

## On the Balance and Seasonal Variation of Dissolved and Particulate Phosphorus in an Eutrophicated Coastal Environment

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(Figs. 1-13; Tables 1-5)

Human activities are the cause of significant changes of marine environments especially in estuaries and coastal regions, where excessive nutrients are introduced through domestic sewage, industrial wastes and river runoff. Although eutrophication increases in these waters through artificial as well as natural addition of nutrients, today its effects on the ecosystem and biological productivity of the area have become top important due to the highly accelerated rate of artificial input. The Seto Inland Sea in Japan is one of the typical areas of eutrophication for reason of its enclosed topography, industrial development and growing population.

Phosphorus is one of the most important nutrient elements. It occurs in the water in relatively low concentrations and often limits the plant growth even in eutrophicated marine environments. Therefore, elucidation of the cycle, the budget and also the accumulation or deposition mechanism of phosphorus in these environments is without doubt an urgent problem.

Although the annual cycle of phosphorus in coastal seas has been studied by ARMSTRONG and HARVEY<sup>1)</sup>, STRICKLAND and AUSTIN<sup>2)</sup>, and others, not so many researches have been made in eutrophicated areas where dense phytoplankton bloom is of frequent occurrence. In the Seto Inland Sea, while a number of observations have been carried out as to reactive phosphate and total phosphorus contents of unprocessed seawater for obtaining indicators of the water quality, so far three forms of phosphorus in seawater have been determined and discussed by UYENO and HAYASHI<sup>3)</sup>.

We have made field observations in the coastal waters off Fukuyama city in the central part of the Seto Inland Sea to find the basic pattern of seasonal variations in the three forms of phosphorus in seawater, namely, dissolved inorganic phosphorus (DIP), dissolved organic phosphorus (DOP) and particulate phosphorus (PP), and also to find the major factors affecting their balance. We have regarded the study as a

first step to the clarification of the phosphorus cycle which is closely related to the water quality control and to the biological productivity in coastal environments. Such factors as chlorophyll *a* content, particulate organic carbon (POC), particulate organic nitrogen (PON) and seston weights were also determined at the same time in order to understand the actual meaning of particulate phosphorus. The results may shed light on some of the unanswered questions concerning the phosphorus cycle in the eutrophicated coastal environment.

This paper deals with the results of the observations at two stations, with special reference to the annual cycle of phosphorus concentrations in the water column, to the balance between three forms of phosphorus and to some of the factors that control the seasonal changes of phosphorus concentrations.

The result of such measurements on the particulate matter as POC, PON and seston weights will be reported in a separate paper.

## MATERIAL AND METHODS

### Field Observation and Collection of Samples

The seawater samples were collected during a period from April, 1972 to February, 1974 at roughly monthly intervals at St. 2 (34° 24.1'N, 133° 24.1'E) and St. BG-1 (34° 18.5'N, 133° 26.3'E) situated in the northern part of the Bingo-nada region of the Seto Inland Sea, Japan (Fig. 1). The former station is situated in a shallow water (6.9 m deep) about 2 km off shore and at approximately 3.5 km from the mouth of the Ashida River, while the latter station (24.3 m deep) is situated about 10 km off the land. Seawater samples were obtained from two depths (surface and 5 m) at St. 2 and three depths (surface, 10 m and 20 m) at St. BG-1 with a 10-liter van Dorn water bottle and a sterile 250-ml J-Z sampler. They were brought to the laboratory on land. Water temperature, chlorinity, dissolved oxygen and sestonic chlorophyll *a* were determined for each sampling depth. Transparency of the upper layer of the sea was recorded by use of the standard Secchi disk.

### Phosphorus Analyses

Within a few hours of collection, each water sample was filtered through the membrane filter (Millipore HA-47, 0.45  $\mu$ m pore dia.), and the filtrate was analysed for the contents of the dissolved total phosphorus and the dissolved inorganic phosphorus (DIP) by the method of MURPHY and RILEY<sup>4)</sup>. The difference was calculated and defined as dissolved organic phosphorus (DOP). The particulate material collected on the membrane filter was digested by the method of FISKE and SUBBAROW<sup>5)</sup>; the resulting phosphate was analysed as above in order to obtain the particulate phosphorus content (PP) of the sample water. These phosphorus analyses were made mostly by single determination except in the preliminary examination of precision and accuracy. Total

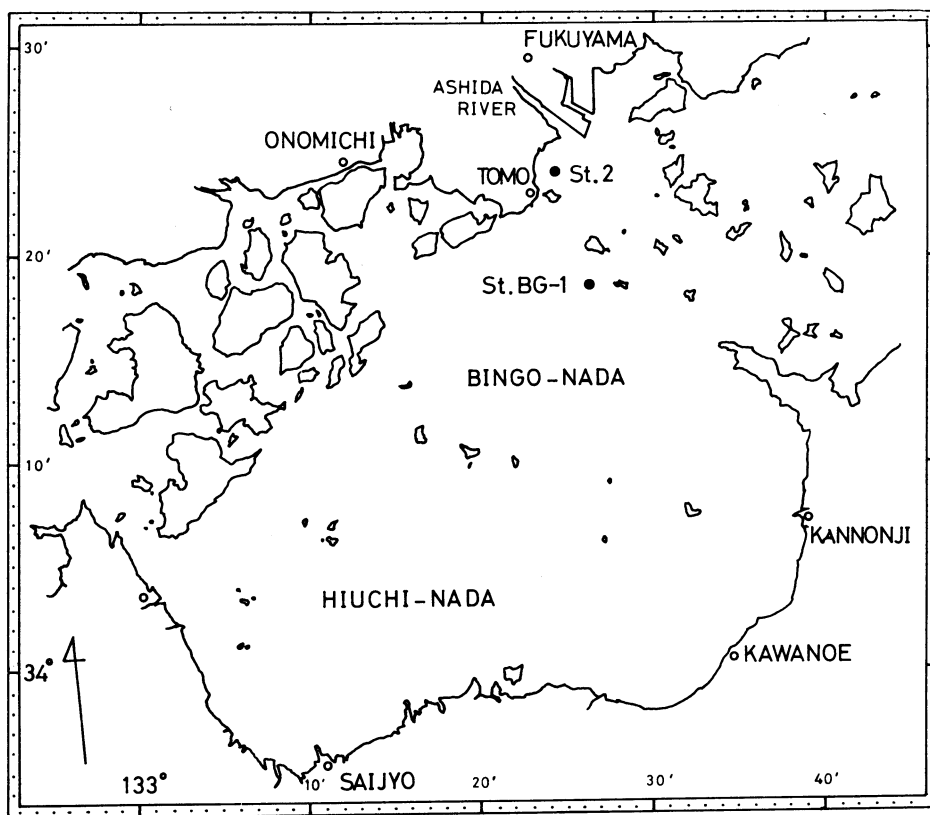


Fig. 1. Location of sampling stations.

phosphorus (TP) in seawater was expressed as the sum of DIP, DOP and PP. Particulate material for PP determination was recovered on a glass-fiber filter paper (Whatman GF/C type) instead of a Millipore filter during April through October in 1972.

#### Other Factors

Sestonic chlorophyll *a* content was determined by trichromatic absorptiometry of 90% acetone extract of the particulate material (STRICKLAND and PARSONS<sup>6</sup>). Organic carbon and organic nitrogen contents and dry weight of the particulate matter were determined, although the results are not presented in this paper.

For the enumeration of heterotrophic bacteria, the seawater sample obtained by the J-Z sampler was successively diluted, and 0.1 ml portions of each dilution were inoculated onto agar plates of Zobell's Medium 2216E with sterile spreading rods (BUCK and CLEVERDON<sup>7</sup>). After 2 weeks incubation at 20°C, the colonies on the plates were counted.

## RESULTS

**Hydrographical Conditions at Sampling Stations**

In the coastal waters where our sampling stations are located, water temperature and chlorinity are profoundly affected by local climate and river runoff, since seawater is exchanged with the outer ocean at very slow rates. Seawater is moved chiefly by the wind and the tide. The latter has a mean spring range of 3.2 m. Tidal currents are slower than 1 knot and reciprocatory in direction. Bottom sediment consists of bluish grey silt, the color being more or less darkened in late summer due to sulfides. This sea area is exposed to the influxes of the Ashida River, the domestic sewage from Fukuyama city and the waste waters from industries (Fig. 1).

Results of hydrographical observation at St. 2 and St. BG-1 are presented in Tables 1 and 2.

At either station, water temperature showed seasonal variation of a typically annual cycle. It rose from the minimum of early spring towards the maximum of August; in the meantime, stratification became established in the water column, particularly at St. BG-1 (Fig. 2). In September, sometimes in late August, vertical mixing set in; the water temperature went down in autumn and winter.

