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Phosphorus and carbon competitive sorption–desorption and associated non-point loss respond to natural rainfall events

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SUMMARY

Long-term application of fertilizer or manure can increase the potential for P loss risk to ground and surface waters due to C and P competitive sorption–desorption. The aim of this study was to investigate the effect of long-term agricultural fertilizer application on dissolved organic carbon (DOC) and dissolved total phosphorus (DTP) loss. The study was conducted at the Yanting Agro-Ecological Experimental Station in Sichuan Province, People's Republic of China, during the 2012 rainy season. The results show that the variations in C and P leaching effects in fertilized soils exposed to natural rainfall events. As expected, application of inorganic and organic fertilizers increases DOC and DTP concentrations in soil and decreases the C:P ratio. Similarly, application of inorganic and organic fertilizers results in greater C and P leaching than that seen in unfertilized soils. The DOC flux was higher in subsurface runoff than in overland flow. In contrast, overland flow was the main pathway for P transport; subsurface runoff accounted for a smaller proportion of the total P transport. The increase of DOC and DTP was higher after use of organic manures than after treatment with inorganic fertilizers. DOC derived from surface-applied organic manures was found to leach at higher rates than that seen for DTP derived from the same source. However, organic manure-derived DOC was found to transport from soil prior to P, when they are surface-applied, demonstrating a higher sorption affinity of P over DOC compared to inorganic fertilization. Therefore, we should pay more attention to the P mobilized through long-term fertilization and enhance the P uptake due to C and P competitive sorption–desorption, and avoid potential leaching loss of P during rainfall process.

1. Introduction

Accumulation of phosphorus (P) in agricultural soils and subsequent P loss by runoff has been long been linked to accelerated eutrophication of local bodies of water (Sharpley et al., 2003; Gao et al., 2009, 2010, and 2012). It is also well-established that application of fertilizer or manure can greatly increase the potential for P loss to surface and ground waters. Sharpley et al. (2003) reported that, after six applications of manure and compost, leachable P reached levels of approximately 100 Mg ha^{-1} under simulated rainfall. Many other reports also have shown that P leaching is correlated with heavy application of manures, as well as with rapid water flow over soils and low P adsorption capacity (Sims et al., 1998; Nelson et al., 2005). The water-extractable P in manure-amended soils transport by runoff during rainfall events would improve P mobilization, and then accelerate water eutrophication (Gao et al., 2013a,b, 2014; Kang et al., 2011).

Water-extractable P is generated when rainwater interacts with a thin layer of surface soil before becoming runoff (Sharpley, 1985). The mobilization and transport of different forms of P found in soil are due primarily to the physicochemical processes of sorption–desorption and precipitation-dissolution (Gao et al., 2009; Kang et al., 2011; Bunemann et al., 2012). Researchers have studied several such processes in detail, focusing on one or another of the many processes that are doubtless happening simultaneously. The decrease on P adsorption in manured soils has been explained as due to competition between organic anions and P for adsorption sites (Iyamuremye et al., 1996; Bhatti et al., 1998) or as due to increased negative charge on soil surface, which can inhibit P adsorption (Jiao et al., 2007). Many researches have pointed to microbial action. According to Easterwood and Sartain (1990), soil

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organic carbon (SOC) can react directly with P sorption sites in soil through microbial action, thus increasing the concentration of dissolved P and the potential leaching effect. Long-term application of fertilizer has been demonstrated to increase SOC accumulation and soil microbial biomass in the agro-ecosystem (Rudrappa et al., 2006; Zhao et al., 2008; Liang et al., 2011), which would affect P sorption and leaching.

Guppy et al. (2005) argue that the ability of DOC to successfully compete with P for soil sorption is mainly determined by the persistence of low-molecular-weight organic acids (LOA) in soil. They assert that DOC would lead to competitive inhibition of P sorption due to the breakdown of organic matter. Kang et al. (2011) also argue that the DOC in manures can decrease P adsorption, thereby enhancing P mobility in the manured soils. According to Staunton and Leprince (1996), P and DOC interaction by means of competitive inhibition is the primary mechanism for releasing P in soil. Schiffman et al. (2001) and Moral et al. (2005) explain that the DOC in manures is a complicated mixture of organic compounds: humic and fulvic acids, amines, polysaccharides, and numerous other C compounds. Although the interactions between P and some organic compounds, such as the humic and fulvic acids in manure, demonstrably reduce P sorption, it is also important to examine the interaction of P with all the DOC compounds created by the application of manure. This can be a complex task, as DOC is not a simple organic acid. The organic matters (OM) in soils which can rapidly sorb applied P improve P bio-availability to plants. Therefore, the effect of OM on P has commonly been contributed to the competition between the decomposition products of OM and P for soil sorption sites leading to increased soil solution P concentrations (Guppy et al., 2005). The evidence has shown that the competitive inhibition of P sorption by DOC compounds is mainly derived from the breakdown of OM, including LOA, humic and fulvic acids, amines, polysaccharides, and numerous other C compounds. They all have a high P sorption capacity.

In the purple soil area of the southwestern People's Republic of China, widespread, serious soil erosion lead to large amounts of nutrients to be washed out and transported with sediment into the fluvial system (Gao et al., 2013a, 2014). This leads to damaging eutrophication for the Three Gorges in China. The P playing an important role in the water eutrophication is of international concern, wherein P losses in particular can negatively affect the water quality, which may put drinking water quality at risk (Gao et al., 2009; Miao et al., 2010, 2011). Therefore, understanding the mechanisms of P sorption and leaching is of immense practical importance to the local water environment quality. In the present study, researchers focused on the long-term effects of fertilizer application on C and P concentrations in soils typical of the purple soil area, as evidenced by measured C and P leaching during natural rainfall events. The specific objectives of the study were: to compare the effect of long-term application of organic and inorganic fertilizers on soil DOC and dissolved total P (DTP) and associated loss by overland flow and subsurface runoff during natural rainfall events; to better understand changes in the stoichiometric C:P ratios in soil and runoff by focusing on competitive sorption mechanisms.

2. Materials and methods

2.1. Study area

This study was conducted at the Yanting Agro-Ecological Experimental Station, which operates under the aegis of the Chinese Academy of Sciences. The station is located in the middle of the Sichuan Basin (105° 27′E, 31° 16′N) (Fig. 1a). The climate of this region is characterized by seasonal subtropical moisture, with an average annual rainfall of 826 mm and a peak rainfall season in the summer (average calculated from meteorological records maintained from 1981 to 2006).

Sichuan Basin soil is rich in minerals, easily cultivable, and highly fertile and productive. It is regarded as one of the more valuable agricultural soil resources in the PRC (Zhu et al., 2008). The soil at the experimental site is locally referred to as purple soil. It is classified as a Pup-Orthic Entisol in the Chinese Soil Taxonomy and Eutric Regosol in the FAO Soil Classification (Gong, 1999). Measured soil parameters were as follows: pH 8.1 ± 0.2; bulk density 1.3 ± 0.03 g cm^{-3}; capillary porosity 38.53 ± 1.10%; non-capillary porosity 11.11 ± 2.00%; total P 0.81 ± 0.3 g kg^{-1}; available P 44.72 ± 5.91 mg kg^{-1}; organic matter 7.8 ± 0.7 g kg^{-1}; and available N 103 ± 4.44 mg kg^{-1}.

