International Journal of Chemical Studies

P-ISSN: 2349–8528
E-ISSN: 2321–4902
www.chemijournal.com
IJCS 2020; 8(3): 1376-1380

Received: 04-03-2020
Accepted: 06-04-2020

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Effect of wood vinegar on the nutrient release of Zn and Fe in a sodic soil

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DOI: https://doi.org/10.22271/chemi.2020.v8.i3s.9388

Abstract
The use of $ZnSO_4$ and $FeSO_4$ either alone or in combination with wood vinegar is incubated to 60 days and it was compared in the present investigation with an aim to increase the nutrient release pattern of micronutrients viz, Fe and Zn under sodic soil conditions. An incubation experiment was conducted during 2019 in ADAC & RI, Trichy, Tamil Nadu. The incubation experiment comprised of 12 treatments replicated twice in a completely randomized design. The treatments included recommended dose of $FeSO_4$ and $ZnSO_4$ alone and their combination and their combination with three levels of wood vinegar viz., 50, 100 and 150 ml/l applied as as spot drenching (SD). Incubated soil sample were analysed for DTPA Zn and Fe at different intervals (0, 15, 30 45 and 60 DAI). The results of the investigation revealed significant differences in wood vinegar release of DTPA Zn and Fe among the treatments in comparison with the $ZnSO_4$ and $FeSO_4$ either alone or in combination of $ZnSO_4$ and $FeSO_4$. Among the treatments, During 0^{th} day of incubation (DAI), the treatment T_{12} receiving the recommended dose of both $ZnSO_4$ and $FeSO_4$ along with wood vinegar (WV) @ 150 ml/l as spot drenching recorded significantly higher value of available Zn content (46.68 mg kg^{-1}). The lowest value was recorded in the treatment T1 (6.72 mg kg^{-1}) which received recommended dose of $FeSO_4$ alone. At 0^{th} day of incubation (DAI), the treatment receiving recommended dose of $ZnSO_4$ alone (T2) recorded the lowest DTPA Fe (7.32mg kg^{-1}) while the highest value(48.28 mg kg^{-1}) was recorded in the treatment receiving recommended dose $FeSO_4$ @ 50 kg /ha along with WV @150 ml/l (T6). Therefore, incorporation of wood vinegar increased the effectiveness of Fe and Zn in sodic soils. The release of DTPA Zn and Fe attained peak at 15 DAI and declined thereafter up to 60 DAI. The experiment received that the DTPA Zn and Fe which contributes to available Zn and Fe considerably increased under wood vinegar drenching in sodic soil.

Keywords: Nutrient release, incubation, wood vinegar, iron, zinc, sodic soil

Introduction
Currently more than 20 per cent of the world's irrigated land is salt affected. Of that about 60 per cent are saline sodic and sodic soils, warranting attention need for efficient, inexpensive and environmentally feasible amelioration. Salt affected soils limit crop growth owing to the presence of soluble salts and / or high amounts of exchangeable sodium (Soil Science Society of America, 1997) [21]. The presence of ions such as Ca^{2+}, Mg^{2+}, Cl^{-}, Na^{+}, sulfate (SO_4^{2-}), bicarbonate (HCO_3^{-}) and in some cases K^{+} and nitrate (NO_3^{-}) further aggravates the problem (Bernstein, 1975) [3]. The amelioration of sodic soils with chemical amendments is an established technology. But very poor farmers are unable to reclaim the soil and use the extra dose of fertilizer for increasing the availability of nutrients. However increasing cost of the chemicals and labor hinders their reclamation to a great extent. The maintenance of optimum levels of soil nutrients plays a key role in sustaining crop yield. The transformation and availability of several plant nutrient elements are affected by soil sodicity. The concentration of micronutrients especially, zinc (Zn), iron (Fe), manganese (Mn) and copper (Cu) is very less or become unavailable in sodic or saline-sodic soil (Ojha *et al.*, 2018) [22]. They also exhibit low levels of solubility in sodic soils, which results in micronutrient deficiencies (Ilavarasi *et al.*, 2019) [9]. The use of organic amendments comprising of crops, stems, straw, green manure, compost, sewage sludge is more viable and effective biological amelioration methods (Matsumoto *et al.*, 1994; Mahdy 2011) [15, 14]. Different types of organic amendments derived from various source differs in their chemical composition and accordingly varies in the extent of changes brought by them. The major drawback in use of organic ameliorants lies in the

