Journal of Hydroscience and Hydraulic Engineering
Vol. 24, No.1 May, 2006, 11-22

EFFECTS OF SUSPENDED SEDIMENTS ON THE BEHAVIOR OF DISSOLVED PHOSPHATE IN THE SEA OFF THE ISHIKARI RIVER MOUTH

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SYNOPSIS

Field observations were carried out to investigate the effects of suspended sediments on dissolved phosphate concentration in the sea near the Ishikari River mouth during the 2004 snowmelt season. Suspended sediments were sampled during the snowmelt runoff at Sapporo-Ohhashi Bridge at the same time water quality was observed in the sea off the river mouth. The combined forms of phosphorus in the sediment were analyzed, and mixing experiments were conducted to examine how the release of phosphate was changed by salinity and pH. Adsorption/desorption process on surface of suspended sediment, which has fast kinetics, is assumed to behave in accordance with Langmuir adsorption isotherm for each condition of salinity and pH. We were able to quantitatively evaluate the input of phosphate to the estuarine water and calculate the dissolved phosphate concentration during the snowmelt runoff.

INTRODUCTION

Fluvial suspended sediments transport much of phosphate to the sea during floods (see Yamashita et.al (8)), therefore, the dissolved phosphate concentration of seawater near the river mouth is significantly influenced by the adsorption/desorption characteristics of suspended sediments. The behavior of desorbed phosphate with fluvial inorganic suspended sediments involves two-step process (see Floelich(3)). The first step, adsorption/desorption on surfaces, has fast kinetics (minutes–hours). The second step, solid-state diffusion of adsorption adsorbed phosphate from the surface into the interior of particles, has slow kinetics (days-months). It is necessary to consider the two-step process for long term release of phosphate from fluvial inorganic suspended sediments. Quantities of the total release of inorganic phosphorus are estimated by comparing fluvial suspended sediments with bottom materials in the estuary (see e.g. Tanaka(6) and Yamazaki and Yamashita(9)). Fox et al. (2) investigated the chemical control of soluble phosphate in the Amazon estuary. The soluble inorganic phosphorous of salinity measured in the estuary was consistently above the conservative mixing value. They developed a one-dimensional dispersion model incorporating input rates derived from the laboratory mixing experiments, assuming that 0.5 g/l of estuarine sediment is resuspended at fixed intervals. Their model predicts that desorption of phosphate from suspended particles within the Amazonian salinity gradient produces an estuarine phosphate input flux. Field observations were carried out to investigate the effects of suspended sediment on dissolved phosphate concentration in the sea near the Ishikari River mouth during the 2004 snowmelt season. The Ishikari River estuary is not as turbid as the Amazon estuary, and much of fluvial suspended sediments discharged during floods from Ishikari River. It is necessary to consider the adsorption/desorption process during flood in the estuary. In the estuary river water remains in a thin layer from the surface and is mixed gradually with sea water offshore, and the salinity remains low in a thin layer and rapidly increases toward the bottom. Fluvial suspended sediments aggregate and precipitate as the river water is mixed with sea water in the estuary. Fluvial suspended sediment concentration is high at the surface and decreases rapidly toward the bottom. The settling time of the fluvial suspended sediments to the bottom lasts one or two days, so it is possible to educe that reaction of desorbed phosphate with fluvial suspended particles occurs on the surface, and that reaction is expected to follow the Langmuir adsorption isotherm. To evaluate quantitatively the input of phosphate to the estuarine water, it is necessary to clarify the relationship between adsorption/desorption characteristics and water quality parameters such as salinity and pH. This paper examines the phosphate adsorption/desorption phenomenon occurring in the Ishikari River estuary during snowmelt runoff by using field data and laboratory experiments with the fluvial suspended sediment.

FIELD SURVEY

Study Area

On April 21, 2004, water was sampled at Sapporo-Ohhashi Bridge, 14 km upstream from the river mouth, during the peak of snowmelt runoff (discharge of approx. 2,000 m^3/s) (see Fig. 1). Approximately 2 m^3 of water was collected from near the surface using a pump (Tsurumi Manufacturing. Co., Ltd., LB3-750) and was centrifuged to separate suspended sediments. The separated sediment was dried by using a freeze-dryer and was stored at a low temperature. On April 22, immediately after the snowmelt runoff discharge peaked, water was sampled from 1 m below the surface and from the intermediate depth at seven points in the sea 1, 2, 3, 4, 5, 7.5, and 10 km from the river mouth. The water samples were analyzed for SS, pH, salinity, T-P, D-T-P, D-PO_4-P, PO_4-P, chl-a, and pheophytin. Bed materials in the Ishikari River were sampled on August 25th and 26th in the river mouth (0.1 km upstream of the river mouth) and at Ishikari-Kakokyo Bridge (5.5 km upstream of the mouth), Sapporo-Ohhashi Bridge, Ishikari-Ohhashi Bridge (26.6 km) and Iwamizawa-Ohhashi Bridge (44.5 km), illustrated in Fig.1.

