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Sediment characteristics, phosphorus types and phosphorus release rates between river and lake sediments

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Abstract

The Han river is 469.7 km long with 26 219-km^2 area watershed, and is the primary drinking water source for the 20 million people that live in Seoul, Kangwon-Do and Kyunggi-Do, Korea. Phosphorus release from sediments impacts water quality, and is endangering the beneficial use of the river. This research measures phosphorus release and predicts future releases from bottom sediments of two tributary areas (Chungpyung Lake (CPL) and Jamsil submerged dam (JSD) area in the Han river). Sediment samples were taken over a 4-year period from four points in the Jamsil dam area and from 92 points in CPL. The sediments were analyzed for total phosphorus, the form of the phosphorus and release rates under different conditions to the water column. Sediment phosphorus distribution from CPL was 3–5% adsorbed-P (Ads-P), 15–20% non-apatite-P (NAI-P), 25–30% apatite-P (A-P) and 45–57% residual-P (R-P). In the JSD area, the phosphorus distribution ranges were 1–3% Ads-P, 22–39% NAI-P, 26–40% A-P and 30–39% R-P. Laboratory experiments showed that phosphorus release rates from 60 to 80 mg/m^2 week in JSD area and ranged from 25 to 40 mg/m^2 week in CPL sediments.

Keywords: Chungpyung Lake; Han river; Non-point sources; Phosphorus release rate; Jamsil submerged dam; Korea

1. Introduction

Various pollutants may be adsorbed to the sediments accumulated on the bottom of rivers or lakes. These sediments may accumulate over long periods and can act as new pollutant sources to the overlying water many years after the water quality has improved (Lijklema et al., 1993; Masunaga et al., 1993; Abrams and Jarrell, 1995). Pollutants such as phosphorus may be transferred from the water column to sediment layer with biochemical and physical reactions such as ion exchange, adsorption, and precipitation (Stumm and Morgan, 1996). The pollutants may be released from the sediments if the overlying water quality changes (Fukushima et al., 1984; Furumai et al., 1989). Mechanisms for reintroduction include advection, ion exchange, molecular diffusion, and biologically mediated changes. The characteristics of sediments, as well as overlying water quality, will affect the release rate.

Phosphorus-laden sediments have accumulated in more than 10 locations in Korea. The Jamsil submerged dam (JSD) area in Han river, upstream of Seoul, and the Chungpyung Lake (CPL) area are such two areas. The water in both areas is of great economic and environmental importance to Korea. Potential release of phosphorus from the sediments is therefore very important, and several funding agencies (see acknowledgements) agreed to collect sediment data to ascertain the extent of the problem.

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In this paper we examine the sediment characteristics in JSD and CPL areas and compare their potential release rates as a function of overlying water quality. Phosphorus release was measured at varying temperature, DO, pH, and physical conditions. This represents the first publication of sediment phosphorous data from these two areas.

2. Background

The Han river, the largest river in Korea, is 469.7 km long with 26 219-km^2 area watershed (Fig. 1). It starts in North–East Kangwon-Do and travels to the Yellow Sea. The river is the primary source for drinking, industrial and agricultural water for more than 20 million people in city of Seoul and the surrounding provinces, Kangwon-Do and Kyunggi-Do. Non-point sources are currently responsible for approximately 80% of the total phosphorus (TP) input (Kim and Choi, 1996). To improve water quality it will be necessary to further reduce phosphorus sources in upstream tributaries and the phosphorus release from sediments. Nitrogen control is more difficult than the phosphorus control in many natural water systems because the nitrogen originates from a greater number of sources. Therefore, it is believed that controlling phosphorus is the best approach to reducing eutrophication (Boers and Vanhese, 1988; Dahl et al., 1993).

Sediment phosphorous accumulation, distribution and release rates were previously reported for the JSD area (Kim and Choi, 1996). The JSD area is 7–9 m deep and approximately 1 km wide. It is adjacent to highly developed urban areas, and its banks have been straightened and channeled for flood control, roads and parks. Paldang dam is located upstream of Seoul which moderates high flows for flood protection. All of these modifications reduce river velocity, which increases the opportunity for sediment accumulation. Treated wastewaters are also discharged into JSD tributaries. The sediments contain 490–1860 mg/kg of phosphorus and released phosphorous at 60–100 mg/m^2 week.

