

Article

Release of Heavy Metals and Metalloids from Two Contaminated Soils to Surface Runoff in Southern China: A Simulated-Rainfall Experiment

Lezhang Wei ^{1,2,3}, Yu Liu ^{1,2,3}, Joyanto Routh ^{1,4}, Jinfeng Tang ^{1,2,3}, Guowei Liu ², Lirong Liu ², Dinggui Luo ^{2,3,*}, Huosheng Li ³ and Hongguo Zhang ^{1,2,3}

- ¹ Linköping University—Guangzhou University Research Center on Urban Sustainable Development, Guangzhou University, Guangzhou 510006, China
- ² School of Environmental Science and Engineering, Guangzhou University, Guangzhou 510006, China
- ³ Key Laboratory for Water Quality and Conservation of the Pearl River Delta, Ministry of Education, Guangzhou University, Guangzhou 510006, China
- ⁴ Department of Thematic Studies, Environmental Change, Linköping University, 58183 Linköping, Sweden
- * Correspondence: ldggq@gzhu.edu.cn

Received: 6 April 2019; Accepted: 26 June 2019; Published: 28 June 2019



Abstract: The release of heavy metals and metalloids (HMs), including Pb, Zn, Cd, As, and Cu, from two typical contaminated soils with different properties, namely red soil and limestone-dominated soil, was characterized through simulated-rainfall experiments in order to investigate the effects of soil properties on HM release. Significant differences in the HM concentrations between the two soils resulted in various concentrations of dissolved and particulate HMs in the runoff. Differences in the dissolved HM concentrations in the runoff were inconsistent with the HM concentrations in the soils, which is attributed to the variable solubilities of HMs in the two soils. However, the HM enrichment ratios were not significantly different. The strong correlation between dissolved organic carbon and dissolved HMs in the runoff, and between the total organic carbon and particulate HMs in sediments, were observed, especially in the limestone-dominated soil. The specific surface area and HM concentrations in sediments were weakly correlated. Acid-rainfall experiments showed that only the limestone-dominated soil buffered the effects of acid rain on the runoff; the concentrations of dissolved Pb, Zn, Cd, and Cu increased in the red soil under acid rainfall and were 60, 29, 25, and 19 times higher, respectively, than under the neutral conditions. The results contribute to the understanding of HM behavior in the two typical soils in southern China, exposed to frequent storms that are often dominated by acid rainfall.

Keywords: enrichment ratio; partition coefficient; red soil; limestone soil; acid rain; southern China

1. Introduction

Anthropogenic activities (e.g., application of fertilizers, mining, and ore processing) often result in the contamination of heavy metals and metalloids (HM) in soils [1]. During rainfall, HMs are released and transported from the upland contaminated soil to riverine systems, resulting in deterioration of water quality, which is a major environmental problem worldwide [2,3]. Hence, understanding the rainfall-derived release of HMs from the topsoil and its subsequent mobilization and transport are essential not only for the sustainable management of contaminated areas, but also important for the conservation of the surrounding water resources and ecosystems.

Heavy metals and metalloid transport in water is conventionally classified into dissolved-HM and particulate-HM transport. The concentration of dissolved HMs is usually defined as HMs passing through a 0.45-µm filter, and it is strongly influenced by the solubility of metal species under specific



physicochemical conditions [4]. Dissolved HM species are generally limited compared with particulate HM in natural systems. Extraction and leaching processes of dissolved and particulate HMs have been the key objectives in previous studies on HM mobilization, and this information has been further related to the bioaccessibility of dissolved HMs to various ecological issues in the environment and the potential risks to groundwater contamination [4–7]. Eroded soils, particularly fine particles, increase the potential for adsorption of contaminants during transport [8]. It is well documented that hydrologic and hydraulic factors (e.g., the intensity of rainfall, raindrop energy, depth and rate of water flow, and stream power) control the detachment, transport, and deposition of soil particles [9–13]. Therefore, knowledge about soil erosion and transport processes indirectly aid in the understanding of soil-bound HM transport processes. Researchers have attempted to analyze the effects of rainfall on HM transport based on simulated-rainfall experiments [14,15]. In addition, these studies analyzed the grain-size in soil samples, which was assumed to be a key factor controlling the physical and chemical transport of HMs during flooding events. Generally, HM concentrations in eroded soils are higher than in parent soils, because soil erosion is a highly size-selective process that enriches the detached HMs in finer particles [16]. However, Huang et al. indicated that the enrichment of cadmium (Cd) in fine particles was absent. Instead, Cd levels increased in the macroaggregates of eroded sediments [15]. In a study focusing on the transport of mercury (Hg) and soil organic matter (SOM), Zheng et al. found that the heavy fraction of SOM has a dominant influence on the enrichment and transport of Hg, whereas the minerogenic clay-rich fraction exhibited a significant indirect influence [17]. These studies highlight that further detailed analyses of the chemical properties in soil are warranted to explain HM behavior during storm events. Although previous studies have shown that chemical properties in the soil such as pH, soil organic matter, and HM species affect the solubility and mobility of HMs [18], it is necessary to examine the effects of these properties on HM release from contaminated soils during rainfall, and thereof, into the runoff. In addition, previous studies on HM release were either based on leaching experiments [14,19] or in artificially polluted soils to understand the mobilization of HMs [15]. Review of current literature indicates that release of HMs from the soil matrix into runoff has not been investigated sufficiently and very little is known about this complex process, which plays an important role in the distribution of HMs in sedimentary environments.