huge volume of manure that is usually required and the transportation and cost of labour that is involved in application. Moreover, there is a great dearth of organic manure that is available for agricultural use. Hence, any alternative resource that is available can be used for the successful amelioration of salt affected soils. In this study, Pyrolysis-derived 'soil interactive product' referred to as wood vinegar and also known as pyroligneous acid is used. It is an acidic, reddish-brown aqueous wood distillate or bio oil (Hagner *et al.*, 2013) [8]. Wood vinegar is the water-soluble fraction of the liquid that is produced during the pyrolysis of organic materials like plant residues, waste woods, coconut shells etc. Depending on the dosage, wood vinegar can act as a biocide against microorganisms Baimark and Niamsa, (2009) [1] weeds, insects (Tiilikkala *et al.*, 2009; Yatagai *et al.*, 2002) [20, 26] or when diluted sufficiently, it can enrich the soil to stimulate plant root and shoot growth, and higher dilution ratios increase microbial activity (Steiner *et al.*, 2008) [17].

In many countries the commonly practice is to apply a mixture of wood vinegar and charcoal to improve soil fertility Kadota and Niimi. (2004) [11]. Despite the long history of applying wood vinegar to soils in Asia, only few studies concerning the effects of wood vinegar in agriculture is available and knowledge about its interactions in physical and chemical properties of the soil is largely unknown. Here we examine the interactions of wood vinegar and micronutrients like Fe and Zn in sodic soil, and their combined effects on the release pattern of the respective micronutrients. We hypothesized that wood vinegar, being a readily usable resource for soil microbiota, increases the chelation of micronutrients due to its various organic functional groups like carboxylic acids, esters, aldehydes, ketones, phenols and lactones (Benzon and Lee, 2017) [2] and facilitate in its sustained availability for crop growth. It may also improve the soil microflora creating a conducive physical, chemical and biological environment for crop growth.

Laboratory incubations are valuable and widely used tools for studying the nutrient release in soils which play a vital role in maintaining soil fertility. In this experiment, soil was incubated with wood vinegar to study the nutrient release pattern of zinc and iron at periodic intervals during incubation. The objective was to ascertain the availability of zinc and iron at critical stages of crop growth. The nutrient release of wood vinegar depends on its chemical and biochemical characteristics (Tian *et al*., 1992, 1995) [19, 18]. Study of nutrient release pattern from wood vinegar is very essential to ensure nutrient supply in adequate quantity and at proper time to crop plants. Wood vinegar plays a prominent role in enhancing the level of soil fertility and sustaining the productivity of soils. It helps in optimizing nutrient efficiency in agricultural crop production systems. Use of wood vinegar is one of the options for reclamation of sodic soil to make these nutrients available to plants. Knowledge of the nutrients released from wood vinegar will enable management strategies to be devised that utilize wood vinegar more effectively and efficiently (Villegas-Pangga *et al.*, 2000) [24] as a green technology.

Materials and methods

An incubation experiment was conducted in the Department of Soil Science & Agricultural Chemistry at Anbil Dharmalingam Agricultural College & Research Institute (ADAC&RI), Trichy to study the influence of wood vinegar in release of DTPA Fe and DTPA Zn. Bulk soil samples for incubation study were collected from the Poongudi village at Manikandam Block in Trichy district of Tamil Nadu. The soil was air dried, finely ground and sieved through 2 mm sieve for incubation study. The experimental soil was sandy clay loam and alkaline in reaction with pH of 8.98 having an electrical conductivity value of 2.54 dS m^{-1}. The soil was high in organic carbon status with a value of 0.75 per cent. The available N ($KMnO_4$ -N) was low (214.6 kg ha^{-1}) while the available P (Olsens-P, 59.6 kg ha^{-1})) and available K (NH_4OAC-K, 739.2 kg ha^{-1}) status was high. Considering the available micronutrient status of the soil, DTPA-Fe was high (6.4269.3 mg kg^{-1}) compared to Zn (2.736 mg kg-1), Cu (0.431 mg kg^{-1}) and Mn (0.932 mg kg^{-1}) (Table 1).

