Phosphorus sorption kinetics and sorption capacity in agricultural drainage ditch sediments in reclaimed land, Kasaoka Bay, Japan
H. V. Nguyen and M. Maeda

ABSTRACT
Equilibrium analysis is essential to evaluate sorption capacity and to determine whether sediment acts as a source or sink of phosphorus (P). This study was carried out to determine whether or not the sediment in drainage ditches acts as a source or sink of P, evaluate phosphorus sorption kinetics, and determine the potential P sorption by using the Langmuir isotherm sorption model. Surface sediment (0–10 cm) and the overlying water were collected from three drainage ditches for the experiments. Results showed that the drainage ditch that was the most contaminated with P had the highest sediment zero-equilibrium phosphorus concentration (EPC0). Because sediment EPC0 of the three ditches was higher than water P concentration, they acted as a sink of P across the sediment interface. The kinetic sorption of sediments consisted of two stages that were quick and slow, regardless of the sampling sites. The amounts of P sorbed to sediments at equilibrium (Qe) ranged from 50.8 to 77.5 mg kg⁻¹. Phosphorus sorption capacity (Qmax) of sediments ranged from 447.0–493.8 mg kg⁻¹ with the constant related to binding energy (K) (0.140–0.171 L mg⁻¹). The results from this study indicate the importance of ditch sediment in controlling P dynamics in discharge from agricultural farms.

Key words | agricultural drainage ditches, phosphorus, sediment, sorption, sorption capacity

INTRODUCTION
Phosphorus (P) is one of the most limiting nutrients contributing to eutrophication of both fresh and estuarine surface waters (Reddy & Delaune 2008; Wang et al. 2008). The eutrophication is often associated with concentration of P in water (House 2005). Agricultural farms are considered to be non-point sources of nutrient loads to rivers and lakes, and drainage ditches are pathways of nutrient loads between farmland and recipient aquatic systems (Smith et al. 2005; Vaughan et al. 2007; Luo et al. 2009; Kröger & Moore 2011). Better water quality can be maintained by reducing the external P inputs (Sharpley et al. 2014). Drainage ditch sediments have capacity to be a sink of P by sorption, and hence potential eutrophication of streams is partially governed by drainage ditch sediments (Nguyen & Sukias 2002).

Whether the sediment acts as a source or sink of P can be determined by measuring the zero-equilibrium phosphorus concentration (EPC0) in sorption experiments of ambient P concentrations (Smith et al. 2005). If the sediment has an EPC0 value higher than water P concentrations, it acts as a source of P. Conversely, sediment is a sink of P when the EPC0 is lower than the overlying water P concentration (Wang Y. et al. 2009). The P equilibrium between sediment and water, functions in the sorption/desorption of P in these drainage systems (Smith et al. 2005). In addition, EPC0 has been used as an indicator to evaluate the sediment’s ability to supply P to the water column (McDowell 2015). Under certain environmental conditions, high EPC0 values resulted from deposition of particulates combined with P from external loadings (Jarvie et al. 2005). House & Denison
(2000) demonstrated that many factors affected the determination of EPC0, such as the presence of ions and manganese under oxic state of sediment, and calcium concentration in solution as a result of precipitation process between calcium and P. Moreover, sediment has a buffering capacity, defined as the resistance of the concentration of the soil/sediment solution to change when phosphate is added to or removed from the labile pool (Holford 1976). Thus, it controls phosphorus behaviors in an aquatic environment (Li et al. 2013). Accordingly, the buffering capacity provides a useful graphic approach for examining P sorption at ambient concentrations (Smith et al. 2005).

Measurement of phosphorus sorption kinetics is used to investigate the effects of sediment on the P concentration in the overlying water during their contact. The sorption kinetics identifies the time dependence of sorption of P onto sediment (Huang et al. 2014). House et al. (1995) suggested that the Elovich equation is the best to describe the kinetic sorption of P and bed sediment controls the influx of P in sediment. Huang et al. (2011) and Yao et al. (2011) reported that the phosphorus sorption kinetics is described satisfactorily by a pseudo-second-order model.

