 137°00' E	26.9	34.59	0.25	0.20	0.02
10°00' N 137°00' E	27.7	34.02	0.37	0.32	0.02
10°01' N 132°43' E	28.0	34.41	0.35	0.30	0.02
07°31' N 137°01' E	27.6	34.26	0.36	0.30	0.02
07°26' N 133°34' E	28.2	34.43	0.42	0.35	0.03
05°01' N 137°01' E	28.1	34.44	0.90	0.58	0.09
04°47' N 134°41' E	28.1	34.36	0.96	0.83	0.07
02°30' N 136°59' E	28.9	34.42	0.93	0.72	0.08
00°00' N 137°05' E	29.2	34.53	1.07	0.90	0.05
(May, 1979)					
39°31' N 144°54' E	11.1	34.30	0.71	0.12	0.04
39°07' N 144°39' E	16.2	34.76	0.73	0.18	0.03
38°21' N 143°58' E	16.1	34.75	0.70	0.21	0.04
38°40' N 144°41' E	16.1	34.75	0.67	0.29	0.04
37°55' N 144°54' E	16.0	34.69	0.61	0.24	0.04
37°47' N 144°46' E	12.1	34.09	0.74	0.34	0.04
37°34' N 144°54' E	15.6	34.69	0.58	0.17	0.04
37°30' N 142°33' E	17.4	34.80	0.69	0.47	0.08
37°14' N 144°58' E	15.4	34.68	0.47	0.18	0.04
37°14' N 144°57' E	15.8	34.69	0.62	0.16	0.05
36°35' N 144°56' E	18.5		0.73	0.59	0.09
36°22' N 141°50' E	16.1	34.72	0.91	0.54	0.07
36°15' N 144°27' E	19.0	34.18	0.59	0.49	0.08
35°39' N 143°37' E	18.4	34.18	0.64	0.50	0.06
(July,1980)					
46°25' N 151°31' E	2.8	33.07	0.33	0.21	0.07
45°50' N 151°54' E	8.9	32.96	0.36	0.17	0.07
45°13' N 152°21' E	9.6	32.41	0.35	0.13	0.08
44°02' N 153°11' E	11.9	33.40	0.42	0.15	0.08
43°26' N 153°53' E	11.3	32.96	0.43	0.19	0.09

(Table 2 continued)

Location	Water temp. (°C)	Salinity	Total	Organic N,B (μg l⁻¹)	A
(Dec.,1977)					
24°60' N 126°57' E	26.9	34.64	0.86	0.47	0.08
20°00' N 121°45' E	28.0	34.51	1.23	0.56	0.05
14°21' N 114°31' E	28.3	34.64	1.07	0.70	0.08
09°56' N 110°00' E	28.4	35.69	1.24	0.48	0.04
04°54' N 106°31' E	27.8	33.24	1.00	0.51	0.05
04°25' N 153°23' E	29.2	34.32	0.94	0.50	0.08
00°04' N 154°24' E	29.2	34.36	0.90	0.44	0.07
05°18' N 151°55' E	28.5	54.36	0.86	0.40	0.08
10°16' N 149°55' E	27.7	34.56	0.82	0.38	0.08
15°21' N 147°28' E	27.0	34.76	0.46	0.27	0.05
20°09' N 145°43' E	25.1	35.15	0.38	0.20	0.05
39°58' N 151°17' E	19.9	35.68	0.69	0.37	0.05
34°57' N 151°09' E	23.8	35.49	1.24	0.74	0.07
30°00' N 153°32' E	26.7	35.41	1.07	0.49	0.05
25°03' N 153°32' E	26.7	35.35	0.64	0.35	0.05
18°30' N 154°42' E	28.0	35.26	0.70	0.40	0.05
12°59' N 154°46' E	28.6	35.06	0.68	0.32	0.07
09°59' N 154°17' E	28.6	34.57	0.42	0.17	0.04
(Jan.,1981)					
30°01' N 137°01' E	19.3	34.95	0.55	0.40	0.05
25°00' N 137°00' E	21.8	34.900	0.56	0.41	0.07
20°01' N 136°59' E	24.5	34.95	0.59	0.31	0.05
15°00' N 137°00' E	26.5	34.33	0.35	0.30	0.05
10°01' N 137°01' E	28.2	33.74	0.37	0.30	0.05
05°01' N 137°01' E	27.6	34.09	0.84	0.53	0.08
00°00' N 137°00' E	28.9	34.32	0.96	0.84	0.09
18°44' N 132°13' E	25.2	34.53	0.42	0.30	0.07
21°19' N 130°45' E	24.0	34.84	0.50	0.42	0.05
23°04' N 129°33' E	23.5	34.70	0.47	0.37	0.05
25°10' N 128°10' E	21.5	34.83	0.53	0.43	0.08
24°23' N 128°03' E	22.2	35.03	0.61	0.44	0.08
23°01' N 128°24' E	22.0	34.99	0.42	0.35	0.06
21°45' N 128°47' E	22.7	34.99	0.47	0.54	0.09
20°57' N 128°00' E	23.7	34.95	0.45	0.39	0.07
22°03' N 129°24' E	23.5	34.86	0.48	0.39	0.08
23°39' N 130°01' E	22.6	34.99	0.51	0.41	0.08
24°50' N 130°34' E	21.5	34.98	0.50	0.39	0.08
25°56' N 131°04' E	20.2	34.98	0.52	0.40	0.07
26°59' N 131°30' E	21.0	34.93	0.51	0.41	0.08
27°19' N 131°04' E	20.6	34.94	0.48	0.42	0.07

