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Experimental studies on the transport of copper down the soil profile and in runoff during rainfall

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Abstract

The widespread use of fertilizers that contain copper have led to concern about the contamination of groundwater. The vertical movement of labile copper down the soil profile has been studied by many researchers. Little research, though, has investigated the mobility of copper in runoff during rainfall. Laboratory experiments were conducted to determine the distribution and transport of copper down the soil profile and in the runoff under conditions of simulated rainfall. Two soils (loam and sandy loam), three initial soil-moisture contents (5%, 15%, and 20%, measured gravimetrically) and three intensities of rainfall (60, 96, and 129 mm h^{-1}) were used to evaluate the effects of these variables and their interactions on the movement of copper vertically down the soil profile and horizontally in runoff. The results indicated that the transport of copper into runoff and movement with the runoff from rainfall was affected by the soil type, soil-moisture content, and intensity of rainfall. The mean copper-ion content in the runoff from the sandy loam was 1.25 times greater than that observed from the loam, increased 0.436 times when the soil-moisture content increased 5% between 5% and 20%, and increased 0.64 times when the intensity of rainfall increased 30 mm h^{-1} between 60 mm h^{-1} and 129 mm h^{-1}. The results from this study show that copper enters and is transported by the runoff from rainfall. The prolonged application of fertilizers containing copper may thus pose an environmental risk.

Keywords: Copper, Vertical transport, Rainfall, Runoff.
Abbreviation: DTPA-diethylenetriaminepentacetic acid; TEA-triethanolamine; SMC-soil moisture content.

Introduction

Fertilizers that contain copper have been widely applied on the Loess Plateau in China for the past two decades to increase crop production (Wei et al., 2007). Copper and zinc are two metals that are consistently added to soils in increasing quantities in the form of fertilizers, pesticides, livestock manures, sewage sludge, and industrial emissions (Adriano, 1989). Continuous heavy use of manure and agrochemicals may pose environmental problems (Tekwa et al., 2010); for example, the pollution of ground and surface waters due to leaching and runoff of organic matter and nutrients, and the accumulation of heavy metals in the soil (Wadman et al., 1987). Heavy metals are significantly toxic to humans, animals, micro organisms, and plants (Shi et al., 2009, Ogbuehi et al., 2011). Studies have shown that applications of fertilizers containing copper have resulted in severe environmental problems in France (Flores-Veles et al., 1996), Australia (Pietrzak and McPhail, 2004), India (Prasad et al., 1984), Sweden (Bengtsson et al., 2006), and the United States (Alva, 1993). The role of heavy metals in the environment is directly related to their physicochemical forms (Stumm et al., 1996; Ure and Davidson, 2002). Copper is present in a variety of forms and is associated with various soil components. The nature of such associations affects the availability and mobility of copper in soils (Kabata-Pendias and Pendias, 1992; Singh, 1997; Ahumada et al., 1999). Although copper is generally considered to be relatively immobile in most soils for short periods, it can be transported rapidly by runoff. Water-soluble and exchangeable forms of copper are readily available and mobile. The distribution of labile copper in the soil profile can be used to assess the vertical transport of copper (Wei et al., 2007). Copper that is present in the crystalline lattice of clays appears to be relatively immobile and unavailable. The various forms in which copper can be present, i.e. precipitated as carbonate, occluded in Fe, Mn, and Al oxides, or complexed with organic matter, can be considered to be relatively labile or unavailable, depending on the actual combination of physical and chemical properties of the soil (Sposito et al., 1982; Shuman, 1985; Wei et al., 2007). Wei et al. (2007) have shown that the upper 15 cm of the soil profile contains approximately 41% of the total and approximately 66% of the labile copper from the long-term application of copper fertilizers in agricultural systems. Copper can thus be readily washed away in runoff and is particularly likely to be transported as a result of rainfall. Many studies have examined the subsurface migration of copper (Karathanasis, 1999; Jenn and Shang, 2001; Wei et al.2007; Businelli et al., 2009; Long et al.2010; Chen et al.2010), but little information is available on the transport of copper associated with runoff and its migration down the soil profile as a result of rainfall. The objectives of this study were: (i) to investigate the vertical movement of labile copper through the soil profile during single rainfalls and to examine the relationship between the transport of labile copper in the soil profile and the initial soil moisture content (SMC), rainfall intensity, and soil type, and (ii) to determine how copper enters and is transported by runoff, its movement in runoff during rainfall, and the effects of initial SMC, rainfall intensity, and soil type on the transport of copper via runoff.