2.2. Experimental design

The experiments were carried out in specially-designed runoff plots (8 m long × 4 m wide × 0.6 m deep) built in 2001. The slope gradient of the plots was 7° (the farmland gradient of the purple soil area in China is normally 3–10°). The plots are hydrologically isolated by partition walls filled with cement and inserted at least 60 cm into the bedrock to avoid unexpected seepage to the individual plot. All the plots were filled with the same local purple soil in 2001. Catchment grooves were built to collect overland flow and subsurface runoff (Fig. 1b and c). Plots are cultivated in a wheat-maize rotation: maize (*Zeamays* L.) is grown from May to September, and wheat (*Triticum aestivum* L.) is grown from October to May of the next calendar year, completing a one-year cycle, which follows local agricultural practices (Fig. 1b and c). The experimental plots were fertilized according to the following treatments: (1) no added fertilizers (CK), (2) 90 kg P_2O_5. hm^{-2} added (IGP1), (3) 90 kg P_2O_5. hm^{-2}, N 150 kg/hm^2 and K_2O 36 kg/hm^2 added (IGP2), (4) 25,000 kg of composted pig manure/hm^2 added (OM) and (5) 7500 kg of chopped wheat straw/hm^2 added (RSD). There were triplicates of each treatment plot. and all the results from each group of three plots were averaged.

Pig manure was collected from the same sty each year and composted for at least two months before being evenly spread onto the soil surface by hand. After application, the pig manure was immediately incorporated into the surface soil (0–20 cm) by plowing. This was done before sowing. Wheat straw, harvested during the winter wheat season, was returned to the same plot prior to planting maize. It was roughly chopped and mixed into the surface soil.

Rainfall events were defined as follows: the rainfall event began when rain started to fall and was deemed to have ended when it was followed by a 24 h period without rain. If the rain stopped for less than 24 h before starting to fall again, the interval was considered to be included in the rainfall event. Hence there were some rainfall events that spanned two or more days; the rain had started and stopped, started and stopped, several times during that period, but none of the dry intervals had lasted 24 h.

2.3. Sampling and analysis

Because soil P is found mostly in the surface layer, soil was sampled at only three depths: 0–10 cm, 10–20 cm and 20–40 cm. Each soil sample was collected by taking soil from a 1 m-radius circle at the specified level until a net weight of 1 kg of wet soil had been collected. The soil samples were stored in a refrigerator until they could be processed for chemical analysis, which was done within the two-month period of the study. The soil samples were completed before maize was planted in May of 2012. The annual fertilizer applications were also completed before the rainfall-related measurements for this study were begun in May of 2012. No recent fertilizer applications affected the measurements taken.

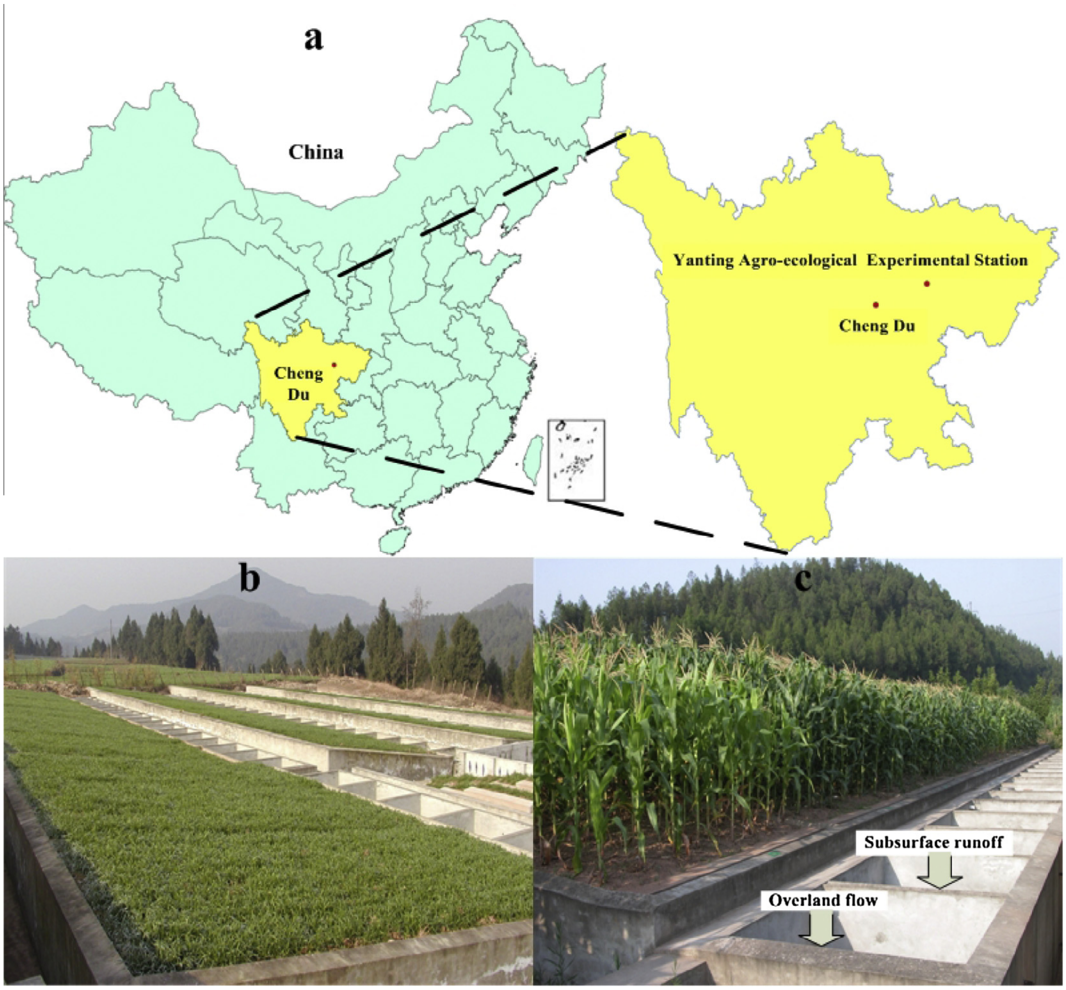

Fig. 1. Yanting Agro-Ecological Experimental Station location (a), plots planted in wheat (b), catchments for overland flow and subsurface runoff (c).

Water samples were collected immediately after each rainfall event stop during the May–September rainy season of 2012. Water catchment levels were measured to calculate the overland flow and subsurface runoff discharge flux. Water samples were analyzed and the average C and P concentrations were used to calculate the C and P load for each rainfall. Sample analysis was conducted as follows: (1) The water samples were stored in a refrigerator at a low temperature (4 °C). Sediment was allowed to settle. The sediment was filtered from the water, dried to a constant weight in an air-forced oven at 105 °C, and weighed and (2) Researchers looked for molybdate reactive P (PO_4–P), DOC, and TDP. Soil DOC was determined using the $K_2Cr_2O_7$ volumetric dilution heating method (Nelson and Sommers, 1982); soil DTP was determined using $H_2SO_4 + HClO_4$ digestion (Olsen and Sommers, 1982). The filtrates of suspended sediment and water mixed sample were analyzed by Auto Analyzer 3 (SEAL, Germany).

2.4. Data analysis

Samples were collected and analyzed from all three plots in each category. After analysis, the results were averaged for each category. The C, P, and sediment loads in the overland flow and subsurface runoff for each rainfall event were calculated by Eq. (1):

$$Q = C \times V \tag{1}$$

where Q is C, P, and sediment loads for each rainfall event (mg); C is concentration of C, P, and sediment in total runoff samples (mg L^{-1}); and V is the water discharge collected in the catchment basins after each rainfall event (L). C, P, and sediment-loss flux were calculated by Eq. (2):

$$F = Q/A \tag{2}$$

where F is C, P, and sediment-loss flux (mg m^{-2}) and A is plot area (m^2).

The C and P stoichiometry for both soil and water was calculated as a molar ratio.