Soil pollution by toxic HMs due to mining, especially cadmium (Cd), lead (Pb), and arsenic (As) has become extremely problematic in China [20]. Acid rain has also been recognized as a serious environmental problem in southern China [21]. The Dabaoshan mine in Guangdong Province is the largest multi-metal mine in southern China which has been operating for several decades (Figure 1). Acid mine drainage from the metal-sulfide ores and tailings ponds have caused severe acidification in nearby soils and streams [22,23]. Furthermore, several areas with high concentrations of HMs (e.g., Pb, Cd, Cu, Zn, and As) have been identified [24]. Recently, soil remediation has been implemented in contaminated agricultural land where concerns persist about the uptake and bioconcentration of HMs in crops grown in these polluted soils. There are two typical contrasting soil types in the contaminated areas, namely red acid soil (equivalent to Ultisol) which has a low pH and abundant Fe oxides [25], and the other is limestone-dominated alkaline soil. Using indoor simulated-rainfall experiments, the present study investigated the release of multiple HMs from two soil samples with different properties contaminated by the mining activities. The main objectives of this study were: (1) to characterize HM release under simulated-rainfall experiments in two contaminated soil types with different chemical properties, and (2) to identify the effects of various soil properties on HM release from the soil matrix during acid- and neutral-rainfall events. Investigations of the release of HMs from the two common types of soil will be beneficial for understanding HM behavior and remediation strategies that can be implemented in the contaminated soils.



Figure 1. Locations of soil-sampling sites in Guangdong Province, southern China (the limestone-rich and red soils were collected from sites A and B, respectively).

2. Materials and Methods

2.1. Soil Samples for Experiments

Soil samples were collected from two agricultural areas where mulberry was planted in the vicinity of mining/smelting locations (Figure 1). The limestone-rich soil (soil A) with a slightly high pH was collected from site A, located close to the mine site. The strongly acidic red soil sample was collected from site B near the river, located downstream from the mine site and contaminated by acid mine drainage (Table 1). Both sites were polluted due to irrigation [24]. Using a stainless-steel grab sampler, the soil samples were collected from the top 0-20 cm layer at 10 different locations covering an area of ca. 200 m² at each site. The samples were mixed and homogenized to represent the soil types at both sites. After returning to the laboratory, the samples were air-dried. Plant matter and large debris was removed from the air-dried soil samples, and later sieved through a 2-mm nylon filter, and stored in plastic containers prior to the experiments. Grain-size distribution in the soils was evaluated with a

laser particle size analyzer (Mastersizer 2000, UK). The saturated hydraulic conductivities in soils (K_s) were measured using the constant head method permeability test [26].

Table 1. Physical and chemical properties of experimental soils.

Soil Type	Grain Size	<i>K_s</i> (m/s)	TOC(mg/g)	pН	Cu(µg/g)	Cd(µg/g)	Pb(µg/g)	Zn(µg/g)	As(µg/g)	Fe(mg/g)
Soil A	2:24:74	0.6×10^{-5}	18.98	7.4	31.1(200)	2.80 (0.60)	94.1(140)	333 (250)	37.3(25.0)	27.8
Soil B	3:34:63	0.8×10^{-5}	13.72	4.5	371(150)	0.39(0.30)	330(80)	269(200)	153(40.0)	56.0

Note: Grain size: %clay:silt:sand in a soil sample; K_s : saturated hydraulic conductivity; TOC: total organic carbon. Values in parentheses are the safe limit for soil contamination in agricultural land (land use is classified other than paddy fields and pH \leq 5.5 for acid soil, pH > 7.5 for alkaline soil) [27]. Values in bold exceed the risk values. The detection limitations were 0.02 µg/g for Cd, 0.2 µg/g for Cu and As, 2 µg/g for Zn, and 5 µg/g for Pb.

2.2. Rainfall Experiment

Simulated-rainfall experiments were conducted using an experimental system composed of a water tank, peristaltic pump, rainmaker, and the soil column as shown in Figure 2. The polymethyl methacrylate soil column had an interior diameter of 19 cm and a height of 8 cm with holes ($d = 1 \mu m$) at the bottom to facilitate leaching. Clean and dry coarse sands ($d > 2.5 \mu$ m) were first placed at the bottom of the column to a height of approximately 2 cm. The soil sample was then stored in the column (bulk density of ~ 1.2 g/cm³). There was no inclination in the packed soil column. When rainfall cannot infiltrate quickly enough into the soil column, excess water on the surface flowing out of the column was collected in the container (S1 Figure 2). The soil column was placed in another container with a slope at the bottom to receive the leachate (L1). To prevent soil and water from splashing out of the column, one more container was placed on top of the soil column. The rainmaker was fixed on a stainless-steel shelf, 3 m above the soil column. The location of the soil column was adjusted to ensure that rainfall was evenly distributed. Raindrops fell from stainless steel syringe needles with an internal diameter of 0.34 mm. Different rainfall intensities were simulated by varying the delivery rate from the pump to the water head. Prior to each experiment, water was pumped at a high rate through the needles for certain time to clear any obstructions (e.g., air bubbles). A container was placed over the soil box for estimating the rainfall intensity (= total volume of precipitation/area/time). The result was used to manually adjust the delivery rate of the peristaltic pump to the desired intensity. The rainfall intensity was checked for > 2 h at an interval of 10–30 min in order to ensure that the intensity was stable. Once the rainfall intensity stabilized, the precipitation volume per second was assumed to be same for the experiment. Set-up of the delivery rate was fixed to ensure a stable rainfall intensity during the different experiments.

In previous studies, rainfall with high intensities e.g., 60 mm/h [28], 90 mm/h [17,29], and 100 mm/h [15] have been used during simulated rainfall experiments. The high rainfall intensity ensures delivery of enough sediments for various analyses. In this study, the rainfall intensity was kept constant at \approx 90 mm/h for approximately 100 min. Approximately 4.2 L of water dripped from the needles and percolated into the soil column. To prevent any chemical reactions deionized water (pH = 7) was used during the simulation experiments. Water samples were collected from the semi-circular outlet using acid washed 100-mL centrifuge tube (S1), starting at 6 and 13 min after the simulated rainfall commenced for soils A and B, respectively and surface runoff was observed. Water samples were collected sequentially, and the times (3–5 min/sample) were recorded. The surface-runoff water collected during the experiment was filtered using 0.45-mm glass filter paper. Two or three samples were combined to obtain a sufficient amount of sediment for chemical extraction. The leachate was also collected during the rainfall simulation experiment for geochemical analyses.



Figure 2. Schematic of the simulated-rainfall experimental setup.