Results and Discussion

Different kinds of soil affect the transport of copper in the soil profile and runoff

Different soil types exhibit different characteristics of copper adsorption. The contents of clay and organic matter differed in the two soils examined, loam and sandy loam; these components play an important role in the adsorption of copper ions (Dhillon et al., 1981; Joshi, 1986; Yu et al., 2002) (table 1). In addition**,** infiltration during rainfall varied according to soil type. The degree of infiltration had a profound impact on the content of copper in the runoff. As a result, the transport of copper down the soil profile and in aboveground flow differed for the two soils when exposed to rainfall. Fig. 1 shows that the copper content in the two soil profiles changed with depth after 90 minutes of rainfall. The results indicate that the transport of copper down the soil profile was affected by soil fractions in different ways, associated with their capacity for adsorption-desorption, precipitation, complexation, and occlusion. These processes depend on factors such as the nature of the mineral and organic constituents, the composition of the soil solution, soil texture, $CaCO_3$ content, pH (Msaky and Calvert, 1990; Alva et al., 2000, Wei et al., 2007), and the rate of water infiltration. Table 1 shows that the amounts of clay and organic matter were higher, and the pH values were lower, in the loam than in the sandy loam. Some researchers (Zou and Mo, 1995; Alva et al., 2000) have shown that soil pH is negatively correlated, and contents of organic matter and clay are positively correlated, with labile copper (Yuan, 1983), which may partly explain the results presented in Fig. 1. The loam contained more labile copper than the sandy loam (Fig. 1) in the 0-15 cm soil layer; the average copper content in loam was 1.089 times higher than in the sandy loam. The results indicate that labile copper is more readily transported in the sandy loam than in the loam under the same conditions of rainfall. Fig. 2 shows the difference in water content of the two soils after rainfall. The water had penetrated deeper in the sandy loam (32 cm) than in the loam (24 cm). The cumulative infiltration was 125.63 mm for sandy loam and 121.85 mm for loam after 90 minutes at an intensity of rainfall of 90 mm h^{-1}. The greater infiltration promoted the transport of copper down the soil profile. Rainfall causes labile copper to move down through the soil profile and to be transported away via runoff. The two soils exhibited different characteristics of copper adsorption and capacities for infiltration, so the copper-ion contents of the runoffs were different (Fig. 3a). The mean copper-ion contents in the runoff were 0.0172 mg l^{-1} from the loam and 0.0215 mg l^{-1} from the sandy loam. The mean content of copper ions in the runoff from the sandy loam was 1.25 times greater than that observed from the loam. These figures indicate that the transport of copper via runoff differs according to the characteristics of copper adsorption of the soil. The copper-ion content in runoff changed with time from the onset of rainfall, as has been recorded for gypsum (Zhang et al.1997), phosphorus (Gao et al., 2004), and bromine (Ahuja, 1990). The copper-ion content in the runoff decreased in the initial few minutes and then became stable. Less copper was transported in the runoff from the sandy loam than from the loam (Fig. 3b). The mean runoff volume per minute for loam and sandy loam were 1.31×10^{-3} and 0.937×10^{-3} m^3 (Fig. 3c), respectively, even though the mean copper content in the runoff was higher from the sandy loam than from the loam. The cumulative loss of copper via runoff from the loam was 1.13 times greater than from the sandy loam (Fig. 3d). Table 2 shows that the average copper contents in the runoffs of the two soils were significantly different, but the average rates of copper loss via runoff were not significantly different. One possible explanation for these observations is that the loam had a stronger affinity for, and contained less, labile copper than the sandy loam. Even though the runoff volume for loam was higher, less copper leached out, so the average rates of copper loss via runoff were nearly the same in the two soils.

Effects of initial soil moisture on the transport of copper in the soil profile and runoff

