Environ Earth Sci (2015) 73:1205–1216
DOI 10.1007/s12665-014-3475-3

ORIGINAL ARTICLE

Phosphorus loss and its estimation in a small watershed of the Yimeng mountainous area, China

Zhernwei Li · Guanghui Zhang · Xingxiu Yu · Qianjin Liu · X. C. Zhang

Received: 4 November 2013 / Accepted: 19 June 2014 / Published online: 8 July 2014

Abstract Non-point source pollution is severe in the Yimeng Mountainous Area of China. Few studies have been conducted to identify and predict phosphorus loss at a watershed scale in this region. The objectives of this study were to identify the characteristics of phosphorus loss and further to develop regression models to estimate phosphorus losses of different forms based on the dataset of measured rainfall, runoff, and sediment of 24 rainfall events during the period of 2010–2011 in a typical small watershed from Yimeng Mountainous Area. The results revealed that phosphorus (P) loss differed considerably with phosphorus forms. The dissolved inorganic phosphorus (DIP) was the dominant form of the total dissolved phosphorus (TDP) loss by runoff, accounting for 72 %. The ratio of particulate phosphorus (PP) to total phosphorus (TP) was 65 %, which indicated that most of phosphorus loss was transported by eroded sediment. Similar to soil loss, rainfall properties influenced phosphorus loss greatly and most of the phosphorus loss was produced by only a few heavy storms. The concentrations of different phosphorus forms during a rainfall event varied with similar trends and reached the maxima prior to the peak runoff. Phosphorus losses of different forms were influenced by rainfall kinetic energy, runoff volume, and sediment loss significantly. DIP, TDP, and TP could be predicted with rainfall kinetic energy and runoff volume satisfactorily ($NSE \geq 0.92$). PP was estimated with rainfall kinetic energy, runoff volume, and sediment loss of rainfall event well ($NSE = 0.90$). Further studies are necessary to assess the performance of the developed models under different conditions.

Z. Li · G. Zhang (✉)
State Key Laboratory of Soil Erosion and Dryland Farming on the Loess Plateau, Institute of Soil and Water Conservation, Chinese Academy of Sciences and Ministry of Water Resources, Yangling 712100, Shaanxi, China
e-mail: ghzhang@bnu.edu.cn

Z. Li
University of Chinese Academy of Sciences, Beijing 100049, China

G. Zhang
School of Geography, Beijing Normal University, Beijing 100875, China

X. Yu · Q. Liu
Shandong Provincial Key Laboratory of Soil Conservation and Environmental Protection, Linyi University, Linyi 276005, China

X. C. Zhang
USDA-ARS Grazinglands Research Laboratory, El Reno, OK, USA

Keywords Rainfall · Runoff · Sediment · Phosphorus loss · Agricultural watershed

Abbreviations

DIP	Dissolved inorganic phosphorus
E	Rainfall kinetic energy
NSE	Coefficient of Nash–Sutcliffe model efficiency
PP	Particulate phosphorus
RV	Runoff volume
SS	Sediment
TDP	Total dissolved phosphorus
TP	Total phosphorus

Introduction

In recent years, non-point source pollution (NPSP) of water bodies has become an issue of global significance;

particularly agricultural NPSP, which covers wider areas, has greater uncertainty and is more difficult to control (Neal and Jarvie 2005). On the global scale, 23–42 Tg nitrogen (N), 2.1–3.9 Tg organic phosphorus (P), and 12.5–22.5 Tg inorganic P are moved by surface runoff and soil erosion each year (Quinton et al. 2010). As a major contributor to agricultural NPSP, the losses of N and P not only impoverish soil nutrient stocks and lower soil productivity, but also cause eutrophication in water bodies (Pimentel et al. 1995). Though phosphorus is an essential nutrient for algal productivity, excess anthropogenic phosphorus loading from contributing watersheds during rainfall events may accelerate eutrophication of freshwater systems (Correll 1998; Jalali and Ranjbar 2011). Consequently, estimation and control of phosphorus loss are vital to minimize surface water degradation (Bowes et al. 2008; Wang et al. 2013).

Phosphorus can be transported to surface water bodies via storm runoff in dissolved and particulate forms. Measurement of different forms of phosphorus concentration is generally undertaken by point sampling. In general, phosphorus concentration exhibits a great variability during a rainfall event due to great variations in phosphorus sources and flow discharge, and thus a continuous monitoring at short interval is required, especially for heavy storms which produce more than 75 % of phosphorus loss from watersheds (Pionke et al. 1999; Vanni et al. 2001). Nevertheless, in reality, the continual measurements at short intervals are seldom done because of the high cost of water sampling and time-consuming chemical analysis. Therefore, it is necessary to develop mathematical models to predict phosphorus loss using available intensive datasets for effective nutrient management decision-making.

Many NPSP models have been developed in the past several decades, which can be arbitrarily grouped into physical-based models and empirical regression models (Zhang 2011). Physical-based models (i.e., AGNPS, ANSWERS, and SWAT) are more suitable to estimate NPSP loss at watershed scale, but they require very extensive data input, dependence of site-specific parameters, and complicated model structures (Worrall and Burt 1999). An alternative to the physical-based model is to use an empirical regression model, especially for management purposes. Site managers often prefer an effective, convenient, and relatively simple model to estimate NPSP loss. Therefore, regression equations with their advantage of simplicity are effective to estimate phosphorus loss in most cases (Beránková et al. 2010; Brezonik and Stadelmann 2002; Girmay et al. 2009; Kim et al. 2006; Zhang et al. 2008).

Phosphorus loss is influenced by many factors. It is critical to identify and quantify these factors to predict phosphorus loss adequately under different conditions (Brezonik and Stadelmann 2002; Zhang et al. 2008). All factors influencing runoff and erosion processes must affect phosphorus loss. These include rainfall property, topography, soil properties, vegetation cover, land use, tillage measure, and fertilizer application. Ahuja et al. (1982) reported that phosphorus loss increased with an increase in slope length or slope gradient. Surface and canopy cover affects phosphorus loss due to its alteration of raindrop impact energy. The results of Girmay et al. (2009) showed that land use influences phosphorus loss significantly and most of the phosphorus loss was produced in the cropland. The ridge till and chisel plow systems were worse than moldboard plow systems in reducing phosphorus loss in runoff (Hansen et al. 2000). Increasing in manure application was associated with a higher total dissolved phosphorus concentration, and it decreased as a linear function with time after manure application due to phosphorus depletion in the soil surface (Kleinman and Sharpley 2003). Zhang et al. (1997a) identified that the chemical transfer from soil solution to surface runoff mainly occurred in the mixing zone, which mixed with rain water, soil solution water, and infiltrated water instantaneously. The rainfall patterns have a significant impact on chemical loss, since the depth of the mixing zone was generally less than 3 mm (Zhang et al. 1997b). Therefore, the changes in phosphorus loss probably strongly relate to the characteristics of rainfall, runoff, and sediment.

The effects of rainfall on phosphorus loss are great. Edwards and Daniel (1993) found that the total phosphorus (TP) loss increased with rainfall intensity, since it was the product of phosphorus concentration and corresponding runoff. Runoff and the dilution factor increased with rainfall intensity, and the phosphorus loss would increase though the phosphorus concentrations probably decreased. Shigaki et al. (2007) demonstrated that both particulate phosphorus (PP) concentration and loss increased with increasing rainfall intensity due to the greater detachment and transport of associated enriched sediment particles. The continuous erosion process made more nutrients extract from the soil solution, resulting in increases in total dissloved phosphorus (TDP) loss. Thus the phosphorus concentration would decrease or increase with increasing rainfall intensity, but the phosphorus loss might increase with rainfall intensity. Phosphorus loss was also related to rainfall amount and duration. Both Zhang et al. (2008), and Brezonik and Stadelmann (2002) found that TDP and TP loss increased as rainfall amount and duration increased under different conditions. Rainfall kinetic energy (Ahuja et al. 1982) and rainfall erosivity (Ramos and Martinez-Casasnovas 2006) also had a great influence on phosphorus loss. The phosphorus concentration increased linearly with rainfall kinetic energy and rainfall erosivity, while the total phosphorus loss increased as a power function of the rainfall erosivity.