CPL is a reservoir created by a large dam in Kangwon-Do. The lake has approximately 71 km shoreline, 15.3 km^2-surface area, and receives runoff from 10 000-km^2 watershed, which is mostly undeveloped. The average water depth is 10 m, which provides an average retention time of 8.5 days. The lake supports 10 fish farms, which act as a source of phosphorus and other pollutants (Honkanen and Helminen, 2000). The river and lake are already stressed and have incidents of low dissolved oxygen (DO) concentration. Both areas receive stormwater and urban runoff, which further increases pollutant concentrations (To, 1974; Williams et al., 1980; Fukushima et al., 1984).

Pollutants released from sediments are another potential source of phosphorus (Furumai et al., 1989; Kim and Choi, 1996). Release of phosphorus from sediments may be caused by environmental changes (low or high pH, water temperature) and may be associated with the release of other pollutants such as metals (Hieltjes and Lijklema, 1980; Lijklema et al., 1993). Phosphorus solubility is a function of pH and redox potential, being generally lowest at neutral pH and highly aerobic conditions, when it precipitates with metals such as aluminum and iron. If the boundary of the sediments and overlying water are aerobic, metal ions such as iron and manganese are oxidized to their higher states [Fe(III) and Mn(IV)] and will precipitate phosphorus with metal hydroxide. Under reducing conditions, the iron and manganese precipitates will dissolve and release PO_4^{3-} (Hieltjes and Lijklema, 1980; Fukushima et al., 1984; Bostrom, 1988; Abrams and Jarrell, 1995; Stumm and Morgan, 1996).

3. Materials and methods

3.1. Study areas

The study areas are JSD, Seoul, and CPL of the Han-river, and are shown in Fig. 1. The JSD area is a sensitive area because it is the primary source of drinking water for Seoul. This area is called "Jamsil Submerged dam area" because a submerged weir maintains minimum water level, and prevents back mixing from the lower sections of the river. It is necessary to prevent back mixing under low flow conditions because the downstream reaches are more polluted. Approximately 25 000 m^3 of sediments have accumulated on the north side (0.128 km^2 area) and 203 000 m^3 have accumulated on the south side (0.507 km^2 area). Sediment depth is approximately 1.5–2 m around fish farms, and 0.5–1 m for other areas (Kim and Choi, 1996).

3.2. Sampling and analysis of sediments and waters

Water samples, disturbed sediment samples and undisturbed sediments samples were collected from the JSD study area over a 5-year period from 1994 to 1999. Four sampling locations were used for the JSD area, and 92 sampling locations were used for CPL area. The disturbed samples were collected with a Ponar Grab style sampler. Divers collected undisturbed samples with acryl tubes, which were 4 cm diameter by 50 cm long. Samples were refrigerated after collection and quickly transported to the laboratory for analysis. The undisturbed samples were cut in 15 cm sections and each section was blended. Portions of the blended sediment were used for analysis, and the remaining portion was dried in the shade to be used later for phosphorus release

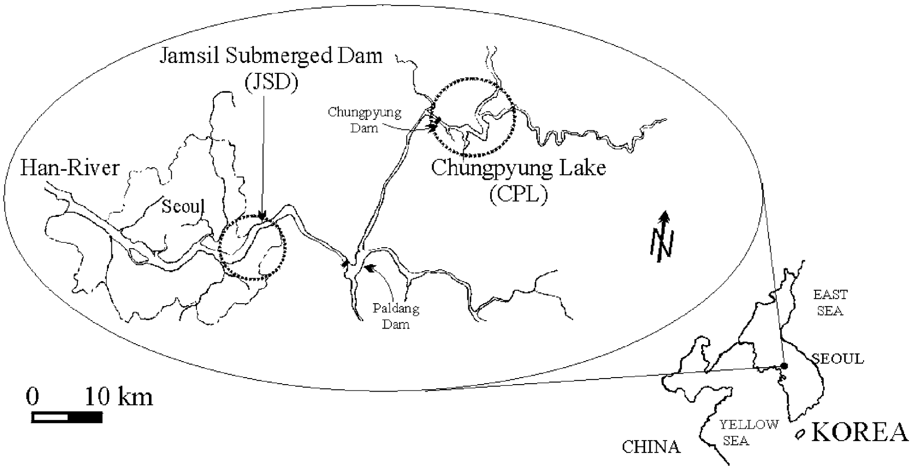

Fig. 1. Sampling areas of JSD and CPL, Korea.