Each soil type has a characteristic ability to adsorb copper ions. The vertical transport of labile copper in this study was affected by rate of infiltration, which was controlled by the initial SMC under standard conditions of rainfall. SMC affects both infiltration and the cohesion of soil particles; the amount of water that can penetrate the soil via infiltration has a profound impact on the mass of sediment and the content of solutes in the runoff. Fig. 4 shows that the copper content for different initial SMCs varies with depth after rainfall. The fluctuation in copper content in the soil profiles for initial SMCs of 15% and 20% was greater than when the initial SMC was 5% (Fig. 4). The average copper content in the 0-15 cm soil layer for an initial SMC of 15% was 1.049 times higher than for an SMC of 5%, and the average copper content in this layer for an initial SMC of 20% was 1.012 times higher than for an SMC of 15%. These results suggest that the amount of infiltration (Fig. 5) has an impact on the downward movement of copper, although the differences were not significant under our experimental conditions. Table 3 shows that both the average copper contents in the runoff and the average copper losses via runoff were significantly different for three water contents. Higher initial SMCs were associated with reduced infiltration and larger volumes of runoff per unit time (Fig. 6a), thus affecting the copper content in the runoff (Fig. 6b). Fig. 6b shows that, in our experiment, the higher the initial SMC, the higher the copper content in the runoff. Inspection of Figs. 6a-c reveals that the copper loss via runoff and the copper content in the runoff stabilised about 21 minutes after runoff commenced, and the runoff volume stabilised after about 13 minutes. These results imply that copper content affects the loss of copper via runoff. The initial SMC thus plays a major role in determining the extent of copper transport via runoff. At an initial SMC of 15%, the copper content in the runoff was about 1.48 times larger than when the initial SMC was 5%. At an initial SMC of 20%, the copper content in the runoff was 1.31 times larger than when the initial SMC was 15%. The mean copper -ion content in the runoff increased 0.436 times when the SMC increased 5% between 5% and 20%. Copper losses via runoff when the initial SMCs were 5%, 15%, and 20% amounted to 0.457, 0.692, and 0.943 mg, respectively, equivalent to 0-0.039, 0-0.060, and 0-0.081 mm layers of labile copper in the soil profile. Fig. 6d shows the changes in cumulative copper transport with runoff since its onset under three initial SMCs. The cumulative losses of copper mass via runoff after 90 minutes of rainfall for the different initial SMCs were, from largest to smallest, 20%>15%>5%.

Effects of rainfall intensity on the transport of copper in the soil profile and runoff

Rainfall intensity had a strong influence on runoff volume and copper losses via runoff because it determined the supply of water to the system and affected the level of erosion. All other things being equal, the heavier the rainfall intensity, the greater will be the flow of water, runoff volume, and the capacity of splashes from raindrops to cause erosion. Heavier rainfall caused increasingly early runoff at a given SMC but also

Table 1. Selected properties of the two soils.

Soil	Particle size distribution (%)			Organic matter g kg^{-1}	$CaCO_3$ g kg^{-1}	Total Phosphorus g kg^{-1}	Total Potassium g kg^{-1}	Total Nitrogen g kg^{-1}	pH	Bulk density g cm^{-3}	Saturated water content cm^{-3}cm^{-3}
	Clay ＜0.002	Silt 0.002-0.05	Sand ＞0.05								
Loam	31.65	64.03	4.32	9.3	26.8	1.1	18.6	0.71	8.35	1.35	0.38
Sandy loam	15.18	60.11	24.71	6.5	93.5	1.2	1.5	0.62	8.5	1.35	0.346

Table 2. Average copper content in the runoff and average copper loss via runoff for two soils.

Soil type	Average copper content in the runoff (mgl^{-1})	Average copper loss via runoff (mgmin^{-1})
Loam	0.0172a	0.00987a
Sandy loam	0.0215b	0.00874a

Means in the same column with different letters are significantly different at p<0.05.

Table 3. Average copper content in the runoff and average copper loss via runoff for three water contents.

Water content	Average copper content in the runoff (mgl^{-1})	Average copper loss via runoff (mgmin^{-1})
5%	0.0089a	0.0051a
15%	0.0132b	0.0077b
20%	0.0172c	0.0105c

Means in the same column with different letters are significantly different at p<0.05.

