Journal of Applied Sciences

ISSN 1812-5654

Journal of Applied Sciences 6 (3): 673-677, 2006
ISSN 1812-5654

Organic Iron-fertilizers from Hornbeam-leaves, Outer Rice-husks and Charcoal

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Abstract: The aim of present study was to optimise the effectiveness of inorganic iron fertilizers by enhancement with amply existing natural organic substances. For this purpose, hornbeam-leaves and outer rice-husks were incubated with increasing quantities of iron-sulphate and plant-available and total iron measured. Additionally, we examined, whether the iron-fertilizer-effect can be increased by addition of charcoal. Present study shows that hornbeam-leaves plus 6.4% iron-sulphate and outer rice-husks plus 5% iron-sulphate yield the best expenses-benefit-relationship. The iron-availability to plants of rotting hornbeam-leaves could be increased by factors of 14 (6.4% $FeSO_4$) and 24 (64% $FeSO_4$ plus 5% char), while the excellent iron-availability of outer rice-husks (84.7%) could not be further increased. With respect to both ecological and economic benefits, the best iron-organic fertilizers can be obtained using hornbeam-leaves plus 6.4% $FeSO_4$ and outer rice-husks plus 5% $FeSO_4$. In both cases an organic iron fertilizer with 0.6% plant-available iron can be obtained.

Key words: Iron-deficiency, alkaline soils, calcareous soils, organic iron fertilizer, charcoal

INTRODUCTION

A wide-spread phenomenon among plants in arid areas is iron-deficiency or even iron chlorosis, which does not appear on the basis of inadequate quantities of total iron in soil in most cases, but on the basis of chemical qualities, such as alkaline milieu or high lime content[1]. The solubility of iron decreases by a factor of 1000 with each pH-increase of one unit in the pH-range between 4-9[2]. Therefore, an inadequate iron-nutrition of the plants often appears in calcareous soils[3] but also on alkaline soils[4]. The reduction of iron-deficiency is of particular economic interest in the cultivation of pistachios, which are especially cultivated in Iran[5].

It has been shown, that a sole application of soluble inorganic iron-salts to soil is not effective against chlorosis[3]. In contrast, synthetic as well as natural organic iron-compounds effectively reduce chlorosis[3]. Thus, from ecological as well as economic points of view, it is important to look for cheap organic materials, which are able to form organic iron complexes. The stability of such complexes, known as chelates, strongly depends on the chemistry of the organic material involved, and thus influences availability of iron to plants. An effective iron chelate is characterised by the fact that iron is not exchanged against other cations in the soil. In comparison to inorganic iron fertilizers, commercially available iron chelates are about five times as effective, but the expenses are 30 to 70 times higher than inorganic iron fertilizers[3]. Thus, with respect to removal of the iron-deficiency, the use of effective organic iron-fertilizers is highly desirable, and the application of iron chelates in arid regions is very popular[5].

However, on the basis of the price, it is not always economically employable[6]. Therefore, gardeners in these areas spend much effort to replace it with cheaper iron-fertilizers. One often observed fact is, that the fertilizer-effect of inorganic iron-fertilizer increases if compost or other organic substances are additionally applied. For instance, Zhenging[7] reported that chlorosis of apple trees in China could be removed after eight to ten applications of iron-sulphate together with animal manure and tree-wool-kernel-cakes.

In most cases, organic iron-fertilizers are synthesized artificially. Beside this synthetic production, also natural organic iron-compounds can be produced upon reaction of inorganic iron-salts with different natural organic materials or organic by-products of the paper-industry like lignosulfonates, polyflavonoids and phenols[3]. The disadvantage of naturallproduced organic iron-fertilizers s that the type of the chemical bonding is not known which might be a chelate or other less effective compounds.

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Among other factors, organic substances has shown to influence iron-availability in soil[3]. However, especially arid soils are poor in soil organic matter content, thus charcoal could be an appropriate soil organic matter substitute. It this context it has been shown that charcoal could increase the cation exchange-capacity and the quantity of the plant-available cations soil[8,9]. Therefore, it can be expected that charcoal exerts an increase of the plant-available iron on locations with iron-deficiency.

The aim of this study was to produce cheap and effective organic iron-fertilizers from rotting organic substances and iron-sulphate. For this purpose, hornbeam-leaves and outer rice-husks seem to be especially favourable, since they are useless waste products in Northern Iran produced in high quantity. Additionally, they become particularly enriched with carboxyl and phenolic hydroxy groups during decomposition (Hosseini, pers. Comm.) which might be able to form organic iron complexes via chelatization[1]. Furthermore, we examined if the effectiveness of organic iron-fertilizers can be further increased by addition of charcoal.