3. Results

3.1. Changes in soil DOC and DTP due to long-term fertilizer use

After twelve years of treatment with inorganic and organic fertilizers, there were significant changes in the concentrations of DOC and DTP at different soil levels (Fig. 2). As Fig. 2a shows, long-term application of organic fertilizers has significantly enhanced soil DTP content, as shown by a comparison of 2012 measurements from the pig-manure-treated (OM) and straw-treated (RSD) plots to those from the unfertilized control plot (DK). Application of inorganic fertilizers can also increase DTP concentration. However, the increased DTP content is concentrated on surface soil layer. There is little difference between the DTP levels in the deepest soil layer in the control plot and those seen in the same layer in the plots treated with inorganic fertilizers. There have been greater increases in DTP content after treatment with

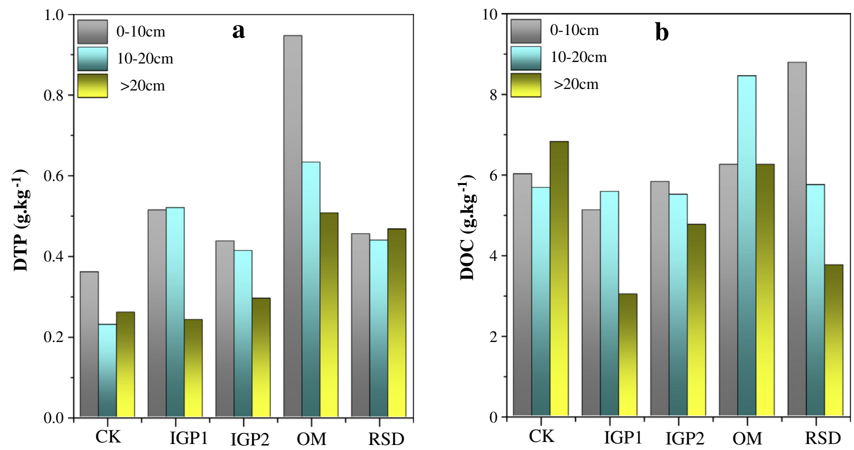

Fig. 2. DTP (a) and DOC (b) concentrations at 0–10 cm, 10–20 cm and 20–40 cm soil depths, following long-term application of inorganic and organic fertilizers. *Note:* CK stands for the control plots which received no fertilizer treatments; IGP1 plots received treatment with inorganic P fertilizers; IGP2 received treatment with inorganic NPK; OM received treatment with composted pig manure; RSD received treatment with chopped straw.

composted pig manure (OM) than after treatment with chopped straw (RSD). Organic fertilizers were also highly effective at increasing DOC concentrations in surface soils, much more so than inorganic fertilizers (Fig. 2b).

3.2. C and P transport during rainfall events

Researchers took overland flow and subsurface runoff catchment samples following six rainstorm events during the 2012 rainy season: (1) May 11th, with 22.0 mm of rainfall, (2) June 30th through July 4th, with 79.4 mm of rainfall, (3) July 6th through 9th, with 112.2 mm of rainfall, (4) July 22nd through 23rd, with 43.8 mm of rainfall, (5) August 21st, with 59.4 mm of rainfall and (6) September 11th, with 160.8 mm of rainfall.

3.3. Change of DOC concentration in overland flow and subsurface runoff.

As Fig. 3 shows, the DOC concentration was lower in overland flow (Fig. 3a) than in subsurface runoff (Fig. 3b). In general, the DOC concentration does not seem to increase as rainfall increases. Indeed, the low-rainfall event of May 11th actually resulted in flow and runoff with a higher DOC concentration than that seen in the high-rainfall events, which may be related with "first flush" effect following dry condition as rainy season coming. It is apparent that the application of either inorganic or organic fertilizer significantly increases the DOC concentration in both overland flow and subsurface runoff (Fig. 3a and b). There was no significant difference between the DOC concentrations from plots that had received inorganic fertilizer and those that had been given organic fertilizer. Measurements of DOC concentration in subsurface runoff were similar to those for overland flow.

3.4. DOC load (total quantity)

As Fig. 4 shows, the DOC load in overland flow and runoff increases as rainfall increases. Application of either inorganic or organic fertilizer increases the DOC load in both overland flow and subsurface runoff. In general, DOC load is higher in subsurface runoff than in overland flow. However, differences between plots treated with organic fertilizers and those treated with inorganic fertilizers emerge when the DOC load measurements are compared. Subsurface runoff from the organic-treated plots contained a higher DOC load than runoff from inorganic-treated

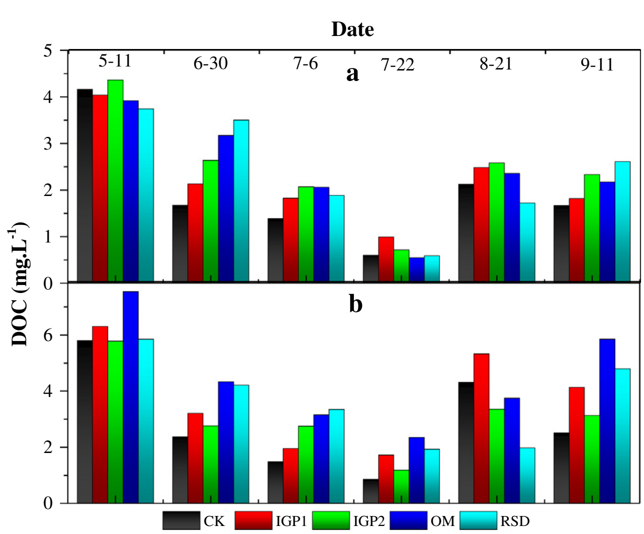

Fig. 3. DOC transport by overland flow (a) and subsurface runoff (b) following six rainfall events in 2012. *Note:* CK stands for the control plots which received no fertilizer treatments; IGP1 plots received treatment with inorganic P fertilizers; IGP2 received treatment with inorganic NPK; OM received treatment with composted pig manure; RSD received treatment with chopped straw.

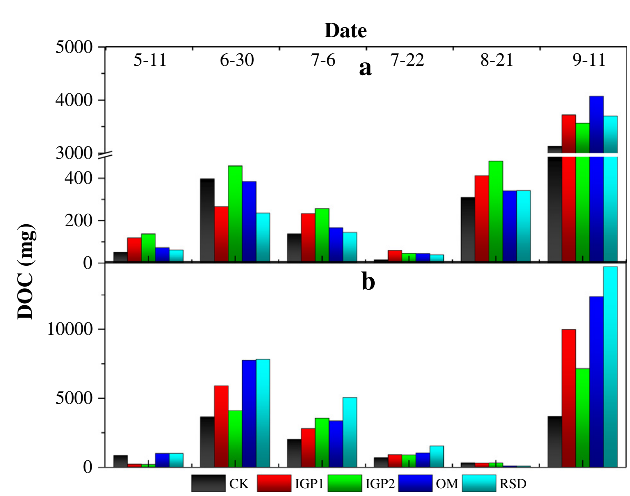

Fig. 4. DOC loads in overland flow (a) and subsurface runoff (b) following six rainfall events in 2012. *Note:* CK stands for the control plots which received no fertilizer treatments; IGP1 plots received treatment with inorganic P fertilizers; IGP2 received treatment with inorganic NPK; OM received treatment with composted pig manure; RSD received treatment with chopped straw.

plots. The DOC load in overland flow from organic-treated plots was lower than the DOC load in flow from inorganic-treated plots.

3.5. Change of TP concentration in overland flow and subsurface runoff.

As Fig. 5 shows, TP concentration was significantly higher in overland flow than in subsurface runoff. The main form of P seen in overland flow was particulate P (PP). Dissolved P (DP) formed a larger proportion of TP transport in subsurface runoff (however, under high rainfall, PP was also seen in subsurface runoff). TP concentration in overland flow and subsurface runoff was lower under high rainfall than it was under low rainfall. Application of organic fertilizers appeared to decrease TP concentration in overland flow. TP concentration in subsurface runoff from plots treated with inorganic fertilizers was higher than that seen from the unfertilized control plots.