The phosphorus sorption capacity of sediment can be predicted by determination of isotherm sorption parameters using the Langmuir model (Bridgham et al. 2001; Luo et al. 2009; Dittrich et al. 2013). Determination of P sorption capacity of sediment is essential for predicting the long-term sustainability of sediment in retaining external P loadings (Lai & Lam 2008). Reddy & Delaune (2008) suggested that phosphorus sorption capacity is not only dependent on available sorption sites of the sediment but also other factors. For example, P may be retained in mineral compositions of sediment by precipitation. The P sorption capacity is correlated with the concentrations of iron and aluminum because P sorption in soil/sediment is associated with amorphous and poorly crystallized forms of iron and aluminum. Chemical reactions of P with CaCO3 are of special significance in calcareous sediment. In addition, under alkaline conditions, PO43−, which easily combines with Ca2+ to form CaHPO4 precipitation, is the dominant form of phosphorus.

Algae blooms have sometimes occurred in the drainage ditches and downstream of the reclaimed land in Kasaoka Bay. More recently, eutrophication tends to occur often because the concentration of PO4-P in water of drainage ditches is 0.3–1.37 mg L−1. Sharpley et al. (1999) noted that the critical phosphorus value for eutrophication was 0.02 mg L−1. The ditch sediment in Kasaoka may have special characteristics because it receives water runoff from agriculture and under alkaline conditions, which differs from lake and river sediments. So far, few studies have been conducted in this region. Maeda et al. (2011) have assessed water quality of drainage ditches. Nguyen et al. (2014) determined P fractions in sediment under different pH and aerobic/anaerobic conditions. Nguyen et al. (2016) reported P fluxes across the sediment–water interface. Information on sediment P sorption capacity is necessary to manage nutrient loadings from agricultural areas. The aims of the present study are to determine whether the sediment in drainage ditches acts as a source or sink of P, evaluate phosphorus sorption kinetics, and determine the potential for P sorption by using the Langmuir model.

MATERIALS AND METHODS

Study area description and sampling methods

Kasaoka Bay is located in the south-western part of Okayama prefecture, Japan. Agricultural activities on the reclaimed land, with an area of 1,191 ha, started in 1990. This area is driven by three main sectors including a livestock-horticulture area (LHA), livestock area (LA), and grassland area (GLA) for dairy cattle. The three drainage ditches are the main component of water transfer networks, which redistributes water within farmlands and links fields with receiving aquatic systems (Figure 1). Each ditch is approximately 1,850 m in length, 5 m in width, and of 0.35 m water level. Our surveys on water quality since 2008 have demonstrated that the ditches were contaminated with nitrogen (N) and P over years (Maeda et al. 2011; Nguyen et al. 2016). The annual precipitation and temperature of the study area from 2000 to 2014 was 1,008 mm and 15.4 °C, respectively, which was obtained from the Automated Meteorological Data Acquisition System (AMeDAS) (http://www.jma.go.jp/en/amedas/). Three drainage ditches flow in the agricultural area and receive discharge water from each sector of LHA, LA, and GLA. Drainage ditches serve mainly for discharge water by

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transferring it from the farmland to the stabilization pond. Water from the stabilization pond is pumped directly out to the sea. Three sites at the end points of each ditch, where nitrogen and phosphorus concentrations were the highest, were selected for water and sediment sampling collection (Figure 1).

