Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.922290

53 (2015) 3054–3065
March

Taylor & Francis
Taylor & Francis Group

Wet weather discharge characteristics of phosphorus and management implications in a mixed land-use watershed

Lady Shanee K. Alfonso[a], Krish J. Madarang[a], Min Yong Lee[a], Dong Hoon Lee[a], Ma. Cristina A. Paule[b], Chang-Hee Lee[b], Joo-Hyon Kang[a,*]

[a]*Department of Civil and Environmental Engineering, Dongguk University-Seoul, Seoul 100-715, Korea, email: joohyon@dongguk.edu (J.-H. Kang)*
[b]*Department of Environmental Engineering and Energy, Myongji University, Yongin, Gyeonggi-do 449-728, Korea*

Received 31 July 2013; Accepted 11 December 2013

ABSTRACT

The diffuse phosphorus (P) load to receiving waters has been of great concern because it is considered the main cause of eutrophication and algal bloom in natural waters. For establishing effective P control strategy, it is the important first step to obtain information on characteristics of diffuse source of P and its discharge behavior during storm events. In this study, wet and dry sampling collection were performed to measure concentrations of P in different types (particulate, dissolved, and soluble reactive P for waters and adsorbed, non-apatite, apatite, and residual P for soil/sediment) in storm water runoff and soil/sediment on the catchment surface from different land uses. The results showed that urban land uses can be the most significant contributor to diffuse P loading because of the high concentration of P in the storm water run-off. Despite minimal wet discharge concentration of P observed, agricultural land-use can be a potentially important P source due to the relatively greater P content in agricultural soil. In addition, it was found that forest land use may discharge significant amount of P during storms unless soil erosion is properly controlled particularly in a large-scale storm. The results also suggested useful P management implications for different land uses. That is, urban site showed a strong first flush phenomenon, implying that first flush enhanced control should be a cost-effective strategy. Agricultural site revealed seasonal first flush of P, suggesting that management actions can be focused more on earlier season that has greater P discharge concentration. In addition, controlling fine particles should be very important because smaller particles contain greater amount of readily bioavailable P.

Keywords: Land use; Non-point source pollution; Phosphorus; Storm water quality assessment

*Corresponding author.

Presented at the 16th International Conference on Diffuse Pollution and Eutrophication (DIPCON) August 18–23, 2013, Beijing, China

1944-3994/1944-3986 © 2014 Balaban Desalination Publications. All rights reserved.

1. Introduction

Pollutant discharge into receiving water bodies due to storm water run-off can only be cost effectively reduced when the sources of the pollutants are properly identified. Absence of such information may lead to improper management or ineffective control scheme, resulting in the degradation of ecosystem. In characterizing and identifying pollutant sources for storm water pollution, complexity arises because pollutant concentration greatly varies for different land uses during rainfall events [1]. Among many pollutants delivered by storm water run-off, nutrients such as nitrogen (N) and phosphorus (P) in particular are of great concern because they are main causes of eutrophication in surface waters [2–5]. Defined as the excessive concentration of nutrients in a water body, eutrophication leads to increased biomass of fresh water phytoplankton and periphyton, changes in vascular plant production, biomass, and species composition, resulting in reduced water clarity, taste and odor problems, depletion of dissolved oxygen, and increased probability of fish kills [6]. Numerous studies have been conducted to reveal the effects of land use on the nutrient load in receiving waters. Sonoda et al. [7] investigated the relationship between surface and subsurface watershed characteristics and stream nutrient concentrations in an urbanizing watershed. They suggested that urbanization contributes to higher P input to stream. Withers et al. [8] reported that the accumulation of surplus P in soils is a major source of P in land run-off causing deterioration in water quality.

Compared to N, P has less mobility in the environment due to the greater affinity for solids and thus tends to be a minor element in natural water. Therefore, P is considered as the primary limiting nutrient for algal bloom in most lakes and reservoirs [9,10]. Sources of P in natural water include wastewater treatment plant, septic tanks, drained wetlands, agronomic soil, and disturbed land areas. Qualitative and quantitative characteristics of P strongly depend on land uses and are highly site specific, significantly varying with respect to anthropogenic pressures and discharge [11]. Classifications with respect to land use, mode of transport, composition, and ecological relevance greatly influence on the applicability of a management strategy. It is therefore important to analyze P distribution of various source areas separately and then to identify governing discharge dynamics.

The goal of this study is to characterize the wet pollutant discharge from different land uses, such as urban, agricultural, and forest, for management implication focusing on P. In line with this goal, dry sampling was performed for the comparison of P concentration in sediment. Careful analysis of various forms of P both in soil/sediment and water was conducted to understand its potential effects to receiving water body. Furthermore, analysis for potential surrogate parameters for prediction P level was performed.

2. Materials and methods

2.1. Study site and sampling strategy

Fig. 1 shows the study watershed and sampling locations in this study, including monitoring sites for storm water run-off, stream water, and sediment sampling sites during dry weather, and soil/sediment sampling sites in different land uses during dry weather. The study area is the Geumhak watershed in Yongin City, Gyeonggi Province which is located at the northeastern part of South Korea. This watershed drains through the Geumhak stream to the Gyung-An stream that eventually flows into Paldang Lake, which is the major source of drinking water for Seoul Metropolitan area and nearby provinces. It covers a total area of 1,407.7 ha with various land-use distributions. To investigate discharge characteristics of P during storms from different land uses, four outlets points corresponding to different land-use compositions were selected. Table 1 displays the four monitoring sites for storm water run-off (S1, S2, S3, and S4) and their land-use compositions based on 2007 Korea Ministry of Environment (MOE) land-use map. S1 was considered as forest dominated site. Within this area is an ongoing large-scale construction which was taken into consideration because of its potential impact on the pollutant characteristics. The catchment for S1 is a sub-catchment for S2, which was categorized as mixed land use, though forest dominated, because the downstream region near the outlet point is mainly urban area which may have a great impact on the characteristic of the run-off. S3 was categorized as agricultural dominated site. S4, representing urban site, solely has exclusive land use classification.

