

# **Combined Effects of Low-molecular-weight Organic Acids on Mobilization of Arsenic and Lead from Multi-contaminated Soils**

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## **ABSTRACT**

A batch experiment was conducted to examine the combined effects of three common low-molecular-weight organic acids (LMWOAs) on the mobilization of arsenic and lead in different types of multi-contaminated soils. The capacity of individual LMWOAs (at a same molar concentration) to mobilize soil-borne As and Pb varied significantly. The combination of the organic acids did not make a marked “additive” effect on the mobilization of the investigated three elements. An “antagonistic” effect on element mobilization was clear in the treatments involving oxalic acid for some soils. The acid strength of a LMWOA did not play an important role in controlling the mobilization of elements. While the mobilization of As and Pb was closely associated with the dissolution of soil-borne Fe, soil properties such as original soil pH, organic matter contents and the total amount of the element relative to the total Fe markedly complicated the mobility of that element. Aging led to continual consumption of proton introduced from addition of LMWOAs and consequently caused dramatic changes in solution-borne Fe, which in turn resulted in change in As and Pb in the soil solution though different elements behaved differently.

**Key words:** Low-molecular-weight organic acids, arsenic, lead, mobilization, contaminated soils

## 1 Introduction

Low-molecular-weight organic acids (LMWOAs) are active components in root exudates of plants (Carson et al., 1992; Gerke et al., 1994; Reichard et al., 2007). LMWOAs could therefore play an important role in the mobilization of nutrients and potentially toxic trace elements in rhizospheric soils (Marschner et al., 1987; Gobran and Huang, 2011). Except for extremely acidic soils such as acid sulfate soils in coastal lowlands and mine sites (Lin et al., 2008), this process may, to a significant degree, control the availability of trace elements for plant uptake in soils. For example, it was demonstrated that the LMWOAs-mediated iron dissolution in the rhizosphere had a potential role in root iron uptake (Jones et al., 1996); Tao et al. (2006) showed that oxalate enhanced uptake of As by wheat plant; Ma et al. (2001) found that LMWOAs could affect the availability of Al to plants; and work by Chen et al. (2015) suggested that Cd uptake by rice plant is influenced by LMWOAs. The mobilized trace elements could also have adverse impacts on soil microbial metabolism, and consequently affect nutrient supply (Liang and Tabatabai, 1978; He et al., 2005) and degradation of organic matter (Gerringa, 1990), including organic pollutants (Perrin-Ganier et al., 2001) in soils. In some circumstances, the LMWOAs-mobilized trace elements can be further transported from the soils to the surface water and groundwater, reaching off-site receptors (Zinder et al., 1986; Slowey et al., 2005; Perelomov et al., 2011). Therefore, understanding the mobility of trace elements by LMWOAs is essential for assessing the phyto-availability of soil-borne trace elements, microbial toxicity of the trace elements in the soils, and the potential for translocation of trace elements from soils to water environments. This is particularly relevant to agricultural, urban and industrial lands that are heavily contaminated by heavy metals and metalloids.

Plant root exudates contain multiple LMWOAs though the dominant LMWOA types may vary with plant species and change over time (Jones et al., 1998; Ash et al., 2016). In the past decade or so, there has been increasing research into mobilization of heavy metals and metalloids by various LMWOAs (Cieśliński et al., 1998; Van Hees et al., 2000; Liu et al., 2008; Wang and Mulligan, 2013;

[Rocha et al., 2015](#)). An extensive review of the relevant literature indicates that the vast majority of available published papers limited their experiments to the examination of trace element mobilization by individual LMWOAs ([Examples are shown in Table 1](#)). This is not sufficient for assessing LMWOAs-driven mobilization of soil-borne trace elements in field systems where multiple LMWOAs are concurrently present in the same space. The combination of different LMWOAs may result in additive, synergistic or antagonistic effects on mobilization of different trace elements. This represents a major knowledge gap that needs to be filled in order to better understand the LMWOAs-driven mobilization of heavy metals in rhizospheric soils.

In this study, the capacities of various combinations of three common LMWOAs (citric acid, oxalic acid and malic acid) to mobilize arsenic and lead were compared using six multi-contaminated soils with different soil properties. The objectives were to understand (a) the integrative effects of the selected LMWOAs on each of the investigated trace elements; (b) whether different types of trace elements respond differently to the exposure of various LMWOA combinations; and (c) how the mobilization of the trace elements is complicated by other soil properties.

## **2 Materials and Methods**

### **2.1 The soil samples**

A total of 6 contaminated soil samples (M1, M2, M3, M4, M5 and M6) were used for the experiment in this study. These 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 ([Mukwaturi and Lin, 2015](#)). 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 homogenize a soil sample prior to analysis. Samples were then stored in an air-tight re-sealable laboratory polythene bags for further use.

Prior to the batch experiment, the soils were characterized and some major chemical characteristics of the soil samples are given in [Table 2](#). The soils were largely acidic with a pH ranging from 3.32 to 5.31. Electrical conductivity was all below 0.15 dS/m. Organic matter content was highly variable with a range of 1.2 – 7.4%. Heavy metal concentration was also highly variable with a range of 494-2285 mg/kg for total As, 393-1931 mg/kg for total Pb, 29-180 mg/kg for total Cu, 133-202 mg/kg for total Cr, 10-150 mg/kg for total Zn, 8792-59013 mg/kg for total Fe and 12-435 mg/kg for total Mn.

## 2.2 Experimental Design

For each sample, 7 treatments were set to observe the release of arsenic and lead by three organic acids (citric acid, oxalic acid and malic acid) and their combinations, as shown in [Table 2](#). The reason for including iron in this report is that reactive iron compounds are the predominant binders for trace elements in soils ([Hartley et al., 2004](#)).

A triplicated batch experiment was conducted. 125 mL plastic bottles were used as batch reactors. The bottles with contents were placed in a covered paper box at room temperature and stood for 7 days after shaking each bottle by hand for 1 minute. After seven days of incubation, each bottle was shaken for 1 minute and then allowed to stand for 1 hour before taking 10 mL of supernatant from each sample. The supernatant was centrifuged for 10 minutes at 3500 rpm to separate the solution and the solid phases. The solution phase was passed through a 0.45 µm filter with polytetrafluoroethylene (PTFE) membrane prior to analysis.

After 10 mL of solution being taken from each bottle, the batch reactors were repacked into the paper box with cover and stood for another 49 days. This was to observe the changes in the investigated trace elements and iron in the solution over time. At the end of the experiment, the pH and electrical conductivity (EC) were measured and then 10 mL of supernatant were taken for analysis following the same procedure, as described above.

### 2.3 Analytical Methods and Statistical Analysis

For the initial soil characterization, pH and EC of the soil samples were measured in a 1:5 (soil : water) extract using a calibrated Mettler Toledo 320 pH meter and a Mettler Toledo EC meter, respectively. Total metal concentration was determined using a Niton XL2 Gold Hand-held XRF Analyzer. The instrument was calibrated by firstly analyzing the 73308 standard reference materials prior to sample analysis. To ensure accuracy and reliability of the results obtained, all analyses were performed in duplicate and the analysis time was set at 240 seconds. Soil organic matter content was determined using a Walkley-Black method.

