



University of
Salford
MANCHESTER

Dynamics of Fe, Mn, and Al liberated from contaminated soil by low-molecular-weight organic acids and their effects on the release of soil-borne trace elements

Qin, J, Enya, O and Lin, C

<http://dx.doi.org/10.3390/app8122444>

Title	Dynamics of Fe, Mn, and Al liberated from contaminated soil by low-molecular-weight organic acids and their effects on the release of soil-borne trace elements
Authors	Qin, J, Enya, O and Lin, C
Publication title	Applied Sciences
Publisher	MDPI
Type	Article
USIR URL	This version is available at: http://usir.salford.ac.uk/id/eprint/49176/
Published Date	2018

USIR is a digital collection of the research output of the University of Salford. Where copyright permits, full text material held in the repository is made freely available online and can be read, downloaded and copied for non-commercial private study or research purposes. Please check the manuscript for any further copyright restrictions.

For more information, including our policy and submission procedure, please contact the Repository Team at: library-research@salford.ac.uk.

Article

Dynamics of Fe, Mn, and Al Liberated from Contaminated Soil by Low-Molecular-Weight Organic Acids and Their Effects on the Release of Soil-Borne Trace Elements

Junhao Qin ^{1,2}, Osim Enya ² and Chuxia Lin ^{2,*}

¹ Key Laboratory of Agro-Environment in the Tropics, Ministry of Agriculture, South China Agricultural University, Guangzhou 510642, China; J_Qin@scau.edu.cn

² School of Environment and Life Sciences, University of Salford, Greater Manchester M5 4WT, UK; o.enya@edu.salford.ac.uk

* Correspondence: C.Lin@salford.ac.uk; Tel.: +44-161-295-5356

Received: 31 October 2018; Accepted: 28 November 2018; Published: 1 December 2018



Abstract: A 15-day batch experiment was conducted to investigate the behaviours of Fe, Mn, and Al oxides upon attack by three common low-molecular-weight organic acids, and their effects on liberation of trace elements from a multi-contaminated soil. While the capacity of malic acid to mobilize soil-borne Fe, Mn, and Al was weaker compared to citric and oxalic acids, a similar trend was observed, showing that the concentration of dissolved Fe, Mn, and Al increased with increasing duration of the experiment. Marked increase in metal concentrations only took place after 5 or 7 days of the experiment. For the same organic acid treatment, Fe, Mn, and Al all showed a very similar temporal variation pattern. The concentration of dissolved Fe, Mn, and Al was markedly controlled by the total Fe, Mn, and Al contained in the soil, respectively. It appears that manganese oxides were more reactive to the organic acids, as compared to their Fe and Al counterparts. However, when multiple organic acids were present, the soil-borne Fe, Mn, and Al were mobilized rapidly within the first 5 or 7 days of the experiment and then tended to decrease. The formation of insoluble Fe, Mn, and Al organic complexes tended to be enhanced due to co-existence of multiple organic acids, resulting in the re-immobilization of the dissolved Fe, Mn, and Al. The organic acid-driven dissolution of Fe, Mn, or Al had a major control on the mobilization of As, Cr, Zn, Ni, Cu, and Cd that were bound to these oxides with a correlation coefficient being frequently greater than 0.9 for As, Cr, Zn, and Ni.

Keywords: arsenic; heavy metals; metal oxides; citric acid; malic acid; oxalic acid

1. Introduction

Oxides of iron (Fe), manganese (Mn), and aluminium (Al) are effective sorbents for trace elements [1,2]. Therefore, they play an important role as the sinks for potentially toxic heavy metals and metalloids in various environmental compartments such as soils, sediments, and aerosols, etc. [3–6]. In soils that are contaminated by potentially toxic elements, the presence of soil-borne Fe, Mn, and Al oxides immobilize pollutants entering soils from external sources, and consequently reduce their bioavailability. This represents a major chemical mechanism through which the toxic effects of trace elements entering a soil system can be attenuated [7]. However, upon changes in environmental conditions, the trace elements bound to these oxides can be released. Soil acidification is an important driver for dissolution of metal oxides [8–10]. For manganese and iron that have variable valence, a drop in redox potential could also destabilize Fe and Mn oxides [11,12].

In vegetated soils, low-molecular-weight organic acids (LMWOAs) contained in root exudates of plants play an important role in mobilizing trace elements bound to Fe, Mn, and Al oxides in rhizospheric soils [13–16]. While localized acidification in rhizospheric soils due to secretion of organic acids from plant roots and rhizobacteria solubilizes Fe, Mn, and Al oxides, complexation of Fe, Mn, and Al with organic ligands is likely to play a more important role in the dissolution of Al, Mn, and Fe oxides [3,17–19]. In addition, certain types of organic acids such as oxalic acid also have a strong capacity to cause reductive dissolution of iron oxides [20,21].

In soil systems, Al, Mn, and Fe oxides, together with other soil minerals, compete for available LMWOAs, resulting in consumption of free organic ligands, and acid neutralization, which causes the increase in solution pH [7,22]. This could, in turn, lead to re-immobilization of the mobilized Al, Mn, and Fe [7,23], and consequently re-immobilization of the previously released trace elements in the soil solutions. So far, there have not been detailed investigations on (a) competitive dissolution among Al, Mn, and Fe oxides upon attack by LMWOAs, (b) temporal variation in LMWOAs-mobilized Al, Mn, and Fe, and (c) effects of (b) on trace elements in soil solutions. The aim of this study was to close the above knowledge gaps.

