

Distribution and dissolution of several forms of phosphorus in coastal marine sediments

Precipitated metal phosphate
Dissolution of phosphorus
Liberation of phosphorus
Anaerobic conditions
Coastal marine sediments

Phosphate métallique précipité
Dissolution du phosphore
Libération du phosphore
Conditions anaérobies
Sédiment marin côtier

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Received 1/9/86, in revised form 23/1/87, accepted 3/3/87.

ABSTRACT

Phosphorus in coastal marine sediments was divided into five forms: Sol-P, Al-P, Fe-P, Ca-P and Org-P. The distribution of phosphorus forms was investigated with sediments from three regions: Hiuchi Nada, Suho Nada and Beppu Bay, in the Seto Inland Sea, Japan. The effects of pH and anaerobic condition on the dissolution of phosphorus forms were studied in laboratory experiments. By comparing *in situ* flux with calculated diffusive flux, the importance of the sediment-water interface to phosphate liberation was considered.

The major form of phosphorus was Org-P, which did not change in concentration with sediment depth. Ca-P was also a major form of inorganic phosphate and did not change in concentration with depth. The concentration of Al-P and Fe-P decreased gradually in the deeper layer of the sediment column. The distribution of several forms of phosphorus in coastal marine sediments differed from that in oceanic sediments. The concentration of T-P, Org-P, Al-P, Fe-P, carbon and nitrogen correlated with each other, but the distribution of Ca-P in sediments did not correlate well. Org-P did not dissolve under the investigated conditions of pH and anaerobic state. Al-P and Fe-P dissolved under weak and strong anaerobic conditions alike. The dissolution of precipitated metal phosphate at the sediment-water interface was significant for the liberation of phosphate, some 60% of which was dependent on this liberation process in summer.

Oceanol. Acta, 1987, **10**, 3, 311-321.

RÉSUMÉ

Répartition et dissolution de plusieurs composés du phosphore dans les sédiments marins côtiers

Le phosphore présent dans les sédiments marins côtiers est divisé en 5 formes moléculaires, Sol-P, Al-P, Fe-P, Ca-P et Org-P dont la répartition a été étudiée dans les sédiments de trois régions, Hiuchi Nada, Suho Nada et Beppu Bay, dans la mer intérieure Seto, au Japon. Les effets du pH et des conditions anaérobies sur la dissolution des composés du phosphore ont été étudiés expérimentalement en laboratoire. Le rôle de l'interface eau-sédiment dans la libération des phosphates a été estimé en comparant le flux *in situ* et la valeur calculée du flux de diffusion.

La concentration du principal composé du phosphore, Org-P, ne varie pas avec la profondeur du sédiment, pas plus que celle d'une autre forme majeure du phosphate inorganique, Ca-P. Les concentrations en Al-P et Fe-P diminuent progressivement dans la couche profonde de la colonne sédimentaire. La répartition de plusieurs composés du phosphore diffère dans les sédiments marins côtiers et dans les sédiments océaniques. Les concentrations en T-P, Org-P, Al-P, Fe-P, carbone et azote sont bien corrélées entre elles, mais pas celle de Ca-P. Dans les conditions expérimentales de

pH et d'anaérobie, Org-P n'est pas soluble. Al-P et Fe-P sont solubles dans des conditions d'anaérobie faibles et fortes. La dissolution du phosphate métallique précipité à l'interface eau-sédiment est significative pour la libération du phosphate, dont 60% dépendent de ce phénomène en été.

Oceanol. Acta, 1987, 10, 3, 311-321.

INTRODUCTION

It is well known that phosphate dissolved in water is adsorbed to sediments under aerobic conditions (Jitts, 1959; Krom, Berner, 1980) and that accumulated phosphate in sediments is again released to overlying water under anaerobic conditions (Aller, 1980; Krom, Berner, 1981). Phosphate exchange across the sediment-water interface affects phosphate concentration in overlying fresh water (Mortimer, 1971; Serruya, 1971) and sea water (Joh, 1984). Phosphate liberation from sediments has been studied in the ocean (Manheim, 1976; Froelich *et al.*, 1982), coastal sea (Klump, Martens, 1981; Krom, Berner, 1981; Joh, 1983), estuaries (Pomeroy *et al.*, 1965; Callender, Hammond, 1982) and lakes (Mortimer, 1971; Fillos, Swanson, 1975; Freedman, Canale, 1977; Hosomi *et al.*, 1982; Quigley, Robbins, 1986). Phosphate liberation is particularly important for estuarine and coastal marine environments, where nutrient regeneration in sediments can supply a significant amount of the nutrient required for primary producers in overlying water (Callender, Hammond, 1982). The distribution and behaviour of various forms of phosphorus in freshwater zone sediments have been studied by many researchers. Williams *et al.* (1976), in their study of phosphorus in Lake Erie, divided it into three forms: apatite; non-apatite phosphates; and organic phosphorus. Hosomi *et al.* (1982) distinguished five forms of phosphorus in the sediments of the lake of Kasumigaura: inorganic phosphate adsorbed on clay particles (Ads-P), inorganic phosphates precipitated with aluminium (Al-P), iron (Fe-P); calcium (Ca-P); and organic phosphorus (Org-P). Non-apatite phosphate or Fe-P was found to be a major component of inorganic phosphates in freshwater sediments. More than 50% of the inorganic phosphate in the surface layer of freshwater sediments comprised non-apatite phosphate or Fe-P. According to Lee *et al.* (1976), Lijkleme (1976) and Banoub (1976), phosphate is precipitated with iron in sediments under aerobic conditions, but dissolves under anaerobic conditions. Hosomi *et al.* (1982) also demonstrated that the rate of phosphate liberation depends on the concentration of Fe-P in the sediments. From these results, it was concluded that Fe-P plays an important role in phosphate liberation in the freshwater zone.

Morse and Cook (1978), studying sediments collected from the continental slope off the eastern United States and the central North Atlantic Ocean, divided the phosphorus into three forms by the method of Williams *et al.* (1976), and demonstrated that apatite phosphate is the dominant component in those marine sediments. Joh (1983) also divided phosphorus into five forms in

coastal marine sediments collected from Osaka Bay in the Seto Inland Sea, Japan, in the same manner as Hosomi *et al.* (1982). According to Joh (1983), the percentage composition of inorganic phosphate in coastal marine sediments was different from that in freshwater sediments, and the concentration of Al-P plus Fe-P was related to that of organic materials in the sediments, any increase in the latter being accompanied by an increase in the former. However, only limited information is available regarding the distribution and behaviour of various forms of phosphorus in marine sediments.

