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LABORATORY EXPERIMENTS ON PHOSPHOROUS RELEASE FROM THE SEDIMENTS OF 9 WETLANDS IN THE LOWER REACHES OF TAMIRAPARANI RIVER REGION, INDIA

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ABSTRACT

Phosphorous (P) has been recognized as the most critical nutrient limiting productivity. In addition, P release from sediments has a significant effect on the water quality and may result in continuous eufrophication in eutrophic wetlands. In this study P release kinetics from sediments and their relationship with sediment composition were investigated, eutrophication risk index (ERI) and degree of phosphorous saturation (DPS) were used to evaluate the eufrophication risk of the studied sediments and other influencing factors were also discussed. The result show that total P (TP), organic matter (OM), $(Al_2O_3+Fe_2O_3)$ and the percentage of sand particles were the important factors affecting the ability of p sorption. P release process was similar for all studied sediments, consisting of the quick and slow reaction process. The quick reaction mainly occurred within 0.5h and slow reaction after 0.5h p release occurred within 20h and then reached the dynamic equilibrium, p release process was slower than p sorption process. Three models (Power function model, parabolic diffusion model and simple Elovich model) can satisfactorily describe P release kinetics. p release was mainly affected TP, OM, sorbed Total phosphorous (STP), DPS and sand particles and quick p release was mainly a physical process. For the slightly polluted sediments, $Al_2O_3+Fe_2O_3$ mainly promoted p release. Both DPS and ERI can be used to evaluate the P-induced wetland eutrophication risk and their threshold values wer 5.9% and 26.1% respectively. Based on the assessment by DPS and ERI most of the studied sediments were in eutrophication risk for the studied sediments. For the heavily polluted sediments, $Al_2O_3+Fe_2O_3$ was significantly correlated with DPS. But for the slightly polluted sediments it was significantly negatively correlated with DPS and OM, and the sand particle percentage was negatively related to ERI.

KEY WORDS: Phosphorous release, kinetics, sediment composition, DPS, ERI, lower reaches of Tamiraparani River region.

INTRODUCTION

One of the most important factors affecting phosphorous (P) concentration of the overlying water in wetlands was the P release from sediments. The P release may have a significant impact on the water quality and may result in continuous eutrophication in eutrophic wetlands, especially when external pollution is reduced. Therefore, the factors affecting p release processes have been extensively studied over the past years. Most of the previous studies focused on the relevant environmental factors *e.g.* temperature, P^H, redox potential and hydrological conditions. However the results from different sediments were sometimes not consistent. Since p release was significantly affected by both physical and chemical properties of the sediments in the middle and lower reaches of Tamiraparani River region. Although indexes such as total P (TP), total nitrogen (TN) and chl were used to evaluate the wetland nutrient status, there is still no suitable assessment system for the eutrophication risk of wetlands. The P induced wetland eutrophication risk and degree of phosphorous saturation (DPS) was used to evaluate the P release risk in soil. The objective of this study was to describe the P release kinetic characteristics and to analyse their relationship with sediment composition. In addition both ERI and DPS were used to evaluate the eutrophication risk of the studied sediments,

and the factors affecting ERI and DPS were also discussed.

MATERIALS & METHODS

9 Wetlands of the lower reaches of Tamiraparani River Region were chosen in this study. The basic characteristics of this region and sediment accumulation rates are about from 0.4 to 1.9 cm per year. Most of those wetlands were p induced and those 9 wetlands represented the major wetland types in this region. The morphometric features and evaluation of eutrophic status for the studied wetlands were carried out using the comprehensive trophic level index methodology that is the common methods.

