

*Full Length Research Paper*

# **Effect of converter sludge, and its mixtures with organic matter, elemental sulfur and sulfuric acid on availability of iron, phosphorus and manganese of 3 calcareous soils from central Iran**

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Accepted 16 December, 2011

**Application of industrial wastes as soil amendment and fertilizers is now a common practice in agriculture. The effect of application of converter sludge, along with organic matter (alfalfa powder), elemental sulfur and sulfuric acid to 3 calcareous soils from central Iran was investigated in an incubation study. Converter sludge used contained 64% iron oxides. Treatments included 0, 2 and 4% pure converter sludge and mixed with organic matter and acidifiers. Results showed that application of 4% pure converter sludge increased soil pH and decreased soil Electrical conductivity (EC) but using a mixture of converter sludge with organic matter or acidifying materials (elemental S and sulfuric acid) decreased soil pH and increased EC. Olsen-P was least affected by the treatments. Application of mixtures of converter sludge with organic matter elemental S and sulfuric acid significantly increased DTPA-extractable Fe and Mn in all 3 calcareous soils with organic matter having the largest effect on DTPA-extractable Fe and elemental S, organic matter and sulfuric acid mixtures having similar effect on DTPA-extractable Mn. Olsen-P and DTPA-extractable Fe and Mn decreased with incubation time for all 3 soils. The rate of decrease was highest for Fe and lowest for P and was different for each soil.**

**Key words:** Calcareous soil, converter sludge, organic matter, elemental sulfur, sulfuric acid.

## **INTRODUCTION**

Iron deficiency (chlorosis) is common in plants growing in calcareous soils of high pH (Marrschner, 1995). Fe deficiency chlorosis (interveinal yellowing of juvenile leaves) has been observed in several plants growing in calcareous soils with moderate to high CaCO<sub>3</sub> content. Under these conditions, soil iron is mostly in the form of well-crystallized iron oxides (e.g., hematite and goethite) and almost insoluble and unavailable to plants (Loeppert et al., 1994). Synthetic chelates are commonly used to correct iron deficiency chlorosis in plants (Mortvedt et al., 1991). Due to high cost of synthetic chelates, their application is, however, limited (Destana et al., 2003).

Steel industries produce large quantities of different types of by-products such as: steel slag, converter sludge, fly ash, and ferosol that contain large amount of iron. Application of industrial wastes as fertilizer and soil amendment has become popular in agriculture (Mahmood and Eliot, 2006). Converter sludge contains appreciable quantities of iron (about 64%) and lime (Das et al., 2006). Parkpian (1983) reported that application of iron dust mixed with sulfuric acid to alleviated iron chlorosis, in sorghum and increased the yield significantly. Wang (2006) showed that moderate use of slag or acidified slag substantially increased corn dry matter yield and uptake of iron. Shariatmadari et al. (2008) reported that application of converter sludge and slag of iron melting factory to calcareous soils increased the soil DTPA-extractable Fe and Mn. Torkashvand et al. (2005) reported that the application of Lintz-Donawitz

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**Table 1.** Chemical analysis of the converter sludge used.

Constituents	Percent (%)
Fe <sub>2</sub> O <sub>3</sub>	44.30
FeO	19.22
CaO	6.12
SiO <sub>2</sub>	1.3
MgO	0.24
Al <sub>2</sub> O <sub>3</sub>	0.1
P <sub>2</sub> O <sub>5</sub>	0.272
MnO	1.02
ZnO	0.03
V <sub>2</sub> O <sub>5</sub>	0.07
S	0.13
Na <sub>2</sub> O	0.20
K <sub>2</sub> O	0.30

(LD) Converter sludge, a byproduct of steel-manufacturing industry, increased the pH of acid soils and AB-DTPA extractable P and Mn. Abouseeda (2002) reported that the application of basic slag in Egypt, increased the pH of the soil and the extractable fraction of Fe by CaCl<sub>2</sub>. Although several studies using converter sludge or other steel factories' by-products as fertilizer or soil amendments are found in literature, however, studies related to their use along with organic matter, and acidifying agents are limited. It was the objective of present study to investigate the effect of pure converter sludge and its mixtures with organic matter, elemental sulfur and sulfuric acid on availability of Fe, P and Mn in 3 calcareous soils of central Iran.

## MATERIALS AND METHODS

The converter sludge was obtained from Isfahan Steel Mill Factory, Isfahan, Iran. Chemical analysis of converter sludge, carried out by the central laboratory of Isfahan Iron Melting factory, is presented in Table 1. The compound contains about 63.5% iron oxides and a pH about 11.6 (pH of 1:10, sludge:water suspension) and some other elements such as Ca, Si, P and Mn. An incubation experiment was carried out for 120 days to evaluate the effect of application of pure converter sludge as well as mixtures of converter sludge with elemental sulfur, organic matter (alfalfa powder) and sulfuric acid. The experiment was conducted with 3 calcareous soils (soil No.1: Najaf abaad (Haplargids), soil No.2: Dastgerd (Haplargids), soil No.3: Ashegh abaad (Haplgypsid) collected from different areas (soil series) of Isfahan region, in central part of Iran. Selected physical and chemical properties of soils are shown in Table 2. Collected surface (0 to 30 cm) soil samples were air-dried and crushed to pass a 2 mm sieve. 500 g subsamples of each soil was treated as explained below and then moistened to field capacity (FC) with deionized water and transferred into the plastic containers and incubated for up to 120 days at room temperature (25 to 35°C). Treatments included control (L0), 2% (w/w) application of converter sludge (L2), 4% (w/w) application of converter sludge (L4), 2% (w/w) application of elemental sulfur powder (S2), 2% (w/w) application of converter sludge plus 2% (w/w) application of elemental sulfur powder (L2S2), 4% (w/w) application of converter sludge plus 2%

