



Effects of simulated acid rain on soil acidification, availabilities and temporal and spatial variations of Cu and Pb in a vegetable field under natural conditions

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Abstract

Under natural conditions, a field trial was introduced to explore influences of soil acidification on availabilities of Cu and Pb and their transferences in soil vertical profiles. Four different levels of simulated acid rain (SAR) were sprayed to the field to acidify the soils so as to observe behaviors of available Cu and Pb. Soil samples were collected from four soil layers: 0~10, 10~20, 20~30 and 30~60 cm. Results indicated that SAR could effectively decrease soil pH of four layers. With the decline of soil pH, contents of available Cu and Pb increased generally and high SAR level resulted in greater increases. In terms of vertical distributions in soil profiles, soil available Cu rose with the depth, indicating a downward movement of Cu to deeper soil layers; while soil available Pb increased only in the layer of 20~30 cm, but decreased dramatically in the deep soil layer (30~60 cm). This suggested that the available Cu was easy to transfer and available Pb was relatively immobile, under the influences of soil acidification. The results also revealed, with the prolongation of soil acidification, contents of soil available Pb increased, whereas contents of soil available Cu decreased, which implied soil available Cu was inclined to be transferred out of soils into groundwater, posing a threat to groundwater system, and soil available Pb was easier to accumulate in soils and be taken up by plants, posing a threat to the food security.

Key words: Field study, soil acidification, heavy metals, Cu, Pb, availability, transference.

Introduction

Soil acidification is getting increasingly common and serious because of environment pollution and unreasonable agricultural practices, which have posed a threat not only to the whole terrestrial ecosystem, but also to farmland quality and food security directly ¹. It has been widely reported that soil acidity highly affected the behavior of heavy metals in soils ²⁻⁷. Soil acidification accelerated activation and release of heavy metals in soils ⁸⁻⁹, which might enter food chain to threaten human and animal health ¹⁰⁻¹³. Copper and lead are considered as greatly hazardous heavy metals and are included in the EPA's list of priority pollutants ¹⁴. They are also major pollutants among various toxic metals in China ¹⁵. Some studies on effects of soil acidification on Cu and Pb drew similar conclusions that low soil pH increased Cu and Pb availabilities and enhanced their release and mobility, and Cu was sensitive to acid and Pb relatively immobile ¹⁶⁻²⁵. However, these conclusions mostly resulted from laboratory experiments or investigations in polluted areas where heavy metals were artificially added. What about natural soils, especially crop soils? To answer the question would be conducive to evaluate and predict the risks of soil acidification and to improve the management of soil resources.

To measure the relationship between soil acidification and availability of heavy metals, most scholars currently adopted soil column experiment in laboratory - reconstructing soil profile in a PVC tube and watering it with simulated acid rain ²⁶, which, however, would unavoidably alter the original soil construction

and components, resulting in great differences in soil acid buffer capacity and water reaction kinetic from natural conditions ¹. Some researchers paid attention to field experiment, under natural field conditions, circling a range of land to be watered with simulated acid rain and then collecting soil samples from the soil profile for determination and analysis ²⁷. The results of field trial were more truthful generally, but the trial was more difficult and expensive ¹.

In this paper, a field experiment was introduced to explore the influences of soil acidification on available contents of soil Cu and Pb, and their transferences in soil vertical profiles, through simulating different levels of acid rain to spray vegetable land under natural conditions.

Materials and Methods

Experimental site description: The site of field trial is at a piece of vegetable field, 500 m away from town of Xinzhou District 114.8° E, 31.84° N, Wuhan City, Hubei Province, central China, with an average annual precipitation of 1240 mm, a mean annual temperature of 16.4°C, and an annual frostless period of 250 days. The surface relief of the whole district, higher in the north than in the south, can be divided into low hills, undulating regions and plains in terms of terrain features, and the highest and the lowest lands are 675 m and 42 m above sea level, respectively. The growing crops include rice, wheat and peanut in low hills and undulating regions, and cotton, rape and vegetable in plains. In recent years, the district witnessed a rapid expansion of the area of vegetable

field to reach 10,000 hectares, which boasts farmland of 46,182 hectares and a population of 956 thousand. The major types of soil comprise the yellow brown soil, alluvial soil, purple soil and paddy soil. The soil type of the experimental field is alluvial soil.