Analytical Methods

Salinity was measured by using a salinometer (The Tsurumi Seiki Co., Ltd., DIGI-AUTO MODEL-5), and pH was measured by using a pH meter with a glass electrode (DKK-TOD Co., Ltd., WM-50EG). Desorbed phosphate was determined by the widely-adopted molybdenum method, after samples were filtered through Membrane Filter (Type 0.45μm HA, Millipore Corporation) (see Japan Industrial Standards Committee(4)). Phosphorus contents in

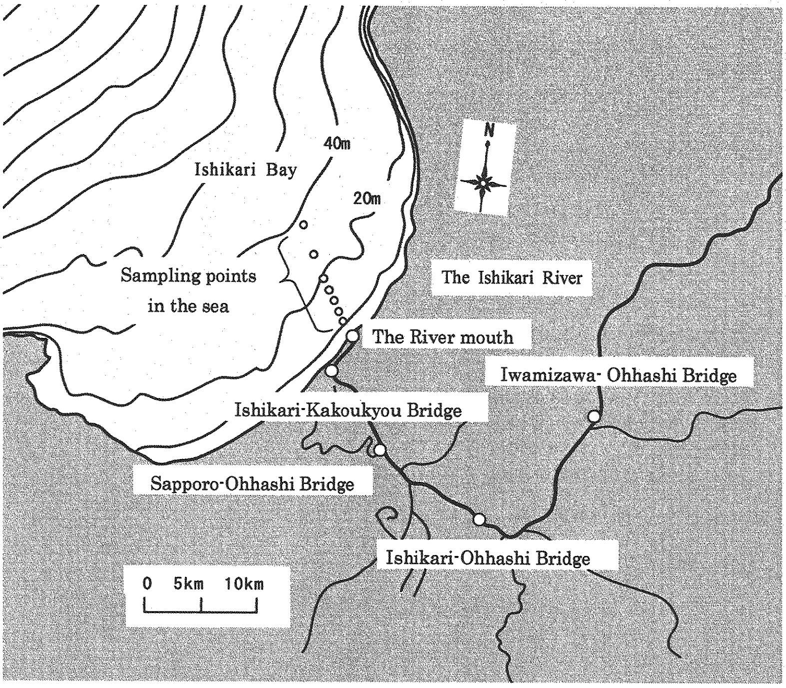

Fig.1 Sampling points in the sea and the Ishikari River

fluvial suspended sediments and bed materials in the river and the sea were determined according to the scheme of Williams et al (10). Phosphorous was divided into four forms: CDB-P (citrate-dithionite-bicarbonate-extractable phosphorous), HCl-P (1N-HCl-extractable phosphorous), NaOH-P (1N-NaOH-extractable phosphorous), and Org-P (Organic phosphorous). Tanaka (7) examined the phosphorous forms using the scheme in the suspended matters in several major rivers in Japan, during high flow stages, and reported that CDB-P load from soil substances discharged during the high flow stages was thought to be the main source of phosphate eluted from the marine sediments. Tanaka also divided CDB-P into two fractions, which were extracted by a seawater extraction technique under aerobic conditions (ads-P) and desorbed under anaerobic conditions. The schemes of Williams et al. and Tanaka are satisfactory for examining the problems of release of phosphate from suspended sediments.

Results of Field Survey

Fig. 2 shows the salinity measured at several specific locations in the sea illustrated in Fig.1, using an immersion water-quality measuring instrument (Alec Electronics Co., Ltd., ACL208-PDK). River water remained in a layer within approximately 2 m from the sea surface, and the salinity rapidly increased toward the bottom. Water quality analysis conducted at Sapporo-Ohhashi Bridge and in the sea are shown in Fig.3. The SS concentration at Sapporo-Ohhashi Bridge was 350 mg/l. However, the SS concentration was only 70 mg/l at the 1km point, suggesting that SS aggregated and precipitated near the river mouth where river water was mixed with seawater. The SS concentration at the intermediate depth was lower than that at the surface, and was approximately 20 mg/l even at the 1km point. The salinity at the 1m depth increased rapidly to 11.7 psu at 1km point, and the rate of salinity increase was gentle offshore. The salinity at the 1m depth was about 18.5 psu at the 10km point. The salinity at the intermediate depth, however, exceeded 32.9 psu, indicating a low mixture rate of river water at that depth even at

