Investigating rainfall duration effects on transport of chemicals from soil to surface runoff on a loess slope under artificial rainfall conditions

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Abstract: The release and transport of soil chemicals in water erosion conditions are important for the local environment, soil and water resources conservation. According to the artificial rainfall experiments with a constant rainfall intensity of 90 mm/h and different rainfall duration (30, 60, 90, 120 and 150 min), the traits of soil PO_4^{3-}, K^+, and Br^- release and transport from soil to surface runoff on the loess slope were analysed, and a model describing the chemical concentration change in surface runoff under soil erosion conditions was developed. The runoff coefficient quickly increased in 15 min or so, and then it was stable in the range of 0.60–0.85. The sediment intensity decreased in 30 min and soon increased after severe sheet erosion occurred on the slope. The concentration curve of Br^- in surface runoff can be divided into two stages, quickly decreasing in the initial 30 min after the surface runoff occurred, and then stable. The concentration curve of PO_4^{3-} and K^+ in surface runoff can be divided into three stages, quickly decreasing like Br^- was decreasing, then stable, and increasing after severe sheet erosion began. Compared with the exponential function, the power function was found more suitable for fitting the change in chemicals in runoff with unsaturated soil; while neither of them could well fit the PO_4^{3-} and K^+ concentration change after severe erosion occurred. The transport of chemicals under complex soil erosion conditions seems to be a dynamic release process between surface runoff and sediment. Based on the convection-dispersion mechanism and desorption kinetics, the polynomial model under soil erosion conditions was created. For adsorbed PO_4^{3-} and K^+, it is more suitable to simulate that process than the power function, while it is not so good for mobile Br^-.

Keywords: influence of rainfall duration; soil chemicals loss; soil erosion; surface runoff; traits and simulation

The loss of agricultural chemicals such as soil nutrients by the surface runoff and the eroded sediment is considered to be one of the major environmental and agricultural problems, leading to available nutrient lessening, soil quality degradation, water pollution and ecological environment deterioration (Ella *et al*. 2017). Some previous studies indicate that there is a mixing zone, which has a certain thickness in the surface soil layer (Green & Houke 1979; Ahuja *et al*. 1981; Sharpley 1985; Yang *et al*. 2016). This theory

assumes that the soil in this layer can interact with rainfall and runoff; as a result, a certain percentage of dissolved chemicals in this zone enter into infiltration water, surface runoff and soil water. By a ^{32}P tracer test on the saturated soil, Ahuja *et al.* (1981) found that the soil chemical placed in the surface layer was the most likely to enter into the surface runoff, and the transported amount exponentially lessened with the soil depth increase. Several models based on the mixing layer theory, such as uniform, incomplete mixing and non-uniform, incomplete mixing, usually represent an exponential function describing the varying process of chemical concentration in surface runoff (Ahuja 1986; Heathman *et al.* 1986; Zhang *et al.* 1999). The transfer of chemicals from soil to surface runoff is considered to be quite a complex result of the rainfall-soil interaction of raindrop strike, runoff scour, soil erosion, including convection-diffusion (Wallach *et al.* 1988; Ahuja 1990; Zhang *et al.* 1999), turbulent mixing caused by raindrop impact (Gao *et al.* 2005; Dong *et al.* 2013; Tao *et al.* 2017) and so on.

The mixing layer theory experiments of Ahuja *et al.* (1981) and Zhang *et al.* (1999), the exchangeable layer theory of Gao *et al.* (2005) and some others were mostly conducted in the conditions of negligibly severe soil erosion. There were always with non-saturated soil and severe soil erosion on the Loess Plateau in China (Zheng *et al.* 2005; Liu *et al.* 2018), so the transport process of soil chemicals in the interaction of surface runoff-infiltration-soil erosion-soil water is particularly complex. Meanwhile, the own physicochemical properties of chemicals aggravate the complexity to a certain degree (Shi *et al.* 2011). The key to improve the simulation accuracy is to study how soil erosion affects the chemical transport. Although relationships between rainfall, runoff, erosion and chemical movement have been reported by many researchers, the main parameter to quantify the chemical loss with different erosion intensities and patterns is the enrichment ratio which is associated with adsorbed chemicals in sediment (Sharpley 1983; Yang *et al.* 2014). The soluble ones in surface runoff are quantified by the models mostly based on the mixing layer theory and putting forward an exponential decrease of chemical concentrations in surface runoff. There are not enough experimental researches on the influence of severe or complex soil erosion on the variable traits and modelling of the migration of mobile and adsorbed chemicals in surface runoff.

Many researchers have reported the influence of rainfall intensity and raindrop energy on soil erosion and loss of chemicals which are the function of the erosive forces of raindrop impact and shallow flowing water and their interaction (Kleinman *et al.* 2006; Shigaki *et al.* 2007; Guo *et al.* 2010; Wang *et al.* 2018; Tao *et al.* 2017). With constant rainfall intensity and raindrop energy, the longer the rainfall duration, the greater is the runoff and the soil erosion types are more complex, leading to an increase of the cumulative chemical loss (Ahuja *et al.* 1982; Sharpley 1985; García-Díaz *et al.* 2017). Therefore, rainfall duration has an important implication in the process of surface runoff, soil erosion and soil chemical transport. However, the existing laboratory experiments with chemical transport along the slope are mostly of short duration (rainfall time was usually around 60 min, no more than 90 min as usual), and are mainly with raindrop splash or coupled with sheet erosion (Zhang *et al.* 1999; Maïga-Yaleu *et al.* 2015; Tao *et al.* 2017). The influence of rainfall duration on the transport of chemicals from soil to surface runoff has received less attention.

