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DEVELOPMENT OF DIFFUSIVE GRADIENT IN THIN FILM AS A NEW METHOD FOR PREDICTION OF PHOSPHATE RELEASE FROM MARINE SEDIMENT

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ABSTRACT
The diffusive gradient in the thin-film (DGT) technique can be used to predict phosphate release from sediment. The phosphate concentration was determined from the dissolved phosphate in the overlying water. The phosphate in overlying water diffused and accumulated in the DGT device. The study of phosphate released from sediment including the effect of temperature, pH, agitation, and phosphate concentration in the overlying water. The sediment was used in this experiment collected from the marine sediment of Jakarta Bay with speciation of phosphate in sediment as water-soluble P (H_2O-P), loosely bound-P (NH_4Cl-P), exchangeable fraction-P ($NaHCO_3$-P), P bound to iron (NaOH-P), and P bound to calcium (HCl-P). The fraction of H_2O-P, NH_4Cl-P, $NaHCO_3$-P, HCl-P, and NaOH-P was 0.16, 0.60, 2.68, 19.23, 1.63, and 0.20 µg/g, respectively. The maximum temperature of phosphate released at 35°C with the concentration of phosphate was 99.88 µg/L, the phosphate accumulation in the DGT device was 8.2569 µg and C_{DGT} was 131.21 µg/L. The range of pH 5-10 resulted in the phosphate released was 59.33-100.16 µg/L, M_{DGT} range 1.8331-2.9734 µg and C DGT range 13.21-22.82 µg/L. The agitation did not influence the phosphate released from the sediment. The phosphate accumulated in the DGT unit for deployment in the overlying water indicated the phosphate release from the sediment. It shows the ability of the DGT unit to absorb phosphate released from sediment to water. It can be inferred from this study that the DGT unit can predict phosphate release from the sediment based on the increase of phosphate accumulation in the DGT unit.
Keywords: Phosphate, DGT, Sediment, Fractionation

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INTRODUCTION

Phosphorus is a very important nutrient in aquatic and it was needed by phytoplankton. The biogeochemical cycling of phosphorus in the water is required for speciation information., mixing behavior and transformation[1]. Phosphate is present in sediments as organic phosphate and inorganic phosphate. The inorganic phosphate is the phosphate bound to minerals in the sediment. These forms are sensitive to pH and redox variation on the sediment and overlying water[2]. Phosphorus is a limiting nutrient in algal growth and caused eutrophication[3].

Eutrophication is a nutrient enrichment process in the aquatic environment. Eutrophication is a kind of water pollution caused by the loss of dissolved oxygen[4]. Phosphate accumulated in sediments and can be released into the water. Sediment act as a sink where P can be stored, but also as a source of P for the overlying water. The release of P from the sediment is an important source for marine sediment. The release of phosphate from sediment may be influenced by dissolved oxygen, redox potential, pH, organic material, and temperature[5,6]. The effect of pH and O_2 has been studied on phosphate release from sediment with determined phosphate concentration in the overlying water by spectrophotometric method[7].

In our research, we will develop a new technique to predict phosphate release with the diffusive gradient in thin-film (DGT). The DGT technique has been used to measure the concentration of an analyte in the water solution[8]. The quantity measured is the mass of analyte accumulated by the binding gel and concentration was calculated by Fick's first law[9]. The objective of our study is to develop a diffusive gradient in thin-film to predict phosphate release from marine sediment including temperature, pH, and agitation effect.

EXPERIMENTAL

Sampling Sediment

Sediment samples were collected from Jakarta Bay (106° 34' 32. 6" E, 06° 01' 24. 2" S). The experiment used a sediment core with a length of 24 cm and a diameter of 8 cm. The sediment characterization was carried out on physical and chemical properties.