2. Materials and Methods

2.1. The Contaminated Soil Used for the Experiment

The selected soil samples were collected from the Moston Brook closed landfill site in the Greater Manchester region, northwestern England. Information about the sampling site was documented in Mukwaturi and Lin [24]. After collection, the soil samples were oven-dried at 40 °C for two days in the laboratory and then ground with a mortar and a pestle to pass through a 2 mm stainless steel sieve. This is done to achieve a very fine and homogenous sample prior to analysis. Samples were later stored in an air-tight re-sealable laboratory polythene bags for further use.

Prior to the batch experiment, the soil was characterized and some major chemical characteristics of the soil samples are given in Table 1. The soils had a pH of 7.1 and an electrical conductivity (EC) value of 0.039 dS/m. The concentrations of Cd, Cu, Ni, Pb, and Zn exceeded the guideline values for soils with plant uptake [25,26].

Table 1. Major physical and chemical characteristics of the soil materials used in this study.

Parameter	Experimental Soil	Guideline Value for Soil with Plant Uptake
pH	7.1	–
EC (dS/m)	0.039	–
Total As (mg/kg)	29.6	43 *
Total Al (mg/kg)	21,013	–
Total Ca (mg/kg)	32,166	–
Total Cd (mg/kg)	6.19	1.8 *
Total Cr (mg/kg)	68.8	130 *
Total Cu (mg/kg)	2768	200 **
Total Fe (mg/kg)	28,131	–
Total K (mg/kg)	1859	–
Total Mn (mg/kg)	3865	–
Total Na (mg/kg)	959	–
Total Ni (mg/kg)	811	230 *
Total Pb (mg/kg)	1498	450 *
Total Zn (mg/kg)	1276	450 **

* CLEA Soil Guideline Value [26], ** EC Directive 86/278/EEC [25].

2.2. Experimental Design

Seven treatments were set to observe the release of Fe, Mn, and Al, other trace elements in the presence of three selected organic acids (citric acid, oxalic acid, and malic acid) and their combinations, as shown in Table 2.

Table 2. Composition of extracting solutions for seven treatments.

Treatment	0.01 M Citric Acid	0.01 M Oxalic Acid	0.01 M Malic Acid
T1	Yes		
T2		Yes	
T3			Yes
T4	Yes	Yes	
T5	Yes		Yes
T6		Yes	Yes
T7	Yes	Yes	Yes

A batch experiment was conducted with 125 mL plastic bottles being used as batch reactors. In each bottle, 10 g of the soil were mixed with 100 mL of a relevant solution (refer to Table 2). The bottle with contents was shaken by hand for 1 min. and then placed in a paper box at room temperature. Various physical and chemical parameters in the extracting solution were monitored during a period of 15 days. In-situ measurement of pH, EC, and Eh was made 1, 3, 5, 7, and 15 days after the commencement of the experiment. Solution samples were also collected for determination of Fe, Mn, Al and other trace elements after each in-situ measurement. Before each in-situ measurement and sampling operation, the bottle with contents was shaken by hand for 1 min. and then allowed to stand for 1 h. An aliquot of supernatant (5 mL) was taken from each bottle. The supernatant was centrifuged for 10 min at 3500 rpm and then passed through a 0.45 µm filter with polytetrafluoroethylene (PTFE) membrane prior to analysis.

2.3. Analytical Methods

For the initial soil characterization, pH/Eh, and EC of the soil samples were measured in a 1:5 (soil:water) extract using a calibrated Mettler Toledo 320 pH/Eh meter and a Mettler Toledo EC meter (Leicester, UK), respectively. Total element concentration was determined using a Niton XL2 Gold Hand-held XRF Analyzer (Winchester, UK). The instrument was calibrated by firstly analysing the 73,308 standard reference materials prior to sample analysis. To ensure accuracy and reliability of the results obtained, all analyses were performed in duplicates and the analysis time was set at 240 s. The pH and Eh in the solutions for the incubation experiment were measured using a Mettler Toledo 320 pH/Eh meter. The EC in the solutions for the incubation experiment was measured using a Mettler Toledo EC meter. Concentrations of Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in the filtrate were determined using a Varian 720 ES inductively coupled plasma optical emission spectrometer (ICP-OES, Palo Alto, CA, USA).

2.4. QA/QC and Statistical Analysis

All the chemicals used in the experiment are of analytical grade. The experiments were performed in triplicate (i.e., each of the 7 treatments in the experiment was independently repeated three times). Repeatability analysis shows that the mean RSD for pH, Eh, EC, Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn was <2.80%, <0.75%, <2.82%, <10.6%, <12.1%, <15.3%, <10.5%, <8.00%, <10.2%, <10.3%, <8.39%, <12.8%, and <4.96%, respectively. Statistical analysis of the experimental data was performed using one-way analysis of variance (ANOVA) and the means compared using significant difference (Duncan) method at 5% level (IBM SPSS software Version 17.0). “Descriptive statistics” followed by “explore” were used to test the data for normality. The “sig” value of Shapiro–Wilk is greater than 0.05. The data in this study is consistent with the test of variance homogeneity using Levene

statistic. All experimental data were presented as mean \pm standard error ($n = 3$). Pearson coefficient of correlation was used to determine the relationship between Al, Mn, or Fe and each of the trace elements investigated in this study.

3. Results

3.1. Temporal Variation in pH, Eh, and EC during the Period of the Experiment

There was a consistent trend showing that pH in the soil solution increased over time during the 15-day incubation experiment. In comparison, the single organic acid treatments (T1–T3) tended to have higher pH compared to the combined organic acid treatments (T4–T7), and the combination of the three organic acid treatment (T7) had the lowest pH on any measurement events among all the 7 treatments (Table 3).

Table 3. Variation in pH, Eh, and EC in the extracting solutions during the period of the experiment.