Experimental design: The experimental field was partitioned into 12 test plots, and each was 20 m² in area with 5 m in length and 4 m in width. Every ditch (40 cm deep, 60 cm wide) between two plots was vertically buried a piece of plastic film which was 80 cm in depth and 5 m in length (equivalent to plot length of 5 m) to avoid influences by groundwater running from each other between the two plots. The related soil properties and background concentrations of Cu and Pb were given as following: soil texture, silt loam; soil pH (0~30 cm), 6.07; organic matter, 18.4 g kg⁻¹; available Cu, 1.124 g kg⁻¹; total Cu, 21.25 g kg⁻¹; available Pb, 0.54 g kg⁻¹; total Pb, 10.34 g kg⁻¹.

The mother solution of simulated acid rain (SARM) consisted of 90 g L⁻¹ citrate, 45 g L⁻¹ oxalic acid, 45 g L⁻¹ tartrate, 90 mL L⁻¹ nitric acid (63%) and 90 mL L⁻¹ sulphuric acid (98%)²⁸.

In order to reduce soil pH differently the SAR was applied to the test plots at four acidity levels, which are: (1) T0 (control)-no SARM, only 80L local irrigation water (pH 6.08), (2) T1-diluting SARM 5000 times to 80L (pH 2.0), (3) T2-diluting SARM 1500 times to 80L (pH 2.5), (4) T-diluting SARM 500 times to 80L (pH 3.0). The water used for irrigation or dilution was from a local irrigation well, and its pH was 6.08. The four treatments were randomly assigned and each had 3 replications.

Each plot was watered homogeneously with 80 L corresponding liquid every ten days, and the watering lasted for one year without any interval (from Nov. 8, 2006 to Nov. 8, 2007).

The plots were grown with vegetables in accordance with local varieties and rotation pattern: celery, Nov. 18, 2006 to Feb. 3, 2007; cucumber, Mar. 4, 2007 to Jul. 23, 2007; cabbage, Aug. 21, 2007 to Oct. 28, 2007. The soils of the plots were not tilled so as not to perturb soil layers in the plots, and the other agricultural measurements were in line with the local practices.

Soil sampling and chemical analysis: Soils were sampled every three months and there were in total four batches of soil samples collected from the trail site, which were: the first batch (Mon3), on

Feb. 8 2007; the second (Mon6), on May 8, 2007; the third (Mon9), on Aug. 8, 2007 and the last (Mon 12) on Nov. 8, 2007. Before each sampling, watering was stopped once in order to stable pH value of the trial soils. Soils were sampled with a layered sampler at four soil depths in each plot: 0~10, 10~20, 20~30 and 30~60 cm. At each soil depth five subsamples were collected and combined into one soil sample. The soils were air-dried and ground to pass through 2 mm sieve prior to analysis.

Soil pH was measured at a soil: water ratio of 1:2.5 by a pH meter (pHS-25, Shanghai Leici Instrument Factory, China). Soil available Cu and Pb were extracted with 0.005 mol L⁻¹ DTPA and determined by atomic absorption spectrophotometer (Varian, AA240FS, USA). Soil organic matter content (OM) was determined following the Walkley Black procedure²⁹.

Statistical analysis: Statistical analyses were conducted using SAS version 8.2 (SAS Institute Inc., 1999-2001). Comparisons of the four different treatments were made using a Least Significance Difference (LSD) t-test on soil pH and available Cu and Pb. All statistical significance levels were set as P < 0.05.

Results and Discussion

Effects of applying simulated acid rain (SAR) on soil pH: The pH values were listed in Table 1. Soil pH values were reduced in all SAR-treated plots, among which T3 had the greatest decrease in soil pH, while control (T0) did the least one, showing soil pH order of T3 < T2 < T1 < T0. With the continuation of watering SAR development, soil pH values in all experimental plots decreased, too. The soils of T3, T2, T1 reduced pH faster in the depths of 10~20 cm and 20~30 cm than in the depths of 30~60 cm and 0~10 cm within 3 months, which could be owing to the short stay of SAR in topsoil (0-10 cm) and the influences of groundwater in deep layer (30-60 cm). The pH differences in all treatments reached the most significant levels in the soil depth of 10~20 cm, having a significant difference between two of all treatments, the second was the depth of 0~10 cm, and, then, the depths of 20~30 cm and 30~60 cm. Generally, soil pH values reduced in the order of T3 < T2 < T1 < T0 and Mon 12 < Mon 9 < Mon 6 < Mon 3.

The result indicated that the application of SAR could effectively decrease soil pH under natural conditions, and the higher rates of

Table 1. Effects on pH of soils treated with simulated acid rain (SAR)*.