The incubation experiment comprised of 12 treatments replicated twice in a completely randomized design. The treatments included recommended dose of $FeSO_4$ and $ZnSO_4$ alone and their combination and their combination with three levels of wood vinegar viz., 50, 100 and 150ml/l applied as as spot drenching.

Table 1: Physicochemical characteristics of soil

S. No.	Particulars	Values
1.	pH	8.98
2.	EC (dS m^{-1})	2.54
3.	Organic carbon (%)	0.75
4.	Alkaline KMnO4- N (kg ha^{-1})	214.8
5.	Olsen - P (kg ha^{-1})	59.6
6.	Neutral N NH4OAc- K (kg ha^{-1})	739.2
7.	Cation exchange capacity (cmol (p^+) kg^{-1})	20.3
8.	DTPA-Fe (mg kg^{-1})	6.426
9.	DTPA-Mn (mg kg^{-1})	0.932
10.	DTPA-Zn (mg kg^{-1})	2.736
11.	DTPA-Cu (mg kg^{-1})	0.431

All the treatments received the recommended dose of NPK uniformly at the start of the experiment. In the incubation study, 100 gm of air-dried soil was weighed and transferred into plastic containers. Distilled water was added to maintain the moisture level at field capacity (60 per cent of the water holding capacity). Subsequently, required quantities of distilled water was added to achieve a final moisture content equivalent to 60% of field capacity. The sampling for analysis of DTPA Fe and DTPA Zn of soil was done at 0, 15, 30, 45 and 60 days after incubation. The DTPA Fe and DTPA Zn were determined with the help of atomic absorption spectrophotometer (Thermo scientific model).

The treatments include

Treat No.	Treatment details.
T_1	RD of $FeSO_4$ @ 50 kg /ha
T_2	RD of $ZnSO_4$ @ 37.5 kg /ha
T_3	50 kg $FeSO_4$/ha + 37.5 kg $ZnSO_4$/ha alone
T_4	T_1 + Wood vinegar @ 50 ml/l as spot drenching (SD)
T_5	T_1 + Wood vinegar @ 100 ml/l as SD
T_6	T_1 + Wood vinegar @ 150 ml/l as SD
T_7	T_2 + Wood vinegar @ 50 ml/l as SD
T_8	T_2 + Wood vinegar @ 100 ml/l as SD
T_9	T_2 + Wood vinegar @ 150 ml/l as SD
T_{10}	T_3 + Wood vinegar @ 50 ml/l as SD
T_{11}	T_3 + Wood vinegar @ 100 ml/l as SD
T_{12}	T_3 + Wood vinegar @ 150 ml/l as SD

*SD= Spot drenching

Results and discussion

DTPA Zn and Fe

During 0^{th} day of incubation (DAI), the treatment T_{12} receiving the recommended dose of both $ZnSO_4$ and $FeSO_4$