Runoff is another important factor affecting phosphorus loss and it is considered as a major variable driving stream hydrochemistry (Wu et al. 2012). Traditionally, the phosphorus concentrations decreased with flow discharge due to greater runoff and the associated dilution (Edwards and Daniel 1993). Nevertheless, some other studies have found different results where the phosphorus concentrations increased with increase of flow discharge (Kim et al. 2006; Shigaki et al. 2007). Compared to the effect of runoff on phosphorus concentrations, most studies have concentrated more on its effect on phosphorus loss. For example, Yang et al. (2009) found that particulate phosphorus loss peaks precede the runoff peaks, while the total dissolved phosphorus loss peaks accompanied the runoff. The difference is caused by the fact that particulate phosphorus loss was transported by sediment, while the total dissolved phosphorus loss was controlled by the runoff process. The ratios of TDP loss to PP loss were closely related to flow discharge, which controlled the sediment transport capacity of flowing water and fluctuated greatly between the dry and rainy seasons (Ellison and Brett 2006; Ide et al. 2007). Based on a simple regression, power functions between phosphorus loss and runoff volume have been developed and used to estimate phosphorus loss in many cases (Beránková et al. 2010; Chun et al. 2010; Kim et al. 2006; Udawatta et al. 2004). Peak flow rate was also used by Fleming and Cox (2001) to predict dissolved and particulate phosphorus loss, and it was regarded as one of the most significant variables to predict particulate phosphorus loss in their study.

Besides rainfall and runoff, phosphorus loss is also strongly influenced by sediment because phosphorus is often strongly adsorbed by sediment (Ide et al. 2008; Yang et al. 2009). The excessive soil erosion from rainstorms could dramatically increase the river sediment loss and the amount of particulate phosphorus flushed into rivers. Some recent studies showed that phosphorus in runoff was mainly governed by sediment, which confirmed the significant correlation between particulate phosphorus concentration and sediment concentration (Withers et al. 2009). Power (Ramos and Martinez-Casasnovas 2006) or linear (Udawatta et al. 2004) function was developed between total phosphorus loss and sediment loss.

According to the classification of Chinese soil erosion, the northern rocky mountainous region is the most susceptible to soil erosion and leaching in China. The Yimeng Mountainous Area is one of the most representative areas of the northern rocky mountainous. This area is characterized by its unstructured and shallow soil layer with great proportion of rock fragments, resulting in a low water-holding capacity. As population increases and economy grows, environmentally damaging human activities (i.e., deforestation, environmentally undesirable utilization of natural resources, and agricultural reclamation) become more and more frequent. Due to natural changes coupled with human influences, NPSP is increasing and becoming more severe in this region (Yu et al. 2012). The total phosphorus concentration in the surface water bodies in the study region was far greater than the threshold of the eutrophication (0.02 mg L^{-1}) during rainfall events. The rich nutrients led to algae outbreak and had a potential threat to deteriorate the water body in the region (Li et al. 2012). In order to develop appropriate regulations to protect water bodies, it was necessary to identify factors affecting phosphorus loss during rainfall events on a watershed scale. However, the quantitative effects of rainfall, runoff, and sediment on phosphorus loss were not clear in this region, which impeded the NPSP control in the Yimeng Mountainous Area.

The objectives of this study were: (1) to quantify the phosphorus loss characteristics of 24 measured rainfall events, especially the five largest storms that contributed most phosphorus loss in the watershed; (2) to determine the quantitative effects of rainfall, runoff, sediment on phosphorus loss; and (3) to develop regression models to estimate phosphorus losses of different forms for small watersheds in the Yimeng Mountainous Area.

Materials and methods

Watershed description

The field experiment was conducted at the Menglianggu watershed (35°20′N, 118°6′E), located in the north of the Yimeng Mountainous Area. This area has a warm temperate continental monsoon climate, with an average annual temperature of 13.4 °C and an average annual precipitation of 757 mm. Precipitation distribution during a year is uneven and more than 60 % of it falls between June and September. The elevation in the watershed increases from 174 m in the southwest to 485 m in the northeast. The watershed has a brown soil (termed Alfisols in the American Soil Taxonomy and Luvisols in the World Soil Taxonomy) derived from acidic granite with a sandy loam texture, a high bulk density (>1.18 g cm^{-3}), and low PH (~5.1). The total area of the watershed is 1.03 km^2, with main land uses (Fig. 1) as forestland (55.8 %), cultivated land (20.5 %), orchard (10.7 %), unused land (9.3 %), residential land (3.5 %), and grassland (0.2 %). Forestland often is located at the upper part of hills, while cultivated land is found at the lower reaches of the watershed. The population density of watershed is only 120 inhabitants per square kilometer and the phosphorus source mainly comes from the fertilizer application on cultivated land and orchard. There is no industrial pollution source and the

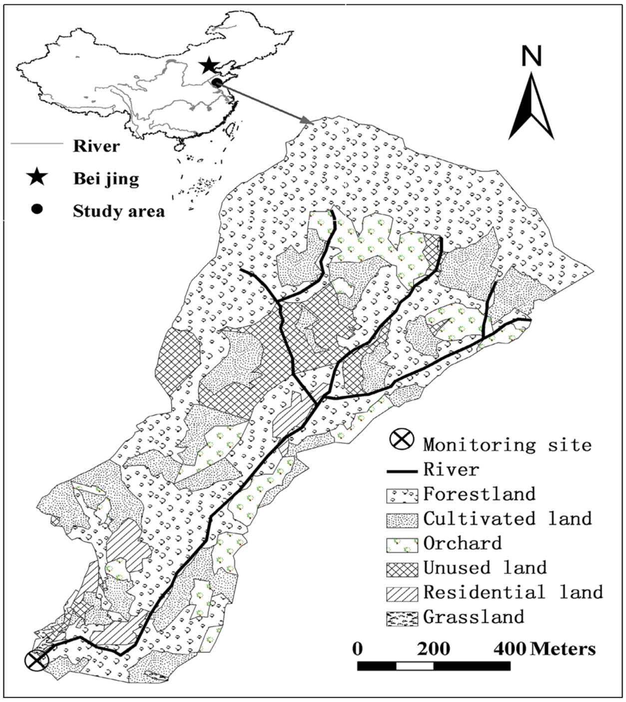

Fig. 1 Land use of the study small watershed

water quality measured at the outlet should represent the non-point source pollution in the watershed.

Measurements of rainfall, water level, sediment, and phosphorus

The rainfall was measured with a siphon precipitation recorder (Shanghai Meteorological Instrument Factory), which was installed on the rooftop of a house in the watershed. Twenty-four natural rainfall events above 2 mm were recorded during the measurement period (2010–2011). Runoff was measured using a normative triangular and trapezoidal weir built at the outlet of watershed. The water level was recorded manually and then converted to runoff discharge using an equation which was derived from the weir types of measurement structures. The sand and sediment in the weirs clear up immediately after a rainfall to ensure the equations accuracy.

For each rainfall event, water samples were collected throughout the runoff process manually by hand. When the water level of the triangular weir increased, water sampling started. Generally, the samples were collected at 5-min intervals, but 3-min intervals were used for heavy storms and 10-min intervals for light rainfall events. When rainfall stopped, sampling was continued at 30-min intervals till the water level returned to the base flow.

