

The elemental composition of plankton

JOHN H. MARTIN* and GEORGE A. KNAUER†

Hopkins Marine Station of Stanford University, Pacific Grove, California 93950, U.S.A.

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Abstract—Phytoplankton samples, collected in Monterey Bay, California, were analyzed for their Pb, Hg, Cd, Co, Ag, Cr, Ti, V, Mn, Ni, Cu, Fe, Zn, Al, Mo, Ba, Sr, K, Ca, Mg, Na and SiO₂ content. The results of these analyses were categorized on a chemical basis and the sample data were placed in three groups: Group I, Ti not detected; Group II, Ti detected; and Group III, Sr concentrators present. Levels of most elements were higher in Groups II and III for a variety of reasons that are discussed in the text. The siliceous frustules, remaining after organic-matter digestion, were also analyzed for the elements listed above. Significant amounts of Al, Ti, Fe, Mn, Cu and Zn were found.

Zooplankton and microplankton samples, collected in Monterey Bay, California; off the coast of Oregon; and on a transect between Hawaii and Monterey, were also analyzed for the elements listed above (except Si). In general, element levels in the inshore and offshore zooplankton were similar; however, the microplankton samples, in which strontium was highly concentrated, were almost always higher in Pb, Hg, Cu, Fe and Zn.

INTRODUCTION

THE PHYTOPLANKTON and zooplankton are of importance in marine biogeochemical cycles not only because they are able to concentrate large quantities of elements (relative to seawater), but also because they can transport them in a variety of ways. These include: the sinking of skeletal structures and organic detritus (e.g. ARRHENIUS, 1963); the moulting of crustacean exoskeletons (FOWLER and SMALL, 1967); the zooplankton's vertical migrations across mixing barriers (PEARCY and OSTERBERG, 1967); the passage of elements to higher trophic levels (e.g. CHIPMAN *et al.*, 1958) and, the incorporation of elements into fast-sinking fecal pellets (OSTERBERG *et al.*, 1963). However, in spite of these possible transport routes, the elemental composition of the phytoplankton and zooplankton is only poorly known; and thus the magnitude of biological transport is difficult to ascertain. Furthermore, because of the specific lack of multielement plankton analyses, parallelisms in biogeochemical pathways have been difficult to detect because in most cases only one or at best a few elements have been analyzed in the same sample (see GOLDBERG, 1957, p. 352).

The reasons for the scarcity of information concerning the elemental composition of the primary producers and primary consumers of the sea are not difficult to ascertain: (1) Because of the microproportions of these organisms, the collection of sufficient material for elemental analyses is often very difficult. (2) When large concentrations of these organisms occur, they are usually in shallow, nearshore waters and abiososton (clay particles, etc.) introduced via runoff and by the resuspension of bottom sediments (see MARTIN, 1969), often contaminate the plankton samples; thus plankton elemental-content data are invalidated. (3) It is often difficult to separate phytoplankton and zooplankton from each other; thus it is impossible to determine which group contains which element. (4) Small paint and rust chips from research vessels often contaminate samples.

* Present address: Moss Landing Marine Laboratories, Moss Landing, California 95039.

† Present address: Department of Oceanography, The Florida State University, Tallahassee, Florida 32306.

In addition to the sampling problems, the establishment of general elemental levels for phytoplankton and zooplankton is made difficult because of the complexities of the relationships between the elements and the organisms. For example, any given sample may contain species from as many as 12 phyla having different morphologies, ash contents, trophic levels, etc.; and the species composition of each sample will change with place, depth and time of sampling. In turn, each group of species can have very different elemental content (see NICHOLS *et al.*, 1959, Table 2, p. 475), as each may have different means available for concentrating a particular element. The rates of uptake via these pathways will, in turn depend upon the amount of the element available for uptake (e.g. GOLDBERG, 1957), various physical factors such as temperature and salinity (e.g. DUKE *et al.*, 1969), population turnover rates (e.g. MARTIN, 1970), and the physiological state of the organisms (for example, the differences in elemental content in senescent and growing diatoms, e.g. GROSS and ZEUTHEN, 1948; HAYWARD, 1970).

Thus it is apparent that the amassing of accurate, plankton–elemental-content data is a difficult and complex task. We have attempted to avoid or lessen the problems mentioned above in a variety of ways that will be described in the methods and results sections. The purpose of this paper is to report the data we have obtained thus far on the concentrations of Pb, Hg, Cd, Co, Ag, Cr, Ti, V, Ni, Mn, Cu, Fe, Zn, Al, Mo, Ba, Sr, K, Ca, Mg and Na we have measured in plankton collected in Monterey Bay, California, the California Current and the open Pacific Ocean.

METHODS

The majority of the plankton samples were collected at a station located 10 miles offshore, over the center of the Monterey Canyon ($36^{\circ}42'N$, $122^{\circ}02'W$, water depth, 1000 m). The collection sites for the open-ocean plankton are shown in Fig. 1. All samples were collected between the hours of 0900–1200 with the exception of 8 Hawaii-transect-zooplankton samples

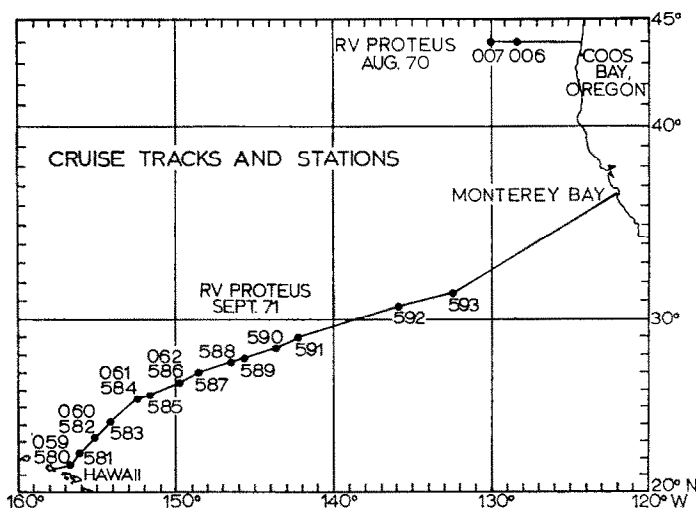


Fig. 1. Cruise tracks and stations. Sample numbers, frequently referred to throughout the text, are shown for each station on the Hawaii–Monterey and Oregon transects. The rest of the samples were collected in Monterey Bay.