Collection of storm water run-off was carried out from June to October 2012. A total of six storm events were monitored. Table 2 provides the hydrological characteristics of the study site throughout the sampling duration. For each event, three representative run-off samples were acquired at three temporal stages in a run-off event—earlier, mid, and later parts of run-off (called “Start”, “Mid”, and “End” samples). Additional stream samples were obtained, representing wet discharge of Geumhak stream during each storm event. Soil samples before and after rain were also obtained in S3.

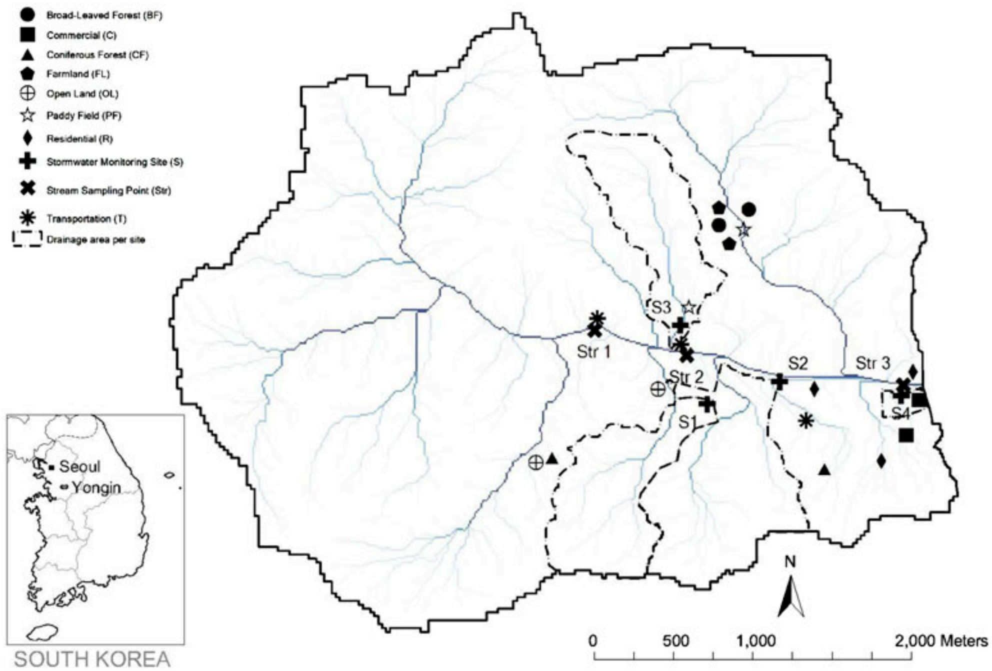

Fig. 1. The study area and the sampling sites.

Table 1
Characteristics of the catchments for the storm water monitoring sites based on MOE land-use map 2007

Site ID	Area (m^2)	Average slope (%)	Longest flow path (m)	Land-use composition
S1	619,000	22.39	1,668	Forest (59%) > Agricultural (24%) > Bare land (10%) > Urban (7%)
S2	1,451,500	20.98	2,275	Forest (52%) > Urban (18%) > Agricultural (18%) > Bare Land (12%)
S3	577,100	17.01	1,882	Forest (47%) > Agricultural (19%) > Public facilities (16%) > Grass Land (13%) > Others (5%)
S4	41,200	1.41	330	Urban (100%)
Outlet of watershed (Str3)	13,473,134	27.18	6,165	Forest (58%) > Urban (18%) > Agricultural (16%) > Public facilities (4%) > Bare land (2.4%) > Others (1.6%)

Sediments and overlaying water samples were collected at the three stream sampling points (Str1, Str2, and Str3 in Fig. 1) during two dry sampling events in May and December 2012. During the dry sampling event in December 2012, soil or sediment samples were collected at a total of 22 sites representing eight different land uses obtained from 2007 MOE land use map, including commercial, residential, transportation, bare land, paddy field, coniferous forest, farm land, and broad leaf forest (see Fig. 1) for P source characterization. The following codes were used: C for commercial, R for residential, T for transportation, OL for open land (or bare land), PF for paddy field, FL for farm land, CF for coniferous forest, and BF for broad leaved forest. C1, C2, C3, R1, R2, R3, T1, T2, and T3 are obtained within the urban area, whereas PF1, PF2, FL1, and FL2 are acquired from the agricultural area and CF1, CF2, BF1, and BF2 are from the forest area. In addition, a sewer sample was collected at a sewer manhole near S4.

2.2. Laboratory analyses

A total of 29 pollutants including ions and metals in storm water run-off samples were measured. Total

Table 2
Hydrological characteristics of the study site for the six storm events

					Site							
					S1		S2		S3		S4	
Event	Date	Antecedent dry period (d)	Average rainfall intensity (mm/h)	Rainfall depth (mm)	Run-off duration (min)	Run-off volume (m^3)	Run-off duration (min)	Run-off volume (m^3)	Run-off duration (min)	Run-off volume (m^3)	Run-off duration (min)	Run-off volume (m^3)
1	29/6/2012	31	5.1	63.7	855	2,656	960	14,727	585	6,065	918	1,026
2	18/7/2012	3	2.64	33.5	385	562	510	11,240	145	5,029	420	789
3	12/8/2012	23	2.24	28.5	280	618	700	11,716	310	1,778	816	1,073
4	9/4/2012	3.8	5.69	74	775	10,811	775	21,610	570	6,173	1,440	933
5	9/13/2012	4	2.63	11	NR	NR	400	5,182	NR	NR	150	17
6	10/22/2012	11	5.68	47.5	NR	NR	490	4,779	252	2,194	630	95

Note: NR—no measurable run-off.

phosphorus (TP), soluble phosphorus (SP), and soluble reactive phosphorus (SRP) were measured using the Ascorbic Acid Method in accordance with the APHA Standard Methods for the Examination of Water and Wastewater (1998). Particulate phosphorus (PP) was obtained by subtracting SP from TP. Dissolved organic phosphorus (DOP) was obtained by subtracting SRP from SP. On-site measurement was done for turbidity (TURB) using a portable water quality meter while total suspended solids (TSS) was analyzed in the laboratory using standard methods. Pre-treatment of storm water run-off samples for the analysis of total and dissolved fractions of the metals (tmetals and dmetals) Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn was performed using standard methods and were then analyzed using ICP-MS 7500ce (Agilent Technologies, Tokyo, Japan). Cations including Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}, and anions including F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-} and SO_4^{2-} were analyzed using IC DX-120 (Dionex, CA, USA).