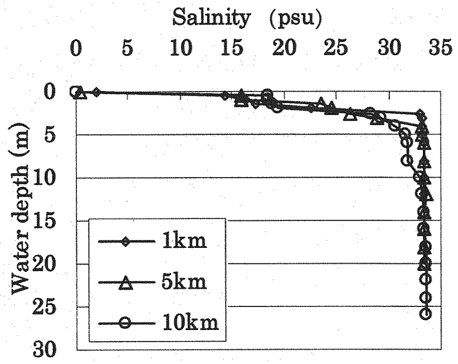

Fig.2 Distribution of salinity in the sea during snowmelt runoff

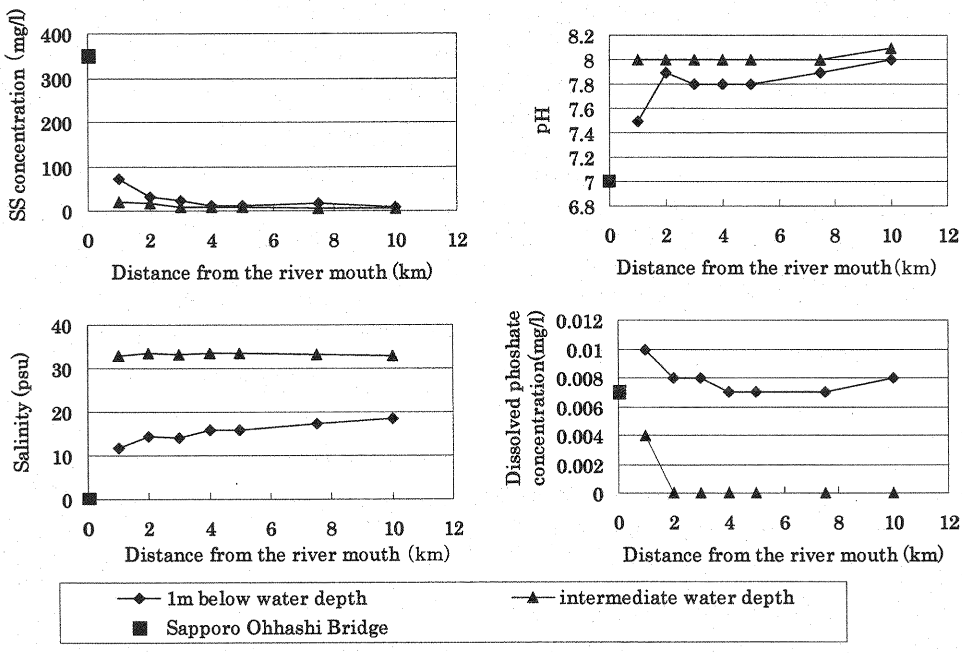

Fig.3 Results of water quality surveys during snowmelt flood conducted in the sea and at Sapporo Ohhashi Bridge. Values at o km from the river mouth represent the data at Sapporo-Ohhashi Bridge.

1km point. The pH, which was 7.0 at Sapporo Ohhashi Bridge, increased in the sea. The pH was about 7.8 at the 2km point and over 8.0 at offshore points. The dissolved phosphate concentration at the 1m depth, which was about 0.007 mg/l at Sapporo-Ohhashi Bridge, was 0.01 mg/l at the 1km point, and 0.007 mg/l at offshore points. The dissolved phosphate concentration at intermediate water depth was below the detection limit (0.003 mg/l) at most of the measuring points. Field surveys conducted in the past revealed that saltwater runs up as far as Ishikari-Ohhashi Bridge. Fig. 4 shows the distribution of average riverbed elevation and the mean grain diameter (d_{50}) of riverbed materials at the lower reaches of the Ishikari River. At Ishikari-Kakokyo Bridge and Sapporo-Ohhashi Bridge, which are located at the lower reaches, the riverbed slope is gentle and the grain size of riverbed materials is as small as that of SS transported from the upper reaches (10 - 20 μm) (see Yamazaki(9)). The data suggested that at the lower reaches SS aggregated and precipitated onto the riverbed during low discharge, after

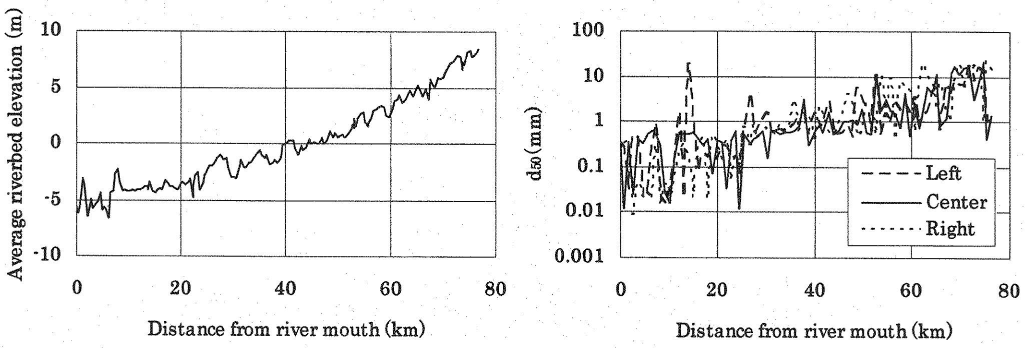

Fig.4 Average riverbed elevation and d_{50} (1997 survey)

coming into contact with saline water running up from the sea, and that at times of flood, such deposited sediments that had small grain size were disturbed and flashed into the sea mixed with SS transported from the upper reaches. Shimizu (5) examined the grain sizes of riverbed materials under different discharges in the Ishikari River, using a one-dimensional riverbed fluctuation model. He educed that the riverbed materials at the lower reaches increased in size when the discharge is about 2,000 m^3/s or greater, which was equivalent to the annual mean discharge of snowmelt runoff. Therefore, we concluded that riverbed material with small grain sizes at the lower reaches is flushed out to the sea every year.

