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Characteristics of contaminant and phosphorus existence types in sediment of a constructed wetland

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ABSTRACT

This research investigated the physical and chemical characteristics of sediment deposited at the bottom soil layer of free water surface flow constructed wetland (CW) treating runoff impacted stream water from an agricultural area which is important when determining the long-term maintenance requirements over the lifetime of the CW. Based on the findings, the influent to the CW still was polluted with high concentration of nutrients with TN and TP exceeding five and two times the water quality standard in rivers and lakes. The accumulation of sediment at the first treatment unit (sedimentation zone) of the CW augmented after the summer season signifying that the dredging of sediment must be conducted after the rainy season or until before the winter season. It was found out that the main phosphorus (P) types existing at the sediment in the CW were residual-P (R-P) and non-apatite-P (NAI-P) constituting to almost 90% of total P. While NAI-P can be released in the natural environment by increasing pH or reducing redox potential, and can be used by aquatic plants; R-P on the other hand exists with organic compounds and is difficult to separate. However, R-P is proportional to the absorption capacity of microorganisms which signifies that microorganisms are highly available in the CW.

Keywords: Agricultural; Constructed wetland; Phosphorus type; Sediment; SEM-EDX; Water quality

1. Introduction

In agricultural areas, surface runoff during storms escalates the release of sediments, nutrients and other pollutants which causes eutrophication. In Korea, almost 20% of the national area is mainly agricultural [1], implying that the country is cultivating intensively. Usually, nonpoint source (NPS) pollutants were carried by runoff from these agricultural areas and washed-off downstream during rainy days. The climate in Korea is Asian Monsoon, which means that most rainfall is concentrated during the summer months from June to September. The timing of fertilizer application to crop in relation to rainfall season, as well as the paddy field waters after being used by the rice plants is usually washed-off to the nearby stream.

Recently, the nutrient control in water quality improvement program is a main policy in Korea to protect the water quality in four major rivers. The total maximum daily load (TMDL) and NPS control programs were legislated by the ministry of environment (MOE) in the 'Act Of Water Quality and Aqua-Ecosystem

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Conservation' to improve the water quality in rivers and lakes from the target pollutants such as biochemical oxygen demand (BOD), total nitrogen (TN) and total phosphorus (TP) [2].

Constructed wetlands (CWs) are particularly suited for treating NPS pollution, such as agricultural runoff since CWs can operate under a wide range of hydraulic loadings, have internal water storage capabilities, and can remove or transform a number of contaminants, including oxygen-demanding substances, suspended solids, and nutrients [3]. Furthermore, as natural treatment systems, CWs are low cost systems, easily operated and maintained and their performance depends on seasonal changes and vegetative cycles [4]. Specifically, the surface flow CW system can treat greater amounts of runoff even it requires a wide area for construction and suitable in agricultural areas and also in temperate climates.

Paddy fields transport predominantly colloidal sediments with high adsorption capacity of chemical elements [5]. Moreover, sediments transported by runoff present higher nutrient enriched to the sediment where they originally came from. This has been attributed, partly, to the fine-sized sediments transported by runoff which, in general, are richer in silt and mainly clay particles [6]. Sediments may accumulate over long periods and can act as new pollutant sources to the overlying water [7]. They may uptake or release contaminants when environmental conditions such as pH, temperature and dissolved oxygen (DO) concentration in the water change [8,9]. 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 [10]. Release of phosphorus from sediments may be caused by environmental changes like to low or high pH, water temperature. It may be associated with the release of other pollutants such as metals [7,11]. 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 [12]. Therefore, to achieve water quality goals, it will be necessary to reduce phosphorus sources further in CW. Reducing or eliminating phosphorus release from sediments may also be required.

This research investigated the characteristics of contaminants and sediments in a surface flow CW receiving runoff impacted stream water from a surrounding agricultural watershed area. Research was conducted to investigate the sediment deposition rates and contaminant retention at the first and final sedimentation zones of the CW to be able to determine the long-term maintenance requirements over the lifetime of the CW. In addition, the specific objective was to recognize the different phosphorus types existing at the accumulated sediment and bottom soil layer to be able to understand the reduction of phosphorus release from sediments at varying DO levels, pH values, and other physical conditions.

