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FOREWORD

Improvement of crop production through sustainable soil management is a challenge faced by the soil science research community. Further, the environmental damage caused by the present market oriented crop production is also a prime concern. Properly planned field research play a key role in filling knowledge gaps pertaining to these research concerns. Especially, studies addressing the environmental threats associated with the present soil fertility management practices and novel approaches for the management of soil fertility to assure long term production potential of low-fertile tropical soils are important. This issue (vol 24) contains four papers submitted and accepted in 2013 to 2014. First two studies address the management and interactions of soil nitrogen and zinc. Third article focuses on exploring the impact of agricultural land uses on the water quality of the cascade tank system and in the forth paper, the authors attempt to investigate the quality of bio-char produced from coconut husk waste.

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CONTENTS

TRANSFORMATION OF APPLIED Zn IN A FLOODED SOIL IN A RAINFED ECOSYSTEM

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ABSTRACT

Transformation of applied Zn to flooded rice soil under rainfed ecosystem was studied in an incubation experiment using a Red soil (Haplusterts, pH 4.5) collected from typical lowland rice fields in Northern Hilly Zone of Karnataka, India after harvest of paddy. The laboratory incubation study was conducted by filling one kilogram of soil into plastic containers and treated with three levels of $ZnSO_4$ (i.e., $Z_1 = 0$, $Z_2 = 5$, $Z_3 = 10$ kg ha^{-1}) and kept under flooded moisture condition. The experiment was in Completely Randomized Design with six replicates. Incubated soil samples were collected periodically at 30, 60 and 90 days after incubation and analysed for pH, total Zn, available Zn using standard analytical methods and different fractions of Zn by sequential Zn fractionation procedur. The results indicated that Water Soluble plus Exchangeable Zn (WSEX-Zn) contributed least to the total Zn followed by Organically Complexed Zn (OC-Zn), Crystalline Sesquioxide bound Zn (CRYOX-Zn), Amorphous Sesquioxide bound Zn (AMOX-Zn), Manganese Oxide bound Zn (MnOX-Zn) and Residual Zn (RES-Zn). Both the content and percent contribution of RES-Zn to the total Zn was the highest among all the Zn fractions studied. In flooded moisture condition, except CRYOX-Zn and RES - Zn, all the other fractions of Zn showed a significant increase with added Zn compared to control. The WSEX-Zn, OC-Zn, and CRYOX-Zn forms significantly decrease and MnOX-Zn, AMOX-Zn forms significantly increase with increase of incubation period. The recovery of applied Zn in WSEX which represents the most readily available pool was relatively low in flooded moisture condition as compared to other forms.

Keywords: Zn fractions, Transformation, Flooded condition, Rice soil, Incubation, Sequential fractionation

INTRODUCTION

Zinc plays an important role in the nutrition of rice (*Oriza sativa L.*). It is one of the essential micronutrients most commonly deficient in flooded rice soils. Widespread occurrence of Zn deficiency in rice soils suggests that both native and applied Zn react with the organic and inorganic phases in the soil and thereby affect the availability of Zn. The availability of Zn in soils is a function of its partition among different fractions (Viets, 1962). Zinc is known to occur in soil in a number of discrete chemical forms differing in their solubility and thus availability to plants (Sarkar and Deb, 1982). According to Viets, (1962), Zn in soils can be divided to different chemical pools, viz., water soluble, easily exchangeable, adsorbed, chelated, or complexed, occluded by or co-precipitated with metal oxides, carbonates or phosphates and other secondary minerals and also held in primary minerals. Zinc in soluble organic complexes and exchange positions are of major importance in maintaining the Zn level sufficient for wetland rice (Murthy, 1982). The water-soluble plus exchangeable Zn (WSEX-Zn), organically complex Zn (OC-Zn), amorphous sesquioxide bound Zn (AMOX-Zn) and crystalline sesquioxide bound Zn (CRYOX-Zn) could account for 95.2 % of the variability of Zn concentration in wetland rice fields (Mandal and Mandal, 1986). The availability of Zn to plants has been observed to vary with different Zn fractions. About five or less than 5 % of total Zn present in soil is available to plants at any given time. The form in which Zn is presented in soil plays a crucial role in determining its availability to plants. The WSEX-Zn and OC-Zn forms are considered to be available, AMOX-Zn form is potentially available and CRYOX-Zn and RES-Zn forms are unavailable to plants (Mandal *et al.*, 1992).