The pH in the solutions for the incubation experiment was measured using a Mettler Toledo 320 pH meter and a Mettler Toledo EC meter, respectively. Concentrations of As, Pb and Fe in the filtrate was determined using a Varian 720ES inductively coupled plasma optical emission spectrometer (ICP-OES). Statistical analysis of the experimental data was performed using IBM SPSS software Version 13.0.

## 3 Results

### 3.1 Extractable Iron in Various Treatments on the 7<sup>th</sup> day

The data on Fe extracted by the 7 extracting solutions (refer to [Table 3](#)) for the 6 soil samples (M1-M6) are shown in [Fig. 1](#). Citric acid (T1) extracted the largest amount of Fe (statistically significant at  $P < 0.05$ ) among the three individual acid treatments for all the 6 samples. Oxalic acid (T2) extracted significantly more Fe than did malic acid (T3) for M2 and M3 while malic acid extracted much more (significant at  $P < 0.05$ ) Fe than did oxalic acid for M1, M4, M5 and M6 from the soil ([Fig. 1](#)).

For the combinations of any two organic acids (T4, T5 and T6), mixed results are observed among the 6 investigated soil samples. For all six investigated samples, the amount of Fe extracted in

the combinations was even significantly ( $P < 0.05$ ) less than that extracted by citric acid (Fig. 1). T7 (the combination of the 3 organic acids) did not extract significantly more Fe than did any two-organic acid combinations for all the six investigated samples (Fig. 1).

Samples M1 and M6 had much greater concentration of Fe for most of the treatments, as compared to the other soil samples (Fig. 1).

### 3.2 Extractable Arsenic in Various Treatments on the 7<sup>th</sup> day

The data on As extracted by the 7 extracting solutions (Table 3) for the 6 samples (M1-M6) are shown in Fig. 2. By comparison among T1, T2 and T3, it can be seen that citric acid (T1) extracted the largest amount of As for all the 6 samples (significantly different at  $P < 0.05$  except for M2 and M6). There was no significant difference ( $P > 0.05$ ) in As between T2 (oxalic acid) and T3 (malic acid) for M1, M3 and M4. Oxalic acid extracted significantly ( $P < 0.05$ ) more soil-borne As than did malic acid for M2 and the opposite was observed for M5 and M6.

For the combinations of any two organic acids (T4, T5 and T6), mixed results are observed among the 6 investigated samples. In general, the amount of As extracted by a combined acid solution was all less than the sum of As extracted by the two individual organic acids. In some situations (T4 and T6 in M1, T5 in M2, T5 in M4), the amount of As extracted in the combinations was even less than that extracted by one of the individual acids (Fig. 2). T7 (the combination of the 3 organic acids) extracted significantly more As than did any two-organic acid combinations for M3, M5 and M6. There was no statistically significant difference in As between T7 and at least one of the combinations in M1, M2 and M4 (Fig. 2).

Samples M1, M2 and M6 tended to extract more As for most of the treatments, as compared to the other three treatments.

### 3.3 Extractable Lead in Various Treatments on the 7<sup>th</sup> day

The data on Pb extracted by the 7 extracting solutions (Table 3) for the 6 samples (M1-M6) are shown in Fig. 3. Citric acid (T1) extracted the largest amount of Pb (statistically significant at  $P < 0.05$ ) among the three individual acid treatments for all the samples except for M2 where there was no statistical significant ( $P > 0.05$ ) difference in Pb among the three individual organic acid treatments. There was no significant difference ( $P > 0.05$ ) in Pb between T2 and T3 for all the samples except for M2, which had higher Pb in T2 than in T3.

For the combinations of any two organic acids (T4, T5 and T6), mixed results are observed among the 6 investigated samples. M1, M4, M5 and M6 showed a similar pattern with the following decreasing order  $T5 > T4 > T6$ . Different trend was observed for M2 ( $T6 > T4 > T5$ ) and M3 ( $T4 > T5 > T6$ ) (Fig. 3). T7 (the combination of the 3 organic acids) did not extract significantly more Pb than did any two-organic acid combinations only for all the six investigated samples except for M3 (Fig. 3).

The amount of Pb extracted was highly variable among the 6 soil samples with Sample M4 having the extractable Pb less than 1 mg/kg for any of the treatments while Sample M6 having the extractable Pb greater than 10 mg/kg for some treatments (Fig. 3).

### 3.4 pH, EC, Iron, Arsenic and Lead in the Solution on the 56<sup>th</sup> day

To reduce the space needed for presenting the complete set of data for the manuscript, only two selected soil samples are reported here: Sample M1 with relatively high organic matter content and pH and Sample M3 with relatively low organic matter content, low pH and high concentration of total As and Pb. The concentrations of iron, arsenic and lead in the solution on the 56<sup>th</sup> day of the experiment are given in Table 4.



The pH in the solution was generally higher in M1 than in M3. For both soils, T7 was consistently the treatment with the lowest pH value among the seven treatments (significant at  $P < 0.05$ ). However, slightly different increasing sequences were observed for the samples; M1 showed the following trend:  $T7 < T5 < T6 < T4 < T2 < T3 < T1$  (the last 3 treatments are not significantly different from each other at  $P < 0.05$ ) while M3 exhibited the following trend:  $T7 < T5 = T4 < T6 \approx T3 \approx T1 < T2$ . EC ranged from 463 to 890  $\mu\text{S}/\text{cm}$  for M1. In contrast, EC in M3 was highly variable with a range of 72-1040  $\mu\text{S}/\text{cm}$ .

For M1, various elements in T2 tended to have the lowest value among the seven treatments though there was no significant difference in all elements among T1, T2 T3, T4 and T6 for M1 except for Pb in T6. For M3, various elements in T2 also tended to have the lowest value among the seven treatments. There was no significant difference in various elements between T2 and T3. Other treatments tended to have greater concentration for each element, as compared to that in T2. T7 had the greatest concentration of each element among the seven treatments except for Fe, which showed no significant difference from that in T1, T4 and T5.

#### 4 Discussion

Under the set experimental conditions, the capacity of individual organic acids (at a same molar concentration) to mobilize soil-borne heavy metals varied significantly. This is consistent with work by others (e.g. Cieśliński et al., 1998; Wu et al., 2003; Vítková et al., 2015). The chemical mechanisms responsible for dissolution of soil-borne heavy metals by organic acids are mainly through acidification, complexation and reduction (Bienfait et al., 1982; Jones and Darrah, 1994; Schwab et al., 2008). The stronger capacity of citric acid to mobilize heavy metals may be attributed to its higher acid strength, as compared to the other two organic acids at the set concentration in this study (Perrin et al., 1981). Apart from acidifying effect, oxalic acid can also facilitate dissolution of iron oxides through formation of soluble iron oxalate when abundant oxalate is present (Paniás et al.,

1996). However, when the oxalate concentration is not sufficiently high, insoluble iron oxalates are formed instead (Onireti and Lin, 2016). The depression of Fe mobilization by oxalic acid in this experiment indicates that a concentration of oxalic acid at 0.01 M was too low to effectively mobilize Fe from most of the investigated soils. Iron oxides play an important role as adsorbents to bind arsenates and heavy metals (Babel and Kurniawan, 2003; Markiewicz-Patkowska et al., 2007; Waterlot et al., 2013; Gong et al., 2016). The corresponding low levels of As and Pb in oxalic acid treatment for the soil samples appears to suggest a link between low iron solubility and low mobility of soil-borne As and Pb in these soils.