experiments. Grab samples were analyzed but not used in phosphorus release experiments. Samples were analyzed using Standard Methods (1995) for pH, chemical oxygen demand (COD), TP, total Kjeldahl nitrogen, total solids (TS), volatile solids (VS), and water content. Phosphorus release experiments are described later. Sediment size distribution of combined disturbed and undisturbed samples was measured on using the Sieve analysis method (Das, 1990). This method separates the sediment into clay (smaller than 0.002 mm), silt (0.002–0.05 mm) and sand fractions (0.05–2 mm).

Water samples were also collected from the top, middle and bottom layers of the water column using a Van Dorn sampler, and analyzed for temperature, DO, total suspended solids, COD, total nitrogen (TN), and TP, using Standard Methods (1995).

3.3. Phosphorus release experiments

Release experiments were performed in 6 cm diameter by 45 cm tall reactor tubes, containing varying amounts of overlying water and previously air-dried sediment, at varying DO concentrations, pHs and temperature. The samples were air-dried; oven drying was not performed in order to avoid increasing release rates (To, 1974). Three different overlying waters, in situ water, distilled water and deoxygenated distilled water (nitrogen gas stripping followed by sodium sulfite addition), were used to perform the tests. The reactor tubes with sediments and overlying water were incubated at constant temperature one week or more. During the incubation, the tubes were sealed with plastic caps and parafilm to prevent oxygen dissolution to the overlying waters. The tubes were not stirred to simulate conditions of the JSD and CPL areas, which are quiescent. Other experimental conditions are shown in figures and tables.

3.4. Analysis of phosphorus type and release studies

Phosphorus type was determined using the procedure of Hieltjes and Lijklema (1980), and our procedure was described previously (Kim and Choi, 1996). The procedure successively extracts phosphorus from sediments using different solvents and conditions. The fractions are called adsorbed-P (Ads-P, extractable by NH_4Cl), non-apatite-P (NAI-P, extractable by NaOH after Ads-P extraction), apatite-P (A-P, extractable by HCl after NAI-P extraction), and residual-P (R-P, non-extractable, calculated by difference with TP, Standard Methods (1995)). The trend from Ads-P to R-P generally corresponds to bioavailabilty in the environment under normal conditions. Large changes in environmental conditions may change the bioavailability.

4. Results and discussion

Fig. 2 shows sediment particle distributions for JSD and CPL areas. The size distribution is important because smaller particles have greater specific surface area for pollutant adsorption (Das, 1990). The sediments are classified as Silty Clay in the JSD area. However, for the case of CPL area, the sediment compositions show various ranges from Sand to Silty Loam.

4.1. Comparison of sediment characteristics between Jamsil submerged dam and Chungpyung Lake areas

Pollutant concentrations except ignition loss (I-L, the organic portion of the sediments) in the JSD area were all higher than CPL area sediments (Table 1). The average COD, TP and TN in JSD area are 29 970, 883 and 1080 mg/kg as compared to 19 760, 480 and 780 mg/kg

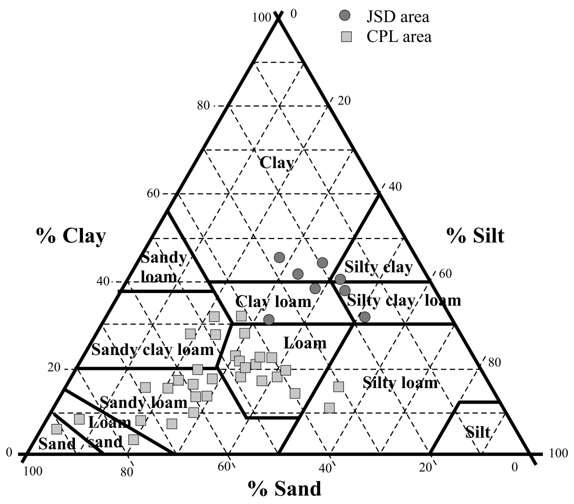

Fig. 2. Sediment particle distributions (US Department of Agriculture Textural Classification).

in the CPL area, respectively. The means are different at the 99% level of confidence in all cases. This was expected because of the greater pollutant inputs to the JSD area than the CPL area (data shown later). Also, the smaller particle sizes in the JSD area should increase pollutant accumulation in sediment layers.