Distribution of Zn forms in soils depends on their chemical and physical properties. The availability of soil Zn to plants is governed by a dynamic equilibrium among the different fractions of soil Zn. Under flooded conditions in paddy soils, a variety of electro chemical changes are taking place. These include a decrease in redox potential, an increase in pH of acid soils and a decrease in pH of alkaline soils, changes in specific conductance and ionic strength, drastic shifts in mineral equilibrium, cation and anion exchange reactions and sorption and desorption of ions (Ponnamperuma, 1972). Such changes may influence the transformation of Zn in soil and thus affect its availability to rice. Therefore, the recovery of applied Zn by rice is very low due to its transformation to different chemical forms. The knowledge of the pattern and magnitude of transformations of applied Zn to different fractions would be helpful in arriving at Zn fertilizer recommendations under flooded rice cultivation. Therefore, the objective of this experiment was to study the transformation of applied Zn to different fractions in flooded rice soils.

MATERIALS AND METHODS

An incubation study was conducted in the laboratory to ascertain the transformation of applied Zn in a soil under continuous flooding. A composite soil sample was collected from typical lowland rainfed rice fields in Hunga taluk located in Northern Hilly Zone of Karnataka, India between 14^0 53' and 14^0 54' N and 75^0 O' and 25^0 1'E and longitude with the altitude of 550 m above mean sea level after the harvest of paddy. Five sampling locations were randomly selected from one hectare of paddy land in each of 23 villages in Hungal taluk. The soil samples were drawn using stainless steel auger upto the depth of 0 – 20 cm from the surface layer.

Properties of the soil used for the incubation study are given in Table 1.

The soil samples were passed through 2 mm nylon sieve just after sampling and mixed thoroughly to get a composite sample. One kilogram of the composite soil was filled into each of the plastic containers. Soils in each container were treated with three levels of $ZnSO_4$ to represent the treatments; $Z_1 = 0$, $Z_2 = 5$, $Z_3 = 10$ kg ha^{-1} and all the soils were treated with a basal dose of 100% RDF (150 : 75 : 75 - N : P_2O_5 : K_2O) in the form of Urea, SSP and MOP and FYM at the rate of 10 tonnes per ha. was mixed with the soil. Zinc sulphate was added in the form of solution and the soils were thoroughly mixed. Soils were kept under flooded condition and the level of standing water in each container was maintained at a height of 5 ± 0.5 cm above the soil surface throughout the period (three months) of incubation. The experimental lay-out was a Completely Randomized Design with six replicates. Soil samples were drawn from the entire depth of the container using a mini-auger periodically at 30, 60 and 90 Days After Incubation (DAI) at 25 ^{0}C and analysed for available Zn in soils by DTPA extractant (Landsay and Norvell, 1978) and total Zn by digesting the soil with HF and $HClO_4$ (Page *et al.,* 1982). The soils were sequentially extracted with 1M $(NH_4)OAc$ at pH 7.0, 0.05 M $Cu(OAC)_2$, 0.2 M $(NH_4)_2C_2O_4.H_2O$ + 0.2 M $H_2C_2O_4$ (pH 3.0) and 0.3 M Sodium citrate + 1.0 M $NaHCO_3$ + 1 g $Na_2S_2O_4$ [Citrate-Bicarbonate-Dithionite] and 0.1 M $NH_2OH.HCl$ (pH 2.0) to extract WSEX - Zn, OC - Zn, AMOX - Zn, CRYOX - Zn and MnOX - Zn respectively by Murthi, (1982) and modified by Mandal and Mandal, (1986). The concentration of Zn in soil extracts were measured using Atomic Absorption Spectrophotometer (GBC 904). Residual fraction of Zn was obtained by deducting all the fractions of Zn from the total Zn. Prior to treatment application, soil was analyzed for above mentioned fractions of Zn, pH, EC, orgnic carbon, cation exchange capacity, free $CaCO_3$ and texture. The Dry Soft Design programme was used to find out the Analysis of Variance (two factor CRD) of the incubation study.