Sediment sampling and analyses

13 sediment cores (ten replicates, 0-10cm) were collected from the 9 wetlands. The core sampler with 30 cm long and 5 cm diameter pleriglass cylinder tube was used. The sediment samples were taken to the laboratory in sealed plastic bags that were put in ice boxes and were then freeze dried and ground. Cationic enchange capacity (CEC) was analyzed using EDTA-NH_4^+ method; total nitrogen (TN) was measured using the concentrated H_2SO_4 digestion method, TP using a modified Williams's method. Organic matter content was estimated as losses on ignition at 550°C. The grain size distribution was determined using a Master sizer 2000 Laser size analyzer

and was classified into clay and sand fractions. The contents of main elements in sediments were measured by ICP-AES (ICP/6500PE)

Phosphorous sorption index (PSI) was derived from a single point P sorption isotherm (P sorbed from a single solution containing 1.5g P Kg^{-1} sediment following a previous procedure reported. Duplicate samples (lg) of air dried sediment were shaken for 18h with 20 ml 0.02 M KCl solution (to maintain certain ionic strength) containing 1.5mg P plug three drops of toluene. The p sorption index (PSI, mg.Kg^{-1} (sorbed p) was calculated by the quotient X/log C, where X, mg.Kg^{-1} (sorbed P) was calculated from the difference between P added and P in the supernatant (C, mg.L^{-1}) at equilibrium. The maximum phosphorous sorption capacity, Qmax (mg.kg-1 dry weight was calculated according to the Langmuir model based on the date of phosphate sorption isotherms 0.5 g dried sediment samples were added in a series of 100 ml acid washed centrifuge tubes with 50ml of phosphate solution (anhydrous KH_2PO_4) The initial concentrations of 0, 2.0, 5.0, 8.0, 10.0, 15.0, 20.0 p mg^{-1} were used respectively. The centrifuge tubes were capped and placed at 25°±1° is an orbital shaker at 250 rpm for 25h to ensure the equilibrium. After equilibrium and centrifugation (5000 g for 10min) the suspension was filtered through 0.45 mm membrane, and its phosphate concentration was measured using the ascorbic acid method (AWWA 1998). The quantity of Sorbed phosphate was calculated through the decreases of the phosphate concentration in the solutions. Triplicate experiments were carried out, standard error deviation was within 5% and the data were reported as their average.

The degree of phosphorous saturation DPS % can be obtained according to the following expressions.

$$DPS (\%) = STP \ 100\% \ /Q \ max + STP \ \text{--------------} \ 1$$

There STP was the sorbed total phosphorous extracted from 1g sediment by 20ml 0.5m NaHCO3 (pH=8.5) for 24h.

Water samples were collected from just above the sediment surface (50cm) with acid-washed 60 ml syringes and were then filtered through 0.45Lm GF/c membranes. Samples were kept in ice bags before analyses. The analyses were performed within 25h, and the methods were according to the ascorbic acid method (AWWA, 1998)

Release kinetic experiments

Phosphorous release experiments were performed in centrifuge tubes. 0.5 dried sediments samples were added in a series of 100ml acid washed centrifuge tubes with 50ml of 0.02M KCl solution (to maintain certain ionic strength). The centrifuge tubes were capped and placed at 25°C ±1°C in an orbital shaker at 250rpm for various time in intervals between 0 and 48h (0.5, 1.5, 3, 5, 7, 12, 24 and 48h). The sampled solution was immediately centrifuged at 5000g for 10 min and was then filtered through 0.45 m G F/c filter membranes. The filtrate was taken for the soluble reactive phosphorous (SRP) analysis using the ascorbic acid method (AWWA, 1998). The quantity of the phosphate released was calculated through the increase of

the SRP concentrations in the solution. Both 0.5M NaHCO$_3$ and 0.02M KCl solutions were used for the extraction of sorbed total phosphorous and the release of the sorbed phosphate respectively. For all samples, triplicate experiments were performed and the data are presented as their average. The results demonstrated the high reproducibility of the methods and the experimental error was within 5%.

RESULTS & DISCUSSION

The general features and chemical composition of the sediments studied. TP varied within a very wide range from 290 to 2050mg kg, TN from 577 to 513 mg.kg^{-1}. Most sediments had TP>500mg kg^{-1} and TN>1000mg kg^{-1}, reflecting a general phosphorous and nitrogen accumulation in the sediments. Organic matter contents ranged from 0.69% to 7.5% and (EC range) from 8.9 to 32.5 meq (100g)$^{-1}$ Al$_2$O$_3$ contents from 8.8 to 15.7 and Fe$_2$O$_3$ from 2.7 to 5.9%. Silt was the major fraction in the sediments, accounting for 53.9% to 84.2% of the total, clay was the minor fraction in the sediments accounting for 3.8% to 7.3% of the total. The determined Q max ranged from 321.8 to 1058.4 mg kg^{-1}, STP from 22.1 to 192.8 mg kg^{-1} PS1. From 16.5 to 37.8mg. 100g^{-1} (µmol.L-1)$^{-1}$. This suggests that the physical and chemical characteristics of the studied sediments in wetlands varied greatly and those chosen wetlands were in various pollution and eutrophication status.