Characterization of Sediment

Characterization of sediment consists of loss on ignition (LOI), phosphate total, Fe, Mn, and Ca content. The LOI was determined with dried in 550°C for 4 hours. Total phosphorus was determined by digestion using nitric acid and perchloric acid[10]. Iron, manganese, and calcium were determined after digestion of potassium persulfate and sulfuric acid by flame atomic absorption spectrometry with Shimadzu AA-6300. The aqueous standard solution of 100 mg/L was used for the quantification of metal in sediment. The fractionation of phosphate concentration in the marine sediment of Jakarta Bay was determined by sequential extraction in the laboratory experiment. The first step was extraction by demineralization of water. The next fraction use NH_4Cl (1.0 M) as the loosely bound-P was extracted and $NaHCO_3$ (0.5M) as the exchangeable fraction. The next extraction using NaOH (2 M) as phosphorus bound to iron (Fe/Al-P). The last extraction using HCl (0.5 M) as phosphorus bound to calcium (Ca-P).

Assembling of DGT Device

The DGT device with a 2 cm diameter was used in this experiment. The DGT unit consists of a diffusive layer, binding gel, and membrane filter. The polyacrylamide hydrogel was used as a diffusive gel. The polyacrylamide pregnated of ferrihydrite was used as a binding gel. The membrane filter was cellulose nitrate with 0,45 μm pore-size. [11,12]

Phosphate Release Experiment

A phosphate release experiment was used in the sampling tubes. The water was added into the tube slowly to avoid sediment resuspension. Phosphate concentration was monitored during the experiment period. Prepared 250 g of sediment in a tube and added 250 mL of distilled water. The pH condition with a range of 5 to 10. The DGT device is put on the surface of the water for 7 days. After 7 days the concentration of phosphate released from sediment was determined. The phosphate mass bound to the binding gel and phosphate concentration diffused to the DGT device was determined by spectrophotometric. The effect of contact time on phosphate release from sediments was carried out with a time variation of 1-15 days. The effect of agitation using a shaker with a speed of 0 to 90 rpm.

Phosphate Analysis

The phosphate ion through the diffusion gel to the binding gel was controlled by Fick's first low diffusion. In this experiment, the phosphate in the binding gel (ferrihydrite) was eluted using 0.25 M H_2SO_4. The concentration of phosphate in acid (*Ce*) was measured by the spectrophotometri[13]. The mass (M) of phosphate fixed in the binding gel of ferrihydrite of DGT device in a solution of concentration C during the time t was calculated (Eq.-1).

$$M = Ce\ (V_{gel} + V_{acid}) \quad (1)$$

The phosphate diffuses in DGT device was calculated in the Eq.-2.

$$C = \frac{M\Delta g}{DtA} \quad (2)$$

M can be obtained to the mass of phosphate species diffused through a known area (A), t was the time of deployment. The Δg was the thickness of the gel membrane and D is the diffusion coefficient.

RESULTS AND DISCUSSION

Characterization of physical and chemical properties gives important information to phosphate released from sediments to the overlying water[14]. Phosphate can be released into the overlying water under certain environmental conditions which leads to continuing water eutrophication.

Tabel-1: Sediment Characteristic

No	Parameters	Content
1	Moisture content	4.89 ± 0.96 %
2	LOI	16.32 ± 0.06 %
3	Fe content	44.68 ± 1.6 mg/g
4	Mn content	1.08 ± 0.10 mg/g
5	Ca content	0.02±0.004 mg/g
6	Phosphate total	898.18 ± 58.80 µg/g

The loss on ignition (LOI) was 16.32 ± 0.06 %. The phosphate in sediment can be associated with Fe, Ca, and Mn. The iron content in sediment was 44.68 ± 1.6 mg/g and Mn content was 1,08 ± 0.10 mg/g. The phosphate concentration in water can control the interaction with minerals in sediment[15,16]. The iron ions dominant in sediment and can interact with phosphate.[17,18]