Because the two experimental soils were acid and alkaline soil types, two additional acid-rainfall experiments were conducted to understand the effects of local acid rainfall on HM release during the storm. The acid rain was produced by adjusting the pH of the deionized water to pH 4 with a mixture of H_2SO_4 , HCl, and HNO_3 ($[SO_4^{2^-}]/[Cl^-]/[NO^{3^-}] = 6.1:1:0.7$, molar ratio) [30]. The replication of rainfall-runoff events is usually not the main consideration in rainfall-runoff studies [17]. Instead, as suggested in previous studies, a typical way to improve the reliability of results is by maintaining a time-series during the sampling procedure. The consistency reflected by the time-series sampling can be an alternative to the consistency expected from replicating the experiment [17,31]. In the current study, we followed a time-series sampling protocol with rainfall simulating different pH conditions.

2.3. Chemical Analysis

The pH of water and soil (in a 1:2.5 soil-to-water suspension) was measured with a calibrated pH meter (IQ150, Scientific Instruments, USA). Following the standard procedure, the total organic carbon (TOC) in the soil and collected sediment and dissolved organic carbon (DOC) in the water samples were measured using a TOC analyzer (Shimadzu 5000A, Japan). The specific surface area (SSA) of soils and sediments was determined by using an ASAP 2460 system (Micromeritics, USA). A 0.5-g soil/sediment sample was digested with a HCl–HNO₃–HF–HClO₄ mixture. Inductively coupled plasma–mass spectrometry was used to determine the HM concentrations in the water and in the digested samples [32]. Soil samples were analyzed using a modified BCR sequential extraction procedure to assess the association of HMs in different fractions of the soil [33]. The HM fractions were divided into (i) exchangeable/acid-extractable fraction (F1), (ii) reducible fraction (F2), (iii) oxidizable fraction (F3), and (iv) residual fraction (F4) [34]. For quality control, standard reference soil (GBW07406) from the National Research Center for Certified Reference Materials in China was used for the recovery test. The recovery for HMs ranged from 91.5% to 103% with a relative standard deviation of less than 7.2%. The detection limits of HM analysis are listed in Table 1.

2.4. Data Analysis

The enrichment ratios (*ER*s) of different soil components were calculated during the simulated-rainfall. Since multiple runoff samples were taken in sequence during each simulated-rainfall event, *ER*s were calculated as [17]:

$$ER = \frac{C'}{C} \tag{1}$$

where *C* denotes the concentration of the target compound (i.e., HM, TOC, and SSA) in the original soil and *C*' represents the concentration in the collected sample [17]. Thus, there were three types of enrichment ratio, i.e., ER_{HM} , ER_{TOC} , and ER_{SSA} .

Statistical and regression analyses of the experimental data were performed using the SPSS v.10.0 software (SPSS, USA) and Excel (Microsoft, USA) to establish the potential relationships between controlling factors and HM released in the experiments. The correlation was performed using Pearson's correlation test. A *t*-test for two groups of samples was also used to compare their differences.

3. Results and Discussion

The physical and chemical properties including the concentration of HMs in the experimental soils are presented in Table 1. The concentrations of Cu, Pb, and As in soil B, and mainly Cd in soil A were several times higher than the screening values for Chinese risk assessment in soils with same pH and land use (Table 1, [27]). Zinc concentration in both soils was comparable and slightly above the designated safe level in Chinese soils. The collected total surface runoff volumes from soils A and B were 2.87 and 2.37 L, respectively, and the total sediment masses collected were 9.10 and 5.00 g, respectively (Figure 3). The relative lower soil hydraulic conductivity of soil A (Table 1) resulted in less infiltration, and consequently more surface runoff and sediment yield during the experiments. The collected runoff water and sediments in the acid-rainfall experiments were similar to those of the neutral-rainfall experiments.



Figure 3. Accumulative (**a**) runoff (mL), and (**b**) sediment (g) collected from soil A and soil B during the simulated-rainfall experiments under acid (pH = 4) or neutral (pH = 7) rainfall.

3.1. Characterization of HMs Release from Soils under Neutral Rainfall

The concentrations of dissolved Zn, Cd, Cu, Pb, and As released from both soils throughout the rainfall simulation are shown in Figure 4. Dissolved Zn had the highest concentration (6.16–19.3 μ g/L; Figure 4d), indicating that Zn had the highest solubility in the runoff experiment irrespective of the soil pH. The lowest dissolved HM concentration was that of Cd (Figure 4b), possibly because of its poor enrichment in both soil samples, which means there is a limited supply of Cd released from the soils to water (Table 1). However, the differences in the dissolved concentrations of HM released from soil A and soil B were inconsistent with the differences in the initial HM concentrations in each soil. For example, Cd in soil A was approximately seven times higher than soil B, but Cd released from soil

A was only 2–3 times higher than Cd levels in the runoff from soil B. This implies that the acidic red soil facilitated the release of Cd into the runoff, although the mobile fractions (i.e., F1+F2+F3) were lower in soil B (Figure 5). The dissolved Cu concentration in soil B was higher than soil A after 40 min of simulated rainfall (Figure 4a). Conversely, the concentration of dissolved Pb in soil B was lower after 40 min of simulated rainfall (Figure 4c), although the initial concentrations of both Cu and Pb in soil A were considerably lower than those in soil B (Table 1). It was evident that the higher enrichment of Cu in soil B was more dominant than in soil A, and the reducible and oxidizable fractions (i.e., F2 and F3) in the two soils were comparable (Figure 5). However, the concentration of Pb in soil B was approximately 3.5-times higher than soil A (Table 1). Thus, the differences of dissolved Pb in the runoff (Figure 4c) may be a result of other factors, such as TOC, which could affect its distribution.



Figure 4. Concentrations of dissolved: (**a**) Zn; (**b**) Cd; (**c**) Cu; (**d**) Pb; and (**e**) As from soil A and soil B during the simulated-rainfall. (The red dash lines represent HM level in water classified as Class V in the Surface Water Environmental Standards in China (GB3838-2002)).

Figure 5. Fractions of Cd, Cu, and Pb in soil A and soil B; F1 = exchangeable acid-extractable fraction, F2 = reducible fraction, F3 = oxidizable fraction, and F4 = residual fraction.