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27°35' N 130°10' E	20.8	34.94	0.56	0.45	0.08
27°54' N 130°10' E	21.6	34.97	0.52	0.40	0.08
28°11' N 129°45' E	21.9	34.90	0.49	0.33	0.08
28°41' N 130°53' E	20.8	34.94	0.50	0.42	0.08
29°08' N 132°15' E	20.6	34.95	0.59	0.41	0.08
29°29' N 133°28' E	20.9	34.90	0.61	0.44	0.08
30°00' N 132°53' E	21.1	34.90	0.57	0.40	0.06
30°25' N 132°23' E	21.3	34.89	0.53	0.42	0.05
30°46' N 132°00' E	21.5	34.88	0.62	0.42	0.11
31°00' N 131°43' E	20.1	34.84	0.71	0.51	0.13
31°10' N 131°30' E	19.0	34.83	0.72	0.48	0.10
(April,1981)					
34°43' N 139°56' E	17.2		0.63	0.47	0.08
33°04' N 142°15' E	17.8		0.57	0.41	0.07
31°38' N 144°21' E	18.2		0.43	0.30	0.07
28°45' N 148°19' E	21.4		0.37	0.30	0.07
27°11' N 150°17' E	21.2		0.36	0.28	0.06
25°44' N 152°09' E	21.4		0.45	0.32	0.07
30°04' N 146°43' E	19.1		0.53	0.37	0.07
31°36' N 143°19' E	18.8		0.47	0.35	0.08
32°39' N 140°52' E	21.4		0.52	0.33	0.08
(Sept.,1981)					
34°40' N 139°46' E	25.4		0.59	0.40	0.05
34°18' N 139°52' E	24.4		0.47	0.31	0.07
33°55' N 139°57' E	27.4		0.52	0.34	0.07
33°29' N 140°04' E	27.3		0.36	0.25	0.05
33°08' N 139°45' E	27.1		0.32	0.26	0.06
34°47' N 141°03' E	26.7		0.44	0.29	0.07
35°26' N 141°49' E	26.8		0.47	0.32	0.07
35°50' N 141°41' E	24.5		0.52	0.31	0.07
36°07' N 141°25' E	21.3		0.53	0.33	0.05
(Dec.,1981)					
33°00' N 137°00' E	21.1	34.49	0.64	0.27	0.08
32°30' N 137°01' E	22.8	34.57	0.50	0.30	0.07
32°00' N 137°01' E	22.1	34.50	0.42	0.22	0.06
31°00' N 136°59' E	22.3	34.78	0.78	0.34	0.07
30°00' N 136°59' E	22.7	34.65	0.62	0.36	0.07
29°00' N 137°00' E	22.2	34.71	0.54	0.41	0.08
28°00' N 137°00' E	22.3	34.74	0.62	0.39	0.07
25°41' N 135°57' E	24.5	34.71	0.62	0.41	0.08
32°57' N 133°35' E	21.9	34.48	0.52	0.37	0.06
32°24' N 133°53' E	22.4	34.82	0.66	0.33	0.06

(Table 2 continued)

Location	Water temp. (°C)	Salinity	Total	Organic (μg l⁻¹) N,B	A
32°29' N 133°42' E	22.6	34.53	0.72	0.40	0.07
32°00' N 133°00' E	22.5	34.77	0.52	0.34	0.07
31°32' N 133°21' E	22.3	34.78	0.60	0.41	0.07
31°35' N 134°00' E	21.8	34.75	0.52	0.42	0.07
32°43' N 133°46' E	22.3	34.57	0.60	0.35	0.06
33°19' N 134°29' E	20.2	34.59	0.62	0.42	0.08
32°55' N 134°49' E	23.3	34.66	0.48	0.33	0.06
32°10' N 135°50' E	21.5	34.78	0.52	0.44	0.07
32°19' N 136°27' E	21.8	34.79	0.61	0.36	0.07
32°54' N 136°28' E	21.1	34.61	0.43	0.29	0.06
33°25' N 136°22' E	19.3	34.58	0.42	0.30	0.07
34°00' N 136°32' E	18.6	34.54	0.56	0.44	0.08
(Jan.,1982)					
34°00' N 137°00' E	17.3	34.71	0.64	0.37	0.06
30°00' N 136°56' E	19.6	34.82	0.54	0.32	0.07
25°00' N 137°00' E	21.5	34.85	0.32	0.26	0.07
21°00' N 137°00' E	24.1	34.78	0.27	0.21	0.05
14°57' N 136°56' E	27.6	34.15	0.30	0.22	0.05
11°00' N 137°00' E	28.8	34.00	0.24	0.20	0.05
07°31' N 137°00' E	28.9	34.08	0.41	0.27	0.05
05°01' N 137°03' E	28.0	34.10	0.37	0.29	0.05
02°31' N 137°01' E	29.2	34.39	0.52	0.31	0.07
00°08' N 137°01' E	28.6	34.13	0.82	0.47	0.08
03°46' N 135°08' E	29.5		0.71	0.42	0.06
16°35' N 130°52' E	27.1		0.62	0.36	0.05
20°46' N 129°26' E	23.4		0.27	0.20	0.05
(March,1982)					
30°19' N 146°47' E	17.8		0.57	0.37	0.07
30°37' N 146°20' E	17.7		0.61	0.34	0.06
30°57' N 145°51' E	18.1		0.49	0.35	0.06
31°12' N 145°18' E	18.2		0.53	0.41	0.07
31°33' N 144°45' E	17.6		0.52	0.47	0.05
31°56' N 144°12' E	17.2		0.50	0.41	0.05
32°18' N 143°39' E	17.2		0.49	0.40	0.05
32°40' N 143°09' E	17.3		0.56	0.41	0.11
33°02' N 142°35' E	17.4		0.58	0.42	0.10
33°25' N 141°57' E	17.5		0.52	0.39	0.12
33°45' N 141°23' E	18.7		0.60	0.41	0.09
34°09' N 140°45' E	19.1		0.49	0.37	0.07
34°30' N 140°15' E	16.1		0.58	0.42	0.08
(April,1982)					
32°15' N 133°57' E	19.1	34.82	0.57	0.42	0.06
32°20' N 133°56' E	20.1	34.87	0.62	0.39	0.07