2. Materials and methods

2.1. Study site description

The CW is located in Kongju city, Chungnam Province, Korea. The climate of the watershed is temperate with average air temperature ranging from 14.1 to 24.6°C in spring and summer, and between –0.5 and 13.6°C in fall and winter. The annual mean precipitation is 1,200 mm of which more than half is concentrated in the summer months of June, July and August. The CW construction was completed in 2008 and the operation started in January 2009. The influent to the CW comes from the agricultural stream flow in the tributaries of Geum River from a 221 ha watershed area comprising of agricultural landuse consisting of 99% wet paddy fields and 1% dry paddy fields. The CW was also designed to treat stormwater runoff during periods of rain storms. Sediment is the main contaminant entering the CW which adsorbed the agrichemicals, fertilizers and by products of crops which is dominant during the field harrowing and rice planting throughout the wet season.

2.2. Constructed wetland design

Fig. 1 shows the composition of the CW including the water quality and sediment sampling locations. Based on the figure, the CW is composed of seven cells designed to treat the runoff impacted stream water from the agricultural watershed. The design description of the treatment cells in the CW was provided in Table 1. The main treatment mechanism employed in the CW is sedimentation of particulates and plant uptake. The wetland plants were selected on the basis of their characteristics such as fast growing, capability of contaminant removal and high tolerance towards toxicities. Four typical wetland plant species were initially transplanted and the locations are shown in Fig. 1b.

2.3. Water quality sampling and sediment analysis

Water quality monitoring was conducted from April to December 2009. Physico-chemical water parameters such as DO, pH, conductivity, turbidity and temperature were measured in the field using portable meters.

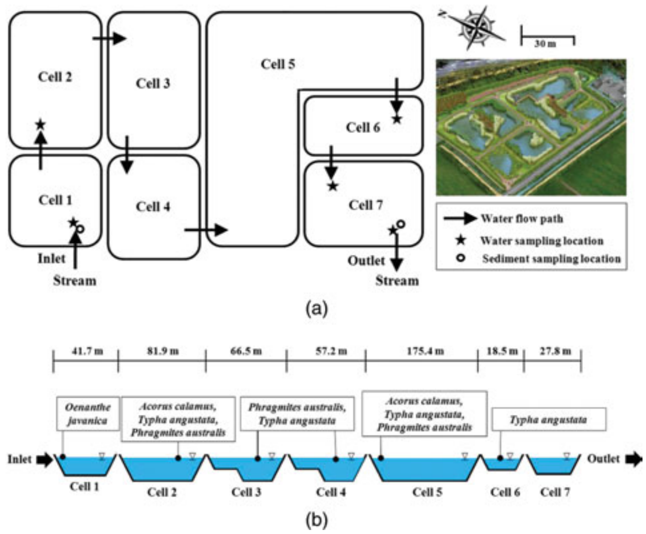

Fig. 1. Representation of the CW showing the (a) sampling locations and water flow path, and (b) composition of the CW with distance of water flow path.

Table 1
Design description of the treatment units of the CW

Cell No.	Function	Surface area (m^2)	Storage volume (m^3)	Water depth (m)	HRT for design flow (h)
1	Sedimentation zone	1168	1155	0.99	2.9
2	Deep marsh	1723	1484	0.86	3.7
3	Shallow & deep marsh	1863	1188	0.64	3
4	Shallow & deep marsh	1634	929	0.57	2.3
5	Deep marsh	4811	5352	1.11	13.5
6	Shallow marsh	553	211	0.38	0.5
7	Sedimentation zone	953	916	0.96	2.3
Total	–	12,705	11,235	–	28.2

Samples were analyzed for water quality parameters including total suspended solids (TSS), biological oxygen demand (BOD), COD, TN, total Kjeldahl nitrogen (TKN), ammonium (NH_4–N), nitrate (NO_3–N), total phosphorus (TP) and phosphate (PO_4–P). Analyses were performed in accordance with ASTM standard methods for the examination of water and wastewater.

Sediment sampling was conducted four times from July to October 2009 summer season after the completion of the CW in 2008. Two sampling points were chosen, at the cell 1 and 7 (sedimentation zones). Undisturbed sediment samples were manually collected using an acryl tube, 5 cm in diameter and 50 cm long. Then, the undisturbed sediment samples were separated from the original bottom soil layer to determine the pollutant amount in the accumulated sediment. The accumulated sediment was measured for each sample and ignition loss, COD, TN and TP were analyzed to determine the chemical characteristics of undisturbed sediments. Additionally, the element-containing phases of the sediment were investigated by direct observation using scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis.