It is interesting to note that the amount of trace elements extracted by the mixed organic acid solutions was much less than the sum of that metal extracted by the individual organic acid solutions, and in some cases, even less than one of the individual organic acid extraction. This suggests that acid strength was not necessary a key factor controlling the mobilization of heavy metals in the presence of the organic acids. Our previous results (Onireti and Lin, 2016) indicated that there was no clear trend showing an increase in extractable arsenic with increasing dosage levels of citric acid and malic acid. It is likely that the capacity of the different organic acids at the concentration level set in the experiment is largely limited to the same highly mobilizable trace element pools. Therefore, the combination of organic acids did not make a marked “additive” effect on the mobilization of the investigated trace elements. In the situations where oxalic acid is involved, an “antagonistic” effect on element mobilization was observed for As in T6 (combined oxalic and malic acids) for Sample M1 although there was no significant difference between T2 (oxalic acid only) and T6.

While there was no clearly relationship between the LMWOA-extractable iron and LMWOA-extractable As when the data from the 6 soil samples are plotted together, certain relationship was observed for each individual soil sample. The  $R^2$  value for the 6 soil samples ranged from 0.4029 to 0.8504 (Fig. 4). Except for M2 that showed no relationship between the LMWOA-

extractable lead and the LMWOA-extractable Fe, the  $R^2$  value for the other 5 soil samples ranged from 0.4814 to 0.8152. These results suggest that the LMWOA-driven release of these two soil-borne trace elements was largely via mobilization of iron compounds (Miller et al., 1986; Pokrovsky et al., 2005).

Sample M2 had the steepest slope for As vs Fe among the 6 soil samples (Figs. 4). This may be attributed to its higher ratio of total As to total iron (Table 2), allowing a larger amount of As being released from a given amount of the mobilized iron. The poor Pb vs Fe relationship in this sample suggests that the Pb contained in this sample was not largely bound to iron compounds.

The total element ratio could also affect the release of Pb by the LMWOAs. This is clearly demonstrated by comparison between Sample M3 and M4; M3 had a much higher total Pb/total Fe ratio, as compared to M4; the Pb released from a given amount of mobilized Fe was markedly greater in M3 than in M4 (Fig. 5). Samples M1 and M6 tended to have more Fe being extracted (Figs. 4 and 5) despite that the total iron concentration in these two samples was much lower than that in Sample M4 (Table 2). These were the two samples with a higher pH value and a higher organic matter content, as compared to other soil samples (Table 2). It is well established that the presence of humic substances can affect crystallization of iron oxides, resulting formation of more reactive amorphous or poorly crystallized iron compounds (Rashid, 2012). This may partly explain the enhanced release of Fe from these organic-rich soils. Our previous work (Mukwaturi and Lin, 2015) showed that the soils in the investigated area frequently contained iron sulfate minerals that was likely to be derived from the coal combustion wastes dumped in this landfill site. The low pH (<4) in Samples M2, M3 and M4 suggests that these soils contained oxidation products of pyrite originally present in the coal (Stucki et al., 2012). Due to their acidic nature, it was likely that the reactive fraction of iron in these soils had been largely leached out of the soils during past rainfall events. This may explain the relatively smaller amounts of Fe being released from M2, M3, M4 and

M5, as compared to M1 and M6 since the LMWOAs-reactive pool of Fe was smaller in the former than in the latter.

It is interesting to note that after aging for another 49 days, the solution-borne Fe changed dramatically and different patterns were observed for M1 and M3. For M1, the concentration of Fe in the solution dropped for all treatments (Fig. 6a). For M2, all treatments involving citric acid showed an increase in solution-borne Fe concentration while others exhibited the opposite (Fig. 6b). This reflects strong influence of the original soil pH on the dynamics of solution-borne Fe in the current reaction systems.

Upon addition into the soils, LMWOAs tended to react with various soil components at different rates. This represents an acid-consuming process, which leads to an increase in solution pH over time until all the likely reactions reach equilibrium. As mentioned previously, the initial rapid release of Fe from M1 indicates the presence of a larger citric acid-reactive iron pool in this soil, as compared to M3. However, as time went by, the proton in the solution was increasingly consumed by other soil components, resulting in an increase in solution pH to >4.5 (4.58-6.74, Table 4) on the 56<sup>th</sup> day of the experiment. The elevated pH conditions drove the dissolved Fe to precipitate and being removed from the solution. This explains the lower solution-borne Fe on the 56<sup>th</sup> day than on the 7<sup>th</sup> day for M1 (Fig. 6a).

In contrast, in M3 that had a smaller citric acid-reactive pool of Fe, the amount of Fe released from the reaction system at the earlier stage (the 7<sup>th</sup> day) was limited (Fig. 6b). This suggests that it required more time to allow reaction between the citric acid and the less reactive Fe pool to take place for the release of Fe from this soil. Since M3 was an acidic soil with a pH of 3.73 (Table 2), much of the acid-neutralizing capacity of the soil had been consumed naturally before the soil was collected. Consequently, the proton introduced from the addition of LMWOAs was not markedly consumed during the period of incubation experiment. This explains the observed low pH (2.53-

4.54) in the solution on the 56<sup>th</sup> day of the experiment. The maintenance of low pH and the continuous liberation of Fe from the soil over time allowed a greater concentration of solution-Fe on the 56<sup>th</sup> day than on the 7<sup>th</sup> day of the experiment. It is realized that the citrate, oxalate and malate might undergo degradation during the period of experiment (Van Hees et al., 2003). The batch reactors were kept in dark during the entire period of the experiment to minimize photo-degradation of these organic ligands from occurring (Powell and Wilson-Finelli, 2003; Shank et al., 2006). Therefore any decomposition of LMWOAs was largely attributed to microbially mediated degradation. The dynamics of various organic ligands during the period of the experiment were not monitored in this work, which is currently being undertaken in separate experiments. However, the remarkable drop in Fe observed in M1 appeared to be partly caused by the weakened complexation effects due to the reduced availability of LMWOA ligands in the solution. There was a good relationship between the pH and Fe in the solution for both M1 and M3 on the 56<sup>th</sup> day (Fig. 7a and 7b), suggesting that over time, the concentration of solution-borne Fe was increasingly influenced by pH.