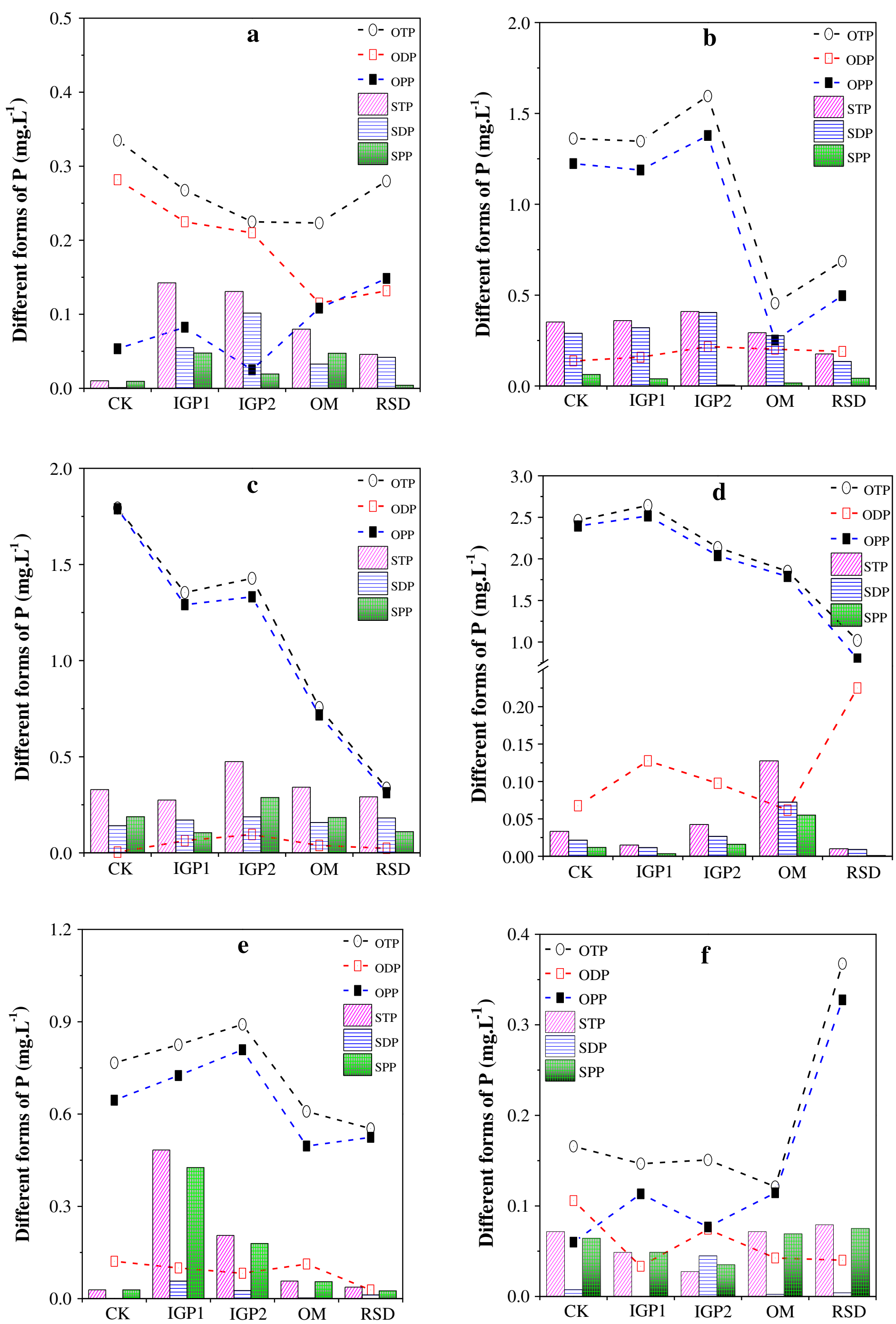

Fig. 5. P concentration transport by overland flow and subsurface runoff following six rainfall events in 2012. *Rainfall events:* (a) May 11th, with 22.0 mm of rainfall; (b) June 30th through July 4th, with 79.4 mm of rainfall; (c) July 6th through 9th, with 112.2 mm of rainfall; (d) July 22nd through 23rd, with 43.8 mm of rainfall; (e) August 21st, with 59.4 mm of rainfall; (f) September 11th, with 160.8 mm of rainfall. Note: The first letter O in legends is overland flow and S is subsurface runoff. CK stands for the control plots which received no fertilizer treatments; IGP1 plots received treatment with inorganic P fertilizers; IGP2 received treatment with inorganic NPK; OM received treatment with composted pig manure; RSD received treatment with chopped straw.

3.6. TP load (total quantity)

However, TP concentration was higher in overland flow than in subsurface runoff, the TP load, shown in Fig. 6, did not follow the same pattern. After rainfall events, TP transport would be higher in subsurface runoff than in overland flow, while overland flow having either similar or higher TP loads than subsurface flow was observed in Fig. 6a and d. PP was the main component of the TP load in subsurface runoff. The amount of rainfall appeared to determine which forms of P would predominate in overland flow, but the same pattern was not seen in P transport by subsurface runoff. Application of NPK fertilizers increased TP load in both overland flow and subsurface runoff compared to the TP load from the unfertilized control plots. However, DP and PP did not vary in the same manner. Compared to the control plots and the inorganic-treated plots, the organic-treated plots showed decreased TP trans-