Therefore, this paper aims to analyse the influence of different rainfall duration on water erosion and soil phosphorus, potassium and bromide (representing an adsorbed, adsorbed-exchangeable, and non-adsorbed soil chemical, respectively) loss with surface runoff and sediment. Meanwhile, one model for describing the driving force of chemical transfer from soil to surface runoff and the concentration in surface runoff under the conditions of soil erosion is put forward. It is hoped that the information of this paper may promote the soil water and fertilizer efficiency, and benefit the research of agricultural nonpoint source pollution in a complex water erosion region.

MATERIAL AND METHODS

Experimental materials and devices. The soil used for experiments was sandy loam collected from the surface to a 0.3-m depth at the Test Station on Soil and Water Conservation of Ansai (latitude 36°51'30'' and longitude 109°19'23''). Ansai County is located on the Loess Plateau, Shaanxi Province, China (latitude 36°30'45''–37°19'3'' and longitude 108°5'44''–109°26'18'') as shown in Figure 1. It is a site with severe soil erosion, the proportion of the water erosion area being about 97% of the total area, the general modulus of soil erosion being 4000~15000 t/(km^2·a), and the average sediment
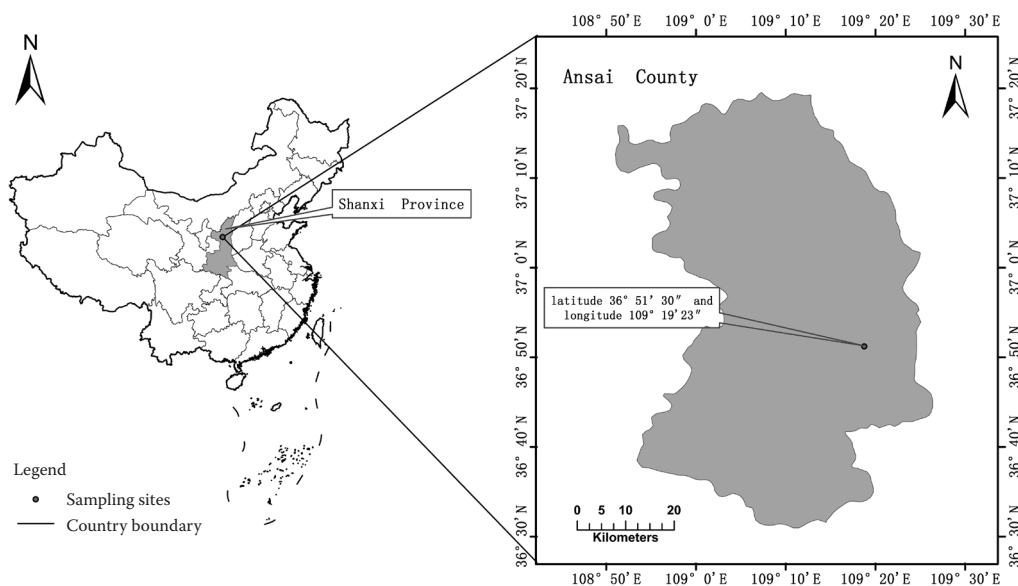
Figure 1. Geographic location of the study region and soil sampling sites

Table 1. Physical properties and nutrient content of the soil used

Particle content levels (%)			Soil texture (%)	pH	Saturated soil moisture (%)	Organic matter	K⁺	Available phosphorus	Br⁻
< 0.002 mm	0.002–0.05 mm	> 0.05mm						(mg/kg)	
2.285	63.122	34.593	sandy loam	8.35	33.9	0.39	95	3.6	1.8

yield being 2.388×10^7 t/a. Selected soil properties are presented in Table 1. The collected soil was air-dried, sieved through a 5-mm sieve and covered by a plastic sheet until used in the experiments.

The artificial rainfall experiments were carried out in the hall of the State Key Laboratory of Soil Erosion and Dryland Farming on the Loess Plateau, Yangling, China. The experimental setup of simulated rainfall included rainfall device, automatic control system (ACS) (simultaneous control of rain intensity and water pressure), water pump, water tank, rainfall intensity rate meter and soil tanks (Figure 2).The rain sprinkler was placed at a height of 16 m. The distribution and size of raindrops had the uniformity above 90%, similar to natural rainfall (Guo *et al.* 2010). For instance, the maximum diameter of the raindrops was up to 5 mm, and the raindrop terminal velocity could reach above 98% of natural raindrops (Pan *et al.* 2010). Water pressure was controlled by ACS so that the rainfall intensity could increase
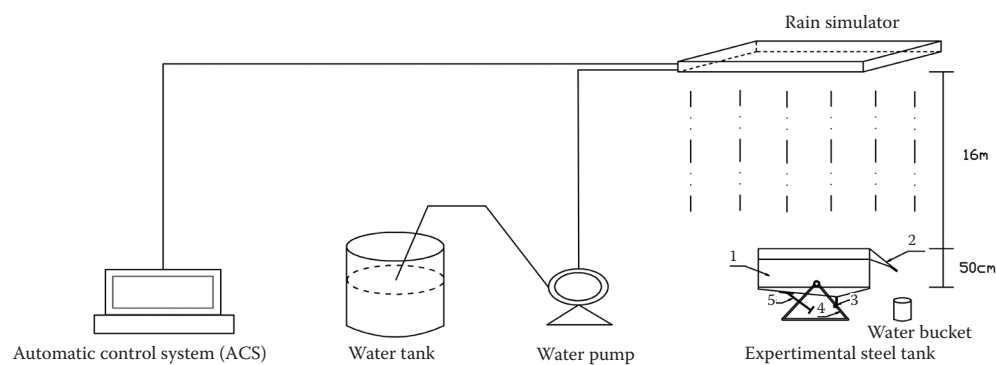