The correlation co efficient of the selected physical and chemical parameters in the sediments are given.

Q$_{max}$ was positively related to TP, OM and Al$_2$O$_3$+Fe$_2$O$_3$ and was negatively related to the percentage of sand particle. PSI was positively related to Al$_2$O$_3$+Fe$_2$O$_3$. This indicates that TP, OM and Al$_2$O$_3$+Fe$_2$O$_3$ may be factors affecting the ability of phosphorous sorption. Higher sand content may result in the decrease of p sorption ability since sediments with different sites had different specific surface areas, and had different effects on the exchange of phosphate between sediments and overlying water. Further grains had greater phosphorous sorption capacity and more suspending potential. Therefore, sediments with higher portion of sand grains and lower ability of phosphorous sorption. These results agree with a previous report. TP was positively related to OM and sand was negatively related to both PP and OM.

The release kinetics of phosphate on sediments

The p release kinetic curves of the studied sediments are studied. P release process was composed of two steps; the quick and slow reaction process. The first process was the quick reaction and then was the slow reaction. The capacity of P released from the sediments increased rapidly within 20h. After 20h the capacity gradually reached a equilibrium. It was reported that the quick sorption process in sediments mainly occurred within 10h in this region. This indicates that the p release process was slower than p sorption process.

Phosphate release from the sediments was often analyzed using kinetic models. In this study the capacity of phosphate released from sediments increased as time increased. Three common kinetic models (power function model, parabolic diffusion model and simple Elovich model) were used to describe the processes (after 24h

equilibrium, the capacity of phosphate released per gram of dry sediment was plotted against time). Those kinetic models were as follows:

Power function model   : $q = kt^a$
Parabolic diffusion model : $q = B + K/t^{1/2}$
Simple Elovich model   : $q = B + K \ln t$

Where t is time (h), q is the p release capacity (mg.kg^{-1} dry weight), a, B and K are the constant. All parameters can be determined by regression of the experimental data. The p release data were fitted using those kinetic models by non linear regression with Microcal origin software (2002). Based on R^2 and SE, it was found that all those three models can satisfactorily describe the p release kinetics. The constant K is the release rate constant and indicates the p release extent, constant B was related to the p sorbed sediments.

The release rates of the sediment samples with different sampling within 0.5h were the highest within 48h, ranging from 0.24 to 12.42 mg/kg.h^{-1}). This indicates the quick release process mainly occurred within 0.5h.

As mentioned earlier the constants K, B and the p release rate can be used to describe the ability the p release from the sediments. p release mainly depended on the physical and chemical properties of the sediments. Both constants K, B of different kinetic models and p release rate within 0.5h had a significant and positive correlation with STP, DPS, TP and OM (r=0.87-0.96), P<0.01), and they all had a strong and negative correlation with a percentage of sand fraction (r=-073-0.94, P<0.01). This suggests that the p release was mainly affected by TP, OM, STP, DPS and the percentage of sand particles. The quick p release was mainly a physical process.

Pearson correlation coefficient between $Al_2O_3 + Fe_2O_3$, the estimated kinetic parameters and p release rates are found. The sediments were divided into two groups, heavily polluted sediments (TP>500 mg.kg^{-1}) and slightly polluted sediments TP<500mg.kg^{-1}). It is interesting to note that the relationship between the estimated kinetic parameters, p release rate and $Al_2O_3 + Fe_2O_3$ was totally different for the heavily and slightly polluted sediments.

For the slightly polluted sediments there existed a significant and negative relationship between them and for the heavily polluted sediments there existed a significant and positive relationship. $Al_2O_3 + Fe_2O_3$ was an important factor affecting the p release due to their specific surface and the higher $Al_2O_3 + Fe_2O_3$ content promoted p sorption and restrained p release. This is true for the slightly polluted sediments but not for the heavily polluted sediments. This may be related to the effects of OM and $Al_2O_3 + Fe_2O_3$. The Affecting factors of the risk of phosphorous release.