The solution-borne As in M1 on the 56<sup>th</sup> day exhibited a different distribution pattern for the seven treatments, as compared to that for the solution Fe. The concentration of As in the solution tended to decrease in the treatments involving citric acid and oxalic acid (Fig. 6c), which was consistent with that for solution-borne Fe. This indicates that re-immobilization of As in these treatments might be associated with precipitation of iron compounds (Fig. 7c). However, those treatments that involved malic acid tended to enhance further release of As from the soil except for T7 (Fig. 6c). The reason for this is unknown but the poor relationship between pH and As in the solution (Fig. 7c) does suggest that the solubility of As in the system was not controlled by pH and the re-immobilization of Fe had little influence on the solution-borne As. Similar to M1, despite that solution-borne Fe in T3 (malic acid treatment) and T6 (combined oxalic acid and malic acid treatment) decreased from the 7<sup>th</sup> day to the 56<sup>th</sup> day, there was an increase in solution-borne As from

the 7<sup>th</sup> day to the 56<sup>th</sup> day in M3 (Fig. 6d). This further demonstrates that malic acid was able to continuously enhance release of soil-borne As under the experimental conditions set for this study regardless the original soil pH. Apart from this, the distribution pattern of As for the seven treatment was very similar to that of Fe. Unlike M1, there was a good relationship between pH and As in the solution in M3 (Fig. 7d), and between Fe and As in the solution (data not shown). Therefore, it is reasonable to state that the further release of As from the soil during the period from the 7<sup>th</sup> day to the 56<sup>th</sup> day was closely related to the dissolution of iron compounds during the same period (Bauer and Blodau, 2006; Pedersen et al., 2006).

There was a close relationship between pH and solution-borne Pb in M1 (Fig. 7e). The marked drop in solution-borne Pb in T5 reflects this pH effects. There was also a good relationship between pH and solution-borne Pb in M3 (Fig. 7f). This soil sample might contain sparingly soluble lead sulfate because the soil was rich in sulfate (data not shown). Perhaps, the reactions between lead sulfate and LMWOAs were kinetically slower (Ali and Dzombak, 1996), as compared to reaction between iron compounds and LMWOAs. This may explain the continuous release of Pb from the soil during the period from the 7<sup>th</sup> day to the 56<sup>th</sup> day.

## 5 Conclusion

Under the set experimental conditions in this study, the capacity of individual LMWOAs (at a same molar concentration) to mobilize soil-borne As and Pb varied significantly. The amount of the investigated element extracted by the mixed LMWOA solutions was much less than the sum of that element extracted by the individual LMWOA solutions, and in some cases, even less than one of the individual organic acid extraction. Where oxalic acid is involved, an “antagonistic” effect on element mobilization was observed for some soils. The acid strength of a LMWOA was not necessary a key factor controlling the mobilization of elements in the presence of the LMWOAs. While the mobilization of the three investigated elements is closely associated with the dissolution of soil-

borne Fe, soil properties such as original soil pH, organic matter contents and the total amount of the element relative to the total Fe could markedly complicate the mobility of that element. Aging led to continuous consumption of proton from the addition of LMWOAs. This caused dramatic changes in solution-borne Fe, which in turn resulted in change in As and Pb in the soil solution though different elements behaved differently. The findings obtained from this study have implications for better understanding the mobilization of potentially toxic trace elements by plant root exudates in multi-contaminated soils.

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## Captions

Fig. 1 Iron extracted by the 7 extracting solutions for the 6 soil samples. (a) M1, (b) M2, (c) M3, (d) M4, (e) M5, and (f) M6.

Fig. 2 Arsenic extracted by the 7 extracting solutions for the 6 soil samples. (a) M1, (b) M2, (c) M3, (d) M4, (e) M5, and (f) M6.

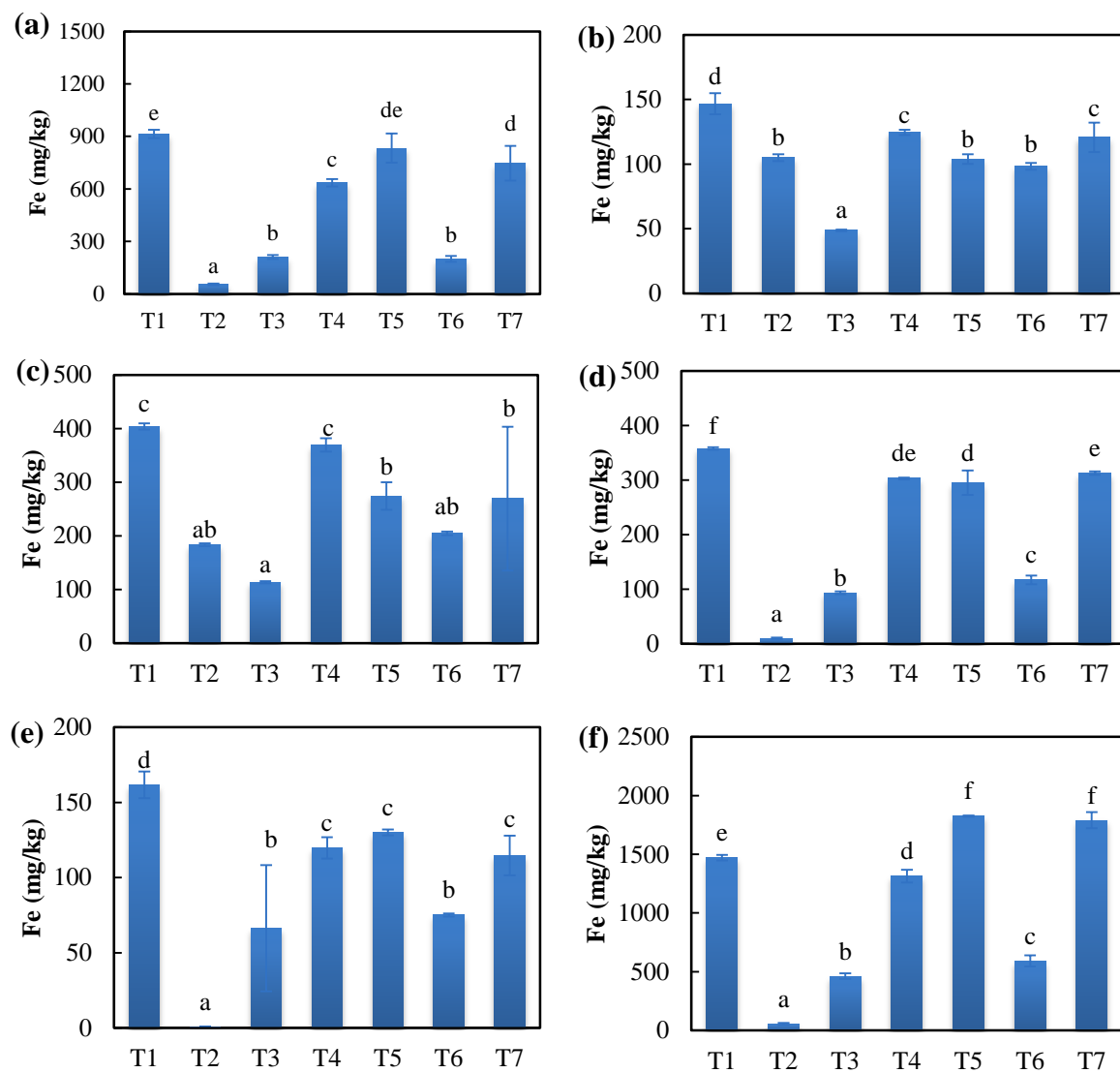
Fig. 3 Lead extracted by the 7 extracting solutions for the 6 soil samples. (a) M1, (b) M2, (c) M3, (d) M4, (e) M5, and (f) M6.