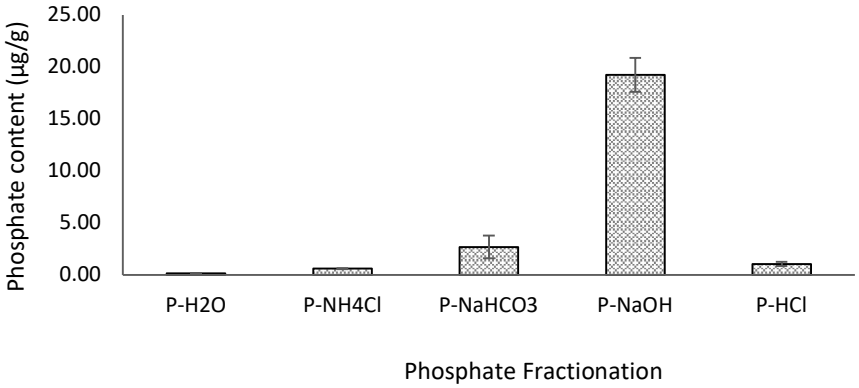
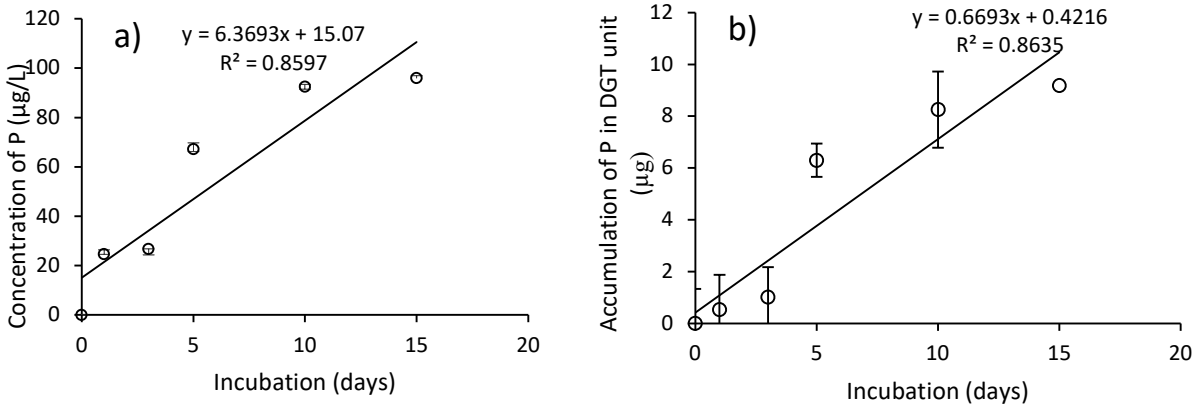


Fig.-1: Phosphate Fractionation of Marine Sediment

Phosphate fractionation in marine sediment with sequential extraction used H_2O, NH_4Cl, $NaHCO_3$, NaOH, and HCl solvents. The phosphate fractionations give the information of associated phosphate with minerals in sediment. Speciations of phosphate in sediment were water-soluble P (H_2O-P), loosely bound-P (NH_4Cl-P), exchangeable fraction-P ($NaHCO_3$-P), P bound to iron (NaOH-P), and P bound to calcium (HCl-P). Based on the experiment, the fraction of H_2O-P, NH_4Cl-P, $NaHCO_3$-P, NaOH-P, and HCl-P was 0.16, 0.60, 2.68, 19.23, 1.63, and 0.20 µg/g, respectively. The fractionation of phosphate can control mobilization phosphate in the sediment to overlying water.[14,19] The extraction using NaOH showed the Fe or Al bound to phosphate and is used for the prediction of bioavailability for algae and phytoplankton.[20,21] Fractionation of HCl-P was sensitive to low pH and indicated the P bound to carbonate and organic-P.[21-23] The Information P fractionation in sediment was important to describe the release and predict the phosphate concentration.[24]



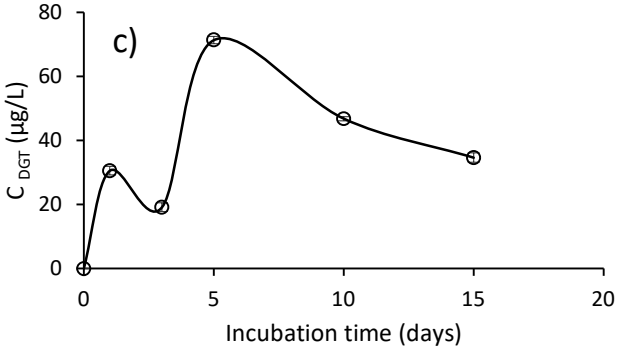


Fig.-2: Effect of Incubation on Parameters (a) Phosphate Release from Sediment (b) Phosphate Accumulation to DGT Unit (c) Phosphate Concentration in DGT Unit