RESULTS AND DISCUSSION

The soil used for the incubation study was acidic in nature with a pH value of 4.5 accompanied by non calcareous nature of the soil with low EC and low $CaCO_3$ content. Texture of the soil was sandy clay loam with low organic carbon and low cation exchange capacity (Table 1).

As shown in the Table 2, among all the Zn fractions, the WSEX-Zn contributed least to the total Zn followed by OC-Zn, CRYOX-Zn, AMOX-Zn, MnOX-Zn and RES-Zn. The contribution of the RES-Zn to the total Zn was the highest among all the Zn fractions studied.

Soil pH

The days of incubation had a significant effect on pH of the soil. pH of the soil significantly increased with increase of incubation period in three levels of Zn. Within 30 days of incubation, pH value of the soil reached above 6 from the initial pH value of 4.5. Thereafter, the soil pH value reached to fairly stable value of 7. Ponnamperuma (1965) stated that when an aerobic soil is flooding, its pH decreases during the first few days, reaches minimum, and then increases asymptotically to a fairly stable value of 6.7 – 7.2 a few weeks later.

The decrease in pH shortly after submergence is probably due to the accumulation of CO_2 produced by respiration of aerobic bacteria; because CO_2 depresses the pH even of cid soils. The subsequent increase in pH of acid soils is due to soil reduction (Ponnamperuma *et al.,* 1966). On flooding, the pH value of the soil was increased which caused a decrease in the solubility of native and applied Zn in soils. Increased pH might have favoured precipitation of some amount of Zn as hydroxides, adsorption on the surfaces of freshly formed hydrated oxides of Fe and Mn which are known to have a strong scavenging action for Zn because of their high specific surface.

Table 1. Average values of Physical and chemical properties of the soil samples used for the incubation study

pH(1:2.5)	EC(dS m^{-1})	OC(%)	CEC(cmol (+) kg^{-1})	Free $CaCO_3$ (%)	Available Zn (DTPA) (mg kg^{-1})	Sand (%)	Silt (%)	Clay (%)
4.5	0.15	0.8	18.9	2.5	2.15	53	18	30

Table 2: Initial status of different fractions of Zn given as the total in soil (mg kg^{-1}) and as a percentage of total Zn.

	WSEX	OC	CRYOX	AMOX	MnOX	Residual	Total	Available
Total (mg kg^{-1})	1.55	2.04	2.84	3.42	5.48	239	326	2.15
% of total Zn	0.47	0.62	0.87	1.05	1.68	73.2	-	0.66

Water Soluble and Exchangeable Zn (WSEX-Zn)

Both the content and percent contribution of this fraction to total Zn was the least among all the Zn fraction studied (Table 2). This might be due to high buffering capacity of soils which resulted in low amount of WSEX-Zn (Deb, 1997). Similar findings were reported by many workers (Iyengar and Deb, 1977; Raja and Iyengar, 1986 and Pal *et al.*, 1997). The variation in the content of this fraction in these treatments may also be due to the soil reaction which determines solubility of Zn (Hazra *et al.,* 1987). The high content of WSEX-Zn fraction than available critical Zn level of 0.4 mg kg^{-1} in this soil may have been due to moderately acidic nature. Similar findings were also made by Singh and Abrol (1986a & 1986b). Added Zn levels had significant effect on most of the Zn fractions in soil. The WSEX-Zn, OC-Zn, MnOX-Zn, AMOX-Zn and Avail.- Zn fractions showed an increased trend with increased level of Zn at flooded moisture regimes during the incubation period (Table 4, 5, 6, 7 & 10). As shown in Table 4 the WSEX-Zn fraction showed an increasing trend for added levels of Zn (Z_2 & Z_3) as compared to control (Z_1). In flooded condition, significantly higher WSEX-Zn content was recorded with Z_3 treatment (3.49 mg kg^{-1}) compared with Z_2 (2.47 mg kg^{-1}) and control (1.27 mg kg^{-1}).