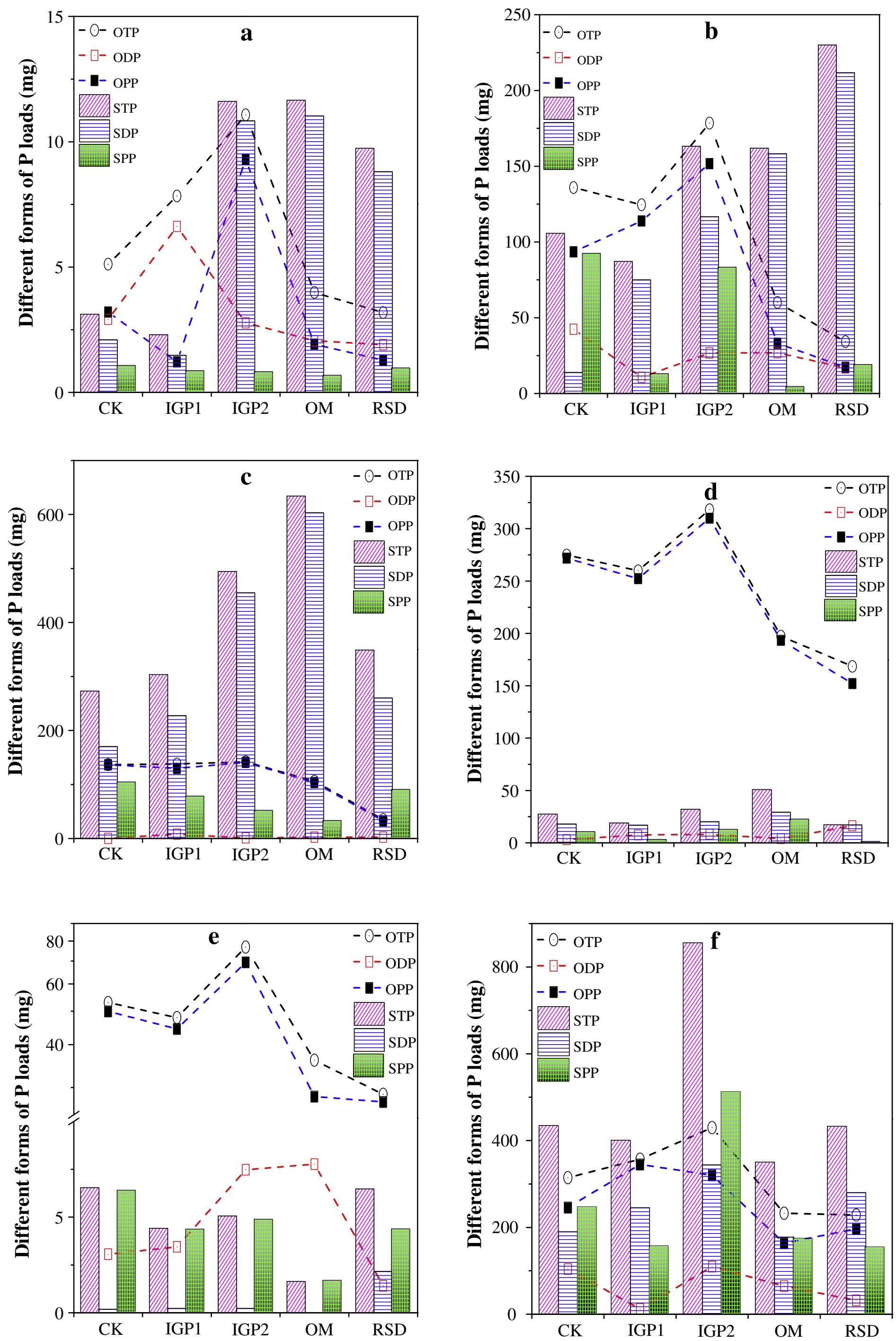

Fig. 6. P loads in overland flow and subsurface runoff following six rainfall events in 2012. *Rainfall events:* (a) May 11th, with 22.0 mm of rainfall; (b) June 30th through July 4th, with 79.4 mm of rainfall; (c) July 6th through 9th, with 112.2 mm of rainfall; (d) July 22nd through 23rd, with 43.8 mm of rainfall; (e) August 21st, with 59.4 mm of rainfall; (f) September 11th, with 160.8 mm of rainfall. *Note:* The first letter O in legends is overland flow and S is subsurface runoff. CK stands for the control plot which received no fertilizer treatments; IGP1 received treatment with inorganic P fertilizers; IGP2 received treatment with inorganic NPK; OM received treatment with composted pig manure; RSD received treatment with chopped straw.

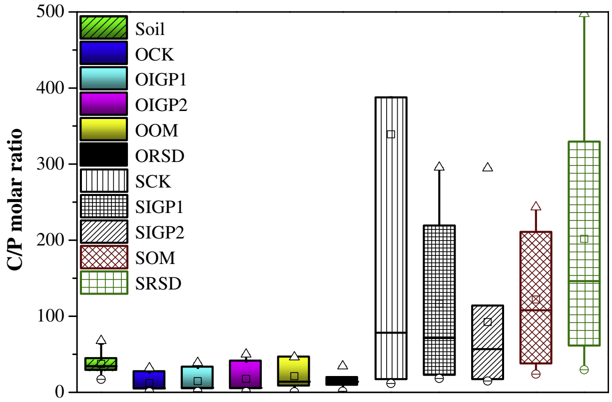

Fig. 7. Soil C:P ratios in overland flow and subsurface runoff following six rainfall events in 2012. *Note:* CK stands for the control plots which received no fertilizer treatments; IGP1 plots received treatment with inorganic P fertilizers; IGP2 received treatment with inorganic NPK; OM received treatment with composted pig manure; RSD received treatment with chopped straw. The first letter O in legends is overland flow and S is subsurface runoff.

port by overland flow (this effect was most pronounced in straw-fertilized plots). However, organic treatment did not seem to decrease TP transport by subsurface runoff.

3.7. Change of C:P ratios

As Fig. 7 shows, C:P ratios in soil and in the transport following rain events were quite different. The soil C:P ratio was higher than the overland flow C:P ratio, but lower than the subsurface runoff C:P ratio. The C:P ratios displayed greater variation in subsurface runoff and less variation in overland flow and soil measurements. The overland flow C:P ratios were higher in transport from fertilizer-treated plots (both inorganic and organic) than in transport from the control plots. The average value of subsurface runoff C:P ratios would be higher for the unfertilized control plots than for the fertilizer-treated plots. The average value of subsurface runoff C:P ratios was higher for organic-treated plots than for inorganic-treated plots. The subsurface runoff C:P ratio was higher for plots fertilized with chopped straw than for plots fertilized with composted pig manure; these results were reversed in measurements of overland flow.

4. Discussion

4.1. C and P competitive sorption

DOC was mainly consisted of humic and fulvic acids, LOAs and numerous others C compounds (Fig. 8). In present study, the composition, concentration, and sorption of organic acids in applied fertilizer and those organic acid persistence in soils determine the competitive capacity of DOC with P in soil; especially, the persistence of LOAs in soils are important in determining if the DOC can successfully compete with P for soil sorption sites (Guppy et al., 2005). Following application of fertilization, the process of microbial activity, metabolic availability of the carbon substrate, and sorption to soil colloids would mainly affect DOC persistence in soil (Fig. 8).

As cations increasing as fertilization, the enhanced interaction of cations with DOC can improve DOC structural stability by linking negatively charged functional groups of DOC together. Thus,

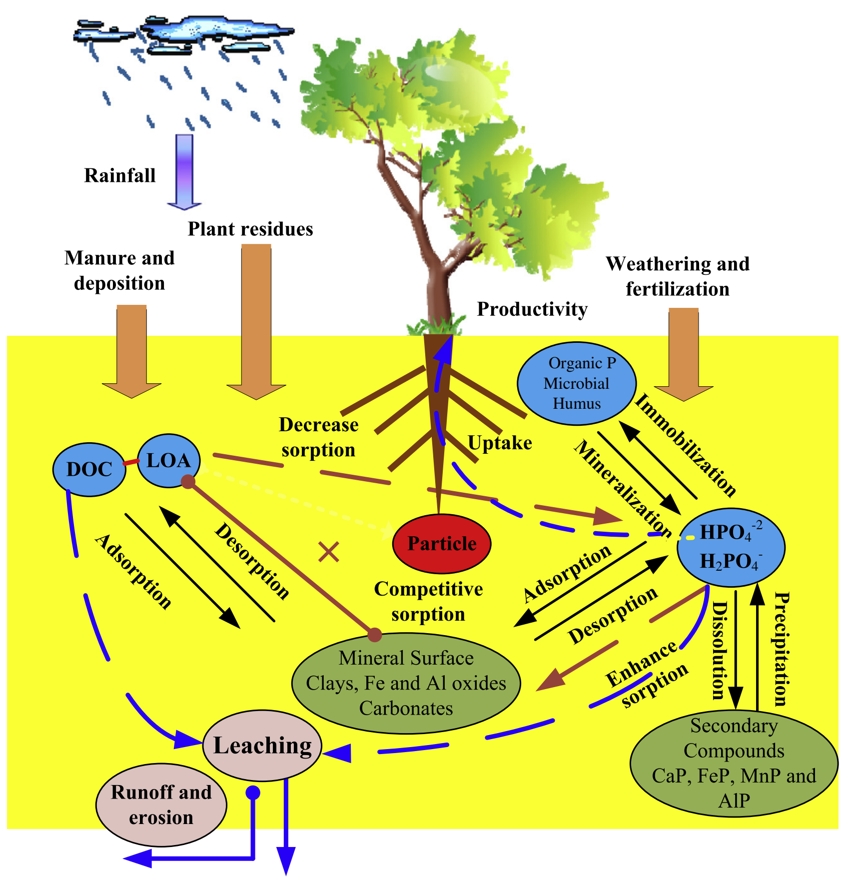

Fig. 8. Effects of organic and inorganic fertilizer use on the P biogeochemical cycle. *Note:* LOA stands for Low-molecular-weight Organic Acids.

the stable metal–DOC complexes can adsorb to soil colloids through cation bridging, which would further decrease the physical accessibility of the DOC to microbial attack (Swift, 1999; Piccolo, 2002) (Fig. 8). The sorption of DOC compounds to soil colloids would avoid the function of microbial degradation to DOC (Kalbitz et al., 2000), and then increases the potential efficacy of competitive reactions for DOC. In addition, microbial activity would greatly influence on the DOC mineralization rate in soil (Kusel and Drake, 1998). Because addition of mineralisable C sources may promote microbial incorporation of P, which result in increased organic P and reduced adsorbable inorganic P concentrations (Chen et al., 2000).