4.2. Concentration versus depth

Fig. 3 shows analysis results of the 45 undisturbed samples with sediment depth. Pollutant concentrations increase with sediment depth in the JSD area. The differences between levels are significant at the 95% confidence level in most cases, as shown by the notched box plots. The meaning of the notches is shown in the figure legend. Outliers are declared when the value is 1.5 times the interquartile distance away from the 25% box (McGill et al., 1978). CPL sediments show the opposite trend in concentration compared to JSD sediments, but the differences are sometimes not significant. Only COD concentration between the surface level (0–15 cm) and the lower levels is significantly less.

Fig. 4 shows water quality for the two areas. The CPL shows very little stratification with depth, except for DO concentrations. The JSD area shows higher pollutant concentrations with water depth, suggesting stratification and sedimentation of pollutants.

Trends in sediment concentration are not sufficient to determine mechanisms for removal, but there are several possibilities. Anaerobic degradation can reduce COD and organic content (e.g. ignition loss) and can increase release rates of TN and TP. If organic content is reduced at greater relative rates than the release of nutrients, the nutrient concentration will increase. Also the sediments represent a history, and higher concentrations at greater sediment depth may represent higher historical water quality contamination. The reason for the difference in trends between the two areas is unknown, but may reflect the age of the sediments, temporal changes in phosphorus inputs or the biodegradability of the organic material. Determining mechanisms is a subject for future research.

4.3. Phosphorus type

Table 2 shows the different forms of phosphorus in the sediments at JSD and CPL study areas. For the sediments from the JSD area, NAI-P, A-P, and R-P were found in about equal distributions. Average R-P was 34% which means that 34% of the phosphorus is unavailable. NAI-P averaged 33% for all samples, which would be available with few environmental changes.

For the sediments from the CPL area, R-P was almost 50%, which was a very high compared to JSD area sediments. Approximately 50% of the phosphorus is unavailable. NAI-P and A-P were found in about equal distributions. NAI-P averaged 21% for all samples, which would be available with few environmental changes.

Table 1
Pollutant concentrations in JSD and CPL sediments

Area	Parameters	Concentration				99% Confidence interval (CI)
		Minimum	Maximum	Mean	Standard deviation	
JSD	COD (mg/kg)	15 640	56 980	29 970	8981	26 911–33 029
	TN (mg/kg)	850	2600	1080	288	982–1178
	TP (mg/kg)	490	1860	883	228	804–960
	Ignition loss (%)	4.2	8.1	5.5	1.1	5.2–5.9
CPL	COD (mg/kg)	6550	29 500	19 760	4856	18 105–21 414
	TN (mg/kg)	310	1120	780	183	717–842
	TP (mg/kg)	230	1310	480	151	428–531
	Ignition loss (%)	3.4	13.2	8.0	1.8	7.3–8.6