Figure 2. The experimental setup of artificial rainfall
Experimental steel tank includes: 1 – soil tank; 2 – V-shaped runoff-collecting device; 3 – infiltration tap; 4 – steel trestle; 5 – slope degree regulator

from 40 to 120 mm/h. The study was conducted on 5 soil tanks that were 100 cm long, 30 cm wide and 55 cm high (Figure 1). There was a 35-cm depth in the soil tank to pack the soil there. The rest 20 cm tall vertical extensions on the two side walls were to prevent the soil from splashing out during the rainfall. Each soil tank had 20 holes on the bottom to allow free drainage. A V-shaped funnel to catch runoff was provided in the outlet of soil tanks.

Preparation and packing of soil. Some air-dried soil (abundant for the 0–25 cm depth of the five tanks) was mixed uniformly with a pre-determined quantity of water. Meanwhile, dissolve a certain amount of KH_2PO_4 and KBr with water, and equally spray the solution on a certain amount of dried soil which is adequate for the remaining 26–35 cm layer of these five tanks. Soil moisture was to the desired level of 10% and the fertilizer applied was equivalent to the amount of 450 kg/ha Br, 110 kg/ha P and 286 kg per ha K in the field. Then these two kinds of soil were stored in covered containers for 2 h to achieve a degree of uniformity in soil moisture and chemical concentration. The treated soil was packed in the soil tank with 5-cm increments with a final bulk density of 1.30 g/cm^3. No fertilized soil was in the bottom 0–25 cm layer and the fertilizer-applied soil was in the upper 26–35 cm layer. After soil packing, the soil surface was covered by a plastic sheet for 24 h to prevent evaporation before the rainfall experiments. It was also provided to ensure the complete dissolution of applied chemicals and to achieve a degree of uniformity in the distribution of both the soil water and the chemicals in the soil profile.

Simulation rainfall processes. The rainfall intensity for all the experiments was 90 mm/h and the slope gradient was fixed at 26.8% (15°), which is typically encountered on the Loess Plateau. The shortest rainfall duration was 30 min and the time increments for other rainfalls were 30 min. At the time of 30, 60, 90 and 120 min after rainfalls began, the soil tanks No. 1–4 were pushed away to the area without rainfall, respectively. The rainfall intensity was calibrated several times with ACS and some rain meters before the experiments began, until the rainfall intensity and uniformity met the need. The runoff samples were collected with small plastic buckets. In the initial 10 min after the surface runoff occurs, collect runoff samples (1 min) at 1-min intervals, being 0–1 min, 2–3 min, 4–5 min, 6–7 min and 8–9 min. In the following 11–30 min, collect runoff samples (1 min) at 5-min intervals, i.e.

10–11 min, 15–16 min, etc. After 30 min, samples were collected at 10-min intervals, i.e. 30–31 min, 40–41 min, 50–51 min, and so on, till to the end of rainfall. The runoff after the rainfall ended was also collected for each slope. The remaining runoff of each soil tank was all collected with five big plastic buckets. To measure the concentration of dissolved chemicals, some rainwater from each small plastic bucket was poured into three plastic bottles of 100 ml. To determine the average concentration of chemicals in surface runoff, three water samples were taken from each big plastic bucket. Finally, the sediment was air-dried, its yield and adsorbed chemical concentration were tested.

Sample testing and calculation methods. Soil particle composition was analysed according to the U.S. land classification system. Texture and mechanical composition of soil were determined by hydrometer method. Soil pH was determined with a pH meter (Sartorius, Göttingen, Germany) (ratio of soil to water was 1 : 2.5). Soil moisture content of the tested soil was measured by drying method (in an oven at 105°C for 10 h). Saturated soil moisture was determined by cutting ring and drying method. Organic matter in soil was determined by the potassium dichromate volumetric method. Available phosphorus in soil and sediment was determined with 0.5 mol/l $NaHCO_3$ and $HClO_4$-H_2SO_4, and assayed using the ammonium molybdate method (Olsen & Sommers 1982). Water dissolved phosphorus PO_4^{3-}-P was determined colorimetrically using ascorbic acid as a reductant for the phosphomolybdate complex. The resulting molybdophosphoric blue colour was measured at 885 nm (Olsen & Sommers 1982). Soil K^+ was extracted with 1 mol/l CH_3COONH_4·K^+ in soil and runoff was determined by atomic absorption spectrophotometer. Soil Br^- was extracted with distilled water (ratio of soil to water was 1 : 5) and filtrated after shaking for 30 min. Br^- in soil and runoff was determined by an ionometer (Model SX-3805, Shanghai Dapu Instrument Co., Ltd, P.R. China).