Treatments	1 d	3 d	5 d	7 d	15 d
pH					
T1	3.63 \pm 0.03 bE	4.11 \pm 0.02 cD	4.44 \pm 0.02 cC	5.38 \pm 0.10 bB	6.83 \pm 0.08 aA
T2	3.34 \pm 0.06 cE	4.78 \pm 0.01 aD	5.18 \pm 0.01 aC	5.88 \pm 0.02 aB	6.70 \pm 0.10 aA
T3	3.88 \pm 0.03 aE	4.50 \pm 0.03 bD	5.04 \pm 0.04 bC	6.01 \pm 0.02 aB	6.76 \pm 0.08 aA
T4	2.86 \pm 0.02 eE	3.36 \pm 0.01 eD	3.58 \pm 0.01 eC	4.29 \pm 0.02 dB	5.27 \pm 0.12 cA
T5	3.33 \pm 0.03 cE	3.77 \pm 0.02 dD	4.06 \pm 0.02 dC	4.81 \pm 0.03 cB	5.66 \pm 0.06 bA
T6	2.99 \pm 0.04 dE	3.71 \pm 0.05 dD	4.07 \pm 0.04 dC	4.83 \pm 0.06 cB	5.87 \pm 0.02 bA
T7	2.73 \pm 0.01 fE	3.26 \pm 0.00 fD	3.50 \pm 0.00 fC	4.22 \pm 0.04 dB	4.86 \pm 0.07 dA
Eh (mV)					
T1	170 \pm 1.70 eA	149 \pm 0.88 dB	128 \pm 0.96 dC	98.1 \pm 4.57 cD	−18.8 \pm 3.33 fE
T2	186 \pm 3.06 dA	112 \pm 0.81 fB	86.4 \pm 0.61 fC	67.5 \pm 1.31 dD	−7.23 \pm 2.02 eE
T3	156 \pm 1.91 fA	127 \pm 1.87 eB	93.9 \pm 2.29 eC	59.4 \pm 1.55 eD	−19.2 \pm 1.03 fE
T4	213 \pm 1.41 bA	192 \pm 0.64 bB	175 \pm 0.38 bC	160 \pm 1.10 aD	60.6 \pm 6.05 bE
T5	187 \pm 1.43 dA	169 \pm 1.17 cB	149 \pm 0.95 cC	130 \pm 0.07 bD	40.1 \pm 3.07 cE
T6	205 \pm 2.41 cA	172 \pm 2.69 cB	147 \pm 2.37 cC	128 \pm 3.31 bD	29.7 \pm 1.02 dE
T7	220 \pm 0.61 aA	197 \pm 0.19 aB	180 \pm 0.12 aC	164 \pm 2.31 aD	81.3 \pm 3.44 aE
EC (μS/cm)					
T1	1374 \pm 43.4 cA	1016 \pm 2.85 dB	1385 \pm 24.0 bA	874 \pm 7.00 cC	25.6 \pm 0.21 cD
T2	839 \pm 17.7 eA	311 \pm 2.03 gC	360 \pm 4.04 eB	196 \pm 3.70 dD	6.83 \pm 0.09 eE
T3	1319 \pm 15.6 cA	977 \pm 7.75 eB	1390 \pm 7.88 bA	867 \pm 3.61 cC	25.8 \pm 0.72 cD
T4	1820 \pm 26.6 aA	1132 \pm 0.88 cC	1528 \pm 4.00 aB	921 \pm 3.18bcD	25.5 \pm 0.43 cE
T5	1375 \pm 48.2 cC	1590 \pm 7.86 aA	1406 \pm 12.9 bB	1093 \pm 169 bD	41.2 \pm 0.37 aE
T6	985 \pm 17.8 dA	941 \pm 3.28 fB	785 \pm 2.96 dC	739 \pm 11.1 cD	18.6 \pm 0.33 dE
T7	1517 \pm 1.53 bA	1526 \pm 2.65 bA	1336 \pm 5.49 cB	1330 \pm 4.67 aB	37.9 \pm 0.18 bC

All values are presented as mean \pm standard error ($n = 3$). Means with different lower-case letters in the same column for each parameter are significantly different at $p < 0.05$. Means with different capital letters in the same row are significantly different at $p < 0.05$.

In contrast, the solution Eh tended to decrease with increasing duration during the incubation experiment. The single organic acid treatments (T1–T3) tended to have lower Eh, as compared to the combined organic acid treatments (T4–T7). The combination of the three organic acid treatment (T7) had the highest Eh on any measurement events among all the 7 treatments (Table 3).

There were different temporal variation patterns for EC among the 7 treatments in the earlier part (until the 7th day) of the experiment. Except for T2 and T6 that showed a continuously decreasing trend over time, EC in the treatments fluctuated markedly until the 7th day and then all the treatments exhibited a consistently decreasing trend toward the end of the experiment with the EC value becoming very low (Table 3).

3.2. Temporal Variation in Solution-borne Al, Fe, and Mn During the Period of the Experiment

For the single acid treatments (T1–T3), the solution-borne Al in T1 (citric acid treatment) and T3 (malic acid treatment) showed the same trend to increase with increasing incubation time though the value was lower in T3 than in T1 during the first 5 days. Unlike T1 and T3, the solution-borne Al in T2 (oxalic acid treatment) showed a gently decreasing trend until the 5th day and then sharply increased to the 7th day; after this, the concentration of Al in the solution slightly decreased to the end of the experiment (Table 4).

Table 4. Variation in Al, Fe, and Mn (mg/L) in the extracting solutions during the period of experiment.