that were taken between 2000–2100 hours (all night sample numbers are shown beneath Hawaii transect line in Fig. 1). Phytoplankton and 'microplankton' (phytoplankton plus small zooplankton forms) samples were collected by means of a $\frac{1}{2}$ -m-dia, No. 20 net (aperture 76 μ). The net was not towed, instead it was suspended by nylon line from the stern of the wooden-hulled research vessel and was repeatedly pulled to the surface, allowed to sink, pulled to the surface, etc. With this slow movement, the phytoplankton did not clog the net's apertures and the cells moved down the sides of the net and were concentrated in the cod end. Zooplankton samples were collected by means of stepped oblique $\frac{1}{2}$ m dia, No. 2 (aperture 360 μ) net tows, covering a depth range of 0–100 m. However, in order to prevent clogging when phytoplankton was abundant, the net was towed beneath the surface, phytoplankton-rich layer (0–30 m). Thus during phytoplankton blooms in Monterey Bay, large amounts (up to 500 g wet weight) of completely separated phytoplankton and zooplankton were collected on the same day.

After collection, the phytoplankton and zooplankton were concentrated on a ring of No. 20 netting and excess water was removed by gentle vacuum. Upon return to the laboratory, samples were dried in an oven at 65°C, ground with mortar and pestle and stored in plastic vials for future analyses. Before digestion, most samples were checked for metal particles by passing a Teflon®-coated magnet over the material that was spread out on a plastic sheet. Metal-particle contamination was found only in a few of the open ocean samples (see results). Paint chips, that were occasionally found, were removed immediately after sample collection.

At least two and often three aliquots of each sample were digested and analyzed as follows. Approximately 1-g samples of dried and ground material plus 5 ml of 90 per cent nitric acid were added to 30 ml beakers. The beakers were covered with watch glasses and the samples were refluxed at 90°C for one hour, followed by evaporation to dryness. The temperature was increased stepwise to a maximum of 400°C and the samples were charred to remove interfering lipid material. The charred samples were redissolved in 5 ml of the HNO₃, and 30 per cent H₂O₂ was added dropwise until the samples remained clear. Cleared solutions were evaporated to 5 ml, 1 ml of concentrated HCl was added, and the final volume of 25 ml was made up with distilled, deionized water.

In the case of the phytoplankton samples, additional procedures were required for the treatment of the silica fractions. Following organic matter digestion, the samples were transferred to acid-cleaned polyethylene tubes and centrifuged to separate the silica from the acid-soluble fraction. The resulting supernatant was returned to the 30 ml beaker, evaporated to 5 ml and made up to a final volume of 25 ml with distilled water. (This is referred to simply as the organic fraction throughout the text, although it must have contained frustule-adsorbed elements, as well.) The remaining silica was washed by resuspending it in 50 ml of distilled water, centrifuging and decanting. This was repeated three times. The washed silica was then dried (65°C for 48 hr) and weighed so that the SiO₂ content of each sample could be estimated. Except in a few instances, the silica residue was found to be chalky white with no signs of other impurities. Ten ml of 50 per cent HF acid were added to dissolve the dried silica. The solution was then transferred to acid-cleaned 25 ml polyethylene beakers and the Si (as the tetrafluoride) and excess HF acid were evaporated off by heating the beakers on a 90°C sand bath. When dry, the residue was redissolved in 10 ml of 1 per cent HNO₃.

The solutions obtained from the digestions described above were then analyzed for their elemental content by atomic absorption spectrophotometry. Various combinations of fuels and oxidants, recommended in the Perkin-Elmer manual, were used for each element. Excesses of various competing ions were added to the samples in order to suppress known interferences, when necessary. Background corrections for light scatter were made at appropriate wavelengths by aspirating a metal-free solution of common sea salts (concentrations approximately equal to that of samples) along with each group of samples.

Samples for mercury determinations were digested using the technique of UTHE *et al.* (1970) and analyzed by STANTON'S (1971) method for flameless atomic absorption. The exact procedures, including modifications necessary for plankton-mercury analyses, have been described in KNAUER and MARTIN (1972a).

We have checked the accuracy of our analytical techniques by analyzing samples of orchard leaves, bovine liver and tuna meal provided by the National Bureau of Standards (NBS). Our

results and those of several other laboratories for Ag, Cd, Co, Cr, Cu, Fe, Hg, K, Mn, Na, Pb and Zn have been published in ANONYMOUS (1972). In addition, we compared the levels of Mg, Ca, Sr and Ni we found in orchard leaves with those reported by NBS. Our means and those of other laboratories and NBS almost always overlapped by one standard deviation. The concentrations of Al, Ba, Mo, Ti and V in the NBS standards have not been reported and thus we have no data to compare ours with.