Soil depth (cm)	Treatment	Mon3	Mon6	Mon9	Mon12
0-10	T0	5.89±0.040a	5.70±0.070a	5.61±0.031a	5.02±0.030a
	T1	5.83±0.047a	5.62±0.035a	5.34±0.056b	4.87±0.060b
	T2	5.62±0.030b	5.20±0.047b	5.02±0.068c	4.61±0.040c
	T3	5.39±0.015c	5.04±0.080c	4.77±0.061d	4.67±0.036d
10-20	T0	5.04±0.090a	4.96±0.076a	4.76±0.040a	4.53±0.050a
	T1	4.94±0.045b	4.73±0.047b	4.52±0.034b	4.38±0.038b
	T2	4.68±0.020c	4.50±0.046c	4.45±0.044b	4.19±0.090c
	T3	4.47±0.083d	4.14±0.053d	4.10±0.045c	4.03±0.099d
20-30	T0	5.01±0.047a	4.84±0.060a	4.50±0.031a	4.42±0.032a
	T1	4.86±0.057b	4.65±0.046b	4.42±0.030ab	4.25±0.055b
	T2	4.86±0.015b	4.45±0.065c	4.41±0.064ab	4.30±0.046b
	T3	4.59±0.027c	4.47±0.053c	4.36±0.057b	4.12±0.059c
30-60	T0	5.62±0.120a	5.02±0.056a	4.53±0.057a	4.89±0.176a
	T1	5.42±0.076ab	4.88±0.085b	4.84±0.056ab	4.79±0.040a
	T2	5.76±0.049bc	4.80±0.080b	4.71±0.161bc	4.82±0.030a
	T3	5.51±0.042c	4.86±0.051b	4.53±0.067c	4.59±0.755b

* Means±SD, different small letters among treatments indicate significant difference at P<0.05 (n=3); T0, T1, T2 and T3 represent no-SAR (simulated acid rain), SAR-5000(dilution times), SAR-150 and SAR-500, respectively; Mon3, Mon6, Mon9 and Mon12 represent sampling time at 3, 6, 9 and 12 months later, respectively.

the SAR application could cause a greater pH decline in soils. Of all four soil layers, the subsurface layer (10~20 cm) had the greatest pH decrease. Quantity and frequency of watering ASR played an important role in process of soil pH fall, more quantity and frequencies favored more decline of soil pH values.

Effects of applying simulated acid rain (SAR) on the soil available Cu concentrations: The variance of contents of soil available Cu for four treatments is shown in Table 2. In topsoil layer (0~10 cm), no significant differences appeared in contents of soil available Cu for all treatments including control (T0), suggesting that application of SAR exerted little effect on availability of Cu in topsoil, which could be due to the shorter stay of SAR in the layer.

In subsurface soil layer (depth of 10~20 cm), the contents of soil available Cu for all SAR-treated treatments (T3, T2 and T1) at Mon3 (sampling at 3 months later) were significantly higher than those in the control (T0). It reflected that the rise of soil available Cu concentration was highly negatively correlated with the fall of soil pH³⁰, demonstrating that soil acidification can effectively increase the release of available Cu, due to complicated soil chemical processes, such as cation exchange and dissolution of minerals at lower pH²². After watering SAR for 6, 9 and 12 months (Mon6, Mon9 and Mon12), the difference of soil available Cu contents between SAR-treated plots and control (T0) shrank until it was almost negligible in the end (Mon12), which may infer that low soil pH values not only induced the increase of soil available Cu, but also the leaching of soil available Cu through the soil profiles.

In the soil layer of 20~30 cm, contents of soil available Cu for SAR-treated plots rose first and fell later. For example, at the first three months (Mon 3), contents of soil available Cu for SAR-treated plots (T3 and T2) were much higher than those of the control (T0). At Mon 6 and Mon 9, those for T3 dropped and at Mon 12, those for all treatments except T1 exhibited no difference. This implied that low soil pH values could elevate availability of Cu, but in the long run, the metal availability depended on

complicated processes of adsorption, desorption, leaching and others⁴.

In the soil layer of 30~60 cm, variation of contents of soil available Cu for treatments was irregular. For instance, at Mon 3, contents of soil available Cu for T3 were adversely lower than those in the control (T0); at Mon 6, the soil available Cu level in T2 treatment was higher than those in T1 and T3 treatments; and at Mon 9 and 12, there were almost no differences among all treatments. The reason for this could be ascribed to the presence of underground water³¹ and complicated status under natural conditions

Table 2 also indicates that with the continuation of applying SAR (from Mon 3 to Mon 12), the soil available Cu concentrations of all treatments decreased regardless of soil depths; but the decrease rates varied from T3 to T0, following as T3 > T2 > T1 > T0. This indicated that the presence of acid was beneficial to removal of heavy metal Cu from soils into groundwater³¹.