Fig. 4 Relationship between the LMWOA-extractable As and the LMWOA-extractable Fe for each of the six soil samples

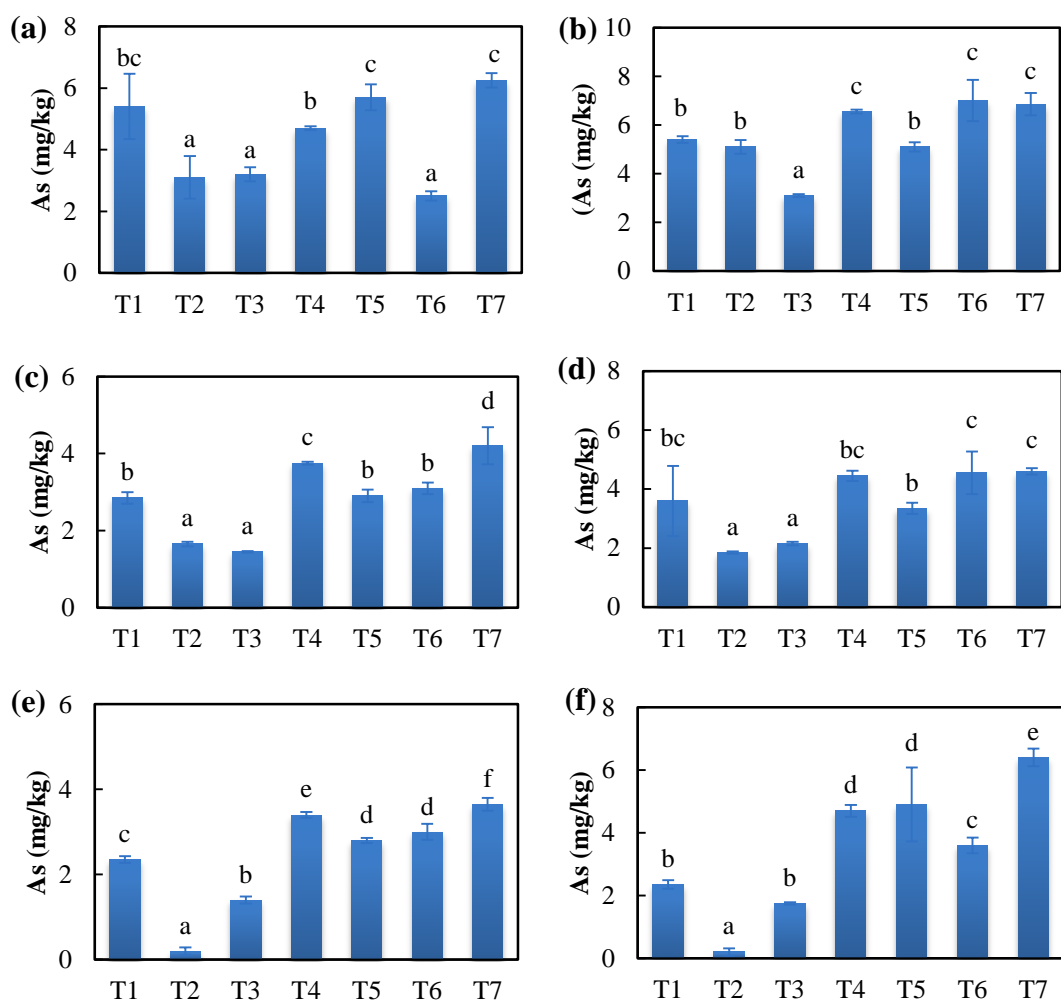
Fig. 5 Relationship between the LMWOA-extractable Pb and the LMWOA-extractable Fe for each of the six soil samples

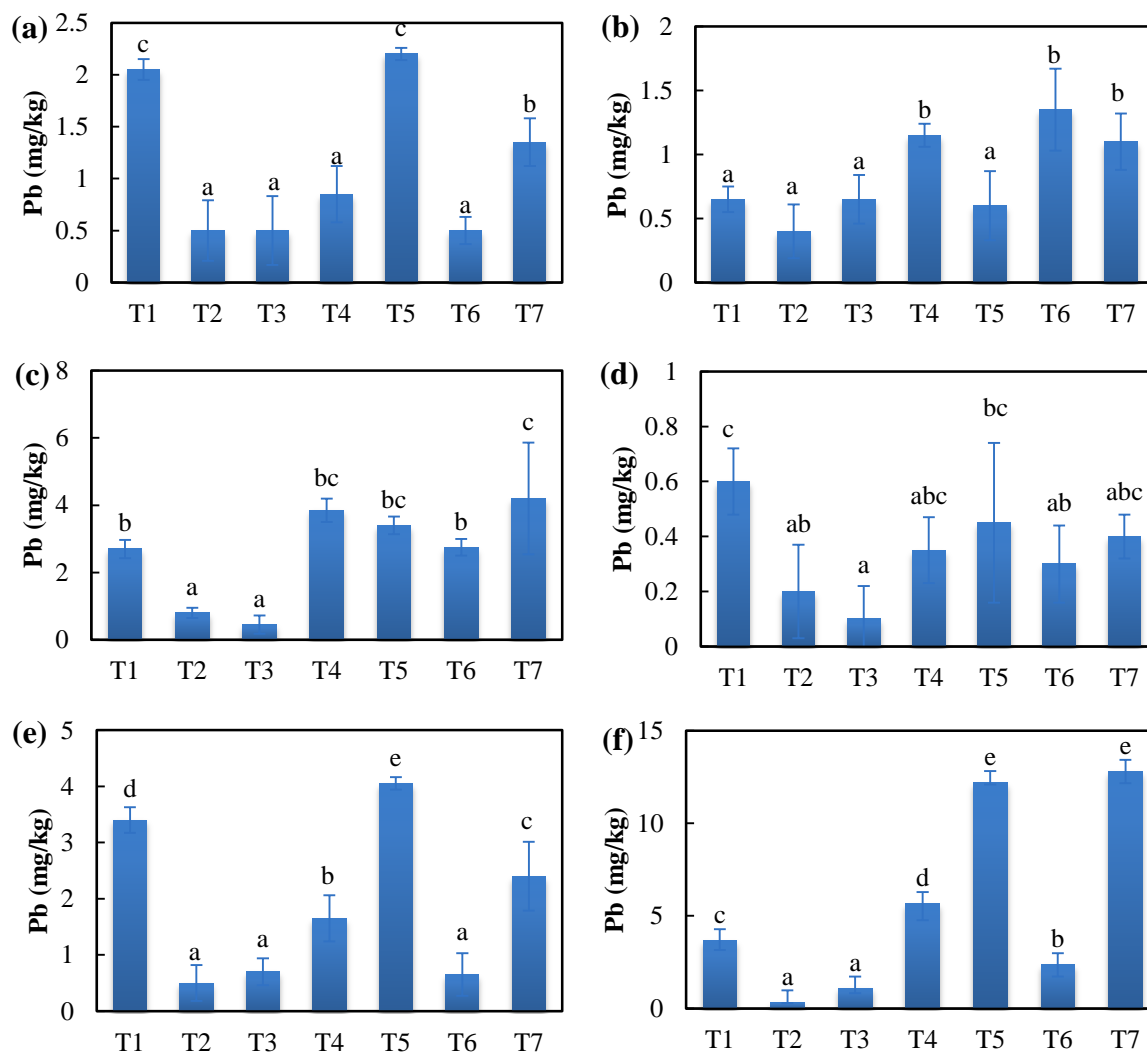
Fig. 6 Comparison of solution-borne elements on the 7<sup>th</sup> day and on the 56<sup>th</sup> day of the experiment. (a) Fe in M1, (b) Fe in M3, (c) As in M1, (d) As in M3, (e) Pb in M1, and (f) Pb in M3.