along with wood vinegar (WV) @ 150 ml/l as spot drenching recorded significantly higher value of available Zn content (46.68 mg kg^{-1}) compared to rest of the treatments in the study. The lowest value was recorded in the treatment T1 (6.72 mg kg^{-1}) which received recommended dose of $FeSO_4$ alone. The treatments T7 to T12 recorded higher available Zn values and the values increased with increasing levels of wood vinegar. At 0^{th} day of incubation (DAI), the treatment receiving recommended dose of $ZnSO_4$ alone (T2) recorded the lowest DTPA Fe (7.32mg kg^{-1}) while the highest value(48.28 mg kg^{-1}) was recorded in the treatment receiving recommended dose $FeSO_4$ @ 50 kg /ha along with WV @150 ml/l (T6). The application of $ZnSO_4$ / $FeSO_4$ either alone or their combination (T1, T2, and T3) recorded lower values in the absence of wood vinegar and showed an overall decreasing trend in the release of available Zn and Fe in soil as the incubation period progressed (Table 3) (Figure 1). The alkaline pH of 8.98 of the soil might have reduced the solubility of Fe and precipitates in alkaline soils (Fageria *et al.*, 2002) [6]. The steep reduction in the DTPA Fe with advancement in incubation period and a steady reduction in DTPA Zn is further corroborated by the fact that solubility of Fe decreases by approximately 1000-fold for each unit increase of soil pH in the range of 4–9 compared to approximately 100-fold decreases in activity of Zn (Lindsay, 1979) [13]. He has also reported minimum solubility of Fe at alkaline soil pH. At alkaline pH, Zn and Fe is precipitated to its unavailable forms which is clearly indicated by the lower values of available Zn and Fe in treatments receiving recommended dose of either $FeSO_4$ or $ZnSO_4$ and its combination (T1, T2 and T3). In soils that are well aerated or of higher pH, Fe is readily oxidized, and is predominately in the form of insoluble ferric oxides (Fageria and Nascente, 2014; Sumona *et al.,* 2018) [7]. However, in soils incubated with wood vinegar at varying levels along with $ZnSO_4$ / $FeSO_4$ either alone or their combination (T4 to T12) recorded an increase in both the DTPA Zn (20.56, 20.26, 20.12, 23.50, 38.08, 45.85, 47.05, 52.55 and 56.29 mg/kg and DTPA Fe values up to 15 DAI which declined steadily thereafter. This sudden increase in the available Zn and Fe may be due to the enhanced solubility of both Zn and Fe due to a decrease in soil pH as a result of application of increasing levels of wood vinegar to the soil (Wei *et al.,* 2010; Theapparat *et al.,* 2018) [25, 23]. The highly acidic pH of the wood vinegar (3.7) would have reduced the pH of soil thereby would have increased the solubility of both DTPA Zn and Fe (Mohan *et al.,* 2006; Jung, 2007) [16, 10] (Table 2). This would have contributed to the increased supply of both the micronutrients immediately to the available pool. Among the various treatments compared, the lowest values of available Zn were recorded in the soils treated with recommended dose of $FeSO_4$ irrespective of the incubation period. On the contrary, all the treatments receiving $ZnSO_4$ at varying levels of WV with or without $FeSO_4$ recorded higher values for DTPA Zn. The proliferation of acid producing soil microorganisms due to addition of wood vinegar to the soils may have decreased the soil pH (Koc *et al*., 2019) [12] thereby increasing the availability DTPA Zn and Fe in sodic soils.

Table 2: Physicochemical characteristics of wood vinegar

S. No.	Particulars	Values
1.	pH	3.7
2.	EC (dS m^{-1})	7.62
3.	Density (%)	3.7
4.	Total Ca (mg kg^{-1})	Nil
5.	Total Mg (mg kg^{-1})	Nil
6.	Total Na (mg kg^{-1})	26.3
7.	Total K (mg kg^{-1})	1.0
8.	DTPA-Fe (mg kg^{-1})	1938
9.	DTPA-Zn (mg kg^{-1})	2.654
10.	DTPA-Mn (mg kg^{-1})	23.307

Table 3: Effect of wood vinegar in DTPA Zinc and Iron content (mg kg^{-1}) of soil at different incubation periods