With ignored evaporation in the rainfall period, the total runoff amount could be calculated by

$$R = Q_r/(1000\ B\ L\ \cos a) \tag{1}$$

where:
R – total runoff (mm)
Q_r – runoff amount collected from each small water bucket and the big one for one slope land (ml)

B – slope width (1 m)
L – slope length (5 m)
a – slope degree (15° for this experiment)

The total sediment amount can be calculated by

$$S = S_r/(B\ L\ \cos a) \tag{2}$$

where:
S – total sediment (t/km^2)
S_r – sediment amount collected from each small water bucket and the big one for one slope land (g)

The transport of chemicals in surface runoff at time t can be described by the loss amount in surface runoff as

$$C_{rt} = r_t \times c(t)/1000 \tag{3}$$

where:
C_{rt} – chemical loss amount in surface runoff (mg/min)
r_t – runoff amount at time t (ml)
$c(t)$ – chemical concentration at the same time (mg/l)

The accumulated loss amount for a dissolved chemical is in all the surface runoff which can be got by the product of runoff and its chemical concentration. Meanwhile that of adsorbed chemical is in all the sediment which can be got by the product of sediment and its chemical concentration. The total chemical surface loss amount for each soil tank is their sum. For the sake of comparison, the loss amount is uniformly converted to that per 1 m^2 of projected area.

Modelling transfer of chemicals from soil to surface runoff. Under the conditions of water erosion, there are usually two forms of soil chemicals coming into surface runoff (Zhang *et al*. 2007; Xing *et al*. 2016). One of them is a dissolved form existing in the soil solution and coming into surface runoff for exchanging. The other is an adsorbed form to the soil particle or eroded sediment and coming into surface runoff for desorption and other driving forces (Wang *et al*. 1998; Liu *et al*. 2018). Therefore, the chemical loss of surface runoff can be expressed as

$$M_r = M_{rw} + M_{rs} \tag{4}$$

where:
M_r – total loss of the chemical in surface runoff (mg)
M_{rw} – dissolved chemical from soil water (mg)
M_{rs} – desorbed chemical from the soil particle or eroded sediment (mg)

The M_{rw} is calculated as

$$M_{rw} = \int_0^t c_{rw}(t) \times r(t)/1000\, dt \tag{5}$$

where:
$c_{rw}(t)$ – concentration of dissolved chemical at time t (mg/l)

$$M_{rs} = \int_0^t c_{rs}(t) \times r(t)/1000\, dt \tag{6}$$

where:
$c_{rs}(t)$ – concentration of desorbed chemical in surface runoff at time t (mg/l)

The loss of dissolved chemical in surface runoff is just like a convective-diffusion mass transfer in the mixing layer (Wallach *et al*. 1988; Tong *et al*. 2010). Wang *et al*. (1998) suggested that the change in dissolved chemical concentration in surface runoff on the loess slope is assumed as a power function without considering the soil adsorption. Then c_{rw} is as

$$c_{rw}(t) = k_m c_{so} t^b \tag{7}$$

where:
c_{so} – soil chemical content in the mixed layer (mg/l)
k_m – mass transfer coefficient
b – coefficient

There is usually a specific relationship between adsorbed chemicals and soil particles (Sharpley 1981). During the dissolution and desorption process, the adsorbed chemical is dispelled from the soil particle or sediment and enters into surface runoff. The adsorption – desorption between the adsorbed chemical, soil particle and erosion sediment are generally believed to take place throughout the entire rainfall-runoff-soil erosion process (Zheng *et al*. 2005). The effect that surface runoff has on a solid chemical before severe soil erosion starts is simply ascribed to the results of desorption between surface runoff and eroded sediment. According to the indoor oscillation test of a certain percent of soil and water, Sharpley (1981) put forward an equation which describes the process of soil P desorption.

$$P_t = A\ P_o\ t^{\alpha}\ W \tag{8}$$

where:
P_t – P desorption amount at time t (mg/kg)
P_o – first desorption amount of soil P (mg/kg)
W – ratio between water and soil
A, α – empirical constants for special soil

Ahjua and Lehman (1983) considered the interaction process of rainfall-runoff-surface soil chemical to be similar to the indoor oscillation. Different rainfall, runoff and soil characteristics impacted on the water to soil ratio and the soil chemical transfer (Sharpley 1985). Soil erosion aggravates the complexity of surface chemical release and transport which is also influenced by physicochemical properties of chemicals to a certain extent (Ahuja & Lehman 1983; Liu *et al.* 2018). According to the experiments of this paper, when severe sheet erosion occurs, the sediment intensity begins to increase. It indicates that the soil erosion has a great influence on the concentration of chemicals (especially adsorbed chemicals) in surface runoff. The turbulent transport of runoff and sediment can be considered as an oscillation extraction process. It means that the influence of soil erosion can be taken as a dynamic release process of chemicals between runoff and sediment. Then Eq. (6) can be simplified like this

$$P_t = k\,t^a \tag{9}$$

where:
k, a – empirical constants

Constant k is associated with sediment ratio and erosive ability of overland flow, while a mostly reflects desorption and dissolution of chemicals from runoff, affected by rainfall, soil physicochemical properties, and properties of chemicals.