The days of incubation had a significant effect on different Zn fractions of the soils. Zinc fractions in WSEX, Avail. OC and CRYOX forms were significantly decreased and Zn fractions in MnOX, AMOX, RES forms were significantly increased with increase of incubation period in three levels of Zn. The significantly highest WSEX-Zn content of 3.36 mg kg^{-1} at 30 DAI followed by 2.31 mg kg^{-1} at 60 DAI and 1.56 mg kg^{-1} at 90 DAI was recorded to flooded moisture regime. The decrease in WSEX-Zn upon flooded might be due to a decrease of pH upon flooded and precipitation of soluble Zn as hydroxide, hydroxyl carbonates, sulphides and franklinite type of compounds (Brar and Sekhon, 1976), its adsorption on the surface of manganese oxides and amorphous sesquioxides (Hazra *et al.,* 1987) and displacement of Zn from exchangeable sites by Fe^{2+} and Mn^{2+} followed by its subsequent precipitation. The conditions prevailing under this situation are favorable for microbial immobilization and formation of $ZnCO_3$ and $Zn(CO_3)_2(OH)_2$ (Brar and Sekhon, 1976) and adsorption of Zn on the surface of organic complexes due to low Eh values (Sims and Patrick, 1978). Similar trend was observed in OC - Zn, CRYOX - Zn and Avail. Zn fraction in soils under flooded moisture regimes.

Organically Complexed Zn (OC-Zn)

The OC-Zn fraction in soil was 2.04 mg kg^{-1} and the percent contribution of this fraction to total Zn was 0.62 %. Percent contribution of this fraction to total Zn was next only to WEX-Zn but lower than oxide bound and residual forms (Table 2). Low content of OC - Zn was due to low organic carbon status of the soils (Katyal and Rattan, 1993). This fraction is known to play a significant role in Zn nutrition of lowland rice (Mandal and Mandal, 1986). Similar values of (0.3 to 6%) of OC – Zn have been reported by Prasad and Shukla (1996). In flooded condition significantly higher OC – Zn was recorded with 10 kg ha^{-1} $ZnSO_4$ (3.69 mg kg^{-1}) compared with 5 kg ha^{-1} (2.39 mg kg^{-1}) and control (1.95 mg kg^{-1}). The OC –Zn showed a decreasing trend with increasing incubation period. The significantly highest value of 3.70 mg kg^{-1} was recorded at 30 DAI followed by 2.39 mg kg^{-1} at 60 DAI and 1.93 mg kg^{-1} 90 DAI (Table 5). The decrease in OC-Zn upon flooded condition might be due to the stability of the Zn – organic complexes decreases under reducing condition and the Zn released from such complexes subsequently undergoes precipitation and adsorption.

Table 3. pH in soils under flooded moisture condition and different Zn levels at 30, 60 and 90 days after incubation

Treatment	30 DAI	60 DAI	90 DAI	Mean
Zn_1	6.99	7.03	7.06	7.02
Zn_2	6.75	6.95	6.99	6.89
Zn_3	6.88	7.00	7.04	6.97
Mean	6.87	6.99	7.03	6.96
Source		S.Em ±		CD at 5 %
Zn levels (Z)		0.021		NS
Days of incubation (D)		0.021		0.083
D x Z		0.021		NS

Table 4. WSEX-Zn in soils under flooded moisture condition and different Zn levels at 30, 60 and 90 days after incubation

Treatment	30 DAI	60 DAI	90 DAI	Mean
Zn_1	1.50	1.29	1.03	1.27
Zn_2	3.22	2.59	1.60	2.47
Zn_3	5.38	3.05	2.06	3.49
Mean	3.36	2.31	1.56	2.41
Source		S.Em ±		CD at 5 %
Zn levels (Z)		0.114		0.421
Days of incubation (D)		0.114		0.421
D x Z		0.114		0.421

Organically bound Zn decrease may partly be due to microbial immobilization of Zn. The declining trend towards latter period might be due to the decrease in stability of Zn – organic complexes at the lower Eh of the soils attained after prolonged flooding and the Zn released from such complexes subsequently undergoes precipitation, adsorption and microbial immobilization of Zn (Reddy and Patrick, 1977). Reddy and Patrick observed that at low redox potentials, Zn and Cu chelates were highly unstable.The declining trend towards latter period might be due to the decrease in stability of Zn – organic complexes at the lower Eh of the soils attained after prolonged flooding and the Zn released from such complexes subsequently undergoes precipitation, adsorption and microbial immobilization of Zn (Reddy and Patrick, 1977). Reddy and Patrick observed that at low redox potentials, Zn and Cu chelates were highly unstable.