(w/w) application of elemental sulfur powder (L4S2), 2% (w/w) application of converter sludge plus 4% (w/w) application of alfalfa powder (L2O4), 4% (w/w) application of converter sludge plus 4% (w/w) application of alfalfa powder (L4O4), 2% (w/w) application of acidified converter sludge (pH = 2) (L2H2) and 4% (w/w) acidified converter sludge (pH = 2) (L4H2). (To acidify converter sludge 5 N sulfuric acid was used). Each treatment was replicated 3 times. Sub samples taken after 30, 60 and 120 days of incubation, were air-dried and crushed to pass a 2 mm sieve and stored for determination of pH, EC (electrical conductivity), DTPA-extractable Fe, Mn, Zn and Cu and Olsen-P. Moisture of containers were kept near FC soil moisture content throughout the incubation period by periodically weighing and replenishing evaporated water with deionized water. At each sampling period (30, 60 and 120 days) equivalent of 100 g dry soil was taken from each container. The samples were air-dried, crush and stored for analysis. Electrical conductivity (EC) and pH were measured in 1:2 (soil:water) suspension using a SELECTA 2005 pH-meter and a Metrohm 644 conductometer, respectively (Rhoads, 1996). DTPA-extractable micronutrients (Fe and Mn,) were extracted as described by (Jones 2001) and measured by Buck 210 atomic absorption spectroscopy (Jones 2001). Available P was extracted by 0.5 M NaHCO<sub>3</sub> (Olsen-P) and was determined using the method described by Morphy and Riley (1988). Calcium carbonate was measured by titration by acid and back titration of remaining acid with NaOH. Data were analyzed in a factorial completely randomized design. Each treatment was replicated three times, by using SPSS software and significant differences were determined based on p < 0.01 level for the least significant difference test.

## RESULTS

### pH

The effect of incubation time and treatments on soil pH is significant at the 1% level in soil No.1 and No.2 and significant at the 5% level in soil No.3. Application of converter sludge significantly increased soil pH. The increase was proportional to the rate of application (Figure 1). Application of sulfur powder, pure or mixed with 2 or 4% (w/w) converter sludge (S2, L2S2, L4S2), 2 to 4% (w/w) acidified converter sludge (L2H2, L4H2) or 4% alfalfa powder mixed with 2 or 4% (w/w) converter sludge (L2O4, L4O4), decreased the soil pH compared to the control (L0). There is a significant difference in soil pH among three incubation times (Figure 6). The highest soil pH was measured in the first month of incubation. pH of the soils initially decreased and then increased by the end of the incubation time, but was still lower for treatments containing S, organic matter (OM) and H<sub>2</sub>SO<sub>4</sub> compared to the first month of incubation. .