Location	Water temp. (°C)	Salinity	Total	Organic (μg l⁻¹) N,B	A
32°25' N 133°56' E	21.2	34.74	0.67	0.47	0.07
32°30' N 133°55' E	21.5	34.78	0.67	0.42	0.09
32°30' N 135°01' E	21.2		0.72	0.48	0.07
32°47' N 135°07' E	22.0		0.70	0.61	0.08
33°02' N 135°11' E	18.5		0.66	0.53	0.07
30°31' N 135°48' E	19.4	34.82	0.52	0.41	0.06
30°59' N 136°10' E	20.1	34.85	0.52	0.39	0.07
31°27' N 136°33' E	21.9	34.71	0.47	0.40	0.05
31°59' N 136°49' E	17.5	34.68	0.42	0.31	0.05
32°31' N 137°04' E	17.7	34.56	0.47	0.30	0.05
33°00' N 137°29' E	18.5	34.66	0.46	0.38	0.05
33°29' N 137°48' E	18.0	34.64	0.52	0.32	0.07
34°01' N 138°11' E	20.3	34.69	0.51	0.37	0.08
34°29' N 138°21' E	21.0		0.48	0.38	0.07
(Jan.,1983)					
33°59' N 137°01' E	17.4	34.66	0.65	0.42	0.08
35°20' N 137°00' E	18.0	34.63	0.59	0.40	0.07
31°00' N 137°01' E	20.6	34.74	0.57	0.40	0.08
29°59' N 137°01' E	20.4	34.75	0.55	0.36	0.07
28°00' N 137°00' E	22.2	34.67	0.54	0.37	0.08
25°58' N 137°00' E	21.7	34.66	0.34	0.25	0.05
24°00' N 137°00' E	22.7	34.66	0.30	0.22	0.05
22°00' N 137°00' E	25.3	34.70	0.28	0.20	0.05
20°00' N 137°00' E	26.5	34.73	0.27	0.22	0.05
17°01' N 137°00' E	26.6	34.67	0.26	0.20	0.05
14°00' N 136°59' E	26.7	34.60	0.28	0.20	0.05
09°55' N 136°58' E	27.1	34.65	0.29	0.20	0.05
09°00' N 137°00' E	27.6	34.58	0.31	0.22	0.05
03°00' N 136°57' E	27.6	34.68	0.40	0.25	0.07
07°00' N 137°00' E	27.6	34.62	0.43	0.29	0.08
06°00' N 137°00' E	27.7	34.59	0.45	0.30	0.08
04°31' N 137°02' E	27.9	34.81	0.54	0.36	0.08
04°00' N 136°59' E	28.0	34.88	0.58	0.36	0.08
02°28' N 137°00' E	28.0	34.90	0.78	0.48	0.06
02°00' N 137°00' E	28.4	34.93	0.80	0.44	0.08
00°00' N 136°59' E	28.6	34.81	0.82	0.46	0.06
01°00' S 137°00' E	28.4	34.41	0.67	0.53	0.05
13°06' N 131°53' E	27.2		0.28	0.20	0.05
(March,1983)					
36°12' N 142°05' E	11.5		0.42	0.20	0.13
36°55' N 143°05' E	16.2		0.43	0.31	0.05
37°41' N 144°14' E	12.3		0.46	0.19	0.09

(Table 2 continued)