Manganese oxide bound Zn (MnOX - Zn)

The percent contribution of MnOX- Zn to the total Zn was next to residual Zn. The percent contribution of this fraction to the total Zn was 1.68% Table 2). This can be attributed to higher amount of Zn adsorption on the surface of the oxides (Marshall, 1977) as these soils reported to be relatively higher in total manganese content (Ananthanarayan and Ravindra, 1988). Under flooded condition significantly higher MnOX-Zn content recorded with 10 kg ha^{-1} $ZnSO_4$ (8.32 mg kg^{-1}) compared with 5 kg ha^{-1} (7.21 mg kg^{-1}) and control (5.85 mg kg^{-1}). In contrast to WSEX-Zn, there was progressive increase in the content of MnOX- Zn with time which might be attributed to the transformation of Zn from WSEX-Zn, OC–Zn and other stable forms to MnOX-Zn form with the passage of time. The MnOX-Zn showed an increasing trend in all treatments with increasing incubation period. Similar trend was observed in AMOX-Zn, RES-Zn and total Zn. The significantly highest value of 8.58 mg kg^{-1} was recorded at 90 DAI followed by at 60 DAI (6.65 mg kg^{-1}) and 30 DAI (6.15 mg kg^{-1}) (Table 6). The increase in MnOX - Zn may be attributed to the reduction of some crystalline form of sesquioxide to less orderly forms upon flooded condition as reported by Willet (1979) and thus releasing some amount of occluded Zn for its subsequent adsorption on the hydrous oxide form. Mandal (1961) and Ponnamperuma (1972) observed that under anaerobic conditions some amount of higher oxides of manganese are converted to lower valent compounds, which are diffused to the oxic region and gets re-oxidized with subsequent formation of Manganese hydroxide having large specific surface area and hence high adsorption capacity. The Zn released from other bound forms might have held by Manganese hydroxide resulting in an increase content of MnOX-Zn. The higher content of MnOX-Zn fraction in this soils could be attributed to the acidic pH in the soil (Singh *et al.,*1988).

Amorphous sesquioxide bound Zn (AMOX-Zn)

The AMOX-Zn in soils was 3.42 mg kg^{-1}**.** The percent contribution of this fraction to total Zn was 1.05 % (Table 2). Under flooded moisture condition significantly higher AMOX-Zn content recorded with 10 kg ha^{-1} $ZnSO_4$ (6.84 mg kg^{-1}) compared with 5 kg ha^{-1} (5.66 mg kg^{-1}) and control (3.04 mg kg^{-1}). The AMOX-Zn showed an increasing trend with increasing incubation period. The significantly highest value of 7.45 mg kg^{-1} was recorded at 90 DAI followed by 4.67 mg kg^{-1} at 60 DAI and 3.42 mg kg^{-1} at 30 DAI (Table 7). The higher content of AMOX-Zn than CRYOX-Zn could be attributed to grater ability of amorphous sesquioxide to adsorb Zn because of their high specific surface area (Devis and Leckie, 1978).

Table 5. OC-Zn in soils under flooded moisture condition and different Zn levels at 30, 60 and 90 days after incubation

Treatment	30 DAI	60 DAI	90 DAI	Mean
Zn1	2.28	1.84	1.72	1.95
Zn2	3.28	2.08	1.82	2.39
Zn3	5.54	3.14	2.26	3.69
Mean	3.70	2.39	1.93	2.67
Source		S.Em ±		CD at 5 %
Zn levels (Z)		0.002		0.005
Days of incubation (D)		0.002		0.005
D x Z		0.002		0.005

Table 6. MnOX-Zn in soils under flooded moisture condition regime and different Zn levels at 30, 60 and 90 days after incubation

Treatment	30 DAI	60 DAI	90 DAI	Mean
Zn1	5.29	5.94	6.31	5.85
Zn2	6.23	6.57	8.83	7.21
Zn3	6.94	7.42	10.61	8.32
Mean	6.15	6.65	8.58	7.130
Source		S.Em ±		CD at 5 %
Zn levels (Z)		0.028		0.081
Days of incubation (D)		0.028		0.081
D x Z		0.028		0.081

Under the reduced condition there was an increase in the formation of hydrated oxides of Fe and Mn. Freshly formed compounds processes large surface area and hence strong adsorption capacity. The WSEX-Zn already present in soil or released from the other forms might have been adsorbed on the surface of these freshly formed hydrated oxides (Hazra *et al.,* 1987).