The primary purpose of this investigation was to determine the distribution of various forms of phosphorus in coastal marine sediments, and the extent to which this distribution is related to other sediment elements, such as carbon and nitrogen. The dissolution of several forms of phosphorus is also studied experimentally under different conditions of pH and the anaerobic state. Further, the significance of the dissolution of precipitated metal phosphate at the sediment-water interface in the processes of phosphate liberation is considered by comparing phosphate liberation due to Fickian diffusion based on the gradient of phosphate concentration in the interstitial water with *in situ* liberation of phosphate.

MATERIALS AND METHODS

Surveyed area

The surveyed areas were in three regions: the eastern part of Hiuchi Nada; Suho Nada; and Beppu Bay in the Seto Inland Sea, Japan. As shown in Figure 1, depths ranged from 15 to 22 m in the eastern part of Hiuchi Nada and from 8 to 28 m in Suho Nada; depths in Beppu Bay were greater, ranging from 45 to 70 m.

The sediments of the investigated stations were silt-clay. The fraction of particles smaller than 0.063 mm accounted for more than 99% of the sediments at the stations in Beppu Bay and the eastern part of Hiuchi Nada, and more than 80% at the stations in Suho Nada.

Total carbon concentrations in the surface layer (0-1 cm) of the sediment column in Hiuchi Nada, Suho Nada and Beppu Bay ranged from 17.2-19.4 mg g⁻¹, 14.8-19.8 mg g⁻¹ and 25.3-26.4 mg g⁻¹ respectively. The ranges of the total nitrogen concentrations in the surface layer of the sediment in the three regions were 2.0-2.4 mg g⁻¹, 1.5-2.4 mg g⁻¹ and 2.2-3.0 mg g⁻¹, respectively (Yamada, unpublished data).

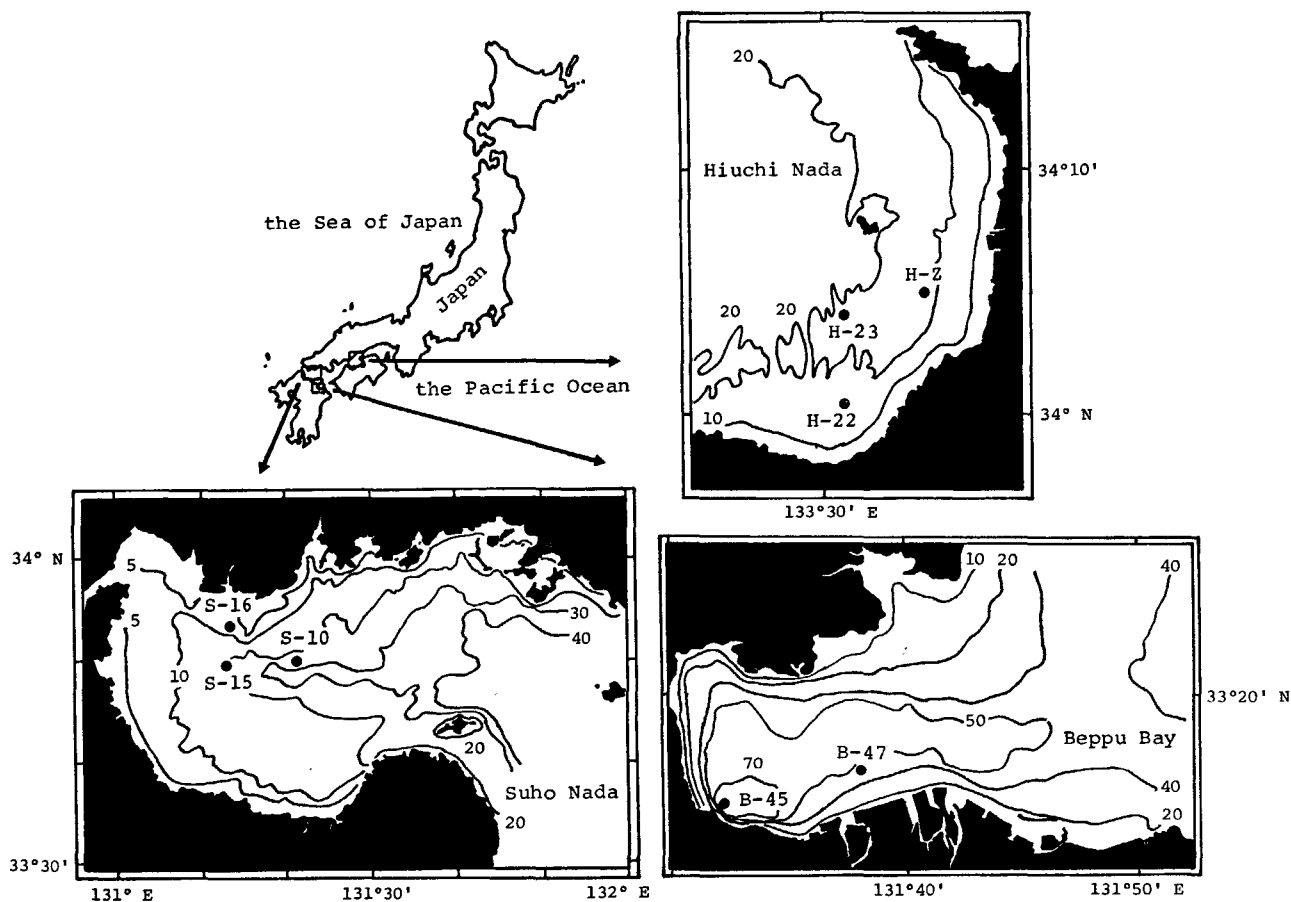


Figure 1
Location of stations and depth distribution in the eastern part of Hiuchi Nada, Suho Nada and Beppu Bay.

Stratification was built up in the shallow layer of the water column (ca. 10 m) during the period from late June to late September. At station B-45 in Beppu Bay, another stratification occurred in the bottom layer of nearly 65 m during the period from June to November. The concentration of dissolved oxygen in the bottom layers at three stations decreased during the warm months, and dissolved oxygen was not recognized in the bottom layer (70 m) of station B-45 in October. The sediment of station B-45 was very anaerobic and the concentration of hydrogen sulphide ranged from 0.55 to 1.21 mg $\text{H}_2\text{S g}^{-1}$ dry sediment. The orthophosphate concentration in the bottom layer (70 m) at station B-45 was especially high in comparison with the other stations during the periods of stratification, amounting to $6.3 \mu\text{mol l}^{-1}$.

Collection of the sediments and the fractionation of phosphorus in sediments

Sediments were collected with a core sampler into a plastic pipe measuring 36 mm in internal diameter. Samplings were carried out on three occasions between August and December 1983 in Beppu Bay; twice, in August 1983 and January 1984, in Hiuchi Nada; and once, in September 1983, in Suho Nada.