Table 1. Concentrations of elements found in the organic fractions of the phytoplankton (for listed in the footnote at

Date 1971	$\mu\text{g/g dry}$								
	$\times 10^3$								
	Na	K	Mg	Ca	Sr	Ba	Al	Fe	Mn
Group I (no Ti)									
8 Feb	50.0	6.7	—	—	203	142	—	125	13.0
16 Feb	140.0	13.0	—	9.0	225	35	—	380	8.5
22 Feb	140.0	11.0	16.0	7.0	149	32	151	281	5.8
19 Mar	103.6	13.3	—	3.9	90	154	630	750	12.0
25 May	—	—	—	—	146	38	47	212	9.0
22 Jun	136.8	13.8	16.4	5.5	115	128	145	236	7.5
28 Jun	119.2	12.0	13.5	4.7	102	18	106	238	9.1
23 Jul	161.7	14.4	—	6.7	138	46	50	99	5.3
6 Aug	158.7	17.6	—	6.5	124	11	27	49	4.9
13 Aug	138.3	14.8	17.8	5.3	133	5	101	170	7.9
19 Aug	187.6	13.3	17.2	6.5	154	11	7	51	2.1
8 Sep	110.8	15.1	—	5.4	260	19	153	248	5.8
15 Sep	133.1	11.1	—	6.8	205	29	240	316	6.4
21 Sep	164.9	12.8	—	8.2	184	70	115	194	5.1
Group II (with Ti)									
27 Jan	106.0	—	—	10.0	—	—	—	1915	22.0
10 Mar	113.5	11.9	13.0	4.2	104	112	2840	2970	32.3
18 May	48.5	13.4	7.4	3.3	53	13	2850	3120	31.3
24 May	127.2	10.4	17.2	6.1	121	16	940	1510	13.3
8 Jun	99.1	12.9	16.1	5.3	127	225	214	446	8.7
15 Jun	115.9	16.3	12.6	5.2	104	27	299	1930	18.9
6 Jul	100.2	14.0	16.9	5.1	120	21	230	500	7.4
12 Jul	153.0	13.3	—	5.3	118	18	530	840	9.9
30 Jul	101.4	14.6	15.5	5.7	133	11	358	520	11.5
Group III (Sr concentrated)									
26 Aug	66.3	1.9	8.8	3.1	3934	490	15	116	3.2
28 Sep	78.5	4.5	11.0	12.6	1970	225	177	790	8.2
15 Oct	98.6	67.3	9.6	6.5	697	30	38	2780	30.0
25 Oct	123.6	14.6	13.6	6.0	354	500	125	231	5.1
8 Nov	—	11.0	17.5	8.7	383	287	11	226	7.7
Medians									
Group:									
I (n = 14)	138.3	13.3	16.4	6.5	147	33	110	224	6.1
II (n = 9)	106.0	13.3	15.5	5.3	119	19	444	1510	13.3
III (n = 5)	88.5	11.0	11.0	6.5	697	287	38	231	7.7
Coefficient of variation (%)									
	15	15	13	12	8	16	25	16	15

* ND = not detected; Ti = <5.7; Cr = <1.0; Ni = <0.5; Ag = <0.1; Pb = <1.0 $\mu\text{g/g dry}$
Mo, Co, and V were not detected in any of these samples (Mo = <2.0; Co = <1.0; V = <3.1 $\mu\text{g/g}$)

RESULTS

Phytoplankton

Results of the individual analyses for the 'organic fractions' of the phytoplankton are presented in Table 1. Although no pronounced temporal trends were found, the data are arranged by date for ease of comparison with the zooplankton values criteria used to establish Groups I-III, see text). Other elements sought, but not detected, are the bottom of the table

weight

Ti	Cr	Cu	Ni	Zn	Ag	Cd	Pb	Hg	% SiO ₂	Date 1971
Group I (no Ti)										
—	—	14.0	—	47	0.4	1.3	13.0	0.27	27	8 Feb
ND*	—	19.0	—	47	0.5	0.6	9.5	0.16	10	16 Feb
ND	—	9.0	1.8	23	—	0.8	ND	0.14	14	22 Feb
ND	1.3	8.7	2.7	54	ND	0.4	ND	0.13	16	19 Mar
—	—	5.0	5.8	28	0.4	1.5	ND	0.17	—	25 May
ND	ND	1.8	0.9	7	0.2	0.6	ND	0.17	13	22 Jun
ND	ND	2.8	2.1	23	0.1	1.1	ND	0.26	18	28 Jun
ND	ND	3.3	1.8	12	0.2	1.5	ND	0.24	5	23 Jul
ND	ND	1.3	ND	3	0.2	2.3	ND	0.27	9	6 Aug
ND	ND	2.3	3.3	8	0.5	2.1	4.7	0.10	12	13 Aug
ND	ND	2.0	1.5	13	0.2	2.3	2.0	0.11	5	19 Aug
ND	ND	4.5	0.6	38	0.1	4.8	3.4	0.23	8	8 Sep
ND	ND	3.1	2.4	13	0.2	2.1	2.3	0.23	7	15 Sep
ND	ND	4.7	2.9	15	0.1	2.8	4.5	0.21	8	21 Sep
Group II (with Ti)										
—	—	30.0	—	127	0.9	3.5	—	0.16	—	27 Jan
117	7.2	41.6	7.6	135	0.2	1.1	7.7	0.31	18	10 Mar
137	21.4	42.0	12.8	122	0.3	3.5	5.4	0.15	17	18 May
44	3.3	5.5	8.6	290	0.6	1.6	11.4	0.24	15	24 May
6	1.0	3.3	8.0	35	0.6	1.5	6.7	0.16	15	8 Jun
16	9.6	22.3	12.5	445	0.6	2.3	46.6	0.48	12	15 Jun
12	3.7	1.7	6.6	17	0.6	1.3	6.5	0.15	9	6 Jul
35	1.5	7.4	2.3	47	0.2	1.5	2.2	0.23	11	12 Jul
19	4.1	1.8	6.1	16	0.6	1.9	8.1	0.12	—	30 Jul
Group III (Sr concentrated)										
ND	—	6.9	1.3	24	ND	2.2	26.4	0.59	5	26 Aug
ND	1.6	18.4	2.3	167	ND	6.3	12.2	0.18	5	28 Sep
ND	—	45.4	8.5	703	—	3.9	9.2	0.14	16	15 Oct
ND	ND	1.8	1.4	11	0.1	6.5	ND	0.16	17	25 Oct
ND	—	14.8	3.5	20	—	3.2	3.9	0.13	11	8 Nov
Medians										
Group:										
ND	ND	3.2	1.9	19	0.2	1.5	ND	0.19	10	I (n = 14)
27	3.9	7.4	7.8	122	0.6	1.6	7.2	0.16	15	II (n = 9)
ND	—	14.8	2.3	24	ND	3.9	9.2	0.16	11	III (n = 5)
Coefficient of variation (%)										
—	15	16	20	11	25	25	30	26	—	