Crystalline sesquioxide bound Zn (CRYOX-Zn)

The CRYOX-Zn content (2.84 mg kg^{-1}) in initial soil was lower than AMOX-Zn content (3.42 mg kg^{-1}). The percent contribution of CRYOX-Zn to total Zn was 0.87 % (Table 2). This fraction was dominant when compared to WSEX-Zn, OC-Zn fractions due to predominance of crystalline iron oxide content. Similar results were obtained by Pal *et al.* (1997). This fraction is more stable particularly in upland condition of soil. The Zn levels had no significant effect on CRYOX-Zn at flooded moisture condition. The CRYOX- Zn showed a decreasing trend in all treatments with increasing incubation period (Table 8). This may be due to the under reduced condition, some of the crystalline sesquioxides might have undergone transformation to amorphous form resulting in the release of a part of the occluded Zn by the former and its subsequent by sorption the latter**.** The possibility of Zn being occluded in the CRYOX becomes comparatively less. Decrease in CRYOX-Zn due to reduction of crystalline Fe-oxides under anaerobic condition and the subsequent release of Zn held by them (Hazra *et al.,* 1987).

Residual Zn (RES-Zn)

As shown in Table 2, Residual Zn was the dominant fraction among all the Zn fractions studied with a content of 239 mg kg^{-1} which is associated with minerals (Sedberry and Reddy, 1976). The percent contribution of this fraction to total Zn was 73.2%. It is considered as the primary form of the native Zn and associated with soil mineral fractions. Type of dominant clay minerals in soil affect the amount of residual Zn fraction in soil (Iyengar *et al.*, 1981). Iyengar and Deb (1977) reported that in some red soils of Karnataka residual Zn fraction was the most dominant fraction and ranged from 43 to 208 mg kg^{-1} and constituted 96.8 % of total Zn. Whereas, calcareous soils of India were found to contain 25 to 81 ppm residual Zn with a mean of 55.7 ppm which constituted 73.4 to 88.0 % of the total Zn (Singh *et al.*, 1988). The effect of Zn levels showed non-significant influence on RES – Zn soil at submerge moisture regime (Table 9). The RES-Zn indicated progressive increase with the advancement of incubation period which indicated considerable mobilization of Zn to residual fraction from other fractions. Similar results were also observed by Saha and Mandal (1996).

Table 7. AMOX-Zn in soils under flooded moisture condition and different Zn levels at 30, 60 and 90 days after incubation

Treatment	30 DAI	60 DAI	90 DAI	Mean
Zn1	1.94	2.55	4.64	3.04
Zn2	3.25	5.22	8.51	5.66
Zn3	5.09	6.24	9.20	6.84
Mean	3.42	4.67	7.45	5.18
Source		S.Em ±		CD at 5 %
Zn levels (Z)		0.178		0.517
Days of incubation (D)		0.178		0.517
D x Z		0.178		0.517

Table 8. CRYOX-Zn in soils under flooded moisture condition and different Zn levels at 30, 60 and 90 days after incubation

Treatment	30 DAI	60 DAI	90 DAI	Mean
Zn1	3.45	3.03	3.15	3.21
Zn2	3.55	2.60	1.86	2.67
Zn3	3.85	3.10	2.64	3.20
Mean	3.61	2.91	2.55	3.02
Source		S.Em ±		CD at 5 %
Zn levels (Z)		0.099		NS
Days of incubation (D)		0.099		1.159
D x Z		0.099		NS

Table 9. RES -Zn in soils under submergence moisture regime and different Zn levels at 30, 60 and 90 days after incubation