Location	Water temp. (°C)	Salinity	Total	Organic N,B (μg l⁻¹)	Organic A (μg l⁻¹)
38°25' N 145°21' E	2.2		0.48	0.12	0.19
35°39' N 145°48' E	11.7		0.43	0.20	0.11
30°10' N 147°08' E	18.1		0.54	0.41	0.06
(Jan.,1984)					
33°59' N 137°00' E	17.0	34.78	0.61	0.42	0.08
31°56' N 137°00' E	20.7	34.87	0.54	0.40	0.08
30°00' N 136°59' E	19.6	34.77	0.56	0.38	0.08
27°01' N 137°02' E	20.6	34.82	0.54	0.38	0.08
24°59' N 137°00' E	23.5	34.96	0.36	0.26	0.05
20°00' N 136°59' E	25.7	34.84	0.29	0.20	0.05
16°57' N 137°00' E	26.4	34.78	0.28	0.20	0.05
14°58' N 136°58' E	28.1	34.64	0.26	0.19	0.05
09°59' N 136°57' E	28.1	34.30	0.29	0.20	0.05
08°02' N 137°00' E	28.6	34.14	0.42	0.27	0.08
05°00' N 136°56' E	28.7	34.19	0.50	0.36	0.08
03°00' N 137°00' E	28.2	34.38	0.73	0.46	0.08
00°02' N 136°58' E	29.7	33.91	0.77	0.30	0.14
31°03' N 131°50' E	20.2	34.90	0.43	0.34	0.07
30°52' N 132°06' E	20.2	34.89	0.50	0.42	0.08
33°29' N 141°30' E	17.1	34.83	0.56	0.44	0.08
34°12' N 140°54' E	17.2	34.83	0.58	0.46	0.08
38°05' N 136°13' E	26.8	34.00	0.32	0.15	0.05
38°50' N 135°39' E	26.2	34.02	0.24	0.05	0.05
39°58' N 134°47' E	25.3	33.74	0.28	0.10	0.05
41°00' N 134°01' E	24.4	33.87	0.23	0.10	0.05
41°00' N 135°40' E	23.5	33.73	0.26	0.12	0.05
40°11' N 136°15' E	25.3	34.05	0.29	0.10	0.10
39°20' N 136°50' E	25.5	33.78	0.27	0.12	0.08
38°32' N 137°26' E	26.5	34.30	0.28	0.10	0.05
37°40' N 138°00' E	27.1	34.18	0.22	0.12	0.05
(July, 1982)					
35°29' N 131°30' E	22.3	34.38	0.26	0.12	0.06
36°00' N 130°59' E	22.1	34.37	0.28	0.12	0.06
36°51' N 130°42' E	20.9	34.57	0.30	0.08	0.08
38°30' N 130°30' E	21.3	34.28	0.34	0.20	0.08
37°58' N 131°00' E	21.0	34.31	0.32	0.18	0.08
36°20' N 132°28' E	23.0	34.48	0.26	0.14	0.06
36°17' N 134°07' E	23.3	34.49	0.28	0.14	0.06
37°22' N 133°16' E	22.2	34.49	0.28	0.12	0.05
38°11' N 132°38' E	23.6	34.27	0.28	0.18	0.06
39°24' N 133°23' E	22.4	34.46	0.30	0.20	0.06
(Oct.,1977)					
45°31' N 144°02' E	12.1	33.05	0.63	0.10	0.02
45°32' N 147°00' E	12.0	33.14	0.51	0.12	0.04
46°45' N 149°00' E	11.5	32.59	0.70	0.14	0.04
46°46' N 145°59' E	11.3	32.94	0.76	0.10	0.04
46°45' N 144°31' E	9.0	32.14	0.60	----	0.05
48°01' N 149°01' E	10.3	32.45	0.67	0.09	0.02
48°40' N 152°40' E	8.6	32.60	0.99	0.12	0.02
50°01' N 151°00' E	9.2	32.29	1.01	0.16	0.03
50°01' N 149°03' E	9.5	31.51	0.46	0.10	0.02
50°45' N 145°40' E	7.3	30.81	0.67	0.14	0.02
50°45' N 147°15' E	8.3	31.80	0.71	0.20	0.04
48°00' N 149°59' E	8.5	32.48	0.71	0.11	0.04
46°57' N 151°03' E	8.1	32.69	0.47	0.12	0.02
45°00' N 153°00' E	6.8	32.70	0.76	0.14	0.02
(Oct.,1978)					
45°31' N 145°00' E	6.8	30.63	0.64	0.12	0.04
45°30' N 147°00' E	10.2	33.02	0.50	0.08	0.02
46°29' N 144°59' E	7.4	32.36	0.68	0.09	0.04
48°00' N 146°03' E	6.4	32.29	0.57	0.14	0.07
48°01' N 148°01' E	8.0	32.74	0.89	0.10	0.03
48°01' N 151°59' E	6.6	32.45	0.64	0.17	0.07
50°02' N 153°02' E	6.6	32.45	0.92	0.11	0.03
50°00' N 145°00' E	5.1	31.46	0.65	0.16	0.09
47°00' N 151°00' E	4.0	33.04	0.90	0.15	0.03
45°00' N 153°02' E	6.8	32.80	0.75	0.09	0.02
44°20' N 151°32' E	7.4	32.73	0.67	0.10	0.04
(July,1980)					
44°51' N 144°58' E	13.7	31.93	0.48	0.24	0.07
45°02' N 146°01' E	10.9	32.51	0.52	0.17	0.08
45°58' N 147°58' E	11.6	32.17	0.44	0.16	0.07
46°25' N 148°56' E	11.3	32.25	0.43	0.20	0.08
46°45' N 149°49' E	10.5	32.09	0.37	0.19	0.09
46°55' N 149°57' E	7.9	32.28	0.42	0.17	0.08
47°20' N 150°20' E	3.6	32.59	0.39	0.18	0.07
46°54' N 151°10' E	2.5	33.19	0.40	0.23	0.08

(Table 2 continued)

Location	Water temp.	Salinity	Total	Organic (µg l⁻¹) N.B	A
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	33.55	0.85	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	0.53	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°57' 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 124°18' E	29.5	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 (µg l⁻¹) N.B	A
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 µg 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

(May,1977) (29°53'N,146°49'E, depth=6030m)

Depth (m)	Water temp. (°C)	Salinity	Total (µg l⁻¹)	Organic N,B	Organic A
0	21.4	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
483	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	0.06
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	0.12
5110	1.5	34.67	0.89	0.48	0.32

(Jan,1978) (04°00'N,134°34'E, depth=4820m)

Depth (m)	Water temp. (°C)	Salinity	Total	Organic N,B	Organic A
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	0.40	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

(May,1978) (29°55'N,146°49'E, depth=6100m)

Depth (m)	Water temp. (°C)	Salinity	Total	Organic N,B	Organic A
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

(Jan.,1979) (13°00'N,131°48'E, depth=5202m)

Depth (m)	Water temp. (°C)	Salinity	Total	Organic N,B	Organic A
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
1096	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
2361	1.9	34.73	0.84	0.17	0.31
3111	1.6	34.75	1.23	0.43	0.29
3976	1.6	34.76	1.47	0.52	0.33
4368	1.6	34.76	1.62	0.49	0.40

(Mar.,1979) (29°53'N,147°05'E, depth=6,160m)

Depth (m)	Water temp. (°C)	Salinity	Total	Organic N,B	Organic A
0	18.8	34.91	0.82	0.62	0.04
89	18.6	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	0.06
706	6.2	34.06	0.96	0.27	0.12
972	4.1	34.23	0.63	0.30	0.12
1468	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

(Apr.,1979) (39°09'N,143°46'E, depth=4,650m)

Depth (m)	Water temp. (°C)	Salinity	Total	Organic N,B	Organic A
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
192	10.8	34.35	0.93	0.10	0.05
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	0.50
3684	1.6	34.65	1.64	0.17	0.48
5512	1.5	34.67	1.70	0.29	0.52
4420	1.5	34.68	1.65	0.37	0.59

(Apr.,1980) (30°00'N,147°02'E, depth=6,211m)

Depth (m)	Water temp. (°C)	Salinity	Total	Organic N,B	Organic A
0	19.2	34.77	0.78	0.56	0.06
100	17.6	34.83	0.63	0.37	0.07
200	16.9	34.73	0.61	0.28	0.06
282	15.8	34.66	0.53	0.51	0.07
471	11.9	34.59	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

(continued)

Depth (m)	Water temp. (°C)	Salinity	Total	Organic N,B
5508	1.5	34.69	0.64	0.32
6021	1.6	34.69	1.04	0.52
6211	1.6	34.69	1.22	0.61

(Jan.,1981) (18°44'N,132°23'E, depth=5760m)