weight.
dry weight).

presented below. Because of the present interest in mercury, this element has been dealt with in a separate paper (KNAUER and MARTIN, 1972a). Fluctuations in Mn, Cu, Pb, Cd and Zn levels in the phytoplankton, in relation to the amounts of these elements in seawater, have also been presented in KNAUER and MARTIN (1972b). Data for these elements are also included here (Table 1) so that they may be related to the other elements not previously discussed. Coefficients of variation for the phytoplankton samples (Table 1) were established for the worst possible case by taking five replicate phytoplankton tows and applying the resulting analytical precision to all samples.

Although aliquots of these samples have been identified, we believe it is more meaningful to classify the data on a chemical rather than a biological basis, since RILEY and ROTH (1971) reported that phytoplankton trace metal distributions were not correlated with taxonomy; and because chemical classifications have proved useful for other materials such as sediments (RILEY and CHESTER, 1971, p. 297). Thus, we have separated the organic-fraction data in Table 1 into three categories: Group I, samples with no detectable Ti; Group II, samples with Ti; and Group III, samples with Sr concentration factors greater than 2. Titanium was not determined in three samples; however, titanium and iron levels were strongly correlated and on the basis of iron content, the 27 Jan. sample was placed in the titanium-present group and the 8 Feb. and 25 May samples in the no-titanium group.

Medians were determined for each group and are presented at the bottom of Table 1. The use of medians rather than means was chosen because data for several elements were not normally distributed. The Group II samples with detectable titanium had the highest median values for Ag, Al, Cr, Cu, Fe, Mn, Ni, Ti, Zn and SiO₂, while the strontium concentrating group (III) was highest in Ba, Cd, Pb and of course, strontium. The mercury median was also slightly higher in this group. Median values for Group I (no-detectable titanium) were considerably lower than one or both other groups with the exception of the major elements Ca, Na, Mg and K.

We have compared our results with those reported by VINOGRADOVA and KOVALSKIY (1962) and RILEY and ROTH (1971). In general, element levels in our Group I samples were quite low in comparison to those of the other investigators, while concentrations in the Group II samples were more similar. RILEY and ROTH (1971) noted that element levels in phytoplankton were correlated with increased amounts in the culture media; thus the lower values we observed for the Group I samples could be expected since natural seawater contains smaller quantities of elements than those present in their culture media. The higher levels found by VINOGRADOVA and KOVALSKIY (1962) in Black Sea plankton, by RILEY and ROTH in Irish Sea plankton and by us in the Group II samples may be the result of clay contamination (see Discussion).

The silica fractions remaining after acid digestion were also analyzed for all elements except mercury. However, levels were usually beneath our detection limits, with the exception of those for Ti, Mn, Fe, Cu, Zn and Al. Sodium, Mg, Ca, K and Sr were also found but, in general, concentrations were insignificant in comparison to those found in the organic fractions (less than 3 per cent). The data for the silica-fraction analyses for the six elements mentioned above were arranged into groups according to the criteria established for Table 1 and are presented in Table 2. Medians

Table 2. Concentrations of Al, Ti, Fe, Mn, Cu and Zn found in the siliceous frustules, together with the percentages of these elements occurring in association with the silica fractions

Date 1971	$\mu\text{g/g}$ dry silica						% found in silica fraction					
	Al	Fe	Ti	Mn	Cu	Zn	Al	Fe	Ti	Mn	Cu	Zn
Group I (no Ti)												
22 Feb	220	250	115	ND*	17.0	10	16	9.7	100	2.2	23	6.7
19 Mar	1210	600	150	3.5	17.0	11	24	11.3	100	4.4	24	3.0
22 Jun	1140	300	120	3.0	1.3	3	47	12.7	100	4.5	8	6.0
28 Jun	175	220	190	2.0	5.0	7	16	9.5	100	3.2	20	10.0
23 Jul	209	ND	88	ND	17.0	5	20	—	100	—	23	2.4
6 Aug	280	ND	ND	ND	5.6	3	49	—	—	—	28	7.0
13 Aug	985	185	119	ND	3.4	2	54	11.8	100	—	15	2.8
19 Aug	20	ND	63	ND	ND	1	13	—	100	—	—	0.5
8 Sep	775	250	244	ND	18.0	10	27	6.8	100	—	22	2.0
15 Sep	1460	430	ND	ND	4.6	5	28	7.9	—	—	9	2.0
21 Sep	620	200	ND	ND	7.0	4	29	7.4	—	—	10	2.0
Group II (with Ti)												
10 Mar	—	1250	850	10.5	59.0	33	—	7.6	60	5.8	21	6.6
18 May	16000	2815	1254	11.5	12.0	11	50	13.6	62	6.0	5	1.5
24 May	8925	1550	471	6.0	3.5	120	59	13.6	62	6.7	9	6.0
8 Jun	1890	305	200	7.0	6.0	7	57	9.0	82	10.7	21	2.6
15 Jun	1900	360	508	ND	80.0	43	43	2.2	80	—	30	1.2
6 Jul	3215	420	150	ND	3.5	5	55	6.8	50	—	15	2.3
12 Jul	1160	640	326	2.6	14.0	9	19	7.8	50	2.8	17	2.0
30 Jul	—	480	255	ND	5.6	4	—	7.4	55	—	21	2.3
Group III (Sr concentrated)												
26 Aug	—	—	ND	11.7	ND	ND	—	—	—	—	—	—
28 Sep	—	—	ND	22.0	11.5	108	—	—	—	11.7	3	3.0
15 Oct	80	500	221	—	—	—	26	2.9	100	—	—	—
25 Oct	110	ND	115	1.2	2.0	4	11	—	100	6.0	16	6.0
8 Nov	105	180	ND	—	—	—	52	8.2	—	1.0	—	—
Medians												
Group I	620	220	115	ND	5.6	5	27	9.6	100	3.8	21	2.8
Group II	2550	560	400	4.3	9	10	52	7.7	61	6.0	19	2.3