Fig. 7 Linear relationship between pH and (a) Fe in M1, (b) Fe in M3, (c) As in M1, (d) As in M3, (e) Pb in M1, and (f) Pb in M3.



**Fig. 1**

**Fig. 2**



**Fig. 3**



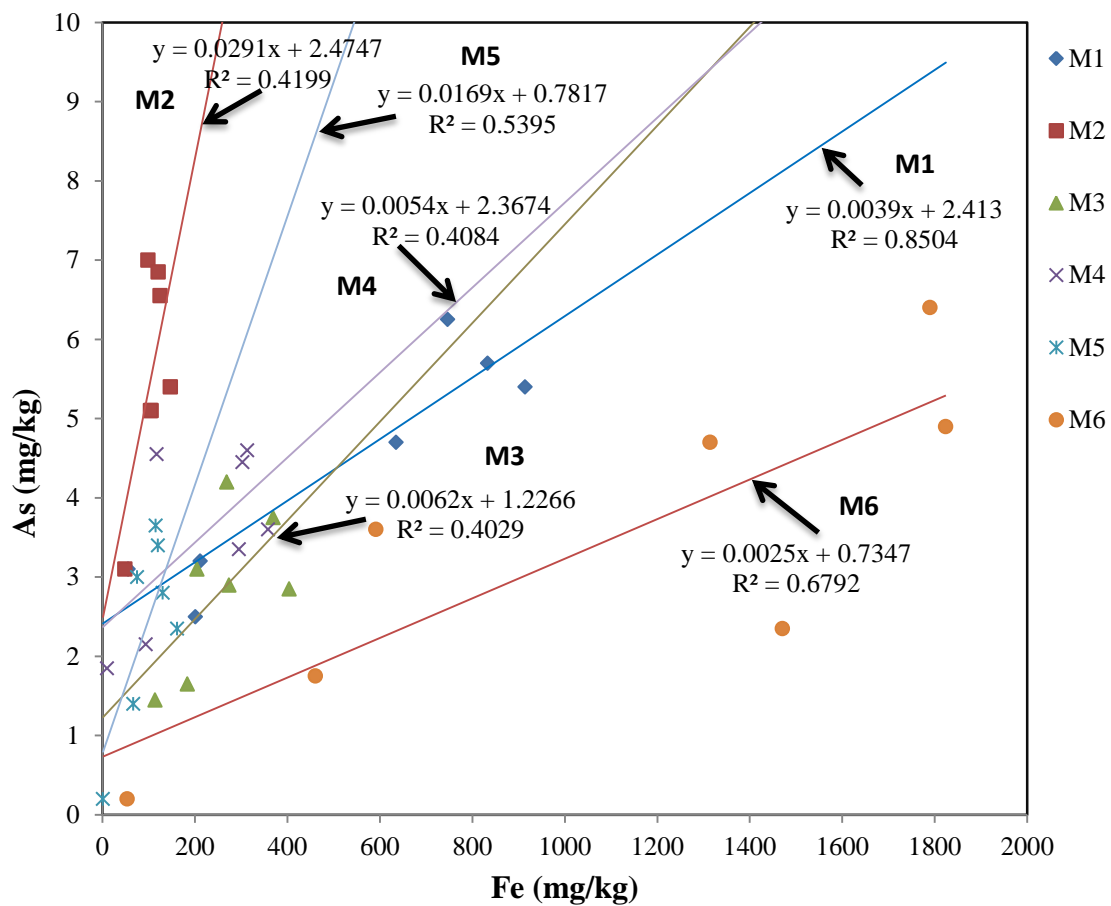


Fig. 4

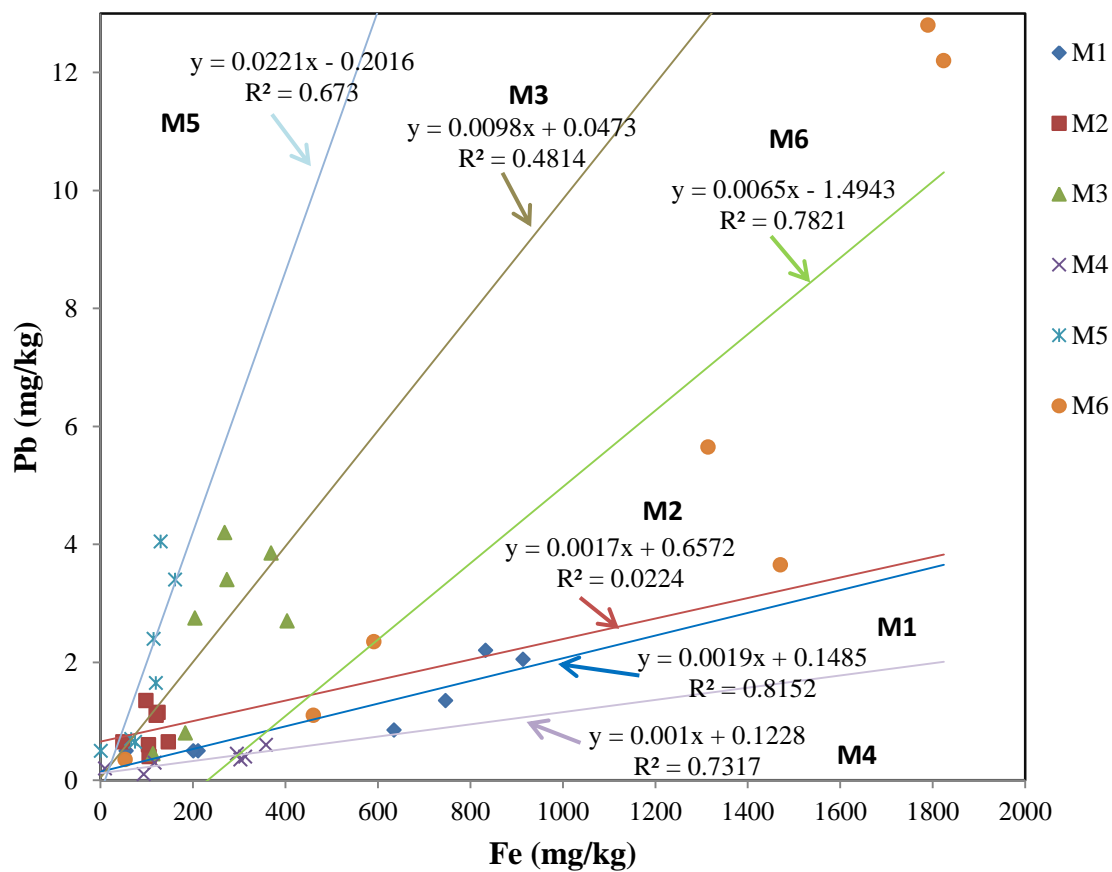


Fig. 5

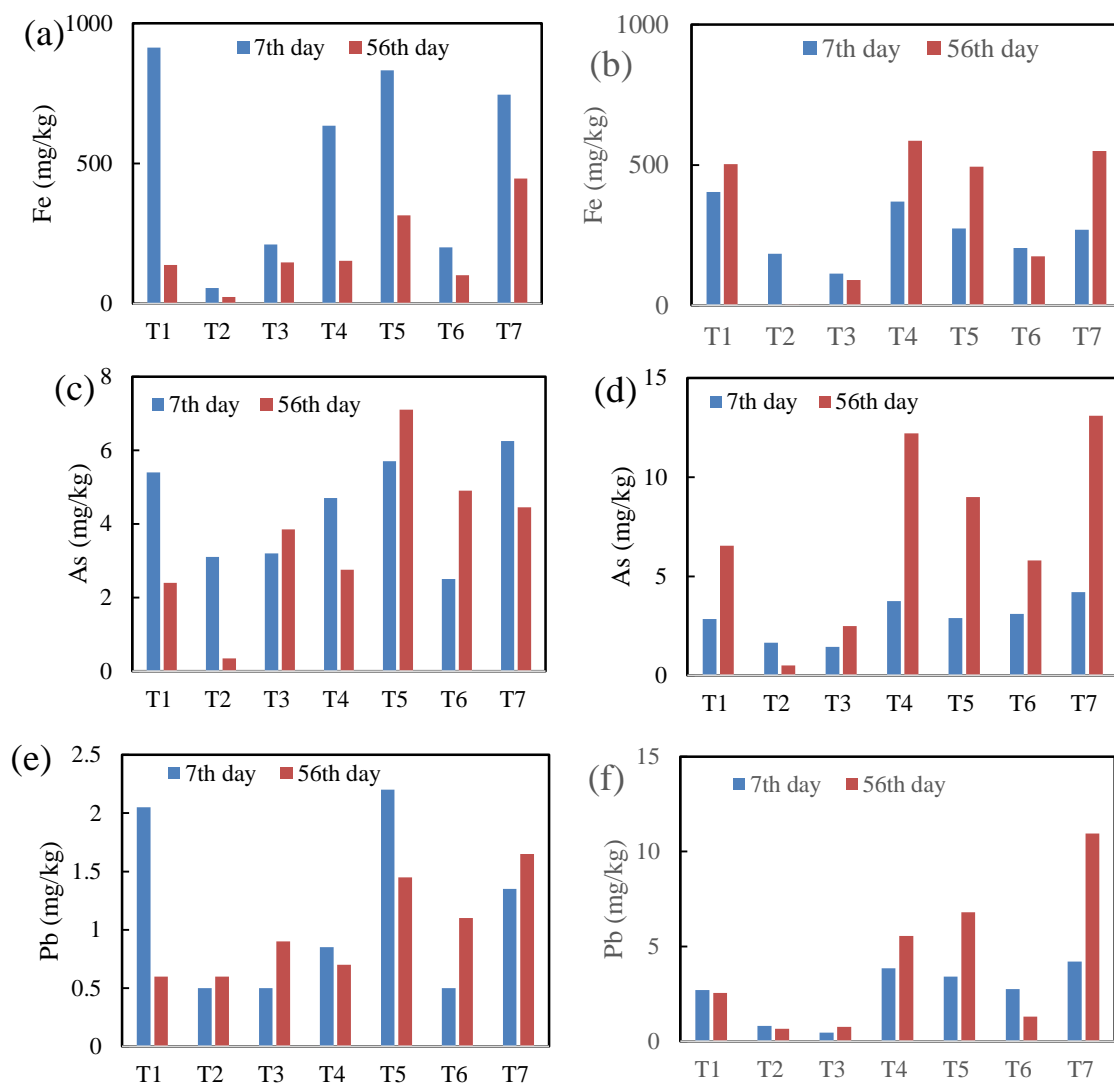


Fig. 6

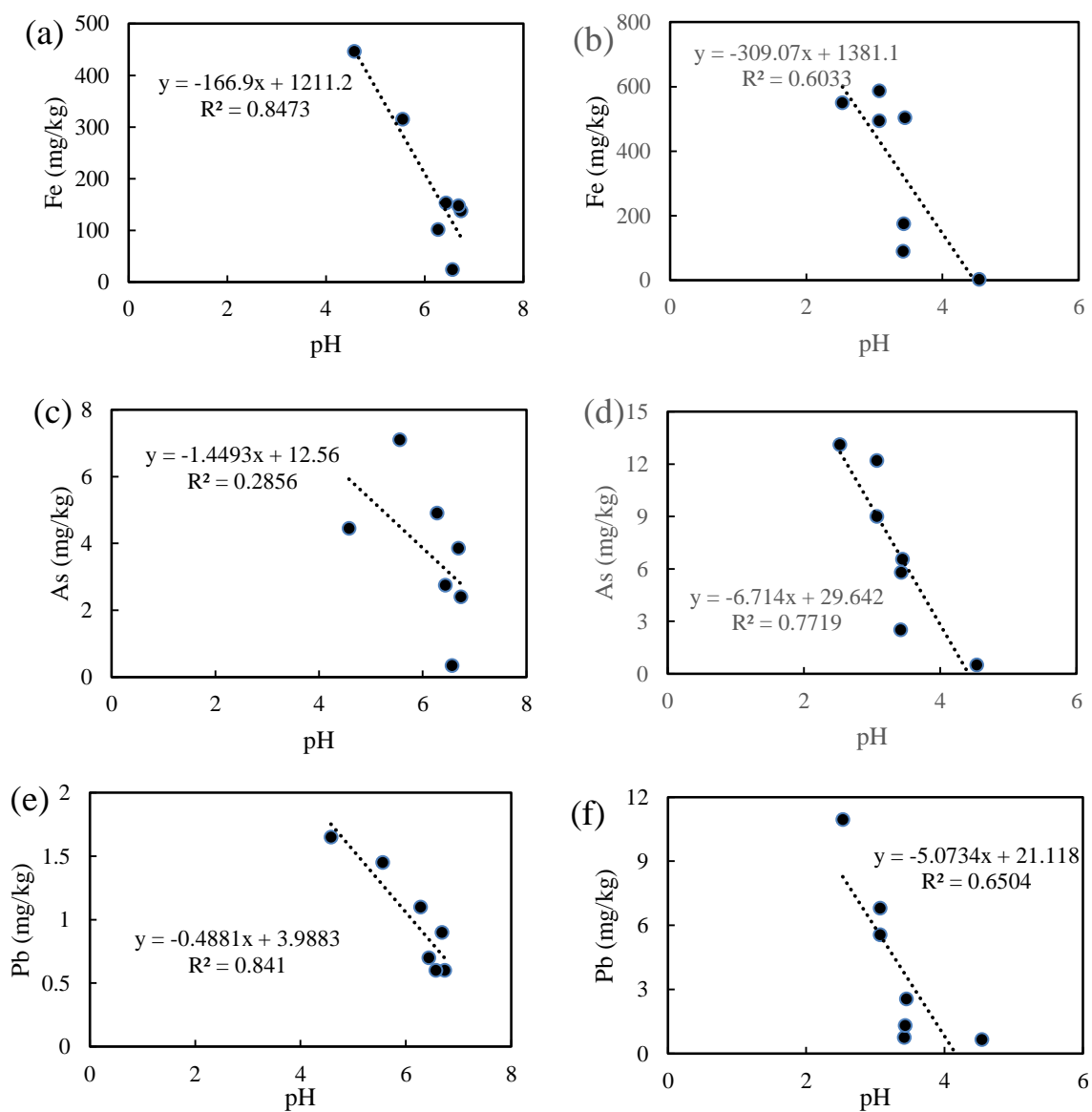


Fig. 7

**Table 1 Example published work on the examination of trace element mobilization by individual LMWOAs**

Organic acid used	Trace element investigated	Reference
Oxalic, fumaric, succinic, L-malic, tartaric, citric, acetic, propionic and butyric acids	Cd	Cieśliński et al., 1998
Citric, oxalic and malic acids	Cu, Zn, Pb and Cd	Wu et al., 2003
Citric and acetic acids	Zn, Cu and Pb	Yang et al., 2006
Citric, malic, tartaric, fumaric and glutaric acids	Zn, Cd and Pb	Schwab et al., 2008
Citric and malic acids	As	Castaldi et al., 2012
Citric acid	Cd, Cu, Fe, Mn, Pb and Zn	Tapia et al., 2013
Citric and tartaric acids	Cu and Zn	Pérez-Esteban et al., 2013
Citric and oxalic acids	Cd	Li et al., 2014
Citric, oxalic and malic acids	Pb	Wei et al., 2014
Caffeic, malic and polygalacturonic acids	Cu	Garau et al., 2015