Treat No.	Treatments	DTPA Zn					DTPA Fe				
		Incubation periods (mg kg^{-1})					Incubation periods (mg kg^{-1})				
		0 DAI	15 DAI	30 DAI	45 DAI	60 DAI	0 DAI	15 DAI	30 DAI	45 DAI	60 DAI
T_1	RD of $FeSO_4$ @ 50 kg /ha	6.72	6.14	4.98	3.84	2.10	17.68	13.82	10.86	9.04	6.24
T_2	RD of $ZnSO_4$ @ 37.5 kg /ha	12.17	9.89	7.15	6.68	4.84	7.32	6.82	5.86	3.68	2.31
T_3	50 kg $FeSO_4$/ha + 37.5 kg $ZnSO_4$/ha alone	13.79	10.82	8.31	7.46	5.61	18.69	15.14	11.69	9.05	6.43
T_4	T_1 + Wood vinegar @ 50 ml/l as spot drenching (SD)	16.55	20.56	19.24	18.66	7.34	39.19	46.93	32.55	21.49	16.49
T_5	T_1 + Wood vinegar @ 100 ml/l as SD	16.80	20.26	18.02	16.91	7.78	46.63	54.34	37.20	25.19	17.52
T_6	T_1 + Wood vinegar @ 150 ml/l as SD	17.05	20.12	17.47	18.03	8.53	48.28	65.31	42.39	29.08	23.23
T_7	T_2 + Wood vinegar @ 50 ml/l as SD	22.05	23.50	22.52	20.78	10.48	21.34	47.94	36.44	23.30	15.32
T_8	T_2 + Wood vinegar @ 100 ml/l as SD	34.14	38.08	18.25	15.87	10.47	26.93	49.66	36.66	24.43	17.32
T_9	T_2 + Wood vinegar @ 150 ml/l as SD	39.15	45.85	20.65	16.04	9.89	28.59	56.38	37.07	25.26	17.82
T_{10}	T_3 + Wood vinegar @ 50 ml/l as SD	40.97	47.05	20.26	19.62	12.06	39.01	41.00	31.15	17.61	14.98
T_{11}	T_3 + Wood vinegar @ 100 ml/l as SD	43.31	52.55	20.88	17.62	12.17	46.56	49.34	38.76	23.05	19.45
T_{12}	T_3 + Wood vinegar @ 150 ml/l as SD	46.68	56.29	19.73	16.08	11.82	47.20	50.25	47.39	31.13	28.14
	SEd	1.05	0.57	0.37	0.23	0.23	0.56	0.69	0.67	0.38	0.36
	CD (.05)	2.16	1.17	0.76	0.47	0.46	1.15	1.43	1.37	0.77	0.75

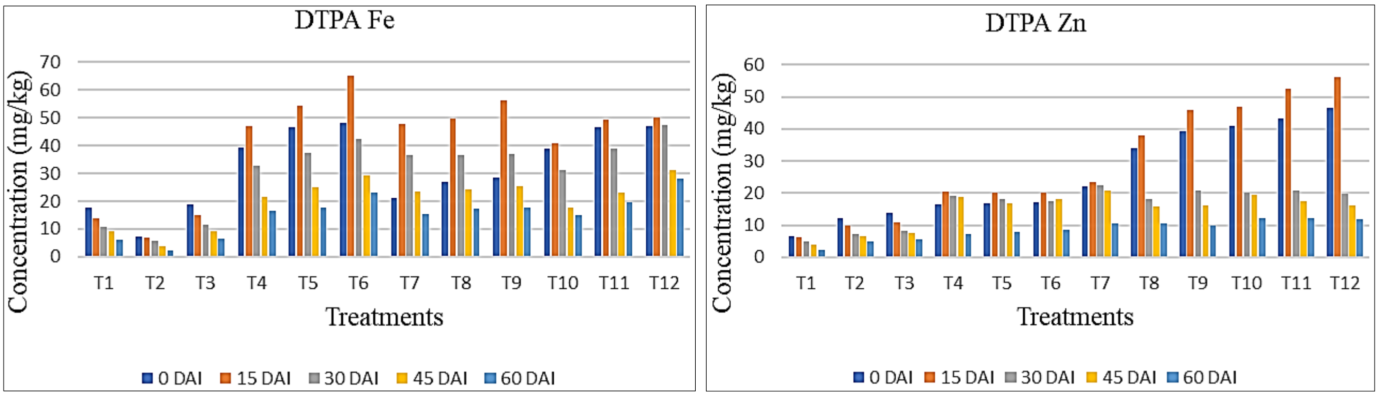

Fig 1: Effect of wood vinegar on release of DTPA Zn & Fe at different incubation periods

Conclusion

Wood vinegar is a natural organic material obtained from agricultural wastes. It contains several organic compounds primarily acetic acid and phenolic compounds. This carbonaceous pyrolysis product obtained from carbonaceous biomass is highly acidic and has been widely used in the areas of medicine, food, and agriculture (Cai *et al*., 2012; Dissatian *et al*., 2018) [4, 5]. The incubation study revealed the potential advantage of wood vinegar in enhancing the solubility of micronutrients viz., Zn and Fe to a sodic soil which is otherwise limiting. The highly acidic pH of wood vinegar helps in moderating the pH of the sodic soil and improves the solubility and availability of the micronutrients in a sustainable manner. The study clearly ascertains the beneficial effect of wood vinegar application to salt affected soils in improving the micronutrient release pattern and increasing the crop growth and productivity.

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