In present study, the effect of application of organic fertilizers and inorganic treatments on increased soil DOC and DTP, especially in the surface soil layer is different. This may be because that the application of organic fertilizers increased DOC concentrations in soil and enhance the extra step of P-mineralization. Accompanying with organic application, microbes may first mineralize organic P to inorganic P before plant uptake, whereas inorganic P would be uptaken rapidly following the inorganic application. P stabilization in soil is achieved through C–P linkages (phosphonates); hence, P is subject to both: (a) biological mineralization through C–P bond breakage (phosphonates) brought about by microbial need for C, and (b) biochemical mineralization through extracellular phosphatase cleavage of the C–O–P bond (Agbenin and Goladi, 1997).Inorganic P and NPK fertilization would halt the production of extracellular phosphatase, so that DTP and DOC would be substantially less than they are after organic fertilizer applications.

Long-term application of organic fertilization would increase organic acids persistence and soil surface area, thereby decreasing the likelihood of P sorption and increasing P phytoavailability; in contrast, inorganic fertilization, especially with N, P, and K, seems to produce negative effects on soil pH, exchangeable bases, and soil acidity (Agbenin and Goladi, 1997; Mokolobate and Haynes, 2003). Although interactions between P and some LOAs, humic and fulvic acids, the interactions due to the application of organic fertilizers, demonstrably reduce P sorption, and the interaction of P with water-soluble DOC compounds derived from animal and green manure is different. This suite of compounds may interact and behave in a manner different with respect to P sorption from the individual compounds considered thus far. This is also why the DOC and DTP concentration due to application of animal manure and chopped straw showed significant differences. Because the greatest effect of inorganic and organic fertilizers on DOC and DTP was seen in the surface soil layer, DOC and DTP in overland flow did not show a regular variation.

4.2. C and P leaching

It is useful to analyze C and P leaching from the agro-ecosystem as consisting of two consecutive steps: infiltration and translocation (Gao et al., 2009, 2010). In the infiltration step, P enters into infiltrating groundwater through its release from the source; in the translocation step, P is carried with soil water and eventually to surface water. As Table 1 shows, the runoff and sediment flux showed an overall increase with increasing rainfall. However, there were some deviations from a strict linear relationship. Although the rainfall starting on June 30th was significantly higher than that measured during the rainfall events of May 11th, 22nd July and August 21st, the sediment and overland flow flux in the smaller rainfall events was not correspondingly less. The rainfall event starting September 11th led to higher than expected. Overland flow, subsurface runoff, and sediment flux. This may have been due to the intensity of the rainfall. The rain fell during a storm, which local residents described as extreme. Short but heavy rainfall would be associated with higher kinetic energy in the raindrops, which would enhance runoff and sediment transport. The rainfall event starting on June 30th was discontinuous and unsteady. Raindrops had little kinetic energy. The infiltration process was prolonged. This resulted in reduced overland flow and increased subsurface runoff (Gao et al., 2010). Overland flow was the main pathway for P transport; subsurface runoff was a subsidiary channel. However, more TP was lost in subsurface runoff. It is possible that increased rainfall duration and intensity strengthen P mobilization. The vegetation in the experimental plots would have increased infiltration and the consequent P transport by subsurface runoff. DOC did not show the same behavior as TP. The DOC flux was higher in subsurface runoff than in overland flow in all rainfall events. This shows a significant leaching effect of DOC under rainfall erosion. Long-duration and high-intensity rainfall would naturally lead to a DOC concentration in runoff.

It is clear from the study results that long-term inorganic fertilizer use has a deleterious effect on soil quality. P introduced by fertilizer is a significant source of the P found in rain runoff (Shigaki et al., 2006). Plots treated with inorganic P treatments showed enhanced P flux in overland flow and decreased P transport in subsurface runoff (in contrast to the increased DOC flux in overland flow *and* subsurface runoff). Application of inorganic P or NPK fertilizers could not arrest the downward slide in soil C and P. Inorganic fertilizers (P and NPK) only added to the easily extractable inorganic C and P in soil; they did not halt the losses of organic N and P (Agbenin and Goladi, 1997). Smith et al. (1998) also reported that soils as long-term application of high rates of inorganic fertilizer showed P enrichment of the subsoil, which is easily leached in rainfall. The relatively higher DOC concentration due to inorganic P treatment, compared to control treatment, was likely to be attributable to desorption of organic C from the soil. The desorption of organic C was probably related to competitive sorption of P for organic C binding sites during P displacement (Beck et al., 1999).

Application of chopped straw reduced overland flow by 15–40%, but increased subsurface runoff by 2–3 times compared to application of either inorganic P or composted pig manure (see Table 1). Treatment with chopped straw would reduce TP and DOC flux in overland flow and increase TP and DOC flux in subsurface runoff compared to other fertilizer treatments. This is because the straw filters rainwater and traps sediment. This leads to a decrease in the availability of freely desorbable P and DOC in overland flow and an increase in P and DOC leaching effects (McDowell and Sharpley, 2002). There is thus a potential for high DOC and P loss to groundwater whenever there is significant down-profile transport of DOC and P.

In present study, the P loss flux from organic-treated plots was characterized by decreased in overland flow but increased subsurface runoff. This is explained by that the enhanced P transport in subsurface runoff may be due to chemical reactions between soil solution and solid phases which P control adsorption and desorption process. Fertilizer application (of both inorganic and organic fertilizers) would increase DOC flux in overland flow and subsurface runoff during and immediately following rainfall. Infiltration of DOC into the soil during rainfall events facilitates competition between P and DOC for soil sorption sites and enhances P (and perhaps DOC) transport. In addition, decomposition of organic matter can also increase soil pH, which can decrease P adsorption, particularly on oxide mineral surfaces with pH-dependent charge (Jiao et al., 2007).

4.3. Stoichiometry

Redfield (1958) reported a C:N:P molar ratio of 106:16:1, both in phytoplankton and in oceanic waters. This ratio is important for studies of C, N, and P export because a stoichiometric ratio

Table 1
Measurements of sediment and compounds in overland flow and subsurface runoff from experimental plots fertilized under different protocols.