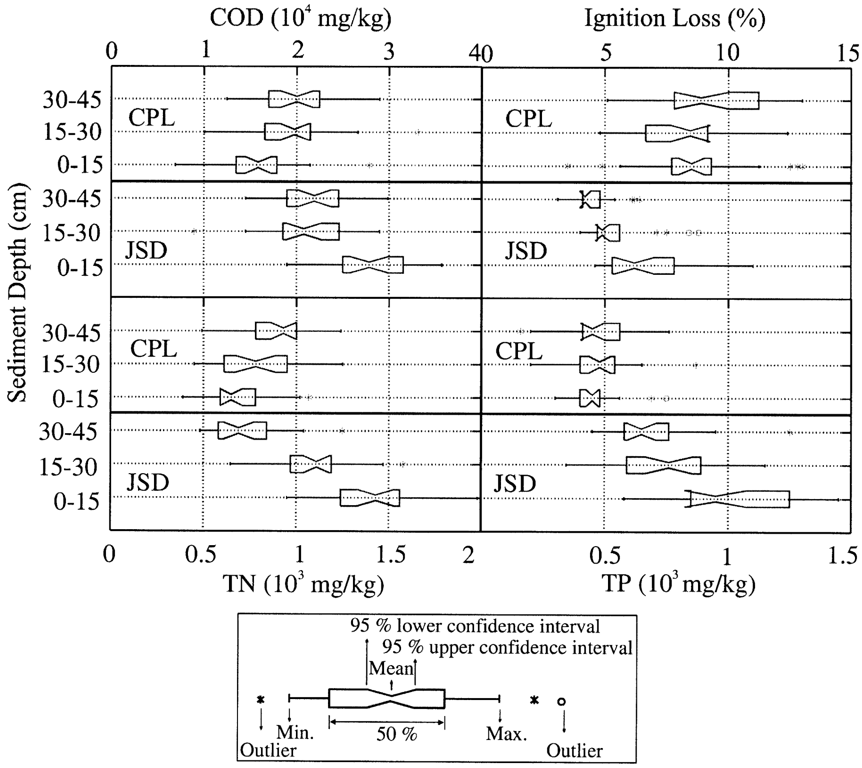

Fig. 3. Average pollutant concentrations versus sediment depth.

4.4. Phosphorus release studies

Fig. 5 shows natural phosphorus release rates for disturbed samples for varying environmental conditions. Fig. 5a shows the phosphorus release rate measured over one week, as a function of DO concentration (at above the sediment). The phosphorus release rates for JSD area are higher than those of CPL area. Table 2 shows the fraction of NAI-P in the JSD area is higher than that of CPL area. The R-P in the JSD area is 34% of the total-P, which is less than the CPL area (50%). As stated earlier, phosphorus types can affect release rate, and the NAI-P is generally more available to aquatic systems than R-P.

The rate in JSD area is approximately 105 mg/m^2 week (to convert mg/m^2 week to mg/m^2 s multiply by 0.6048) at anaerobic conditions, but decreases to 40 mg/m^2 week when DO is increased to 7 mg/l. Phosphorus was released 2.5 times faster under anaerobic conditions.

High temperature is known to affect phosphorus release. Fig. 5b shows phosphorus release rate as a function of temperature at pH 8 and DO = 0.5 mg/l. The phosphorus release rate increases fivefold between 2 and 25–35 °C. The release rates for the CPL area, which were slightly lower at low DO concentration, are greater at higher temperatures than the release rates for the JSD. The releases were measured over one-week exposure, and replicates are needed to determine the statistical significance of the differences.

Extreme pHs also affects phosphorus release. The release rate of phosphorus as a function of pH is shown in Fig. 5c. The rate varies from 40 to 125 mg/m^2 week. The release rate shows a minimum at pH = 8 for JSD area sediments. Only three data points were collected for the CPL area, and a comparison is not possible. Phosphorus release is affected by pH if it is precipitated with Fe, Al, or metals. Sediment metal content was measured in the CPL area sediments and found to be 4.75 $\pm$ 0.3 mg Fe/kg, 9.94 $\pm$ 0.8 mg Al/kg, 0.55 $\pm$ 0.1 mg Ca/kg and 1.1 $\pm$ 0.4 mg Mg/kg. At high pH, phosphate can be exchanged with OH^- and released to the water column (Bostrom, 1988).

Fig. 6a shows the total release as a function of time for varying DO concentration and temperature for CPL area samples. The rate of phosphorus release decreases with time, gradually reaching equilibrium with the overlying water column. The DO and temperature dramatically affect the total release as well as the initial rate of release. This figure shows the importance of maintaining high DO concentration in overlying water to minimize release.