Analytical results for Suspended Sediments and Riverbed Materials

Fig. 5 shows the contents of CDB-P, HCl-P, and NaOH-P in SS in the Ishikari River and in the surface layer of bed materials in the sea. These samples were collected in previous surveys. The contents of HCl-P and NaOH-P were almost constant both in the river and in the sea. CDB-P content correlated with T-P content and was lower in the seabed materials than in the river suspended sediments and bed materials. The minimum CDB-P content in the surface layer of the seabed material is thought to be about 0.1 mg/g, and the residual content is expected to be the fraction that dissolves under anaerobic conditions and does not readily dissolve under aerobic conditions. Fig. 6 shows the phosphorous fractions of the suspended sediments and bed materials in the Ishikari River. The contents of T-P and CDB-P at Ishikari-Kakokyo Bridge and Sapporo-Ohhashi Bridge which were at the lower reach of the river were higher than those of the suspended sediments during the flood, suggesting that suspended sediments with high phosphorus content flowed into the river during periods of irrigation and at other times, and aggregated and

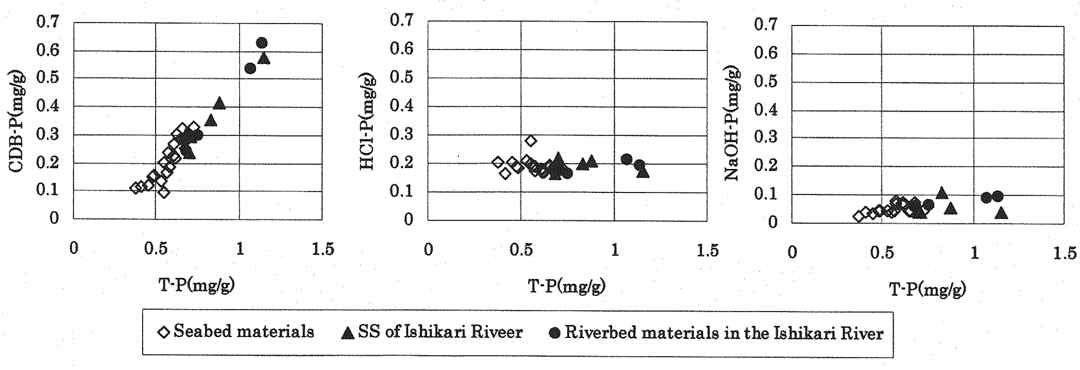

Fig.5 Contents of phosphorus in different forms

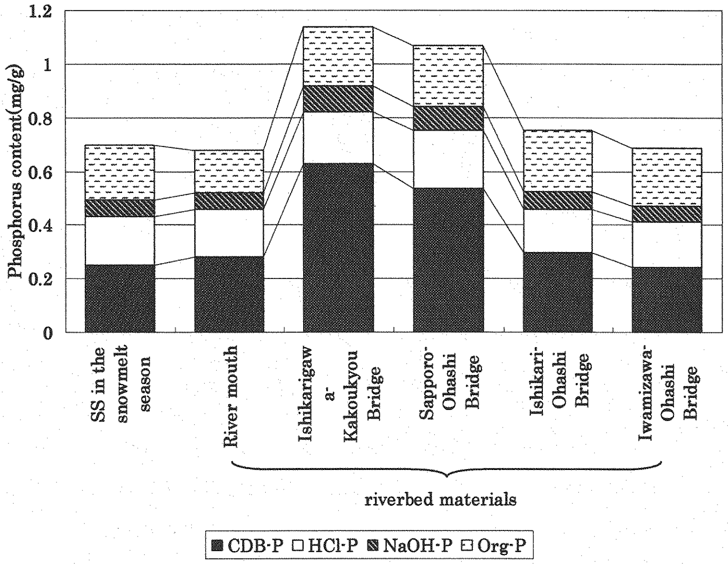

Fig.6 Analysis of suspended sediment (SS) and riverbed materials in the Ishikari River

precipitated to the river bed during the period when saltwater was running up. During floods, sediments deposited on the riverbed at the lower reaches, and suspended sediments transported from the upstream probably flow out to the sea, carrying phosphates in great amounts.