As soon as possible, the sediment column was divided from the top, surface to 1 cm, 1 to 2 cm, and every 2 cm to the depth of 14 cm. The interstitial water

was separated by centrifuging the divided sediments at 3,000 rpm (ca., $1,800 \times G$) for 15 min (Kubota Co., Model KCF-62) within 12 hours of sampling, and then stored at -20°C after filtering with a glass fibre filter (Whatman GF/F). The separation of the interstitial water was carried out under N_2 atmosphere. Phosphate in the supernatant fraction was defined as dissolved inorganic phosphate (DIP).

The sediments having been separated the interstitial water was dried at 110°C in an oven. Inorganic phosphate adsorbed (Ads-P) or precipitated on the sediments was fractionated with 1 N NH_4Cl , 0.5 N NH_4F , 0.5 N NaOH and 0.5 N H_2SO_4 , and defined as Ads-P, Al-P, Fe-P and Ca-P, respectively, using the procedure of Chang and Jackson (1957) and Hosomi *et al.* (1982) as shown in Figure 2. Phosphate extracted from 0.5 g of sediment sample by shaking with 20 ml of 1 N HCl for 24 hours at room temperature was defined as total inorganic phosphate (TIP) in sediments. A comparison between the concentration of TIP and the sum of the concentrations of Ads-P, Al-P, Fe-P and Ca-P in the sediment samples from the three surveyed areas is presented in Table 1. Although the sum of fractionated inorganic phosphates was less than the concentration of TIP, the difference was less than 10%.

Dried sediment (0.1 g) was digested with 10 ml of 10 N H_2SO_4 in a kjeldahl flask for 24 hours. Total phosphorus (T-P) in the sediment was determined by measuring

Table 1
Comparison of inorganic phosphorus concentrations.

Sample No.	Inorganic phosphorus ($\mu\text{g g}^{-1}$)		Difference between A and B ($\mu\text{g g}^{-1}$)	Percentage error of phosphorus content (%) ^{*3}
	A ^{*1}	B ^{*2}		
1	419.97	449.49	29.52	6.6
2	371.73	405.47	33.74	8.3
3	375.85	387.79	11.94	3.1
4	444.45	463.34	18.89	4.1
5	335.42	362.62	27.20	7.5
6	332.90	342.72	9.82	2.9
7	306.45	309.72	3.27	1.1
8	310.74	326.72	15.98	4.9
9	305.25	318.20	12.95	4.1
10	303.33	307.35	4.02	1.3
11	335.91	362.76	26.85	7.4
12	335.71	347.82	12.11	3.5
13	340.13	377.60	37.47	9.9
14	341.30	349.63	8.33	2.4
15	363.41	364.33	0.92	0.3

*1: Sum of phosphorus extracted with 1N NH_4Cl , 0.5N NH_4F , 0.5N NaOH and 0.5N H_2SO_4 .

*2: Phosphorus extracted with 1N HCl .

*3: $(B-A)/B \times 100$.

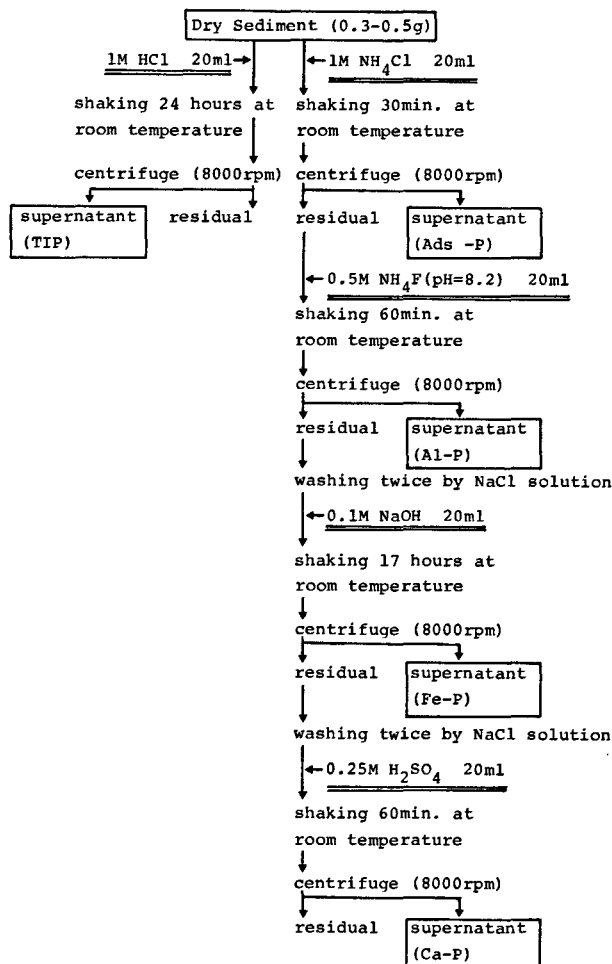


Figure 2
Flow diagram for the sequential extraction of various forms of phosphorus in sediments.

the concentration of phosphate in the digested materials. The concentration of Org-P was determined by subtracting the sum of Ads-P, Al-P, Fe-P and Ca-P from T-P.

The various forms of phosphorous in the sediments were classified in six fractions: DIP, Ads-P, Al-P, Fe-P, Ca-P, and Org-P. The summation of DIP and Ads-P was expressed as soluble inorganic phosphate (Sol-P), and total inorganic phosphate in the sediments was expressed as the sum of Sol-P, Al-P, Fe-P and Ca-P.

Determination of phosphate liberation from sediments

The liberation rate of phosphate was determined at station H-Z in Hiuchi Nada by using the *in situ* chamber method according to Sonzogni *et al.* (1971). The apparatus used for the phosphate liberation consisted of a nutrient trap and reference bag. The sea water in the reference bag did not enter into contact with the sediments, while that in the nutrient trap did; both waters were sampled through a polyethylene tube with a large glass syringe once a day. The sea water samples were filtered by a glass fibre filter (Whatman GF/C) and stored at -20°C . The difference between the rates of increase of phosphate in the samples of the nutrient trap and the reference bag provides the liberation rate of phosphate.

Factors affecting the dissolution of the various forms of phosphorus

The factors affecting the dissolution of the various forms of phosphorous were studied by modifying the anaerobic condition and pH. Sediments and sea water used in the experiments were obtained at the pier of the Nansei Regional Fisheries Research Laboratory, Hiroshima Prefecture. Wet sediment (0.5 g) was placed in a 100 ml BOD bottle. One group of bottles was filled with sea water, from which dissolved oxygen was excluded by bubbling nitrogen gas after filtration with glass fibre filter (Whatman GF/C). Another group of bottles was filled with sea water containing 0.01% sucrose after filtration and exclusion of dissolved oxygen.