The sediment will continually be deposited along with the transport process. Soil chemicals are leached and desorbed by surface runoff; meanwhile the sediment also has some adsorption for chemicals. Thus, the dynamic process can be described as

$$c_{rs}(t) = \sum_{i=1}^{n} k_i t^{\alpha i} \tag{10}$$

where:
k_i, a_i – parameters

Substitute Eq. (7) and (10) into Eq. (5) and (6), respectively. Then unify them into Eq. (2). The result is

$$M_r = \int_0^t \left(k_m c_{so} t^b + \sum_{i=1}^{n} k_i t^{\alpha_i} \right) \times r(t)/1000\,dt \tag{11}$$

The derivative is

$$c_r = k_m c_{so} t^b + \sum_{i=1}^{n} k_i t^{\alpha_i} \tag{12}$$

RESULTS AND DISCUSSION

Soil and water loss in the runoff process. Surface runoff occurs when the rainfall intensity exceeds the infiltration capacity of soil (Kleinman *et al.* 2006). It is evident that the runoff occurred in about 4 min after the rainfall began (Figure 3A and Table 2). The runoff coefficient, the ratio of surface runoff to rainfall, quickly increased from 0.18 to 0.60 in the following 15 min or so, and then it was stable in the range of 0.60–0.85. The total runoff of each slope nearly linearly increased with the rainfall duration as shown in Table 2. It is consistent with the former studies (Guo *et al.* 2010; Zhao *et al.* 2014). The splash erosion was dominant in the initial stage of the rainfall. Then the soil particles were rushed away by the surface runoff and the sheet erosion tended to be dominant in the following rainfall. On the other hand, the soil may become compacted by raindrop strikes, so resulting in crust formation and a decrease in erosion consequently (Luk & Cai 1990; Tao *et al.* 2017). With the sustained rainfall, in 60 min or so after the rainfall began, severe sheet erosion occurred in the lower part of the slope; some slight ditches even appeared later. Although there was

Table 2. Soil and water loss, loss of chemicals in surface runoff and sediment

Rainfall duration	t_p	Rainfall amount	Runoff amount	Average sediment content in runoff	Chemical loss amount in runoff			Enrichment ratio of chemical in sediment		
					Br^-	PO_4^{3-}	K^+	Br^-	PO_4^{3-}	K^+
(min)		(mm)		(kg/m³)	(mg/m²)					
30	4.18	45	14.33	7.24	15.25	3.68	18.1	0.51	1.95	0.76
60	4.30	90	44.90	4.09	22.08	6.12	23.28	0.37	1.93	0.82
90	3.93	135	83.37	3.74	25.34	18.56	56.8	0.35	1.99	0.74
120	4.75	180	120.95	3.34	27.12	31.44	71.98	0.34	2.35	0.90
150	4.62	225	144.51	4.23	31.76	35.76	83.42	0.35	2.99	1.07

t_p – the time surface runoff begins on the slope

not an evident increase of the runoff coefficient, the sediment intensity (g/min), eroded sediment yield per 1 min, increased as a result of some soil particles below the surface soil entering into the runoff (Figure 3B). Because of the increasing runoff yield, the average sediment content in runoff for each slope decreased with the duration, on the whole.

Total loss of chemicals in runoff and sediment. As shown in Table 2, the total loss of chemicals in runoff increases with the duration of rainfall, especially that of PO_4^{3-} and K^+. Because the soil tank is so small, there was no severe rill erosion. The sediment yield of 1-min sample was so small to test all the chemical content, so we mixed all the sediment samples for each slope. With the longer duration of rainfall, the enrichment ratio of Br^- in sediment decreased, while those of PO_4^{3-} and K^+ increased on the whole. There was not any enrichment with Br^- in sediment, most of the enrichment ratios of K^+ were less than 1, and the enrichment ratio of PO_4^{3-} was more than 1.9. The loss amount of Br^- in sediment was always 13%~26% of that in surface runoff; the ratio of PO_4^{3-} was 2.98~12.05 and that of K^+ was 4.91~12.91. It indicates that Br^- (representing a non-adsorbed chemical) is mainly transported with surface runoff and PO_4^{3-} (representing an adsorbed chemical) is mostly transported with sediment (Ahuja 1982; Havis *et al*. 1992; Guo *et al*. 2010). Because K^+ is an adsorbed exchangeable chemical and the soil on the Loess Plateau in China usually has plenty of K^+, more K^+ is adsorbed in sediment than in surface runoff.

Loss of chemicals and concentration change in surface runoff. The surface release of Br^- into surface runoff occurred mainly in the initial 60 minutes of rainfall duration, especially within the first 30 minutes

(Figure 4A). The cumulative loss of Br^- for the rainfall duration of 30 min experiment was 72.1%, 51.0%, 48.5%, and 42.7% of that of 60, 90, 120, and 150 min experiment, respectively. With the strongest adsorption, the loss of PO_4^{3-} in the initial stage of surface runoff is mainly from the solid state (hit by raindrop splash or driven by sheet erosion), and some liquid state in topsoil. With the longer duration of rainfall, mobile PO_4^{3-} in the topsoil was diminished and there was no subsequent replenishment from the lower layers of soil; and the suspended soil particles were moved away one by one. Therefore, the content of soluble PO_4^{3-} and the loss of PO_4^{3-} in runoff decreased rapidly nearly to zero within 30 min after the surface runoff occurred. Because severe sheet erosion occurred at the time of 60 min or so after the rainfall began, the topsoil came into surface runoff and the lower soil lost its protective layer, then the loss of PO_4^{3-} began to increase (Figure 4B). The cumulative loss of PO_4^{3-} in 60 min of rainfall duration for each slope was 70.4%, 47.3% and 36.3% of that in 90, 120 and 150 min of rainfall duration, respectively. It shows that for the adsorbed chemicals, the time when the severe sheet erosion occurred was the increasing time of the loss amount curve. It reveals that much more PO_4^{3-} release and transport with surface runoff was in the period when it was dominated or controlled by severe or complex soil erosion. The surface output of K^+ was between that of Br^- and PO_4^{3-} (Figure 4C). The cumulative loss of K^+ in 30-min rainfall duration experiment is 77.7%, 31.9%, 25.1% and 21.7% of that in 60, 90, 120 and 150 min, respectively. The cumulative release amount of K^+ in 90-min duration is 72.2% and 51.7% of that in 120 min and 150 min, respectively.