Date	11-May, 2012				
Rainfall (mm)	22				
Treatment	CK	IGP1	IGP2	OM	RSD
Overland flow (m^3)	0.005	0.007	0.009	0.017	0.003
Subsurface runoff (m^3)	0.027	0.022	0.031	0.087	0.061
Sediment (g)	41.01	32.25	36.98	38.34	23.76
Sediment flux ($g\ m^{-2}$)	1.71	1.34	1.54	1.2	0.99
OTP flux ($mg\ m^{-2}$)	0.21	0.33	0.46	0.17	0.13
STP flux ($mg\ m^{-2}$)	0.13	0.1	0.28	0.49	0.41
ODOC flux ($mg\ m^{-2}$)	2.14	4.95	5.71	3.02	2.56
SDOC flux ($mg.m^{-2}$)	5.77	9.13	8.58	31.4	41.4
Date	30-Jun to 4-Jul, 2012				
Rainfall (mm)	79.4				
Treatment	CK	IGP1	IGP2	OM	RSD
Overland flow (m^3)	0.147	0.098	0.128	0.087	0.116
Subsurface runoff (m^3)	1.534	1.853	1.57	1.844	1.57
Sediment (g)	43.14	27.13	33.52	29.04	27.27
Sediment flux ($g\ m^{-2}$)	1.8	1.13	1.4	1.21	1.14
OTP flux ($mg\ m^{-2}$)	5.17	5.69	7.44	2.51	1.43
STP flux ($mg\ m^{-2}$)	4.41	3.63	2.63	6.75	9.58
ODOC flux ($mg\ m^{-2}$)	16.51	11.05	19.05	16.01	19.81
SDOC flux ($mg\ m^{-2}$)	151.78	245.99	170.68	323	325.91
Date	6-Jul to 9-Jul, 2012				
Rainfall (mm)	112.2				
Treatment	CK	IGP1	IGP2	OM	RSD
Overland flow (m^3)	0.177	0.173	0.128	0.199	0.127
Subsurface runoff (m^3)	1.848	1.564	1.848	1.28	1.738
Sediment (g)	63.17	51.96	59.11	59.91	26.97
Sediment flux ($g\ m^{-2}$)	2.63	2.17	2.47	2. 50	1.12
OTP flux ($mg\ m^{-2}$)	4.69	5.75	5.92	4.43	1.46
STP flux ($mg\ m^{-2}$)	11.37	12.65	18.31	26.42	14.54
ODOC flux ($mg.m^{-2}$)	5.72	9.73	10.66	6.91	6.01
SDOC flux ($mg\ m^{-2}$)	84.18	116.61	147.86	140.02	210.6
Date	22-Jul to 23-Jul				
Rainfall (mm)	43.8				
Treatment	CK	IGP1	IGP2	OM	RSD
Overland flow (m^3)	0.042	0.058	0.08	0.073	0.078
Subsurface runoff (m^3)	0.841	0.577	0.79	0.499	0.84
Sediment (g)	33.54	45.5	40.83	39.01	41.7
Sediment flux ($g\ m^{-2}$)	1.4	1.9	1.7	1.63	1.74
OTP flux ($mg\ m^{-2}$)	9.46	11.83	13.26	8.22	7.02
STP flux ($mg\ m^{-2}$)	1.15	1.79	1.33	2.12	0.72
ODOC flux ($mg\ m^{-2}$)	0.64	2.48	1.91	1.88	1.63
SDOC flux ($mg\ m^{-2}$)	28.98	38	37.02	43.02	63.93
Date	21-Aug, 2012				
Rainfall (mm)	59.4				
Treatment	CK	IGP1	IGP2	OM	RSD
Overland flow (m^3)	0.066	0.058	0.087	0.062	0.057
Subsurface runoff (m^3)	0.042	0.055	0.06	0.04	0.077
Sediment (g)	48.85	34.06	45.38	40.03	21.54
Sediment flux ($g\ m^{-2}$)	2.04	1.42	1.9	1.67	0.9
OTP flux ($mg\ m^{-2}$)	2.21	3	3.2	1.5	1.19
STP flux ($mg\ m^{-2}$)	0.27	0.18	0.21	0.17	0.27
ODOC flux ($mg\ m^{-2}$)	12.89	17.18	20.02	14.17	14.21
SDOC flux ($mg\ m^{-2}$)	13.57	13.02	13.34	3.39	3.14
Date	11-Sep, 2012				
Rainfall (mm)	160.8				
Treatment	CK	IGP1	IGP2	OM	RSD
Overland flow (m^3)	1.908	1.403	1.523	1.504	1.616
Subsurface runoff (m^3)	1.557	2.34	2.043	2.053	3.043
Sediment (g)	3355.08	3420.39	3550.95	3609.78	1612.65
Sediment flux ($g\ m^{-2}$)	139.8	142.52	147.96	150.41	67.2
OTP flux ($mg\ m^{-2}$)	10.12	14.88	17.91	9.69	9.52
STP flux ($mg\ m^{-2}$)	18.12	16.7	35.65	14.6	18.04
ODOC flux ($mg\ m^{-2}$)	130.27	154.98	148.53	169.73	153.98
SDOC flux ($mg\ m^{-2}$)	153.16	415.93	297.96	516.16	606.09

Fertilizer protocol codes: CK stands for the control plots which received no fertilizer treatments; IGP1 plots received treatment with inorganic P fertilizers; IGP2 received treatment with inorganic NPK; OM received treatment with composted pig manure; RSD received treatment with chopped straw.
Transport flux codes: OTP stands for TP transport by overland flow; STP stands for TP transport by subsurface runoff; ODOC stands for DOC transport by overland flow; SDOC stands for DOC transport by subsurface runoff.

closer to the Redfield ratio is a good indicator of the water's capacity to support higher trophic levels and thus eutrophication (Vink et al., 2007). Many researchers have looked for this ratio, or variations on this ratio, in terrestrial ecosystems (Gao et al., 2013b, 2014). Out results show that soil C:P ratios ranging from 20 to 43,overland flow C:P ratios ranging from 8 to 40, and subsurface runoff C:P ratios ranging from 11 to 500. This shows a clear divergence of nutrient composition between terrestrial and aquatic systems.

The ratios of C:P in soil during long-term fertilization and in overland flow due to rainfall, which may be the effect of inorganic and organic fertilization on C and P competitive sorption mainly occur at surface soil layer, so large number of P desorption from surface soil. The ratios of C:P was significantly higher in subsurface runoff compared to overland flow. This was explained by that only little P transport by subsurface runoff due to absorbed by soil particle and DOC can transport by subsurface runoff due to leaching effect. The C:P ratio in runoff or soil was significantly higher or lower than the Redfield ratio, suggesting that P is ordinarily limited in purple soil watersheds. Under rainfall events, however, significant P leaching and release were seen. In addition, rainfall-induced changes in the C:P stoichiometry and percentages of dissolved nutrients will also benefit some algal species more than others, which could affect water quality.

5. Conclusion

Our results show that the long-term application of organic fertilizers significantly increased soil DOC and DTP content, which would also benefit plants. However, fertilizer application, whether of inorganic or organic fertilizers, also results in greater P and C leaching than seen in the control (unfertilized) plots. Researchers believe that these results are due to C and P competitive sorption. Organic-manure-derived DOC was found to leach from soils at a higher rate than P (when organic fertilizers are surface-applied), which demonstrates that organic fertilizers facilitate a higher sorption affinity of P over DOC than do inorganic fertilizers.

The competitive inhibition of P sorption through fertilizer use is of great significance to potential plant uptake. Long-term application of organic fertilizers increases the persistence of LOAs in soil. These in turn increase the amount of P in solution, which is more available to plants. The change of C:P ratios were significantly higher in subsurface runoff than in overland flow, which is a strong indicator of C and P competitive sorption. This study sheds some light on the soil processes that predict the environmental fate of P. It also presents a strong argument for the use of organic fertilizers to enhance P uptake and avoid potential leaching of P from agricultural soils.