LABORATORY EXPERIMENT ON THE ADSORPTION/DESORPTION CHARACTERISTICS OF PHOSPHATES

Adsorbed phosphate content on the sediment and dissolved phosphate concentration in the seawater are known to change with the salinity and pH in solution (see Tanaka (7)). To clarify the change in dissolved phosphate concentration in the sea off the river mouth, it is necessary to understand the adsorption/desorption characteristics of fluvial suspended sediments. Considering the fact that the settling time of the fluvial suspended sediments to the seabed lasts one or two days, it is then possible to assume that reaction of desorbed phosphate with fluvial suspended particles occurs on the surface, and that this reaction follows the Langmuir adsorption isotherms. The Langmuir adsorption isotherm is expressed as follows:

$$\Gamma_i \,/\, (\Gamma_s - \Gamma_i) = b\, C_i \qquad (1)$$

where Γ_s is saturated adsorbed phosphate content, Γ_i is adsorbed phosphate content in equilibrium, b is constant term of free energy, C_i is dissolved phosphate concentration in solution in equilibrium. This following relationship can also be derived as follows:

$$\Delta C = -[SS] \cdot \Delta \Gamma \qquad (2)$$

where ΔC is difference in dissolved phosphate concentration of solution between initial and equilibrium conditions, $\Delta \Gamma$ is difference in adsorbed phosphate content of SS between initial and equilibrium conditions, $[SS]$ is SS concentration in solution. Γ_i and C_i in equilibrium can be expressed as follows:

$$\Gamma_i = \Gamma_{i0} + \Delta \Gamma \tag{3}$$

$$C_i = C_{i0} + \Delta C \tag{4}$$

where Γ_{i0} is initial adsorbed phosphate content, C_{i0} is initial dissolved phosphate concentration in solution.

Initial Amount of Phosphate Adsorption

To calculate the relationship between the amount of adsorbed phosphate and the dissolved phosphate concentration in solution, the initial adsorbed phosphate content (Γ_{i0}) needs to be estimated. Tanaka (7) extracted the adsorbed phosphate (Ads-P) by the seawater extraction technique. The procedure is as follows: ① sediments are added to filtered fresh (PO_4-P=0) seawater, ② seawater with sediments is mixed for 24hours, ③ after the mixing the solution is filtered, ④ the residue is centrifuged, ⑤ procedures ①~④are repeated for ten times, ⑥ Ads-P is the amount of dissolved phosphate concentration. In a similar experiment conducted for this study, we found that the release of adsorbed phosphate continued even after 10 times. We educed that the relationship between each extracted phosphate concentration and the adsorbed phosphate content in SS followed Eq.1 to 4. Therefore, we conducted an experiment using Tanaka's method and estimated the values that best fit the Langmuir adsorption isotherm. Considering Eq.1 to 4, it was predicted that extracted phosphate would increase with decreasing SS concentration in solution. We conducted experiments with the SS concentration of 500 mg/l as well as that of 2,000 mg/l. Fig. 7 shows the Langmuir adsorption isotherm and experimental values when an initial adsorbed phosphate

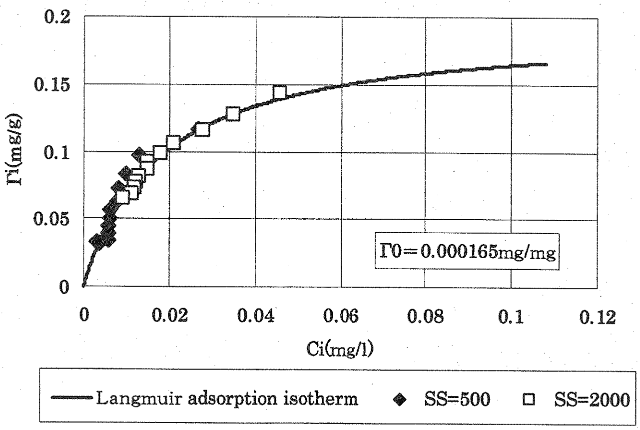

Fig.7 adsorbed phosphate content vs. dissolved phosphate concentration (Langmuir adsorption isotherm of Γ0=0.165 mg/g is assumed.)

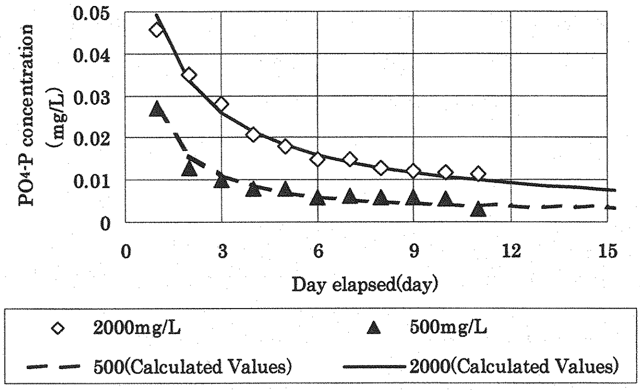

Fig.8 Temporal changes of desorbed phosphate for each 24hours mixing from the sediments

(Γ_{i0}) of 0.165 mg/g is assumed. Fig. 8 shows the temporal changes in phosphate desorbed from sediments in two kinds of SS concentration, and the curves calculated from the Langmuir adsorption isotherm. Phosphate continued to be released even after the release rate of phosphate became low. The minimum CDB-P content of seabed materials measured near the surface was about 0.1 mg/g, and the CDB-P content of the SS collected was 0.25 mg/g (see Fig. 5). Therefore, the maximum content of adsorbed phosphate desorbable in the sea under aerobic condition is estimated to be about 0.15 mg/g, which is almost consistent with the experimental results.