Treatment	1 d	3 d	5 d	7 d	15 d
Al					
T1	347 ± 14.8 cD	533 ± 7.06 eC	648 ± 6.64 dB	744 ± 19.6 dB	1632 ± 27.7 aA
T2	368 ± 7.52 cC	348 ± 4.69 fD	273 ± 7.55 fE	1279 ± 14.3 bA	1144 ± 10.5 cAB
T3	156 ± 9.59 dE	261 ± 6.04 gD	322 ± 2.16 eC	794 ± 2.99 dB	1436 ± 3.93 bA
T4	634 ± 25.9 aC	929 ± 11.3 bAB	1048 ± 12.2 bA	1157 ± 20.8 cA	631 ± 20.4 fC
T5	494 ± 14.1 bC	751 ± 8.26 cB	885 ± 5.99 cA	337 ± 4.10 eD	688 ± 13.0 eB
T6	480 ± 21.7 bC	624 ± 16.7 dB	662 ± 22.3 dB	1135 ± 21.0 cA	312 ± 8.78 gD
T7	674 ± 3.10 aE	1055 ± 15.9 aC	1237 ± 10.5 aB	1603 ± 20.4 aA	791 ± 23.7 dD
Fe					
T1	287 ± 10.9 eE	527 ± 3.63 dD	714 ± 10.9 dC	1066 ± 28.2 dB	2583 ± 40.9 aA
T2	339 ± 4.11 dC	190 ± 7.80 eD	94.4 ± 3.18 gE	1487 ± 11.5 cB	2340 ± 33.2 bA
T3	105 ± 6.19 fE	208 ± 5.20 eD	328 ± 31.2 fC	682 ± 5.85 eB	1674 ± 23.3 cA
T4	639 ± 22.3 bD	982 ± 23.2 bC	1132 ± 14.7 bB	1556 ± 17.0 bA	1170 ± 17.3 dB
T5	406 ± 5.77 cD	757 ± 54.9c AB	883 ± 8.77 cA	364 ± 38.6 fD	589 ± 19.5 eC
T6	414 ± 9.97 cB	522 ± 17.4 dA	568 ± 18.2 eA	400 ± 0.03 fBC	381 ± 16.7 fC
T7	707 ± 15.9 aD	1100 ± 2.77 aC	1346 ± 6.66 aB	1967 ± 18.2 aA	1142 ± 6.54 dC
Mn					
T1	183 ± 10.9 eD	323 ± 7.24 dC	416 ± 7.44 dB	472 ± 30.1 cB	1054 ± 11.9 aA
T2	158 ± 0.20 eC	125 ± 1.70 fCD	83.7 ± 2.95 gE	616 ± 42.4 bB	885 ± 5.87 bA
T3	80.6 ± 3.35 fE	144 ± 3.22 eD	225 ± 2.60 fC	491 ± 32.1 cB	746 ± 16.6 cA
T4	325 ± 13.2 bD	507 ± 8.45 bBC	543 ± 4.66 cB	700 ± 19.9 bA	73.8 ± 4.84 fE
T5	288 ± 9.84 cD	501 ± 4.04 bB	563 ± 4.01 bA	341 ± 39.9 dCD	372 ± 9.07 eC
T6	244 ± 9.73 dC	354 ± 6.28 cB	359 ± 6.76 eB	96.8 ± 6.86 eD	369 ± 7.05 eA
T7	370 ± 1.02 aD	641 ± 6.14 aC	702 ± 6.34 aB	954 ± 6.81 aA	688 ± 3.24 dB

All values are presented as mean ± standard error ($n = 3$). Means with different lower-case letters in the same column for each parameter are significantly different at $p < 0.05$. Means with different capital letters in the same row are significantly different at $p < 0.05$.

For the combined two acid treatments (T4–T6), T4 (citric acid-oxalic acid treatment) and T6 (oxalic acid-malic acid treatment) showed a similar trend where solution-borne Al increased from the 1st day to the 7th day and then decreased to the end of the experiment. However, T5 (citric acid-malic acid treatment) exhibited a different temporal variation trend, showing that solution-borne Al increased from the 1st day to the 5th day and then increased to the 7th day, followed by a re-increase to the end of the experiment (Table 4).

For the combined three acid treatment (T7), there was a clear trend that solution-borne Al increased from the 1st day to the 7th day and then decreased to the end of the experiment with a value being very close for the 1st and the 15th day (the end of the experiment) (Table 4).

Similar to Al, the solution-borne Fe showed a consistent trend to increase over time for T1–T3. However, unlike Fe, the concentration of solution-borne Fe was consistently in T1 than in T3 during the period of incubation experiment. The temporal variation pattern for solution-borne Fe was also very similar to that for solution-borne Al (Table 4).

The temporal variation pattern in solution-borne Fe in T4–T6 was also very similar to that in solution-borne Al in T4 and T6, respectively. However, there was no marked variation in solution-borne Fe for T5, which is different from the solution-borne Al in T5 that had a strong peak on the 7th day of the experiment (Table 4). There was a high level of similarity in solution-borne Fe and solution-borne Al for T7 (Table 4).

In general, the temporal variation in solution-borne Mn showed a similar pattern to that of solution-borne Al for T1–T3 (Table 4). However, for the combined two acid treatments (T4–T6), the temporal variation in solution-borne Mn was more similar to that of solution-borne Fe but the peaks on the 5th day were much more evident, as compared to the latter (Table 4). For T7, the temporal variation pattern in solution-borne Mn was highly consistent with that for either Al or Fe (Table 4).

3.3. Relationships Among Solution-Borne Al, Fe, and Mn at Different Sampling Times

There was a close relationship among the solution-borne Fe, Mn, and Al (significant at $p < 0.01$) for any of the sampling occasions during the period of the experiment. However, there was a tendency showing that the correlation coefficient between the two elements decreased over time. The lowest correlation coefficient ($r = 0.576$) was for the pair of solution-borne Al vs. solution-borne Mn on the 7th day of the experiment (Table 5).