Water samples were collected using 500 mL polyethylene plastic bottles. For each bottle, 0.5 mL of 98 % H_2SO_4 was added to suppress microbial activity and then it was stored in a portable freezer at 2–4 °C. Water samples were transported to the laboratory to measure dissolved inorganic phosphorus (DIP), total dissolved phosphorus (TDP), particulate phosphorus (PP), total phosphorus (TP), and sediment (SS). DIP, DP, and TP were all determined by the molybdenum-blue (ascorbic acid) method (Murphy 1962), but with different pre-treatments. For TP, water samples were digested using potassium peroxodisulfate ($K_2S_2O_8$) at 120 °C for 0.5 h and then TP was measured using molybdenum-blue (ascorbic acid) method (Murphy 1962). For TDP, water samples were filtered through a filter of 0.45 μm pore size just prior analysis, and then TDP was digested and measured following the same procedure of total phosphorus (Murphy 1962). The collected water samples were filtered through a filter of 0.45 μm pore size and then DIP was measured directly using molybdenum-blue method without digesting (Murphy 1962). The DIP, TDP and TP concentrations were all determined with the ultraviolet and visible spectrophotometer (UV 1206) (Chun et al. 2010). PP was calculated as the difference between TP and TDP. Water samples were filtered with glass fiber disks with a 0.70 mm pore size, oven-dried at 120 °C for 24 h till no change in weight and then weighed to obtain the sediment. Altogether, 826 samples were tested and analyzed separately.

Data analysis

The mass of each phosphorus form (DIP, TDP, PP, and TP) transported by runoff for a rainfall event was calculated as follows:

$$M = \int_0^T C_t \times Q_t \mathrm{d}t \approx \sum_{i=1}^{i=n-1} (C_i + C_{i+1})/2 \cdot (Q_i + Q_{i+1})/2 \cdot \Delta t_i \Big/ A \quad (1)$$

where M is the mass of the different phosphorus transported by runoff of a rainfall event (g km^{-2}), T is the duration of rainfall (s), C_i is the phosphorus concentration at time of the ith sample (mg L^{-1}), Q_i is the runoff discharged at time of the ith sample (m^3 s^{-1}), Δt_i is the interval of runoff sampling (s), n is the total number of sampling, and i (1, 2, … $n - 1$) is the sampling sequence number, A is the area of the watershed (km^2).

To assess effects of rainfall on phosphorus loss, the rainfall characteristics of both single and compound factors were obtained or computed from rainfall data set. The single factors were precipitation amount (*PR*), rainfall duration (*DR*), average rainfall intensity (*I*), the maximum x-min rainfall intensity (I_x including I_5, I_{10}, I_{30}, I_{60}), the rainfall kinetic energy (E), and the maximum 60-min rainfall kinetic energy (E_{60}). The rainfall kinetic energy, E (MJ ha^{-1}), was calculated by the following equations:

$$E = \sum_{r=1}^{n} e_r v_r \tag{2}$$

$$e_r = 0.29[1 - 0.72\exp(-0.05 i_r)] \tag{3}$$

where e_r is the unit rainfall energy (MJ ha^{-1} mm^{-1}), v_r is the rainfall amount for the rth part of a storm (mm), and i_r is the breakpoint rainfall intensity for the rth part of a storm (mm h^{-1}).

The compound factors were product of rainfall kinetic energy and average rainfall intensity (EI), product of the maximum 60-min rainfall kinetic energy and average rainfall intensity ($E_{60}I$), product of precipitation and average rainfall intensity (PI), product of rainfall kinetic energy and the maximum x-min rainfall intensity (EI_x including EI_5, EI_{10}, EI_{30}, EI_{60}), product of the maximum 60-min rainfall kinetic energy and the maximum x-min rainfall intensity ($E_{60}I_x$ including $E_{60}I_5$, $E_{60}I_{10}$, $E_{60}I_{30}$, $E_{60}I_{60}$), and product of precipitation and the maximum x-min rainfall intensity (PI_x including PI_5, PI_{10}, PI_{30}, PI_{60}).

The runoff discharge of each rainfall event was computed from water level recorded by weirs. When water level was below the height of triangular weir, it was calculated using Eq. (4), and when water level surpassed the height of triangular weir, the runoff was estimated using Eq. (5) (Li et al. 2012).

Triangular weir:

$$Q = 1.4H^{2.5} \tag{4}$$

Trapezoidal weir:

$$Q = 21.44H_a^{1.6} \tag{5}$$

where Q is the runoff discharge (m^3 s^{-1}); H is the water level of the triangular weir (m); H_a is the water level of the trapezoidal weir (m).

The runoff volume, peak flow rate, and sediment loss were used to analyze the potential effects of those factors on phosphorus loss. The runoff volume and sediment loss for a rainfall event were calculated:

$$RV = \sum_{i=1}^{i=n-1} (Q_i + Q_{i+1})/2 \cdot \Delta t_i \Big/ A \tag{6}$$

$$M_{SS} = \sum_{i=1}^{i=n-1} (SC_i + SC_{i+1})/2 \cdot (Q_i + Q_{i+1})/2 \cdot \Delta t_i \Big/ A \tag{7}$$

where RV is the runoff volume (m^3 km^{-2}), M_{SS} is the mass of sediment loss for a rainfall event (kg km^{-2}), and SC_i is the sediment concentration at time of the ith sample (kg m^{-3}).

Statistical analysis

Statistical analysis was conducted using SPSS version 17.0. Relationships between phosphorus loss and rainfall characteristics, runoff, or sediment were analyzed by a simple regression method. A multi-variable, nonlinear regression was applied to develop the relationships between each form of phosphorus and rainfall, runoff, and sediment. The coefficient of determination (R^2) and the coefficient of Nash–Sutcliffe model efficiency (NSE) were used to evaluate the performance of the regression equations. The calculation formulae for those statistical indices were found in Zhang et al. (2009).

Results and discussion

Phosphorus loss characteristics

The statistical properties of each form of phosphorus loss for 24 rainfall events were presented in Table 1. It was clear that the phosphorus loss varied between the forms of phosphorus. The dissolved inorganic phosphorus changed significantly from 0.08 to 1.31 × 10^3 g km^{-2} with a mean of 182 g km^{-2} per event. As the inorganic phosphorus fertilizers made the largest fraction of total dissolved phosphorus in this agricultural watershed, the contribution of the DIP to TDP was 72 % for all 24 events. The total dissolved phosphorus also varied greatly from 0.38 to 1.54 × 10^3 g km^{-2} with a mean of 253 g km^{-2}. Compared with DIP, PP, and TP, the variation in TDP between different rainfall events was the minimum. On the average of 24 events, the ratio of TDP to TP was approximately 35 %, which implied that most of the lost phosphorus was associated with eroded sediment. For 24 rainfall events, the TDP and TP losses were equal in 6 light rainfall events since the sediment was not observed in these events. Thus, particulate phosphorus was observed only in 18 events, which increased from 8.23 to 4.36 × 10^3 g km^{-2} with a mean of 619 g km^{-2}. The ratio of particulate phosphorus to total phosphorus loss was 65 % for all 24 events. In rocky mountainous region as in this study, the loose soil layer with earth–rock structure and steep valleys likely led to a great particulate phosphorus loss due to severe water erosion (Ma et al. 2012). Much attention should be paid to control of water erosion for water quality conservation in those areas.