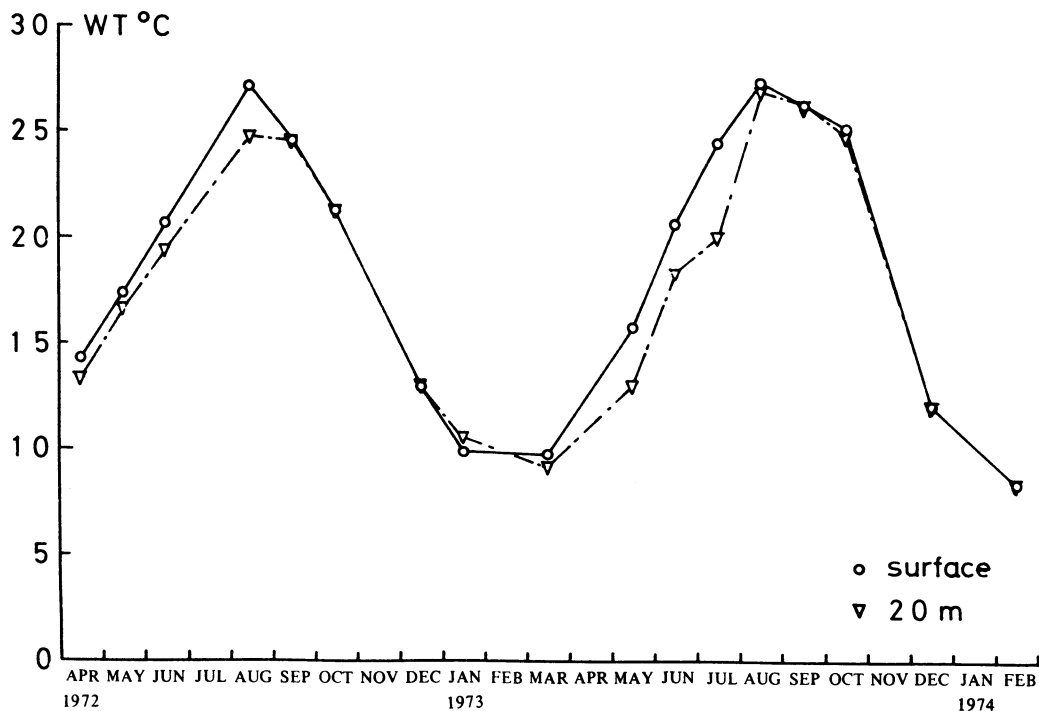


Fig. 2. Seasonal variation of water temperature at St. BG-1.

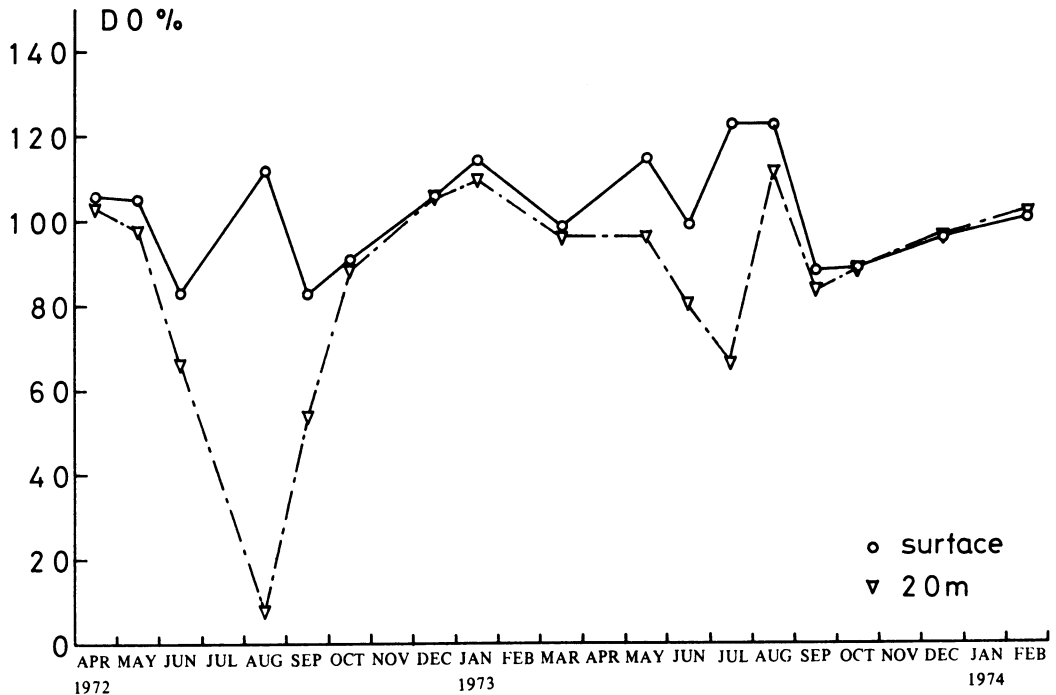


Fig. 3. Seasonal variation of dissolved oxygen at St. BG-1.

For the sake of convenience the annual cycle was divided into the following halves on the basis of the water temperature:

High temperature season (Water temperature higher than 15°C): May to October

Low temperature season (Water temperature lower than 15°C): November to April  
Incidentally, rich crops of phytoplankton (chlorophyll *a* exceeding about 6 mg/m<sup>3</sup>) seldom occurred at water temperature below 15°C. Three forms of phosphorus in the seawater were measured on 10 and 6 occasions respectively in the high and the low temperature season at both stations.

The annual cycle was distinguished also into the period of stratification and that of vertical mixing:

Stratification period: April to August, 1972; March to July, 1973.

Vertical mixing period: September, 1972 to January, 1973; August, 1973 to February, 1974.

The stratification period almost overlapped the high temperature season.

At St. 2 the influence of inflowing land water was stronger than at St. BG-1. This was evidenced by the lower level and greater seasonal variation of chlorinity. Vertical differences of water temperature and chlorinity indicated that the mixing effect of wind waves was often active down to the sea-bottom at this station even during the stratification period. Standing crops of phytoplankton were rich, especially in the

high temperature season; Secchi disk visibility and chlorophyll *a* content averaged respectively 2.1 m and 13.5 mg/m<sup>3</sup> during the stratification period. Red tide consisting of monotonous or mixed bloom of flagellate micro-algae such as *Heterosigma*, *Gymnodinium*, *Ceratium*, *Exuviaella*, *Prorocentrum*, *Eutreptiella*, etc. as well as diatoms such as *Skeletonema* etc., occurred several times at this station-site in the high temperature season of 1972. Dissolved oxygen was usually within 10% of saturation level throughout the year, except that considerable supersaturation at the surface and undersaturation at 5 m depth were recorded in midsummer.

Compared with St. 2, St. BG-1 was situated farther in sea, had a greater water depth and showed poorer crops of phytoplankton. Secchi disk visibility averaged 5.0 m and chlorophyll *a* content 3.4 mg/m<sup>3</sup> in the stratification period. Dissolved oxygen was usually within 20% of saturation level and was almost the same at the surface, 10 m and 20 m depth; in the later part of stratification period, however, a marked undersaturation was observed at 20 m (Fig. 3).

Differences in Secchi disk visibility and chlorophyll *a* content, as well as the counts of heterotrophic bacteria (averaging 10<sup>5.3</sup> and 10<sup>4.05</sup> per ml respectively at St. 2 and St. BG-1 in the stratification period), point to a more eutrophic condition at St. 2 than at St. BG-1.

Seasonal variations of some variables from April, 1972 to February, 1973 were not identical to those of the following year. The fact that the summer of 1973 was exceptionally dry should be taken notice of in this connection.

#### Seasonal Variation of Phosphorus Contents of Seawater

The results of phosphorus analyses are presented in Tables 3 and 4 and Figs. 4 to 7. From these results the phosphorus contents for the entire water column were calculated (AC in Tables 3 and 4; Figs. 8 and 9), and their averages for high and low temperature seasons are shown in Table 5.

#### Particulate Phosphorus (PP)

Seasonal variation in the PP content of sample water was roughly correlated to the water temperature and the chlorophyll *a* content.

At St. 2 (Fig. 4) the minima of PP content were observed in the surface water in April and December, 1972 (0.09 and 0.14  $\mu\text{g-at/l}$ ). The PP content for the water column of this station averaged 0.22 for the low and 0.56  $\mu\text{g-at/l}$  for the high temperature season (Table 5). Seasonal averages of chlorophyll *a* content for the water column also showed a similar trend (5.7 for the low and 12.5 mg/m<sup>3</sup> for the high temperature season).

Maximal PP values at St. 2 were observed at the surface and 5 m depth in June, August and September, 1972 (0.91 – 1.06  $\mu\text{g-at/l}$ ). At the time of these high values the sea was discolored by the dense bloom of phytoplankton (i.e., red tide), and chlorophyll *a* contents were as high as 19.5 – 30.7 mg/m<sup>3</sup>. On such occasions PP accounted for large proportions of TP, and DIP tended to be exhausted, as it was typically

Table 1. Hydrographical conditions observed at St. 2

Date	Depth m	Tr*m	Layer m	WT °C	Cl‰	DO ml/l	DO %	E**x10 <sup>6</sup>
Apr. 25, 1972	6.0	2.0	0	14.0	16.84	6.91	112.8	+ 12
			5.0	14.0	16.89	6.63	108.3	
May. 23	7.0	2.4	0	17.5	17.07	6.17	107.5	+ 4
			5.0	17.6	17.10	5.96	104.1	
Jun. 29	7.9	1.2	0	21.6	15.97	6.45	99.0	+195
			6.0	21.1	16.73			
Jul. 28	8.0	2.5	0	26.1	15.86	5.63	111.8	+201
			7.0	24.4	16.53	4.13	80.3	
Aug. 30	6.5	1.9	0	27.6	15.29	7.23	146.4	+460
			5.0	26.0	16.62	3.04	60.8	
Sep. 26	8.0	2.0	0	23.8	16.17	6.16	118.1	+ 12
			6.0	23.9	16.25	5.54	106.5	
Oct. 24	7.0	1.8	0	20.0	16.38	4.71	86.9	+ 22
			6.0	19.7	16.43	4.74	85.1	
Dec. 19	8.0	3.1	0	10.0	16.73	6.78	102.3	+ 75
			6.5	10.8	17.17	6.70	103.3	
Jan. 27, 1973	6.0	3.3	0	9.3	16.35	7.50	110.9	+114
			5.0	9.5	16.78	7.58	113.2	
Mar. 20	8.0	2.8	0	9.3	17.52	6.48	97.2	+ 54
			5.0	8.8	17.65	6.44	95.9	
May. 2	6.0	1.5	0	15.9	16.63	6.58	111.1	+100
			5.0	15.6	16.95	6.63	111.6	
Jun. 17	6.0	2.9	0	21.6	17.32	6.05	113.3	+ 30
			5.0	21.3	17.36	5.50	102.5	
Jul. 4		1.6	0	23.7	16.59	7.25	139.4	+146
			5.0	23.2	17.02	4.77	91.4	
Aug. 24	4.8	1.8	0	27.9	17.68	6.06	126.8	0
			4.0	28.1	17.69	5.69	119.5	
Sep. 13	6.0	2.0	0	25.7	17.48	4.73	95.0	- 8
			5.0	25.7	17.46	4.69	94.2	
Oct. 2	7.0	2.2	0	24.8	17.09	4.53	89.3	+ 86
			5.0	24.0	17.23	4.79	93.3	
Dec. 24	8.0	1.8	0	11.0	18.37	6.09	95.7	0
			6.0	11.0	18.37	6.12	96.2	
Feb. 23, 1974	7.0	3.0	0	8.4	18.19	7.23	107.5	+ 4
			5.0	8.3	18.19	7.28	108.0	

\* Tr: Transparency or Secchi disk visibility.