Mixing Experiments

We examined the change of release rate of phosphate in an experiment where the fluvial suspended sediment was put into solutions with different salinity and pH. The initial phosphate content of the suspended sediment was assumed to be 0.165 mg/g. In the experiment, initial concentrations of desorbed phosphate were 0, 0.02, 0.04, and 0.1 mg/l, concentrations of SS in solution were 200, 700, and 2,000 mg/l, and the stirring time was 4 hours. Salinity of filtered seawater was controlled by addition of deionized water. Saturated adsorbed phosphate content (Γ_s) and a constant (b) of the adsorption isothermal were determined from phosphate adsorption/desorption experiments in which salinity and pH were controlled. However, since pH fluctuated markedly before and after the mixing experiment, the distribution of Γ_s and b due to changes in pH under constant salinity could not be expressed. Fig. 9 shows the relationship between salinity and pH during floods in the sea off the mouth of the Ishikari River. The pH was about 7.0 when the salinity was low and increased to about 8.0 as the salinity approached to that of the seawater, and pH was assumed to be related to salinity in the Ishikari River estuary. The experiments followed the field relation between salinity and pH. Langmuir adsorption isotherms and the data of mixing experiments for various controlled salinity are shown in Fig. 10, where the adsorption behavior of phosphate approximately follows the Langmuir adsorption isotherm. Fig. 11 shows the relationship between salinity and Γ_s or b. Γ_s and b at 0 psu are different from those of other salinity conditions. At the salinity of 0 psu, b is largest, and it means that Γ_i is tend to approaches the saturated content even at low Ci. At the salinity of 1 psu or more, Γ_s decreases as salinity increases, which means the ability of adsorption decreases with increasing salinity, consequently facilitating the release of phosphate. Tanaka (8) reported that the adsorption of phosphate by bed materials is greatest when the salinity is one-fiftieth of that of seawater. In this study, too, the amount of phosphate adsorption was largest at low salinity (1psu).

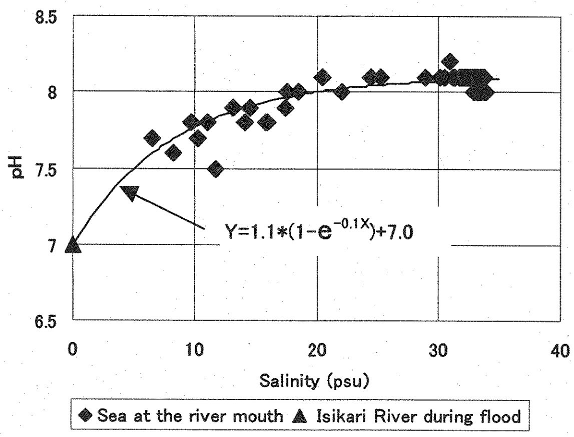

Fig.9 Salinity vs. pH level during the flood in the sea at the river mouth

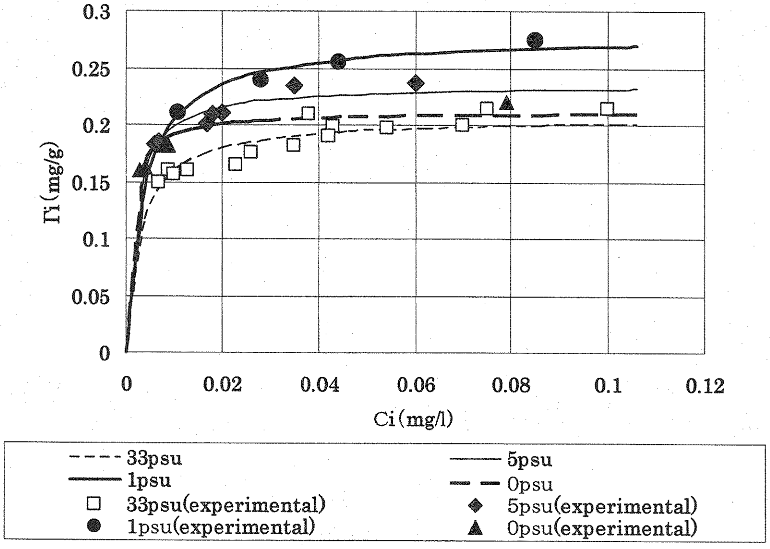

Fig.10 Langmuir adsorption isotherms and the data of mixing experiments for various controlled salinity