For the analysis of TP in soil and sediment, the samples were digested at 180℃ using mixture of acids (nitric acid and hydrochloric acid), and then were analyzed colorimetrically using Vanadomolybdophosphoric Acid Method from APHA Standard Methods [12]. P fractions, adsorbed-P (Ads-P), non-apatite P (NAP), and apatite-P (AP) in the samples were analyzed as suggested by Hieltjes and Lijklema [13]. Residual P (Res-P) was obtained by subtracting other P types to TP.

Five types of P in water were considered for the characterization study namely, TP, PP, SP, SRP, and DOP. TP includes both organic and inorganic P in both dissolved and particulate form. SP is the dissolved fraction that passed through 0.45 μm filter, consisting of SRP and DOP. PP is the remaining P fraction greater than 0.45 μm. SRP is the molybdate-reactive P form which is mostly inorganic. DOP is the dissolved non-reactive P which is sometimes referred as soluble organic P.

P fraction in soil and sediment consists of TP, Ads-P, NAP, AP, and Res-P. TP contains all forms of P in the soil, obtained after acid digestion to convert to dissolved P form. Successive P extraction is required to quantify Ads-P, NAP, and AP in soil and sediment samples. Ads-P is the loosely sorbed P easily removed by shaking the sample with NH_4Cl within 2 h. NAP is the algal-available P which is metal oxide bound, normally with Fe and Al. This fraction is highly controlled by the pH. For about 17-h shaking with NaOH allows the extraction of NAP. AP is also known as Calcium-bound P which usually attached to organic

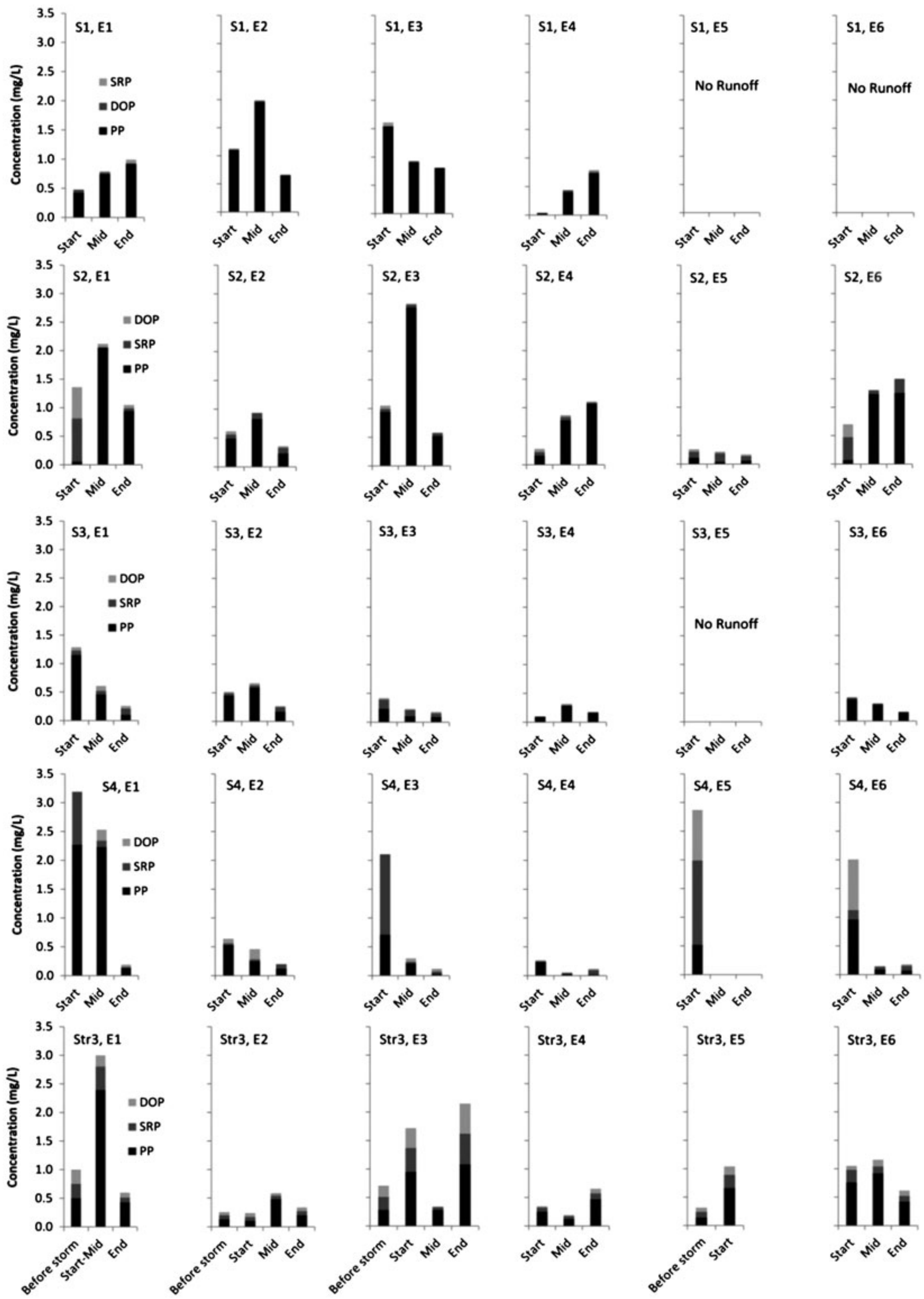

Fig. 2. P concentrations in the run-off at different stages (Start, Mid, and End) of each storm for the storm water monitoring sites.

salts. It is extracted using HCl after 24-h shaking. Res-P or organic-P is very difficult to quantify experimentally hence obtained by subtracting other P types from TP.

2.3. Statistical data analysis

With the aim of obtaining potential surrogate parameters for each examined P type, all analyzed physico-chemical parameters in the water samples were used to determine correlation with each type of P. Correlation analyses were performed using SYSTAT v10.2 (Adage Technologies, Inc., IL, USA).