The phosphorus loss varied considerably from event to event. The ratios of DIP, TDP, PP, and TP losses from the five maximum events (serial number: 20100717, 20100719, 20100812, 20110725, and 20110811) to the total 24 events were 69, 66, 84 and 79 %, respectively. This result indicated that only a few heavy storms caused

Table 1 Summary statistics of each form of phosphorus loss for 24 rainfall events

Items	Min. (g km^{-2})	Max. (g km^{-2})	Mean (g km^{-2})	Sum (g km^{-2})	Std.	CV	*n*
DIP	0.08	1,312	182	4,370	300	1.65	24
TDP	0.38	1,541	253	6,066	383	1.51	24
PP	8.00	4,356	619	11,144	1,079	1.74	18
TP	0.38	5,897	717	17,210	1,331	1.86	24

DIP dissolved inorganic phosphorus, *TDP* total dissolved phosphorus, *PP* particulate phosphorus, *TP* total phosphorus, *CV* coefficient of variation, and *n* number of the rainfall events

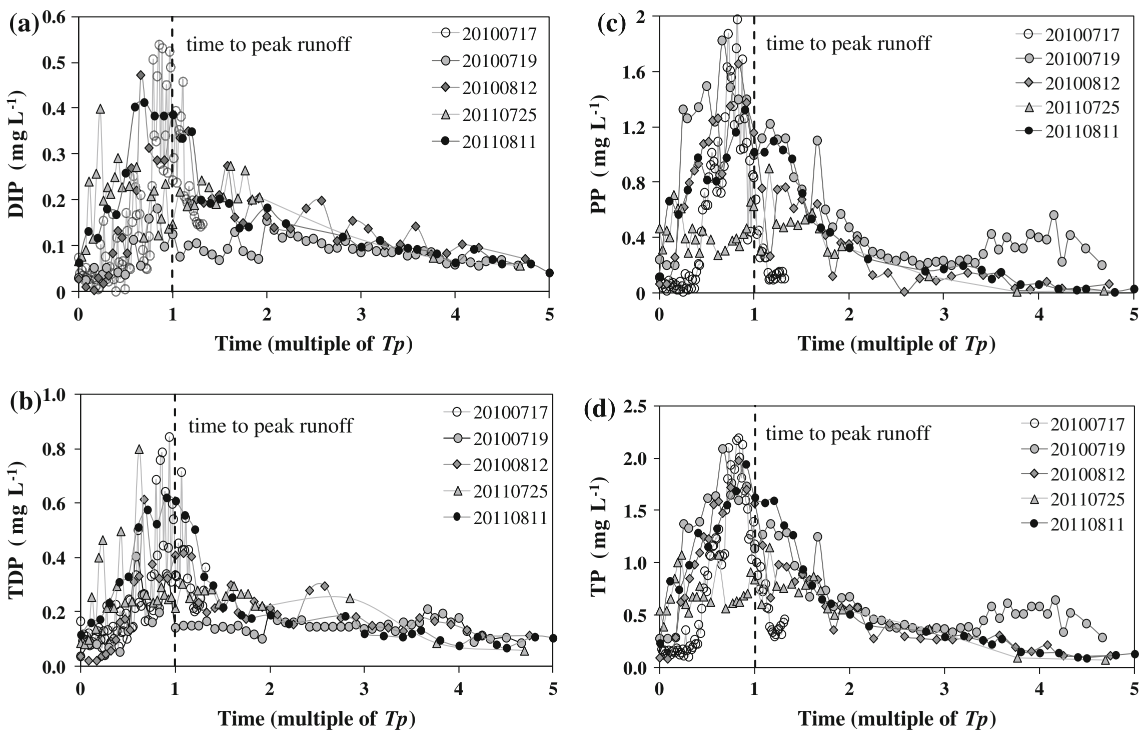

Fig. 2 The processes of phosphorus concentrations as a function of the time to peak runoff rates (T_p) for five maximum rainfall events. **a** Dissolved inorganic phosphorus (DIP). **b** Total dissolved phosphorus (TDP). **c** Particulate phosphorus (PP). **d** Total phosphorus (TP)

the most phosphorus loss, which was first found in our studied area. Similar results also have been found by Pionke et al. (1999), Ramos and Martinez-Casasnovas (2004) and Vanni et al. (2001) in other regions. Thus, it was important to analyze the processes of these five rainfall events to understand the dynamic changes in phosphorus concentration and to control phosphorus loss in the Yimeng Mountainous Area.

To analyze the variations of phosphorus concentrations during the five maximum rainfall events, the phosphorus concentrations were plotted against time (Fig. 2). The time scale in Fig. 2 was calculated as a multiple of time to peak runoff rate (T_p). This approach was easy to compare the variation in phosphorus concentrations between different rainfall events with different T_p. Furthermore, it provided a more uniform scale for comparing various storms having extreme variations in runoff durations (Pathak et al. 2004; Han et al. 2010). The variation patterns of different phosphorus losses were similar for all the five rainfall events. The phosphorus concentration increased rapidly and reached a maximum. Then it declined gradually and became stable. Due the first flush effect (Lee and Bang 2000), the appearance of DIP, TDP, PP, and TP concentration peaks preceded the peak runoff for all five rainfall events, There were some small differences between different rainstorms. For the events of 20100719, 20100812, and 20110811, the DIP, TDP, PP, and TP changed as a dissymmetric "∧"shape with only one concentration peak (Fig. 2). However, for the other two events of 20100717 and 20110725, the concentration of DIP, TDP, PP, and TP fluctuated and had several peaks. This phenomenon was probably caused by the fact that these two events were the first erosive rainstorms in the rainy season in 2010 and 2011. Due to the increasing capacity of phosphorus storage, as a result of increasing availability of fine sediments, the fine material (i.e., clays contain high phosphorus content) was initially removed preferentially from the soil surface by the small flow energy and caused the first phosphorus concentration peaks (Nash et al. 2002). Detachment controlled by the availability kinetic energy from the flowing water became greater as rainfall continued and led to expose more phosphorus-enriched material to be eroded, and then the next peaks appeared. An alternative explanation was that the phosphorus transfer from soil solution to runoff could be described as a two-rate process. A fast rate sub-process prevailed at the early stage of rainfall and produced the first peak due to an exponential depletion of phosphorus from the mixing zone. However, a slow rate sub-process became significant as rainfall continued and the next peaks appeared, attributing to transport the phosphorus from the underlying soil to the mixing zone (Zhang et al. 1997a, 1999). This result implied that a rainstorm following a long dry period tended to cause a great loss of phosphorus.

The variation in concentration of PP (2.5×10^{-3}–2.0 mg L^{-1}) was greater than that of TDP (2.0×10^{-2}–0.8 mg L^{-1}) (Fig. 2). This result could be explained by a dynamic equilibrium mechanism for phosphorous between soil adsorption and the dissolution via soil–water interactions (Yang et al. 2009), which led to a greater variation in TDP than PP for runoff with high sediment. It was generally accepted that the critical level of TP was 0.02 mg L^{-1} to accelerate the eutrophication of surface waters. In this study, TDP concentration (0.02–0.8 mg L^{-1}) was 1–40 times greater than the critical level, which would certainly pollute the local water bodies (such as Andi Reservoir near the watershed providing water for life).

Effects of rainfall characteristics on phosphorus loss

All single factors and compound factors of rainfall events influenced various phosphorus losses significantly, except rainfall duration. This result agreed with the findings of Ramos and Martinez-Casasnovas (2006), whereas it differed from the results of Brezonik and Stadelmann (2002) and Zhang et al. (2008), who found that the total dissolved phosphorus loss correlated with precipitation and rainfall duration significantly, but not with rainfall intensity. These differences were probably caused by the land use of the studied watershed. In this study, a typical agricultural small watershed was selected and both phosphorus fertilizers and manure were applied on croplands. Nevertheless, forest and urban watersheds were utilized in their studies.