Depth (m)	Water temp. (°C)	Salinity	Total	Organic N,B
0	25.2	34.58	0.42	0.30
89	24.9	34.71	0.48	0.41
259	18.1	34.87	0.56	0.23
518	8.4	34.21	0.53	0.18
658	5.6	34.21	0.54	0.17
886	4.2	34.43	0.58	0.18
1365	2.9	34.57	0.50	0.15
1889	2.1	34.62	0.47	0.18
2574	1.8	34.66	0.48	0.17
3415	1.6	34.68	0.44	0.17
4309	1.6	34.68	0.42	0.16
5264	1.8	34.69	0.45	0.17

(Apr.,1981) (23°36'N,151°08'E, depth=6100m)

Depth (m)	Water temp. (°C)	Salinity	Total	Organic N,B
0	22.3	35.06	0.37	0.31
100	19.3		0.52	0.23
193	17.2	34.83	0.48	0.12
289	15.7	34.69	0.48	0.12
476	11.2	34.33	0.51	0.13
715	5.7	34.06	0.47	0.19
780	5.1	34.10	0.49	0.15
1104	3.5	34.35	0.48	0.14
1483	2.5	34.52	0.49	0.14
2341	1.7	34.63	0.43	0.14
3932	1.5	34.68	0.41	0.13
4892	1.5	34.68	0.45	0.10
5382	1.5	34.69	0.44	0.11
5875	1.6	34.69	0.43	0.11

(Mar.,1982) (30°15'N,146°51'E, depth=6210m)

Depth (m)	Water temp. (°C)	Salinity	Total	Organic N,B
0	18.4	34.87	0.67	0.48
92	18.0	34.80	0.58	0.39
248	16.3	34.61	0.56	0.40
488	12.4	34.44	0.61	0.27
716	5.4	34.10	0.66	0.28
978	4.0	34.21	0.66	0.28
2010	2.0	34.61	0.59	0.26
3045	1.7	34.59	0.60	0.36
4010	1.6	34.67	0.70	0.42
4980	1.5	34.68	0.72	0.48

(Jan.,1983) (03°52'N,135°03'E, depth=4840m)

Depth (m)	Water temp. (°C)	Salinity	Total	Organic N,B
0	27.9	34.90	0.82	0.86
81	23.6	34.75	0.66	0.48
177	17.3	34.75	0.60	0.46
299	8.2	34.44	0.58	0.44
749	5.6	34.54	0.78	0.46
1244	3.7	34.58	0.54	0.30
1741	2.5	34.62	0.50	0.26
2240	1.9	34.67	0.52	0.26
2527	1.8	34.68	0.50	0.22
3555	1.5	34.69	0.54	0.24
4542	1.5	34.70	0.58	0.28
4839	1.6	34.70	0.62	0.34

(Mar.,1983) (38°31'N,145°29'E, depth=5320m)

Depth (m)	Water temp. (°C)	Salinity	Total	Organic N,B
0	2.6	33.204	0.42	0.10
100	3.5	33.30	0.44	0.12
200	3.4	33.28	0.52	0.10
300	3.1	33.55	0.48	0.12
500	3.0	33.95	0.50	0.18
750	3.1	34.15	0.54	0.20
1000	2.3	34.35	0.58	0.24
1500	1.7	34.51	0.68	0.17
2000	1.6	34.51	0.72	0.17
3000	1.7	34.58	0.74	0.12
4000	1.6	34.54	0.68	0.12
5140	1.6	34.64	0.68	0.10

(May,1983) (36°59'N,144°02'E) (depth=6000m)

Depth (m)	Water temp. (°C)	Salinity	Total	Organic N,B
0	12.4	34.69	0.42	0.18
48	5.4		0.44	0.30
98	3.3		0.52	0.24
240	3.9		0.48	0.32
480	3.5		0.56	0.24
720	3.0		0.54	0.20
960	2.7		0.58	0.17
1100	2.0		0.50	0.17
2000	1.8		0.52	0.12
2500	1.7		0.56	0.12

(Jan.,1984) (23°59'N,128°18'E, depth=2450m)

Depth (m)	Water temp. (°C)	Salinity	Total	Organic N,B
0	21.3	34.84	0.58	0.40
22	21.3	34.85	0.54	0.37
49	21.4	34.85	0.48	0.38
102	21.3	34.85	0.52	0.38
155	20.1	34.82	0.47	0.27
207	18.0	34.81	0.50	0.24
269	16.7	34.75	0.49	0.24
323	15.6	34.67	0.48	0.20
539	10.0	34.29	0.53	0.20
819	5.0	34.28	0.61	0.16
1206	3.1	34.46	0.57	0.16
1779	2.2	34.58	0.52	0.16

(Table 3 continued)