\*\* E: Average increase in the seawater density per meter of increase in the depth.

$$E = \frac{\Delta \rho}{\Delta z(m)}$$

illustrated by the surface water on September 26, 1972 in which PP represented 63% of TP and DIP had dropped to 0.12  $\mu\text{g-at/l}$  (Table 3).

At St. BG-1 (Fig. 5) the PP content of seawater was usually lower than at St. 2: PP content for the water column averaged 0.13 in the low and 0.26  $\mu\text{g-at/l}$  in the high temperature season (Table 5), accounting for 14.9 and 23.2% of TP respectively. These figures are lower than those at St. 2, but they resemble the latter in the tendency of

Table 2. Hydrographical conditions observed at St. BG-1.

Date	Depth m	Tr*m	Layer m	WT °C	Cl <sub>00</sub> ‰	DO ml/l	DO %	E* ×10 <sup>6</sup>
Apr. 25, 1972	24.0	7.0	0	14.3	17.69	6.37	105.7	+ 26
			10.0	13.4	17.74	6.37	104.0	+ 7
			20.0	13.3	17.78	6.32	103.0	
May. 23	24.0	6.5	0	17.4	17.69	5.99	105.0	+ 5
			10.0	17.0	17.66	5.98	104.0	+ 18
			20.0	16.6	17.72	5.66	97.8	
Jun. 29	26.0	2.9	0	20.7	17.27	5.34	83.0	+ 29
			10.0	20.2	17.39	4.72	73.6	+ 36
			20.0	19.4	17.50	4.21	65.9	
Aug. 30	20.0	4.2	0	27.2	16.81	5.45	111.5	+ 62
			19.0	24.8	17.13	0.38	7.5	
Sep. 26	25.6	6.0	0	24.6	16.64	4.22	82.4	+ 1
			10.0	24.6	16.65	3.75	73.3	+ 10
			20.0	24.6	16.72	2.72	53.2	
Oct. 24	25.0	5.0	0	21.3	16.89	4.89	90.7	+ 3
			10.0	21.2	16.90	4.71	87.2	+ 4
			20.0	21.2	16.92	4.76	88.1	
Dec. 19	26.0	6.2	0	13.0	17.65	6.54	105.8	+ 1
			10.0	13.0	17.66	6.50	105.2	0
			20.0	13.0	17.66	6.50	105.2	
Jan. 27, 1973	24.0	5.0	0	9.9	17.48	7.48	114.0	+ 18
			10.0	10.2	17.64	7.09	108.6	+ 7
			20.0	10.6	17.74	7.06	109.2	
Mar. 20		4.2	0	9.8	17.80	6.47	98.5	+ 16
			10.0	9.1	17.83	6.43	96.6	+ 1
			20.0	9.1	17.84	6.39	96.0	
May. 2	26.0	3.0	0	15.8	17.47	6.76	114.5	+ 40
			10.0	14.9	17.61	6.80	113.6	+ 84
			20.0	13.1	17.96	5.88	95.9	
Jun. 17	25.0	8.0	0	20.7	17.64	5.34	98.9	+ 20
			5.0	20.5	17.67	5.29	97.7	+ 58
			10.0	19.6	17.71	4.86	88.4	+ 37
			20.0	18.4	17.76	4.48	79.9	
Jul. 5	24.0	4.1	0	24.6	17.18	6.24	122.6	+176
			5.0	23.0	17.48	5.73	110.0	+ 92
			10.0	21.8	17.61	4.80	90.4	+ 84
			22.0	20.0	17.77	3.63	66.5	
Aug. 24	24.5	8.0	0	27.4	17.80	5.90	122.6	- 8
			10.0	27.5	17.80	5.95	123.7	+ 18
			20.0	27.0	17.81	5.40	111.4	
Sep. 13	24.0	4.0	0	26.4	17.75	4.32	88.1	+ 2
			10.0	26.4	17.76	4.24	86.5	+ 2
			20.0	26.4	17.78	4.09	83.5	
Oct. 2	24.0	6.1	0	25.3	17.79	4.44	88.9	+ 18
			5.0	25.0	17.79	4.38	87.3	+ 8
			10.0	24.9	17.80	4.28	85.2	+ 5
			20.0	24.8	17.81	4.46	88.6	
Dec. 24	24.0	5.5	0	12.2	18.39	5.96	95.9	- 1
			10.0	12.4	18.41	6.11	98.7	+ 1
			20.0	12.3	18.40	6.00	96.7	
Feb. 23, 1974	23.0	4.5	0	8.5	18.50	6.74	100.8	+ 2
			10.0	8.5	18.51	6.77	101.3	+ 3
			20.0	8.5	18.53	6.85	102.5	

\* Tr and E are as in Table 1.



Table 3. Phosphorus data and other factors observed at St. 2.

Data	Layer m	DIP	DOP $\mu\text{g-at/l}$	PP	TP	Chl. <i>a</i> $\text{mg/m}^3$	Bacteria $\log(\text{no./ml})$
Apr. 25, 1972	0	0.70	0.57	0.09	1.36	9.03	<5.00
	5	0.45	0.75	0.14	1.34	7.89	<5.00
	AC*	0.55	0.68	0.12	1.35		
May. 23	0	0.22	0.56	0.48	1.26	7.17	<5.00
	5	0.15	0.51	0.48	1.14	6.47	<5.00
	AC	0.18	0.53	0.48	1.18		
Jun. 29	0	0.29	0.37	0.94	1.60	30.74	6.57
	6	0.37	0.26	0.91	1.54	19.46	5.01
	AC	0.34	0.30	0.93	1.56		
Jul. 28	0	0.15	0.42	0.57	1.14	13.14	5.32
	7	0.18	0.45	0.59	1.22	10.30	4.94
	AC	0.17	0.44	0.58	1.19		
Aug. 30	0	0.11	0.68	1.06	1.85	25.00	5.46
	5	0.51	0.58	0.97	2.06	16.38	4.84
	AC	0.36	0.62	1.00	1.98		
Sep. 26	0	0.12	0.51	1.06	1.69	22.95	4.89
	6	0.16	0.66	1.01	1.83	20.84	4.58
	AC	0.15	0.60	1.03	1.78		
Oct. 24	0	0.71	0.61	0.29	1.61	3.73	4.56
	6	0.67	0.60	0.44	1.71	6.04	4.69
	AC	0.69	0.60	0.38	1.67		
Dec. 19	0	0.52	0.24	0.14	0.90		5.18
	5	0.50	0.24	0.17	0.91		4.93
	AC	0.51	0.24	0.16	0.91		
Jan. 27, 1973	0	0.45	0.26	0.25	0.96	5.50	5.61
	5	0.45	0.33	0.31	1.09	5.34	5.63
	AC	0.45	0.30	0.29	1.04		
Mar. 20	0	0.30	0.40	0.18	0.88		4.77
	5	0.20	0.39	0.31	0.90		4.13
	AC	0.23	0.39	0.27	0.89		
May. 2	0	0.16	0.38	0.25	0.79	6.92	5.37
	5	0.19	0.32	0.22	0.73	6.19	4.46
	AC	0.18	0.35	0.23	0.76		
Jun. 17	0	0.33	0.59	0.17	1.09	8.26	5.00
	5	0.13	0.45	0.17	0.75	6.90	4.21
	AC	0.21	0.51	0.17	0.89		
Aug. 24	0	0.34	0.75	0.42	1.51		5.65
	4	0.33	0.53				
	AC	0.33	0.62	0.42	1.51		
Sep. 13	0	0.83	0.82	0.43	2.08	22.36	5.15
	5	0.67	0.66	0.43	1.76	20.44	4.93
	AC	0.4	0.73	0.43	1.89		
Oct. 2	0	1.10	0.70	0.44	2.24	4.02	5.07
	5	0.81	0.76	0.38	1.95	6.69	4.90
	AC	0.91	0.74	0.40	2.05		
Dec. 24	0	0.78	0.76	0.21	1.75	2.61	4.06
	6	0.78	0.71	0.22	1.71	2.70	3.11
	AC	0.78	0.73	0.22	1.72		
Feb. 23, 1974	0	0.16	0.41	0.28	0.85	5.65	5.02
	5	0.13	0.47	0.29	0.89	6.99	5.30
	AC	0.14	0.45	0.29	0.88		

\* AC: Average for the water column.

Table 4. Phosphorus data and other factors observed at St. BG-1.