Five bottles were used for each incubation period. The bottles of the two groups were incubated at 25°C for 5, 10, 15 and 20 days in an incubator. After 20 days incubation, the bottles were unsealed and oxygen gas was bubbled once a day into the bottles until day 29. After incubation, pH and dissolved oxygen in sea water were measured. The sea water was separated from the sediments by centrifuging for 15 min at 3,000 rpm (ca., $1,800 \times G$). The different forms of phosphorus in the sediments were fractionated in the manner described above; phosphate in the sea water and fractionated phosphorus were then determined.

An experiment was carried out to determine the dissolved fraction of several forms of phosphorus under different conditions of pH. One gram of the sediment obtained from the coast near the Nansei Regional Fisheries Research Laboratory was mixed with buffer solutions in a BOD bottle for 24 hours at room temperature. After mixing, the buffer solution was decanted. The various forms of phosphorus in the residual sediments were fractionated as described above. Buffer solutions of pH 5.0, 6.0 and 6.7 were prepared by using 0.1 M sodium citrate and 0.1 M sodium hydroxide.

Buffer solutions of pH 8.0 and 9.0 were also prepared as follows: 4.0 and 21.4 ml of 0.2 M sodium hydroxide were added to 50 ml containing 0.2 M boric acid and 0.2 M potassium chloride respectively, the solutions then being diluted to 200 ml with distilled water.

Analytical procedure

Phosphate in sea water and interstitial water was determined spectrophotometrically using the ascorbic acid-molybdenum blue method (Koroleff, 1976). Interstitial water was diluted as appropriate with artificial sea water (25 g NaCl and 8 g MgSO₄ per litre of redistilled water) before the determination.

Measurement of Ads-P, Al-P, Fe-P, Ca-P, T-P and TIP in sediment was carried out by the ascorbic acid-molybdenum blue method. Before the determination, the extracted sample solutions were diluted with redistilled water; the pH of the solution was neutralized with 1 N NaOH and/or 1 N H₂SO₄. For the determination of Ads-P, Al-P, Fe-P, Ca-P, T-P and TIP, optimum analytical conditions for the practical sample were established; a calibration curve was prepared by standard phosphate solution under the same conditions and was used for determination of the practical sample.

Total carbon and total nitrogen were determined by a CHN Corder (Yanagimoto Co., Model MT-3, Kyoto, Japan). Sulphide in the sediments was determined by using a Gastec detector tube (Kitazawa Sangyo Co., Tokyo, Japan), in which lead acetate coated on silica gel of supporting materials was contained as a reactor. Sulphide concentration was determined by the length of the tube blackened by hydrogen sulphide (Arakawa, 1980).

RESULTS AND DISCUSSION

Distribution of fractionated phosphorus in the sediments

The vertical distributions of the fractionated phosphorus in Hiuchi Nada, Suho Nada and Beppu Bay are shown in Figures 3, 4 and 5. The concentration of T-P in sediments at all stations decreased gradually with

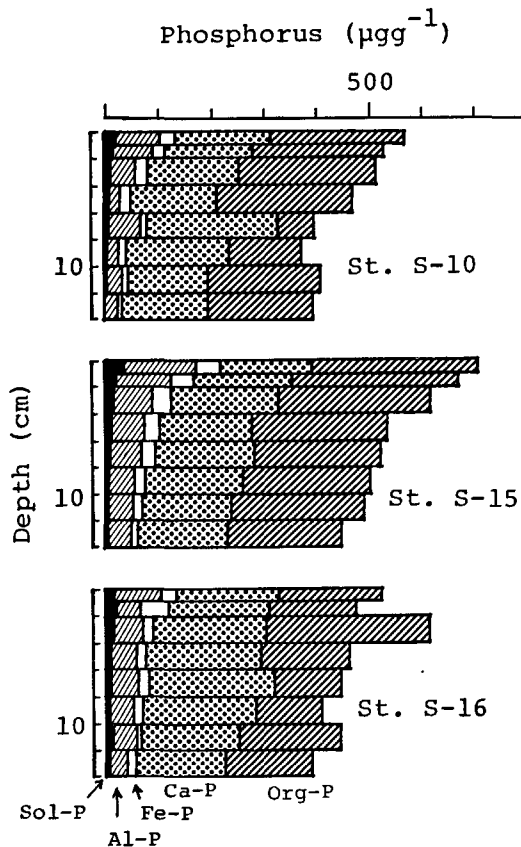


Figure 4
Vertical distribution of phosphorus forms in sediment at stations S-10, S-15 and S-16.

increased depth in the sediment column; the results were same as those described by Williams *et al.* (1976) and Hosomi *et al.* (1982) for freshwater, and Joh (1983) for seawater regions. In descending order of importance, T-P concentration in the surface sediments amounted to 770-1005 µg.g⁻¹, 644-704 µg.g⁻¹ and 525-709 µg.g⁻¹ in Beppu Bay, Hiuchi Nada and Suho Nada, respectively.

Almost 40-50% of T-P were in the form of Org-P, which comprised a major constituent in the sediments as shown in Figures 3, 4 and 5. Vertical change of

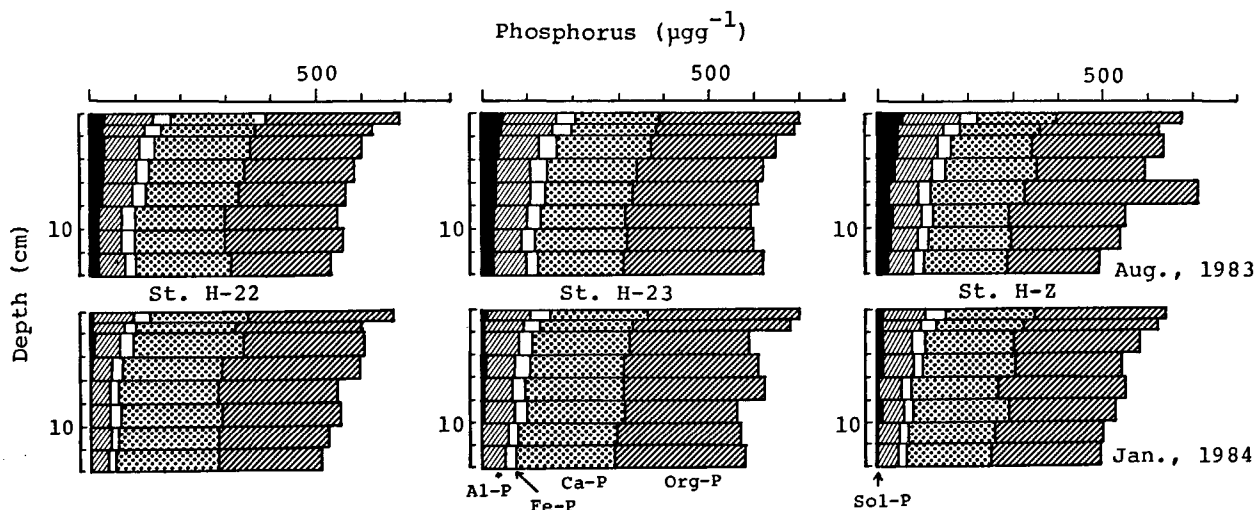


Figure 3: Vertical distribution of phosphorus forms in sediment at stations H-22, H-23 and H-Z.