Our surveys in 2014 indicate that P concentrations in drainage water are higher in summer than in other seasons (Tables 1 and 2) because higher P release occurs during summer (Ogdahl et al. 2014) due to effects of temperature on P release from sediments (Wu et al. 2014; Wang et al. 2015). Surface sediment (0–10 cm) and the overlying water were collected downstream of the ditches for the experiments. These sampling points were selected because the highest concentration of nitrogen and P were detected in the ditches. Water and sediment samples were collected in triplicate by a hand corer (5.5 cm in diameter) in September 2014, immediately placed in an ice-box, and transported to the laboratory within 3 h. The initial physiochemical characteristics of sediment were determined. Sediment samples were subjected to measurements of pH and electrical conductivity (EC) at soil:water ratio of 1:5 after shaking for 1 hour at 175 rotations per minute (rpm), using a digital pH meter (F-23, Horiba, Japan) and EC meter (DS-14, Horiba, Japan), respectively. The total carbon (TC) and total nitrogen (TN) were determined with a C:N Coder.
(CMT-700, Yanaco, Japan). Approximately 1 g air-dried sediment was digested with sulfuric acid and hydrogen peroxide at 300°C for the analysis of total P (TP) (Rydin 2000). The soil particle-size distributions were analyzed by the pipette method (Dane & Topp 2002).

### Phosphorus sorption experiments

#### Sorption at ambient P concentrations (low-range P concentrations)

The first experiment was conducted with approximately 2.5 g air-dried sediment and 25 mL solution of (anhydrous) KH₂PO₄ with different P concentrations (C₀: 0.025, 0.05, 0.1, 0.5, 1.0, and 2.0 mg L⁻¹) to determine the EPC₀ and P buffering capacity. The blank control tubes were set up, including two centrifuge tubes with sediment added with deionized water and two other centrifuge tubes without sediments and only P solution added, to determine P released from sediments and sorbed by plastic centrifuge tubes. Samples were placed in 50 mL Erlenmeyer flasks, sealed with parafilm, and then shaken at 175 rpm for 24 h (25 ± 1°C). Phosphorus sorption behavior of sediment including EPC₀ and P buffering capacity were determined according to the method developed by Bridgham et al. (2001). The x-intercept is termed the EPC₀, when the amount of P sorbed by sediment (Qₑ, mg kg⁻¹) is graphed on the y-axis against C₀ or Cₑ (equilibrium concentration). Qₑ is determined from the difference between concentrations at C₀ and Cₑ.

\[
Qₑ = \frac{(C₀ - Cₑ)V + CₑV}{M}
\]

where M is the mass of a known weight of sediment (kg), Cₑ is concentration of P in blank control tubes and V is the volume of solution (L). When (C₀ – Cₑ) is graphed on the y-axis versus C₀ on the x-axis, the slope of the regression line indicates buffering capacity.

#### Sorption kinetic measurement

The second experiment was carried out to describe the P sorption kinetics using 1 g air-dried sediment placed in a series of 50 mL centrifuge tubes with 25 mL solution containing 5 mg L⁻¹ of P. The centrifuge tubes were capped...
and incubated at 25 ± 1°C in a shaker at 175 rpm for various time intervals between 0 and 48 h of sorption (0, 0.25, 0.5, 1.0, 2.5, 5, 10, 15, 24, 32 and 48 h). The sampled solutions were immediately centrifuged at 5,000 rpm for 10 min and filtered through a 0.2 μm membrane filter, and the P concentration of the filtrate was determined.

The amount of P sorbed onto sediment was calculated using Equation (1). Experimental data were tested by the common kinetic models of pseudo-first-order, Elovich equation, and pseudo-second-order to describe sorption kinetics, and to calculate sorption rates and the amount of phosphorus sorbed to sediments at equilibrium. However, only the pseudo-second-order equation was satisfactorily suitable to determine the parameters, which are represented by the following equations:

\[
\frac{dQ_t}{dt} = k(Q_e - Q_t)^2
\]  

(2)

where \( k \) is the rate constant of sorption (kg\(^{-1}\) mg\(^{-1}\) h), and \( Q_e \) and \( Q_t \) are the amounts of P sorbed at equilibrium and at time \( t \) (h), respectively. For the initial condition at \( t = 0 \), \( Q_t = 0 \), the integration of Equation (2) gives the following form:

\[
t = \frac{1}{kQ_e^2} + \frac{t}{Q_e}
\]  

(3)

\[
\frac{Q_t}{t} = \frac{kQ_e^2}{1 + kQ_e t}
\]  

(4)

A plot of \( t/Q_t \) versus \( t \) of Equation (4) gives a linear relationship with a slope \( 1/Q_e \) and an intercept of \( 1/kQ_e^2 \).