Date	Layer m	DIP	DOP $\mu\text{g-at/l}$	PP	TP	Chl. <i>a</i> $\text{mg/m}^3$	Bacteria log (no./ml)
Apr. 25, 1972	0	0.54	0.26	0.14	0.94	1.39	< 4.00
	10	0.23	0.63	0.17	1.03	2.37	< 4.00
	20	0.22	0.69	0.12	1.03	2.92	< 4.00
	AC*	0.29	0.58	0.15	1.01		
May. 23	0	0.10	0.54	0.24	0.88	1.61	< 4.00
	10	0.13	0.43	0.29	0.85	1.74	< 4.00
	20	0.12	0.42	0.29	0.83	2.62	< 4.00
	AC	0.12	0.45	0.28	0.85		
Jun. 29	0	0.08	0.52	0.30	0.90	6.06	4.74
	10	0.16	0.44	0.27	0.87	3.55	4.60
	20	0.19	0.44	0.31	0.94	2.34	4.15
	AC	0.16	0.46	0.29	0.91		
Aug. 30	0	0.09	0.61	0.38	1.08	7.46	4.43
	10	0.10	0.61	0.51	1.22		4.51
	20	1.26	0.52	0.57	2.35	3.52	3.60
	AC	0.39	0.59	0.49	1.42		
Sep. 26	0	0.59	0.91	0.43	1.93	8.91	4.18
	10	0.49	0.58	0.50	1.57	9.36	4.04
	20	1.10	0.56	0.34	2.00	5.77	4.02
	AC	0.76	0.64	0.42	1.82		
Oct. 24	0	0.37	0.49	0.24	1.10	4.60	4.20
	10	0.38	0.59	0.21	1.18	3.89	3.43
	20	0.49	0.46	0.25	1.20	4.42	3.21
	AC	0.42	0.52	0.23	1.17		
Dec. 19	0	0.49	0.10	0.09	0.68		3.69
	10	0.46	0.11	0.10	0.67		4.23
	20	0.44	0.15	0.10	0.69		3.60
	AC	0.46	0.13	0.10	0.68		
Jan. 27, 1973	0	0.30	0.25	0.16	0.71	4.55	4.70
	10	0.46	0.24	0.13	0.83	3.38	5.02
	20	0.56	0.19	0.12	0.87	3.43	4.99
	AC	0.46	0.22	0.13	0.82		
Mar. 20	0	0.17	0.34	0.11	0.62		2.70
	10	0.22	0.41	0.14	0.77		3.38
	20	0.18	0.34	0.14	0.66		3.23
	AC	0.19	0.37	0.13	0.70		
May. 2	0	0.08	0.26	0.11	0.45	2.33	4.26
	10	0.06	0.32	0.15	0.53	4.56	3.70
	20	0.12	0.27	0.10	0.49	3.72	2.90
	AC	0.09	0.29	0.12	0.50		
Jun. 17	0	0.19	0.33	0.10	0.62	1.28	4.23
	10	0.28	0.36	0.11	0.75	1.44	4.04
	20	0.31	0.32	0.08	0.71	1.34	3.92
	AC	0.27	0.34	0.10	0.71		
Aug. 24	0	0.27	0.40	0.21	0.88		5.83
	10	0.30	0.46	0.25	1.01		
	20	0.80	0.48	0.21	1.49		
	AC	0.49	0.46	0.23	1.17		

Date	Layer m	DIP	DOP	PP	TP	Chl. <i>a</i> mg/m <sup>3</sup>	Bacteria log (no./ml)
		μg-at/l					
Sep. 13	0	0.60	0.47	0.27	1.34	2.99	2.95
	10	0.55	0.48	0.27	1.30	2.72	3.93
	20	0.53	0.46	0.28	1.27	2.57	3.88
	AC	0.55	0.47	0.27	1.30		
Oct. 2	0	0.54	0.68	0.15	1.37	2.28	4.07
	10	0.53	0.66	0.18	1.37	2.90	4.12
	20	0.45	0.52	0.19	1.16	3.05	3.88
	AC	0.50	0.61	0.18	1.29		
Dec. 24	0	0.65	0.49	0.11	1.25	2.49	3.78
	10	0.68	0.62	0.22	1.52	2.34	2.78
	20	0.74	0.51	0.06	1.31	2.48	2.30
	AC	0.70	0.55	0.14	1.38		
Feb. 23, 1974	0	0.36	0.30	0.13	0.79	1.64	3.82
	10	0.29	0.28	0.14	0.71	1.55	3.51
	20	0.28	0.39	0.14	0.81	1.49	3.66
	AC	0.30	0.32	0.14	0.76		

\* AC: Average for the water column.

Table 5. Average concentrations of three forms of phosphorus for the high and the low temperature season in the water column of St. 2 and St. BG-1.

Station	Phosphorus Form	Average Concentration (μg-at/l)		Ratio H.T.S./L.T.S.
		H.T.S.*	L.T.S.**	
St. 2	PP	0.56	0.22	2.55
	DIP	0.39	0.44	0.89
	DOP	0.54	0.46	1.17
	TP	1.49	1.13	1.32
St. BG-1	PP	0.26	0.13	2.00
	DIP	0.38	0.40	0.95
	DOP	0.48	0.36	1.33
	TP	1.12	0.89	1.26

\* H.T.S. : High temperature season.

\*\* L.T.S. : Low temperature season.

growing two times bigger in the high temperature season. The PP content remained at a low level of about 0.1 μg-at/l during the low temperature season. The PP content of the surface water attained the annual maximum in September both in 1972 and 1973 (0.43 and 0.27 μg-at/l).

Though the PP content did not differ significantly between the three sampling depths of St. BG-1, the water from 10 m and/or 20 m depth gave greater PP contents than the surface water in a few cases (e.g., August and September, 1972; December, 1973).

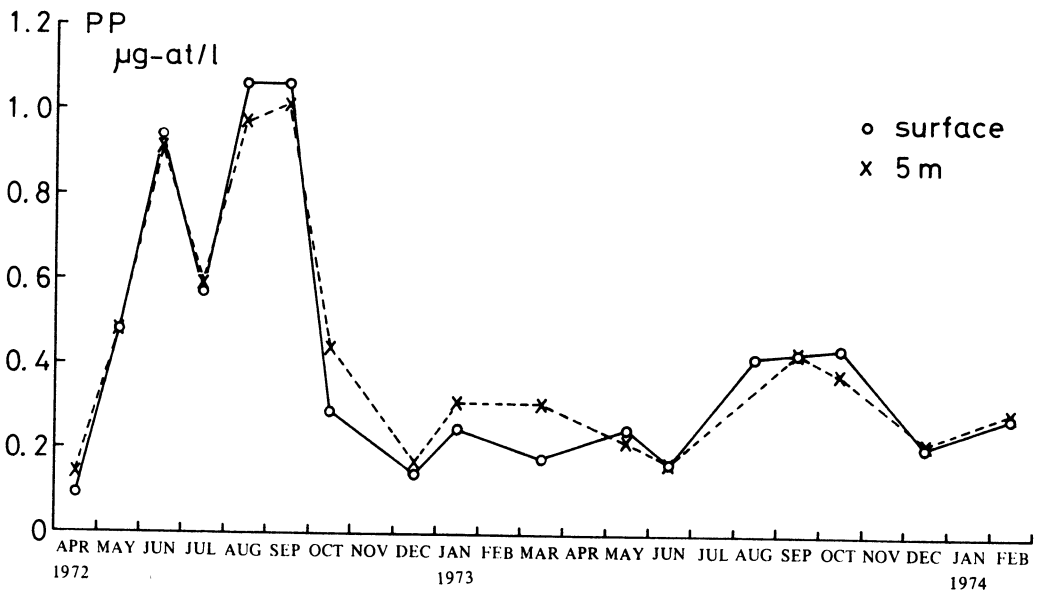


Fig. 4. Seasonal variation of particulate phosphorus (PP) at St. 2.

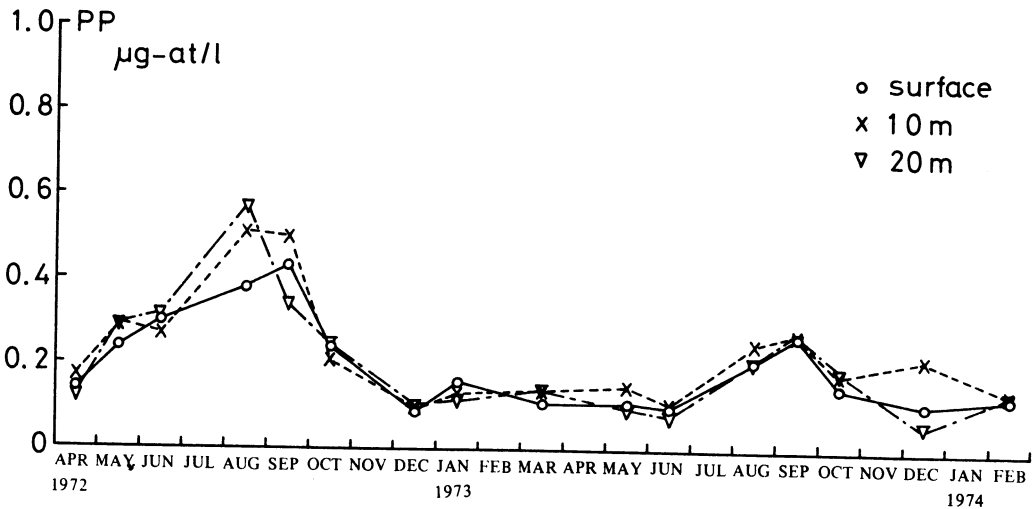


Fig. 5. Seasonal variation of particulate phosphorus (PP) at St. BG-1.

#### Dissolved Inorganic Phosphorus (DIP)

At St. 2 (Fig. 6), DIP in surface water decreased to less than  $0.15 \mu\text{g-at/l}$  in July, August and September in 1972 apparently synchronizing with the dense blooming of phytoplankton, and then rose up markedly in October. Again in 1973, DIP was low during the summer months, rose in September and reached its maximum ( $1.10 \mu\text{g-at/l}$ ) in October.