Afterwards, we determined the plant-availability of the organic iron-fertilizers. For this purpose we applied an extraction-method using NH_4HCO_3 and DPTA which has been particularly proven to be suitable for arid soils. Al-Mustafa and Abdalah[10] investigated 42 representative calcareous soils in Saudi Arabia with different extraction-methods for the estimation of the iron-deficiency of sorghum and showed that 1 M NH_4HCO_3 and 0.005 M DPTA at pH 7.6 had the highest correlation with the iron-uptake of sorghum. The critical level for sorghum was estimated to 3.4-4.8 mg kg^{-1} with this extraction method[10]. Presumably, the alkaline pH of the extraction-solution is responsible for the good correlation, reflecting the natural pH of calcareous soils.

MATERIALS AND METHODS

Production of organic iron-fertilizers on the basis of hornbeam-leaves and outer rice-husks: Hornbeam-leaves (*Carpinus betulus* L., 5.7 g each on a dry-weight basis) were incubated with increasing amounts (0, 6.4, 12.8, 32 and 64 weight) of iron as $FeSO_4$ in free-draining lysimeters in three-fold replication. The same tests were repeated with addition of 5% charcoal. Additionally, hornbeam-leaves were incubated with increasing amounts of charcoal (1, 2, 5 and 10% weight) without $FeSO_4$.

The incubation was carried out during 49 days in a greenhouse at constant temperature (28°C). The pots were irrigated with deionised water daily (50 mL). After 45 days, irrigation was stopped and incubation continued for another 4 days. After day 49, rotted leaves were dried at 65°C, weighed and ground for determination of total and available iron contents.

Outer rice-husks (*Oryza sativa* L., 90 g each on a dry-weight basis) were incubated with increasing amounts (0, 5, 10, 25 and 50% weight) of iron as $FeSO_4$ in free-draining lysimeters in three-fold replication. The same tests were repeated with addition of 5% charcoal.

The incubation was carried out during 6 months in a greenhouse at constant temperature (28°C). The pots were irrigated with deionised water daily (50 mL). After the first month, irrigation was only carried out when the pots were dry. After day 158, rotted rice-husks were dried at 65°C, weighed and ground for determination of total and available iron contents.

Chemical characterization of the produce organic iron-fertilizers: For the determination of total iron, about 100 mg of ground residue was placed into quartz-digestion tubes and digested with 1 mL of 65% HNO_3 in a high-pressure digestion apparatus for 8 h at 170°C[11]. The digestion solution was diluted to 25 mL with deionised water and kept in polyethylene bottles.

The extraction of plant-available iron was achieved with a solution containing 0.005 M DPTA as chelating reagent and 1.0 M NH_4CO_3 to keep the pH at 7.6[12]. About 100 mg of organic iron-fertilizer was shaken with 20 mL of extraction solution for 15 min, filtered, and diluted to 50 mL. Both total and plant-available iron concentrations were measured by atomic absorption (Varian SpectrAA400). Calibration was carried out using five standard solutions with increasing concentrations and the same matrix as the samples.

Total organic carbon and total nitrogen was determined by dry combustion on an Elementar Vario EL C/N-analyser.

RESULTS AND DISCUSSION

Decomposition of organic matter: Decomposition of both organic materials is strongest if no iron was added (Table 1 and 2) although the decomposition of rice-husks is generally lower, probably due to the high C/N ratio (Table 2). The more iron was added, the less hornbeam-leaves are decomposed (Table 1). Therefore, iron seems to slow down decomposition of labile organic matter. This observation can be explained by sorption of iron to the organic matter of the hornbeam-leaves[13,14] and/or by complexation of iron-ions with carboxylic and phenolic groups of decomposing hornbeam-leaves. The retardation of organic matter decomposition at the occurrence of metals is a well-known phenomenon. For instance, Boudot *et al.*[15] described that the decomposition of citric acid and melanin is delayed when iron or aluminum is present. Another possible explanation for reduced

Table 1: Composition of hornbeam-leaves/iron-sulphate/charcoal mixtures after 49 days of incubation with respect to weight loss, organic matter composition reflected by the C/N-ratio and total and plant available iron