The solubility of As increases with pH [35], which may explain the higher As concentration released from the limestone-dominated soil A than from the more acidic soil B (Figure 4e). Overall, a decreasing trend in the dissolved HM concentrations was observed during the rainfall (Figure 4a–e) although there were some outliers, possibly due to the experimental uncertainty. This is however consistent with the "first flush" phenomenon, which is an episodic discharge of acidic metal-rich fluids caused by the quick dissolution and flushing of soluble salts built up on the surface of mine wastes and soils when the first major rainfall occurs [36]. At the beginning of the experiment, HM concentrations from soil A were higher in all cases than those from soil B, implying that soil properties in the limestone-dominated soil B had a greater effect on HM concentrations during the "first flush."

With the exception of Zn, the HM concentrations in soils A and B differed considerably (Table 1), resulting in large differences in the concentrations of particulate HMs in sediments during the experiment (Figure 6). The enrichment ratios of HMs (ER_{HM}) were in the range of 1.21-2.44, as shown in Figure 7. The average ER_{HM} values were 1.64 and 1.63 for HMs derived from soils A and B, respectively. Although the HM concentrations in the soils varied, the difference in HM enrichment ratios was not significant (*t*-test, p > 0.05). The HM concentrations in the soils decreased slightly at the beginning of the experiments and fluctuated thereafter (Figure 7). However, the decreases in the HM concentrations in this study differed from observations in other rainfall experiments (e.g., [17,31]) in which the HM concentrations in the first sample were reported to be the highest. This may be a result of combining several samples in the present study, whereby the peak concentration of the initial sample was averaged. This trend was more obvious in soil B, for which the first measurement was obtained 15 min after the runoff was observed (Figure 3); less runoff and particulate matter was produced by this sample.

Figure 6. Cont.

Figure 6. Concentrations of particulate: (**a**) Zn; (**b**) Cd; (**c**) Cu; (**d**) Pb; and (**e**) As in runoff from soils A and soil B during the simulated-rainfall experiment. Note: different scales on secondary y-axes.

Figure 7. Enrichment ratios of heavy metals and metalloids (*ER*_{HM} values) of eroded particulate matter during the simulated-rainfall experiment.

3.2. Impact of Soil Chemical Properties

Chemical properties such as pH, organic matter content, and total metal burden in the soils affect the partitioning coefficients (K_d) in metals. K_d is defined as the total contaminant bound to the soil particles relative to that found in the soil solution [37,38]. In the present study, pH was relatively stable (± 0.1) throughout the experiment. Thus, pH was not a decisive factor that affected the release of HMs during the simulated-rainfall event.

The dissolved organic carbon (DOC) in the runoff decreased exponentially with rainfall, possibly resulting in the first flush of dissolved HMs during the experiments. A strong correlation between DOC and dissolved HMs was observed in soil A (p < 0.05). However, in soil B (which had less organic matter content; Table 1), DOC correlated strongly only with dissolved Cu and Cd (Table S1). Dissolved organic matter forms strong complexes with HMs including competition for available adsorption sites, formation of aqueous complexes, and/or changes in the redox potential of surface sites [39–41]. However, these factors can vary for different HMs and soil types. Hence, further studies should focus on factors which control the release of dissolved Zn, Pb, and As from the acidic red soils. Although

there was a slight temporal variation in particulate HM concentrations during the runoff (Figure 6), dissolved HM concentrations were probably unaffected because the correlation coefficients were low (Table S1). The enrichment ratio of TOC (ER_{TOC}) of the sediments from soil A in the runoff was a useful variable for predicting ER_{HM} (excluding the outliers with the highest ER_{TOC} and low ER_{HM}) as shown in Figure 8 ($R^2 \ge 0.89$). Unlike ER_{TOC} , the correlation between ER_{SSA} and ER_{HM} was relatively weak (0.73 $\ge R^2 \ge 0.25$).

Figure 8. Relationships between the enrichment ratios for (**a**) heavy metals and metalloids (ER_{HM}) and total organic carbon (ER_{TOC}), and (**b**) heavy metals (ER_{HM}) and specific surface area (ER_{SSA}) in soil A. Note the y-axis in the left represents Cd, As, Cu, Pb and in the right it represents Zn; the data in the dashed circles were obtained from the first sample since the runoff and sediment yield were not stable, the data were assumed as outliers for model estimation.

Based on the equations listed in Table S2, ER_{HM} values in the runoff in soil A can be estimated via the two dependent variables (i.e., ER_{TOC} and ER_{SSA}). In contrast, the results for soil B were inconclusive ($R^2 \le 0.55$), implying that more complicated factors affected the HM release during rainfall, and further studies are recommended to ascertain these relationships. Red soils in south China feature an abundance of Fe and Al oxides [21], and transformations in Fe-bearing minerals can significantly affect the mobility of Cd in soils [42]. The HMs released from soil B can, therefore, be attributed to the high Fe levels in red soil (soil B), which was twice the concentration in the limestone-dominated soil A (Table 1).

The total metal content in the soil samples resulted in differences in HM concentrations in the particulate fraction in the runoff from soils A and B (Figure 6). The value of $\log K_d$ during the experiments, which were mainly determined by ER_{HM} in the experimental soils (Table 2), are comparable with those reported in previous studies [37,43]. The high $\log K_d$ values indicated that particulate HMs were dominant in HM released during rainfall. The results of accumulative mass indicated that >90% of HMs were released from the soil in particulate form during both experiments.

Table 2. Average value of heavy metal and metalloid (HM) partition coefficients ($\log K_d$; L/Kg). The standard deviations are listed in the parentheses.