* ND = not detected.

were determined for Groups I and II but, because of the lack of data none were calculated for Group III. As expected, medians for the group (II) with titanium present in the organic fraction were substantially higher than those in Group I. Of the six elements, titanium and aluminum values were especially high in both groups, and it is interesting to note that Ti was almost always detected in all samples regardless of group.

The amounts of these elements in both the organic and silica fractions were totalled and the percentages of each element occurring in the silica fractions were calculated (Table 2). The high levels of Ti and Al in the silica fractions were also reflected in the percentages: 27 per cent of the Al and 100 per cent of the Ti in the Group I samples were found in the silica fractions, while in Group II, 52 and 61 per cent, respectively, were found. In comparison, relatively low percentages of Mn, Fe and Zn occurred

with the silica fractions; however, Cu values were surprisingly high (medians, Group I = 21; Group II = 19 per cent).

Zooplankton

The results of the individual, Monterey-Bay-zooplankton analyses are presented in Table 3. Although no regular temporal trends were evident, the data were arranged by date for ease of comparison with the phytoplankton data presented in

Table 3. Concentrations of elements found in zooplankton collected in Monterey Bay, California. Detection limits for other elements sought but not found are listed in the footnote at the bottom of the table

Date 1971	$\mu\text{g/g}$ dry weight													Ag	Cd	Pb	Hg
	$\times 10^3$					Sr	Ba	Al	Fe	Mn	Cu	Ni	Zn				
Na	K	Mg	Ca														
Euphausiids																	
18 May	95.3	12.3	9.1	7.9	154	4	36	144	2.2	9.8	5.0	80	ND*	2.8	3.5	0.15	
25 May	41.3	11.9	6.1	6.3	130	28	62	92	3.2	7.5	6.0	64	ND	0.8	1.0	0.08	
1 Jun	36.6	12.3	4.9	10.2	163	8	20	63	3.6	21.3	0.5	69	ND	1.7	1.2	0.08	
8 Jun	45.2	13.3	6.0	8.6	166	38	31	94	3.2	16.0	2.7	83	0.2	2.0	2.4	0.07	
22 Jun	61.7	15.7	6.7	8.3	156	24	66	121	3.5	15.6	0.6	64	ND	3.5	ND	0.05	
6 Jul	60.0	14.0	8.9	9.1	172	104	31	84	4.5	14.8	6.6	66	0.5	3.7	10.9	0.11	
23 Jul	—	8.1	8.0	9.1	152	10	16	54	3.8	19.9	ND	53	ND	2.8	ND	—	
13 Aug	52.3	10.4	8.3	12.5	204	60	ND	84	4.3	18.0	5.8	75	0.5	4.0	6.7	0.10	
19 Aug	91.5	11.5	8.8	9.0	182	20	85	236	3.9	13.1	3.8	82	ND	5.5	2.1	0.08	
Copepods																	
18 May	85.6	14.7	9.7	7.7	100	21	115	282	3.3	22.6	6.3	170	ND	2.8	5.2	0.11	
25 May	58.0	11.8	6.0	4.7	100	8	115	230	4.1	10.2	5.4	127	ND	3.9	1.4	0.11	
1 Jun	40.6	10.3	5.0	8.4	118	16	42	114	4.3	9.6	1.0	86	ND	1.6	ND	0.10	
8 Jun	77.2	12.5	8.0	5.7	114	6	63	161	2.8	9.0	5.3	115	0.1	6.0	2.9	—	
15 Jun	61.3	10.8	6.5	5.3	83	19	90	257	4.5	10.7	11.9	158	0.2	4.6	9.0	0.16	
22 Jun	83.8	11.4	9.5	7.8	158	21	83	247	6.6	10.1	2.0	112	ND	4.3	7.0	0.06	
6 Jul	94.2	12.2	9.2	5.2	132	27	55	182	10.4	10.0	1.4	144	ND	5.7	3.7	0.15	
12 Jul	50.4	12.3	6.3	10.0	156	5	36	141	5.6	16.5	1.7	89	ND	3.4	1.8	0.09	
23 Jul	71.4	7.1	10.9	10.1	170	12	20	55	3.6	11.7	ND	62	ND	2.9	ND	—	
13 Aug	81.0	13.8	9.4	12.9	290	26	78	213	4.5	16.5	2.1	96	ND	7.5	5.2	0.12	
Radiolarians																	
15 Jun	87.8	13.1	8.6	7.2	151	—	313	1070	12.4	12.4	ND	168	ND	3.0	ND	—	
28 Jun	81.1	12.0	7.9	6.6	139	55	242	436	7.3	6.5	3.2	141	ND	3.4	1.6	0.18	
30 Jul	127.4	11.3	17.0	10.6	153	127	91	269	5.2	6.5	5.5	63	0.4	8.2	5.4	0.08	
6 Aug	118.9	8.9	12.1	9.2	192	30	113	307	4.6	4.9	1.8	80	0.1	9.6	2.3	0.10	
26 Aug	183.0	10.8	20.1	12.5	810	257	106	324	7.9	4.4	4.2	74	0.1	6.8	12.2	0.29	
15 Oct	79.0	8.4	10.3	7.9	173	77	162	270	5.6	11.4	7.1	279	ND	6.0	2.0	0.14	
Mixed																	
28 Jun	113.3	14.2	11.1	6.0	132	16	94	199	10.6	6.3	3.5	104	ND	6.0	5.0	0.12	
28 Sep	87.8	10.5	10.8	9.0	206	39	154	490	5.1	4.5	4.4	73	0.4	6.4	8.8	0.12	

