Study of phosphate release from Bogor botanical gardens' sediment into pore water using diffusive gradient in thin film (DGT)

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Abstract. Eutrophication is one of the environmental problems caused by the excessive nutrients in aquatic ecosystems. In most lakes, phosphate is a limiting nutrient for algae photosynthesis. Even though the concentration of phosphate from external loading into the water body has been reduced, eutrophication could still be occurred due to internal mobilization of phosphate from the sediment pore water into the overlying water. Therefore, the released phosphate from sediments and their interaction in the pore water must be included in the monitoring of phosphate concentration in aquatic system. The released phosphate from sediment into pore water has been studied by DGT device with ferrihydrite as binding gel and N-N’-methylenebisacrylamide as crosslinker. The results showed that DGT with 15% acrylamide; 0.1 % N-N’-methylenebisacrylamide and ferrihydrite as binding gel was suitable for the measurement of the released phosphate from sediment into pore water. The result of the deployed DGT in oxic and anoxic conditions in seven days incubation showed the released phosphate process from the sediment into pore water was affected by incubation time and the existence of oxygen in the environment. The released phosphate from the sediment into pore water in anoxic condition has a higher value than oxic condition. The experimental results of the deployed DGT in natural sediment core at a depth of 1 to 15 cm from the surface of the water for 7 days showed that the sediment has a different phosphate mass profile based on depth. The concentration of phosphate tends to be increased with depth. The maximum $C_{DGT}$ of phosphate released in oxic and anoxic conditions at 7th day period of incubation are 29.23 $\mu$g/L at 14 cm depth and 30.19 $\mu$g/L at 8 cm depth, respectively.

Keywords: sediments, phosphates release, DGT, pore water

1. Introduction

Eutrophication is one of the environmental problems that causing damage to aquatic ecosystems, especially to freshwater. Eutrophication occurs when the aquatic environment is enriched with nutrients. Nitrates and phosphates are nutrients that needed to grow the plants. In sufficient amounts they are beneficial to many ecosystems, but in excess amounts can cause eutrophication [1]. Agricultural residual waste such as fertilizers is one of the cause of eutrophication, mostly they are dissolved into a nearby water system causing the increase of nutrient content [2]. Eutrophication stimulates an explosive growth of algae (algal blooms), may cause the oxygen content on the water to be consumed by algae, also block the sunlight from photosynthesizing the aquatic plant that lead to the depletion of the dissolved oxygen.
in water. This bloom disrupts normal ecosystem function and causes many problems. Some algae even produce toxins that are harmful to the higher forms of life. This can cause problems along the food chain and affect any animal which uses them as the food source [3].

In most lakes, phosphate becomes the limiting factor in the algae photosynthesis process because its presence is relatively small compared with the number of aquatic organisms that need them. Phosphate controls the growth of biomass in the overlying water [4], so it necessary to monitor the presence of phosphate in the water. Even though the presence of phosphate has been reduced, eutrophication can still continue to occur due to the mobilization of phosphate from the sediment into pore water through the physics, chemistry and biochemistry processes [5]. Sediments play an important role in the presence of phosphate in the water because it acts as a source and reservoir of phosphate. Therefore, the release of phosphate from the sediment into the pore water must be included in the process of monitoring phosphate pollution. Pore water defines as water that presents between sediment particles, the phosphate is released into pore water and then diffused into overlying water, in which algae could consume orthophosphate as the available phosphate that required by plants [6].

Orthophosphate in the water occurs from the dissolution of apatite mineral and mineralization of organic phosphate [7]. Rumhayati [8], Edlund and Carman [9] and Suzumura and Kamatani [10] found that organic phosphate mineralization in sediments occurs in anoxic condition. It is well known that phosphorous cycle in water is affected by Fe (III) reduction in the sediment and Fe (II) oxidation in the water [11]. The accurate determination of phosphate is difficult to obtain because the dynamic interaction during storage could change the concentration of phosphate. Zhang et al. [12] has developed the Diffusive Gradient in Thin Films (DGT) device for in situ measurement of reactive phosphorus species in natural waters, sediments and soils. The principle of phosphate measurement using DGT technique is that phosphate ion diffuses through the membrane filter and diffusive layer to reach the ferricydrite gel. Mass of phosphate absorbed by binding gel was analyzed by colorimetry method after being eluted by acid. Concentration of phosphate obtained is considered to be equal to the phosphate which may diffuse into algae, therefore DGT can be used for measuring the bioavailability.