3. Results and discussion

3.1. P characterization with respect to land use

Concentrations of P in different forms (i.e. PP, DOP and SRP) in the storm water run-off from different sites and storm events were compared in Fig. 2. PP was the dominant form of P in the run-off from S1 to S3. Moreover, the later stage of the run-off from S3 also showed greater particulate fraction in P. The result implies that PP is the dominant form of P in the agricultural or forest run-off. Physical mechanisms primarily explain the large fraction of PP in the run-off, proportional to the intensity of the physical mode of transport [14]. Furthermore, PP dominated flow in agricultural areas is typically observed in small catchments while in larger catchments, SP can be dominant due to the longer residence time allowing larger SS deposition [15,16]. In comparison to S1 and S3, S2 and S4 had greater dissolved P fraction especially during the initial stage of each storm event, though flow is still PP dominated. A relatively large fraction of dissolved P in the run-off might reflect particular characteristics of urban run-off. Desorption–dissolution reactions might explain the significant SP delivery [14] in the storm water run-off for these sites.

No indicative pattern was observed in S1 but significant amount of P was measured, implying that with such a large area, the impact of forest region must not be ignored. Rapid flushing can induce soil erosion hence delivering P bound in the forest soils to the outlet. When the rainfall amount is not sufficiently high, there was no run-off occurred. Thus, it could be concluded that at a sufficiently large rainfall, forest area can be a significant P source. S2 reflects combined impact of urban and forest areas on the temporal variation of P concentration in the storm water run-off. Dissolved fraction of P was greater in the earlier part of the storm, reflecting the influence from the urban area located near the outlet point. As a storm developed, total concentration and particulate fraction of P in the run-off generally increased probably due to the fact that P mobilized in the upper forest area under high flow condition was delivered to the outlet point after a certain travel time. No first flush effect was observed in S2 because of the combined effect of urban and forest areas.

In S3, a gradual decrease in P concentration was observed as the season changed. Mean TP concentration of approximately 0.75 mg/L at the first event dropped to 0.3 mg/L at the last event. This seasonal P first flush in agricultural dominated site is further supported by the temporal change of the TP concentration in surface agricultural soils in the catchment during the same storm events, as shown in Fig. 5. The seasonal P first flush implies that management practice should be focused more on the earlier season with higher P discharge. Conversely, S4 shows no seasonal trend but exhibits first flush phenomenon at each storm event. First flush phenomenon is the initial period of storm water run-off where concentration of pollutants is higher than later stages [17]. It is typical of a small urban catchment [18] and first flush enhanced management can be effective strategy for urban storm water run-off [19,20].

Overall, the TP concentration of storm water run-off from the urban site (S4) was higher compared to that in the less urbanized areas, such as S1 and S3. Ranking in terms of maximum TP concentration is given by S4 > S2 > S1 > S3. Greater P discharge from the completely urbanized (S4) and partly urbanized (S2) areas compared to the less urbanized areas (S1 and S3) might be due to the several reasons; Storm drain system in urban areas may help efficiently deliver pollutants including P during storm events. Furthermore, anthropogenic sources allow continuous and rapid regeneration of P in the system through the build-up mechanism. Additionally, sediments deposited in urban areas can be relatively finer compared to those in forest and agricultural areas, providing greater surface area for P adsorption and more efficient mobilization from the catchment surface during the run-off.

3.2. Land-use specific pollutant profiles

Profiles of physical and chemical parameters in each land use may be used to describe specific source sites. S1 and S2 were dominant in terms of TSS and TURB concentration, almost 15 times greater than that in the urban site (S4), which showed the lowest TSS concentration. This is in relation to the construction area in S1; Soils were disturbed due to construction activities and easily eroded during the rainfall run-off process. Moreover, for the metal concentration, Zn and Pb were dominant in S4 and S2 (completely and partly urbanized areas). Both of these are prominent heavy metal pollutants mainly from roof run-off [21]. High Zn concentration in urban storm water run-off is mainly from Zn roofing material, galvanized gutters, and bulk deposition while Pb inputs are primarily

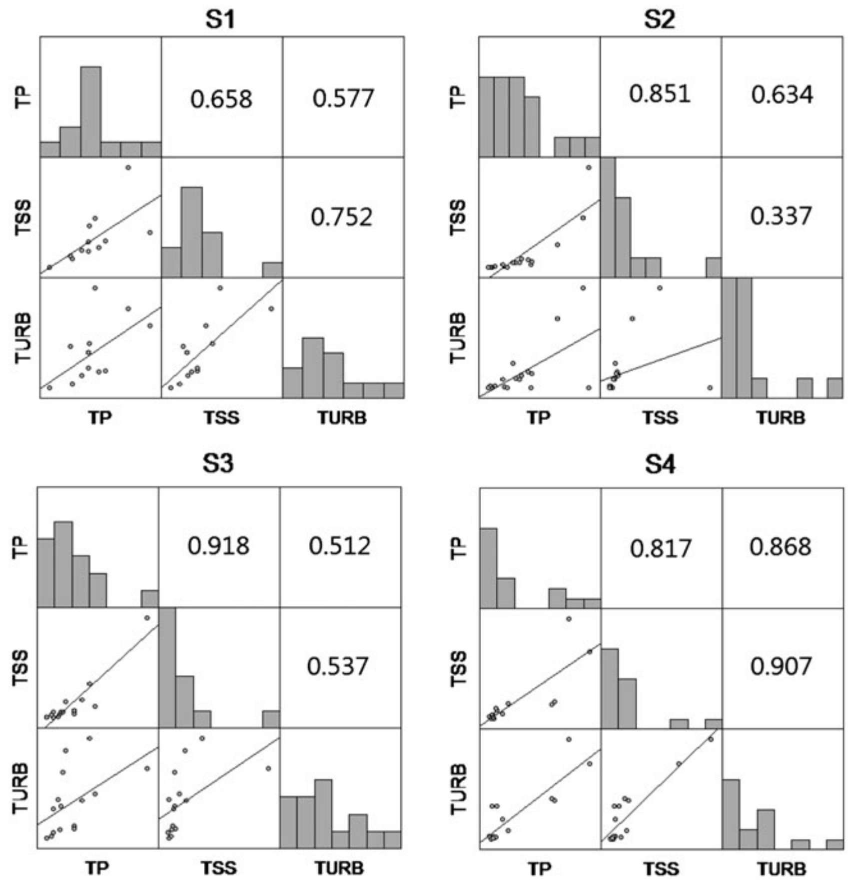

Fig. 3. Correlation matrices for TP, TSS, and TURB in each source sites.