Depth	Water temp. (°C)	Salinity	Total	Organic (µg l⁻¹) N,B	A
(July,1977)(41°00'N,135°40'E, depth=3560m)					
0	23.5	33.73	0.26	0.12	0.05
50	3.6	34.00	0.42	0.30	0.08
100	1.0	34.00	0.40	0.30	0.05
200	0.5	34.04	0.44	0.28	0.06
300	0.4	34.05	0.44	0.30	0.06
500	0.3	34.06	0.40	0.26	0.08
750			0.48	0.24	0.08
1000			0.48	0.20	0.10
1250			0.44	0.20	0.10
1500	0.1	34.07	0.40	0.20	0.08
2000	0.3	34.08	0.44	0.18	0.12
2500			0.46	0.18	0.10
3400			0.46	0.18	0.10
(Oct.,1978)(46°30'N,147°00'E)					
0	9.2	32.61	0.55	0.10	0.06
50	7.2	32.85	0.60	0.12	0.06
187	0.9	32.90	0.52	0.28	0.10
466	0.8	33.58	0.48	0.40	0.06
947	2.2	34.19	0.50	0.16	0.16
1949	2.0	34.50	0.52	0.14	0.22
2917	1.8	34.60	0.50	0.12	0.14
(51°30'N,147°00'E)					
0	3.1	32.09	0.44	0.23	0.06
100	-1.4	33.04	0.58	0.44	0.08
188	0.4	33.37	0.62	0.38	0.08
498	1.8	33.89	0.60	0.30	0.10
1110	2.3	34.37	0.56	0.16	0.22
(July,1980)(42°50'N,153°59'E)					
0	14.6	34.10	0.54	0.28	0.08
102	6.4	33.79	0.43	0.20	0.07
200	4.0	33.64	0.62	0.15	0.09
300	4.5	33.92	0.56	0.09	0.08
505	3.9	34.14	0.47	0.09	0.07
817	3.0	34.30	0.45	0.11	0.08
1035	2.8	34.41	0.51	0.08	0.07
1680	2.1	34.47	0.50	0.08	0.08
1900		34.58	0.48	0.08	0.08
2900		34.64	0.53	0.08	0.08
3200					
3900		34.64	0.55	0.09	0.08
4200					
4900		34.68	0.53	0.08	0.08
(Aug.,1978)(29°53'N,124°30'E)					
0	27.9	30.71	3.24	0.24	0.22
30	23.6	33.54	0.78	0.20	0.10
50	20.9	34.41	0.56	0.20	0.12
(28°25'N,126°55'E)					
0	29.7	34.33	0.46	0.20	0.10
50	26.3	34.52	0.48	0.24	0.12
100	22.8	34.78	0.50	0.22	0.12

Fig. 4   The vertical distribution of total and organic copper compounds at the differnet locations (a and b).

5,000 m depth are mainly due to the decrease of neutral and basic copper organic compounds. A maximum observed in the layer just below the seasonal thermocline is the result of an increase in neutral and basic copper organic compounds in the layer.

The concentration of copper incorporated in the acidic organic fraction shows a nearly constant value with depth from the surface to 5,000 m. A small maximum is also observed near the salinity minimum layer.

In the deeper layer from 5,000 m to the bottom, the concentration of both the neutral and basic fractions and the acidic fraction increased with depth, and about 60% of the increment is due to the increasing concentration of neutral and basic copper organic compounds near the bottom layer.

The concentration of inorganic copper is low at the surface and reaches a maximum at the salinity minimum layer. In the intermediate and deep layer the concentration is nearly a constant value. As seen in the tables, everywhere in the ocean the major fraction of organically bound copper in sea water is involved in the neutral and basic fraction.

The subarctic waters in the western North Pacific are characterized by a relatively high concentration of inorganic copper concentration, and this may be due to the high concentration of copper in the salinity minimum layer of the subtropical water. The concentration of total and organic copper in the Japan Sea water is similar to the concentration in the subarctic water.

In the Southern Ocean water, the concentration both of total and organic copper is higher than in any other area of the ocean, and it is also notable that the major fraction of organically bound copper is involved in neutral and basic organic matter.

Molecular size distribution of copper organic compounds

As described in the first section, most of organic copper species are involved in the macromolecular fraction and these are adsorbed in such a way on the XAD-2 resin that they can be analyzed quantitatively. To obtain further information on the organically bound copper in sea water, the copper organic compounds adsorbed on the resin were examined in more detail using gel-filtaration chromatography.

Surface water

The results of the molecular size distribution of
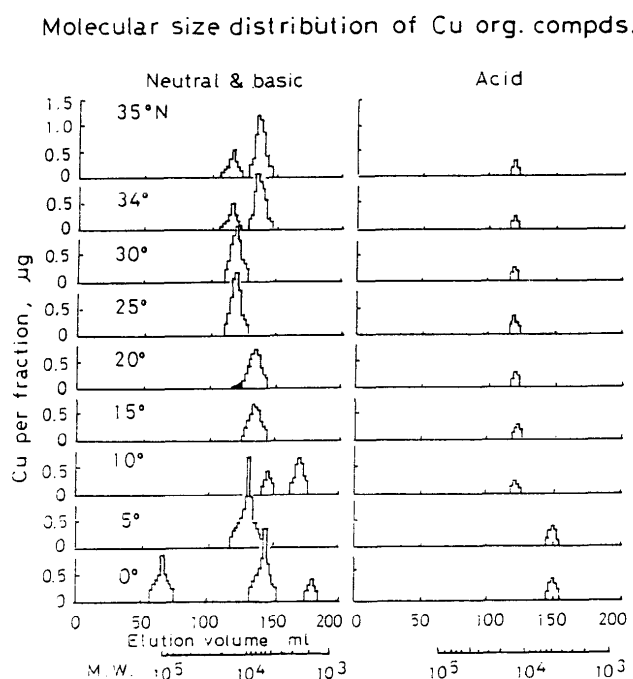
Molecular size distribution of Cu org. compds.

Fig. 5 The molecular size distribution of organic copper compounds in surface water.

organic copper adsorbed on the XAD-2 resin are shown in Fig. 5 together with the UV absorption value as an indicator of the presence of organic matter in the samples collected along 137°E.

As seen in the figure, several groups of organic matter were observed in the neutral and basic organic species, with molecular sizes ranging from 1 $\times 10^3$ to 1×10^5.

In the acidic fraction, there are a few groups of organic matter with molecular sizes ranging from 2 $\times 10^3$ to 2×10^4.

Although several groups of organic matter with different molecular sizes were observed in surface waters, it seems that only a limited number of groups of organic matter are associated with copper-organic complexes. Most copper-organic compounds in the neutral and basic fraction have molecular sizes ranging from 5×10^3 to 2×10^4.

In tropical water, about 30% of organically bound copper is associated with macromolecular organic matter with a molecular size of about 1×10^5, and water near the equator, at 10°N, contained a smaller size of organic-copper compounds with molecular size 2 to 3 $\times 10^3$.

Unlike the organic matter distribution, water between 30°N and 15°N contained only one molecular size group of copper-organic compound. It thus appears that the molecular size of copper-organic compounds in the surface water of the western North Pacific is distributed zonally.