Among all rainfall characteristics, rainfall kinetic energy was the best variable to estimate DIP, TDP, PP, and TP loss compared to the other 23 variables. Various phosphorus losses increased as a power function of rainfall kinetic energy with high coefficients of determination of 0.90, 0.90, 0.90, and 0.89, respectively (Fig. 3). When the rainfall kinetic was <6 or >20 MJ ha^{-1} the estimated DIP and TDP losses were slight smaller than the observed values (Fig. 3a). When the rainfall kinetic energy was greater than 10 MJ ha^{-1}, the predicted PP and TP losses matched the

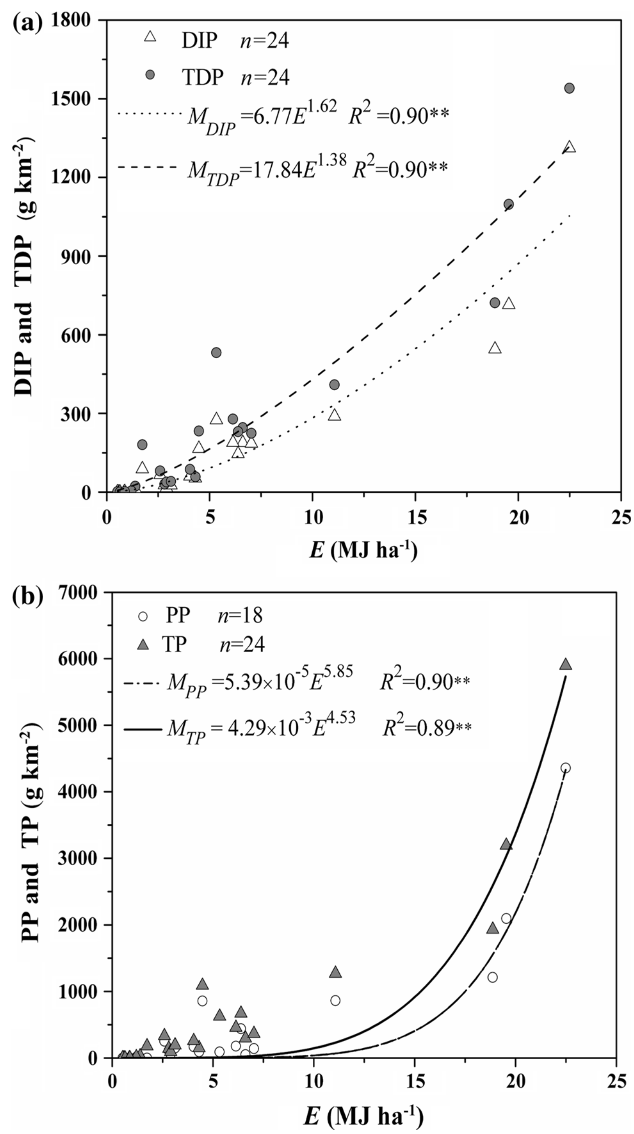

Fig. 3 Measured losses of phosphorus as a function of rainfall kinetic energy (E). **a** Dissolved inorganic phosphorus loss (M_{DIP}) and total dissolved phosphorus loss (M_{TDP}). **b** Particulate phosphorus loss (M_{PP}) and total phosphorus loss (M_{TP}). **$p < 0.01$

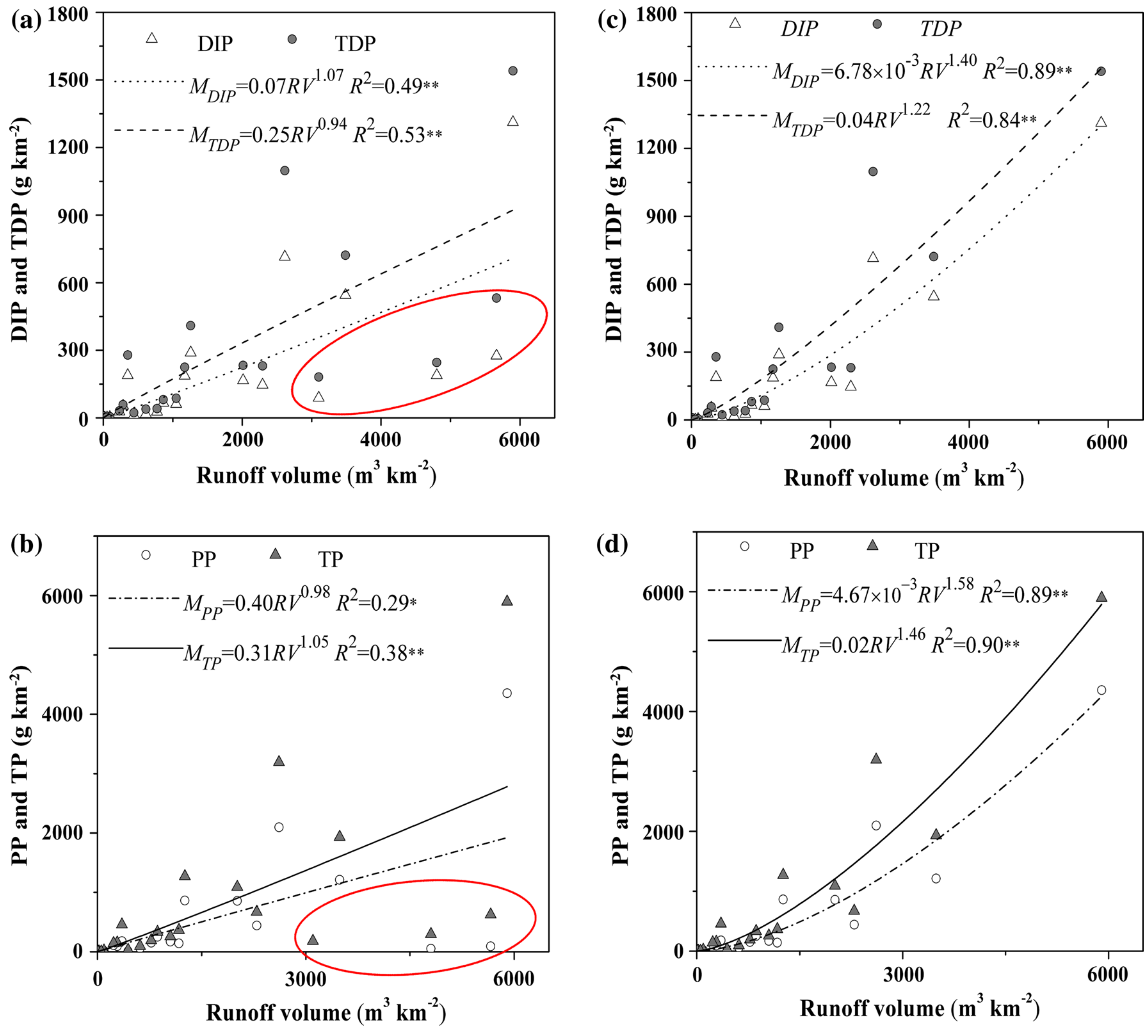

Fig. 4 Measured losses of phosphorus as a function of runoff volume (*RV*). **a** Dissolved inorganic phosphorus loss (M_{DIP}) and total dissolved phosphorus loss (M_{TDP}) for all 24 events. **b** Particulate phosphorus loss (M_{PP}) and total phosphorus loss (M_{TP}) for all 24 events. **c** DIP and TDP loss with three events deleted from regressions. **d** PP and TP loss with three events deleted from regressions. *$p < 0.05$; **$p < 0.01$

measured ones satisfactorily. However, when the rainfall kinetic energy was low, the phosphorus losses were greatly underestimated (Fig. 3b). The increases in phosphorus of different forms with rainfall kinetic energy could be explained by two aspects. On one hand, with the increase in rainfall kinetic energy, the soil structure was severely destroyed and phosphorus could be well mixed and extracted by runoff water. The transfer of phosphorus from soil solution to surface runoff increased significantly (Ahuja 1990). On the other hand, increase in rainfall kinetic energy probably leads to an increase in runoff, which results in increase in flow velocity and runoff depth and, consequently, widening of the runoff volume to phosphorus source ratio. Therefore, the increase in equilibration time of soil phosphorus and a solution leads to an increase in phosphorus loss (Dougherty 2002; Nash et al. 2002). Also, increase in runoff would increase the detachment and transport capacities of overland flow (Zhang et al. 2003, 2009) and, therefore, increase sediment and phosphorus loss (Ahuja et al. 1982).