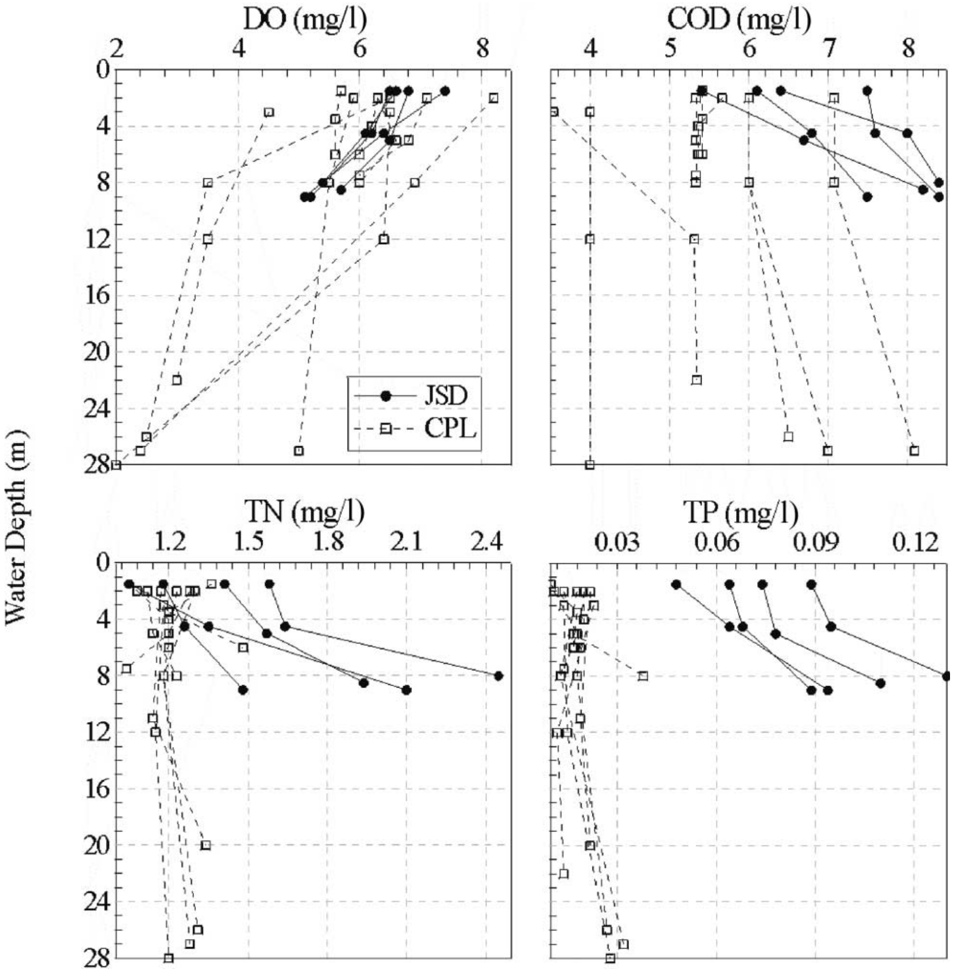

Fig. 4. Water quality with water depth.

Table 2
Average phosphorus existence types of sediment

Concentration (mg/kg)	JSD				CPL			
	Minimum	Maximum	Average	% of average concentration	Minimum	Maximum	Average	% of average concentration
Total-P	490	1860	883	–	230	1310	480	–
Ads-P	1	12	10	1	13	39	28	6
NAI-P	110	450	289	33	22	269	100	21
A-P	205	320	282	32	57	156	112	23
R-P	210	390	302	34	120	860	240	50

4.5. Release rate studies

Fig. 6b shows natural phosphorus release as a function of time for aerobic (DO = 6 mg/l) and anaerobic conditions (DO < 0.5 mg/l) in the overlying waters for both study areas. After 120 h, the anaerobic and aerobic mass releases are approximately 90 and 30 mg P/m^2 for JSD area sediments and 50 and 22 mg P/m^2 for CPL area sediments. The instantaneous release rates are equal to the slopes of the two concentrations. The rate of release declines, suggesting that equilibrium is being obtained. The initial release rate is more than several hundred mg/m^2 week (the data are insufficient to calculate release rate precisely).