reduced the cumulative infiltration prior to the onset of runoff, as shown in Table 4. Little difference in water content in the soil profile was seen under different rainfall intensities (Fig. 7). The transport of labile copper down the soil profile for the different intensities was not significant due to the small differences in infiltration and the strong adsorption of copper, as shown in Fig. 8. The average copper contents in the soil profile were 20.637, 20.633, and 20.626 mg kg^{-1} for rainfall intensities of 60, 96, and 129 mm h^{-1}, respectively. The copper content in the runoff for different rainfall intensities varied with time, as shown in Fig. 9a. Higher rainfall intensities increased the copper content in the runoff. During the first few minutes, the copper content in the runoff decreased sharply as the rainfall intensity increased. Once the copper content had stabilised, heavier rainfall was associated with higher copper content in the runoff (Fig. 9b). The mean copper contents in the runoff for the three rainfall intensities (60, 96, and 129 mm h^{-1}) were 0.016, 0.019, and 0.043 mg l^{-1}, respectively. The total copper lost via runoff for the three rainfall intensities (60, 96, and 129 mm h^{-1}) was 0.533, 1.075, and 3.252 mg, respectively, equivalent to 0-0.046, 0-0.094, and 0-0.283 mm layers of labile copper in the soil profile. The runoff volume increased as rainfall intensity increased, as shown in Fig. 9c. The average runoff volume for the three rainfall intensities (60, 96, and 129 mm h^{-1}) were 0.364x10^{-3}, 0.616x10^{-3}, and 0.834x10^{-3} m^{3}, respectively. At a rainfall intensity of 96 mmh^{-1}, the mean copper content in the runoff was about 1.19 times higher than at a rainfall intensity of 60 mm h^{-1}; the mean copper content in the runoff was 2.24 times higher at a rainfall intensity of 129 mm h^{-1} than at 96 mm h^{-1}. The mean copper-ion content in the runoff increased 0.64 times when the rainfall intensity increased 30 mm h^{-1} between 60 and 129 mm h^{-1}. These results suggest that the copper content in the runoff and the mass of copper lost via runoff were positively correlated with rainfall intensity. Since the loss of copper mass from the soil increased with rainfall intensity, raindrops may promote the transfer of copper into the runoff. The splashing caused by rainfall may have a profound effect on the loss of copper via runoff by virtue of its influence on the desorption of copper from the soil. Fig. 9d clearly shows that the cumulative loss of copper mass via runoff at a rainfall intensity of 129 mm h^{-1} was markedly higher than losses at rainfall intensities of 60 and 96 mm h^{-1}. Table 5 shows that both the average copper contents in the runoff and the average losses of copper via runoff were significantly different under the three rainfall intensities. The cumulative copper lost via runoff at a rainfall intensity of 96 mm h^{-1} was 2.037 times more than at an intensity of 60 mm h^{-1}. The cumulative copper lost via runoff at an intensity of 129 mm h^{-1} was 3.029 times more than at an intensity of 96 mm h^{-1}. These results suggest that when rainfall is sufficiently intense, its capacity to cause erosion (together with that of the water flow) increases, causing the rapid transport of copper from the soil via runoff.

Material and methods

Experimental equipment

Experiments to artificially simulate rainfall were conducted in the laboratory from April to September 2010 at the Institute for Soil and Water Conservation of the Chinese Academy of Sciences, Shaanxi Province, China. The basic equipment used in the experiments was a rainfall simulator (Fig. 10), which could generate a variable intensity of rainfall. The nozzles used to simulate rainfall were 15 m from the soil surface. Six steel soil flumes were used; each flume was 1.0 m long, 0.4 m wide, and 0.5 m high. They were filled with soil to a depth of 0.35 m; this depth allowed infiltration without saturating the lower parts of the flumes and left a 0.15 m 'lip' above the soil level to prevent water losses from splashing. The angle of inclination of the flumes could be varied between 0º and 30º.

Experimental design

Three treatments were designed to allow us to study the relationships among copper content in runoff, soil profile, soil type, initial SMC, and rainfall intensity. One treatment was designed to assess the influence of soil type; two soils, loam and sandy loam, were investigated, with a rainfall intensity of 90 mm h^{-1}, an initial (gravimetric) SMC of 10%, and a gradient of 5^{o}. In a second treatment, three levels of initial gravimetric soil moisture (5%, 15%, and 20%) were used to study the influence of initial SMC on copper loss at a rainfall intensity of 90 mm h^{-1} and a gradient of 5^{o}. The third treatment was designed to investigate the influence of variations in rainfall intensity on the copper content in runoff; three different rainfall intensities (60, 96, and 129 mm h^{-1}) were examined with an initial SMC of 10% and a gradient of 5^{o}.

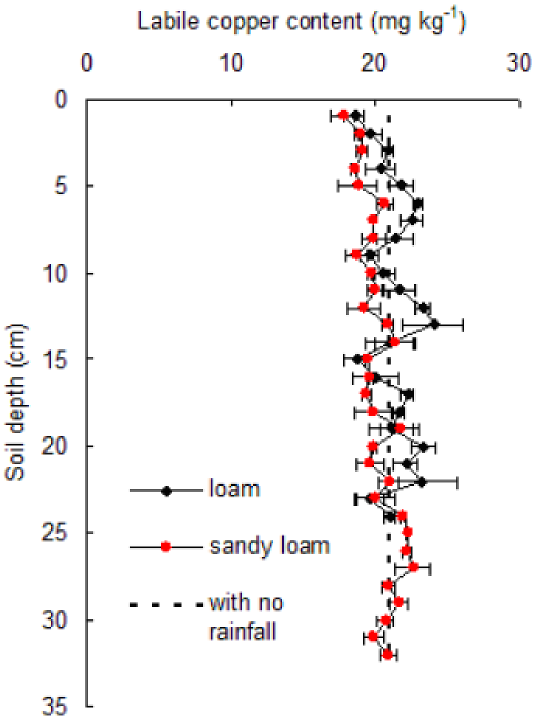

Fig 1. Copper content down the profiles of two soil types after 90 minutes of rain once runoff had commenced. Error bars indicate standard errors.