There was also a trend that the available Cu concentrations of all treatments increased with the soil depth particularly from the topsoil to depth of 20~30 cm, but the difference in soil available Cu concentrations among soil layers became narrow while more irrigation occurred (Table 2). The results could deduce that the available Cu in soil transferred vertically through the profiles and accumulated at the deep soil layers (20~30 and 36~60 cm) due to the influences of the presence of acid, which might result in an increasing potential of Cu leaching into groundwater.

In conclusion, soil acidification enhanced available Cu activation and accelerated its mobility from upper soil layer to deeper layer and then into groundwater, which posed a threat to groundwater system.

Effects of applying simulated acid rain (SAR) on the soil available Pb concentrations: Table 3 lists the contents of DTPA extractable Pb of soils in different treatments. It indicates that after watered SAR for three months (Mon 3) and six months (Mon 6), the top soil (0-10 cm) in the high level SAR-treated plot (T3) had a distinctly higher soil available Pb concentration than the other treatments (T0, T1, T2). After nine months (Mon 9) and

Table 2. Contents of available Cu (mg kg⁻¹) for soils treated with simulated acid rain (SAR)*.

Soil depth (cm)	Treatment	Mon 3	Mon 6	Mon 9	Mon 12
0-10	T0	1.355±0.030a	1.266±0.012a	1.268±0.040a	1.156±0.139a
	T1	1.420±0.037a	1.130±0.008b	1.215±0.039a	1.171±0.233a
	T2	1.418±0.016a	1.292±0.041a	1.238±0.016a	0.982±0.031a
	T3	1.443±0.056a	1.261±0.017a	1.248±0.018a	1.100±0.116a
10-20	T0	1.492±0.011c	1.528±0.028b	1.486±0.022ab	1.231±0.231a
	T1	1.590±0.063b	1.555±0.054b	1.545±0.041a	1.186±0.006a
	T2	1.726±0.046a	1.633±0.014a	1.458±0.049b	0.902±0.081b
	T3	1.751±0.041a	1.431±0.018c	1.475±0.023b	1.218±0.026a
20-30	T0	1.564±0.031b	1.652±0.033a	1.550±0.036ab	1.226±0.146b
	T1	1.611±0.088b	1.636±0.034a	1.610±0.046a	1.537±0.181a
	T2	1.840±0.055a	1.662±0.020a	1.546±0.054ab	1.119±0.057b
	T3	1.813±0.022a	1.547±0.023b	1.471±0.057b	1.149±0.133b
30-60	T0	1.610±0.044a	1.554±0.033ab	1.596±0.029a	1.227±0.128ab
	T1	1.649±0.068a	1.516±0.170b	1.491±0.113a	1.393±0.240a
	T2	1.742±0.120a	1.719±0.068a	1.462±0.093a	1.089±0.109b
	T3	1.574±0.074b	1.407±0.070b	1.535±0.102a	1.212±0.087ab

* Mean±SD, different small letters among treatments indicate significant difference at P<0.05 (n = 3); T0, T1, T2 and T3 represent no-SAR (simulated acid rain), SAR-5000(dilution times), SAR-150 and SAR-500, respectively; Mon3, Mon6, Mon9 and Mon12 represent sampling time at 3, 6, 9 and 12 months later, respectively.

Table 3. Contents of available Pb (mg kg⁻¹) for soils treated with simulated acid rain (SAR)*.