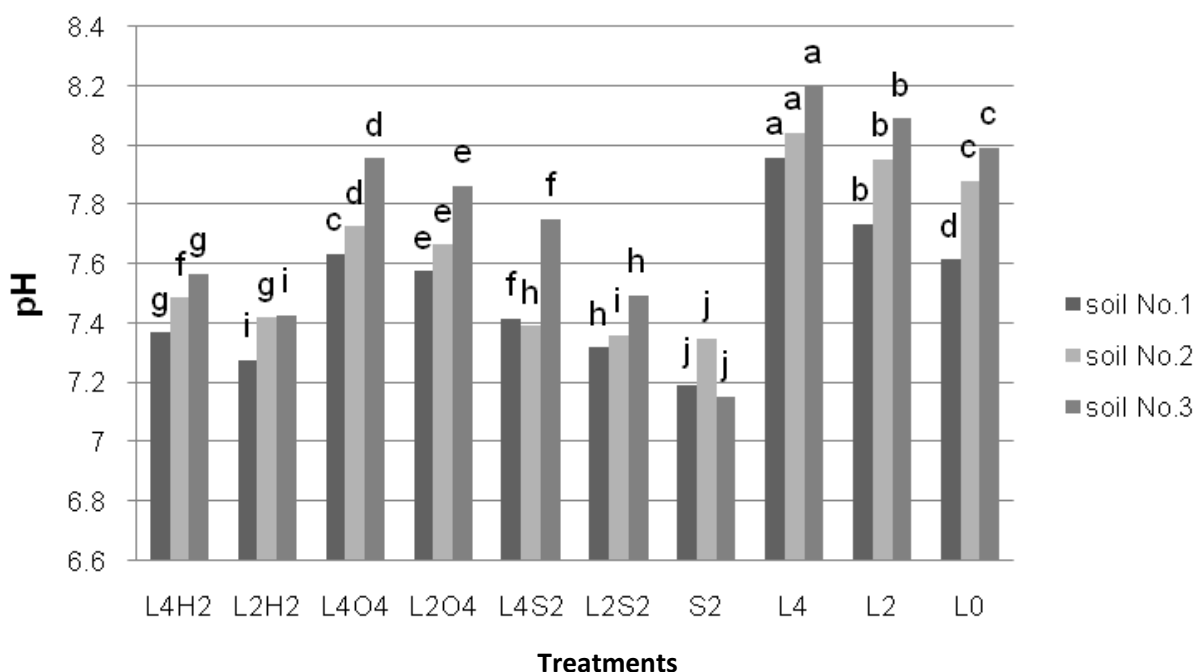
### EC

The effect of incubation time and treatments on soil EC is significant at 1% level in soil No.1 and No.3 and at 5% level in soil No.2. Application of pure converter sludge (2 to 4% w/w) had little or no effect on EC of 3 soils (Figure 2). Application of converter sludge mixed with S, sulfuric acid and alfalfa powder increased EC of all 3 soils

**Table 2.** Selected physical and chemical properties of soils used.

Soil no.	1	2	3
Soil series	Najaf abaad	Dastgerd	Ashegh abaad
Texture	Sandy Loam	Sandy Loam	Sandy Clay
Classification	Haplargids	Haplargids	Haplgypsid
pH	7.8	7.9	8.0
EC (dS/m)	2.1	3.3	2.8
CaCO <sub>3</sub> (%)	40	40	42
P (mg kg <sup>-1</sup> )	18.5	21.0	12.1
Fe (mg kg <sup>-1</sup> )	12.2	5.1	8.2
Mn (mg kg <sup>-1</sup> )	11.2	7.1	4.2

DTPA-extractable Fe and Mn. available (Olsen)-P.



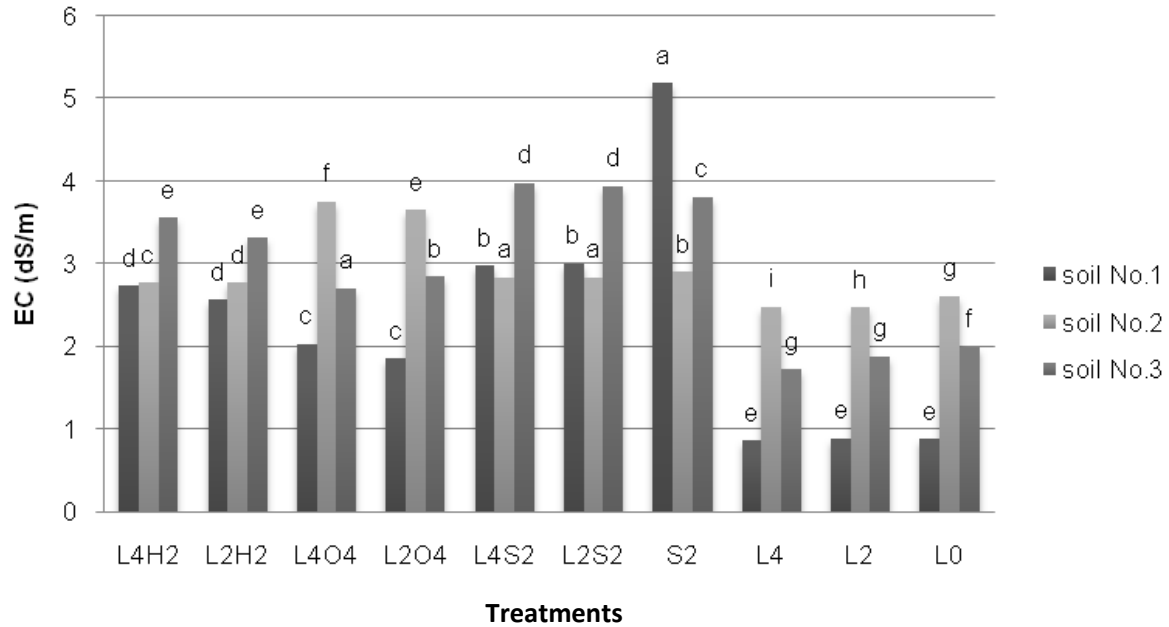
**Figure 1.** Effect of treatments on soil pH. For each soil, bars (treatments) with the same letter indicate no significant difference.

significantly. The largest increase was observed in elemental S (S2) in soil No.1, L4O4 in soil No.2 and L2S2 and L4S2 in soil No.3. EC of soils No.1 and No.3 significantly decreased after 2 month of incubation and then increased after 4 month of incubation but in soil No.3, the highest EC was measured in the second month of incubation (Figure 7).