2.4. Phosphorus type analysis

Phosphorus existence types were determined using the procedure of Hieltjes and Lijklema [11] used to analyze the concentrations of total phosphorus and the phosphorus fraction in sediments. The procedure successively extracts phosphorus from sediments using different solvents and conditions into four fractions [13]. The first step, adsorbed-P or NH_4Cl extractable P, is the most available phosphorus which is adsorbed to the surface of clays and small particles. The second step is the separation of non-apatite-P (NAI-P) or NaOH-P that is the phosphorus precipitated with metal ions, such as Fe or Al. NAI-P is generally less available than adsorbed-P, but can be released in the natural environment by increasing pH or reducing redox potential, and can be used by aquatic plants. The third step is the apatite-P or HCl extractable P that is usually precipitated with inorganic salts such as calcium and included in mineral. The last step is the residual-P (R-P) or organic-P that exists with organic compounds and it is difficult to separate [14].

3. Results and discussion

3.1. Influent water quality

The box and whisker plot in Fig. 2 shows the statistical summary of the influent pollutant concentrations entering the CW. The average concentrations (mean ± standard deviation) for pH, DO, TSS and BOD were 7.0 ± 0.5 mg/l, 6.9 ± 2.0 mg/l, 20.3 ± 12.9 mg/l and 4.3 ± 1.8 mg/l, respectively; while the mean concentrations for COD, TN and TP were 16.5 ± 5.9 mg/l, 4.5 ± 1.9 mg/l and 0.5 ± 0.35 mg/l, respectively. Provided in Table 2 is the list of water quality standards for rivers and lakes in Korea. The agricultural water quality standards should be within the level IV [15]. Comparing the CW influent to the water quality standard, the organic and particulate parameters passed the level IV (less than 8 mg/l). However, the nutrient levels of the influent did not pass the water quality standard. In the case of TN, the influent concentration was five times greater than the

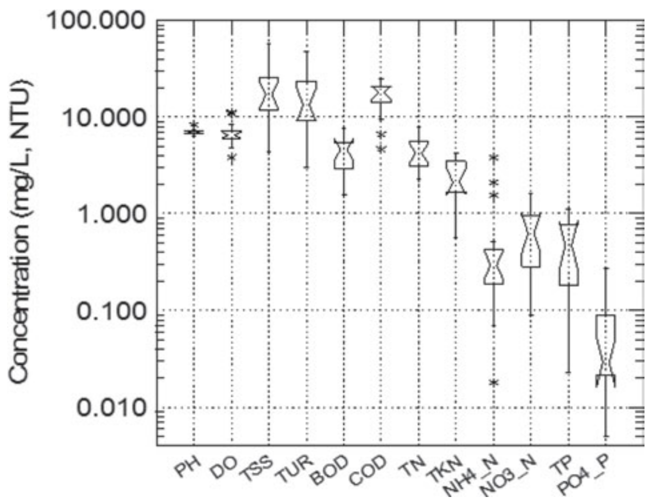

Fig. 2. Water quality characteristics of influent (n = 15).

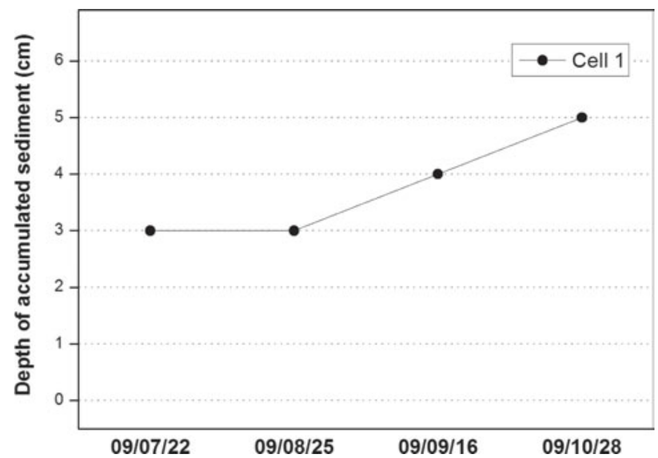

Fig. 3. Depth changes of the accumulated sediment at the sedimentation zones in cells 1 and 7.

permissible water quality standard of 1.0 mg/l; while more than twice for TP. Therefore, the results implied that the influent necessitate prior treatment to meet the nutrient water quality standards.