* ND = not detected; Al = <8.0 ; Ni = <0.5 ; Ag = <0.1 ; Pb = $<1.0 \mu\text{g/g}$ dry weight.

Mo, Ti, Co and Cr were not detected in any of the samples (Mo = <2.0 ; Ti = <5.7 ; Co = <1.0 ; Cr = $<1.0 \mu\text{g/g}$ dry weight). V was not detected ($<3.1 \mu\text{g/g}$ dry weight) except in samples collected: 28 June = 16.4; 6 July = 10.1; 30 July = 14.9; 26 Aug = 41.5 $\mu\text{g/g}$ dry weight.

Table 1. The samples were also classified according to the dominant forms present: Large euphausiids (mostly *Euphausia pacifica*); copepods and immature euphausiids; and radiolarians. Median values were determined for each of these groups and will be compared with the levels for open-ocean zooplankton below.

The individual values for the open-ocean zooplankton (predominantly copepods) are presented in Table 4. In general, levels for each element within these samples were quite constant, with the exception of five samples that contained elevated levels of Ni and Cr. Because of this combination of elements we suspected that particles of stainless steel might be contaminating some of our collections. Since such particles should be magnetically attracted, an acid-cleaned, Teflon[®]-coated, magnetic, stirring bar was passed over 0.89 g of dried and ground zooplankton that was spread out in a thin layer on a plastic sheet; 9.4 mg of metal were attracted to the magnet. The following concentrations were found in this material: 276,000 $\mu\text{g Fe}$; 44,000 $\mu\text{g Zn}$; 1700 $\mu\text{g Ni}$; 1150 $\mu\text{g Pb}$; 250 $\mu\text{g Cr}$; 600 $\mu\text{g Mn}$; and 180 $\mu\text{g Cu/g}$ of metal. As it was readily apparent that the slightest amount of this material would invalidate any plankton elemental content data, we began looking for these particles in other samples. Varying amounts were found in a few other open-ocean samples, but usually less than 1 mg. These contaminants were never found in our Monterey Bay samples, in spite of the use of the same ship and sampling gear.

In order to find the source of these particles we analyzed several metal items commonly found aboard ships, such as shackles, nico-press fittings, thimbles, paint, and of course, hydrowire. Our research vessel, *Proteus* is equipped with regular steel hydrowire, with the exception of the last 100 meters which is stainless steel. When both types of wire were flexed, particles fell out that were easily picked up with a magnet. The elemental composition of this material is quite similar to that of particles we removed from our zooplankton samples (Table 5). Thus, we conclude that we are contaminating some of our samples with rust particles from hydrowire. However, these particles can easily be removed with a magnet and thus accurate data for zooplankton can be obtained in most cases providing this precaution is taken. We also analyzed *Proteus* hull paint and open-ocean oil particles (Table 5); these appear to be relatively minor sources of contamination.

Nine samples were reanalyzed after the magnetic removal of metal particles; Cu, Mn and Ni levels were essentially the same and Cr was not detected. For the other elements median values for these nine samples in comparison to those of the original 14 were: Fe = 100 vs 210; Zn = 180 vs 240; and Pb = 2.1 vs 6.1 $\mu\text{g/g}$ dry weight. The Fe, Zn and Pb medians for the nine decontaminated samples and the nine Ni values in samples apparently free of contamination will be used for comparison with the other sample types observed in this study.

Individual values for four samples collected with a phytoplankton net are also included in Table 4, since they contained small zooplankton forms (radiolarians, copepod nauplii, etc.) as well as phytoplankton and detritus. The four 'microplankton' samples were collected with a net suspended by nylon line and thus were not subject to hydrowire contamination. Median values determined for the Monterey Bay groups and the Hawaii transect zooplankton and microplankton are compared in Table 6. The results of the individual analyses for two samples collected (using nylon line) approximately 400 km (No. 006) and 600 km (No. 007) off the coast of Oregon

Table 4. Concentration of elements in zooplankton and microplankton collected on a Hawaii-listed in the footnote at

Sample no.	$\mu\text{g/g dry}$								
	$\times 10^3$				Sr	Ba	Al	Fe	Mn
	Na	K	Mg	Ca					
Zooplankton									
580	89.0	10.7	9.0	20.3	1600	97	15	90	4.5
581	72.6	10.4	7.9	22.0	2000	40	19	870	7.0
582*	95.6	9.7	10.4	27.7	3000	38	31	1490	7.1
583*	68.1	9.2	8.1	31.0	1150	17	9	1720	6.4
584	79.7	11.0	7.9	14.5	810	24	9	145	3.3
585	84.7	11.7	9.5	27.8	740	14	9	220	4.0
586	74.5	9.5	7.2	14.6	550	27	14	580	4.3
587	81.9	9.6	10.2	31.6	620	10	15	620	4.7
588*	74.7	10.3	8.8	19.1	750	63	17	130	3.6
589*	80.7	9.9	10.0	26.0	610	15	27	190	3.6
590*	79.9	9.6	8.7	20.2	690	43	13	205	3.3
591	53.6	9.9	7.8	19.7	580	19	17	120	2.9
592	120.3	10.8	13.8	17.7	450	18	14	115	2.9
593	80.1	10.3	9.8	21.1	380	30	24	380	5.8
Microplankton									
059	103.6	5.7	11.9	10.4	9300	51	102	1030	6.9
060	123.0	10.6	13.7	15.7	9650	52	102	2510	23.6
061	107.9	8.3	12.9	11.5	8500	70	72	1460	32.7
062	124.9	7.4	14.9	12.7	6800	66	108	4000	3.4