Table 5. Correlation coefficient among Fe, Mn, and Al in the solution samples ($n = 7$).

Time	Element	Al	Fe	Mn
1 d	Al	1		
	Fe	0.982 **	1	
	Mn	0.982 **	0.953 **	1
3 d	Al	1		
	Fe	0.984 **	1	
	Mn	0.977 **	0.976 **	1
5 d	Al	1		
	Fe	0.985 **	1	
	Mn	0.970 **	0.978 **	1
7 d	Al	1		
	Fe	0.770 **	1	
	Mn	0.576 **	0.915 **	1
15 d	Al	1		
	Fe	0.885 **	1	
	Mn	0.822 **	0.797 **	1

** Correlation is significant at the 0.01 level

3.4. Relationship between Fe, Mn, or Al and Various Potentially Toxic Elements in the Solutions

From Table 4, it can be seen that there was a close relationship between the solution-borne As and any of the solution-borne Fe, Mn, and Al though there was a trend showing that the correlation coefficient increased from the 1st day to the 5th day and then decreased to the end of the experiment (the 15th day).

For solution Cd, a closer relationship with the solution-borne Al, Fe, or Mn was only observed in the sampling occasion before the earlier part of the experiment (the first 5 days). No significant relationships were observed on the 7th and the 15th days of the experiment. The solution-borne Mn tended to be more closely related to the solution-borne Cd, as compared to the solution-borne Al and Fe, which also showed no significant relationship with the solution-borne Cd on the first day of the experiment (Table 6).

Table 6. Correlation coefficient between each selected trace metal and each of other elements investigated in this study ($n = 7$).

Time	Element	As	Cd	Cr	Cu	Pb	Zn	Ni
1 d	Al	0.907 **	0.397	0.954 **	0.964 **	0.077	0.979 **	0.972 **
	Fe	0.941 **	0.351	0.929 **	0.923 **	−0.026	0.944 **	0.943 **
	Mn	0.841 **	0.552 **	0.980 **	0.934 **	0.227	0.998 **	0.987 **
3 d	Al	0.986 **	0.744 **	0.961 **	0.889 **	0.232	0.965 **	0.943 **
	Fe	0.977 **	0.800 **	0.943 **	0.884 **	0.296	0.968 **	0.956 **
	Mn	0.978 **	0.850 **	0.983 **	0.944 **	0.392	0.993 **	0.974 **
5 d	Al	0.980 **	0.524 *	0.967 **	0.732 **	0.248	0.962 **	0.923 **
	Fe	0.978 **	0.556 **	0.947 **	0.767 **	0.292	0.963 **	0.942 **
	Mn	0.989 **	0.619 **	0.970 **	0.865 **	0.418	0.991 **	0.971 **
7 d	Al	0.658 **	−0.109	0.565 **	0.093	−0.065	0.637 **	0.586 **
	Fe	0.925 **	0.249	0.890 **	0.643 **	0.366	0.934 **	0.923 **
	Mn	0.944 **	0.340	0.950 **	0.829 **	0.393	0.943 **	0.962 **
15 d	Al	0.790 **	−0.270	0.864 **	0.322	0.077	0.852 **	0.808 **
	Fe	0.909 **	−0.097	0.889 **	0.257	0.400	0.934 **	0.863 **
	Mn	0.838 **	0.216	0.894 **	0.116	0.414	0.636 **	0.970 **

** Correlation is significant at the 0.01 level

Similar to As, the solution-borne Cr had a close relationship with solution-borne Al, Fe, and Mn on any of the five sampling occasions. The correlation coefficient tended to be relatively smaller on and after the 7th day than before and on the 5th day (Table 6).

There was a general trend that the correlation coefficient between solution-borne Cu and solution-borne Al, Fe, and Mn decreased over time during the period of the experiment. The relationship was significant at $p < 0.01$ except for the sampling occasion on the 15th day and on the 7th day for Al (Table 6).

There was no significant relationship ($p > 0.05$) between the solution-borne Pb and any of the solution-borne Al, Fe, and Mn on any sampling occasions though the solution-borne Mn tended to have a larger correlation coefficient with the solution-borne Pb, as compared to the solution-borne Al and Fe (Table 6).

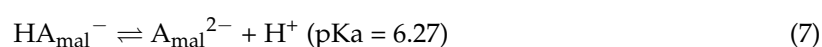
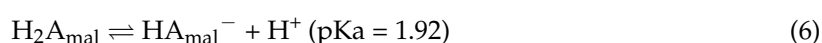
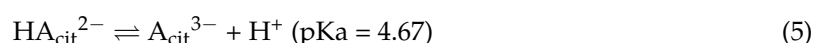
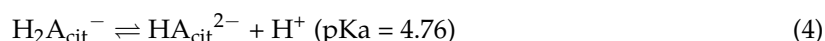
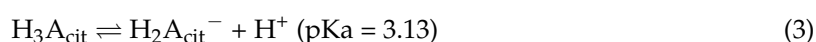
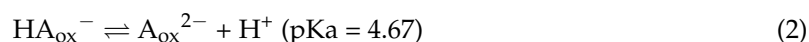
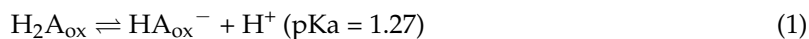
Both Zn and Ni in the solutions were closely related to any of the solution-borne Fe, Mn, and Al on any sampling occasions (significant at $p < 0.01$), although the correlation coefficient with the solution-borne Al was relatively smaller on the 7th day of the experiment (Table 6).