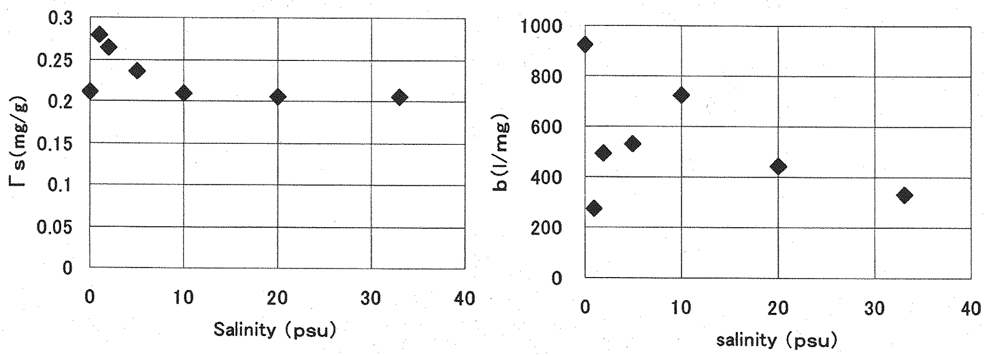

Fig.11 Relationship between salinity and Γ_s or b determined in the mixing experiment

DISTRIBUTION OF DISSOLVED PHOSPHATE IN THE SEA OFF THE ISHIKARI RIVER DURING SNOWMELT RUNOFF

We examined the water quality change in the sea off the river mouth based on the adsorption/desorption characteristics of fluvial suspended sediments determined in the laboratory experiment. When the phosphate adsorption/desorption is in equilibrium, C_i and Γ_i can be calculated by Eq.1 to 4, using given values of Γ_0 , C_{i0}, and SS concentration. By repeating this calculation, changes in the dissolved phosphate concentration in the sea near the river mouth where salinity and pH change can be calculated. The ratio of seawater to river water was determined by the salinity at that point, and the initial dissolved phosphate concentration (C_{i0}) was obtained under the assumption that no SS was present. Pre-reacted phosphate content in SS (Γ_0) and SS concentration at each measuring point were used to calculate C_i and Γ_i. Γ_s and b in different salinity were calculated using a regression curve of a cubic polynomial that was established using the values in Fig. 11 (excluding the values of 0 psu). The reason why we adopted a short stirring time (4 hours) was that phenomenon was assumed to be the results of sequential reactions in a short time under different conditions of solution during floods in the sea off the river mouth where seawater and river water mixed. In contrast, offshore, where constant salinity and pH persist for many hours and the SS concentration is low, the phosphate release from SS will not be a dominant phenomenon. Fig. 12 shows the temporal changes in dissolved phosphate concentration in the desorption experiment at the salinity of 33 psu, SS concentration of 500 mg/l, and initial dissolved phosphate concentration of less than 0.003 mg/l. Over 70% of the adsorbed phosphate was released in initial four hours, before reaching equilibrium within about 12 hours. Fig. 13 shows measured and calculated values for dissolved phosphate concentrations in the sea off the river mouth. The measured dissolved phosphate concentration was highest in the sea 1 km off the river mouth, and gradually decreased toward the offshore points. Simple dilution with seawater can not account for this increase in dissolved phosphate concentration in the sea off the river mouth. The adsorption/desorption characteristics can explain roughly this change in the water quality in the sea off the river mouth. Fig. 14 shows the Langmuir adsorption isotherm at each measuring point and its value under adsorption/desorption equilibrium. In the river water, the adsorption/desorption equilibrium is thought to be at the point marked ① on the line denoted Isikari River, as the dissolved phosphate concentration in the river was 0.007 mg/l. At 1km point from the river mouth, salinity increased and Langmuir adsorption isotherm shifted to the line denoted 1km. The dissolved phosphate concentration

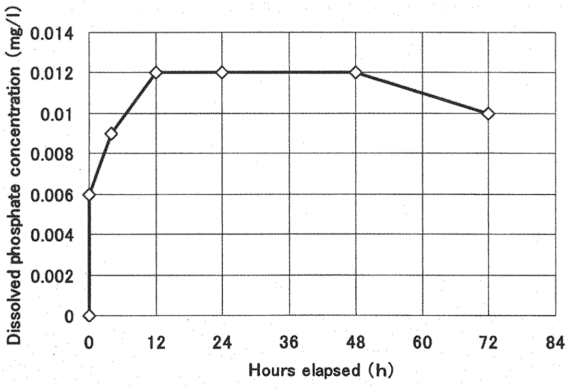

Fig.12 Temporal changes in dissolved phosphate concentration after suspended sediment (SS) was added to the seawater

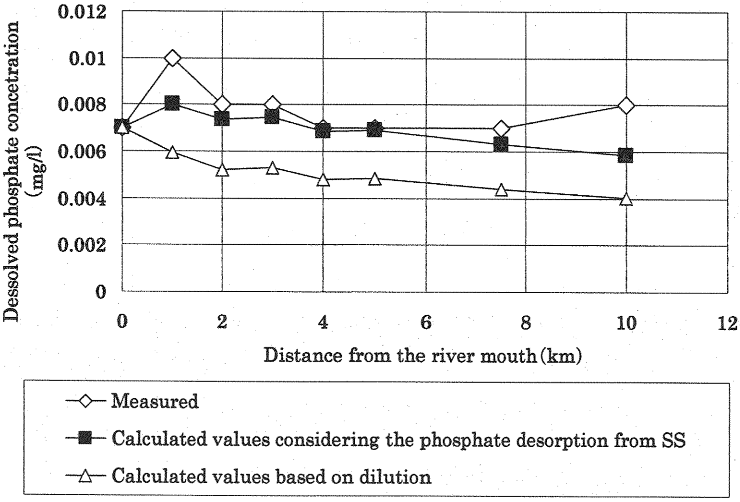

Fig.13 Measured and calculated dissolved phosphate concentrations in the sea off the river mouth