Soil Type	Cu	Cd	Pb	Zn	As
Soil A	3.87 (0.21)	4.55 (0.09)	5.47 (0.07)	4.72 (0.15)	4.36 (0.04)
Soil B	4.86 (0.06)	3.99 (0.08)	6.26 (0.15)	4.63 (0.03)	5.15 (0.05)

3.3. Effect of Acid Rainfall on Heavy Metal and Metalloid Release from Soil

The pH buffering capacity in soils is an intrinsic property that quantifies the ability of a soil to resist pH changes [44]. Following acid rainfall, it has been reported that the pH of leachate could increase because of the soil buffering capacity [45,46]. In this study, we found that the pH values of the leachate were 7.1 and 6.7 for soils A and B, respectively, after the acid-rainfall (pH = 4) event. This implied that both these soil types could absorb/complex H^+ and increase the pH, and thereby neutralize some of

the effects of acid rainfall. Furthermore, the pH of the surface runoff in these experiments with soil A were in the range of 6.7–7.2 and 5.9–6.3, respectively, under the neutral and acid-rainfall conditions. In contrast, the pH of surface runoff in the experiments with soil B was in the range of 6.7–7.1 and 4.2–4.7, respectively. These results indicate that the limestone-dominated soil (soil A; pH = 7.4) had a high buffering capacity that was sufficient to offset the effects of acid rain on the runoff acidity. However, such a buffering capacity was less in the red soil (soil B; pH = 4.5). Consequently, the K_d values of HMs in runoff from the experiment using soil B was more sensitive than the experiment using soil A by comparing the experiments using neutral and acid-rainfall events (Figure 9).

Figure 9. Comparison of heavy metal and metalloid (HM) partition coefficient (log K_d) calculated for soil A and soil B under neutral (pH = 7) and acid (pH = 4) rainfall conditions.

Previous leaching studies found that acid rain may break down the red soil aggregates and decrease soil infiltration [47,48], resulting in the release of HMs. In this study, however, the effect of acid rain on the runoff and sediment yield was negligible (Figure 3). Only a slight increase in particulate HM concentrations was observed after acid-rainfall (Figure 10). However, the dissolved HMs released from soil A and soil B varied significantly (Figure 11). The buffering effect in soil A resulted in a slight increase in dissolved HM concentrations. In contrast, with the exception of As, HM concentrations released in the runoff increased considerably for soil B because of the substantial decrease in pH from 6.7–7.1 to 4.2–4.7.

Figure 10. Comparison of concentrations of particulate heavy metals and metalloids (HMs) from soil A and soil B under the neutral (pH = 7) and acid (pH = 4) rainfall conditions.

It is well known that metals such as Cd, Pb, Cu, and Zn become more soluble under acidic conditions [49,50]. Sukreeyapongse et al. reported that with the decrease in pH, a pronounced increase in release rates was observed in the order of Cd > Pb > Cu [51]. In the present study, the concentrations of dissolved Pb, Zn, Cd, and Cu from soil B under the acid-rainfall condition were 60, 29, 25, and 19 times higher, respectively, than those under neutral conditions. It has been established that Pb has a high affinity for iron-oxides [52]. In this study, the Fe-Mn oxide fraction (F2) for Pb (37%) in the acidic red soil (soil B) was readily released under low-pH conditions. Consistent with this trend, Cd in the

F2 fraction was low (11%). Moreover, it was reported that the effect of acidification on leaching of Zn was more significant than for Cu, and the release of Zn commenced when pH was <6.0 [53]. The solubility of Zn and Cu increased exponentially at pH values of 4.5–3.8 and 6.5–6.2, respectively [19]. Thus, in this study, the solubility of Zn increased much more than Cu at pH 4.2–4.7.

Figure 11. Comparison of concentrations of dissolved heavy metals and metalloids (HMs) under neutral (pH = 7) and acid (pH = 4) rainfall conditions.

3.4. Potential Implications

The study sites located in southeast China are subjected to a sub-tropical monsoon climate. Heavy rainstorms as typhoons occur very frequently from April to September. According to the measurements taken during the period 2009–2015 at the long-term ecological observatory in Mt. Nanling which is not far from this study area, the recorded maximum 15-min rainfall can be up to 24 mm. During such heavy precipitation events, concentrations of all dissolved HMs in the runoff in the present study were higher than the levels of the most polluted water (i.e., Class V) according to the Surface Water Environmental Standards in China (GB3838-2002) [54] as shown in Figure 4. Although the simulated runoff is not completely representative of real conditions, the outcomes highlight the urgency to be aware of the potential environmental risks of HM release from contaminated soils during such short episodic high-impact events. The results of the experiments suggest that different remediation strategies are needed for treating the contaminated soils. For example, decrease in DOC following the application of a coagulant for DOC can decrease the phytoavailablity of HM concentrations because the humic and fulvic acids in DOC are very active in binding ions, organic molecules, and solid surfaces [55]. However, in the present experiments, the correlation coefficients of DOC and dissolved HMs released from the red soil were low, suggesting that the efficiency of DOC coagulant on soil remediation might be different for soils A and B. Water-derived soil erosion dominated HM release from the contaminated soils in the present rainfall-simulation experiment, implying that further investigations about particulate contaminant transport combined with the chemical and physical properties of soil are vital. The limitation of this laboratory experiment with disturbed soils cannot provide a comprehensive picture about the release and transport of HMs. Nevertheless, field observations coupled to model simulations help to identify the critical areas prone to intense soil erosion and likely occurrences of 'hot spots' for HM contamination [13]. Hence, further investigations will be a good way to understand the environmental problems about HMs release and transport from contaminated soil types around mining areas.