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References

Agbenin, J.O., Goladi, J.T., 1997. Carbon, nitrogen and phosphorus dynamics under continuous cultivation as influenced by farmyard manure and inorganic fertilizers in the savanna of northern Nigeria. Agric. Ecosyst. Environ. 63, 17–24.
Beck, M.A., Robarge, W.P., Buol, S.W., 1999. Phosphorus retention and release of anions and organic C by two Andisols. Eur. J. Soil Sci. 50 (1), 157–164.
Bhatti, J.S., Comerford, N.B., Johnston, C.T., 1998. Influence of oxalate and soil organic matter on sorption and desorption of phosphate onto a spodic horizon. Soil Sci. Soc. Am. J. 62 (4), 1089–1095.
Bunemann, E.K., Oberson, A., Liebisch, F., Keller, F., Annaheim, K.E., Huguenin-Elie, O., Frossard, E., 2012. Rapid microbial phosphorus immobilization dominates gross phosphorus fluxes in a grassland soil with low inorganic phosphorus availability. Soil Biol. Biochem. 51, 84–95.
Chen, G.C., He, Z.L., Huang, C.Y., 2000. Microbial biomass phosphorus and its significance in predicting phosphorus availability in red soils. Commun. Soil Sci. Plant Anal. 31, 655–667.
Easterwood, G.W., Sartain, J.B., 1990. Clover residue effectiveness in reducing orthophosphate sorption on ferric hydroxide coated soil. Soil Sci. Soc. Am. J. 54, 1345–1350.
Gao, Y., Zhu, B., Zhou, P., Tang, J.L., Miao, C.Y., 2009. Effects of vegetation cover on phosphorus loss from a hillslope cropland of purple soil under simulated rainfall: a case study in China. Nutr. Cycl. Agroecosyst., 263–273.
Gao, Y., Zhu, B., Wang, T., Tang, J.L., Zhou, P., Miao, C.Y., 2010. Bioavailable phosphorus transport from a hillslope cropland of purple soil under natural and simulated rainfall. Environ. Monit. Assess. 171, 539–550.
Gao, Y., Zhu, B., Wang, T., Wang, Y.F., 2012. Seasonal change of non-point source pollution-induced bioavailable phosphorus loss: a case study of Southwestern China. J. Hydrol. 420–421, 373–379.
Gao, Y., He, N.P., Wang, Q.F., Miao, C.Y., 2013a. Increase of external nutrient input impact on carbon sinks in Chinese coastal seas. Environ. Sci. Technol. 47, 13215–13216.
Gao, Y., Yu, G.R., He, N.P., 2013b. Equilibration of the terrestrial water, nitrogen, and carbon cycles: advocating a health threshold for carbon storage. Ecol. Eng. 57, 366–374.
Gao, Y., Zhu, B., Yu, G.R., Chen, W.L., He, N.P., Wang, T., Miao, C.Y., 2014. Coupled effects of biogeochemical and hydrological processes on C, N, and P export during extreme rainfall events in a purple soil watershed in southwestern China. J. Hydrol. 511, 692–702.
Gong, Z.T., 1999. Chinese Soil Taxonomy. Science Press, Beijing, pp. 160–166, 756–759 (in Chinese).
Guppy, C.N., Menzies, N.W., Moody, P.W., Blamey, F.P.C., 2005. Competitive sorption reactions between phosphorus and organic matter in soil: a review. Aust. J. Soil Res. 43, 189–202.
Iyamuremye, F., Dick, R.P., Baham, J., 1996. Organic amendments and phosphorus dynamics: I. Phosphorus chemistry and sorption. Soil Sci. 161 (7), 426–435.
Jiao, Y., Whalen, J.K., Hendershot, W.H., 2007. Phosphate sorption and release in a sandy-loam soil as influenced by fertilizer sources. Soil Sci. Soc. Am. J. 71 (1), 118–124.
Kalbitz, K., Solinger, S., Park, J.H., Michalzik, B., Matzner, E., 2000. Controls on the dynamics of dissolved organic matter in soils: a review. Soil Sci. 165, 277–304.
Kang, J., Amoozegar, A., Hesterberg, D., Osmond, D.L., 2011. Phosphorus leaching in a sandy soil as affected by organic and inorganic fertilizer sources. Geoderma 161, 194–201.
Kusel, K., Drake, H.L., 1998. Microbial turnover of low molecular weight organic acids during leaf litter decomposition. Soil Biol. Biochem. 31, 107–118.
Liang, B., Yang, X.Y., He, X.H., Zhou, J.B., 2011. Effects of 17-year fertilization on soil microbial biomass C and N and soluble organic C and N in loessial soil during maize growth. Biol. Fertil. Soils 47, 121–128.
Miao, C.Y., Ni, J.R., Borthwick, A.G.L., 2010. Recent changes in water discharge and sediment load of the Yellow River basin. China. Prog. Phys. Geography 34 (4), 541–561.
Miao, C.Y., Ni, J.R., Borthwick, A.G.L., Yang, L., 2011. A preliminary estimate of human and natural contributions to the changes in water discharge and sediment load in the Yellow River. Global Planet. Change 76 (3–4), 196–205.
Mokolobate, M.S., Haynes, R.J., 2003. A glasshouse evaluation of the comparative effects of organic amendments, lime and phosphate on alleviation of Al toxicity and P deficiency in an Oxisol. J. Agric. Sci. 140, 409–417.
Moral, R., Moreno-Caselles, J., Perez-Murcia, M.D., Perez-Espinosa, A., Rufete, B., Paredes, C., 2005. Characterization of the organic matter pool in manures. Bioresour. Technol. 96 (2), 153–158.
Nelson, D.W., Sommers, L.E., 1982. Total carbon, organic carbon and organic matter. In: Page, A.L., Miller, R.H., Keeney, D.R. (Eds.), Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties, 2nd ed. American Society of Agronomy, Madison, WI, USA, pp. 539–577.
Nelson, N.O., Parsons, J.E., Mikkelsen, R.L., 2005. Field-scale evaluation of phosphorus leaching in acid sandy soils receiving swine waste. J. Environ. Qual. 34 (6), 2024–2035.
Olsen, S.R., Sommers, L.E., 1982. Phosphorus. In: Page, A.L., Miller, R.H., Keeney, D.R. (Eds.), Methods of Soil Analysis. Part 2: Chemical and Microbiological Properties, 2nd ed. American Society of Agronomy, Madison, WI, USA, pp. 403–430.
Piccolo, A., 2002. The supramolecular structure of humic substances: a novel understanding of humus chemistry and implications in soil science. Adv. Agron. 75, 57–134.
Redfield, A.C., 1958. The biological control of chemical factors in the environment. Am. Sci. 46, 205–211.
Rudrappa, L., Purakayastha, T.J., Singh, D., Bhadraray, S., 2006. Long-term manuring and fertilization effects on soil organic carbon pools in a typic Haplustept of semi-arid sub-tropical India. Soil Till. Res. 88, 180–192.
Schiffman, S.S., Bennett, J.L., Raymer, J.H., 2001. Quantification of odors and odorants from swine operations in North Carolina. Agric. Forest Meteorol. 108 (3), 213–224.
Sharpley, A.N., 1985. Depth of surface soil-runoff interaction as affected by rainfall, soil slope and management. Soil Sci. Soc. Am. J. 49, 1010–1015.
Sharpley, A.N., Weld, J.L., Beegle, D.B., Kleinman, P.J.A., Gburek, W.L., Moore, P.A., Mullins, G., 2003. Development of phosphorus indices for nutrient management planning strategies in the U.S. J. Soil Water Conserv. 58 (3), 137–152.
Shigaki, F., Sharpley, A.N., Prochnow, L.I., 2006. Source-related transport of phosphorus in surface runoff. J. Environ. Qual. 35, 2229–2235.

Sims, J.T., Simard, R.R., Joern, B.C., 1998. Phosphorus loss in agricultural drainage: historical perspective and current research. J. Environ. Qual. 27 (2), 277–293.
Smith, K.A., Chalmers, A.G., Chambers, B.J., Christie, P., 1998. Organic manure phosphorus accumulation, mobility and management. Soil Use Manag. 12, 154–159.
Staunton, S., Leprince, F., 1996. Effect of pH and some organic anions on the solubility of soil phosphate: implications for P bioavailability. Eur. J. Soil Sci. 47, 231–239.
Swift, R.S., 1999. Macromolecular properties of soil humic substances: fact, fiction and opinion. Soil Sci. 164, 790–802.
Vink, S., Ford, P.W., Bormans, M., Kelly, C., Turley, C., 2007. Contrasting nutrient exports from a forested and an agricultural catchment in south-eastern Australia. Biogeochemistry 84, 247–264.
Zhao, M.X., Zhou, J.B., Kalbitz, K., 2008. Carbon mineralization and properties of water-extractable organic carbon in soils of the south Loess Plateau in China. Eur. J. Soil Biol. 44, 158–165.
Zhu, B., Wang, T., You, X., Gao, M.R., 2008. Nutrient release from weathering of purplish rocks in the Sichuan Basin. China Pedosphere 18 (2), 257–264.