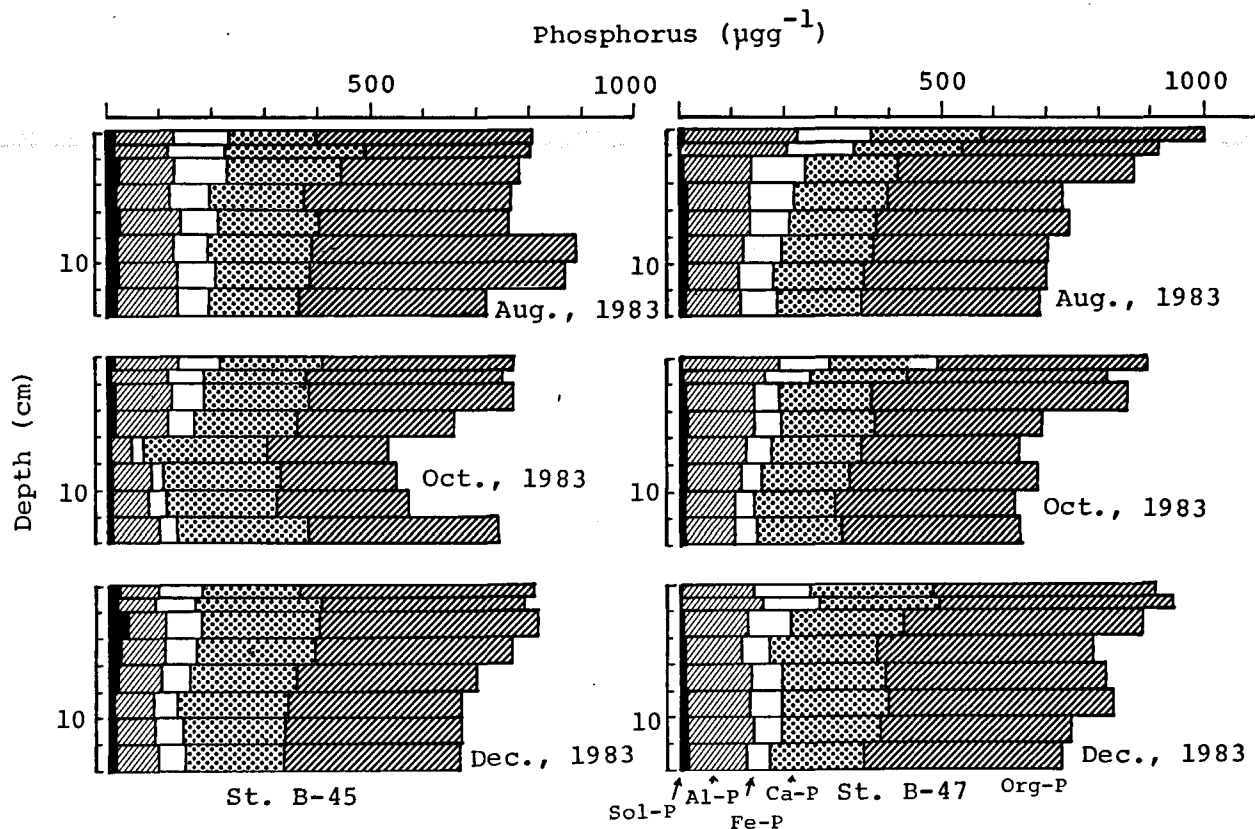


Figure 5: Vertical distribution of phosphorus forms in sediment at stations B-45 and B-47.

Org-P concentration was not observed. It was concluded from these results that Org-P was not easily decomposed by bacteria in the sediment and might be fairly stable compound. The secondary major component of phosphorus in the sediment was Ca-P, followed by Al-P, amounting to 20-37% and 9-21% of T-P, respectively. The concentration of Fe-P in the sediments of Beppu Bay was not as low (11-15% of T-P) as those in the sediments of Hiuchi Nada and Suho Nada (5-7% of T-P). According to Morse and Cook (1978), Org-P amounted to 4-13% of T-P in ocean sediments, and to 35% of T-P in sediments of the continental slope. On the other hand, apatite-P accounted for 44-68% of T-P in these sediments. Therefore, it was obvious that inorganic phosphate formed a major component of these oceanic sediments. The composition of phosphorus in the coastal marine sediments differed from that in the oceanic sediments, and the former contained a considerable amount of Org-P. Sol-P concentration in all sediments was generally low (8% of T-P), although the fraction was observed to increase during the warm months when the sediment became more anaerobic with decreasing dissolved oxygen in the overlying water. In August, Sol-P (5-8% of T-P) was comparable to Fe-P (6% of T-P) in the sediment of Hiuchi Nada.

Al-P and Fe-P concentrations decreased gradually in the deeper layer of the sediment column. The vertical distribution of Ca-P in the sediments was somewhat different from those of Al-P and Fe-P. The concentra-

tion of Ca-P did not change remarkably in the deeper of the sediment column.

The percentage composition of inorganic phosphorus at various stations in Hiuchi Nada is shown in Figure 6. Ca-P was the major component of inorganic phosphate accounting for more than 50%. Since the concentrations of Al-P and Fe-P decreased with increasing depth in the sediment column, and since the concentration of Ca-P did not change remarkably in the deeper strata as shown in Figures 3, 4 and 5, the percentage of Ca-P to inorganic phosphorus showed a consequent increase in the deeper strata. This tendency was the same as that reported by Joh (1983) in Osaka Bay in the Seto Inland Sea, Japan. Sol-P was recognized as a minor constituent and this fraction increased in warm months at the stations in Hiuchi Nada. The percentage of Sol-P at station B-45 was larger than at station B-47.

The Sol-P fraction must therefore have increased in the anaerobic sediments, the precipitated metal phosphate dissolving under anaerobic conditions.