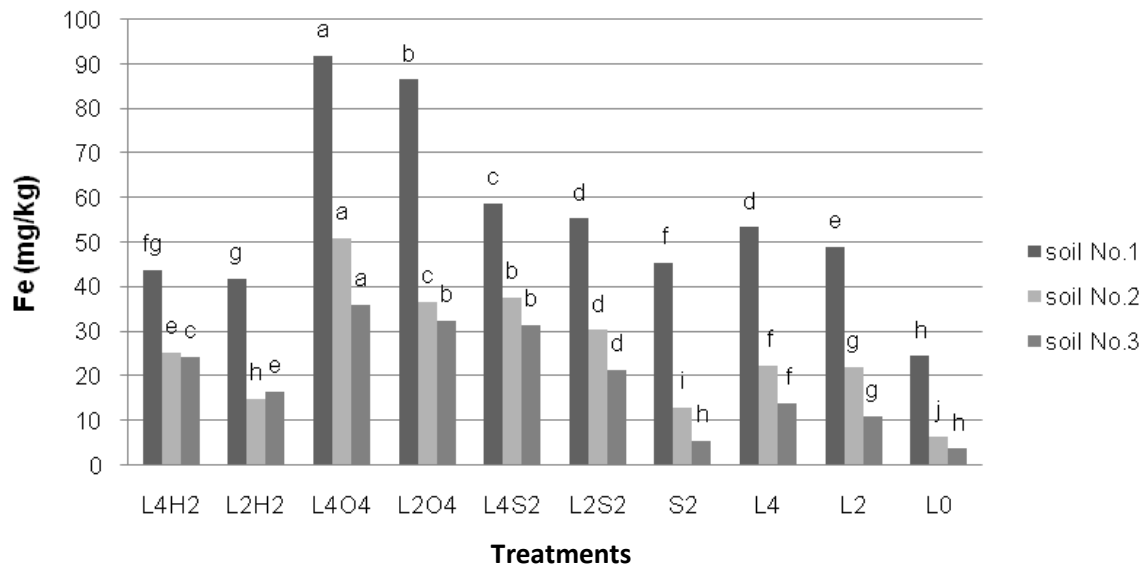
## Fe

Effect of treatments and incubation time on soil DTPA-extractable Fe was significant at  $p \leq 0.01$ . Application of pure converter sludge (2 or 4%) increased DTPA-

extractable Fe and the increases were proportional to the application rates. Application of 4% alfalfa powder mixed with 2 or 4% converter sludge (L2O4, L4O4) caused the highest increase in DTPA-extractable Fe. L4O4 treatment increased DTPA-extractable Fe, about 3.9 times in soil No.1, 3.5 times in soil No.2 and 7.3 times in soil No.3 as compared with the control (Figure 3). Application of mixtures of converter sludge with elemental S increased DTPA-extractable Fe as compared to the control and pure converter sludge treatments. The increases, however, were lower as compared to the mixture of organic matter and converter sludge. Effect of elemental S application was minimal and significant only in soil No.1. Application of acidified sludge (with sulfuric acid)



**Figure 2.** Effect of treatments on soil EC. For each soil, bars (treatments) with the same letter indicate no significant difference.



**Figure 3.** Effect of treatments on DTPA-extractable Fe. For each soil, bars (treatments) with the same letter indicate no significant difference.

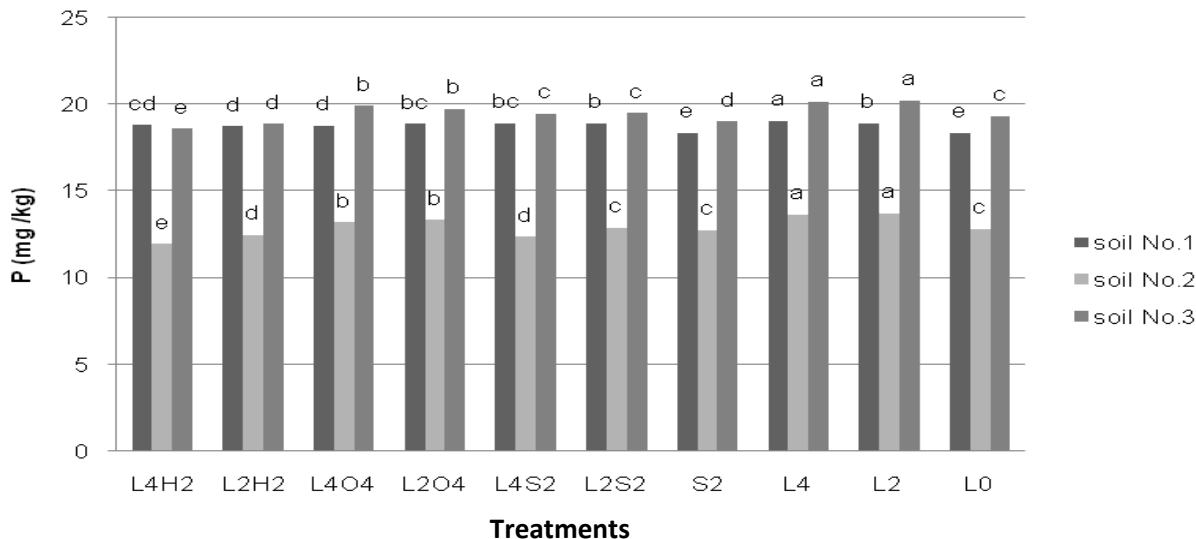
increased DTPA-extractable Fe significantly. The increases were, however, less than the mixtures of converter sludge with organic matter and elemental sulfur (Figure 5). Overall treatments effect on DTPA-extractable Fe on soil No.1 was highest and on soil No.3 lowest with soil No.2 being intermediate (Figure 8).