3.2. Accumulated sediment

Fig. 3 shows the monthly trend of the depth of the accumulated sediment at cells 1 and 7 from July to October 2009. It can be observed that the accumulated sediment at cell 1 increased after the summer season with an average accumulation rate of 0.0014 mm/ha-day. It has to be noted that it was during the summer season in Korea when frequent rain storms occurred that could possibly washed off more pollutants from the surrounding watershed area and deposited them to the CW. Consequently, if the CW needs to be dredge for maintenance, it might be appropriate to do the dredging after the summer season between end of October to early November or before the winter season. Apparently, no sediment accumulated at cell 7 indicating that sediment deposition did not actually took place since it was the final treatment stage of the CW. Nevertheless, other factors include the low concentration of particulates (mean concentration = 20.3 mg/l) entering the CW and the CW was still in its early stage of operation.

3.3. Chemical characteristics

Comparisons on the chemical characteristics between the accumulated sediment and bottom soil layer of cell 1 were made since there was no accumulated sediment at cell 7. As revealed by the plots in Fig. 4, the pollutant concentration of accumulated sediment was higher than the bottom soil layer indicating that lots of particulates precipitated at the first sedimentation zone. In the CW, sedimentation is the main treatment mechanism enhanced by plants reducing the flow velocity of water. The accumulated pollutants in the sediments can be degraded by microbial activities and plant uptake during

Table 2
Korea water quality standard in rivers and lakes (unit: mg/l except for pH) [15]

Level	pH	BOD*	COD	TSS	DO	TP	TN**
I_a	6.5–8.5	≤1	≤2	≤25 (≤1)	≥7.5	≤0.02 (≥0.01)	≤0.2
I_b	6.5–8.5	≤2	≤4 (≤3)	≤25 (≤5)	≥5.0	≤0.04 (≥0.02)	≤0.3
II	6.5–8.5	≤3	≤5 (≤4)	≤25 (≤5)	≥5.0	≤0.1 (≥0.03)	≤0.4
III	6.5–8.5	≤5	≤7 (≤5)	≤25 (≤15)	≥5.0	≤0.2 (≥0.05)	≤0.6
IV	6.5–8.5	≤8	≤9 (≤8)	≤100 (≤15)	≥2.0	≤0.3 (≥0.10)	≤1.0
V	6.5–8.5	≤10	≤11 (≤10)	Non-float litter	≥2.0	≤0.5 (≥0.15)	≤1.5
VI	–	>10	>11 (>10)	–	<2.0	>0.5 (>0.15)	>1.5

*only river.
**only lake.

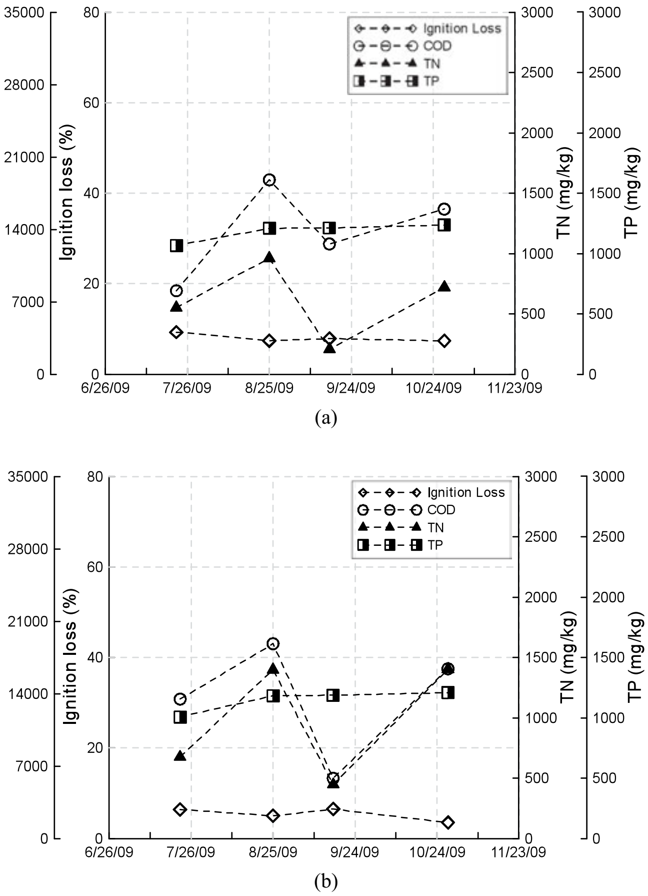

Fig. 4. Contaminant changes of the (a) undisturbed accumulated sediment, and (b) bottom soil layer at the first sedimentation zone in cell 1.

photosynthesis. Even though sedimentation plays an important function in the CW, the soil and groundwater pollution can be an issue when the CW treats highly concentrated wastewaters. In order to prevent the soil and groundwater pollution, the soil liner systems in the wetlands should be carefully considered when designing the CW.