Based on Fig.-2, it can be seen the effect of incubation time on phosphate release from sediment. The experiment condition with dissolved oxygen was 8.3 mg/L, pH was 7, and temperature of 25° C. After incubation for 1 day showed the phosphate release was 25.59 µg/L. Incubation for 5 days indicated the phosphate release of 67.24 µg/L. Incubation for 15 days showed an increase of phosphate concentration in the overlying water of 95.98 µg/L. It can be inferred from this experiment, the increase of incubation time caused the increase of phosphate released from the sediment. Phosphate released from sediment showed the phosphate in pore water was diluted to the overlying water.

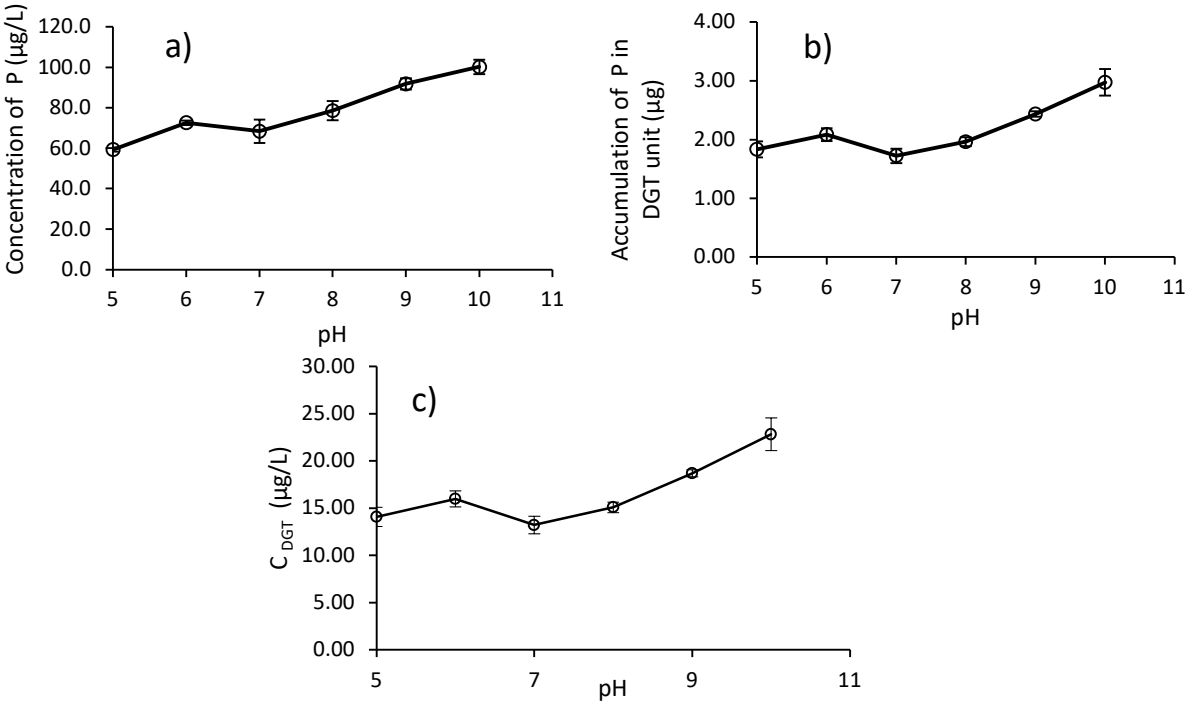


Fig.-3. Effect of pH to Parameters (a) Phosphate Release from Sediment (b) Phosphate Accumulation in DGT Unit (c) C_{DGT} After Released from Sediment.