DTPA-extractable Fe decreased significantly with the incubation time (Figure 8). The decreases were larger between first and second month of incubation than

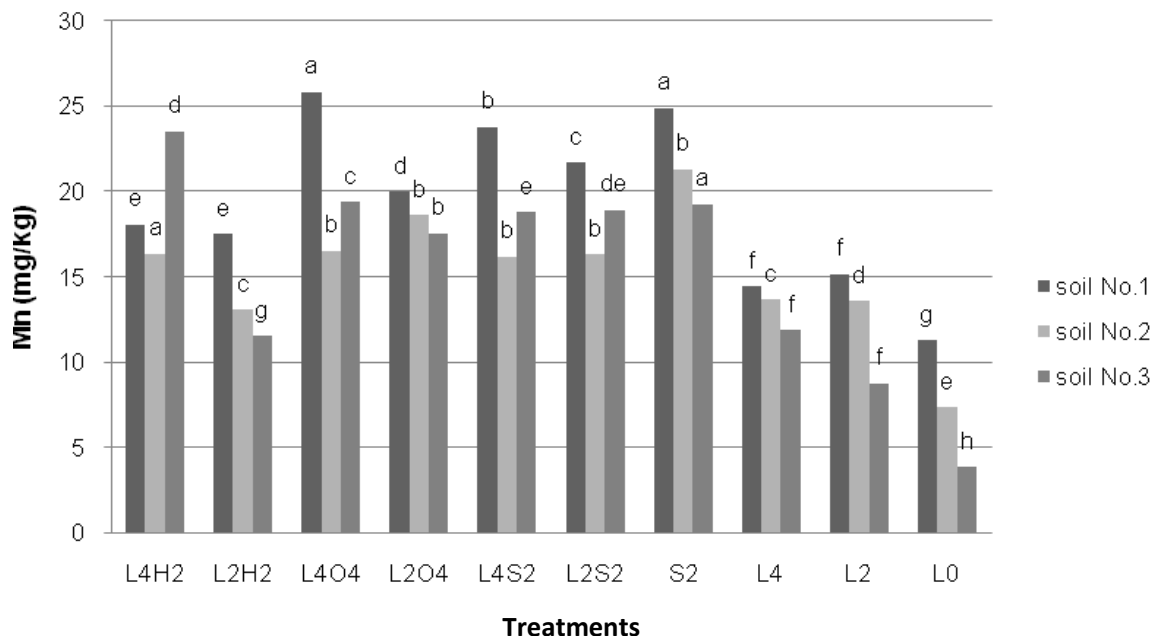
between the second and fourth month of incubation. The amount of decrease was largest in soil No.1 as compared to the other 2 soils.

**P**

Olsen-P was least affected by the treatments. While it slightly increased in some treatments it either decreased



**Figure 4.** Effect of treatments on Olsen-P. For each soil, bars (treatments) with the same letter indicate no significant difference.



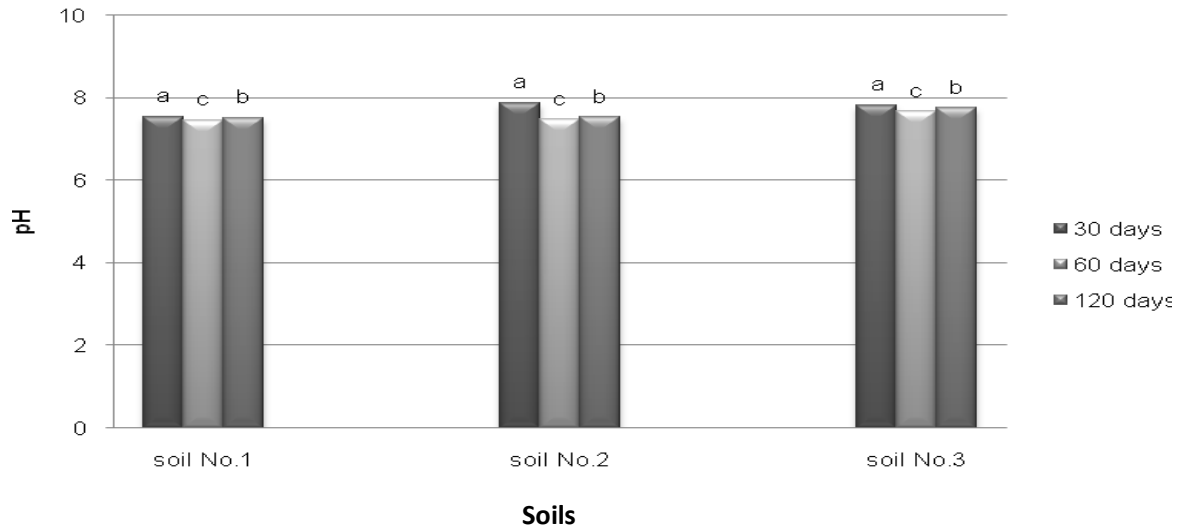
**Figure 5.** Effect of treatments on DTPA-extractable Mn. For each soil, bars (treatments) with the same letter indicate no significant difference.

or did not change in some other treatments (Figure 4). Olsen-P decreased with incubation time. The rate of decrease was lowest in soil No.1 and highest in soil No.3 (Figure 9).