* These samples appear to be contaminated because of the high Ni and Cr levels that were found
 † ND = not detected; Cr = $<1.0 \mu\text{g/g dry weight}$.

V, Mo and Co were not detected in any of these samples (V = <3.1 ; Mo = <2.0 ; Co = $<1.0 \mu\text{g/g}$
 microplankton: 059 = 13.0; 060 = 5.4; 061 = 18.0; 062 = 21.0 $\mu\text{g/g dry weight}$).

Table 5. Concentrations of elements found in plankton-sample contaminants

Material description	ppm						
	Fe	Zn	Ni	Pb	Cr	Mn	Cu
Metal particles in zooplankton samples	196,000	55,000	900	1500	150	340	180
Rust from stainless hydrowire	142,000	29,000	590	660	460	1370	350
Rust from nonstainless hydrowire	147,000	20,500	190	ND*	ND	3670	470
Hull paint†	29	209	2.5	485	1.0	5.4	45
Open-ocean tar balls	8540	185	ND	ND	ND	75	43

* ND = not detected.

† The presence of paint chips is easily detectable because of high Ti (1700 ppm) and Co (140 ppm) levels.

Monterey transect (see Fig. 1). Detection limits for other elements sought but not found are the bottom of the table

weight								
Cu	Ni	Cr	Zn	Ag	Cd	Pb	Hg	Sample no.
Zooplankton								
6.6	5	ND†	50	0.1	2.3	1.5	0.15	580
58.4	10	ND	260	0.1	1.9	6.2	0.13	581
19.9	608	137.0	660	0.2	2.5	14.2	0.10	582*
13.0	179	31.0	750	0.4	3.1	11.5	0.16	583*
6.2	5	ND	140	0.1	2.8	2.2	0.08	584
8.6	9	ND	260	0.4	2.3	4.3	0.05	585
6.7	8	ND	385	0.1	2.2	7.9	0.04	586
11.1	10	ND	250	0.3	2.7	9.2	0.45	587
9.4	136	17.0	120	0.3	2.6	3.4	0.13	588*
12.0	87	8.0	255	0.3	1.9	6.5	0.17	589*
10.4	283	55.0	110	0.3	2.3	6.0	0.17	590*
17.4	6	ND	165	0.2	2.0	3.4	0.10	591
14.8	8	ND	60	0.3	2.0	10.1	0.08	592
21.6	13	ND	225	0.3	3.5	14.4	0.08	593
Microplankton								
70	11.8	ND	285	ND	1.0	24.6	0.53	059
40	11.8	3.7	725	0.4	1.3	37.5	0.11	060
46	10.8	ND	840	0.2	2.2	16.9	0.24	061
104	11.5	0.6	4190	0.2	2.0	38.8	0.44	062

(see text).

dry weight). Ti was not detected in the zooplankton ($<5.7 \mu\text{g/g}$ dry weight), but was not found in the

(Fig. 1) in August of 1970 are also included as they were of special interest; they consisted of practically pure phytoplankton detritus and protozoans (radiolarians?) which we believe were feeding on this material. The Sr levels we report for 006 and 007 may be low since we were unable to dissolve a white precipitate with HNO_3 , HCl or HF ; we believe it was SrSO_4 .

Medians for the three groups of Monterey Bay zooplankton were quite similar to the open-ocean zooplankton with the exception that Sr and Ca values were higher in the latter. Zinc and Ni levels were somewhat higher and Al lower in the offshore zooplankton. In contrast, the Hawaii-transect and Oregon microplankton usually contained far greater quantities of Sr, Fe, Zn, Cu, Pb and to a lesser degree Hg. Barium was also markedly higher in the Oregon samples.

DISCUSSION

The reasons for the various elemental levels in the three groups of phytoplankton (Table 1) appear obvious in the cases of Group I (no titanium) and III (strontium concentrators present). The former consisted of practically pure phytoplankton which were actively growing and because of rapid turnover rates, trace element levels were relatively low (see Pb, Cd, Ag, Ni, Cu and Zn values, Table 1). The presence of strontium-concentrating organisms (radiolarians and dinoflagellates) in

Table 6. Median values determined for the groups of plankton presented in Tables 3 and 4 plus 2 individual microplankton samples collected off the coast of Oregon

Element	$\mu\text{g/g}$ dry weight						
	Monterey Bay			Hawaii		Oregon	
	Euphausiids $n = 9$	Copepods $n = 10$	Radio- larians $n = 6$	Zoo- plankton $n = *$	Micro- plankton $n = 4$	Microplankton No. 007 $n = 1$	Microplankton No. 006 $n = 1$
Pb	2.1	3.3	2.1	2.1†	31.0	27.7	4.3
Hg	0.08	0.11	0.14	0.11	0.34	0.71	0.48
Cd	2.8	4.1	6.4	2.3	1.6	1.1	0.4
Ag	<0.1	<0.1	<0.1	0.26	0.17	0.24	0.12
Ni	3.8	2.0	3.7	8.4‡	11.6	5.7	2.0
Mn	3.6	4.4	6.4	4.3	15.0	7.4	5.2
Cu	15.6	10.5	6.5	11.5	57.5	45.8	24.1
Fe	92	197	315	100†	1985	745	290
Zn	69	113	110	180†	780	970	163
Al	31	70	137	15	102	25	17
Ba	24	17	17	26	59	314	323
Sr	163	125	163	720	8900	1800	3600
K	12,300	12,000	11,000	10,000	7900	12,900	6900
Ca	9000	7770	8500	20,500	12,000	7000	6500
Mg	8000	8600	11,200	8900	13,300	18,000	17,300
Na	56,100	74,300	103,300	80,000	115,000	133,100	111,300
Average wet:dry ratio	8.45	10.78	13.05	9.98	16.90	20.31	22.77

* $n = 9$ for Pb, Fe, Ni and Zn; $n = 14$ for remaining elements.