4. Discussion

The clear trend that the pH in soil solutions increased over time for all the 7 treatments suggests that proton consumption took place continuously during the period of the 15-day incubation experiment after mixing the soil with either the single or combined LMWOA solutions. This was accompanied by the enhancement of reducing conditions over time, as indicated by the consistent trend that the solution Eh decreased with increasing duration of the experiment. The temporal variation in both solution pH and Eh appeared to markedly complicate the mobilization-immobilization of various soil constituents, resulting in irregular variation in the EC value. Different organic acids or combinations of organic acids had differential effects on these chemical processes. However, as a whole, the EC value tended to decrease over time, and at the end of the experiment (the 15th day), EC dropped to a very low value for all the treatments. This suggests that, at this point, hydrolytic polymerization of metal complexes dominated as a result of rising pH [27,28]. For the single organic acid treatments (T1–T3), no removal of Fe, Mn, and Al from the solutions took place at this point because their concentrations remained high in the solutions. However, for the combined organic acid systems, removal of these metals from the solutions occurred, as evidenced by the facts that their

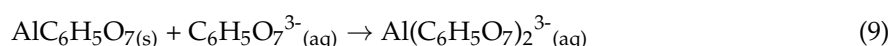
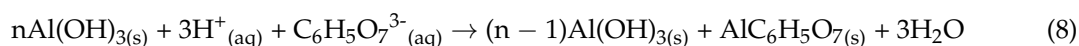
concentrations tended to decrease after either 5 or 7 days of the experiments. This suggests that the presence of multiple organic acid ligands enhanced the precipitation of solution-borne Fe, Mn, and Al.

The lower initial pH for oxalic acid treatment can be attributed to the greater acid dissociation constant (Ka) or lower pKa, as compared to the other two individual acid treatments (Equations (1)–(7)) [29].



The sharp increase in pH during the first 3 days for the oxalic acid treatment indicates rapid consumption of H^+ generated from dissociation of oxalic acid (Equations (1) and (2)). This could involve protonation of variably charged organic and inorganic soil colloids (including oxides of Fe, Mn, and Al) and reactions with carbonate and silicate minerals [30,31]. The slight decrease in solution-borne Fe, Mn, and Al prior to the 5th day of experiment suggests that release of soil-borne Fe, Mn, and Al to the solutions was inhibited.

The reaction between the soil-borne Fe/Mn/Al oxides/hydroxides and individual organic acids could lead to the release of these metals into the solution, as illustrated in the following example for the reaction of aluminium hydroxide with citric acid:



In Equation (8), the attack of aluminium hydroxide by citric acid results in the formation of insoluble aluminium citrate, which further reacts with another citrate ion to form soluble aluminium citrate complex (Equation (9)). Therefore, Equation (9) represents the rate-limiting step for the organic acid-driven dissolution of aluminium hydroxide. At least before the 7th day of the experiment, the reaction equilibrium was not reached because the concentration of dissolved Al kept increasing from the 7th day to the 15th of the experiment. The malic acid treatment showed a similar trend to the citric acid, suggesting that both citric acid and malic acid behaved similarly in terms of solubilizing the Al in the investigated soil. The delayed release of Al in the oxalic acid treatment could be attributed to the smaller acid dissociation constant (Ka), as compared to the other two organic acids [27].

The close correlation among the solution-borne Fe, Mn, and Al suggests that these metals were solubilized consistently from the oxides of these metals upon contacts with the organic acids. The reduced correlation coefficient during the later stage of the experiment may reflect differential rate of precipitation for these metals. By comparison, the amount of three metals mobilized during LMWOA extraction was in the following decreasing order: $\text{Al} > \text{Fe} > \text{Mn}$. This was consistent with the total concentration of these three metals contained in the investigated soil (Table 1), suggesting the strong control of the soil-borne metals on the solution-borne metals. However, when considering the ratio of solution-borne metal to soil-borne metal ($M_{\text{solution}}:M_{\text{soil}}$), it is clear that Mn had much stronger affinity to the LMWOAs, as compared to either Al or Fe; $M_{\text{solution}}:M_{\text{soil}}$ was more than 0.23 for Mn while $M_{\text{solution}}:M_{\text{soil}}$ for either Al or Fe was only 0.07.

The fact that solution-borne Pb was not related to any of the solution-borne Fe, Mn, and Fe suggests that Pb was not predominantly bound to the oxides of these metals. This is not in agreement

with many other findings that show Pb is favourably bound to oxides of iron and manganese [32–36]. Previous investigation suggested that Pb in contaminated soils at this site was mainly in the form of lead sulfate [37]. Consequently, the mobilization of Pb was not related to the dissolution of Fe, Mn, and Al oxides. In contrast, As, Cr, Zn, and Ni showed a close correlation with Fe, Mn, or Al, suggesting the LMWOA-driven dissolution of Fe, Mn, or Al had a major control on the mobilization of these elements of potential toxicity. It is interesting to note that the correlation coefficient for Cu vs. Fe/Mn/Al and Cd vs. Fe/Mn/Al varied over time. During the earlier stage of the experiment, a close correlation was observed, suggesting that the solution-borne Cu and Cd were essentially of Fe/Mn/Al oxide sources. In particular, it is likely that Cd was mainly bound to Mn oxides given the closer correlation between these two metals. The poor correlation between Cd or Cu and Fe/Mn/Al during the later stage of the experiment may be attributed to different immobilization rate between Cd/Cu and Fe/Mn/Al.