Mutual relationships between forms of phosphorus, carbon and nitrogen in sediments

Relationships between various forms of phosphorus and organic materials in sediments were studied by simple correlation analysis; the results are shown in Table 2. T-P concentration was related to the concentrations of carbon and nitrogen in sediments. The

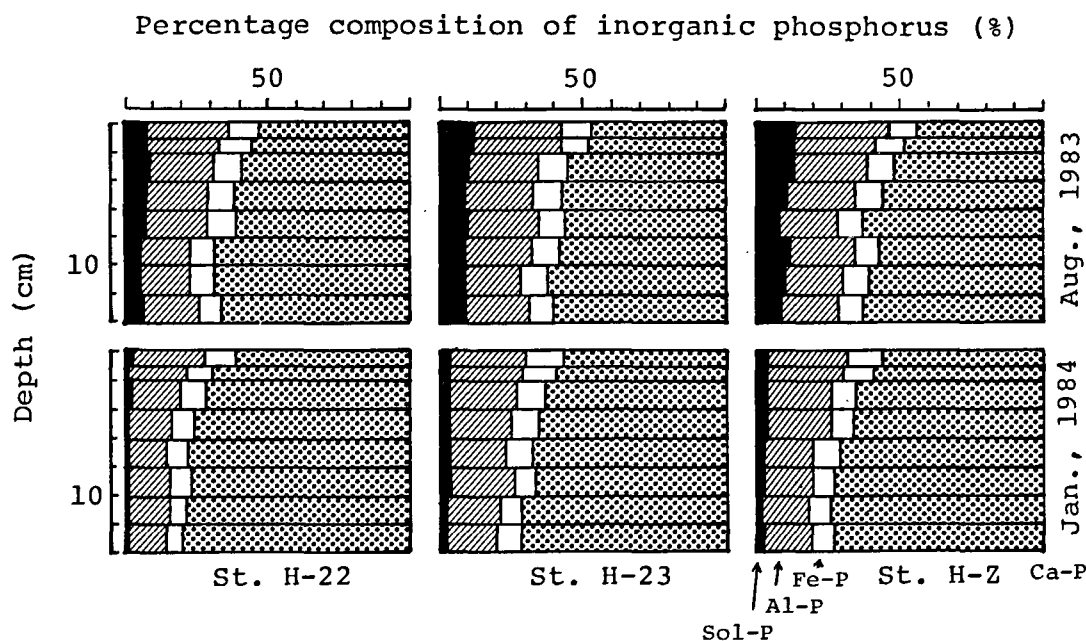


Figure 6: Vertical distribution of the percentage of Sol-P, Al-P, Fe-P and Ca-P to inorganic phosphorus in the sediment of Hiuchi Nada.

concentration of Org-P was also closely to T-P, carbon and nitrogen concentrations, and Org-P in the sediments increased with the increase of carbon and nitrogen.

The conclusion was thus drawn that the phosphorus in sediments of these coastal areas was supplied by the deposition of suspended materials containing phosphorus, carbon and nitrogen.

As regards the relationships between Al-P, Fe-P, Ca-P, carbon and nitrogen, the concentrations of Fe-P and Al-P but not of Ca-P were proportionally related to carbon, nitrogen and T-P. Precipitated metal phosphates such as Fe-P and Al-P were high in sediments containing considerable amounts of carbon and nitrogen, although the concentration of Ca-P did not necessarily increase in company with carbon, nitrogen and T-P. It is obvious from the results shown in Table 2 that the percentage of Ca-P to inorganic phosphorus correlated with the concentrations of Fe-P, Al-P, Org-

P, T-P, carbon and nitrogen, and decreased in sediments containing large amounts of Fe-P, Al-P, Org-P, T-P, carbon and nitrogen. From the findings that Fe-P and Al-P concentrations were high in sediments containing considerable amounts of carbon and nitrogen and that the concentration of Ca-P was not related to carbon and nitrogen, it was concluded that the percentage of Ca-P to inorganic phosphorus decreased in sediments rich in carbon and nitrogen. From the results of simple correlation analysis, it is considered that the behaviour of Ca-P is different from that of Fe-P and Al-P in sediments.

Dissolution of several forms of phosphorus

The effect on dissolution of phosphorus was studied experimentally by varying the factors of pH and the anaerobic state.

Table 2
Results of simple correlation analysis.

Fe-P ($\mu\text{g g}^{-1}$)	Al-P ($\mu\text{g g}^{-1}$)	Al-P + Fe-P ($\mu\text{g g}^{-1}$)	Ca-P		Org-P ($\mu\text{g g}^{-1}$)	T-P ($\mu\text{g g}^{-1}$)	C (mg g^{-1})	N (mg g^{-1})
			($\mu\text{g g}^{-1}$)	(%) ^{*1}				
Fe-P	0.83	0.94	0.48	-0.79	0.81	0.90	0.84	0.75
	Al-P	0.79	0.09	-0.89	0.70	0.88	0.72	0.72
		Al-P+Fe-P	0.08	-0.86	0.78	0.93	0.84	0.77
			Ca-P	0.19	0.11	0.25	0.14	-0.06
				Ca-P	-0.71	-0.82	-0.74	-0.83
					Org-P	0.93	0.84	0.70
						T-P	0.86	0.77
							C	0.79
								N

*1: Percentage of Ca-P to inorganic phosphorus.

The dissolution of phosphorus in relation to pH is shown in Figure 7. Although the fraction of Org-P was independent of pH, those of Al-P, Fe-P and Ca-P decreased with the lowering of pH towards acidic conditions. The Al-P and Fe-P fractions decreased slightly in the range of pH 8 to 9. It was recognized from these results that phosphate was mainly dissolved from precipitated metal phosphate and that dissolution was lowest under condition of neutral pH.

The influence of anaerobic state on the dissolution of precipitated inorganic phosphorus is shown in Figure 8. Weak and strong anaerobic states were prepared in the laboratory: sucrose was added to sea water to create a strong anaerobic state. The dissolved oxygen in sea water containing sucrose decreased more remarkably than that in the sea water without sucrose, reaching zero during the anaerobic incubation period of 5 to 20 days. In the sea water containing sucrose, pH decreased from 8.2 to 7.0 during the initial 5 days, 7.0 to 7.2 being maintained during the further incubation period of 5 to 29 days. In the sea water without sucrose, pH did not remarkably change, remaining steady at 8.0 to 8.2.

Since Org-P concentration in the sediments did not change in either of the experiments, Org-P was supposed not to decompose during the incubation period. Although the amount of total inorganic phosphorus (sum of Sol-P, Al-P, Fe-P and Ca-P) was nearly constant in both experiments, the individual percentages of the fractionated phosphorus changed. The percentage of Sol-P increased, while those of Al-P and Fe-P decreased, during the anaerobic incubation period. Joh (1983) studied the forms of phosphorus liberated under anaerobic conditions, and recognized that Al-P and Fe-P dissolved under anaerobic conditions of 0.17 to 0.27 O₂ ml.l⁻¹. The present study was coincident with Joh's results. Several forms of precipitated metal phosphate were dissolved by organic acid produced by bacteria (Harrison *et al.*, 1972). The percentage of Ca-P decreased in the experiment containing sucrose, but did not change to such an extent in the experiment without sucrose. The influence on the dissolution of Ca-P of organic acid produced by bacteria from sucrose should be studied to elucidate further the behaviour of Ca-P under anaerobic conditions.