Figure 5 shows that the concentration of chemicals in surface runoff was rapidly reduced in 30 min after
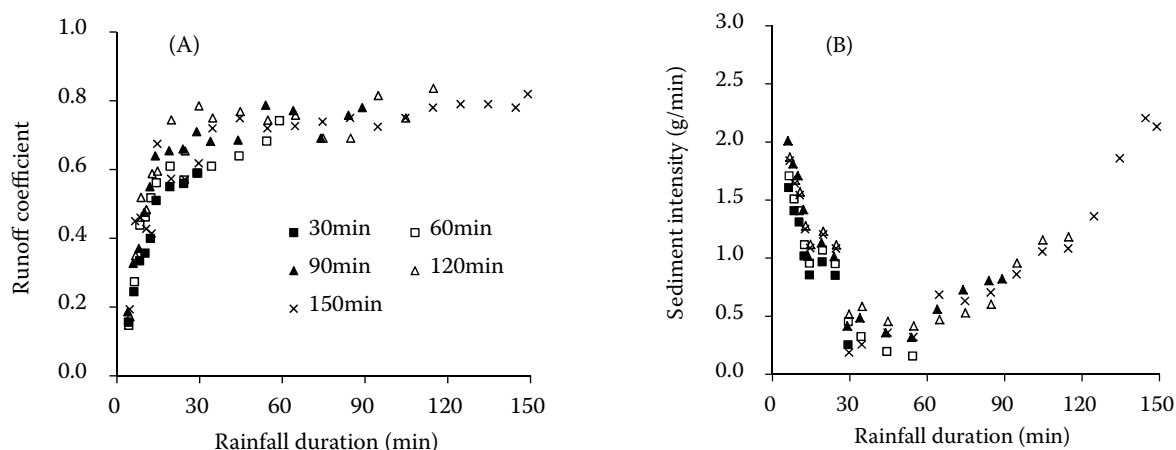

Figure 3. Runoff coefficient (A) and sediment intensity (B) during the runoff process
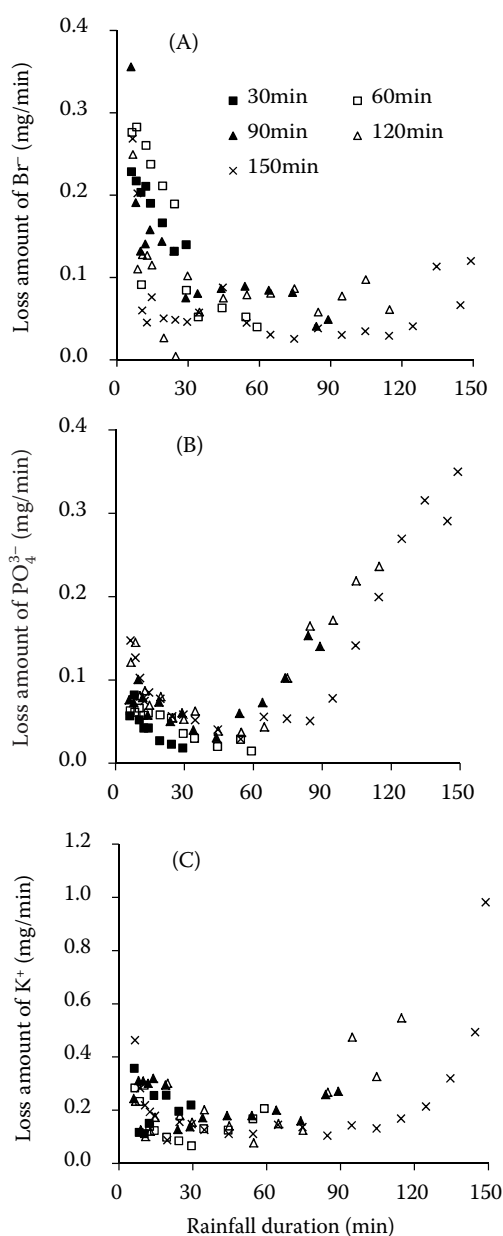
Figure 4. Loss of chemicals in surface runoff during the runoff process: Br⁻ (A), PO₄³⁻ (B), K⁺ (C)

Figure 4. Loss of chemicals in surface runoff during the runoff process: Br^- (A), PO_4^{3-} (B), K^+ (C)