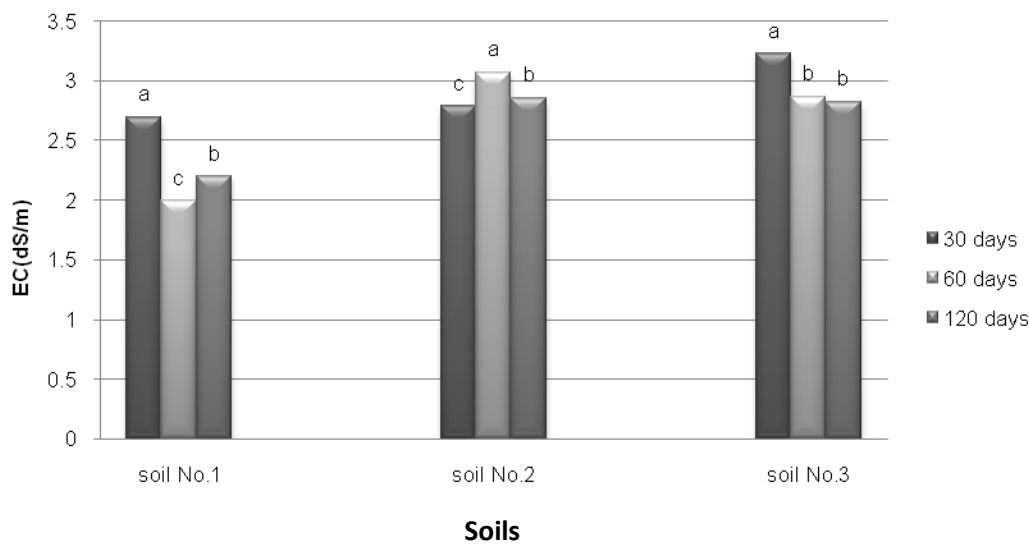
**Mn**

Effect of treatments on DTPA-extractable Mn is shown in

Figure 5. DTPA-extractable Mn increased significantly for all the treatments compared to the control. The magnitude of increased was, however, different for various treatments. The lowest increase was for 2 and 4% pure converter sludge while the largest increases were for the mixtures of converter sludge and alfalfa powder or elemental S. Effect of acidified converter sludge with sulfuric acid was intermediate. Elemental S treatment also had significant effect on DTPA-extractable



**Figure 6.** Effect of incubation time on soil pH. For each soil, bars (treatments) with the same letter indicate no significant difference.



**Figure 7.** Effect of incubation time on EC. For each soil, bars (treatments) with the same letter indicate no significant difference.

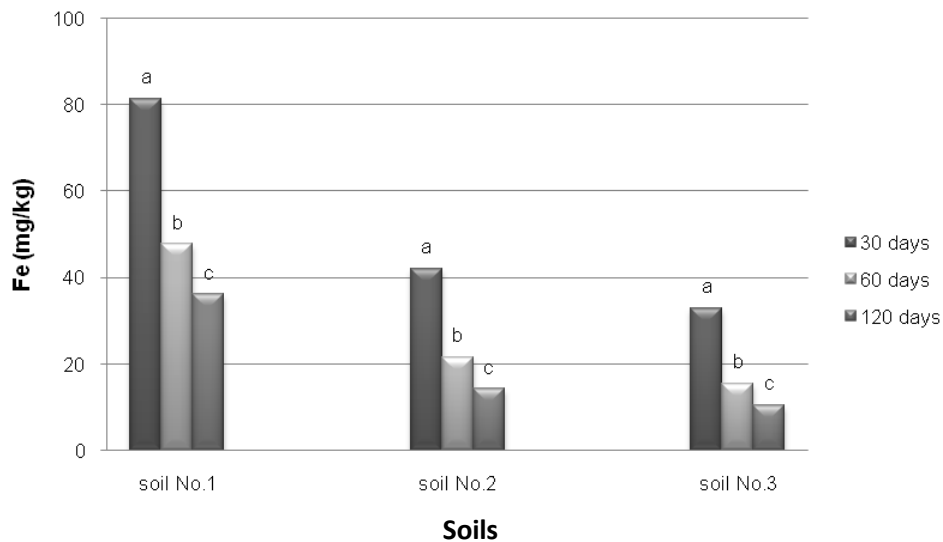
Mn. DTPA-extractable Mn decreased significantly with the incubation time. The decrease was larger in soil No.2 and 3 as compared with soil No.1.