from roofs with PVC gutters [22]. In S3, Zn also dominated but compared to the other sites, S3 has less Zn concentration. The concentration of Mn is also high in S3. This site actually provided the highest Mn concentration among all the monitoring sites. In S1, only Mn showed a noticeable contribution to metal discharge but the concentration is almost half the concentration in S3. Furthermore, for the ion concentration, S4 showed the highest ion concentration which is much greater than the other sites, specifically for Cl^-, Na^+, and SO_4^{3-}. In S2, Cl^-, and SO_4^{2-} also dominated the ion concentration in the site, including Ca^{2+} and NO_3^-. The same ions were also observed in S3 including Na^+, Ca^{2+}, Cl^-, and SO_4^{3-}. S1 exhibited the lowest ion concentration which was dominated by Na^+, SO_4^{2-}, and Ca^{2+}. A large ionic strength might be a specific property of urban run-off.

3.3. Potential surrogate parameters

The applicability of potential surrogate parameters for predicting the P level can be different among different land uses. Overall TP was well correlated with TSS for all sites. S4 exhibited highest correlation for both TP and TSS ($r = 0.817$) and TP and TURB ($r = 0.868$) as shown in Fig. 3. In S2 and S4, TP correlation for TSS ($r > 0.817$) and TURB ($r > 0.634$) were good but in S1 and S3, TP is only well correlated with TSS ($r > 0.658$).

Since TP is typically governed by PP in all sites, and SP with SRP, most correlation analyses for each set resemble. In the urban and partly urban sites, S2 and S4, SP and SRP are both well correlated with the ionic species. In S2, SP and SRP both showed high correlation with Na^+ ($r > 0.933$), K^+ ($r > 0.925$), Cl^- ($r > 0.935$), and PO_4^{3-} ($r > 0.939$). Furthermore, good correlation was noted for NH_4^+ ($r > 0.832$), Br^- ($r > 0.838$), SO_4^{2-} ($r > 0.832$), and Mg^{2+} ($r > 0.689$). In S4, good correlation was noted for Na^+ ($r > 0.841$), NH_4^+ ($r > 0.796$), K^+ ($r > 0.836$), Cl^- ($r > 0.892$), PO_4^{3-} ($r > 0.897$) Br^- ($r > 0.824$), SO_4^{2-} ($r > 0.807$) and Mg^+ ($r > 0.889$). Soluble P fraction in S1 and S3 showed little correlations with other parameters.

Correlation results for TP and PP against total and dissolved metals are shown in Table 3. Least correlation was observed in S1. TP and PP in S2 and S4 are

Table 3
Pearson product of moment coefficient of correlation (r) for TP and PP against total and dissolved metals

		Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
tmetals												
S1	TP	0.628	–	–	–	–	–	–	–	0.605	–	–
	PP	0.627	–	–	–	–	–	–	–	0.611	–	–
S2	TP	0.824	0.716	0.751	0.794	0.740	0.734	0.647	–	0.665	0.667	–
	PP	0.836	0.745	0.757	0.791	0.746	0.746	0.675	–	0.697	0.673	–
S3	TP	0.860	0.717	0.625	0.857	–	*0.934*	–	–	–	–	0.691
	PP	0.887	0.721	0.651	0.889	–	*0.904*	–	–	–	–	0.644
S4	TP	–	–	0.669	0.681	–	–	–	0.666	–	–	–
	PP	–	0.724	0.876	0.887	–	0.749	–	0.912	–	–	–
dmetals												
S1	TP	–	–	–	–	–	–	–	–	–	–	0.683
	PP	–	–	–	–	–	–	–	–	–	–	0.700
S2	TP	–	–	–	–	0.677	–	–	–	–	–	–
	PP	–	–	–	–	0.655	–	–	–	–	–	–
S3	TP	–	0.692	–	–	–	0.738	0.681	–	–	–	–
	PP	–	0.671	–	–	–	0.734	0.677	–	–	–	–
S4	TP	0.648	–	0.751	0.748	0.754	0.798	–	–	0.745	–	–
	PP	0.860	–	0.875	*0.956*	*0.904*	*0.927*	–	–	0.687	–	–

Note: Dashed cells corresponds to $r < 0.60$.

similarly well correlated with a number of total metals (tmetal). tNi is highly correlated with TP ($r > 0.934$) and PP ($r > 0.904$) in S3. In S4, PP is also highly correlated with dissolved metal (dmetal) fractions of Fe ($r > 0.956$), Co ($r > 0.904$), and Ni ($r > 0.927$).

3.4. P concentration in stream water during wet and dry event

Fig. 4 shows P profiles in bottom sediments and overlying waters at three stream sampling sites (Str1, Str2, and Str3) along Guemhak stream during dry sampling periods. In comparison to Fig. 2, P concentration during wet event was higher compared to that obtained during dry sampling. P concentrations in surface waters do not follow a consistent seasonal pattern [23] rather, stronger precipitation accounts to higher P concentration.

Higher TP concentration was observed on the first dry sampling in May 2012, with the greatest TP concentration in the upstream. Upstream probably tends to receive mostly particulate form of P originated from upstream forest areas. Higher soluble P concentration was observed in Str2 and Str3, probably due to the impact of urban discharge as well as deposition of particulate P on the upper stream bed. The impact of urbanization offers a greater soluble P concentration, specifically SRP [7]. Moreover, low flow condition during spring season might increase the retention of P upstream [24] resulting in lower TP concentration downstream in the dry event. Additionally, higher water consumption of agricultural fields provides less dilution capacity in the stream. On the contrary, TP concentration during the second dry sampling event in December 2012 noticeably dropped, but showed less spatial variability with slightly greater concentration in the downstream, probably due to the dry discharge from the downstream urban areas. Generally, water bodies have higher flow during winter allowing dilution of P concentration [11].