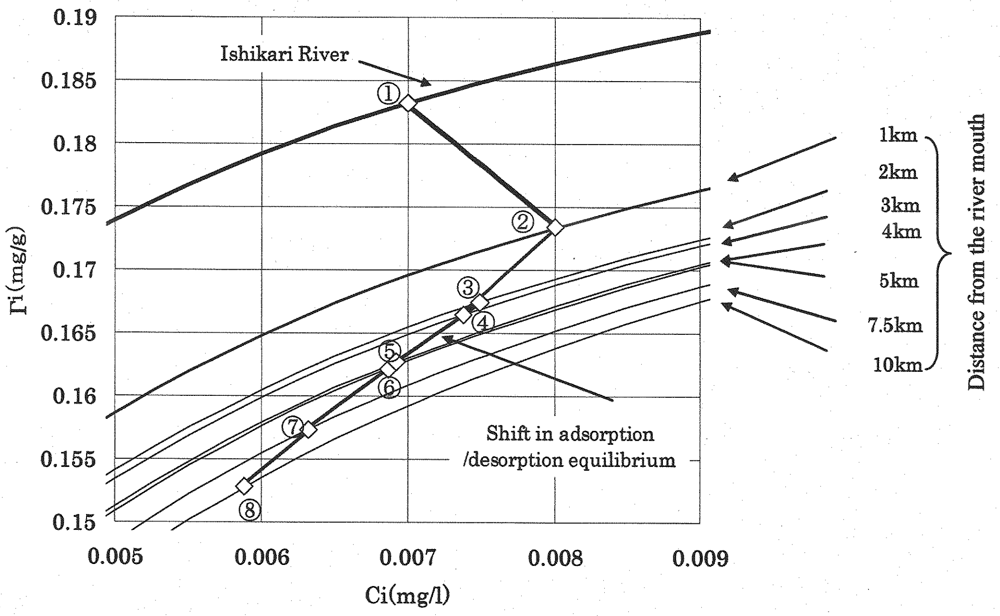

Fig.14 Langmuir adsorption isotherms at measuring points, and shift in adsorption/desorption equilibrium.

increased due to the release of phosphate with high SS concentration, the equilibrium point sifted to marked ②. As leaving from the river mouth, salinity increased, the isotherm adsorption curves shifted, the dissolved phosphate concentration in the seawater gradually decreased toward the offshore point, and the equilibrium point shifted from ② to ⑧. Due to low SS concentration, the effects of dilution by seawater exceeded the effect of phosphate desorption. The adsorbed phosphate content at the river was 0.185 mg/g, higher than that obtained by SS analysis (0.165 mg/g). The result suggested that riverbed materials that contained high adsorbed phosphate at the lower reaches was flushed out to sea during flood mixing with suspended sediments. We confirmed that the SS discharged from the Ishikari River supplied phosphate to the Ishikari River estuary during the snowmelt runoff.

CONCLUSIONS

It was possible to express phosphate adsorption/desorption characteristics in the short time by Langmuir adsorption isotherm, and the release rate changed by salinity and pH were examined by laboratory experiments. Based on these results, we were able to quantitatively reproduce the distribution of dissolved phosphate concentration in the sea off the river mouth. We were able to confirm that fluvial suspended sediments, when discharged from the Ishikari River during snowmelt runoff, release phosphate into the seawater. The data obtained in this study corroborated the role of SS in supplying phosphates to seawater during the snowmelt runoff. However, further studies will be necessary to estimate the desorbed phosphate with fluvial inorganic suspended sediments during floods in summer and at other times. In this study, Γ_s and b, which determine the Langmuir adsorption isotherm, were used to clarify the relationship between adsorption/desorption characteristics and salinity and pH. The effect of water temperature is also a factor that determines Γ_s and b, because the desorbed phosphate adsorption under low-salinity conditions is reported to vary by temperature(see Bale(1)). When investigating the effects of summer floods, it is also necessary to consider organic phosphorus as well as inorganic phosphorus in SS. It is not easy to directly analyze organic phosphorus, because they decompose and contain some refractory components, and analyzed data showed different results between those estimated by the subtraction using T-P, D-T-P, PO_4-P, and D-PO_4-P data, and those obtained by the scheme of Williams et al. Analytical methods of organic phosphorus need to be improved.

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(Received September 14, 2005 ; revised February 22, 2006)