The phosphate released from sediment to the overlying water will be accumulated in the DGT unit. Phosphate in the overlying water diffused to diffusive gel in the DGT unit and accumulated to binding gel. The phosphate concentration released from sediment to the overlying water was detected by the DGT device. Based on the experiment showed the increase in incubation time caused the increase of phosphate accumulation in the DGT unit. Incubation for 1 day showed the accumulation of phosphate in the DGT

unit was 0.5393 µg. After 5 days, the mass of phosphate increase to 6.2989 µg. The maximum phosphate accumulated to the DGT unit for incubation of 15 days with the mass of phosphate was 9.1750 µg. Incubation for 1 day showed the diffused phosphate from solution to DGT unit with the concentration of 30.56 µg/L. The incubation of 3 days causes the decrease of phosphate concentration diffused to the DGT unit. The maximum phosphate concentration in the DGT unit occurred in 6 days with a concentration of 71.38 µg/L. From the curve occurred fluctuation in the diffusion of phosphate because of the incubation process in a long time, which can reduce the diffusion process.

The effect of pH was controlled by the addition of NaOH and HCl. The pH range was 5-10. Fig.-3 showed the correlation between pH and phosphate released from sediment to the overlying water. In the pH neutral was 7 the phosphate release from sediment was 68.34 µg/L. The highest phosphate release occurred at pH 10 with a concentration of 100.16 µg/L. The phosphate accumulation in the DGT unit at pH 5 was 1.8331 µg. Based on the curve seen in an alkaline condition, there was an increase in phosphate accumulation mass to 2.9734 µg. Based on the experiment, it showed a positive correlation between the increase of pH and phosphate accumulation in the DGT unit. The binding gel in the DGT unit can accumulate the phosphate released from sediment in acidic, neutral, and alkaline pH conditions. The amount of accumulated mass is influenced by the amount of phosphate released from the sediment.

In the high pH, the phosphate released was influenced by the ferrous content in the sediment. Phosphate was precipitated and bounded as $FePO_4$ and occurred ion-exchanged with hydroxide Na_3PO_4. The sodium phosphate will be solute in the water and hydroxyl ion reacted with ferrous to make $Fe(OH)_3$ with the low solubility and deposited in the sediment. The phosphate ion in sediment was interacted with ferrous and adsorb at ferrihydroxide. The high pH caused desorption of phosphate from ferric hydroxide to the overlying water.[25,26]

The pH 5 resulted in the phosphate accumulation of 1.8331 µg. The minimum accumulated phosphate was pH=7 with a mass of 1.7215 µg. Overall, the binding gel can interact with phosphate in pH neutral, acid, and base. The phosphate accumulated in the DGT unit was influenced by the rate of phosphate release in the sediment.