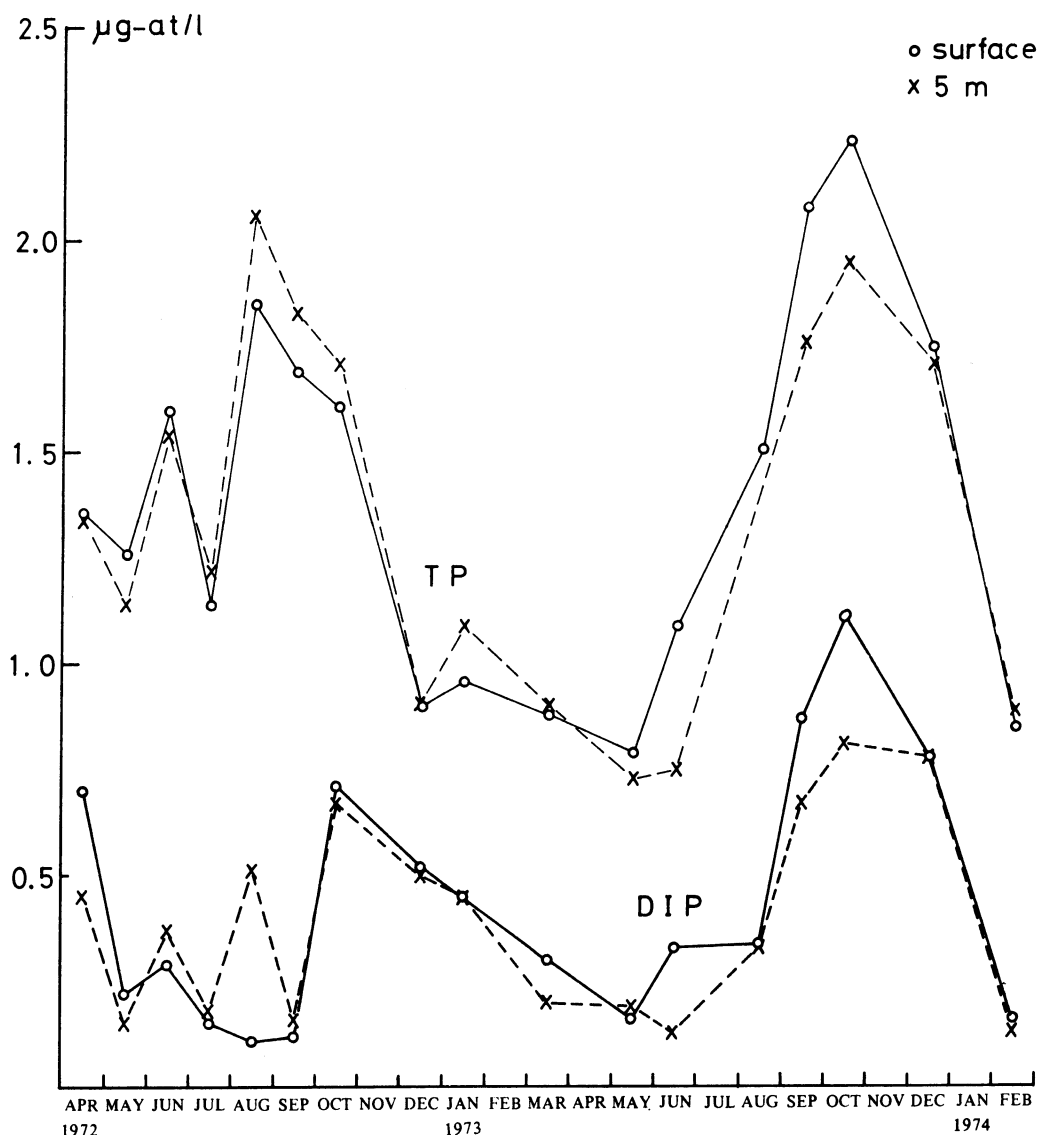


Fig. 6. Seasonal of total phosphorus (TP) and dissolved inorganic phosphorus (DIP) at St. 2.

At St. BG-1 (Fig. 7), DIP at the surface and 10 m depth followed almost the same pattern of seasonal variation as at St. 2. At 20 m depth, however, DIP showed itself in quite a different way. It increased to high values of 0.80 or 1.26  $\mu\text{g-at/l}$  in August; most probably this increase was due to the liberation of DIP from bottom sediment under low oxygen tensions. Subsequently, DIP attained high concentrations at every depth of St. BG-1 in September or October; this seems to be the consequence of vertical mixing. Increase of DIP concentration in the water column of St. 2 in September or October (Fig. 6) may be due to a similar mechanism.

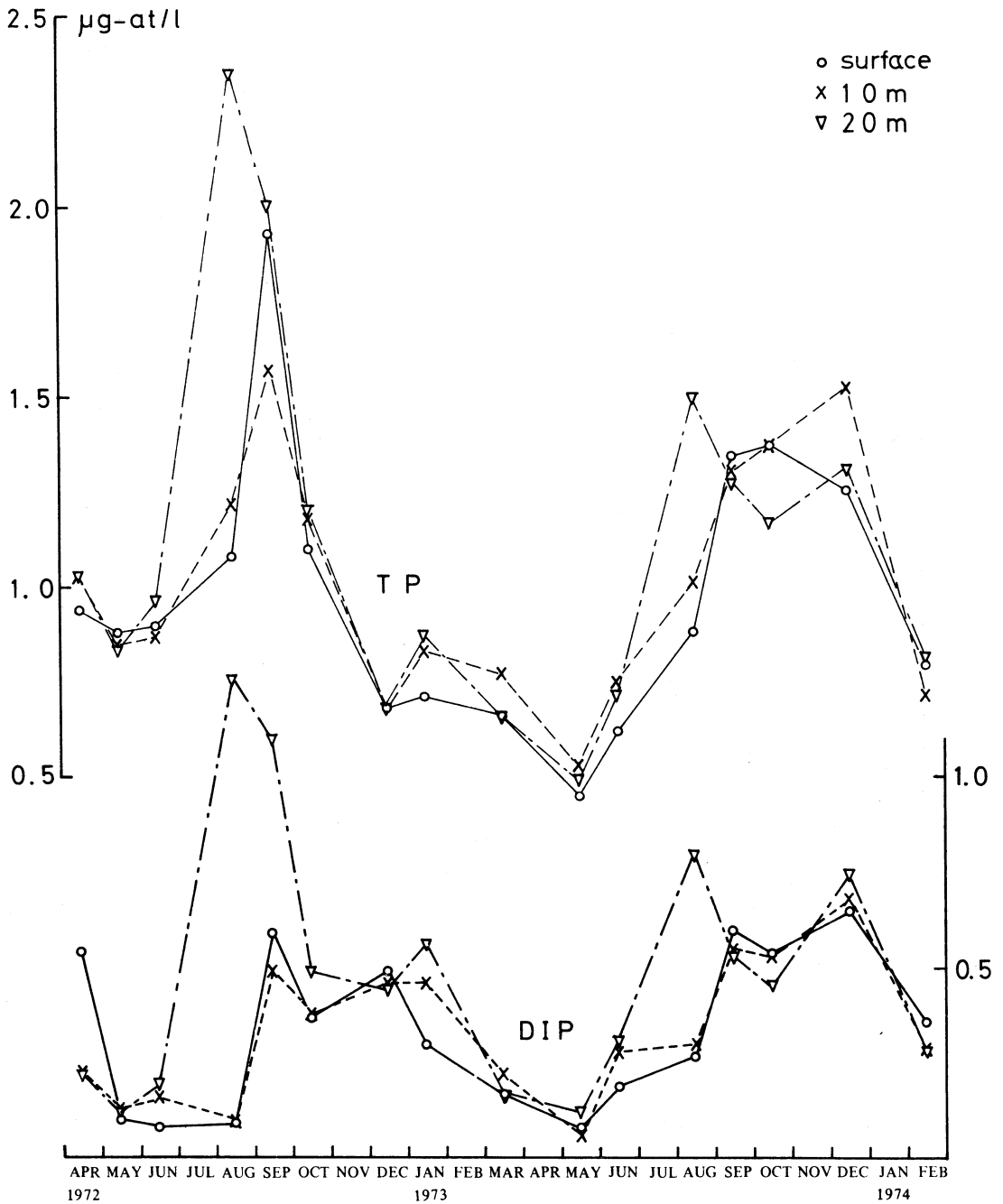


Fig. 7. Seasonal variation of total phosphorus (TP) and dissolved inorganic phosphorus (DIP) at St. BG-1.

From these data we may infer that in the waters under study the low level of DIP in the upper layers during the summer was induced largely through biological activities which transformed DIP into other forms of phosphorus, mostly PP, and also that liberation of DIP from bottom sediment was an important factor affecting DIP concentrations in the water column.

DIP concentrations at different depths were probably conditioned at least by the following factors which acted independently: namely, (1) consumption by growing plants, (2) dilution by the admixing offshore water, (3) supply by inflowing land water, (4) mineralization of organic phosphorus, and (5) liberation from bottom sediment. It is difficult, however, to trace the immediate effects of the factors (2), (3) and (4) from the mere inspection of Figs. 6 and 7.

#### **Dissolved Organic Phosphorus (DOP)**

DOP accounted for considerable portions of TP all the year round. Seasonal variation of DOP concentration was not so conspicuous as that of DIP.

At St. 2 the average concentration of DOP in the water column for all seasons was 0.53  $\mu\text{g-at/l}$  and accounted for 38.7% of TP. The average for the high temperature season was a little higher than that for the low temperature season (Table 5). The situation was much alike at St. BG-1: the general average of all seasons was 0.43  $\mu\text{g-at/l}$  or 41.7% of TP, and the average for the high temperature season was somewhat higher than that for the low temperature season.

At St. 2 (Fig. 8) it is pointed out that in 1972 the high level of DOP during August–October was almost synchronous with the high PP values in August–September, and also that in 1973 the high level of DOP from August to December was synchronous with, or a little preceded by, the high level of PP from August through October. At St. BG-1 (Fig. 9), rise and fall of DOP concentration during 1972 were generally synchronous with those of PP content, and in 1973, high DOP of October was immediately preceded by the high PP in September. From these findings, we may induce that there is a tendency that an increase of DOP in the water column coincides with—or follows with a short delay—an increase in the standing crop of phytoplankton. Such a tendency fits in the hypothesis that DOP might be constituted chiefly by metabolites and decomposition products of organisms (PARSONS and TAKAHASHI<sup>8</sup>).