DGT is a device that consists of a membrane filter, diffusive gel and adsorbent, packed in a probe. Diffusive gel used was an acrylamide polymer in the form of a hydrogel. Generally, DGT Crosslinker from DGT research used as a crosslinker in the synthesis of acrylamide polymer. According to Ratshania, N,N'-methylenebisacrylamide can be used as a crosslinker in the synthesis of acrylamide polymer for DGT [13]. In this study, the authors used DGT probe technique using ferricydrite as binding gel and N,N'-methylenebisacrylamide as crosslinker for the measurement of the phosphate release from sediment into pore water sediment in oxic and anoxic conditions. Measurement of the phosphate release was carried out at different depths of 1-15 cm.

2. Materials and methods

2.1. Chemicals

All reagents were of analytical grade. The reagents and materials employed for the preparation of in-house manufactured DGT gels were acrylamide (Sigma–Aldrich, Germany), ammonium persulfate (Sigma–Aldrich, Germany), tetramethylethylenediamine (Sigma–Aldrich, Germany), N,N'-methylenebisacrylamide (Sigma–Aldrich, Germany), cellulose nitrate membrane filter (Whatman), Sodium Nitrate from Merck, and Fe(NO$_3)_2$.9H$_2$O (Merck, Germany). The reagents for PO$_4$ determination were potassium hydrogen phosphate (Merck, Germany), sodium hydroxide (Merck, Germany), sulphuric acid (Merck, Germany), ammonium molybdate (Merck, Germany), potassium antimonyl tartrate (Merck, Germany), and ascorbic acid (Merck, Germany).

2.2. Experimental

The preparation of diffusive gel and ferricydrite was conducted using the procedure by Zhang et al. [12]. The available phosphate species was measured using a DGT technique with ferricydrite as a diffusive gel. The gel contains 15% acrylamide and 1.0% crosslinker. For binding gel, the gel solution was added by ferricydrite. 70 μL of ammonium persulfate (10% in water) and 20 μL of tetramethylethylenediamine were added to initiate the polymerization reaction. The prepared gel
solution was then maintained at 45°C for 1 hour. Resin gels were hydrated in demineralized water for 24 h, the diffusive gels disks were stored in the demineralized water and the binding gel was stored in 0.1 M NaNO\textsubscript{2} solution. The thickness of the prepared gels was 0.23 cm.

Sediment sample from Bogor Botanical Gardens’ lake was sampled as core sediment to attain the undisturbed sample. DGT probe was deployed for 7 days in oxic and anoxic conditions with bubbling of oxygen and nitrogen. For initial data, DGT probe was deployed for 2 hr without bubbling of oxygen and nitrogen. At each retrieval time, the binding gel was removed from the probe and then cut into 1 cm size. The binding gel was eluted by 0.25 M H\textsubscript{2}SO\textsubscript{4} solution and the concentration of PO\textsubscript{4} was measured by spectrophotometer UV-Visible with blue molybdenum method.

3. Results and discussion

3.1. Assembly of DGT probe for sediment

DGT is a device that consists of a membrane filter, diffusive gel and adsorbent, packed in a plastic probe. Diffusive gel is the acrylamide polymer and the binding gel is diffusive gel which added with adsorbents. In this research, ferrihydrite was used as adsorbent for phosphate binding. DGT probe sediment used in this research was plastic assembled with an open window of 2.6 cm x 16 cm. The schematic representation of asection of the DGT assembly can be seen in figure 1.

DGT probe sediments were assembled by the following stages, the first stage is to put ferrihydrite gel on the probe, continued with the placement of diffusive gels, cellulose nitrate membrane and finally it was closed using window probe. The DGT probe sediments assembly process can be seen in figure 2.