Citric, malic and oxalic acids	Cd and Cu	Najafi et al., 2015
Malic and acetic acids	Cd	Hawrylak-Nowak et al., 2015
Acetic, lactic, citric, malic, formic acids	Pb, Zn, Cu, Cd and As	Vítková et al., 2015
Citric, oxalic and malic acids	As	Olaronke and Lin, 2016

**Table 1 Some major chemical characteristics of the soil samples used in the experiment**

<b>Sample</b>	<b>pH</b>	<b>EC (dS/m)</b>	<b>OMC (%)</b>	<b>As (mg/kg)</b>	<b>Pb (mg/kg)</b>	<b>Cu (mg/kg)</b>	<b>Cr (mg/kg)</b>	<b>Zn (mg/kg)</b>	<b>Fe (mg/kg)</b>	<b>Mn (mg/kg)</b>
<b>M1</b>	5.31	0.069	5.2	494	500	35	214	74	29271	315
<b>M2</b>	3.64	0.035	2.2	777	679	29	202	10	8792	12
<b>M3</b>	3.73	0.034	1.2	1230	1931	46	180	22	21357	36
<b>M4</b>	3.90	0.112	4.2	1999	894	117	199	63	59013	213
<b>M5</b>	4.19	0.139	5.2	790	572	86	166	98	37626	423
<b>M6</b>	5.06	0.089	7.4	567	393	61	161	74	37197	281

OMC: organic matter content

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OMC: organic matter content

**Table 3 pH, EC ( $\mu\text{S}/\text{cm}$ ) and various trace elements in the solution after 56 days of incubation**

Sample		T1	T2	T3	T4	T5	T6	T7