TP concentration in stream sediment showed relatively little temporal variation when compared to that in the overlying water. Episodic occurrence of large NAP fraction in the sediment (e.g. sediment in Str2) implies that stream sediment may become a P source available for algal growth in downstream water bodies.

3.5. P concentration in agricultural soil

For each storm event, representative soil samples before and after rainfall were collected in a farm land site in S3 for P analyses. At each stage (i.e.

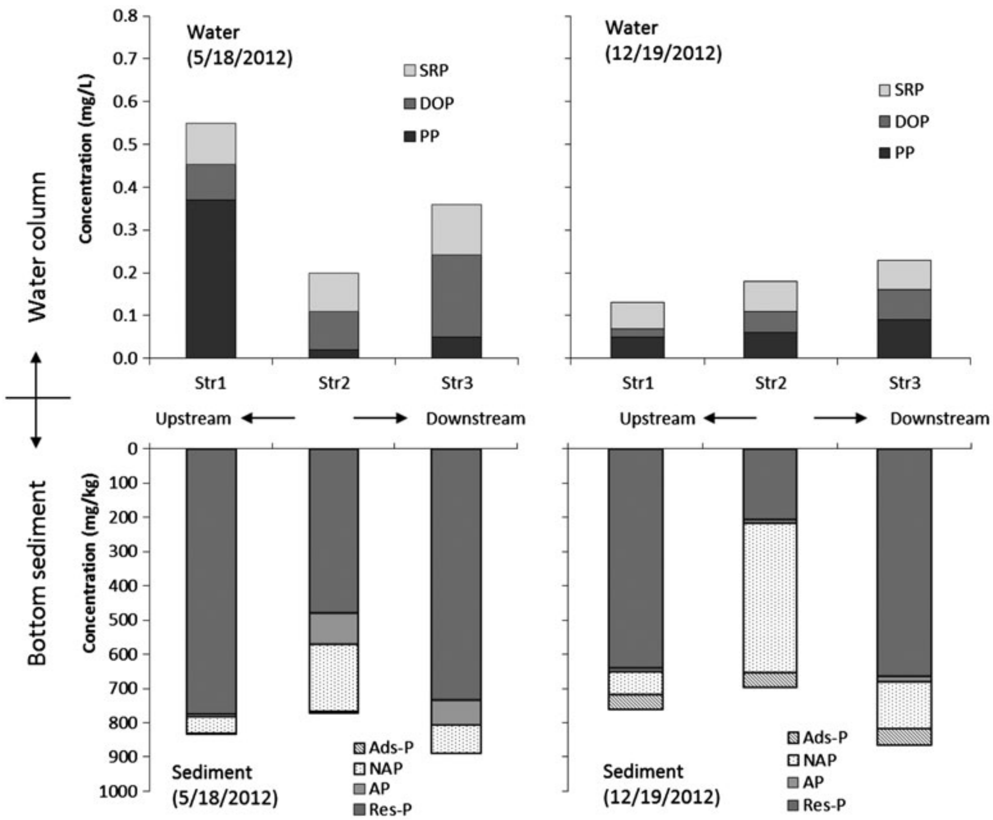

Fig. 4. P concentration in water column and bottom sediment in the main stream during dry days.

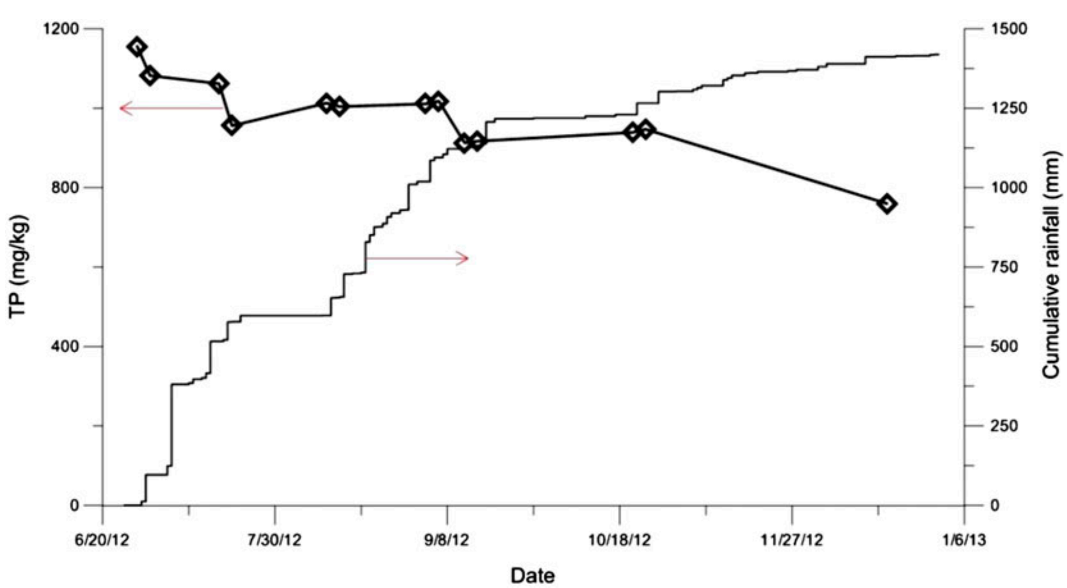

Fig. 5. Temporal change in the TP concentration of surface soils in the agricultural area.