Soil depth (cm)	Treatment	Mon 3	Mon 6	Mon 9	Mon 12
0-10	T0	0.380±0.020b	0.407±0.042b	0.430±0.020d	0.493±0.025c
	T1	0.393±0.015b	0.397±0.015b	0.467±0.012c	0.520±0.020c
	T2	0.400±0.010b	0.457±0.051b	0.507±0.015b	0.583±0.015b
	T3	0.449±0.016a	0.530±0.010a	0.597±0.021a	0.643±0.015a
10-20	T0	0.613±0.031a	0.610±0.026b	0.617±0.021b	0.633±0.012b
	T1	0.679±0.071a	0.617±0.031b	0.640±0.000ab	0.640±0.040b
	T2	0.607±0.031a	0.620±0.053b	0.660±0.120ab	0.693±0.031b
	T3	0.645±0.022a	0.690±0.020a	0.750±0.030a	0.813±0.042a
20-30	T0	0.727±0.012a	0.667±0.012ab	0.773±0.031a	0.840±0.020b
	T1	0.693±0.042a	0.653±0.031b	0.693±0.081a	0.855±0.018ab
	T2	0.720±0.125a	0.724±0.026a	0.767±0.031a	0.880±0.053ab
	T3	0.717±0.025a	0.627±0.050b	0.733±0.058a	0.900±0.020a
30-60	T0	0.480±0.060a	0.530±0.036b	0.690±0.020a	0.717±0.021a
	T1	0.487±0.046a	0.607±0.076ab	0.693±0.170a	0.720±0.020a
	T2	0.493±0.023a	0.633±0.012a	0.683±0.074a	0.687±0.023a
	T3	0.427±0.061a	0.533±0.031b	0.610±0.030a	0.727±0.042a

* Mean±SD, different small letters among treatments indicate significant difference at P<0.05 (n = 3); T0, T1, T2 and T3 represent no-SAR (simulated acid rain), SAR-5000(dilution times), SAR-150 and SAR-500, respectively; Mon3, Mon 6, Mon 9 and Mon12 represent sampling time at 3, 6, 9 and 12 months later, respectively.

twelve months (Mon 12) of SAR treatment, the soil available Pb concentrations in all treatments were raised and the variation among treatments were distinguishable with the order of soil available Pb concentration as T3>T2>T1>T0. This showed that availability of Pb in topsoil was effectively enhanced by inputs of acid (SAR), and the higher the acidity level was, the higher the contents of available Pb was elevated.

In the soil depth of 10~20 cm, the soil available Pb concentrations of high level SAR-treated plot (T3) was still higher than the other treatments, significantly, after watering SAR for 12 months, the available Pb concentration for the high level SAR-treated plot (T3) developed much higher than the others. This showed that the presence of acid rain still increased available Pb in this soil layer, but the effect relatively attenuated compared with topsoil layer.

In depths of 20~30 and 30~60 cm, the effect of SAR on soil available Pb concentration was nearly negligible regardless of the watering SAR frequency, so the soil acidification did not play an important role in soil Pb availability of deep soil layers.

Compared with the decrease of soil available Cu concentration with the time, contents of soil available Pb appeared a completely opposite change pattern - the available Pb concentration of all treatments at all sampling time (Mon 3, Mon 6, Mon 9, Mon 12) increased with the time of watering SAR, the sequence of increase rate was T3>T2>T1>T0, while the control (T0) increased very little (Table 3). The results might deduce that soil acidification played more important role in increasing the availability of soil Pb than accelerating its transference. This result was similar to the report that Pb will remain relatively immobile in soil profiles even in the presence of a strong complex agent²⁰.

Table 3 also presents the distribution and transference of soil available Pb in soil vertical profiles. From topsoil to 20~30 cm layer, the variation trend was similar to that of soil available Cu, while soil available Pb altered more sharply than soil available Cu, it indicated that soil acidification influenced on availability of soil Pb more effectively than soil Cu because the organic acid is easier

to combine with Pb than Cu¹⁶. However, compared with the upper soil layer of 20~30 cm, contents of soil available Pb in the depth of 30~60 cm declined dramatically, implying that soil available Pb accumulated in the soil layer of depth 20 ~30 cm.

To sum up, under the influences of soil acidification, soil available Pb increased sharply in the upper layers (0~30 cm), accumulated in the layer of 20~30 cm. It was relatively immobilized compared with Cu, suggesting that more Pb would be taken up by plants, enter into the food chain and pose a threat to human and animal health.

Conclusions

Under natural conditions (without artificial addition of heavy metals), the field study indicated that application of simulated acid rain can overcome soil acid buffering capacity and reduce soil pH values by 1.4 unit at most. Soil acidification could lead to the elevation of the availability of Cu and Pb and accelerate their transferences in soil vertical profiles. Under the same influences of acidification, contents of available Pb rose much larger than those of available Cu, demonstrating that the former (Pb) was more sensitive to soil acidification than the later (Cu). With the development of time, available Pb increased and available Cu decreased, implying that available Pb was inclined to accumulate in soils, be taken up by plants and pose a threat to food security, while available Cu was inclined to move downward to deep soil layers or leaching out of soils into the groundwater, posing a threat to groundwater system, under the impact of soil acidification.

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