In the acidic organic fraction, two groups of copper-organic compounds were observed from 35°N

to the equator. In water from 35°N to 10°N, copper-organic compounds were involved in organic matter with a molecular size 1.2×10^4, and a slightly smaller size group of copper-organic compounds was observed (5×10^3) in the waters from 5°N to the equator.

The molecular size distribution of copper-organic compounds in surface water might be controlled by the balance of biological production and decomposition of organic matter, the stability of metal organic compounds in sea water and lateral mixing of water from different source waters. Therefore, the distribution in surface water might reflect the biochemical nature of waters in the source regions.

Vertical distribution

An example of the vertical distribution of molecular sizes of copper-organic compounds is shown in Fig. 6. As seen in the figure, the major part of the copper-organic species dissolved in sea water is involved in neutral and basic organic matter with a molecular size of 8×10^3 from the surface to 5,000 m depth.

A small maximum observed just below the seasonal thermoline is a consequence of the appearance of copper-organic species with a slightly smaller molecular size of 5×10^3.

In the intermediate water, the concentration of copper-organic species gradually decreased to 0.15 $\mu g \ l^{-1}$. Below 5,000 depth, the concentration increased toward the bottom, and it is of interest to note that the species of copper-organic compound in the deeper water are not the same as those in upper water, but most of them are involved in organic matter with a molecular size of 2×10^3.

With respect to the acidic organic fraction, most of copper-organic compounds are in the form of macromolecular organic matter with a molecular size of 2×10^4 from the surface to 5,000 m depth. A small maximum around the oxygen minimum layer may be due to the addition of a slightly smaller size of copper-organic species size of 5×10^3.

In the water below 5,000 m depth to the bottom, the copper-organic species with higher molecular sizes in the upper layer were replaced with other compunds with molecular size of 2×10^3, and the concentration increased toward the bottom.

Summarizing the vertical distribution of copper-organic species dissolved in the total water column, 50% of copper-organic species are associated with a organic matter with molecular size of 8×10^3, 30% with 2×10^3, 16% with 2×10^4 and only a small fraction with 5×10^3.

3.4. Relation between copper-organic compounds and combined amino acids

Because of the similarities of distribution in sea water and elution behavior from gel-chromatography of the combined amino acids or protein-
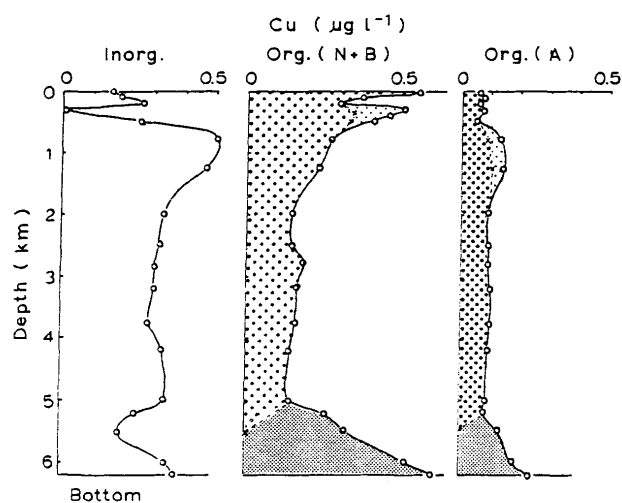
Fig. 6 The vertical distribution of organic copper compounds with different molecular size (coarse stippling: high molecular weight, fine stippling: low molecular weight).
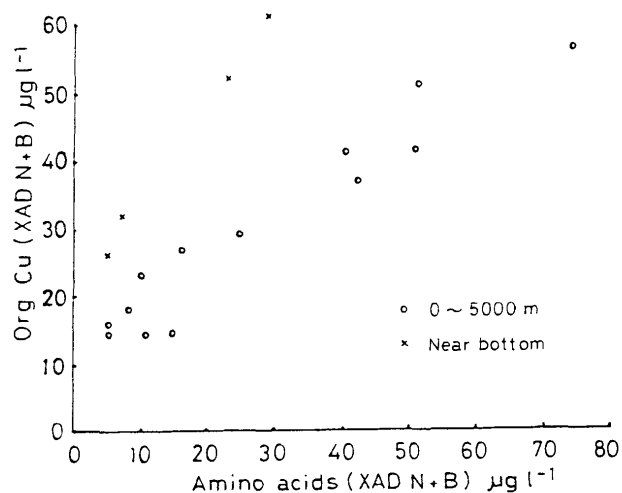

Fig. 7 The relationship between amino acids concentration and organic copper compounds absorbed on the XAD-2 resin.

Composition of amino acids in each molecular size

M.W.	AA composition	AA $_{nM}$	Cu
(N+B)			
8×10^3	$Lys_9 Ser_{10} Pro_9 Gly_{33} Ala_{13} Val_{10} Cys_3 Met_{13}$	180	8.8
2×10^3	$Arg_5 Lys_6 Asp_{10} Gly_{25} Ala_{26} Ile_{10} Leu_1 Tyr_7 Phe_9$	150	9.6
(A)			
2×10^4	$Gly_{58} Leu_{20} Met_{11} Trp_{11}$	60	0.9
2×10^3	$Arg_7 Lys_5 Asp_{14} Gly_{51} Leu_{12} Trp_{11}$	160	3.8

Fig. 8 The compositions of amino acids abosorbed on the XAD-2 resin in each molecular size fraction.

& SUZUKI 1984; KREMLING et al. 1982).

The meridional distribution of copper-organic compounds and combined amino acids along 137°E in the western North Pacific indicates that the high concentration of copper in surface water corresponds with the high concentration of combined amino acids adsorbed on the resin. The low concentration of copper-organic species in waters between 10°N and 20°N may be consistent with the low concentration of combined amino acids adsorbed on the resin in the water, although the total concentration of amino acids is high in this region (SUGIMURA & SUZUKI 1983).

3.4.1. Individual amino acid composition

The detailed report on the composition of individual amino acids in sea water is given elsewhere (SUGIMURA & SUZUKI 1983).