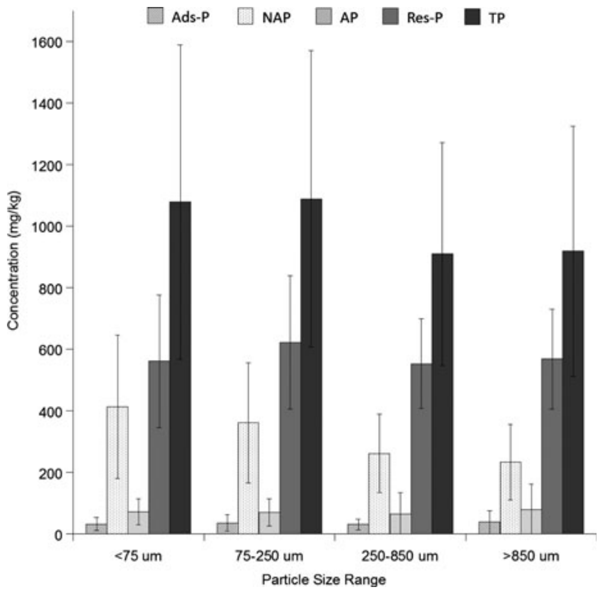

Fig. 6. Concentrations of different P types for different particle size ranges in the surface soils from the agricultural area. Mean values with one-standard deviations for 12 samples.

before and after rainfall), soil samples were collected at three different locations and combined into a single composite sample to represent agricultural soil characteristics. As mentioned before, P concentration in the run-off from the agricultural area showed a seasonally decreasing trend as the P availability in soil decreased. This is also supported by the results of P analysis in soil as shown in Fig. 5. TP concentration in the agricultural soil showed a decreasing trend as the cumulative precipitation increased through the year (from 1,100 to 780 mg/kg). This is because P was released from the soil during each rainfall event, continuously decreasing total P amount sorbed in the soil as the season developed.

Agricultural soil samples were sieved into four size ranges (<75, 75–250, 250–850, and >850 μm) for measuring different types of P with respect to particle size. Fig. 6 illustrates the distributions of Ads-P, NAP, AP, and Res-P for different particle size ranges. Mean values with one-standard deviations for the 12 samples including samples before and after rainfall for the six storm events are shown in the figure below. As for the distribution, Ads-P, AP, and Res-P relatively have small variation. There was a measurable difference in NAP for different size ranges; NAP concentration increases as the particle size decreases, implying that controlling smaller particles should be important to reduce readily bioavailable P load in receiving water bodies.

3.6. P types in solids on different land uses

P in soil originates from the weathering of parent materials, manure, and inputs of fertilizers. There are many possible source sites with high P concentration in soil, other than agricultural soil. This dictated the analysis of P distribution in various land

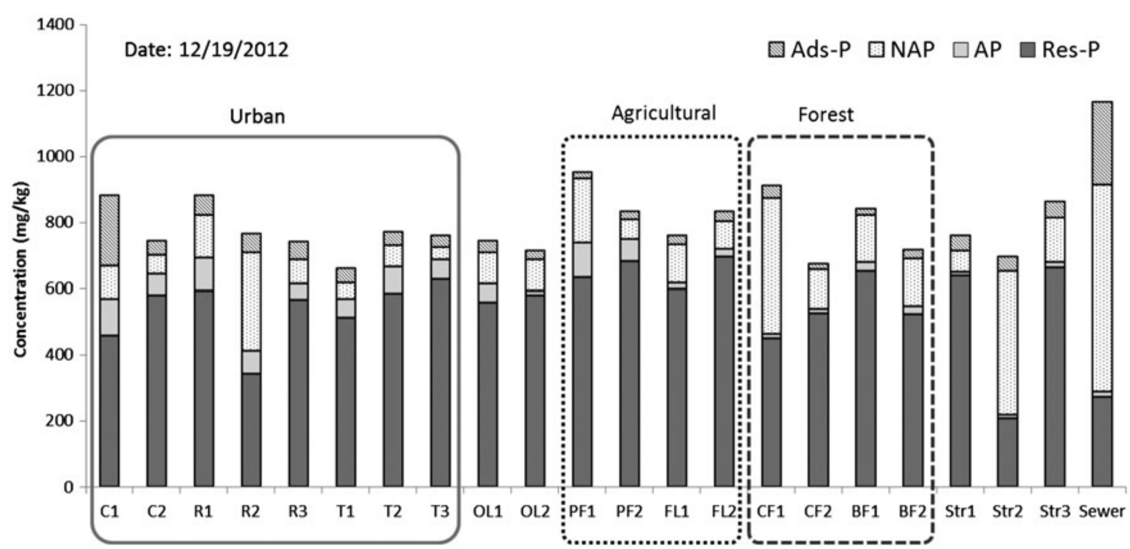

Fig. 7. Compositions of different P types in the sediments or surface soils in different land uses.

uses. Soil or sediment samples were collected during dry periods in winter last December 2012. Sampling locations for the soil/sediment samples are shown in Fig. 1. The distributions of different P types (Ads-P, NAP, AP and Res-P) in soil/sediment samples from various land uses are displayed in Fig. 7.

Small variation in TP concentration in soil/sediment was noted among all the sites. In the urban area, maximum sediment TP concentration was 882.68 mg/kg from a residential land use while minimum concentration of 659.66 mg/kg was found in a transportation land use. Commercial area showed a sediment TP concentration of 882.24 mg/kg, which is very close to that from the residential area. Forest area presented maximum soil TP concentration of 912.02 mg/kg found in the coniferous forest area. Soil sample from the agricultural land use provided the highest concentration for the whole watershed area, which was 951.87 mg/kg from paddy field. In consideration of the time of the year, since agricultural site was concluded to have seasonally decreasing trend in the soil P content, the TP concentration in agricultural land uses measured from this sampling event can be considered as lower than that in the earlier seasons. Note that this is not the same location where agricultural soil samples were collected during the wet sampling events.

In spite of small variability in TP concentration in soil/sediment among different land uses, there was a measureable difference in the distribution of P types among different land uses. Commercial and residential land uses usually contained greater fraction of readily bioavailable P (i.e. Ads-P and NAP) compared to other land uses while transportation land use showed relatively smaller fraction of those types of P. Agricultural area generally had greater concentration of Res-P although the fraction of readily bioavailable P was slightly greater than those of the transportation land use. It should be noted that the forest soils contain moderate amount of TP and readily bioavailable P as opposed to other land uses, reflecting that forest land use can also be an equally important source of P load into receiving waters. All dry soil/sediment samples were smaller in TP concentration and fraction of readily bioavailable P than sewer.