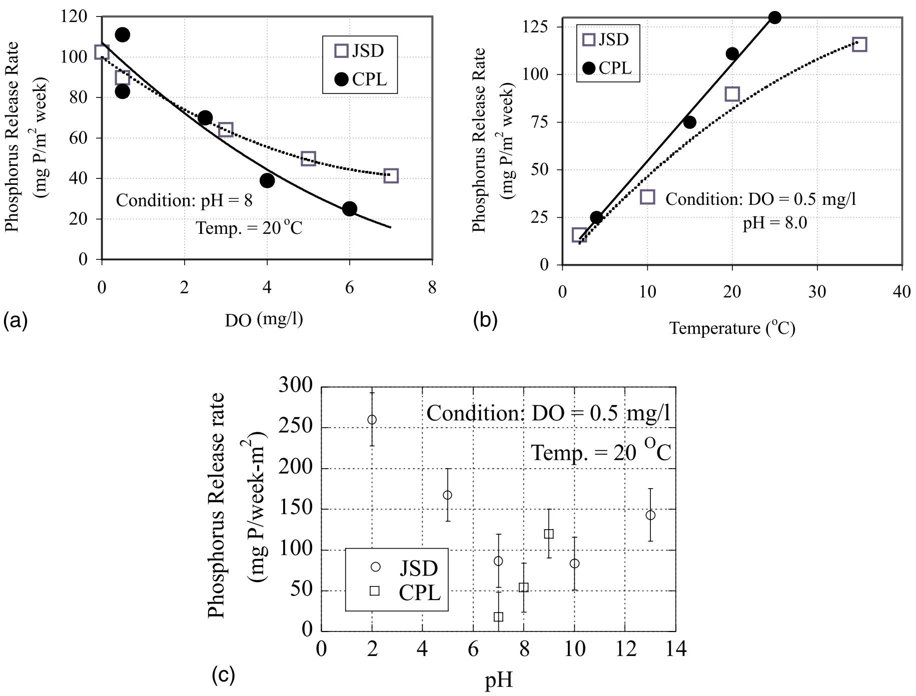

Fig. 5. Phosphorus release rates with condition changes: (a) DO changes, (b) temperature changes and (c) pH changes.

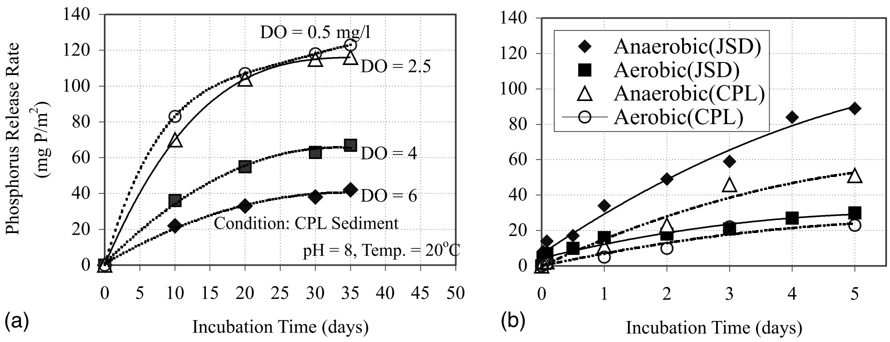

Fig. 6. Phosphorus release rates with incubation time: (a) for different DO and (b) for aerobic and anaerobic conditions.

The annual release rate for the JSD sediment area can be estimated using the previously described results. In order to evaluate the impact of sediments on water quality, it is necessary to compare release rates from sediments to other inputs. If one assumes the average release rate measured over one-week exposure, and the sediment areas for the JSD areas, the minimum release is 1.4 tonnes/year for aerobic conditions (DO = 7 mg/l, pH = 6.2). The maximum release rate is 5.5 tonnes/year for anaerobic conditions (DO = 0 mg/l, pH = 5). The input of phosphorus from the Han river flowing through the JSD area can be determined from the water quality. Fig. 7 shows the water quality for the JSD and CPL areas, and flow rate from the JSD areas (flow not available for CPL area).