Based on the results, the average concentrations at the accumulated sediment were 22,381 mg/kg for COD, 1376 mg/kg for TP and 877 mg/kg for TN while 13,855 mg/kg COD, 1181 mg/kg TP and 610 mg/kg TN for the bottom soil layer. There was no significant trend observed during the duration of the sampling period. Though in July 2009, a heavy storm happened that generated almost 98 mm rainfall and since the watershed area is large it could take longer time for the runoff to reach the CW. Rainfall affected the deposition of sediment to the CW because of washed off rates. The relationship between COD and TN was evident in cells 1 and 7; disregarding the first sampling event, at cell 1: r^2 = 0.98 and at cell 7: r^2 = 0.82. Certainly, 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 because of wash off which can affect and change the conditions in the CW [12].

SEM and EDX analysis were performed to determine the chemical compositions useful to know the status of soil pollution by sedimentation and biodegradation at cell 1. The SEM photographs of the sediment samples were shown in Fig. 5. Smaller components were detected on the surface area of the accumulated sediment particles, greater in comparison with the bottom soil layer

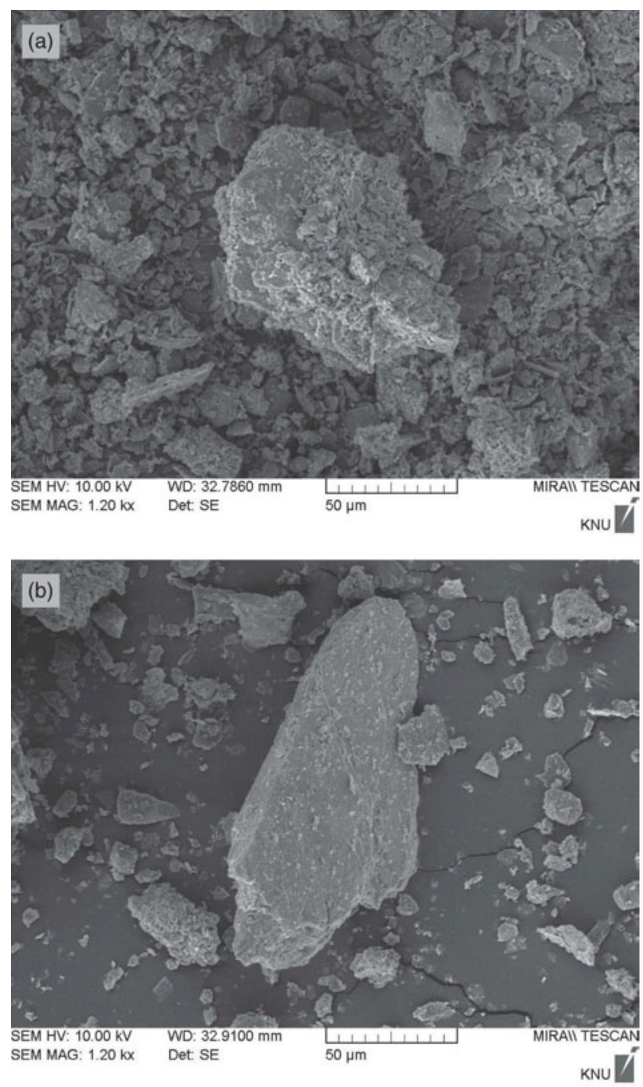

Fig. 5. SEM photographs of the (a) undisturbed accumulated sediment, and (b) bottom soil layer at the first sedimentation zone in cell 1.

Table 3
Average element composition of samples collected at the sedimentation zone in cell 1

Sample	O	Si	C	Al	Fe	K	Mg	Cr	Ni	Cu	Zn	Cd	Hg	Pb
	Atomic (%)													
Accumulated sediment	52.3	14.0	14.1	9.7	2.3	1.2	1.3	0.3	0.1	0.4	2.1	0.1	2.0	0.02
Bottom soil layer	56.8	13.7	11.4	8.1	2.7	0.9	1.6	0.3	0.4	0.5	1.6	0.1	1.5	0.01

at cell 1. These components suggested the evidence of adsorption by positively charged particles.