#### **Total Phosphorus (TP)**

Figs. 6 and 7 illustrate the seasonal variation of TP content for each depth at St. 2 and St. BG-1. In these graphs, all the ups and downs in the first year do not recur exactly in the next year; for example, we have a plateau in December, 1973, in contrast to a sharp drop in December, 1972.

Nevertheless, apparently the general trend at both stations for the average TP content in the water column is to remain at an annual minimal level during February

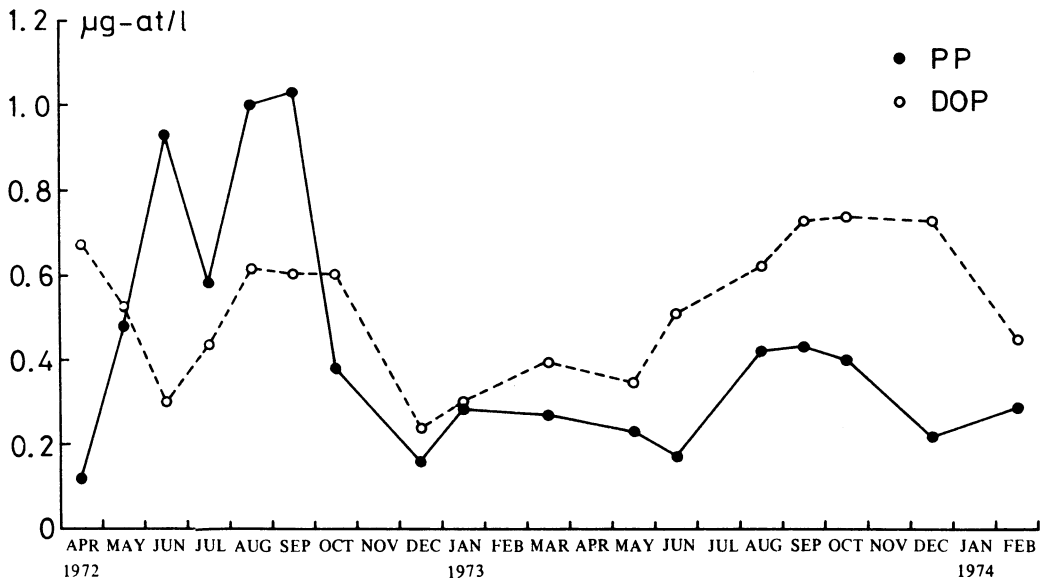


Fig. 8. Seasonal variation of particulate phosphorus (PP) and dissolved organic phosphorus (DOP) for the water column at St. 2.

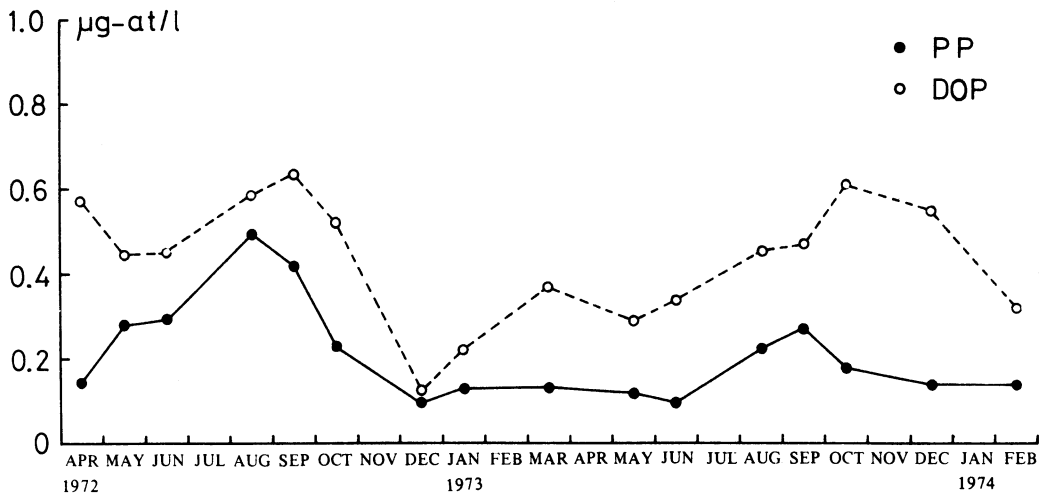


Fig. 9. Seasonal variation of particulate phosphorus (PP) and dissolved organic phosphorus (DOP) for the water column at St. BG-1.

through May and to reach the annual maximal level from August through October. TP content for the water column varied seasonally between 0.76 and 2.05  $\mu\text{g-at/l}$  at St. 2 and between 0.50 and 1.82  $\mu\text{g-at/l}$  at St. BG-1.

Such wide range of seasonal variation points to seasonal addition or removal of



phosphorus in the water column. It then follows that the seasonal variations in PP, DIP and DOP concentrations as described in the preceding sections depended not only on the transformation amongst the three forms of phosphorus, but also on net increase and decrease of phosphorus in the water column. For instance, in the case of phytoplankton bloom at St. 2 in June, 1972, PP content of the water column increased by  $0.45 \mu\text{g-at/l}$  over the level in May, whereas concurrent decrease of dissolved phospho-

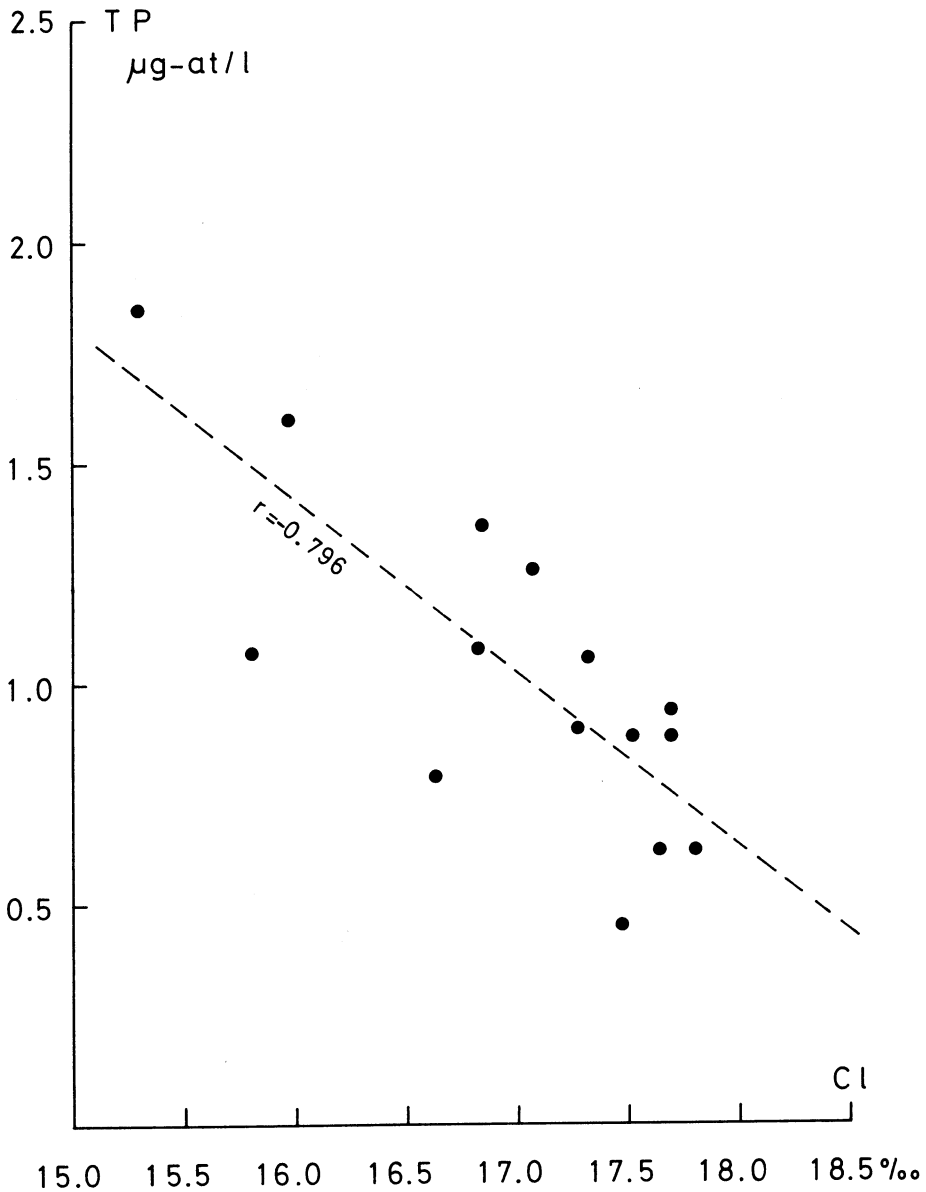


Fig. 10. Relationship between total phosphorus (TP) and chlorinity in the surface water in stratification period.

rus (DIP + DOP) was less than  $0.06 \mu\text{g-at/l}$ ; total phosphorus increased concurrently by  $0.38 \mu\text{g-at/l}$ , indicating that phosphorus was supplied from an outside source and that such supply was required for the blooming to occur.

As we do not yet understand the complete picture of the seasonal variation of TP in the waters under study, reference is made only to a few factors whose role is known qualitatively.

One possible route of phosphorus supply to the water column might be the admixing of land water. When TP content was plotted against chlorinity in all the surface water samples taken during the stratification period, a negative regression coefficient of  $-0.796$  was obtained (Fig. 10), suggesting the importance of admixing land water as a factor that increases TP content in seawater.

Liberation of dissolved phosphorus from the bottom sediment might be another route of supply. Reference has already been made to this process in connection with the seasonal variation of DIP. The fact that TP and DIP concentrations behaved in much the same way at different depths of St. BG-1 in August and September (Fig. 7) suggests that TP contents were considerably affected by the DIP liberated from the bottom sediment, at least during these months.