Mixture	Weight loss [%]	Total iron [mg g^{-1}]	Total iron [g]	Plant-available iron [mg g^{-1}]	Plant-available iron [g]	Plant available/ total iron [%]	C/N
Hornbeam leaves (HL)	34.4±0.8	5.24±0.3	0.026	0.083±0.01	0.4	1.6	12.8
HL + 6.4% Fe	32.8±0.6	28.69±0.7	0.144	6.45±0.3	32.0	22.5	14.7
HL + 12.8% Fe	23.45±0.5	30.5±0.4	0.152	7.23±0.2	36.0	23.7	15.3
HL + 32% Fe	16.2±0.6	52.89±0.8	0.264	14.04±0.5	70.0	26.5	15.3
HL + 64% Fe	9.9±0.4	63.82±0.7	0.319	16.68±0.5	83.0	26.1	15.2
HL + 6.4% Fe + 5% char	17.4±0.7	25.00±0.6	0.125	5.55±0.5	27.0	22.2	17.4
HL + 12.8% Fe + 5% char	11.5±0.5	35.2±0.7	0.176	9.54±0.4	47.0	29.6	17.9
HL + 32% Fe + 5% char	5.8±0.8	39.94±0.5	0.197	13.621±0.5	68.0	34.1	16.0
HL + 64% Fe + 5% char	26.5±0.7	49.94±0.9	0.294	18.93±0.6	94.0	37.9	16.9
HL + 1% char	n.d.	3.89±0.4	0.019	0.1291±0.02	0.6	3.3	12.8
HL + 2% char	n.d.	5.69±0.5	0.028	0.1197±0.02	0.6	2.1	14.6
HL + 5 % char	n.d.	4.92±0.2	0.024	0.162±0.02	0.8	3.2	15.1
HL + 10 % char	n.d.	5.45±0.4	0.027	0.23±0.03	1.2	4.2	19.6

n.d. not determined

Table 2: Composition of outer rice-husks/iron-sulphate/charcoal mixtures after 158 days of incubation with respect to weight loss, organic matter composition reflected by the C/N-ratio and total and plant available iron.

Mixture	Weight loss (%)	Total iron [mg g^{-1}]	Total iron (g)	Plant-available iron [mg g^{-1}]	Plant-available iron (g)	Plant available/ Total iron [%]	C/N
Outer rice-husks (RH)	0	1.4±0.3	(0.13)	1.2±0.5	(0.108)	83.1	62.0
RH + 5% Fe	7.06±0.7	6.0±0.4	(0.54)	4.8±0.6	(0.432)	80.0	84.8
RH + 10% Fe	9±0.6	7.9±0.4	(0.71)	6.1±0.7	(0.549)	77.3	87.9
RH + 25% Fe	16.55±0.9	13.0±0.5	(1.18)	7.9±0.5	(0.731)	61.9	92.2
RH + 50% Fe	3.6±0.4	22.8±0.6	(2.05)	11.2±0.6	(1.008)	49.2	76.9
RH + 5% char	0	1.9±0.3	(0.17)	1.6±0.5	(0.144)	84.7	72.4
RH + 5% Fe + 5% char	3.9±0.7	7.9±0.5	(0.71)	6.5±0.7	(0.585)	82.4	79.7
RH + 10% Fe + 5% char	0	9.7±0.5	(0.87)	7.8±0.4	(0.622)	71.5	85.0
RH + 25% Fe + 5% char	15.4±0.5	15.7±0.4	(1.85)	8.5±0.5	(0.767)	41.4	84.0
RH + 50% Fe + 5% char	4.3±0.3	27.9±0.5	(2.51)	9.2±0.5	(0.828)	33.0	82.4

organic matter decomposition at the presence of metal ions could be toxicity of the metals at high concentrations[15]. Also Miltner [16] showed that Al-hydroxide and Fe-oxide (ferrihydrite) retarded beech litter decomposition while Mn-oxide (birnessite) accelerated the decomposition of organic matter.

Further evidence for the formation of stable iron-organic complexes is given by increasing C/N ratios of hornbeam-leaves with increasing iron addition (Table 1). While without iron addition, hornbeam-leaves showed a C/N ratio of 12.8, this ratio increased to 15.3 at the highest iron addition. This trend is not so clear for the rice-husks (Table 2). The formation of stable organic matter at the presence of high iron concentrations would have an additional beneficial effect on the stability of the organic iron-fertilizer.

Plant-available iron levels: Rotted hornbeam-leaves (83 mg kg^{-1}) and rice-husks (1200 mg kg^{-1}) alone already contained plant-available iron levels above the critical level reported for sorghum and pistachios 3.4-4.5 mg kg^{-1}[10]. Thus, rotted hornbeam-leaves and rice-husks alone would be appropriate organic iron-fertilizers to reduce iron-deficiency on alkaline soils. After beech, hornbeam is the second most abundant tree in Northern Iran. However, due to the high decomposition rates, the sole use of hornbeam-leaves for iron-fertilization purposes is hardly economically useful while rice-husks decompose very slowly, making them suitable for iron fertilization. Nevertheless, it is desirable to design a stable and more iron-rich organic fertilizer which could be produced in Northern Iran and transportation to the south would be more economic with respect to a certain iron level.