Table 3 shows the average element compositions of the undisturbed sediment and soil samples collected at cell 1 of the CW. In comparison to the bottom soil layer, the accumulated sediment has higher carbon and heavy metal fractions such as Zn, Hg and Pb than the bottom soil layer. Hence, the bottom soil layer also exhibited higher fractions of other elements like oxygen, Si, Fe, K, Mg and Cd. The heavy metals were usually attached to the sediment and washed-off from the surrounding watershed area. Phosphate fertilizers are an important source of heavy metals entering agricultural soil, especially Cd, Cu and Zn. Other sources may include inorganic fertilizers (e.g., nitrogen or potash), atmospheric deposition. Heavy metal contents are also located near roads that have a high traffic density and are probably affected by vehicle fumes [16]. According to Facchinelli et al. [17], heavy metals such as Cu and Zn were associated with specific agronomic practices and could be derived from car exhausts, and related with human activities and associated with parent rocks that seem to have both natural and anthropic origin. K and Mg were from phosphate fertilizers, especially, K dissolves and transported more easily in no-till systems. Also, crop residue burning, as with phosphorus, increased K losses by runoff water [18]. On the other hand, Cr, and Ni were associated with and controlled by parent rocks. Hg from agricultural chemical residues, sediment Methyl mercury (MeHg) is inversely related to agricultural land, indicating that the generally low sediment Total Hg concentrations in these areas will be characterized by even smaller amounts of MeHg [19].

3.4. Phosphorus existence types

Table 4 shows the proportion of phosphorus existence types in the undisturbed accumulated sediment and soil samples from the sedimentation zone at cell 1. As can be seen, the dominant phosphorus types at the accumulated sediment and bottom soil layer were R-P and NAI-P. On the other hand, adsorbed-P and apatite-P constituted a very small proportion that was only less than 6%. It is known that R-P is related with organic compounds from raw water. Thus, R-P is proportional to the absorption capacity of microorganisms which signifies that microorganisms are highly present in the CW. In comparison, the bottom soil layer has more R-P than the accumulated sediment, though only about 10% greater. A previous study showed that much more R-P was present in the soil solution of manured soils than soils that had received the same quantity of P as inorganic fertilizer, but it is unavailable [20]. Especially, R-P exists with organic compounds and it is difficult to separate. On the other hand, NAI-P and adsorbed-P forms increased at the accumulated sediment. NAI-P precipitated with metal ions, such as Fe or Al is separated. Commonly, the agricultural catchments were found to exhibit higher mean concentrations of Fe and Al [21]. Also the increased metal concentrations (i.e., caused NAI-P) may be promoted by increased weathering and erosion rates, and this was further supported by observations of dramatically higher turbidity in the stream water draining the agricultural catchments. Because of that reason, the NAI-P at the accumulated sediment was higher than the bottom soil later by almost 6%. NAI-P can be released in the natural environment by

Table 4
Average concentration (mg/kg) for each phosphorus existence types for samples collected at the sedimentation zone in cell 1 with relative percentages in parenthesis

Sample	TP	Adsorbed-P	NAI-P	Apatite-P	Residual-P
Accumulated sediment	1376 (100)	80 (5.9)	556 (40.6)	1 (0.1)	739 (53.4)
Bottom soil layer	1181 (100)	15 (1.3)	406 (34.4)	1 (0.1)	759 (64.3)

increasing the pH or reducing redox potential, and can be used by aquatic plants. It would also be available with few environmental changes.

4. Conclusions

This research was conducted to determine the physical and chemical characteristics of contaminants that accumulated at the sedimentation zones of a CW designed for treatment of runoff impacted stream water from agricultural area. Based on the findings, the nutrient levels especially TN and TP concentration entering the CW failed to meet the allowable agricultural water quality standard set by the government indicating a necessary treatment of nutrients from the watershed area. During the initial monitoring period, it was found out that sediment was accumulated only at the first sedimentation zone (cell 1) which increased abruptly in late summer (August) and peaked in early fall season (October). However, no sediment has accumulated at the final sedimentation zone near the outlet of the CW. The results implied the importance of sedimentation zone that should be located near the inlet and not necessary at the final or end unit of the system. For maintenance purposes, it is suggested that the dredging of sediment should be done more frequently at the first sedimentation zone than at the final sedimentation zone and should be conducted before the winter season. Since a larger percentage of phosphorus was in residual form, biological treatment could also take place at the bottom soil layer of the CW; however, the separation process was still limited because of the nature of phosphorus that exist with organic compounds.

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