The P sorption on sediments was related to many factors. Among them the physical and chemical properties of the sediments were the most important factors. For the whole sediments and the heavily polluted sediments. DPS was significantly correlated with TP, OM and STP. But it was negatively related to the sand fraction percentage. $Al_2O_3 + Fe_2O_3$ were not correlated to DPS for the whole sediments. But it was significantly correlated for the heavily polluted sediments. For the slightly polluted sediments DPS was only significantly correlated to OM

and the significant and negative relationship between DPS and $Al_2O_3 + Fe_2O_3$ was observed. This may be because there was a notable accumulation of $Al_2O_3 + Fe_2O_3$ precipitation process when wetlands were developed. Similar results were also reported in other areas. $Al_2O_3 + Fe_2O_3$ was a main factor affecting the phosphate sorption capacity due to it specific surface. In some cases, the phosphate sorption sites were occupied by Al_2O_3 and Fe_2O_3 and DPS was higher. PSI was positively related to Fe, Fe+Al, TOC, CEC, TP and IP. Therefore ERI may be also related to the physical and chemical properties of the sediments. But in this study, the expected correlations were not observed except the percentage of sand fraction.

Correlated for the heavily polluted sediments, for the slightly polluted sediments, DPS was only significantly correlated to OM and the significant and negative relationship between DPS and $Al_2O_3 + Fe_2O_3$ was observed. In some cases, the phosphate sorption sites due to its specific sites were occupied by Al_2O_3 and Fe_2O_3 and DPS was higher. The phosphate sorption capacity was negatively related to Al_2O_3 and Fe_2O_3. This process may be an important mechanism for the removal of P from the overlying water in this region, although this aspect needs to be further investigated.

PS_1 was positively related to Fe, Fe+Al, TOC, CEC, TP and IP. Therefore ERI may also be related to the physical and chemical properties of the sediments. But in this study, the expected correlations were not except the percentage of sand fraction. This indicates that among the physical and chemical properties in the studied sediments, only the relationship between sediments, only the relationship between the percentage of sand fraction ERI was significant and negative (R^2=0.84, P<0.01). It is suggested that the great variety of the selected physical and chemical characteristics of the studied sediments was one of the reasons. In this study, ERI had a strong and negative correlation with the percentage of sand particles. This suggests that the p release was mainly a physical process. The higher the percentage of the sand particles in the sediments, the cower the P release risk.

CONCLUSION
The selected physical and chemical characteristics of the studied sediments varied greatly. TP, OM, $Al_2O_3 + Fe_2O_3$ and the percentage of sand particles were the important factors affecting the ability of P sorption.

P release process from the sediments was similar; the first process was the quick reaction and mainly occurred within 0.5h, and then the slow reaction. The P release occurred within 20h and then reached a dynamic equilibrium, and P release process was slower than P sorption process.

Both power function model, parabolic diffusion model and Simple Elovich model can satisfactorily describe the P release kinetics in the sediments. The P release was mainly affected by TP, OM and STP, DPS and the percentage of sand particles, and the quick P release was mainly a physical process. For the slightly polluted sediments $Al_2O_3 + Fe_2O_3$ restrained P release, and for the heavily polluted sediment organic matter and $Al_2O_3 + Fe_2O_3$ promoted P release.

Both DPS and ERI can be used to evaluate the P-induced wetland eutrophication risk, and the threshold values were 6.6% and 25%, respectively. The results shows that most

of studied sediments were in eutrophication risk. For the whole sediments and the heavily polluted sediments DPS was significantly correlated with TP, OM and STP, and it was negatively related to the sand fraction percentage. $Al_2O_3+Fe_2O_3$ was not correlated to DPS for the whole sediments, but they were significantly related for the heavily polluted sediments. For the slightly polluted sediments DPS was only significantly correlated to OM, and there existed a significant and negative relationship between DPS and $Al_2O_3+Fe_2O_3.$ The percentage of the sand particle was negatively related to ERI.

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