**DISCUSSION**

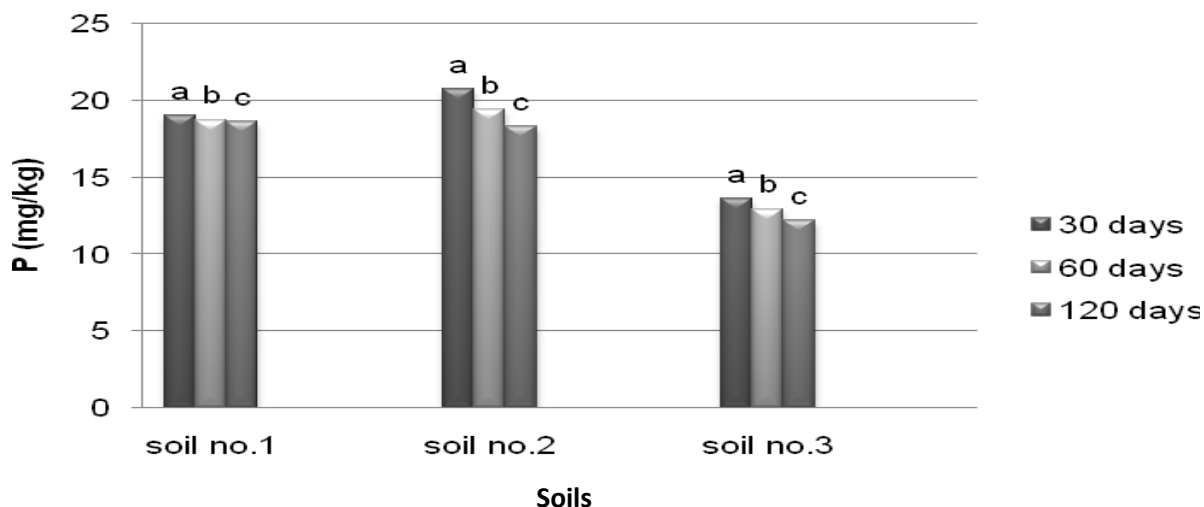
**pH**

Slight and proportional increase of pH as the result of converter sludge application is likely due to the high pH of converter sludge (pH=11/6). Similar results have been reported for calcareous and acid soils (Torkashvand and

Sedaghat Hoor (2007). Significant decrease in pH as the result of application of elemental S and its mixtures with converter sludge is likely due to the biological oxidation of elemental S and production of sulfuric acid during the incubation period. The decrease was largest for 2% S treatment probably because some of the acids produced by oxidation of S had been neutralized by base content of converter sludge. Similar discussion could be stated for mixtures of sulfuric acid and converter sludge. Slight decrease in pH of L2O4 and L4O4 treatments could be due to the formation of organic acids as the result of organic matter decomposition. Abbaspour et al. (2004) reported similar results when applied acidified converter



**Figure 8.** Effect of incubation time on DTPA-extractable Fe. For each soil, bars (treatments) with the same letter indicate no significant difference



**Figure 9.** Effect of incubation time on Olsen-P. For each soil, bars (treatments) with the same letter indicate no significant difference.

sludge to a calcareous soil.

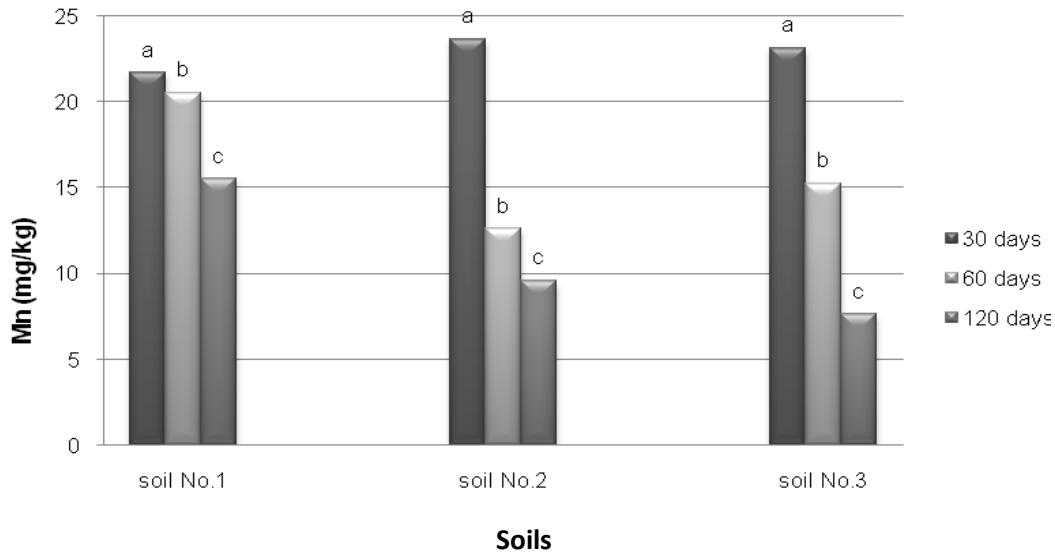
## EC

Except pure converter sludge which did not change or slightly decreased EC of soil, the rest of treatments especially those containing elemental S increased EC of soil solution. The increases are likely due to the formation of acids and increasing solubility of minerals in the soil or in the converter sludge. The acids formed (sulfuric in S containing treatments and organic in alfalfa containing treatments) could solubilize minerals such as  $\text{CaCO}_3$  in soil and increase the EC. Decrease in EC of soils treated

with pure converter sludge could be due to the precipitation of some minerals as the result of pH increase in these treatments (Figure 1). Similar results were reported by Abbaspour et al. (2004) who treated the calcareous soil with converter sludge. Slight decrease of EC with incubation time was likely due to the neutralization of acids added or formed in the treatments containing S, sulfuric acids or organic matter.