Significance of the dissolution of precipitated metal phosphate at the sediment-water interface

Phosphorus-liberation from sediments to overlying water depends on the process of diffusion based on the difference of phosphate concentration between overlying water and interstitial water (Aller, 1980; Krom, Berner, 1981; Klump, Martens, 1981; Callender, Hammond, 1982), while phosphate is released to the overlying water by the dissolution of precipitated metal phosphate at the sediment-water interface. It is important to estimate these two processes affecting phosphate liberation separately. The liberation rate of phosphate and the profile of phosphate concentration in the interstitial water were determined at St. H-Z in Hiuchi Nada in August 1983, when the sediment temperature

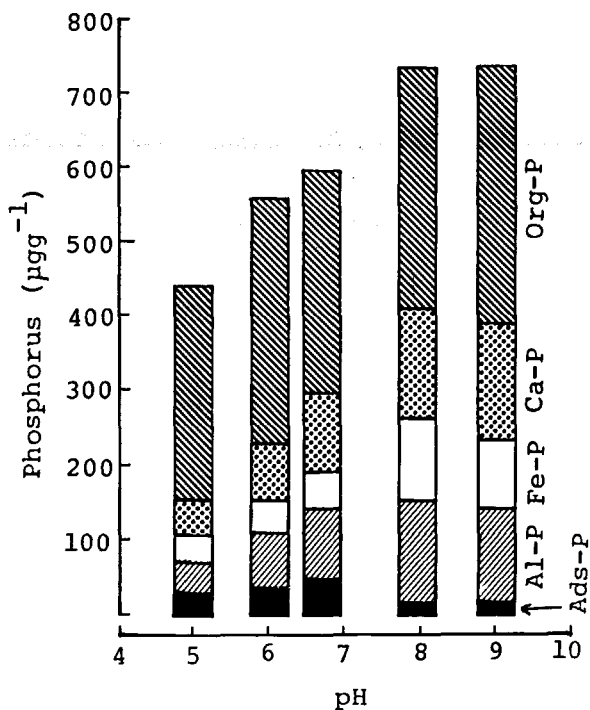


Figure 7
Dissolution of phosphorus in relation to pH.

was 25°C. The results are shown in Table 3. Following the argument of Kester and Pytkowicz (1967) that most of dissolved inorganic phosphate exists as HPO₄²⁻, calculations were carried out on HPO₄²⁻.

According to Li and Gregory (1974), the diffusion coefficient of phosphate ions in free solution (Do) is related to temperature, the relationships being shown as follows:

$$D_o(\text{HPO}_4^{2-}) = 7.34 + 0.16(T - 25^\circ\text{C}) \times 10^{-6} \quad (1)$$

The diffusion coefficient in sediment (Ds) is related to porosity, and Ds is estimated from Do by the following equation (Ullman, Aller, 1982):

$$D_s = \theta^2 D_o, \quad (2)$$

where θ is the porosity of the sediment.

From the above relationships, Do of HPO₄²⁻ at 25°C was determined as $7.34 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$. According to equation (2), Ds in the sediment of Hiuchi Nada in August 1983 was determined as $6.08 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ from Do.

The liberation rate of phosphate by diffusion (J_{id}) was estimated by Fick's first law.

$$J_{id} = -D_s \theta (dC/dz). \quad (3)$$

The diffusive flux of phosphate across the sediment-water interface was calculated by using the values of Ds, θ and dC/dz , and found to be $2.16 \times 10^{-6} \mu\text{g cm}^{-2} \cdot \text{s}^{-1}$. The liberation rate of phosphate, using the nutrient trap (J_{it}), was found to be $5.56 \times 10^{-6} \mu\text{g}$

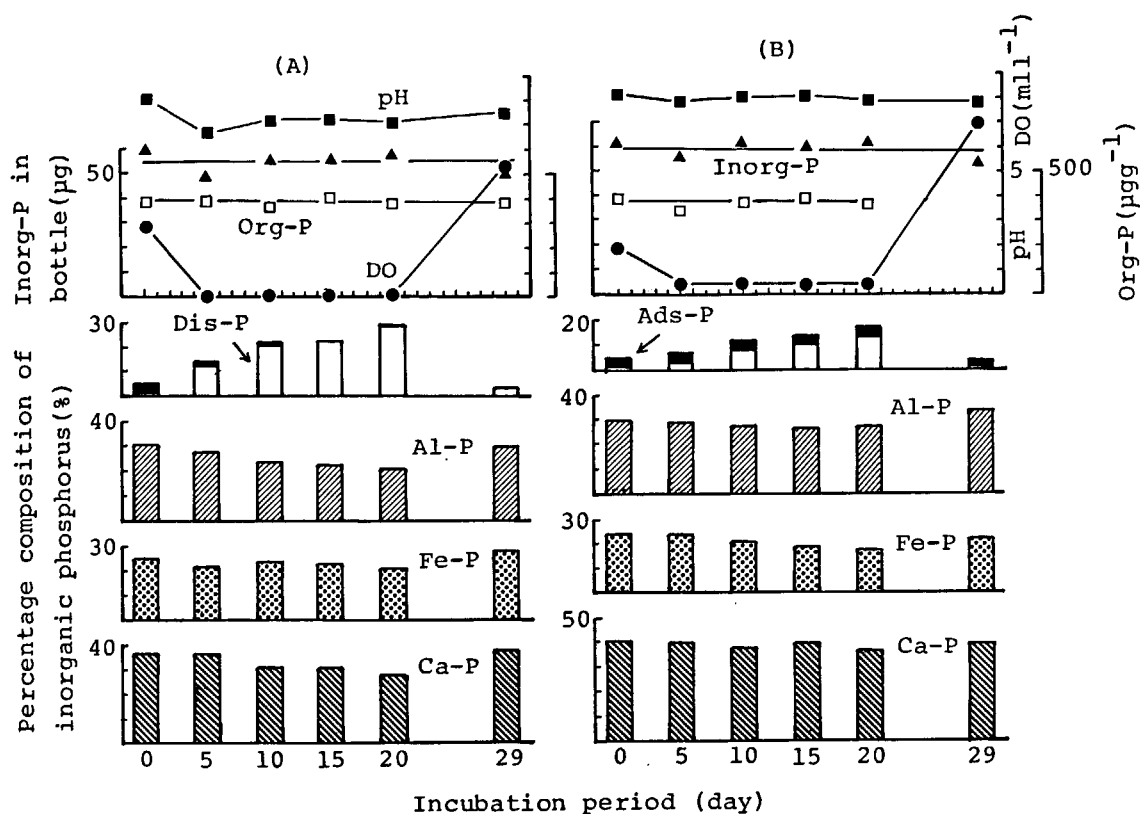


Figure 8: Dissolution of precipitated inorganic phosphorus in relation to anaerobic intensity. A) strong anaerobic condition; B) weak anaerobic condition.