† Medians determined after metal particles were removed (see text).

‡ Median determined with Nos. 582, 583, 588-590 omitted.

the Group III samples can be used to explain the elevated levels of Pb, Cd, Cu, Ba and of course, Sr. Simple explanations for the Group II organisms (titanium present in organic fraction) are impossible, however, since several factors, or combinations thereof, may exist. At first glance, the elevated levels of Fe, Mn, Al, and Ti suggest that these samples were contaminated with abiosteston such as clay particles. This may well be the case. However, there was no readily apparent source of such material since there was no runoff; and, because of the water depth (1000 m) at the sampling station, resuspension of sediments by bottom currents can also be disregarded. Other evidence that the samples may not be clay-contaminated is suggested by the work of RILEY and ROTH (1971) who found high concentrations of Fe, Mn, Al and Ti in phytoplankton raised in laboratory cultures. Obviously these organisms were not contaminated with clays and there is no reason why natural phytoplankton should not also highly concentrate these elements. Therefore, we believe that there is a good possibility that these samples represent phytoplankton populations in which active growth has stopped, and because of slow turnover rates of the population, sufficient time has elapsed for greater uptake of several elements.

Two uptake mechanisms acting singly or in concert could be adsorption and/or the formation of hydroxy complexes on the surfaces of senescent phytoplankton and detritus. For example, adsorption could account for the elevated zinc levels, as this element is known to be readily adsorbed to at least some types of dead organic material (i.e. euphausiid exoskeletons, FOWLER *et al.*, 1969). The formation of hydroxy complexes on phytoplankton and detritus also is feasible since several of the elements that were elevated in Group II are believed to be present in such complexes in seawater (i.e. Al, Fe, Mn, Ti, Cr and Cu; see RILEY and CHESTER, 1971, pp. 64-65). Other elements (e.g. Ni, Zn, Ag) could be concentrated by occlusion with such hydroxy complexes via the 'chemical scavenger' mechanism described by GOLDBERG (1954). On the other hand, the silica fraction data (Table 2) suggests that these elements (except Cr) are well incorporated in the frustules. However, this does not necessarily suggest that the elements were concentrated by means other than surface adsorption. Indeed, LEWIN (1961) has demonstrated that acid-cleaned diatom walls readily adsorb aluminum and the presence of this element prevents the silica in the frustules from dissolving. In living diatoms, adsorbed elements could be incorporated into the silica lattices as the frustules thicken with increased age.

The reasons for the various zooplankton elemental levels we found are very complex as they probably involve differences in geographical location and biological turnover rates as well as species composition. However, the latter appears to be the most important factor for Ba, Sr and Ca; e.g. the high Ca levels found in the Hawaii transect zooplankton are probably due to the calcareous pteropods in these samples. The various Sr and Ba levels in Monterey Bay, Hawaii and Oregon radiolarians are also due to species differences. Those from Monterey Bay are siliceous and little Sr and intermediate levels of Ba were concentrated; the Hawaii radiolarians contained large quantities of Sr but little Ba, and the Oregon radiolarians concentrated large quantities of both Sr and Ba. Species composition also appears to be primarily responsible for the high levels of Pb, Hg, Cu, Fe and Zn as these appeared only in association with the Sr-concentrating radiolarians.

The data for the Monterey Bay euphausiids and copepods and the Hawaii transect zooplankton can be used for the estimation of element transport rates within the water column via the means of food-chain amplification and zooplankton vertical migrations. However, the amounts of elements actually removed to the sediments in conjunction with the organic remains of these organisms cannot be estimated until element levels in organic detritus and the amounts of this material reaching the sediments are better known.

In contrast to the lack of knowledge concerning the amounts of organic detritus reaching deep-ocean sediments, there is abundant evidence that inorganic skeletal structures reach the deep-sea floor. Thus the Hawaii and Oregon microplankton samples are of special interest as they contained large numbers of radiolarians whose skeletal remains are often found in deep-sea sediments (e.g. REVELLE *et al.*, 1955, see p. 223). In this light, the elevated levels of Sr, Pb, Hg and Cu found in these samples are of interest since the biological removal of these elements from the water column to the sediments has been suggested; i.e. CHESTER and MESSIHA-HANNA (1970) note that more than 80 per cent of the Sr in deep-sea sediments is held in calcareous shell material; TATSUMOTO and PATTERSON (1963) estimate that biological organisms

annually remove 2×10^{11} g of Pb from the surface waters of the world's oceans; KLEIN and GOLDBERG (1970) suggest that biological transport is responsible for the increased Hg concentrations on the East Pacific Rise; REVELLE *et al.* (1955), TUREKIAN and IMBRIE (1966) and BURNETT (1971) have noted the relationship between Cu and sediments of biological origin. Thus much of the material in the microplankton samples may have been ready for transport to the sea floor. We plan to collect and analyze additional microplankton samples in order to better estimate their importance in the biogeochemical cycling of elements in the world's oceans.

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