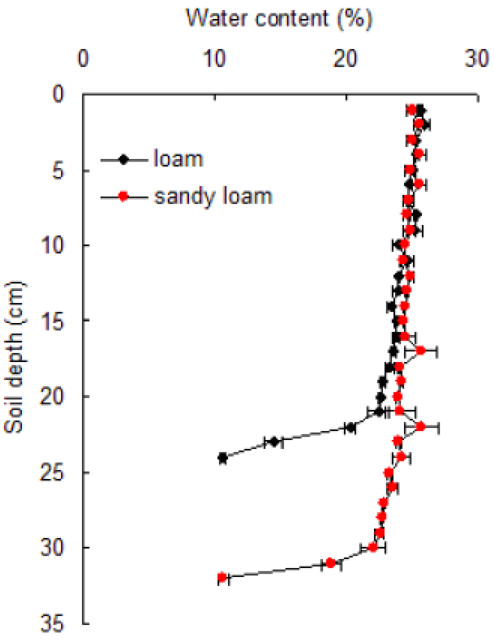

Fig 2. Water content down the profiles of two soil types after 90 minutes of rain once runoff had commenced. Error bars indicate standard errors.

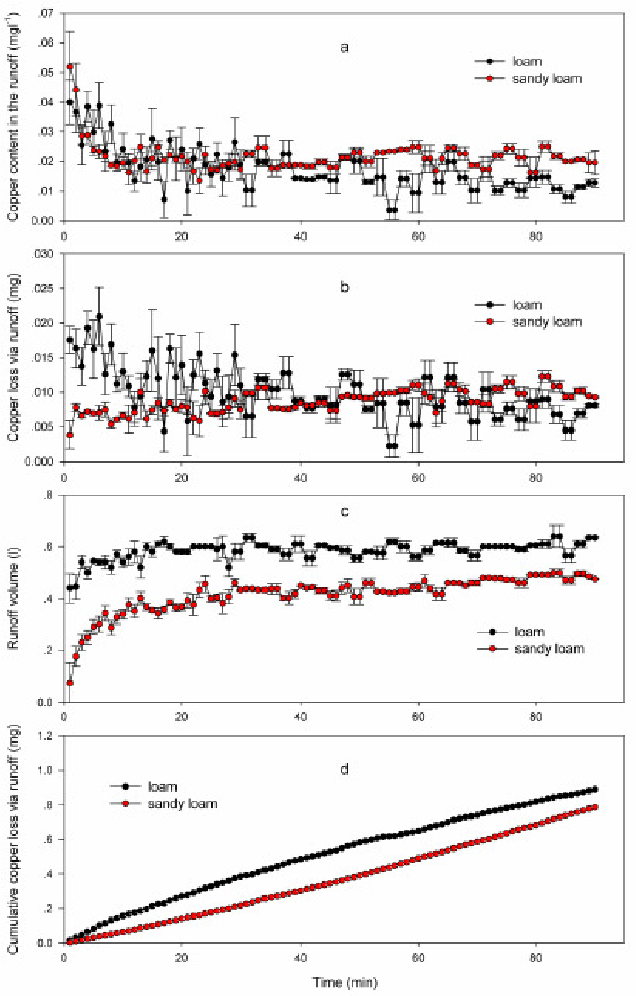

Fig 3. Copper content in the runoff (a), copper mass loss via runoff (b), runoff volume (c), and cumulative copper loss via runoff (d) against time since the onset of runoff and with rainfall continuing. Error bars indicate standard errors.

Experimental process

Samples of loam soil were collected from unfarmed land in Yangling, Shaanxi Province, China. Samples of sandy loam were collected from Ansai, which is also in Shaanxi Province. The physical and chemical properties of the soils are shown in Table 1. The soil samples were passed through a 0.004 m aperture sieve to remove coarse rock and debris, then air-dried (to about 2%, gravimetrically). Cupric nitrate, used as a tracer, was dissolved in water and added to the test soils based on their intended soil water content and the required concentration of cupric nitrate. The soil was then thoroughly mixed. The soil flume was filled with the prepared soil in layers to achieve a dry bulk density of 1.35 g cm^{-3}. To obtain a flat surface, a sharp-edged straight blade was used to remove excess soil. The soil surface was covered with plastic for approximately 24 hours, after which the rainfall experiment was conducted. During the experiment, the outflow from one of the holes in the flume was collected in a fresh plastic container for each one-minute period from runoff onset to 30 minutes and

Table 4. The time between the commencement of rainfall and the onset of runoff, along with cumulative infiltration during this period at different rainfall intensities.