Figure 5. Concentration of chemicals in surface runoff during the runoff process: Br^- (A), PO_4^{3-} (B), K^+ (C)

the surface runoff occurred. Most of Br^- in the surface soil was lost with infiltrating water before the runoff began, and immediately after it began (Ahuja 1982). Then the loss of Br^- became stable till to the end of rainfall events, less susceptible to the later soil erosion (Figure 5A). The concentrations of PO_4^{3-} and K^+ decreased rapidly nearly to zero in 30 min and then they also remained stable later (Figure 5B, C). At the time of 60 min after the rainfall began, the concentration of PO_4^{3-} started rising while that of K^+ rose in 90 min or so. As mentioned above, both the
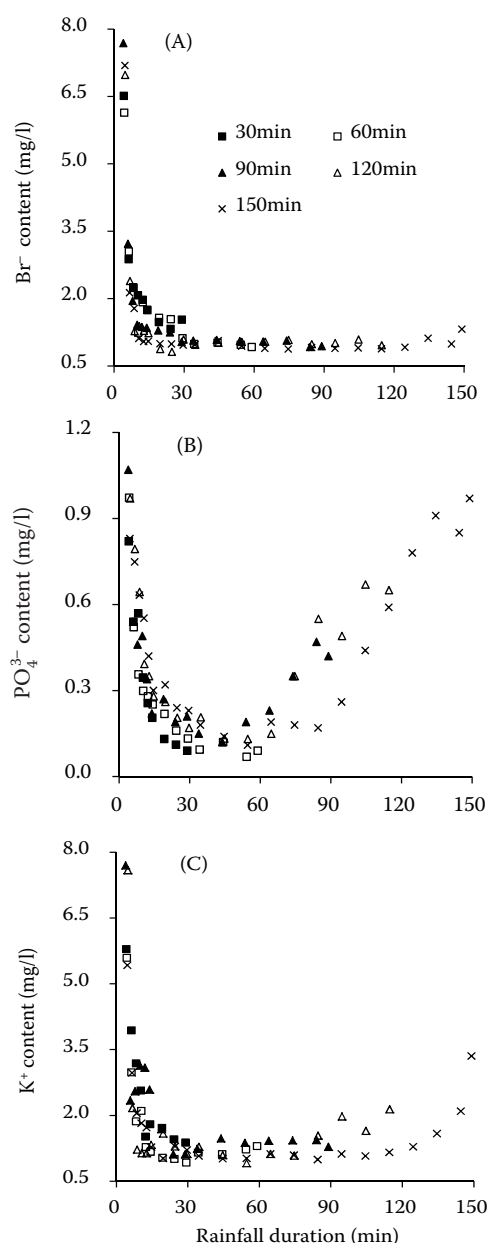
strong runoff scouring and the complex soil erosion play important roles in the release and transport of adsorbed chemicals with runoff (Zheng *et al.* 2005). It reveals that the output process of adsorbed chemicals can reflect the soil erosion change to a certain extent, especially for PO_4^{3-}.

Comparison of power function and exponential one in modelling the concentration of chemicals in surface runoff. Several studies have indicated that the transport of chemicals on a loess slope with unsaturated soil usually has two forms under the

rainfall conditions (Wang *et al.* 1998; Liu *et al.* 2018). On the one hand, the soil chemical is moving with infiltration water after the rainfall begins. On the other hand, when the soil infiltration capacity is lower than the rainfall intensity, the surface runoff occurs (Kleinman *et al.* 2006). The soluble chemicals are transported with surface runoff, and the adsorbed ones are transported with erosion sediment (Guo *et al.* 2010; He *et al.* 2014).

Due to severe soil erosion and usual drought on the loess slope the concentration of chemicals in surface runoff does not decrease there as quickly as that under slight erosion and high soil moisture. Wang *et al.* (1998) stated that the power function describes the chemical concentration change in surface runoff much better than does the exponential function. It is so because the exponential model is good at simulating the process that changes rapidly with time and is not suitable to describe the concentration in a stable stage. The power function and the exponential one are used to model the concentration of chemicals in surface runoff during the whole runoff process (Table 3). The results show that when the rainfall duration is 30 min or 60 min, both these functions can well reflect the chemical concentration change, while the power function does better than the exponential one to some extent. For non-adsorbed Br^-, when the rainfall time is more than 90 min, the correlation of exponential function decreases from the most significant correlation to a non-significant level. For adsorbed PO_4^{3-}, when the rainfall time is more than 60 min, its concentration increases by the influence of soil erosion, and neither power function nor exponential one can well describe the variation process. For adsorbed exchangeable K^+, neither of them is suitable for 120- and 150-min experiments.

Modelling the concentration of chemicals in surface runoff by polynomial equation. When surface runoff occurs, molecular diffusion and mechanical dispersion is assumed to be the primary migration drive of chemicals within the mixed layer (Wallach *et al.* 1988; Zhang *et al.* 1999). Soil erosion in early rainfall is mainly raindrop splash erosion or slight sheet erosion, which drives some dispersed soil particles into the surface runoff (Gao *et al.* 2005; Yang *et al.* 2016). Therefore, according to Eq. (12) formulated in this paper, the concentration of chemicals in the early stage is determined by the first right item of the equation. When severe soil erosion appears, more and more soil particles are released into the surface runoff and the erosion modulus increases (Zheng *et*