In this way, plant-available iron increased with increasing iron amendments. The most effective increase, however, appears in both cases with the lowest iron addition in which the total amount of plant-available iron increased by a factor of 80 at 6.4% iron addition to hornbeam-leaves, while at the tenfold iron addition, only a factor of 208 is reached (Table 1). For rice-husks, 5% iron addition caused a four-fold increase in total plant-available iron while 50% iron addition lead to a nine-fould increase (Table 2). Since inorganic iron-salts (150-300 US\$ t^{-1}) are normally more expensive than organic substances (about 25 US\$ t^{-1}) in Iran, a relative maximum should always be reached for practical purposes for plant-available iron. Additionally, as both iron-sulphate and waste organic materials such as hornbeam-leaves and rice-husks are readily available in Iran, the production of organic iron fertilizers might be economically feasible with potential for exportation to other countries such as Saudi Arabia, Morocco, Egypt etc. as well. In comparison, one ton of commercially available iron-chelates would cost about 10,000 US$.

Using $FeSO_4$ alone for fertilization, approximately 90% is washed out or is fixed in the soil. Present experiments showed that at the lowest $FeSO_4$ addition to hornbeam-leaves, iron losses can be reduced to 60% (Table 1), a relative increase of potentially plant-available iron of 50%. This corresponds to an economic benefit of about 1,700 Euro t^{-1} of necessary iron. Converting this economic efficiency on the quantity of the plant-effective iron, even an increase of about factor four can be reached ($FeSO_4$: 10% effective corresponding to 2250 US$ t^{-1} of effective iron, $FeSO_4$ and hornbeam-leaves 40% effective, 563 US$ t^{-1} of effective iron). The iron losses using rice-husks were in the same order of magnitude as using $FeSO_4$ alone (Table 2). However, the irrigation water containing the leached iron could be recycled. Additionally, as mentioned above, rice-husks might be used solely as organic iron-fertilizer due to their high plant-available Fe content.

Since iron is a micro-nutrient, one can expect that in both cases, the iron-concentration is satisfactory in the fertilizer. Although commercially available organic iron-fertilizers contain up to 13% water-soluble iron, the extractability with NH_4CO_3/DPTA at pH 7.6 and thus the plant-availability under alkaline conditions would decrease tremendously. Additionally, these iron-chelates are very expensive (10,000 US$ t^{-1}) and thus unaffordable for pistachio-farmers in Iran.

Total iron contents: The contents of total iron increased from 0.5% in the control sample to 6.382% with 64% added iron in the hornbeam-leaves (Table 1) and from 0.14 to 2.28% in the rice-husks (Table 2). These results show that the more iron added, the more iron-ions were bound to both organic materials and it can be assumed that all iron is bound in organic forms, since the lysimeters used in both experiments were heavily irrigated and thus, free inorganic iron was leached quickly. Consequently, organic iron-fertilizers with 6.3 and 2.3% total iron with 26.1 and 49.2% available iron has originated for hornbeam-leaves and rice-husks, respectively.

Influence of charcoal: Addition of 5% charcoal to decomposing hornbeam-leaves with increasing iron levels obviously does not increase total and plant-available iron concentrations (Table 1). However, the relative contribution of plant-available iron increased with increasing iron addition from 22.2 to 37.9% (Table 1). Thus, charcoal has a positive effect on iron complexation in a plant-available form. For the rice-husks,charcoal addition does increase the total amount of iron after incubation but there is no effect on plant-availability (Table 2).

CONCLUSIONS

Present study shows that addition of hornbeam-leaves increases the plant-availability of inorganic iron-fertilizers in alkaline soils from 10 to approximately 20%. Another increase to approximately 40% can be reached through addition of 5% charcoal. Besides this ecological potential, also the economic benefit is enormous, since approximately one ton of hornbeam-leaves costs 25 US$ in Iran, while one ton $FeSO_4$ costs about 225 US$ and has a very low efficiency. Therefore, the application of $FeSO_4$ in combination with hornbeam-leaves and charcoal reduces the total costs by a factor of about for at the same effective iron-quantity. Additionally, rice-husks should be used without additional iron addition as cheap organic iron-fertilizer.

ACKNOWLEDGEMENTS

We are indebted to the German Academic Exchange Program for providing a grant for Pirouz Azizi and to Prof. Wolfgang Zech for using his laboratory facilities. The patience and help of Tanja Gonter and Karin Jeschke during laboratory work is kindly acknowledged.

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