4. Conclusions

The release of HMs from two soil types with different chemical properties under simulated-rainfall was investigated in this study. A comparison of the HM concentrations in the two experimental soils and its runoff exhibited significant differences between them. The two soils exhibited various concentrations of dissolved and particulate HMs in the runoff. Differences in the concentrations of dissolved forms of HMs released from the two soils in the runoff were inconsistent with differences in the HM concentrations in soils. Although the HM concentrations in both soils varied, the differences in ER_{HM} in the soils were not statistically significant. The average ER_{HM} values of the experiments with the two soils were approximately 1.63. The "first flush" of dissolved HMs occurred for both soils at the beginning of the simulated-rainfall. The HM concentrations in the soils decreased slightly at the beginning of the experiments and then fluctuated for the remaining period. Significant correlations were found between DOC and dissolved HMs, as well as between the TOC and particulate HMs, especially in the experiments using soil A ($R^2 \ge 0.53$). Thus, the organic matter content in soils could possibly be a useful variable to predict HM release. Acid-rainfall experiments showed that soil A (limestone-dominated soil) could offset the effects of acid water on the runoff acidity. However, no buffering effect was observed for soil B (red soil). Consequently, with the exception of As, HMs released in the runoff increased substantially for soil B. For soil B, the concentrations of dissolved Pb, Zn, Cd, and Cu under the acid-rainfall conditions were, respectively, 60, 29, 25 and 19 times higher than those under neutral conditions. These results provide valuable information that aids our understanding of HM behavior and release from two typical soil types in southern China, impacted by mining, frequent heavy storms, and acid rainfall.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4441/11/7/1339/s1, Table S1: Pearson correlation coefficient between dissolved heavy metals and metalloids (HMs) and dissolved organic carbon (DOC) and particulate HMs in runoff from soil A and soil B. Table S2. Relationships between the dependent variable (enrichment ratio of heavy metals and metalloids; *ER*_{HM}) and independent variables.

Author Contributions: Conceptualization, L.W. and D.L.; Methodology, L.W., Y.L., G.L., L.L. and H.L.; Writing—Original Draft Preparation, L.W., J.R. and D.L.; Writing—Review and Editing, L.W., J.R. and J.T.; Funding Acquisition, L.W., D.L. and H.Z.

Funding: This research was funded by the National Natural Science Foundation of China (No. 41807463), the Natural Science Foundation of Guangdong Province, China (No. 2018A030310309) and the Collaborative Project between Guangzhou University and Linköping University (2018–2019).

Acknowledgments: We also would like to thank Xiaodong Wu and Kengqiang Zhong for the technical work. We also thank the four anonymous reviewers for the constructive comments which improved the quality of the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Alloway, B.J. Sources of heavy metals and metalloids in soils. In *Heavy Metals in Soils*; Springer: Dordrecht, The Netherlands, 2013; pp. 11–50.
- Barber, L.B.; Paschke, S.S.; Battaglia, W.A.; Douville, C.; Fitzgerald, K.C.; Keefe, S.H.; Roth, D.A.; Vajda, A.M. Effects of an extreme flood on trace elements in river water-from urban stream to major river basin. *Environ. Sci. Technol.* 2017, *51*, 10344–10356. [CrossRef] [PubMed]
- 3. Gray, C.W.; Monaghan, R.M.; Orchiston, T.; Laurenson, S.; Cavanagh, J.A. Cadmium losses in overland flow from an agricultural soil. *Environ. Sci. Pollut. Res.* **2017**, *24*, 24046–24053. [CrossRef] [PubMed]
- 4. Kerr, J.G.; Cooke, C.A. Erosion of the Alberta badlands produces highly variable and elevated heavy metal concentrations in the Red Deer River, Alberta. *Sci. Total Environ.* **2017**, 596, 427–436. [CrossRef] [PubMed]
- 5. Dijkstra, J.J.; Meeussen, J.C.; Comans, R.N. Leaching of heavy metals from contaminated soils: An experimental and modeling study. *Environ. Sci. Technol.* **2004**, *38*, 4390–4395. [CrossRef] [PubMed]
- Bolan, N.; Kunhikrishnan, A.; Thangarajan, R.; Kumpiene, J.; Park, J.; Makino, T.; Kirkham, M.B.; Scheckel, K. Remediation of heavy metal (loid)s contaminated soils? To mobilize or to immobilize? *J. Hazard. Mater.* 2014, 266, 141–166. [CrossRef] [PubMed]