In the water column of both stations (Table 5), the average content of TP was about 30% higher for the high temperature season than for the low temperature season. And the average content at St. 2 was about 30% higher than that at St. BG-1 for either season.

## DISCUSSION

One of the characteristic features of this work lies in the fact that the annual cycle of phosphorus concentration was traced in an artificially eutrophicated marine environment where PP attained a high concentration of about  $1.0 \mu\text{g-at/l}$  owing to the dense phytoplankton bloom. STRICKLAND and AUSTIN<sup>2)</sup> studied the annual cycle of phosphorus concentration in naturally eutrophic coastal waters where total phosphorus was as high as  $2.5 \mu\text{g-at/l}$ . The balance between PP, DIP and DOP concentrations was studied in the natural and the experimentally induced phytoplankton bloom by KETCHUM and CORWIN<sup>9)</sup> and ANTIA et al.<sup>10)</sup>, respectively.

In our research, the contrast between the high and the low temperature season was more conspicuous in the concentration of PP than in that of TP, DIP or DOP (Table 5).

As shown in Fig. 11, PP content was positively correlated to chlorophyll *a* content in the euphotic zone of St. 2 and St. BG-1 (i.e., the data for 20 m depth at St. BG-1 are excluded). When the chlorophyll *a* contents were higher than  $10 \text{ mg/m}^3$ , PP were usually higher than  $0.5 \mu\text{g-at/l}$ . At lower values of chlorophyll *a* content, however, the

PP: chl. *a* ratio fluctuated considerably; this seems rather natural because particulate matter is constituted not only by living phytoplankton but also by less pigmented organic material. It is also probable that the PP: chl. *a* ratio was affected by the seasonal succession of the dominant species of phytoplankton. The regression line in Fig. 11 is expressed by

$$\text{PP } (\mu\text{g-at/l}) = 0.117 + 0.0317 \text{ chl. } a \text{ ( mg/m}^3 \text{ )}.$$

If this regression is accepted, the particulate phosphorus of our water samples was composed of approximately 0.1  $\mu\text{g-at/l}$  independent of chlorophyll *a* content and the remainder dependent of chlorophyll *a*.

The gradient of the regression line in Fig. 11 is equivalent to 1.054 ( $\mu\text{g PP}/\mu\text{g chl. } a$ ), which is a little larger than the conversion factor proposed by STRICKLAND<sup>11)</sup> for computing PP from an observed value of chlorophyll *a* content, i.e.  $0.75 \pm 0.2$  ( $\mu\text{g PP}/\mu\text{g chl. } a$ ). When, neglecting the above-said regression, the ratio PP: chl. *a* is calculated for each set of the data plotted in Fig. 11 and averaged for St. 2 and St. BG-1, we obtain 1.26 and 2.63 respectively. The PP: chl. *a* ratio obtained by ANTIA et al.<sup>10)</sup> on the phytoplankton bloom grown in a large plastic sphere was of comparable magnitude (i.e. 0.93 – 2.26). The smaller value of the ratio at St. 2 suggests that active phytoplankton may have represented a larger proportion of particulate matter at St. 2

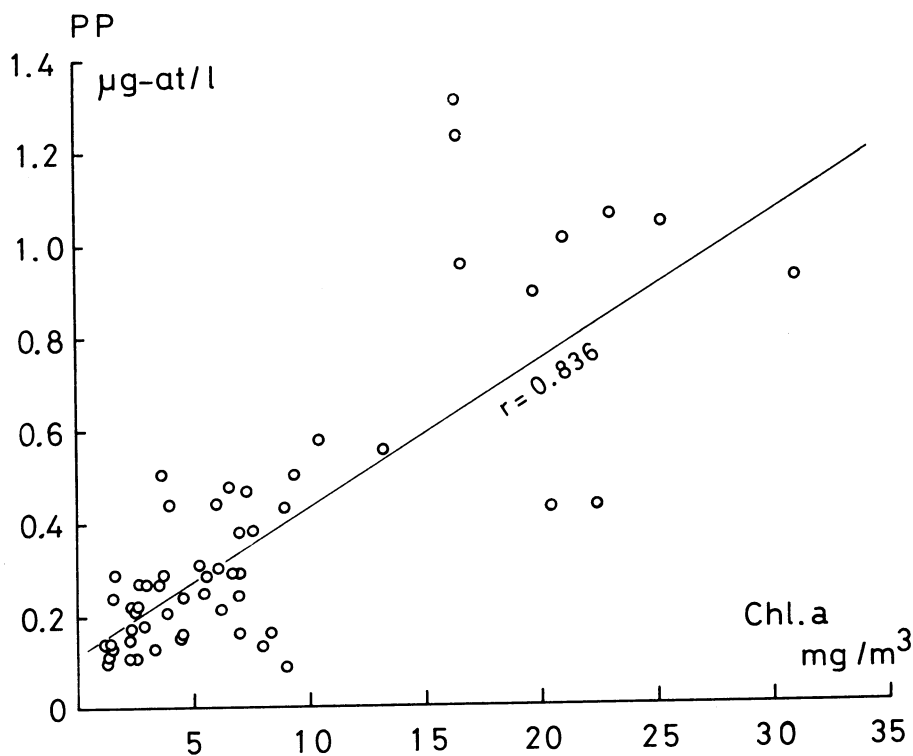


Fig. 11. Relation between sestonic chlorophyll *a* content and particulate phosphorus.

than at St. BG-1.

Judging from the data on the viable counts of heterotrophic bacteria (Tables 3 and 4), the contribution of bacterial cells to PP seemed to be very small. Correlation was not found between PP and the bacterial number. The amount of phosphorus obtained by multiplying bacterial number by the conversion factor of  $10.35 \times 10^{-9}$   $\mu\text{g-P/cell}$  were insignificantly small.

The values of POC and PON varied on the whole in a parallel way with the value of PP. This result supports the idea that usually organic matter accounted for a large proportion of particulate phosphorus.

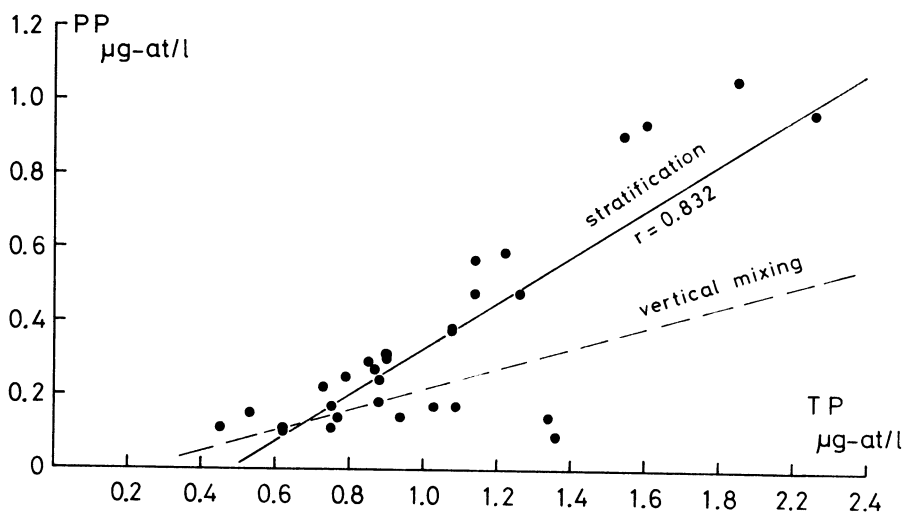


Fig. 12. Relationship between total phosphorus (TP) and particulate phosphorus (PP) in upper layers in stratification period.

As we have seen already, in certain cases a marked increase of PP was made possible by concurrent increase of TP. In order to understand the effects of TP upon the variation of PP, the relation between PP and TP has been plotted in Fig. 12 for the euphotic zone during the stratification period, in which the data for 20 m depth at St. BG-1 are not included. The graph indicates, although its theoretical basis is not clear, that PP is positively correlated to TP. In addition, the regression line intersects the axis of abscissa at the TP values of about  $0.5 \mu\text{g-at/l}$ , which is approximately the average concentration of DOP. Although similar plots were made for the vertical mixing period, they are not shown, and only the regression line is indicated by a broken line in Fig. 12.

Regarding the effect of TP upon the phytoplankton crop, UYENO and HAYASHI<sup>3)</sup> have already pointed out the tendency that chlorophyll *a* content tended to vary in parallel with TP content at the surface and 10 m depth in the Hiuchi-nada region of the Seto Inland Sec.

As has been already pointed out, the concentration of PP often varied inversely with that of DIP in their seasonal variation. This relationship is essentially the same as was reported by STRICKLAND and AUSTIN<sup>2)</sup> from Departure Bay. In order to examine this relationship, all of our data on DIP are plotted against PP in Fig. 13, in which both DIP and PP are expressed in percentages of TP. The distribution of the plots is such that the increase of PP from about 5% to about 40% is accompanied by the gradual increase in percent DOP and by the relatively sharp decrease in percent DIP. At high percentages of PP (i.e., above 45%) both DIP and DOP are low; these plots represent the measurements taken in the phytoplankton bloom at St. 2.