Effects of runoff on phosphorus loss

Various phosphorus losses increased significantly with both runoff volume and peak flow rate. Simple regression analysis showed that runoff volume was more closely related to phosphorus loss compared to the peak flow rate. DIP and TDP losses increased as a power function of runoff volume with the coefficient of determination of 0.49 and 0.53. However, the measured data were scattered greatly when runoff was greater than 1,000 m^3 km^{-2} (Fig. 4a). This result was consistent with the results of Ide

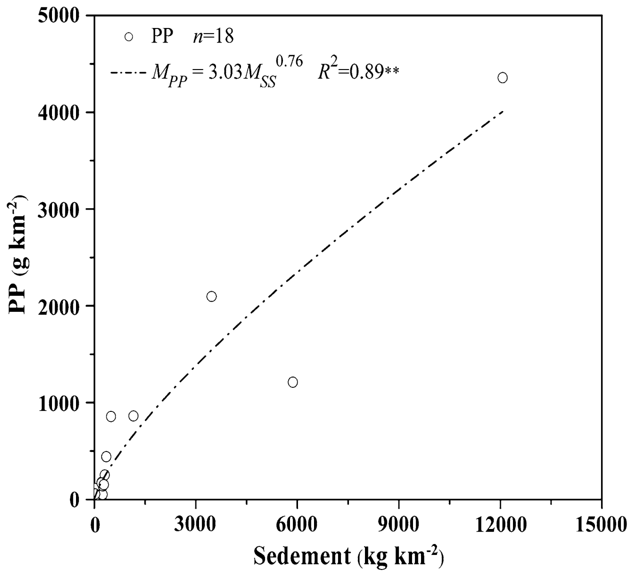

Fig. 5 Measured particulate phosphorus loss (M_{PP}) as a function of sediment loss (M_{SS}). $^{**}p < 0.01$

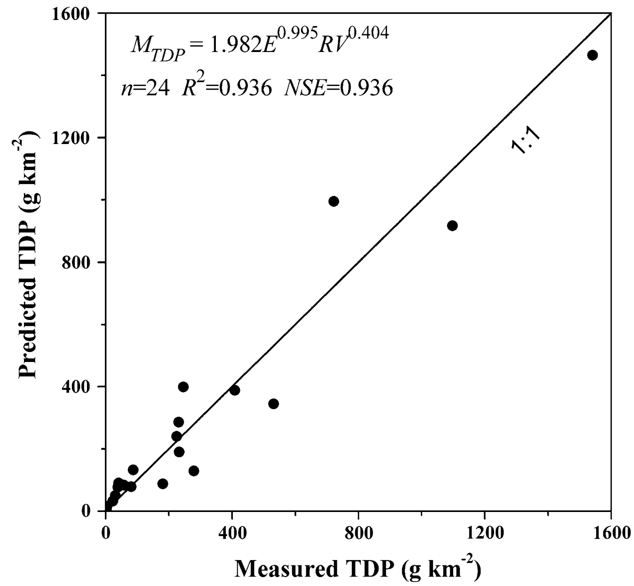

Fig. 7 Measured vs. predicted [using Eq. (9)] total dissolved phosphorus loss (M_{TDP}). *E* rainfall kinetic energy, *RV* runoff volume

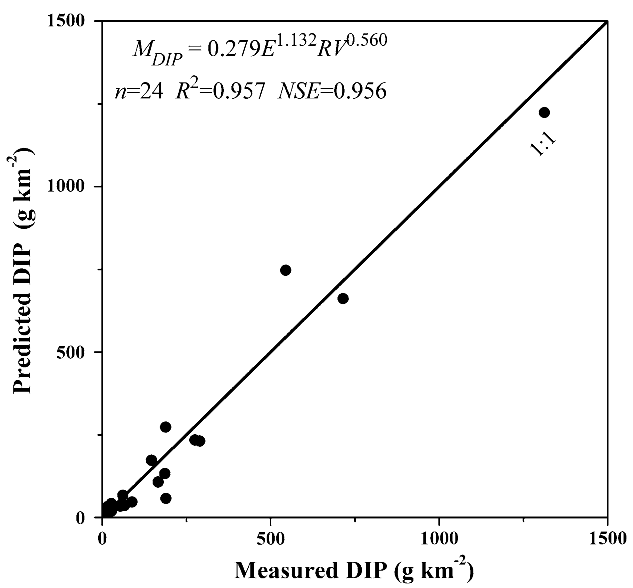

Fig. 6 Measured vs. predicted [using Eq. (8)] dissolved inorganic phosphorus loss (M_{DIP}). *E* rainfall kinetic energy, *RV* runoff volume

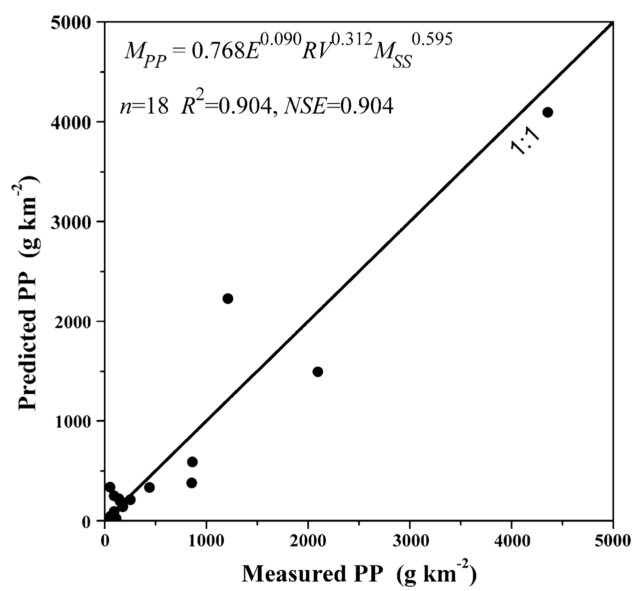

Fig. 8 Measured vs. predicted [using Eq. (10)] particulate phosphorus loss (M_{PP}). *E* rainfall kinetic energy, *RV* runoff volume, M_{SS} sediment loss

et al. (2007), who showed that total dissolved phosphorus loss was related to runoff volume significantly.

Compared to DIP and TDP, PP and TP losses were poorer, estimated by runoff volume with a coefficient of determination of 0.29 and 0.38 (Fig. 4b). In small watershed, runoff volume of rainfall event was usually closely related to eroded sediment, which was the carrier of PP. But it is difficult to express PP loss as a simple function of discharge, since factors except runoff, such as antecedent sediment depletion and replenishment, probably affect the processes of phosphorus transport and supply (Nisror and Church 2005). As a result, it may lead to the particulate phosphorus loss varying by several orders of magnitude at a given runoff volume. Thus, a loose relationship between runoff volume and PP loss was exhibited (Fig. 4b). The same result was also reported by Prairie and Kalff (1988).

In our study, some events had a large runoff volume with small phosphorus loss as in the three rainfall events marked with red ellipse in Fig. 4a and b. If these three events are separated from the others, the regressions show excellent relationships between PP, TP loss, and runoff volume (Fig. 4c, d).