- Kim, R.Y.; Yoon, J.K.; Kim, T.S.; Yang, J.E.; Owens, G.; Kim, K.R. Bioavailability of heavy metals in soils: Definitions and practical implementation? A critical review. *Environ. Geochem. Health* 2015, 37, 1041–1061. [CrossRef] [PubMed]
- 8. Rickson, R.J. Can control of soil erosion mitigate water pollution by sediments? *Sci. Total Environ.* **2014**, *468*, 1187–1197. [CrossRef] [PubMed]
- 9. Nearing, M.A.; Foster, G.R.; Lane, L.J.; Finkner, S.C. A process-based soil erosion model for USDA-Water Erosion Prediction Project technology. *Trans. ASAE* **1989**, *32*, 1587–1593. [CrossRef]
- Rose, C.W. Research progress on soil erosion processes and a basis for soil conservation practices. In *Soil Erosion Research Methods;* Routledge: Abingdon, UK, 2017; pp. 159–180.
- Lu, J.; Zheng, F.; Li, G.; Bian, F.; An, J. The effects of raindrop impact and runoff detachment on hillslope soil erosion and soil aggregate loss in the Mollisol region of Northeast China. *Soil Tillage Res.* 2016, 161, 79–85. [CrossRef]
- 12. De Lima, J.L.; Singh, V.P.; de Lima, M.I.P. The influence of storm movement on water erosion: Storm direction and velocity effects. *Catena* **2003**, *52*, 39–56. [CrossRef]
- 13. Wei, L.; Kinouchi, T.; Velleux, M.L.; Omata, T.; Takahashi, K.; Araya, M. Soil erosion and transport simulation and critical erosion area identification in a headwater catchment contaminated by the Fukushima nuclear accident. *J. Hydro Environ. Res.* **2017**, *17*, 18–29. [CrossRef]
- 14. Meite, F.; Alvarez-Zaldivar, P.; Crochet, A.; Wiegert, C.; Payraudeau, S.; Imfeld, G. Impact of rainfall patterns and frequency on the export of pesticides and heavy metals from agricultural soils. *Sci. Total Environ.* **2018**, *616*, 500–509. [CrossRef] [PubMed]
- 15. Huang, B.; Yuan, Z.; Li, D.; Nie, X.; Xie, Z.; Chen, J.; Liang, C.; Liao, Y.; Liu, T. Loss characteristics of Cd in soil aggregates under simulated rainfall conditions. *Sci. Total Environ.* **2019**, *650*, 313–320. [CrossRef] [PubMed]
- 16. Quinton, J.N.; Catt, J.A. Enrichment of heavy metals in sediment resulting from soil erosion on agricultural fields. *Environ. Sci. Technol.* **2007**, *41*, 3495–3500. [CrossRef]
- 17. Zheng, Y.; Luo, X.; Zhang, W.; Wu, X.; Zhang, J.; Han, F. Transport mechanisms of soil-bound mercury in the erosion process during rainfall-runoff events. *Environ. Pollut.* **2016**, *215*, 10–17. [CrossRef] [PubMed]
- Strobel, B.W.; Borggaard, O.K.; Hansen, H.C.B.; Andersen, M.K.; Raulund-Rasmussen, K. Dissolved organic carbon and decreasing pH mobilize cadmium and copper in soil. *Eur. J. Soil. Sci.* 2005, 56, 189–196. [CrossRef]
- 19. Zhang, M.; Calvert, D. Simulation study on copper and zinc release from contaminated sandy soils due to acidification. *J. For. Res.* **2005**, *16*, 289–292.
- 20. Yang, Q.; Li, Z.; Lu, X.; Duan, Q.; Huang, L.; Bi, J. A review of soil heavy metal pollution from industrial and agricultural regions in China: Pollution and risk assessment. *Sci. Total Environ.* **2018**, *642*, 690–700. [CrossRef]
- 21. Zhang, J.E.; Ouyang, Y.; Ling, D.J. Impacts of simulated acid rain on cation leaching from the Latosol in south China. *Chemosphere* **2007**, *67*, 2131–2137. [CrossRef]
- 22. Chen, M.; Lu, G.; Guo, C.; Yang, C.; Wu, J.; Huang, W.; Yee, N.; Dang, Z. Sulfate migration in a river affected by acid mine drainage from the Dabaoshan mining area, South China. *Chemosphere* **2015**, *119*, 734–743. [CrossRef]
- 23. Chen, T.; Lei, C.; Yan, B.; Li, L.L.; Xu, D.M.; Ying, G.G. Spatial distribution and environmental implications of heavy metals in typical lead (Pb)-zinc (Zn) mine tailings impoundments in Guangdong Province, South China. *Environ. Sci. Pollut. Res.* **2018**, *25*, 36702–36711. [CrossRef] [PubMed]
- Zhao, H.; Xia, B.; Fan, C.; Zhao, P.; Shen, S. Human health risk from soil heavy metal contamination under different land uses near Dabaoshan Mine, Southern China. *Sci. Total Environ.* 2012, 417, 45–54. [CrossRef] [PubMed]
- 25. Xu, R.; Zhao, A.; Li, Q.; Kong, X.; Ji, G. Acidity regime of the Red Soils in a subtropical region of southern China under field conditions. *Geoderma* **2003**, *115*, 75–84. [CrossRef]
- 26. Klute, A. Laboratory measurement of hydraulic conductivity of saturated soil. In *Methods of Soil Analysis*. *Part 1. Physical and Mineralogical Properties, Including Statistics of Measurement and Sampling, (Methods of Soil Analysis);* American Society of Agronomy: Madison, WI, USA, 1965; pp. 210–221.
- 27. Mahdi, K.N.; Commelin, M.; Peters, R.J.; Baartman, J.E.; Ritsema, C.; Geissen, V. Transport of silver nanoparticles by runoff and erosion—A flume experiment. *Sci. Total Environ.* **2017**, *601*, 1418–1426. [CrossRef] [PubMed]