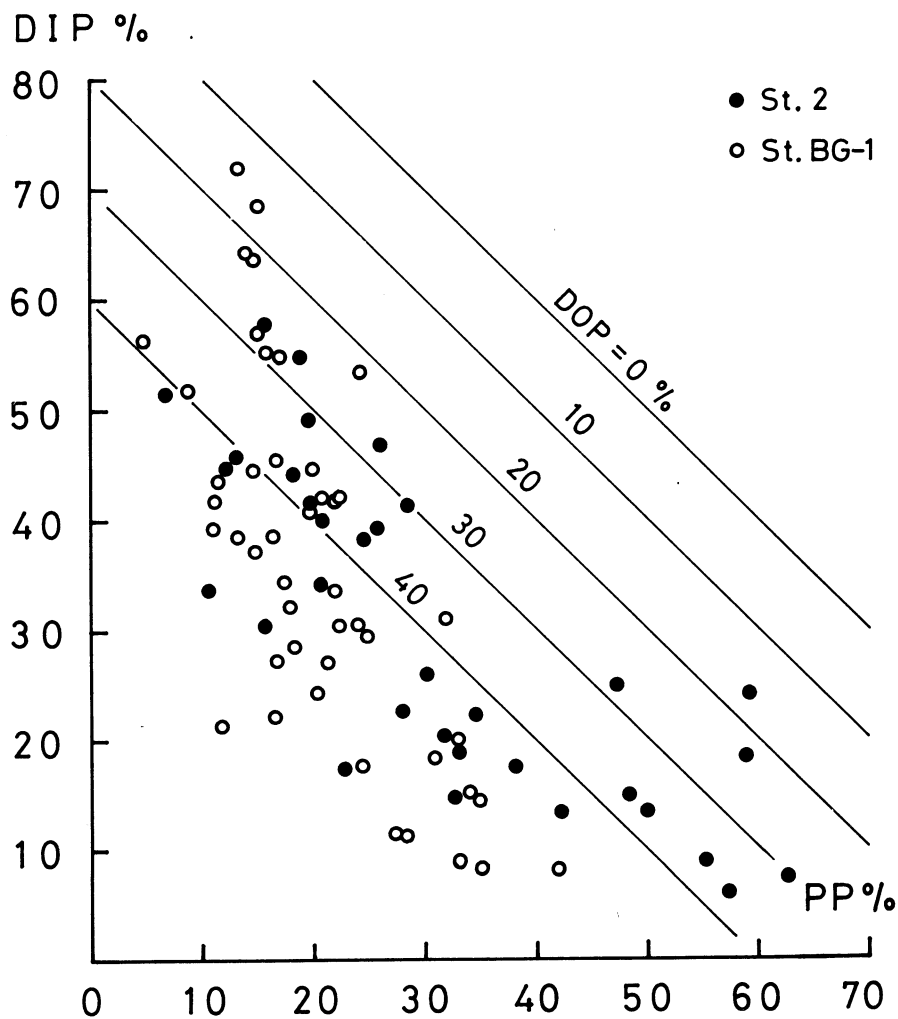


Fig. 13. Relationship between particulate phosphorus (PP) and dissolved inorganic phosphorus (DIP).

Our measurements indicate that the percentage of DOP to TP was pretty high throughout the year. This result agrees for the essential with the one obtained by UYENO and HAYASHI<sup>3)</sup> in the Hiuchi-nada region. But our result does not conform to the one obtained by ARMSTRONG and HARVEY<sup>1)</sup> in the English Channel, in which DOP showed marked seasonal variation. In view of the results obtained experimentally by WATT and HAYES<sup>12)</sup> and JOHANNES<sup>13)</sup> that there is no direct transformation of DIP to DOP, high DOP percentages in the presently studied waters might be due to those high PP contents which were largely referable to rich phytoplankton crop. If such be the case, it may be said that rather constant concentration of DOP and relatively high percentage of DOP to TP are characteristics features of an eutrophicated environment.

#### ACKNOWLEDGEMENT

Field collection of the data for this study was mostly made on board the Toyoshio Maru (82 gross tons), a training vessel of the Faculty. The invaluable cooperation and assistance rendered by Captain Zen'ichi Kamiryō, Captain Yoshiyuki Fukuura and the crew members are most gratefully acknowledged.

#### SUMMARY

Field observations were made during two years on the seasonal variation and the balance of three forms of phosphorus (particulate phosphorus, PP; dissolved inorganic phosphorus, DIP; and dissolved organic phosphorus, DOP) in the water column at two stations situated in the eutrophicated coastal region of the Seto Inland Sea, Japan.

In the high temperature season concentration of PP was definitely higher than in the low temperature season. High correlation between the concentrations of PP and chlorophyll *a* suggested that PP was mostly composed of the phosphorus contained in the phytoplankton, especially at high PP levels. Maximal PP values were observed in dense phytoplankton blooms, and were as high as 0.91 – 1.06  $\mu\text{g-at/l}$ .

Proportion of DOP in the total phosphorus of seawater was considerably high throughout the year, averaging 38.7 and 41.7% at each station. An increase of DOP in the water column coincided with, or followed with a short delay, an increase of PP.

DIP was consumed in the course of the growth of phytoplankton in upper layers during stratification period. There was indication that DIP was supplied to the water column from the outside during September through October. The influx of land water and the liberation of dissolved phosphorus from the bottom sediments were suggested as two main routes of phosphorus supply to the water column.

In conclusion, then, it appears that in this sea region the production and decomposition of phytoplankton played a important role in the annual cycle of phosphorus.

## REFERENCES

- 1) ARMSTRONG, F. A. J. and HARVEY, H. W.: The cycle of phosphorus in the waters of the English Channel. *J. mar. biol. Ass. U. K.*, **29**, 145–162 (1950).
- 2) STRICKLAND, J. D. H. and AUSTIN, K. H.: On the forms, balance and cycle of phosphorus observed in the coastal and oceanic waters of the northeastern Pacific. *J. Fish. Res. Bd. Canada*, **17**, 337–345 (1960).
- 3) UYENO, F. and HAYASHI, K.: Relation between various forms of phosphorus compounds and phytoplankton and bacteria in Hiuchi-nada. Annual Report of JIBP-PM-CG Group for 1969, 113–125 (1970). (in Japanese).
- 4) MURPHY, J. and RILEY, J. P.: A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta.*, **27**, 31–36 (1962).
- 5) FISKE, C. H. and SUBBAROW, Y.: The colorimetric determination of phosphorus. *J. Biol. Chem.*, **66**, 375–400 (1925).
- 6) STRICKLAND, J. D. H. and PARSONS, T. R.: A practical handbook of seawater analysis. *Fish. Res. Bd. Canada Bull.*, **167**, 311pp., Ottawa (1968).
- 7) BUCK, J. D. and CLEVERDON, R. C.: The spread plate as a method for the enumeration of marine bacteria. *Limnol. Oceanogr.*, **5**, 78–80 (1960).
- 8) PARSONS, T. R. and TAKAHASHI, M.: Biological oceanographic processes. 186pp., Pergamon Press, Oxford (1973).
- 9) KETCHUM, B. H. and CORWIN, N.: The cycle of phosphorus in a plankton bloom in the Gulf of Maine. *Limnol. Oceanogr.*, suppl. to Vol. **10** (REDFIELD anniversary volume), 148–161 (1965).
- 10) ANTIA, N. J., MCALLISTER, C. D., PARSONS, T. R., STEPHENS, K. and STRICKLAND, J. D. H.: Further measurement of primary production using a large-volume plastic sphere. *Limnol. Oceanogr.*, **8**, 166–183 (1963).
- 11) STRICKLAND, J. D. H.: Measuring the production of marine phytoplankton. *Fish. Res. Bd. Canada Bull.*, **122**, 172pp. (1960).
- 12) WATT, W. D. and HAYES, F. R.: Tracer study of the phosphorus cycle in sea water. *Limnol. Oceanogr.*, **8**, 276–285 (1963).
- 13) JOHANNES, R. E.: Uptake and release of dissolved organic phosphorus by representatives of coastal marine ecosystem. *Limnol. Oceanogr.*, **9**, 224–234 (1964).

## 富栄養沿岸海域におけるリンの存在様式と その季節変動

松田 治・遠藤拓郎・小山治行

瀬戸内海の備後灘北部の2定点において、1972年4月から約2年間、リンの基本的変動様式を知るために、約1カ月間隔で、海水中のリンを懸濁態リン(particulate phosphorus, PP), 溶存態無機リン(dissolved inorganic phosphorus, DIP), 溶存態有機リン(dissolved organic phosphorus, DOP)の3態に分別して定量した。結果を要約すると次のとおりである。

1. 本海域における海水中のリンの季節変動の一つの特長として、海水中の chlorophyll *a* 濃度が高い暖季(5~10月, 水温15℃以上)にPPの濃度が寒季におけるよりも、顕著に高かった。chlorophyll *a* とPPの間の高い相関などから、懸濁態リンの主部分は植物プランクトンに含まれていたと推定された。富栄養化の進んだ測点で、chlorophyll *a* が20 mg/m<sup>3</sup>以上の赤潮状態を呈した場合PPは1.0 μg-at/l前後の高い値を示した。
2. DIPの変動にはいくつかの要因が考えられるが、全リン(total phosphorus, TP)中に占めるDIPとPPの割合が逆の変動を示したことは、DIPの減少が、PPの主体をなす植物プランクトンの生産に強く支配されていたことを示唆する。事実、植物プランクトン現存量が大きく、3態中でPPの割合が卓越している場合にはDIPの濃度はしばしば著しく低下した。  
また、DIPの濃度は9月から12月にかけて高かったが、これは夏季に流入陸水および底泥から補給されたリンの影響が残存する時期に、植物プランクトンの生産が低下したためと考えられた。
3. DOPが海水中のリンに占める割合は周年かなり高かった。DOPの濃度は比較的季節変化に乏しかったが、その増減はPP濃度の変化と同時に、あるいは多少の遅れを伴って、生じた。この結果は、DOPの主体が植物プランクトンおよびその他生物の代謝・分解産物から成る、との考えと矛盾しない。
4. 海水中の各態リン濃度の季節変化は、各態相互間の変換によってだけでなく、3態の和である全リン(TP)も季節変化を示した。そのさい、リンの補給経路としては、夏季底泥からの溶出、および陸水の流入が指摘された。海水の成層期には光合成層ではTPの増加分にほぼ比例してPPが増加した。
5. これらの結果から、本海域におけるリンのサイクルには植物プランクトンの生産とその分解過程が極めて重要な位置を占めていると考えられる。