The major fraction of copper-organic compounds is involved in macfomolecular organic matter with molecular sizes of 8×10^3 and 2×10^2 in the neutral and basic fraction, and 2×10^4 and 2×10^3 in the acidic fraction; the individual amino acid composition was determined in each molecular size group.

As shown in Fig. 8, among the 14 species of amino acids in the original fraction, only eight — Lys, Ser, Pro, Gly, Ala, Val, CysH and Met — are detected in the neutral and basic organic matter with molecular size 8×10^3.

In the deep water, organic matter with molecular size 2×10^3 is another important compound in the neutral and basic organic matters. The amino acids consisted of Arg, Lys, Asp, Gly, Ala, Ile, Leu, Tyr and Phe.

In the acid organic fraction with molecular size 2×10^4, four species of amino acids — Trp, Gly, Leu and Met — were observed. In the deep water, Arg, Lys, Asp, Gly and Leu were detected in the fraction with molecular size 2×10^3.

These results indicate that only a limited number of species of amino acids are concerned with metal complexation in combined forms in sea

aceous matter with those of copper-organic compounds, it is of interest to examine the relationship between organic matter and copper-organic species dissolved in sea water.

As seen in Fig. 7, an intimate correlation was observed between copper-organic compounds and combined amino acids or proteinaceous matter adsorbed on the XAD-2 resin. This suggests that the organic ligand of copper-organic species dissolved in sea water may be related with some of the combined amino acids or polypeptide-like matter. In this connection, it is reported that after chemical or photochemical decomposition of the organic matter, no detectable amount of copper was adsorbed on the resin or some other adsorbent (SUGIMURA

water. It is of interest to note that the sulphur-containing amino acids in surface water are 2 to 3 % of the total in molar ratio, but in the metal-organic fraction, the ratio increased to 10 to 15 % in the neutral and basic organic matter. The higher stability constant of sulphur-containing amino acids with copper relative to that those of other amino acids may suggest a role for these amino acid residues in the cause of the intimate correlation observed between combined amino acids and copper-organic compounds in sea water.

Inorganic copper and reactive nutrients

Recently, the distribution of trace elements in sea water has often been discussed in relation to those of the reactive nutrients, whose concentration is low at the surface and high in the intermediate and deep layer (c.f. BRULAND 1983). However, no consideration has been given to the existence of organic species of trace metals and nutrients.

As revealed by the recent work (SUGIMURA et al. 1978, 1980; SUGIMURA & SUZUKI 1984; KREMLING et al. 1981, 1983; HIROSE et al. 1983), every element dissolved in sea water is present in inorganic and organic forms. The total concentration of the element [M] is expressed as follows:

$$[M]_{total} = [M]_{org.} + [M]_{inorg.} \tag{1}$$

The relationship between the total and inorganic forms of elements in sea water is expressed in following equation for the case of Cu and carbon, nitrogen and phosphorus (HIROSE & SUGIMURA 1983):

$$[Cu]_{inorg} = [Cu]_b/[C,N,P]_b \times [C,N,P]_{inorg}$$
$$+ [Cu]_{total} - [Cu]_b/[C,N,P]$$
$$\times [C,N,P]_{total} \tag{2}$$

where the subscript b represents the concentration in marine organisms.

If the oceanic residence time of these elements is long enough compared with the ocean mixing time, then the total concentrations of carbon, nitrogen, phosphorous and copper should not significantly vary with depth. Therefore, as seen in Eq. 2, the concentration of inorganic forms of copper would be linearly related with that of reactive (inorganic) nutrients.

As seen in the previous section, the total concentration of copper dissolved in sea water is almost constant from the surface to the bottom, though the vertical profile of inorganic forms shows surface depletion and a deep water maximum.

In Fig. 9 is plotted the concentration of reactive nitrate (NO₃-N) against that of inorganic copper in sea water in the western North Pacific. As seen in the figure, there is an intimate correlation between reactive nutrients and inorganic copper from the surface to the oxygen minimum layer, but no positive correlation was observed in the deeper layer. One of the causes of these differences
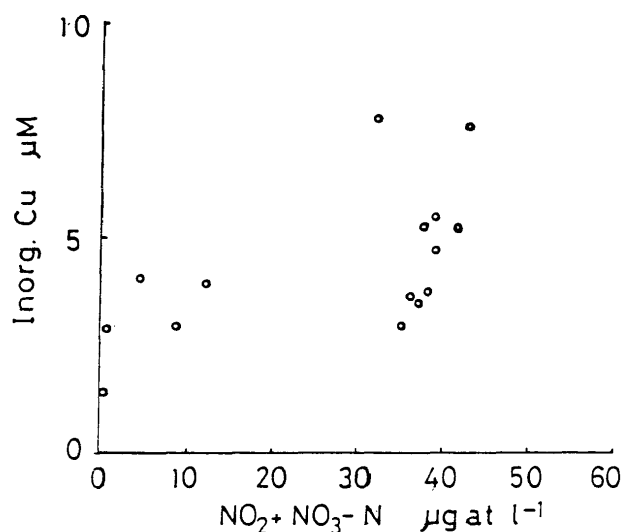

Fig. 9 The relationship between inorganic copper compounds and inorganic nitrogen (nitrate and nitrite) in sea water.

between the surface and deep layers may be explained if most transformation from organic to inorganic forms of the elements occurrs in the upper 1,000 m of the ocean, and if the mixing of water between surface and deep layers is rather slow.

The proposed relasionship between metallic elements and reactive nutrients given by previous researchers (cf. BRULAND 1983) is valid only in the case of inorganic species of metallic elements and nutrients.

CONCLUSION

The average concentration of total copper dissolved in surface water is $0.5\,\mu g\ l^{-1}$ for the western North Pacific, $0.7\,\mu g\ l^{-1}$ for the Indian Ocean and $1.3\,\mu g\ l^{-1}$ 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 2×10^3 to 2×10^4. 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 combined states, in polypeptides or polynucleotides accompanied with carbohydrates. It is concluded that most copper in sea water is present organic metal compounds.

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