![Figure 1. Schematic Representation of a section of the DGT Assembly [14].](image)

![Figure 2. Schematic representation of asection through the DGT assembly.](image)
3.2. FTIR characterization of diffusive gel and ferrihydrite gel

FTIR characterization of diffusive gel and ferrihydrite gel can be seen in figure 3. Based on the results, there are two peaks at the wavenumber of 3337 cm$^{-1}$ and 3188 cm$^{-1}$ for sample diffusive gels. For gel sample of ferrihydrite gel, two peaks are also appear at wavenumber 3338 cm$^{-1}$ and 3181 cm$^{-1}$ which is a typical absorption of the primary amine (NH$_2$) at wavenumber 3300-3600 cm$^{-1}$ with a medium intensity. Peak at wavenumber 1648 cm$^{-1}$ for sample of diffusive gel and 1649 cm$^{-1}$ for sample of ferrihydrite gel indicated an absorption of carbonyl amide (-CONH-) at the wavenumber 1690-1650 cm$^{-1}$ with a strong intensity. Peak at wavenumber 1186 cm$^{-1}$ for sample diffusive gel and 1187 cm$^{-1}$ for sample ferrihydrite gel showed an absorption of aliphatic amine (C-N) at the wavenumber 1250-1020 cm$^{-1}$ with medium intensity. Functional groups that appear in the spectra are the main functional groups of the acrylamide polymer. Functional groups that appear on diffusive gels and ferrihydrite gel showed no significant difference, so it can be concluded that no changes took place in the structure of the polymer in the presence of ferrihydrite. The data also showed that interaction between ferrihydrite and acrylamide polymer is a physical interaction.

3.3. DGT deployment on nature sediment sample

During the deployment of DGT probe, the dissolved oxygen, temperature and pH of the water surface were monitored. The result can be seen in table 1. After seven day period of deployment of DGT probes in sediment, the probe was removed from the DGT system then rinsed using aquabidest. The binding gel was removed from the devices and then sliced for each 1 cm layer of depth to be analyzed for concentration of phosphate using spectrophotometer UV-Visible after eluted with 0.25 M sulphuric acid. Data of phosphate concentrations absorbed by the ferrihydrite binding gel ($C_{DGT}$) during deployment in oxic condition are showed in table 2 and figure 3.

![FTIR Spectra](image.png)

**Figure 3.** FTIR Spectra diffusive gel (grey line) and ferrihydrite gel (black line).

**Table 1.** Data of the dissolved Oxygen, temperature and pH.

| No. | Parameter     | Result               |
|-----|---------------|----------------------|
|     | Initial (2 hour) | Oxic (7 day) | Anoxic (7 day) |
| 1   | Temperatur ($^\circ$C) | 25.0 – 25.5 | 25.0 – 25.5 | 25.0 – 25.5 |
| 2   | Dissolved Oxygen (mg/L) | 7.38 – 7.56 | 6.73 – 7.82 | 0.12 – 0.90 |
| 3   | pH             | 7.05 – 7.10 | 6.93 – 7.20 | 7.60 – 7.92 |

Data of phosphate concentrations absorbed by the ferrihydrite binding gel ($C_{DGT}$) during deployment in oxic condition are showed in table 2 and figure 3.
Table 2. Mass of PO$_4$ during DGT deployment.

| Depth (cm) | Initial (2 jam) | Oxidic (7 hari) | Anoxic (7 hari) |
|------------|-----------------|-----------------|-----------------|
| 1          | 0.00 ± 0.00     | 0.33 ± 0.09     | 1.74 ± 2.34     |
| 2          | 0.00 ± 0.00     | 0.31 ± 0.07     | 4.43 ± 4.98     |
| 3          | 0.08 ± 0.07     | 0.32 ± 0.13     | 9.17 ± 1.45     |
| 4          | 0.22 ± 0.08     | 6.44 ± 5.05     | 10.44 ± 2.59    |
| 5          | 0.34 ± 0.58     | 5.10 ± 4.49     | 9.79 ± 1.95     |
| 6          | 0.08 ± 0.14     | 6.93 ± 3.14     | 8.05 ± 4.92     |
| 7          | 0.00 ± 0.00     | 6.93 ± 2.35     | 10.22 ± 3.38    |
| 8          | 0.00 ± 0.00     | 7.38 ± 1.41     | 10.84 ± 1.78    |
| 9          | 0.40 ± 0.47     | 9.59 ± 1.98     | 9.05 ± 1.95     |
| 10         | 0.29 ± 0.06     | 5.90 ± 2.27     | 8.44 ± 5.45     |
| 11         | 0.09 ± 0.15     | 7.46 ± 1.16     | 7.18 ± 1.31     |
| 12         | 0.11 ± 0.18     | 9.46 ± 3.45     | 7.19 ± 1.80     |
| 13         | 0.00 ± 0.00     | 8.62 ± 2.41     | 10.72 ± 3.69    |
| 14         | 0.00 ± 0.00     | 10.50 ± 1.89    | 9.25 ± 2.83     |
| 15         | 0.00 ± 0.00     | 9.14 ± 4.08     | 8.90 ± 1.98     |

Note: *0.00 ± 0.00 means phosphate was below detection limit.