### High-range P concentrations for sorption capacity

To determine the phosphorus sorption capacity of sediment, a similar experiment to the first one was performed with various higher initial P concentrations (\( C_0 \): 0, 2, 5, 10, 20, 30, and 40 mg P L\(^{-1}\)), shaken at 175 rpm room temperature (25 ± 1°C) for 24 h (Yoo et al. 2006; Luo et al. 2009). The Langmuir, Freundlich, and Redlich–Peterson models are widely used to describe experimental data. Previous works showed that the Langmuir model tended to fit the data better at higher concentration and seems to be best-fitted with the data than others because of the minimal deviations.

The Langmuir model:

\[
Q_e = \frac{Q_{\text{max}}K_Ce}{1 + KC_e}
\]  

(5)

\( Q_e \): amount of P sorbed onto sediment at equilibrium (mg kg\(^{-1}\)).

\( K \): a constant related to binding energy (L mg\(^{-1}\)).

\( C_e \): concentration at equilibrium (mg L\(^{-1}\)).

\( Q_{\text{max}} \): P sorption capacity or maximal sorption onto sediment (mg kg\(^{-1}\)).
In the present study, non-linear regression analysis was used by OriginPro version 8.5.1 to estimate the parameters. Correspondingly, a plot was drawn between \( C_e \) and \( Q_e \) using experimental data and predicted value by non-linear regression. Moreover, the Langmuir model allows the estimation of potential sorption of sediments (\( Q_{max} \)). In addition, the study used the coefficient of determination, \( r^2 \), which is widely used to determine the relationship between the experimental data and optimum isotherm models.

**Sample analysis**

All samples were filtered through a 0.2 \( \mu \)m membrane filter. The concentration of P in filtrates was determined by spectrophotometry using a continuous flow autoanalyzer (QuAAtro 2-HR, Bltec, Japan). The experiments were performed in triplicate. The amount of P sorption onto sediments was determined after subtracting the blank control (Equation (1)). Means and standard deviations (SD) were calculated and expressed as a mean \( \pm \) SD.

**RESULTS AND DISCUSSION**

**Drainage water and sediment properties**

Table 1 shows the temporal and spatial variations of water quality parameters of the studied drainage ditches. The highest concentration of N and P occurred in the LA ditch, followed by LHA and GLA ditches. Phosphorus concentration of the three ditches was higher in September (summer) than other sampling dates. Table 2 describes sediment properties that showed similar patterns of concentrations as those of N and P in water. While clay and silt contents of GLA were greater than other ditches, the concentration of N and P in LA sediment was the highest. The pH and EC values of sediment indicate that the drainage ditches are affected by sea water from inflow (Figure 1). Concentration of PO\(_4\)-P in agricultural drainage water from reclaimed land in Kasaoka, Japan, exceeded the eutrophication threshold (0.02 mg L\(^{-1}\)). These concentrations were higher than that of agricultural drainage ditches in other countries (Table 3). This demonstrated that agricultural activities in Kasaoka discharge a large quantity of P. The silt fraction dominated in all ditch sediments at more than two-thirds. A high percentage of the silt component was attributed to sediment runoff from agricultural areas (Kröger & Moore 2011).

**Ambient phosphorus concentration sorption parameters**

Figure 2 and Table 4 show the differences in EPC\(_0\) values and buffering capacity of different sediments that received different polluted wastewaters. Sediment EPC\(_0\) is the concentration at which no net sorption or desorption of P occurs. The highest value of EPC\(_0\) was seen for LA, followed by LHA and GLA sediments, indicating that the higher the EPC\(_0\) of the sediment, the more polluted it was (Luo et al. 2009). Jin et al. (2005) reported that sediment EPC\(_0\) had a strongly positive correlation with the nutrient level of sediments. Silt and clay contents in sediment had strong correlations with EPC\(_0\), and higher PO\(_4\)-P concentrations in the overlying water increased sediment EPC\(_0\) (Smith et al. 2005). The order of the sediment EPC\(_0\) was the same as the order of PO\(_4\)-P concentrations in the three ditch waters. The sediment EPC\(_0\) values of the three drainage ditches were lower than the PO\(_4\)-P concentrations of the ditch water. The data are comparable to the results of Luo et al. (2009), who reported EPC\(_0\) values ranging from 0.001 to 0.108 mg L\(^{-1}\) in agricultural headwater drainage ditches or to those of Yoo et al. (2006) of marsh sediment (0.02–0.26 mg L\(^{-1}\)).