5. Conclusions

Although the capacity of malic acid to mobilize Fe, Mn, and Al in the contaminated soil was weaker compared to citric and oxalic acids, there was a general trend showing that the concentration of dissolved Fe, Mn, and Al increased over time during the 15-day experiment with marked increase in metal concentrations only occurring after 5 or 7 days of the experiment. For the same LMWOA treatment, the three metals showed a very similar temporal variation pattern. The total amount of Fe, Mn, and Al contained in the soil had an important control on the concentration of the dissolved Fe, Mn, and Al, respectively. Manganese oxides appeared to be more prone to LMWOA attack. However, in the presence of multiple LMWOAs, the soil-borne Fe, Mn, and Al were mobilized rapidly within the first 5 or 7 days of the experiment and then tended to decrease. The co-existence of multiple LMWOAs appeared to enhance the formation of insoluble Fe, Mn, and Al organic complexes, leading to their precipitation. The LMWOA-driven dissolution of Fe, Mn, or Al had a major control on the mobilization of As, Cr, Zn, Ni, Cu, and Cd, but not Pb, which was not largely derived from oxides of iron, manganese, and aluminium in the investigated soil.

Author Contributions: Conceptualization, C.L. and J.Q.; Methodology, J.Q.; Validation, C.L., J.Q. and O.E.; Investigation, J.Q. and O.E.; Data Curation, J.Q.; Writing—Original Draft Preparation, C.L.; Writing—Review & Editing, J.Q.; Visualization, J.Q.; Supervision, C.L.

Funding: This research received no external funding

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

References

1. Lee, G.; Bigham, J.M.; Faure, G. Removal of trace metals by coprecipitation with Fe, Al and Mn from natural waters contaminated with acid mine drainage in the Ducktown Mining District, Tennessee. *Appl. Geochem.* **2002**, *17*, 569–581. [[CrossRef](#)]
2. Suda, A.; Makino, T. Functional effects of manganese and iron oxides on the dynamics of trace elements in soils with a special focus on arsenic and cadmium: A review. *Geoderma* **2016**, *270*, 68–75. [[CrossRef](#)]
3. Violante, A.; Ricciardella, M.; Pigna, M. Adsorption of heavy metals on mixed Fe-Al oxides in the absence or presence of organic ligands. *Water Air Soil Pollut.* **2003**, *145*, 289–306. [[CrossRef](#)]
4. Hartley, W.; Edwards, R.; Lepp, N.W. Arsenic and heavy metal mobility in iron oxide-amended contaminated soils as evaluated by short-and long-term leaching tests. *Environ. Pollut.* **2004**, *131*, 495–504. [[CrossRef](#)] [[PubMed](#)]
5. Feng, X.H.; Zhai, L.M.; Tan, W.F.; Liu, F.; He, J.Z. Adsorption and redox reactions of heavy metals on synthesized Mn oxide minerals. *Environ. Pollut.* **2007**, *147*, 366–373. [[CrossRef](#)]
6. 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](#)]