Effects of sediment on phosphorus loss

In general, the runoff containing more sediment did not cause higher TDP loss, since the DIP and TDP were dissolved material (Yang et al. 2009). In addition, the TP includes TDP, so only the effects of sediment on PP losses were analyzed in this study. Analysis results indicated that sediment loss influenced PP loss significantly. PP loss increased with increasing sediment loss as a power function with a coefficient of determination of 0.89 (Fig. 5). Phosphorus was relatively insoluble and strongly absorbed by soil minerals and organic matter. Thus, particulate phosphorus loss certainly increased, associated with sediment loss of rainfall events. This result corroborated the conclusion of Ramos and Martinez-Casasnovas (2006).

Estimating phosphorus loss

As discussed above, DIP and TDP were affected by rainfall kinetic energy and runoff volume significantly. Thus, these two variables were selected as predictors to predict DIP and TDP loss in this study. Nonlinear regression indicated the best-fit relationships between DIP, TDP loss and rainfall kinetic energy, and runoff volume as shown in Figs. 6 and 7:

$$M_{\mathrm{DIP}} = 3.901E^{1.132}RV^{0.560},\ n = 24, R^2 = 0.957,\ NSE = 0.956 \tag{8}$$

$$M_{\mathrm{TDP}} = 19.613E^{0.995}RV^{0.404},\ n = 24, R^2 = 0.936,\ NSE = 0.936 \tag{9}$$

where M_{DIP} (g km^{-2}) and M_{TDP} (g km^{-2}) are the masses of the DIP and TDP loss, respectively. The predicted dissolved inorganic phosphorus and total dissolved phosphorus matched the observed values satisfactorily and the points were close to the 1:1 line. This result indicated that both Eqs. (8) and (9) could be used to predict DIP and TDP losses at an event scale.

Multivariate, nonlinear regression analyses between PP loss and rainfall kinetic energy, runoff volume, and sediment loss was produced (Fig. 8):

$$M_{\mathrm{PP}} = 0.944E^{0.090}RV^{0.312}M_{\mathrm{SS}}^{0.595},\ n = 18,\ R^2 = 0.904, NSE = 0.904 \tag{10}$$

where M_{PP} is the mass of the PP loss (g km^{-2}) and M_{SS} is the mass of the sediment loss (kg). As shown in Fig. 8, Eq. (10) predicted particulate phosphorus very well with *NSE* of 0.904. However, the performance of Eq. (10) was a little worse than Eqs. (8) and (9).

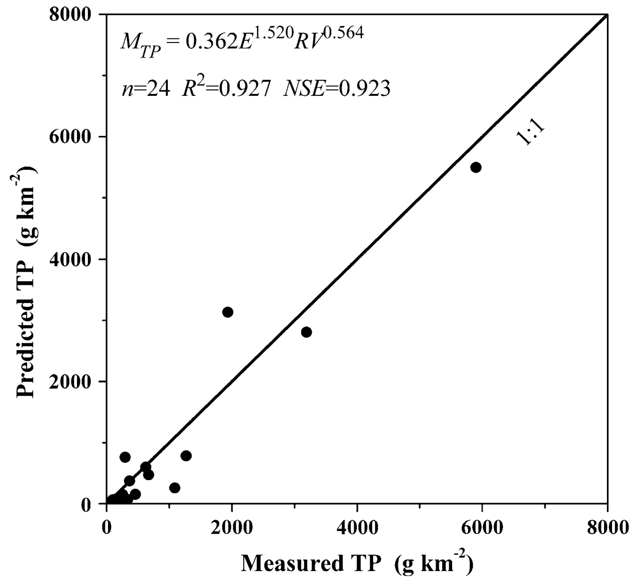

Fig. 9 Measured vs. predicted [using Eq. (11)] total phosphorus loss (M_{TP}). *E* rainfall kinetic energy, *RV* runoff volume

For the total phosphorus loss of rainfall event, it could be predicted satisfactorily by rainfall kinetic energy and runoff volume using a power function (Fig. 9):

$$M_{\mathrm{TP}} = 11.988E^{1.520}RV^{0.564},\ n = 24, R^2 = 0.927,\ NSE = 0.923 \tag{11}$$

where M_{TP} is the mass of the TP loss (g km^{-2}). The *NSE* of Eq. (11) was 0.923 and the points evenly distributed on both sides of 1:1 line (Fig. 9), which implied that Eq. (11) could be used in the study region to predict total phosphorus for a rainfall event. The agricultural watershed, characterized by loose soil layer with a great proportion of rock fragments, is widely distributed in Yimeng Mountain and Northern Plain of China; therefore the developed equations could be used in those regions. However, both runoff and sediment were strongly affected by catchment characteristics and land use. Thus, these models cannot be directly used for other watersheds with different topography and land use without calibration.

Conclusion

This study was conducted to identify the characteristics of phosphorus loss and further to develop regression models to predict phosphorus losses of different forms based on the measured rainfall, runoff, and sediment of 24 rainfall events in a typical small watershed from the Yimeng Mountainous Area, China. The results showed that phosphorus loss varied greatly with phosphorus forms. The dissolved inorganic phosphorus was the dominant form of total dissolved phosphorus loss by runoff (72 %). More than 65 % of phosphorus was lost in the particulate form, associated with the eroded sediment. The phosphorus loss varied considerably from event to event and most of the phosphorus loss was produced by only a few heavy storms. The dynamics of different forms of phosphorus loss during a rainfall event were similar and the concentration reached the maximum prior to the runoff peak. Phosphorus loss was affected by rainfall kinetic energy, runoff volume, and sediment loss significantly. Dissolved inorganic phosphorus, total dissolved phosphorus, and total phosphorus could be predicted with rainfall kinetic energy and runoff volume satisfactorily ($NSE \geq 0.92$). Particulate phosphorus was estimated well with rainfall kinetic energy, runoff volume, and sediment loss of the rainfall event ($NSE = 0.90$).

Acknowledgments Financial assistance for this work was provided by the Hundred Talents Project of the Chinese Academy of Sciences and the National natural Foundation (41271287).

References

Ahuja LR (1990) Modeling soluble chemical transfer to runoff with rainfall impact as a diffusion process. Soil Sci Soc Am J 54(2):312–321

Ahuja LR, Sharpley AN, Lehman OR (1982) Effect of soil slope and rainfall characteristics on phosphorus in runoff. J Environ Qual 11(1):9–13

Beránková T, Vogel RM, Fiala D, Rosendorf P (2010) Estimation of phosphorus loads with sparse data for agricultural watersheds in the Czech Republic. Hydrol Sci J 55(8):1417–1426

Bowes MJ, Smith JT, Jarvie HP, Neal C (2008) Modeling of phosphorus inputs to rivers from diffuse and point sources. Sci Total Environ 395(2–3):125–138

Brezonik PL, Stadelmann TH (2002) Analysis and predictive models of stormwater runoff volumes, loads, and pollutant concentrations from watersheds in the Twin Cities metropolitan area, Minnesota, USA. Water Res 36(7):1743–1757

Chun JA, Cooke RA, Kang MS, Choi M, Timlin D, Park SW (2010) Runoff losses of suspended sediment, nitrogen, and phosphorus from a small watershed in Korea. J Environ Qual 39(3):981–990

Correll DL (1998) The role of phosphorus in the eutrophication of receiving waters: a review. J Environ Qual 27(2):261–266

Dougherty WJ (2002) The mobilization of soil phosphorus in surface runoff from intensively managed pastures in south-east Australia. PhD Thesis, University of Adelaide, pp 88–98

Edwards DR, Daniel TC (1993) Effects of poultry litter application rate and rainfall intensity on quality of runoff from fescue grass plots. J Environ Qual 22:361–365

Ellison ME, Brett MT (2006) Particulate phosphorus bioavailability as a function of stream flow and land cover. Water Res 40(6):1258–1268