Accordingly, sediments of the study sites acted as a sink for P, so they can accept new P loading. Phosphorus
buffering capacities among the locations were not greatly different. The P-buffering capacity controlled P sorption and release in sediment and is related to the pollution level (Wang S. et al. 2013). Smith et al. (2005) reported that P-buffering capacity of sediment increased with high fractions of fine particle (clay and silt) and organic matter contents. Moreover, the P-buffering capacity of sediment was increased by chemical treatment (aluminum sulfate, calcium carbonate) or by dried sediment treatment (Hama et al. 2015).

The sorption kinetics is important because it provides insights into the mechanism of sorption reactions. The kinetics of phosphorus sorption by sediment is defined as a time-dependent process (Lai & Lam 2009), which has been widely reported as a multiple kinetic process to determine the reaction time required for completion of the sorption reaction (Huang et al. 2014). Figure 3 illustrates the time-course of the sorption kinetics of three sediments, described by the pseudo-second-order model. The sorption reached equilibrium and stayed stable after 5 h.

The sorption kinetics can be divided into two stages based on the geometric shape of the sorption curve (Wang Y. et al. 2009; Huang et al. 2014). The first stage is described as the quick sorption of P onto sediment, about 78% of P was sorbed onto the sediment. The second stage started to follow slow sorption of P in the solid phase before reaching equilibrium concentration in the water phase. Almost 100%

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**Table 4** Zero equilibrium P concentration (EPC₀) and buffering capacity of sediments

<table>
<thead>
<tr>
<th>Sediment location</th>
<th>LHA</th>
<th>LA</th>
<th>GLA</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPC₀ (mg L⁻¹)</td>
<td>0.146</td>
<td>0.275</td>
<td>0.060</td>
</tr>
<tr>
<td>Buffering capacity (L kg⁻¹)</td>
<td>0.944</td>
<td>0.934</td>
<td>0.951</td>
</tr>
</tbody>
</table>

LHA: livestock and horticulture area; LA: livestock area; GLA: grassland area; EPC₀: zero-equilibrium phosphorus concentration.

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**Figure 2** EPC₀ of sediments (a) LHA, (b) LA, and (c) GLA. LHA: livestock and horticulture area, LA: livestock area, GLA: grassland area. EPC₀: zero-equilibrium phosphorus concentration. C₀: initial phosphorus concentration (mg L⁻¹), Qₑ: amount of phosphorus sorbed onto sediment (mg kg⁻¹).

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**Phosphorus sorption kinetics**

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of P sorption onto sediment occurred within the first 24 h of the experiment. This suggests that the sorption kinetic between solid and solution phases can be attained after 24 h. Jin et al. (2005) reported that 80% of P sorption onto sediment occurred in the first stage. Likewise, Wang et al. (2006) found that about 70% of P sorption capacity onto the sediment occurred within 2.5 h. About 60% P was sorbed onto sediment in the first stage (30 min) according to House et al. (1995). Table 5 describes parameters of P sorption kinetic that were obtained from the pseudo-second-order model. The highest amount of P sorbed onto the sediment at equilibrium was seen for the GLA sediment, followed by LA and LHA sediments (77.52, 64.52, and 50.76 mg kg⁻¹, respectively). In this study, the pseudo-second-order model fitted with the experimental data ($r^2 > 0.998$) better than the pseudo-first-order, Elovich, and power function models.