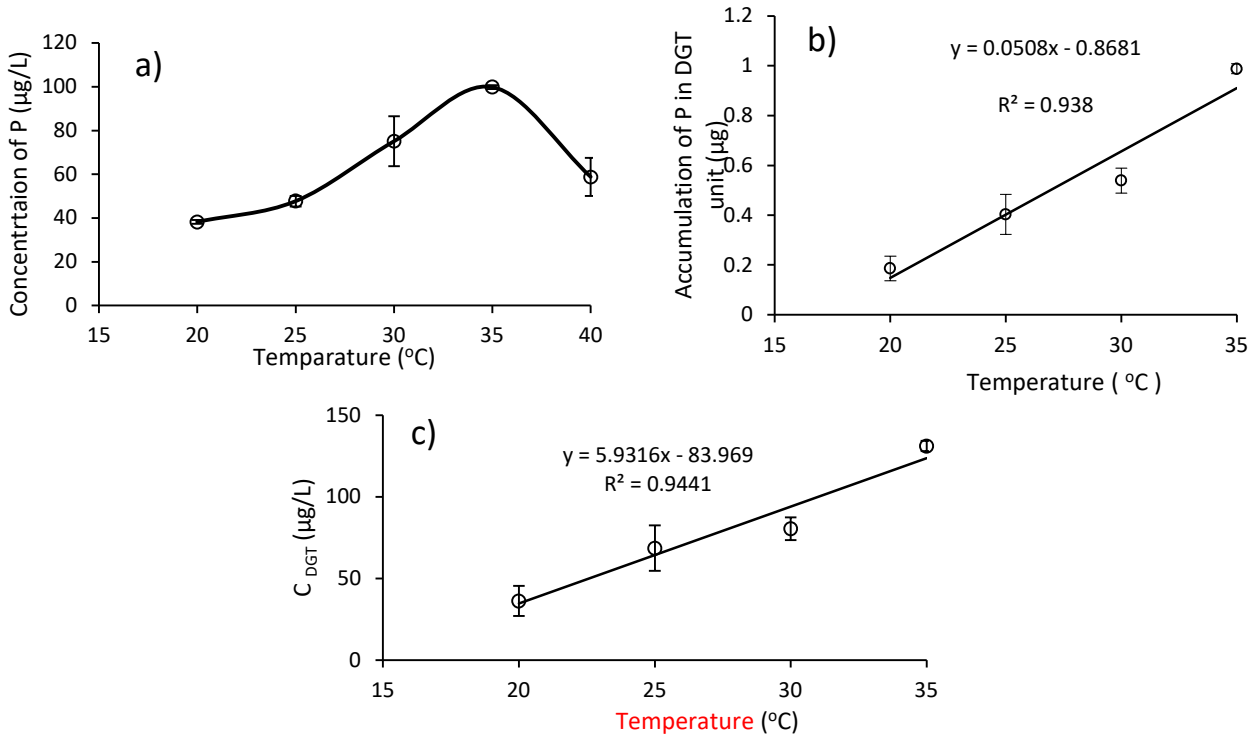


Fig.-4: Effect of Temperature on Parameters (a) Phosphate Release from Sediment (b) Phosphate Accumulation in DGT Unit (c) Phosphate Concentration in DGT Unit

The experiment resulted in the minimum phosphate concentration at pH 7 of 13.21 µg/L. The maximum phosphate concentration was found at pH 10 with C_{DGT} of 22.82 µg/L. The diffused phosphate can be analogous to phosphate released from sediment into the overlying water and diffused to the biota in the aquatic environment. In general, species form diffused to DGT unit at pH 5-6 as $H_2PO_4^-$, pH 7-10 as HPO_4^2. These species can be absorbed by biota in the aquatic that can be described in the DGT unit. In acidic conditions with pH below 7, the phosphate release process is affected by the presence of carbonate ions in the sediment. Ca-bound P in sediments is easier to release under acidic conditions than alkaline conditions.[27] The release of phosphate from sediment influences pH and phosphate speciation.[28,29]

Based on Fig.-4 showed the influence of temperature on phosphate release from the sediment. At the temperature of 20ºC, the concentration of phosphate released from the sediment was 38.28 µg / L. The higher of temperature, the greater of phosphate released from the sediment. The optimum phosphate release was obtained at 30ºC with a concentration of 99.88 µg/L. There is a decrease in phosphate concentration released from sediment at the temperature of 40^0C because of the adsorption of phosphate into the sediment. Based on the correlation between temperature and phosphate accumulation in the DGT unit shows a positive correlation. The results indicated that the higher of temperature, the greater of accumulation phosphate in the DGT unit for a range of 20-35ºC. The DGT device is placed in a solution to accumulated phosphate mass released from the sediment. Phosphate accumulated at temperatures of 20 to 35ºC with a range of 0.5393- 8.2569 µg. The linearity relationship between temperature and phosphate mass accumulated in gel oxide in DGT units with a correlation value of 0.9386 and the equation y = 0.0508x-0.8681. Temperature affected the microbial process in sediments. The microbial activity indirectly affects the process of reducing Fe (III) to Fe (II) as an alternative electron acceptor. The range of temperature was 20 – 35 ºC resulted in the phosphate diffused of 36.32-131.21µg/L. The linear correlation between temperature and phosphate diffused in DGT with $R^2 = 0.9441$ and equation of y = 5.316x-83.968.