Figure 4. The comparison mass of phosphate absorbed on initial, oxic and anoxic conditions.

Based on the data in table 2, the maximum mass of phosphate after 7 days on oxic and anoxic conditions are 10.50 µg at a depth of 14 cm and 10.84 µg at a depth 8 cm, respectively. Figure 4 shows that mass of phosphate tend to be increased by the depth in both oxic and anoxic treatments. In oxic condition, mass of phosphate increased sharply compared to the increase in anoxic condition. Observation at a depth of 1-8 cm showed that difference mass phosphate absorbed in anoxic condition was much greater than oxic condition.
Phosphate mobilization from sediment into pore water is strongly influenced by environmental redox condition [15]. According to Baken et al. [11] the dynamics of phosphate and iron in the aquatic environment is affected by the Fe (III) reduction in the sediment and Fe (II) oxidation in the water. In anoxic condition, the sediment will release phosphate which bind with iron hydroxides [10] and increase the concentration of phosphate in the water. While in oxic condition, Fe (II) will be oxidized to Fe (III) to form iron oxyhydroxide (FeOOH) which adsorbs phosphate from the water. Therefore, in oxic condition the phosphate concentration became lower than phosphate in anoxic condition. Moreover, the process of release of phosphate from the sediment into the water was not only caused by dissolution and precipitation of apatite mineral, but also occurred by mineralization of organic phosphate compounds. Phosphorus bound by the organic phase is released from microbial activity during the degradation of organic matter [16]. Suzumura and Kamatani [10] found that at 60 days of incubation, myo-inositol hexaxis phosphate (IP₆) are mineralized in oxic and anoxic conditions. In oxic condition, the IP₆ mineralization was at 48% and in anoxic condition at 95%.

The concentration of phosphate absorbed by binding gel (C_{DG'T}) is calculated using the following equation (1) bellow:

\[
C_{DG'T} = \frac{M \times \Delta g}{D \times t \times A}
\]

where:
- \(C_{DG'T}\) = concentration of phosphate absorbed by binding gel
- \(M\) = mass of phosphate absorbed by binding gel
- \(\Delta g\) = the thickness of the diffusive gel plus the thickness of the filter membrane
- \(D\) = diffusion coefficient of phosphate in the gel
- \(t\) = deployment time
- \(A\) = exposure area

Data of the concentration of phosphate absorbed by binding gel (C_{DG'T}) during seven days of deployment can be seen in table 3. The concentration profile of C_{DG'T} of phosphate at various depths after seven days period of deployment can be seen in figure 5.

Based on the data in table 3, the maximum of C_{DG'T} of phosphate after 7 days period of oxic and anoxic conditions are 29.23 g/L at a depth of 14 and 30.19 g/L at a depth of 8 cm, respectively. Based on profile of C_{DG'T} Phosphate at various depths after seven days of deployment in oxic and anoxic conditions, it showed that CDGT phosphate tends to increase by the depth. Observation at depth of 1-8 cm showed

![Figure 5. Profile C_{DG'T} phosphate at various depths after seven days period of deployment.](image-url)
Table 3. C\textsubscript{DGT} during seven days period of deployment.