7. Violante, A.; Ricciardella, M.; Pigna, M.; Capasso, R. Effects of organic ligands on the sorption of trace elements onto metal oxides and organo-mineral complexes. In *Biogeochemistry of Trace Elements in the Rhizosphere*; Huang, P.M., Gobran, G.R., Eds.; Elsevier B.V.: Amsterdam, The Netherlands, 2005; pp. 157–182.
8. Cook, F.J.; Hicks, W.; Gardner, E.A.; Carlin, G.D.; Froggatt, D.W. Export of acidity in drainage water from acid sulphate soils. *Mar. Pollut. Bull.* **2000**, *41*, 319–326. [[CrossRef](#)]
9. Mosley, L.M.; Shand, S.; Self, P.; Fitzpatrick, R. The geochemistry during management of lake acidification caused by the rewetting of sulfuric (pH < 4) acid sulfate soils. *Appl. Geochem.* **2014**, *41*, 49–61.
10. Sukitprapanon, T.; Suddhiprakarn, A.; Kheoruenromne, I. Partitioning and potential mobilization of aluminum, arsenic, iron, and heavy metals in tropical active and post-active acid sulfate soils: Influence of long-term paddy rice cultivation. *Chemosphere* **2018**, *197*, 691–702. [[CrossRef](#)]
11. Davies, S.H.R.; Morgan, J.J. Manganese (II) oxidation-kinetics on metal-oxide surfaces. *J. Colloid Interface Sci.* **1989**, *129*, 63–77. [[CrossRef](#)]
12. Burton, E.D.; Bush, R.T.; Sullivan, L.A.; Mitchell, D.R.G. Schwertmannite transformation to goethite via the Fe(II) pathway: Reaction rates and implications for iron-sulfide formation. *Geochim. Cosmochim. Acta* **2008**, *72*, 4551–4564. [[CrossRef](#)]
13. Kuan, W.H.; Wang, M.K.; Huang, P.M.; Wu, C.W.; Chang, C.M.; Wang, S.L. Effect of citric acid on aluminum hydrolytic speciation. *Water Res.* **2005**, *39*, 3457–3466. [[CrossRef](#)] [[PubMed](#)]
14. Mimmo, T.; Del Buono, D.; Terzano, R.; Tomasi, N.; Vigani, G. Rhizospheric organic compounds in the soil-microorganism-plant system: Their role in iron availability. *Eur. J. Soil Sci.* **2014**, *65*, 629–642. [[CrossRef](#)]
15. Clarholm, M.; Skyllberg, U.; Roslin, A. Organic acid induced release of nutrients from metal-stabilized soil organic matter—the unbutton model. *Soil Biol. Biochem.* **2015**, *84*, 168–176. [[CrossRef](#)]
16. Dotaniya, M.L.; Meena, V.D. Rhizosphere effect on nutrient availability in soil and its uptake by plants: A review. *Proc. Natl. Acad. Sci. India Sect. B Biol. Sci.* **2015**, *85*, 1–12. [[CrossRef](#)]
17. Perez-Benito, J.; Arias, F.C.; Amat, E. A kinetic study of the reduction of colloidal manganese dioxide by oxalic acid. *J. Colloid Interface Sci.* **1996**, *177*, 288–297. [[CrossRef](#)]
18. Saad, E.M.; Sun, J.; Chen, S.; Borkiewicz, O.J.; Zhu, M.Q.; Duckworth, O.W.; Tang, Y.Z. Siderophore and organic acid promoted dissolution and transformation of Cr (III)-Fe (III)-(oxy) hydroxides. *Environ. Sci. Technol.* **2017**, *51*, 3223–3232. [[CrossRef](#)]
19. Novo, L.A.B.; Castro, P.M.L.; Alvarenga, P.; da Silva, E.F. Plant growth-promoting rhizobacteria-assisted phytoremediation of mine soils. In *Bio-Geotechnologies for Mine Site Rehabilitation*; Elsevier: Amsterdam, The Netherlands, 2018; Volume 1, pp. 281–295.
20. Lee, S.O.; Tran, T.; Jung, B.H.; Kim, S.J.; Kim, M.J. Dissolution of iron oxide using oxalic acid. *Hydrometallurgy* **2007**, *87*, 91–99. [[CrossRef](#)]
21. Lee, J.C.; Kim, E.J.; Kim, H.W.; Baek, K. Oxalate-based remediation of arsenic bound to amorphous Fe and Al hydrous oxides in soil. *Geoderma* **2016**, *270*, 76–82. [[CrossRef](#)]
22. Gu, B.H.; Schmitt, J.; Chen, Z.H.; Liang, L.Y.; McCarthy, J.F. Adsorption and desorption of natural organic matter on iron oxide: mechanisms and models. *Environ. Sci. Technol.* **1994**, *28*, 38–48. [[CrossRef](#)]
23. Rengel, Z. Availability of Mn, Zn and Fe in the rhizosphere. *J. Soil Sci. Plant Nutr.* **2015**, *15*, 397–409. [[CrossRef](#)]
24. Mukwaturi, M.; Lin, C.X. Mobilization of heavy metals from urban contaminated soils under water inundation conditions. *J. Hazard. Mater.* **2015**, *285*, 445–452. [[CrossRef](#)] [[PubMed](#)]
25. Euro. Council Directive of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture (86/278/EEC). *Off. J. Eur. Commun.* **1986**, *181*, 6–12.
26. Jeffries, J. *CLEA Software (Version 1.05) Handbook*; Environment Agency: Bristol, UK, 2009.
27. Spiro, T.G.; Pape, L.; Saltman, P. Hydrolytic polymerization of ferric citrate. I. Chemistry of the polymer. *J. Am. Chem. Soc.* **1967**, *89*, 5555–5559. [[CrossRef](#)]
28. Chang, C.A.; Wu, B.H.; Kuan, B.Y. Macrocyclic lanthanide complexes as artificial nucleases and ribonucleases: Effects of pH, metal ionic radii, number of coordinated water molecules, charge, and concentrations of the metal complexes. *Inorg. Chem.* **2005**, *44*, 6646–6654. [[CrossRef](#)]
29. Goldberg, R.; Kishore, N.; Lennen, R. Thermodynamic Quantities for the Ionization Reactions of Buffers. *J. Phys. Chem. Ref. Data* **2002**, *31*, 231–370. [[CrossRef](#)]
30. Swift, R.S.; McLaren, R.G. Micronutrient adsorption by soils and soil colloids. In *Interactions at the Soil Colloid—Soil Solution Interface*; Springer: Dordrecht, The Netherlands, 1991; pp. 257–292.

31. Hill, D.M.; Aplin, A.C. Role of colloids and fine particles in the transport of metals in rivers draining carbonate and silicate terrains. *Limnol. Oceanogr.* **2001**, *46*, 331–344. [[CrossRef](#)]
32. Lofts, S.; Tipping, E. Solid-solution metal partitioning in the Humber rivers: Application of WHAM and SCAMP. *Sci. Total Environ.* **2000**, *251–252*, 381–399. [[CrossRef](#)]
33. Weng, L.P.; Temminghoff, E.J.M.; van Riemsdijk, W.H. Contribution of individual sorbents to the control of heavy metal activity in sandy soil. *Environ. Sci. Technol.* **2001**, *32*, 4436–4443. [[CrossRef](#)]
34. Ash, C.; Tejnecký, V.; Šebek, O.; Houška, J.; Chala, A.T.; Drahot, P.; Drábeka, O. Redistribution of cadmium and lead fractions in contaminated soil samples due to experimental leaching. *Geoderma* **2015**, *241–242*, 126–135. [[CrossRef](#)]
35. Gunawardana, C.; Egodawatta, P.; Goonetilleke, A. Adsorption and mobility of metals in build-up on road surfaces. *Chemosphere* **2015**, *119*, 1391–1398. [[CrossRef](#)] [[PubMed](#)]
36. Tiberg, C.; Sjöstedt, C.; Gustafsson, J.P. Metal sorption to Spodosol Bs horizons: Organic matter complexes predominate. *Chemosphere* **2018**, *196*, 556–565. [[CrossRef](#)] [[PubMed](#)]
37. Onireti, O.O.; Lin, C.X.; Qin, J.H. Combined effects of low-molecular-weight organic acids on mobilization of arsenic and lead from multi-contaminated soils. *Chemosphere* **2017**, *170*, 161–168. [[CrossRef](#)] [[PubMed](#)]



© 2018 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/>).