Fleming NK, Cox JW (2001) Carbon and phosphorus losses from dairy pasture in South Australia. Soil Res 39(5):969–978

Girmay G, Singh BR, Nyssen J, Borrosen T (2009) Runoff and sediment-associated nutrient losses under different land uses in Tigray, Northern Ethiopia. J Hydrol 376(1–2):70–80

Han JG, Li ZB, Li P, Tian JL (2010) Nitrogen and phosphorous concentrations in runoff from a purple soil in an agricultural watershed. Agric Water Manag 97(5):757–762

Hansen NC, Gupta SC, Moncrief JF (2000) Snowmelt runoff, sediment, and phosphorus losses under three different tillage systems. Soil Tillage Res 57(1–2):93–100

Ide J, Nagafuchi O, Chiwa M, Kume A, Otsuki K, Ogawa S (2007) Effects of discharge level on the load of dissolved and particulate components of stream nitrogen and phosphorus from a small afforested watershed of Japanese cypress. J For Res 12(1):45–56

Ide J, Haga H, Chiwa M, Otsuki K (2008) Effects of antecedent rain history on particulate phosphorus loss from a small forested watershed of Japanese cypress. J Hydrol 352(3–4):322–335

Jalali M, Ranjbar F (2011) Effect of addition of organic residues on phosphorus release kinetics in some calcareous soils of western Iran. Environ Earth Sci 62:1143–1150

Kim JS, Oh SY, Oh KY (2006) Nutrient runoff from a Korean rice paddy watershed during multiple storm events in the growing season. J Hydrol 327(1–2):128–139

Kleinman PJ, Sharpley AN (2003) Effect of broadcast manure on runoff phosphorus concentrations over successive rainfall events. J Environ Qual 32(3):1072–1081

Lee JH, Bang W (2000) Characterization of urban stormwater runoff. Water Res 34(6):1773–1780

Li ZW, Yu XX, Liu QJ, Jing GH (2012) Output characteristics of non-point phosphorus from a typical small watershed in Yimeng Mountainous Area under the special rainfall (in Chinese with English abstract.). Environ Sci 33(4):1152–1158

Ma Q, Yu XX, Lü GA, Liu QJ (2012) The changing relationship between spatial pattern of soil erosion risk and its influencing factors in Yimeng mountainous area, China 1986–2005. Environ Earth Sci 66(5):1535–1546

Murphy J (1962) A modified single solution method for the determination of phosphorus in natural waters. Anal Chim Acta 27:31–36

Nash DM, Halliwell D, Cox J (2002) Hydrological mobilisation of pollutants at the slope/field scale. In: Haygarth PM, Jarvis SC (eds) Agriculture, hydrology and water quality. CABI Publishing, UK, pp 225–242

Neal C, Jarvie HP (2005) Agriculture, community, river eutrophication and the water framework directive. Hydrol Process 19(9):1895–1901

Nisror CJ, Church M (2005) Suspended sediment transport regime in a debris-flow gully on Vancouver Island, British Columbia. Hydrol Process 19:861–885

Pathak P, Wani SP, Singh P, Sudi R (2004) Sediment flow behavior from small agricultural watersheds. Agric Water Manag 67:105–117

Pimentel D, Harvey C, Resosudarmo P, Sinclair K, Kurz D, McNair M, Crist S, Shpritz L, Fitton L, Saffouri R, Blair R (1995) Environmental and economic costs of soil erosion and conservation benefits. Science 267:1117–1123

Pionke HB, Gburek WJ, Schnabel RR, Sharpley AN, Elwinger GF (1999) Seasonal flow, nutrient concentrations and loading patterns in stream flow draining an agricultural hill-land watershed. J Hydrol 220(1–2):62–73

Prairie YT, Kalff J (1988) Particulate phosphorus dynamics in headwater streams. Can J Fish Aquat Sci 45(2):210–215

Quinton JN, Govers G, Van Oost K, Bardgett RD (2010) The impact of agricultural soil erosion on biogeochemical cycling. Nat Geosci 3:311–314

Ramos MC, Martinez-Casasnovas JA (2004) Nutrient losses from a vineyard soil in Northeastern Spain caused by an extraordinary rainfall event. Catena 55(1):79–90

Ramos MC, Martinez-Casasnovas JA (2006) Nutrient losses by runoff in vineyards of the Mediterranean Alt Penedès region (NE Spain). Agric Ecosyst Environ 113(1–4):356–363

Shigaki F, Sharpley AN, Prochnow LI (2007) Rainfall intensity and phosphorus source effects on phosphorus transport in surface runoff from soil trays. Sci Total Environ 373(1):334–343

Udawatta RP, Motavalli PP, Garrett HE (2004) Phosphorus loss and runoff characteristics in three adjacent agricultural watersheds with claypan soils. J Environ Qual 33(5):1709–1719

Vanni MJ, Renwick WH, Headworth JL, Auch JD, Schaus MH (2001) Dissolved and particulate nutrient flux from three adjacent agricultural watersheds: a five-year study. Biogeochemistry 54(1):85–114

Wang WL, Liang T, Wang LQ, Liu YF, Wang YZ, Zhang CS (2013) The effects of fertilizer applications on runoff loss of phosphorus. Environ Earth Sci 68:1313–1319

Withers PJA, Jarvie HP, Hodgkinson RA, Palmer-Felgate EJ, Bates A, Neal M, Howells R, Withers CM, Wickham HD (2009) Characterization of phosphorus sources in rural watersheds. J Environ Qual 38(5):1998–2011

Worrall F, Burt TP (1999) The impact of land-use change on water quality at the catchment scale: the use of export coefficient and structural models. J Hydrol 221(1–2):75–90

Wu XY, Zhang LP, Yu XX (2012) Impacts of surface runoff and sediment on nitrogen and phosphorus loss in red soil region of southern China. Environ Earth Sci 67:1939–1949

Yang JL, Zhang GL, Shi XZ, Wang HJ, Cao ZH, Ritsema CJ (2009) Dynamic changes of nitrogen and phosphorus losses in ephemeral runoff processes by typical storm events in Sichuan Basin, Southwest China. Soil Tillage Res 105(2):292–299

Yu XX, Qi SZ, Xu YT (2012) Soil erosion hazard in the Yimeng mountainous region, North China. Nat Hazards 64:1963–1967

Zhang T (2011) Distance-decay patterns of nutrient loading at watershed scale: regression modeling with a special spatial aggregation strategy. J Hydrol 402(3–4):239–249

Zhang XC, Norton LD, Nearing MA (1997a) Chemical transfer from soil solution to surface runoff. Water Resour Res 33(4):809–815

Zhang XC, Norton LD, Hickman M (1997b) Rain pattern and soil moisture content effects on atrazine and metolachlor losses in runoff. J Environ Qual 26(6):1539–1547

Zhang XC, Norton LD, Lei T, Nearing MA (1999) Coupling mixing zone concept with convection–diffusion equation to predict chemical transfer to surface runoff. Trans ASAE 42(4):987–994

Zhang GH, Liu BY, Liu GB, He XW, Nearing MA (2003) Detachment of undisturbed soil by shallow flow. Soil Sci Soc Am J 67(3):713–719

Zhang Z, Fukushima T, Onda Y, Mizugaki S, Gomi T, Kosugi K, Hiramatsu S, Kitahara H, Kuraji K, Terajima T, Matsushige K, Tao F (2008) Characterization of diffuse pollutions from forested watersheds in Japan during storm events—its association with rainfall and watershed features. Sci Total Environ 390(1):215–226

Zhang GH, Liu YM, Han YF, Zhang XC (2009) Sediment transport and soil detachment on steep slopes: I. Transport capacity estimation. Soil Sci Soc Am J 73(4):1291–1297