| Depth (cm) | C\textsubscript{DGT} PO\textsubscript{4} (µg/L) |
|------------|----------------------------------|
|        | Oxic        | Anoxic        |
| 1       | 0.92 ± 0.25 | 4.85 ± 6.52  |
| 2       | 0.86 ± 0.21 | 12.35 ± 13.86|
| 3       | 0.90 ± 0.37 | 25.53 ± 4.05 |
| 4       | 17.94 ± 14.07 | 29.08 ± 7.22 |
| 5       | 14.20 ± 12.51 | 27.25 ± 5.43 |
| 6       | 19.29 ± 8.74 | 22.42 ± 13.71|
| 7       | 19.29 ± 6.53 | 28.45 ± 9.41 |
| 8       | 20.55 ± 3.92 | 30.19 ± 4.96 |
| 9       | 26.71 ± 5.50 | 25.21 ± 5.43 |
| 10      | 16.43 ± 6.32 | 23.49 ± 15.16|
| 11      | 20.78 ± 3.22 | 20.00 ± 3.64 |
| 12      | 26.35 ± 9.60 | 20.02 ± 5.01 |
| 13      | 24.00 ± 6.71 | 29.84 ± 10.27|
| 14      | 29.23 ± 5.26 | 25.76 ± 7.89 |
| 15      | 25.44 ± 11.36| 24.77 ± 5.51 |

that CDGT phosphate in anoxic condition was greater than oxic condition. This is due to at the increasing depth the oxygen concentration decreases, so both two core sediment samples are in anoxic condition. According to Effendi, at the water surface, oxygen levels will be higher due to the diffusion process of water with free air. Furthermore, the surface layer exposed to sunlight allows the process of photosynthesis to produce oxygen. At the increasing depth, the level of dissolved oxygen is decreased, caused by the decreasing sunlight that would inhibit the process of photosynthesis. The dissolved oxygen is used by the aquatic biota for breathing process and the oxidation of organic and inorganic materials [17]. At a depth of 9-15 cm the absorbed mass phosphate was relatively the same, it could be due to the influence of oxygen and nitrogen bubbling was reduced at the higher depths, therefore the oxygen cannot diffuse to the higher depths. This causes the environmental conditions on both treatments to be relatively equal.

Redox potentials in natural waters range from about -400 mV to +800 mV at pH 7 to 8. They are bounded in the negative range by the reduction of H\textsubscript{2}O to H\textsubscript{2} (g) and in the positive range by the oxidation of H\textsubscript{2}O to O\textsubscript{2} (g). According to Wetzel, Stumm and Morgan have classified the representative ranges of redox potentials in water and sediment at pH 7 to 8. The first range redox potentials are from about 710 to 800 mV the second range redox potentials are from about -100 to 710 mV, and the third range redox potentials are from about -240 to -100 mV. In the first range, where saturated with oxygen, the soluble iron II (Fe\textsuperscript{2+}) was oxidized to solid iron III (Fe\textsuperscript{3+}) which adsorb phosphate. In the second range, where some oxygen has been consumed, the solid iron III (Fe\textsuperscript{3+}), manganese III and IV (Mn\textsuperscript{3+}, Mn\textsuperscript{4+}) were reduced to soluble iron II (Fe\textsuperscript{2+}) and manganese II (Mn\textsuperscript{2+}) in which organic matter was mineralized. Phosphorus, which initially bound to Fe\textsuperscript{3+} hydroxide, was released to the pore water and diffused to overlying water as a result of the reduction of Fe\textsuperscript{3+} solid phases. The third range, under even more reduce conditions, the concentration of Fe\textsuperscript{2+} and Mn\textsuperscript{2+} were further increased; SO\textsubscript{4}\textsuperscript{2-} was started to be reduced, accompanied by the precipitation of Manganous Sulfide (MnS) and Ferrous Sulfide (FeS) and the formation of pyrite [18].

4. Conclusions
DGT with 15% acrylamide; 0.1 % N-N'-methylenbisacrylamide and ferricydrite as binding gel were suitable for the measurement of the phosphate release from sediment into pore water. The result of the deployed DGT in oxic and anoxic conditions in seven days period of incubation showed the released phosphate process from the sediment into pore water was affected by incubation time and the existence
of oxygen in the environment. The released phosphate from the sediment to the water in anoxic condition has a higher value than oxic condition. The experimental results of the deployed DGT in natural sediment core at a depth of 1 to 15 cm from the surface of the water in 7 days period of incubation showed that the sediment has a phosphate mass profile difference based on depth. The concentration of phosphate tends to be increased with depth. The maximum $C_{DGT}$ of phosphate release in oxic and anoxic conditions at 7th days are 29.23 $\mu$g/L at 14 cm depth and 30.19 $\mu$g/L at 8 cm depth, respectively.

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