Table 3. Parameters, correlation coefficient and correlation significance of power function and exponential function simulating the concentration of chemicals in surface runoff

| | Br⁻ | | | | | | | | PO₄³⁻ | | | | | | | | K⁺ | | | | | | | |
| | $C_r(t)=at^b$ | | | | $C_r(t)=ce^{dt}$ | | | | $C_r(t)=at^b$ | | | | $C_r(t)=ce^{dt}$ | | | | $C_r(t)=at^b$ | | | | $C_r(t)=ce^{dt}$ | | | |
t	a	b	r	$s.$	c	d	r	$s.$	a	b	r	$s.$	c	d	r	$s.$	a	b	r	$s.$	c	d	r	$s.$
30	11.685	−0.686	0.907	++	4.001	−0.045	0.776	+	5.337	−1.213	0.985	++	0.939	−0.090	0.964	++	15.754	−0.762	0.931	++	4.876	−0.052	0.849	++
60	8.685	−0.583	0.897	++	2.798	−0.023	0.773	++	2.708	−0.884	0.978	++	0.512	−0.037	0.896	++	6.060	−0.479	0.780	++	2.194	−0.015	0.616	+
90	6.028	−0.458	0.825	++	2.145	−0.012	0.623	++	0.759	−0.287	0.504	+	0.347	−0.004	0.186	–	7.103	−0.421	0.807	++	2.759	−0.011	0.549	+
120	3.659	−0.321	0.660	++	1.601	−0.006	0.434	–	0.588	−0.161	0.252	–	0.319	0.002	0.084	–	2.528	−0.156	0.330	–	1.541	−0.001	0.058	–
150	3.065	−0.268	0.631	++	1.433	−0.004	0.381	–	0.424	−0.037	0.060	–	0.288	0.004	0.291	–	2.859	−0.180	0.415	–	1.569	−0.001	0.105	–

t – rainfall duration; a, b – parameters of the power function; c, d – parameters of the exponential function; r – correlation coefficient between $C_r(t)$ and t; the number of runoff samples for these 5 rainfall experiments was 9, 13, 16, 18 and 22, respectively; $r_{0.01}$ – correlation coefficient of critical test statistics at the 0.01 significance level, and $r_{0.05}$ is correlation coefficient at the 0.05 level; for the number of these samples, $r_{0.01}$ is 0.798, 0.684, 0.623, 0.59 and 0.537, respectively; $r_{0.05}$ is 0.666, 0.553, 0.497, 0.468 and 0.423, respectively; $s.$ – correlation significance; ++ the most significant correlation with $r \geq r_{0.01}$; + significant correlation with $r_{0.01} > r > r_{0.05}$; – non-significant correlation with $r < r_{0.05}$

Table 4. Coefficients of the relationship and fitting effect of the polynomial function between the concentration of chemicals in surface runoff and rainfall duration

Modeling polynomial	Relation coefficient of Br^-			Relation coefficient of PO_4^{3-}			Relation coefficient of K^+		
	90 min	120 min	150 min	90 min	120 min	150 min	90 min	120 min	150 min
Quadratic	0.629++*	0.519+†	0.499+	0.796++	0.806++	0.925++	0.703++	0.659++	0.704++
Cubic	0.756++	0.656++	0.594++	0.879++	0.930++	0.970++	0.799++	0.736++	0.728++
Quartic	0.849++	0.757++	0.695++	0.905++	0.940++	0.970++	0.831++	0.797++	0.865++
Quintic	0.913++	0.841++	0.776++	0.948++	0.964++	0.98++	0.847++	0.881++	0.891++

++ the most significant correlation; + significant correlation

al. 2005). The major transfer mechanism of chemical output may be desorption when the surface runoff works on chemicals adsorbed by eroded sediment, which can be reflected by the second item in Eq. (12). So there is an evident increase of the concentration of chemicals in surface runoff.

The process of a change in the surface runoff chemical concentration was simulated by 2, 3, 4 and 5 polynomials in experiments with 90-, 120- and 150-min rainfall duration in which severe sheet erosion occurred (Table 4). At the same time, the results are compared with those of the power function as shown in Table 3. It shows that for adsorbed PO_4^{3-} and K^+ the correlation coefficient can achieve the most significant correlation level by these polynomials, better than the results of the power function. However, it is not so good for non-adsorbed Br^- by 2 polynomial equations.

Obviously, under the conditions of complex or severe water erosion, for the loss of adsorbed chemicals in runoff, it is necessary to study all the complex dynamic mechanism, convection – dispersion – desorption, and so on; for mobile chemicals, convection – dispersion should be mainly taken into account. There is often a heavy rainfall during summer and earlier autumn causing severe and complex soil erosion (sheet, rill or shallow gully, etc.) on the Loess Plateau of China (Zheng *et al.* 2005). These different soil erosion patterns usually have different soil detachment and transport capacities; therefore, they will have different impacts on the loss of soil chemicals (Zheng *et al.* 2005). The future studies should combine the simulation with field experiments on the Loess Plateau.

CONCLUSION

The runoff volume of each soil tank is linearly increasing with the rainfall duration, while the sediment content in runoff is decreasing on the whole. After severe sheet erosion occurs on the slope, sediment intensity will soon increase. Under the conditions of splash erosion and severe sheet erosion, the concentration of Br^- in surface runoff can be divided into two stages, firstly decreasing and then flat. The PO_4^{3-} and K^+ concentration curve can be divided into three stages, firstly decreasing, then flat, and finally increasing. Their increase occurs after severe sheet erosion begins.

Experiments validated that compared with the exponential function, the power function is more suitable for fitting the change of chemical concentration in runoff with non-saturated soil on the loess slope, while neither of them can fit the concentration change of adsorbed chemical if severe erosion began. The chemical transport under severe soil erosion conditions seems to be a dynamic release process between surface runoff and sediment. The polynomial model under the conditions of water erosion, based on convection-dispersion and desorption kinetics, was established. It was found more suitable to simulate that process than the power function, especially for adsorbed chemicals. Obviously, under the conditions of complex or severe water erosion, a different dynamic mechanism for the release and transport of adsorbed chemicals and mobile ones in surface runoff should been taken into account.

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