Rainfall intensity (mm h^{-1})	Time between rainfall initiation and onset of runoff (min)	Cumulative infiltration prior to onset of runoff (mm)
60	4.00	4.00
96	2.40	3.84
129	1.70	3.66

Table 5. Average copper content in the runoff and average copper loss via runoff under three rainfall intensities.

Rainfall intensity (mm h^{-1})	Average copper content in the runoff (mgl^{-1})	Average copper loss via runoff ($mgmin^{-1}$)
60	0.016a	0.0059a
96	0.019a	0.0119b
129	0.043b	0.0361c

Means in the same column with different letters are significantly different at $p<0.05$.

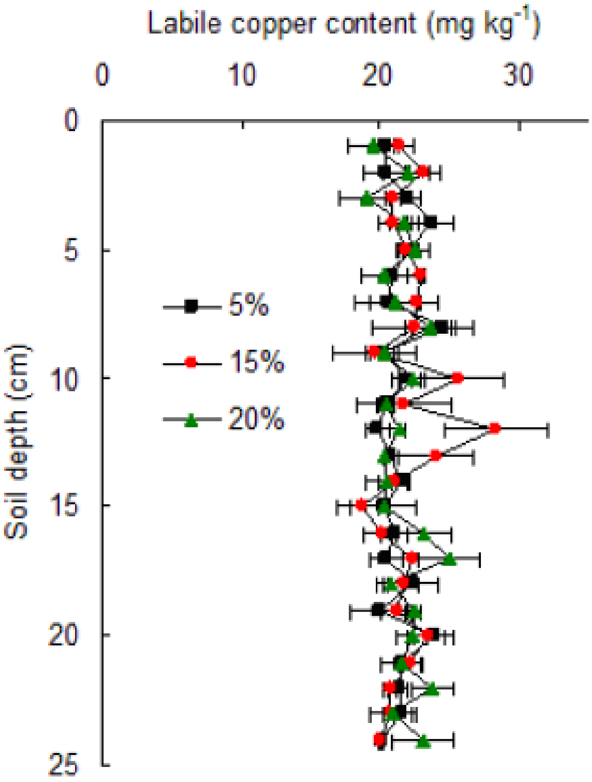

Fig 4. Copper content for three initial soil-moisture contents (5%, 15%, and 20%) in the soil profiles after 90 minutes of rainfall after the onset of runoff. Error bars indicate standard errors.

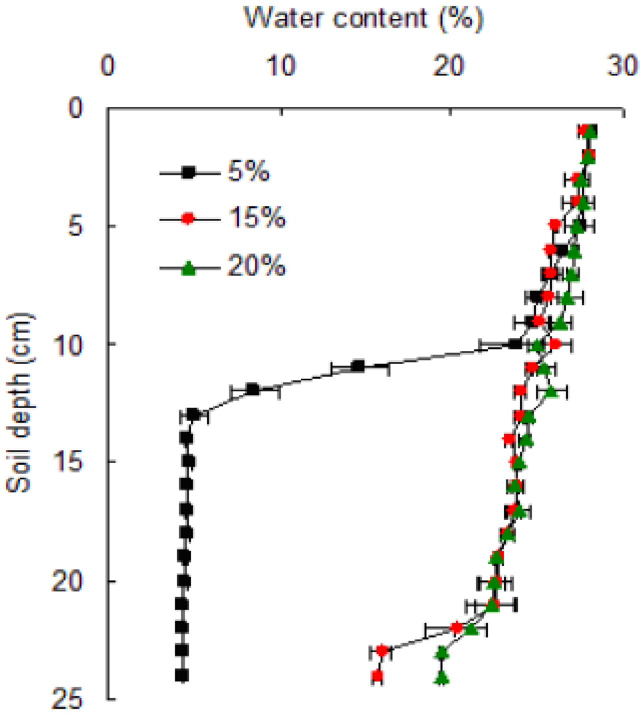

Fig 5. Water content for three initial soil-moisture contents (5%, 15%, and 20%) in the soil profiles after 90 minutes of rainfall after the onset of runoff. Error bars indicate standard errors.

two-minute period from 30 to 90 minutes to measure the volume of runoff and its sediment and the concentration of copper. The time between the onset of runoff and the cessation of rainfall was 90 minutes. Immediately after the rainfall was halted, soil samples were taken at 10 mm intervals along a vertical profile to determine the water and copper contents within the soil. The copper content in the runoff and soil samples was measured using an atomic absorption spectrophotometer. The soil was dried overnight in an ovenat 105 °C for determining water content.