## Fe

DTPA-extractable Fe increased significantly in all treatments including pure converter sludge. This was likely



**Figure 10.** Effect of incubation time on DTPA-extractable Mn. For each soil, bars (treatments) with the same letter indicate no significant difference.

due to the high content of iron oxides (about 64%) which contains both Fe (II) and Fe (III) oxides with possible lower level of crystallization (as compared to Fe oxides in soil) which results in a higher solubility. Iron could precipitate as  $\text{Fe}(\text{OH})_3$  as the result of pH increase. However, very high pH results in formation of  $\text{Fe}(\text{OH})_4^-$  which results in increase in Fe solubility (Norvell and Lindsay, 1982). Enhanced increase in DTPA-extractable Fe in treatments containing or producing acids is likely due to the lower pH of these treatments compared to the control or pure converter sludge application. Decrease of DTPA-extractable Fe with incubation time in treatments containing or producing acid treatments was possibly due to the neutralization of acids and increase of pH. Application of 4% organic matter mixed with 4% converter sludge (L4O4) was the most effective treatment in increasing DTPA-extractable Fe in calcareous soils probably due to the formation of soluble Fe-organic acid complexes. Melali and Shariatmadari (2008) reported that application of converter sludge mixed with vermicompost increased DTPA-extractable Fe in calcareous soil. Abou Saeeda et al. (2002) found that the extractable fraction of Fe by  $\text{CaCl}_2$  increased with organic matter addition to soil. In all three soils, DTPA-extractable Fe decreased with incubation time, indicating the pH effect and possible organic matter decomposition effect on Fe solubility.

## P

Moderate and proportional increase in Olsen-P in treatments containing converter sludge could be due to the high Si content of converter sludge (Table 1). The increase was especially significant in the first month of incubation. This increase could be due to the release of P

from specific adsorption site by Si (Subramanian and Copalswamy, 1990). Kristen and Erstad (1996) also reported that the effect of slag on soil P was probably due to the Si content of slag. Application of organic matter or acid producing treatments (containing S or sulfuric acid) caused the highest increase on soil P during four months of incubation. Rayan and Stroehlein (1976) reported that the extractable P increased by adding Sulfuric acid to the soil. Increased Olsen-P in treatments containing organic matter was likely due to the increased microbial activity and possible mineralization of organic P (Aliasgharzadeh, 1997). Olsen-P decreased with time in all soils. It seems that P could have re-precipitated as calcium phosphate. Torkashvand and Sedaghat (2007) reported the same results. Abou Seeda et al. (2002) reported that increasing rates of slag increased the mobile fraction of P, during the incubation period.

## Mn

Increase in DTPA- extractable Mn as the result of application of acid containing or producing treatments (L2S2, L4S2, L2H2, and L4H2) was probably due to the lower pH of these treatments that increased solubility of Mn containing minerals. This could also be due to the effect of pH on reduction of Mn (IV) to Mn (II). Lower pH promotes reduction of Mn (Lindsay, 1979). Effect of elemental S containing treatments was more stable than  $\text{H}_2\text{SO}_4$  containing treatments. Abbaspour et al. (2004) reported that application of converter sludge mixed with elemental S powder increased extractable Mn in calcareous soils. Enhanced effect of organic matter mixtures with converter sludge could be due to the formation of complexes of Mn with organic acids and



other form of organic liqands. Mellali and Shariatmadari (2008) reported that the highest rate of the plant Mn uptake was observed in treatments containing 5% iron from converter sludge mixed with vermicompost.

## Conclusion

Converter sludge is an inexpensive source of Fe that could provide enough available Fe for calcareous soils. When mixed with organic matter (plant residue or organic fertilizers) or acid producing materials (elemental S or H<sub>2</sub>SO<sub>4</sub>) the effect on availability of Fe and Mn is greatly enhanced. Although the effect on availability of Fe and Mn is time dependent and decreases with time but the effect lasts long enough that most crop could benefit from its application. Application of acidified converter sludge or a mixture of converter sludge with proper amount of organic matter could be a beneficial method to provide Fe and other nutrients in calcareous soils. This, however, needs further research in the field and with various crops to determine the effect directly on the crop and also investigate the residual and environmental impact of long term application of this compound to calcareous soils.

## ACKNOWLEDGEMENTS

Partial support of this research by a grant from the Isfahan Iron mill factory is appreciated.

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