4. Conclusion

In this study, we investigated the discharge characteristics of P from different land uses during storm events. Additionally, concentrations of different P types in soil and sediment from different land uses were measured to provide information on potential sources of P in a mixed land-use watershed. The results showed that the run-off P concentration was greatest in urban land uses compared to non-urban land uses including forest and agricultural areas. However, a measurable concentration of P was also observed in the storm water run-off and soil from the forest areas, implying that forest land use can be an important source of P loading to receiving waters particularly in a relatively large-scale storm event. Agricultural soil showed greater P concentration compared to soils or sediments from urban or forest land uses, although the P concentration in the storm water run-off was relatively smaller than that of other land uses. Smaller particles contained greater amount of readily bioavailable P in the agricultural soils. In addition, the agricultural soil showed a seasonal first flush phenomenon due to the continued P release from the soil during repeated storm events as the season developed. The results indicated that it is important to properly control soil erosion in agricultural and forest area to reduce P discharge from these land uses. In particular, the storm water management should be focused more on fine particles and on earlier season for agricultural land uses. In urban areas, first flush enhanced management for each storm event should be a useful strategy. Stream bed contained comparable amount of P, reflecting that it can also be a potential P source.

Acknowledgment

This research was supported by the Korean Ministry of Environment, as “Eco-Innovation Projects” (No. 413-111-003).

References

[1] S. Wang, H. Qiang, A. Hainan, W. Zhentao, Q. Zhang, Pollutant concentrations and pollution loads in stormwater runoff from different land uses in Chongqing, J. Environ. Sci. 25(3) (2012) 502–510.

[2] D.L. Correll, T.E. Jordan, D.E. Weller, Transport of nitrogen and phosphorus from Rhode River watersheds during storm events, Water Resour. Res. 35(8) (1999) 2513–2521.

[3] A.L. Heathwaite, R.M. Dils, Characterising phosphorus loss in surface and subsurface hydrological pathways, Sci. Total Environ. 251–252(5) (2000) 523–538.

[4] J.N. Houser, P.J. Mulholland, K.O. Maloney, Upland disturbance affects headwater stream nutrients and suspended sediments during baseflow and stormflow, J. Environ. Qual. 35(1) (2006) 352–365.

[5] P. Jordan, A. Arnscheidt, H. McGrogan, S. McCormick, Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrol. Earth Syst. Sci. 11 (2007) 372–381.

[6] V.H. Smith, G.D. Tilman, J.C. Nekola, Eutrophication: Impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems, Environ. Pollut. 100 (1998) 179–196.

[7] K. Sonoda, J.A. Yeakley, C. Walker, Near-stream land-use effects on streamwater nutrient distribution in an urbanizing watershed, J. Am. Water Resour. Assoc. 37 (6) (2001) 1517–1532.

[8] P.J.A. Withers, H. Hartikainen, E. Barberis, N.J. Flynn, G.P. Warren, The effect of soil phosphorus on particulate phosphorus in land runoff, Eur. J. Soil Sci. 60 (2009) 994–1004.

[9] D.W. Schindler, Evolution of phosphorus limitation in lakes, Science 195 (1977) 260–262.

[10] R.E. Hecky, P. Kilham, Nutrient limitation of phytoplankton in freshwater and marine environments: A review of recent evidence on the effects of enrichment, Limnol. Oceanogr. 33(4 part 2) (1988) 796–822.

[11] P.J.A. Withers, H.P. Jarvie, Delivery and cycling of phosphorus in rivers: A review, Sci. Total Environ. 400 (2008) 379–395.

[12] Standard Methods for the Examination of Water and Wastewater. 20th ed., American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, 1998.

[13] A.H.M. Hieltjes, L. Lijklema, Fractionation of inorganic phosphates in calcareous sediments, J. Environ. Qual. 9(3) (1980) 405–407.

[14] A.N. Sharpley, S.J. Smith, O.R. Jones, W.A. Berg, G.A. Coleman, The transport of bioavailable phosphorus in agricultural runoff, J. Environ. Qual. 21(1) (1992) 30–35.

[15] H.P. Jarvie, C. Neal, P.J.A. Withers, Sewage-effluent phosphorus: A greater risk to river eutrophication than agricultural phosphorus? Sci. Total Environ. 360 (1–3) (2006) 246–253.

[16] H.P. Jarvie, P.J.A. Withers, R. Hodgkinson, A. Bates, M. Neal, H.D. Wickham, S.A. Harman, L. Armstrong, Influence of rural land use on streamwater nutrients and their ecological significance, J. Hydrol. 350(34) (2008) 166–186.

[17] A. Deletic, C.T. Maksimovic, Evaluation of water quality factors in storm runoff from paved areas, J. Environ. Eng. 124(9) (1998) 869–879.

[18] J.H. Lee, K.W. Bang, L.H. Ketchum, J.S. Choe, M.J. Yu, First flush analysis of urban storm runoff, Sci. Total Environ. 293 (2002) 163–175.

[19] J.-H. Kang, M. Kayhanian, M.K. Stenstrom, Implications of a kinematic wave model for first flush treatment design, Water Res. 40(20) (2006) 3820–3830.

[20] Y. Li, J.-H. Kang, S.-L. Lau, M. Kayhanian, M.K. Stenstrom, Optimization of settling tank design to remove particles and metals, J. Environ. Eng. Sci. 134(11) (2008) 885–894.

[21] M.C. Gromaire-Mertz, S. Garnaud, A. Gonzalez, G. Chebbo, Characterisation of urban runoff pollution in Paris, Water Sci. Technol. 39(2) (1999) 1–8.

[22] K. Lampria, V. Ruban. Micro pollutants in atmospheric deposition, roof runoff and storm water runoff of a suburban Catchment in Nantes, France, 11th International Conference on Urban Drainage, Edinburgh, Scotland, UK, 2008.

[23] L.B. Owens, W.N. Edwards, R.W. Van Keuren, Sediment and nutrient losses from an unimproved, all-year grazed watershed, J. Environ. Qual. 18 (1989) 232–238.

[24] W. House, F.H. Denison, Phosphorus dynamics in a lowland river, Water Res. 32(6) (1997) 1819–1830.