Labile copper in the soil-profile samples was extracted by the DTPA procedure designed for calcareous soils (Lindsay and Norvell, 1978). A volume of 20 mL of 0.005 $molL^{-1}$ DTPA (diethylenetria- minepentaacetic acid) + 0.1 mol L^{-1} TEA (triethanolamine) + 0.01 mol L^{-1} $CaCl_2$ (pH 7.30) was added to 10 g soil (<1.0 mm), and the suspensions were shaken for 2 h at 25°C and then filtered through Whatman No. 5 filter paper. All treatments were replicated three times. The values we present in the results were the averages of the three replicates.

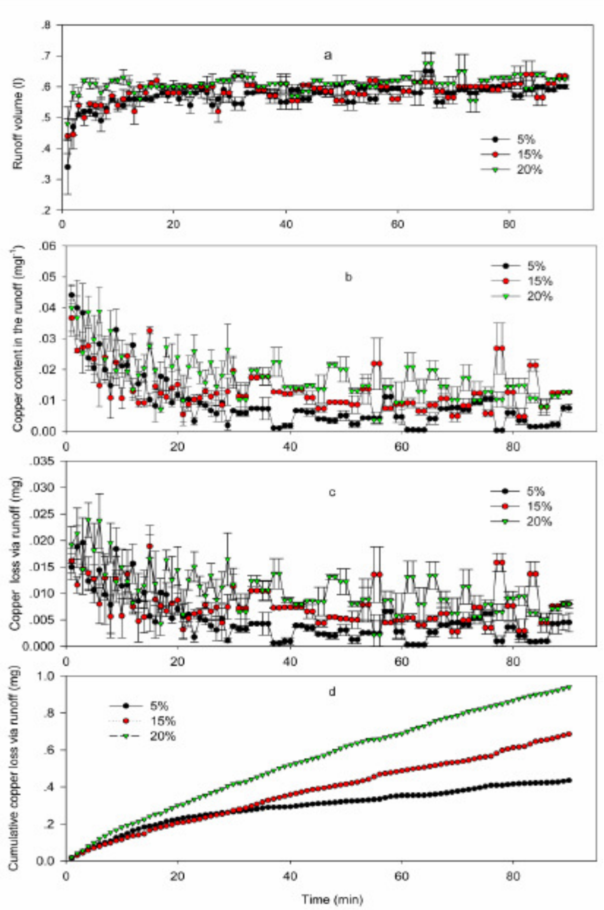

Fig 6. Runoff volume (a), copper content in the runoff (b), copper mass loss via runoff (c), and cumulative copper loss via runoff (d) against time since the onset of runoff and with rainfall continuing under different initial soil-moisture contents (5%, 15%, and 20%). Error bars indicate standard errors.

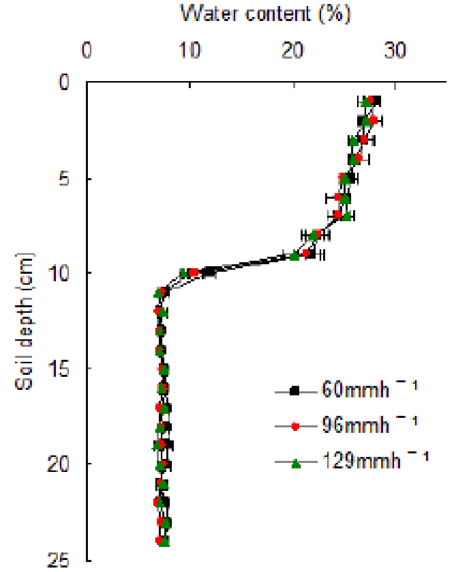

Fig 7. Soil water content for three rainfall intensities (60, 96, and 129 mm h^{-1}) down the soil profile after 90 minutes of rainfall following the onset of runoff. Error bars indicate standard errors.