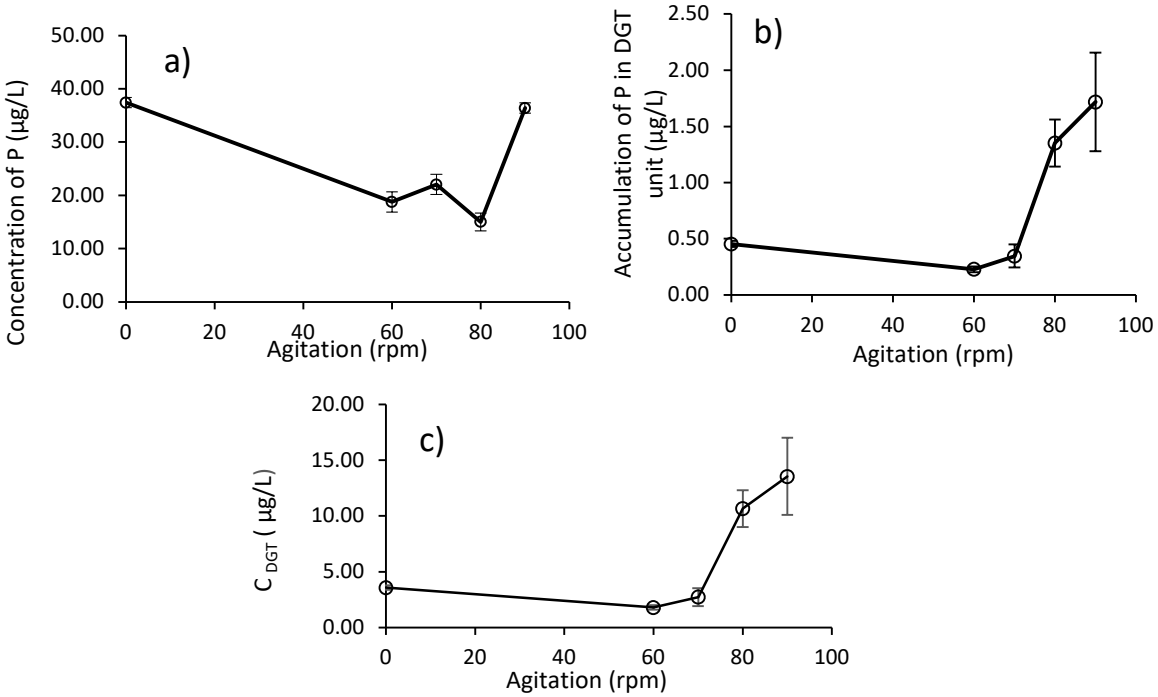


Fig.-5: Effect of Agitation on Parameters (a) Phosphate Release from Sediment (b) Phosphate Accumulation in DGT Unit (c) Phosphate Diffused in DGT Unit

Fig.-5 shows the effect on agitation to phosphate released from the sediment. The phosphate released from sediment without agitation was 37.41 µg/L. Agitation with 60 rpm causes a decrease of phosphate concentration to 18.79 µg/L. The greater agitation speed, the concentration of phosphate released from the sediment varies and fluctuates up and down. The effect of agitation does not give a significant correlation with phosphate release because it only involves physical interactions between sediment and water.

Increased agitation showed an increase in phosphate accumulation to the binding gel. This indicated the effect of agitation can increased absorption in aquatic biota but this number is less than the amount released to the overlying water. The water absence stirring resulted in phosphate accumulation and agitation at 90 rpm caused the phosphate to accumulate of 1.7174 µg. The increasing of phosphate accumulated in the DGT unit because the phosphate released from the sediment was increasing. Increased agitation causes an increase of phosphate diffused to DGT from 5.58 µg/L to 13.54 µg/L. The effect of agitation causes an increase of phosphate release from sediment, so the phosphate diffused to DGT becomes higher. The phenomena diffused phosphate to DGT unit mimic the uptake phosphate in the organism in the aquatic environment.

CONCLUSION

The diffusive gradient in thin-film (DGT) technique can be used to predict phosphate release from sediment. The concentration of phosphate was measured from the dissolved phosphate in the overlying water. The phosphate in overlying water diffused and accumulated in the DGT unit. The study of phosphate released from sediment including the effect of temperature, pH, agitation, on phosphate concentration in the overlying water.

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