$\text{cm}^{-2} \cdot \text{s}^{-1}$ at station H-Z in August. The diffusive flux across the sediment-water interface was determined as 38.8% of the phosphate liberation of $5.56 \times 10^{-6} \mu\text{g cm}^{-2} \cdot \text{s}^{-1}$ obtained from the measurement of the nutrient trap.

The difference between *in situ* flux (*Jit*) and calculated diffusive flux (*Jid*) in phosphate liberation was also recognized by Klump and Martens (1981) in sediments of Cape Lookout Bight, and by Callender and Hammond (1982) in sediments of the Potomac River Estuary. Aller (1980) also determined *in situ* and diffusive fluxes of phosphate in the sediments of Long Island Sound. According to his results, it was obvious that the *in situ* flux of phosphate was 1.4-1.9 times larger than the diffusive flux of phosphate in summer. The *in situ* liberation of phosphate depends not only on the diffusive flux but also on macrofaunal irrigation, gas bubble ebullition and the direct dissolution of precipitated metal phosphate at the sediment-water interface.

The increased amount of phosphate in the nutrient trap over a period of 5 days was calculated at $6000 \mu\text{g}$ by using $5.56 \times 10^{-6} \mu\text{g cm}^{-2} \cdot \text{s}^{-1}$. As the surface area of the sediment covered by the nutrient trap was 0.25 m^2 , the diffusive flux across the sediment-water interface during that period was estimated at $2332 \mu\text{g}$ by using the diffusive flux of $2.16 \times 10^{-6} \mu\text{g cm}^{-2} \cdot \text{s}^{-1}$. If the difference between the increased amount of phosphate

in the nutrient trap during 5 days ($6000 \mu\text{g}$) and the diffusive flux ($2332 \mu\text{g}$) is due to dissolution of the precipitated metal phosphate (Fe-P plus Al-P) in the surface of sediment within the nutrient trap, the depth (*z*) of the surface sediment for dissolution may be estimated by using the following mass balance equation of phosphate between the overlying water and sediments in the nutrient trap.

$$z = (Jit - Jid) / \rho \cdot (1 - \theta) \times A \cdot (Al-P + Fe-P),$$

where *Jit*-*Jid* is the increased amount of phosphate in the nutrient trap by dissolution of precipitated metal phosphate, ρ is the density of the sediment particle, θ is the porosity of the sediments, *A* is the area of the sediments covered by the nutrient trap, and Al-P plus Fe-P is the concentration of precipitated metal phosphate available for dissolution in the sediments. Since the dissolved oxygen concentration was of the order of $1.0 \text{ ml} \cdot \text{l}^{-1}$ in the water of nutrient trap, it was considered that Ca-P was not available for dissolution in the sediments. The values used for calculation are presented in Table 3. As a result, it was recognized that Al-P and Fe-P in the top 0.4 mm of the sediment column were released to overlying water during the 5-day experiment using the nutrient trap. Thus, the dissolution

Table 3

Results of phosphate liberation rate and characteristics of sediment at station H-Z.

Liberation rate by nutrient trap (J _{it}) (μgcm ⁻² s ⁻¹)	Liberation rate by diffusion (J _{id}) (μgcm ⁻² s ⁻¹)	Concentration gradient (dC/dz) (μgml ⁻¹ cm ⁻¹)	Porosity* ¹ (θ)	Diffusion coefficient (D _s) (cm ² s ⁻¹)	Density* ² (ρ) (gcm ⁻³)	Concentration of Al-P+Fe-P (μgg ⁻¹)	Area covered by nutrient trap (A) (m ²)
5.56 × 10 ⁻⁶	2.16 × 10 ⁻⁶	3.91 × 10 ⁻¹	0.91	6.08 × 10 ⁻⁶	2.645	154.14	0.25

*¹: Porosity was determined by applying the data of water amount, densities of interstitial water (1.024) and sediment particle (2.645) at the surface of sediments in the following equation; $\theta = (\alpha/\rho_w)/((1-\alpha)/\rho_s + \alpha/\rho_w)$ where α is water amount in sediments, ρ_w and ρ_s is density of interstitial water and sediment particle, respectively.

*²: Density was determined by a pycnometer at the surface layer of sediments.

process of the precipitated metal phosphate at the sediment-water interface is important for the liberation of phosphate from the sediments during the warm months when oxygen concentration decreases in the bottom layer of the water column.

CONCLUSIONS

1) T-P concentration was highest in Beppu Bay, followed by Hiuchi Nada and Suho Nada, and decreased gradually with increasing depth in the sediment column. Almost 40-50% of T-P comprised Org-P, which was a major constituent in the sediments; and the vertical distribution of Org-P did not markedly change. Ca-P was the major component of the inorganic phosphorus in the sediments, the second being Al-P. Al-P and Fe-P concentration decreased gradually in the deeper layer of the sediment column, whereas that of Ca-P did not. The distribution of the various forms of phosphorus in coastal marine sediments was found to be different from that in oceanic sediments.

2) T-P, the fractions of Org-P, Al-P and Fe-P, carbon and nitrogen were correlated to each other, but Ca-P was independent of these elements. The findings indicated that the distribution of Ca-P in sediment was determined different by from that of Al-P, Fe-P and Org-P.

3) The dissolution of precipitated metal phosphate was influenced by pH and the degree of anaerobic state of the sediment; Org-P did not dissolve under the investigated conditions of pH and anaerobic state. Al-P and Fe-P dissolved under weak and strong anaerobic conditions alike.

4) The dissolution of precipitated metal phosphate at the sediment-water interface was important for phosphate liberation from sediments. It was found from the results obtained at station H-Z in August that some 60% of the phosphate liberation depended on the dissolution of precipitated metal phosphate at the sediment-water interface.

Acknowledgements

The authors are grateful to Dr. H.J. Ceccaldi (Endoume Marine Institute, Centre of Oceanography of Marseilles), Prof. Dr. Hiroshi Sunahara (Faculty of Engineering, Hiroshima University) and Dr. Yoshihiro Satomi (Water Pollution Division, Tokai regional Fisheries Research Laboratory) for their helpful advice and critical reading of this paper. Grateful acknowledgement is made to the crew of the research vessel "Shirafuji Maru" (Nansei Regional Fisheries Research Laboratory) for assistance in obtaining the sediment samples.

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