- Li, Y.; Zhang, F.; Yang, M.; Zhang, J.; Xie, Y. Impacts of biochar application rates and particle sizes on runoff and soil loss in small cultivated loess plots under simulated rainfall. *Sci. Total Environ.* 2019, 649, 1403–1413. [CrossRef] [PubMed]
- 29. Ministry of Ecology and Environment of the People's Republic of China, State Administration for Market. *Regulation Soil Environmental Quality-risk Control Standard for Soil Contamination of Agricultural Land (GB 15618-2018);* Ministry of Ecology and Environment of the People's Republic of China, State Administration for Market: Beijing, China, 2018. (In Chinese)
- 30. Lu, Y.; Luo, D.; Lai, A.; Liu, G.; Liu, L.; Long, J.; Zhang, H.; Chen, Y. Leaching characteristics of EDTA-enhanced phytoextraction of Cd and Pb by Zea mays L. in different particle-size fractions of soil aggregates exposed to artificial rain. *Environ. Sci. Pollut. Res.* **2017**, *24*, 1845–1853. [CrossRef]
- 31. Shi, P.; Schulin, R. Erosion-induced losses of carbon, nitrogen, phosphorus and heavy metals from agricultural soils of contrasting organic matter management. *Sci. Total Environ.* **2018**, *618*, 210–218. [CrossRef] [PubMed]
- 32. Wu, Q.; Tam, N.F.; Leung, J.Y.; Zhou, X.; Fu, J.; Yao, B.; Huang, X.; Xia, L. Ecological risk and pollution history of heavy metals in Nansha mangrove, South China. *Ecotoxicol. Environ. Saf.* **2014**, *104*, 143–151. [CrossRef]
- 33. Rauret, G.; López-Sánchez, J.F.; Sahuquillo, A.; Barahona, E.; Lachica, M.; Ure, A.M.; Davidson, C.M.; Gomez, A.; Lück, D.; Bacon, J.; et al. Application of a modified BCR sequential extraction (three-step) procedure for the determination of extractable trace metal contents in a sewage sludge amended soil reference material (CRM 483), complemented by a three-year stability study of acetic acid and EDTA extractable metal content. *J. Environ. Monit.* 2000, 2, 228–233.
- 34. Liu, J.; Wang, J.; Xiao, T.; Bao, Z.A.; Lippold, H.; Luo, X.; Yin, M.; Ren, J.; Chen, Y.; Linghu, W. Geochemical dispersal of thallium and accompanying metals in sediment profiles from a smelter-impacted area in South China. *Appl. Geochem.* **2018**, *88*, 239–246. [CrossRef]
- 35. Moldovan, B.J.; Hendry, M.J. Characterizing and quantifying controls on arsenic solubility over a pH range of 1–11 in a uranium mill-scale experiment. *Environ. Sci. Technol.* **2005**, *39*, 4913–4920. [CrossRef] [PubMed]
- Nordstrom, D.K. Hydrogeochemical processes governing the origin, transport and fate of major and trace elements from mine wastes and mineralized rock to surface waters. *Appl. Geochem.* 2011, 26, 1777–1791. [CrossRef]
- 37. Sauvé, S.; Hendershot, W.; Allen, H.E. Solid-solution partitioning of metals in contaminated soils: Dependence on pH, total metal burden, and organic matter. *Environ. Sci. Technol.* **2000**, *34*, 1125–1131. [CrossRef]
- Degryse, F.; Smolders, E.; Parker, D.R. Partitioning of metals (Cd, Co, Cu, Ni, Pb, Zn) in soils: Concepts, methodologies, prediction and applications? A review. *Eur. J. Soil Sci.* 2009, 60, 590–612. [CrossRef]
- 39. Aiken, G.R.; Hsu-Kim, H.; Ryan, J.N. Influence of dissolved organic matter on the environmental fate of metals, nanoparticles, and colloids. *Environ. Sci. Technol.* **2011**, *45*, 3196–3201. [CrossRef] [PubMed]
- Chen, W.; Habibul, N.; Liu, X.Y.; Sheng, G.P.; Yu, H.Q. FTIR and synchronous fluorescence heterospectral two-dimensional correlation analyses on the binding characteristics of copper onto dissolved organic matter. *Environ. Sci. Technol.* 2015, 49, 2052–2058. [CrossRef] [PubMed]
- 41. Wang, S.; Mulligan, C.N. Effect of natural organic matter on arsenic release from soils and sediments into groundwater. *Environ. Geochem. Health* **2006**, *28*, 197–214. [CrossRef]
- 42. Yu, H.Y.; Liu, C.; Zhu, J.; Li, F.; Deng, D.M.; Wang, Q.; Liu, C. Cadmium availability in rice paddy fields from a mining area: The effects of soil properties highlighting iron fractions and pH value. *Environ. Pollut.* **2016**, 209, 38–45. [CrossRef]
- 43. Velleux, M. Spatially Distributed Model to Assess Watershed Contaminant Transport and Fate. Ph.D. Thesis, Colorado State University, Fort Collins, CO, USA, January 2005.
- 44. Wang, X.; Tang, C.; Mahony, S.; Baldock, J.A.; Butterly, C.R. Factors affecting the measurement of soil pH buffer capacity: Approaches to optimize the methods. *Eur. J. Soil Sci.* **2015**, *66*, 53–64. [CrossRef]
- Qiu, Q.; Wu, J.; Liang, G.; Liu, J.; Chu, G.; Zhou, G.; Zhang, D. Effects of simulated acid rain on soil and soil solution chemistry in a monsoon evergreen broad-leaved forest in southern China. *Environ. Monit. Assess.* 2015, 187, 272. [CrossRef]
- 46. Jiang, J.; Wang, Y.P.; Yu, M.; Li, K.; Shao, Y.; Yan, J. Responses of soil buffering capacity to acid treatment in three typical subtropical forests. *Sci. Total Environ.* **2016**, *563*, 1068–1077. [CrossRef] [PubMed]
- 47. Lin, L.; Zhang, J.; Xu, H.; Bai, W.; Liu, W. The impact of simulated acid rain leaching on aggregate stability of the latosolic red soil. *Chin. J. Soil Sci.* **2013**, *44*, 799–806. (In Chinese)

- 48. Wang, H.; Gong, E.; Liu, C.; Yuan, H. Effect of simulating acid rain leaching repeatedly on infiltration characteristics of Red soil. *J. Soil Water Conserv.* **2016**, *30*, 127–130. (In Chinese)
- 49. Wilson, M.J.; Bell, N. Acid deposition and heavy metal mobilization. *Appl. Geochem.* **1996**, *11*, 133–137. [CrossRef]
- 50. Bakshi, S.; He, Z.L.; Harris, W.G. Particulate copper in soils and surface runoff from contaminated sandy soils under citrus production. *Environ. Sci. Pollut. Res.* **2013**, *20*, 8801–8812. [CrossRef]
- Sukreeyapongse, O.; Holm, P.E.; Strobel, B.W.; Panichsakpatana, S.; Magid, J.; Hansen, H.C.B. pH-dependent release of cadmium, copper, and lead from natural and sludge-amended soils. *J. Environ. Qual.* 2002, *31*, 1901–1909. [CrossRef] [PubMed]
- Allen, H.E.; McGrath, S.P.; McLaughlin, M.J.; Peijnenburg, W.J.G.M.; Sauvé, S.; Lee, C. Speciation of metals in soils. In *Bioavailability of Metals in Terrestrial Ecosystems: Importance of Partitioning for Bioavailability to Invertebrates, Microbes, and Plants*; Society of Environmental Toxicology and Chemistry: Pensacola, FL, USA, 2002; pp. 7–37.
- Fernández-Calviño, D.; Pateiro-Moure, M.; Nóvoa-Muñoz, J.C.; Garrido-Rodriguez, B.; Arias-Estévez, M. Zinc distribution and acid-base mobilisation in vineyard soils and sediments. *Sci. Total Environ.* 2012, 414, 470–479. [CrossRef]
- 54. Environmental Quality Standards for Surface Water of China. Available online: http://kjs.mee.gov.cn/hjbhbz/ bzwb/shjbh/shjzlbz/200206/W020061027509896672057.pdf (accessed on 27 June 2019).
- 55. Kim, H.S.; Seo, B.H.; Kuppusamy, S.; Lee, Y.B.; Lee, J.H.; Yang, J.E.; Owens, G.; Kim, K.R. A DOC coagulant, gypsum treatment can simultaneously reduce As, Cd and Pb uptake by medicinal plants grown in contaminated soil. *Ecotoxicol. Environ. Saf.* **2018**, *148*, 615–619. [CrossRef]

© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).