The flow and concentrations vary generally, but can be used to estimate phosphorus mass rates. The mass rates ranges from 17 to 33 tonnes/month for total-P and 1.9–3.3 tonnes/month for PO_4-P in the winter to 280–430 tonnes/month for total-P and 18.7–37.6 tonnes/month in the summer, respectively. The total sediment phosphorus accumulation is approximately 50% of the yearly load from the Han river. The yearly load from the river is much greater than the release rate estimated from the batch experiments. To more precisely estimate the release rates and compare them to other inputs, it

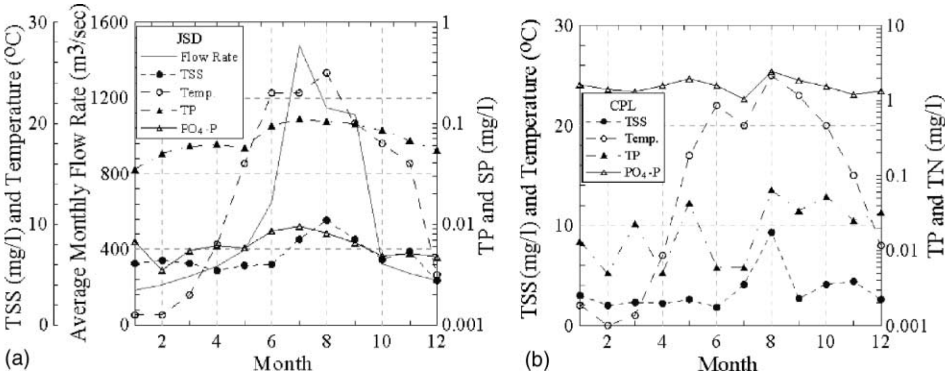

Fig. 7. Average monthly flow rate and water quality. (a) JSD area and (b) CPL area.

will be necessary to better characterize the in situ conditions and water phase concentration just above the sediments. Using the existing results, the sediments contribution appears small compared to the mass inputs from upstream tributaries.

5. Conclusions

This investigation evaluated the mass, composition and release rates of phosphorous-laden sediments in the JSD and CPL areas of the Han river. Large amounts of phosphorus originating from point and non-point sources exist in the sediments. The release rate, as measured in laboratory reactors with long exposures, is low, as compared to the current TP load in the river. Additional rate studies are needed to determine the release rates at short exposures, which may be significant compared to the current phosphorus load. The low release rate of soluble phosphorus is due to the existing environmental conditions in the river. If conditions such as pH or DO change, the release rate could increase by as much as five times. Maintaining good water quality in the river and lake is important to minimize phosphorus release. The following specific conclusions are made:

1. Sediments from the JSD area are much more polluted than CPL area sediments. The average COD, TP and TN concentrations in JSD sediments are 29 970, 883 and 1080 mg/kg, respectively, as compared to 19 760, 480 and 780 mg/kg in CPL sediments. Ignition loss is the only exception; average ignition loss of CPL sediments is 8% as compared to 6% in JSD sediments.
2. Sediments were classified using the Unified Soil Classification System and US Department of Agriculture Textural Classification. JSD sediments are classified as Silty Clay as compared to CPL sediments, which varied between Sand and Silty Loam.
3. JSD sediments are low in adsorbed phosphorous, and remaining sediment phosphorus is nearly equally distributed among NAI-P, A-P and R-P. Phosphorus in CPL sediments is 6% Ads-P, 21% NAI-P, 23% A-P and 50% R-P.
4. The phosphorus release rates are generally higher from JSD sediments, but varied for different environmental conditions. The DO concentration in the overlying water dramatically impacted release rates. The release rate is as high as 105 mg/m^2 week for anaerobic conditions but decreases to 40 mg/m^2 week for highly aerobic conditions (DO = 7 mg/l). In equilibrium studies of CPL sediments, the release rate decreases to zero after 25–35 days; total released phosphorus is a function of DO concentration and ranges from 120 mg/m^2 at 0.5 mg/l to 40 mg/m^2 at 6 mg/l.
5. Temperature also impacts phosphorus release rates. The release rate increases fivefold between 2 and 25–35 °C. This is an important result, since rate will be greatest during the summer (>20 °C in both areas), when phosphorus can most effectively stimulate plant growth.
6. Phosphorus release rate is a function of pH. The release rate is lowest in the 7–10 range (~75 mg/m^2 week) and increases fourfold at pH 2 and doubles at pH 13.
7. Phosphorus release can be minimized in both areas by maintaining good water quality. Aerobic conditions at neutral pH will minimize the release rates.

Acknowledgements

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