M1	pH	6.74 $\pm$ 0.03e	6.57 $\pm$ 0.04de	6.69 $\pm$ 0.05e	6.44 $\pm$ 0.06d	5.56 $\pm$ 0.10b	6.28 $\pm$ 0.05c	4.58 $\pm$ 0.01a
	EC	890 $\pm$ 6.00e	538 $\pm$ 10.0b	464 $\pm$ 18.0a	663 $\pm$ 17.0c	814 $\pm$ 14.0d	463 $\pm$ 8.00a	517 $\pm$ 12.0b
	Fe	27.5 $\pm$ 4.63ab	4.82 $\pm$ 0.83a	29.5 $\pm$ 4.25ab	30.5 $\pm$ 8.91ab	62.9 $\pm$ 16.3bc	17.7 $\pm$ 8.13ab	89.2 $\pm$ 31.2c
	As	0.48 $\pm$ 0.07ab	0.07 $\pm$ 0.02a	0.77 $\pm$ 0.05ab	0.55 $\pm$ 0.22ab	1.42 $\pm$ 0.82b	0.73 $\pm$ 0.38ab	0.89 $\pm$ 0.23ab
	Pb	0.13 $\pm$ 0.00ab	0.12 $\pm$ 0.01a	0.19 $\pm$ 0.02abc	0.14 $\pm$ 0.01ab	0.29 $\pm$ 0.07cd	0.25 $\pm$ 0.02bcd	0.33 $\pm$ 0.06d
M3	pH	3.45 $\pm$ 0.07c	4.54 $\pm$ 0.02d	3.42 $\pm$ 0.02c	3.07 $\pm$ 0.02b	3.07 $\pm$ 0.01b	3.43 $\pm$ 0.04c	2.53 $\pm$ 0.02a
	EC	365 $\pm$ 8.00c	72.0 $\pm$ 2.00a	146 $\pm$ 6.00b	682 $\pm$ 10.0d	721 $\pm$ 8.00e	382 $\pm$ 8.00c	1040 $\pm$ 15.0f
	Fe	100 $\pm$ 2.17b	0.54 $\pm$ 0.07a	18.0 $\pm$ 1.34a	117 $\pm$ 7.40b	98.7 $\pm$ 7.89b	34.9 $\pm$ 1.40a	110 $\pm$ 30.0b
	As	1.31 $\pm$ 0.02b	0.10 $\pm$ 0.01a	0.50 $\pm$ 0.20a	2.44 $\pm$ 0.19c	1.80 $\pm$ 0.10b	1.17 $\pm$ 0.02b	2.62 $\pm$ 0.47c
	Pb	0.51 $\pm$ 0.06abc	0.13 $\pm$ 0.03a	0.15 $\pm$ 0.00a	1.11 $\pm$ 0.14bc	1.36 $\pm$ 0.32cd	0.27 $\pm$ 0.04ab	2.19 $\pm$ 0.67d