### Phosphorus sorption capacity

The Langmuir sorption isotherms have been widely applied to evaluate the phosphorus sorption capacity of drainage sediment (Nguyen & Sukias 2002; Vaughan et al. 2007; Luo et al. 2009; Dittrich et al. 2013) because this adsorption isotherm has some advantages for describing P sorption behavior and estimating sorption capacity by non-linear methods of the sediments, as shown in Figure 4.

Overall, the sorption data from the experiments showed that higher initial P concentrations in solution increased the amounts of P sorbed onto sediments. Potential sorption is usually dependent on available sorption sites and concentrations of minerals of the sorbent (Reddy & Delaune 2008). Table 6 illustrates the sorption parameters of P onto sediments by using the Langmuir non-linear sorption...
According to $Q_{\text{max}}$, the potential sorption capacities of LHA, LA and GLA sediments were 447.0, 473.9, and 493.8 mg kg$^{-1}$, respectively. The $Q_{\text{max}}$ of GLA sediment was the highest, followed by LA, and then LHA sediment. This can be attributed to its clay and silt contents and concentration of P in sediments (Table 2). These values were much higher than the data reported by Kröger & Moore (2011), who found P sorption capacity of agriculture drainage ditches was only 18–28 mg kg$^{-1}$, but much lower than those of Nguyen & Sukias (2002) (2,225–4,194 mg kg$^{-1}$).

This result agrees with those obtained by many researchers studying sorption of P onto sediments. Clay and silt contents were correlated with sorption capacity of sediment (Nguyen & Sukias 2002; Kröger & Moore 2011). When the available surfaces of the sorption sites were completely covered, increasing potential sorption resulted from increased concentrations of minerals by precipitation reactions (Wang Y. et al. 2013). Similarly, $Q_{\text{max}}$ increased with increasing mineral content (House et al. 1995; Lopez et al. 1996; Wang Y. et al. 2009). Stone & Mudroch (1989) found that the clay particle fraction contains a greater amount of minerals. However, $Q_{\text{max}}$ decreased when the ionic strength increased (Wang et al. 2009). Huang et al. (2014) reported that $Q_{\text{max}}$ increased with increasing temperature due to greater amorphous contents of Fe and Al. In addition, along with the minerals, bacteria contributed to the uptake of P in sediment (House et al. 1995). On the other hand, the constant $K$ of the current study ranged from 0.140 to 0.171 L mg$^{-1}$. These values were lower than in previous reports of agricultural drainage ditches by Luo et al. (2009).
of the present study fitted well with non-linear regression analysis (0.992–0.995) (Figure 4, Table 6). The highest coefficient of determination was for LA sediment, followed by LHA, and then GLA sediments. Ho (2006) noted that using transformation of non-linear Langmuir to linear forms may impact the final determination of parameters, where use of the non-linear method would avoid such errors. Similarly, it is suggested that the non-linear method is the best way to get the actual isotherm parameters. According to Diaz et al. (1994), the precipitation of P increased as the pH increased >9.0. In particular, calcium and phosphorus were precipitated at the higher pH levels associated with higher Ca concentrations.

CONCLUSIONS

The sediments from three drainage ditches of reclaimed land in Kasaoka Bay were two-thirds silt. The contents of TC, TN, and TP in the LA sediment were the highest, followed by LHA and GLA sediments. The pseudo-second-order model could describe the P sorption kinetics of sediments. The kinetic sorption of sediments consisted of two stages: quick and slow stages. The EPCo values indicate that sediments of the three ditches, act as P sinks. The Langmuir model by the non-linear method described sorption isotherms of sediments in this study ($r^2 > 0.99$) and provided a good theoretical estimate of the P sorption capacity of the sediments. Our results indicate the significance of ditch sediment in controlling the dynamics of P discharged from agricultural farms; when P concentrations in sediments are relatively high, sediment still tended to sorb more P from drainage water. Further information on environmental characteristics, such as the fate of P and transport processes within drainage ditches, needs to be reassessed in further studies so that an appropriate solution can be selected.

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