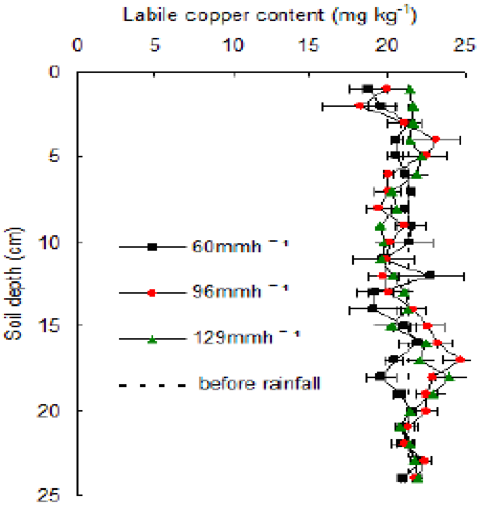

Fig 8. Copper content in the soil profiles for three rainfall intensities (60, 96, and 129 mm h^{-1}) after 90 minutes of rainfall following the onset of runoff. Error bars indicate standard errors.

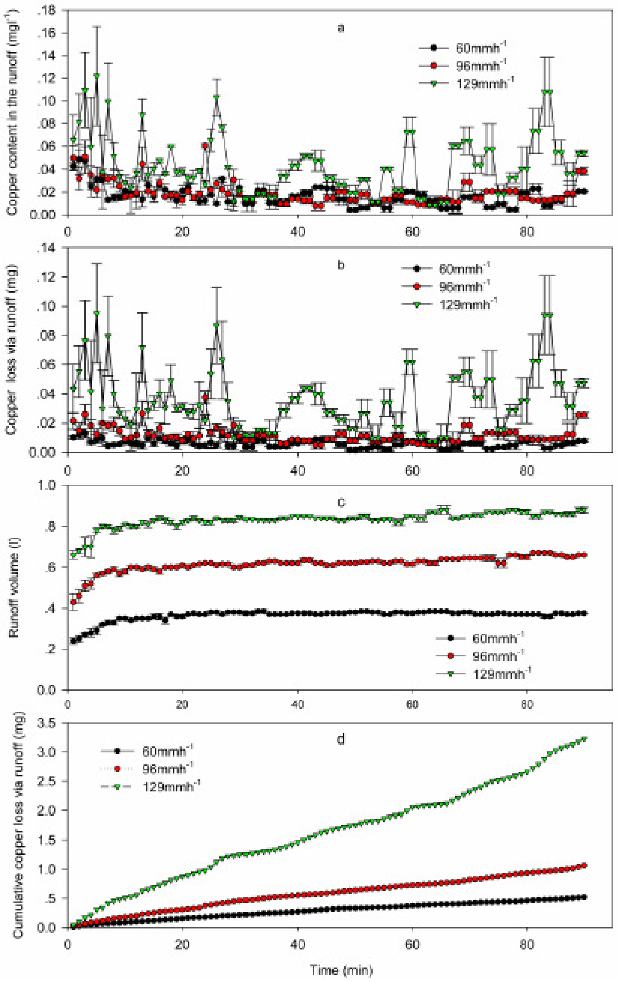

Fig 9. Copper content in the runoff (a), copper mass loss via runoff (b), runoff volume (c), and cumulative copper loss via runoff (d) against time since the onset of runoff and with rainfall continuing under three rainfall intensities (60, 96, and 129 mm h^{-1}). Error bars indicate standard errors.

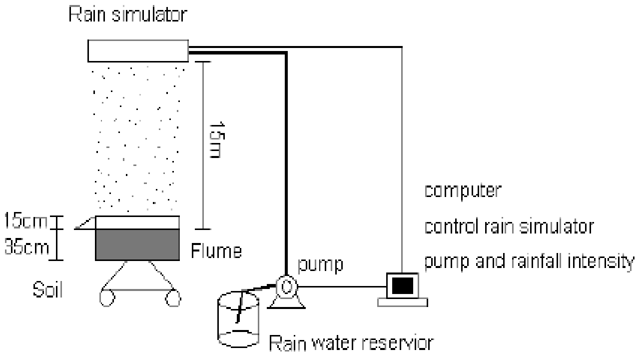

Fig 10. Schematic of the experimental apparatus and setup.

Conclusions

The transport of copper into runoff and the movement of copper with the runoff were examined under experimental conditions of rainfall. The transport of copper down the soil profile was not significant under our conditions of rainfall, but different conditions (soil type, initial SMC, and rainfall intensity) had different effects on the copper transported via runoff. Less copper was lost in the runoff from sandy loam than from loam for different soil characteristics under rainfall. Both copper content in the runoff and copper mass lost via runoff were positively correlated with initial SMC and rainfall intensity when other conditions did not vary. Different conditions produced significant differences in copper content in the runoff and copper lost via runoff. The results of this study suggest that understanding the means by which copper enters runoff and how it is transported in runoff under varying conditions of rainfall is important not only for optimising plant nutrition in agricultural systems but also for avoiding environmental problems.

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