Treatment	30 DAI	60 DAI	90 DAI	Mean
Zn_1	240	276	298	271
Zn_2	318	322	328	323
Zn_3	325	333	342	333.
Mean	294	310	323	309
Source	S.Em ±			CD at 5 %
Zn levels (Z)	2.160			NS
Days of incubation (D)	2.160			6.280
D x Z	2.160			NS

Table 10. Available Zn in soils under submergence moisture regime and different Zn levels at 30, 60 and 90 days after incubation

Treatment	30 DAI	60 DAI	90 DAI	Mean
Zn_1	2.06	1.89	1.78	1.91
Zn_2	2.18	2.01	1.88	2.02
Zn_3	2.23	2.88	1.95	2.35
Mean	2.16	2.26	1.87	2.03
Source		S.Em ±		CD at 5 %
Zn levels (Z)		0.037		0.107
Days of incubation (D)		0.037		0.107
D x Z		0.037		NS

Total Zn

Total Zn content of soils depends on the parent material. Although total Zn content is considered as a poor indication of Zn supplying capacity of soil for long term management of a cropping system, it may help. The flooded moisture condition had no significant effect on total Zn content in soils during the incubation period. Zinc levels significantly increase the total Zn content in soils. Total Zn content in soil was 326 mg kg^{-1}. Significantly higher total Zn was recorded in soils with 10 kg ha^{-1} $ZnSO_4$ (333 mg kg^{-1}) than 5 kg ha^{-1} $ZnSO_4$ (323 mg kg^{-1}) and control (271 mg kg^{-1}).

Available Zn

The available Zn (DTPA) content in this soil was 2.15 mg kg^{-1} comprising 0.66% to the total Zn (Table 2). Under flooded moisture condition, significantly higher available Zn recorded with 10 kg ha^{-1} $ZnSO_4$ (2.35 mg kg^{-1}) compared with 5 kg ha^{-1} (2.02 mg kg^{-1}) and control (1.91 mg kg^{-1}). The amount of DTPA extractable Zn recorded a gradual decrease from their initial amounts at flooded moisture condition with time. Decrease in DTPA extractable Zn in soil on flooded moisture condition may be due to their precipitation as hydroxides, hydroxy carbonates, sulphides and franklinite type of compounds in presence of excess amount of soluble Fe and Mn (Dutta *et al.,* 1989)

CONCLUSIONS

Among all the Zn fractions studied in Red soil (Haplusterts) which collected from typical lowland rice fields in Northern Hilly Zone of Karnataka in India, WSEX- Zn contributed least to the total Zn followed by OC-Zn, CRYOX-Zn, AMOX-Zn, MnOX-Zn and RES-Zn. All the Zn fractions except crystalline sesquioxide and residual Zn fractions showed an increased trend with increased level of Zn under flooded moisture condition during the incubation period. The days of incubation had significant effect on soil pH and different Zn fractions of the soils at 30, 60 and 90 days after incubation. The WSEX-Zn, OC-Zn, CRYOX-Zn and Avail. Zn fractions decreased with increased incubation period. The pH of soil, MnOX-Zn, AMOX-Zn RES-Zn and total Zn showed an increasing trend with increasing incubation. The recovery of applied Zn in WSEX which represents the most readily available pool was relatively low in flooded moisture condition as compared to other forms.

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THE RESPONSE OF SELECTED RICE VARIETIES TO PARTIAL NITRATE NUTRITION AND THEIR ABILITY TO SUPPRESS NITRIFICATION

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ABSTRACT

Nitrogen use efficiency in rice can be improved by supplying N-form matching the requirement of plant. Response of thirteen lowland rice varieties to different mixtures of NH_4^+ and NO_3^- and the ability of selected varieties to suppress nitrification, a transformation governing NH_4^+:NO_3^- in the root-zone, were studied. Plant performance was measured after growing rice hydroponically supplying same level of N in different NH_4^+:NO_3^-(100:0, 50:50, and 0:100 percent ratio). The effect of root derived compounds from 14 days old rice seedlings on soil nitrifiers was assessed. Response of rice to NH_4^+:NO_3^- in the root-zone differed across varieties. Soil nitrification was differently affected by water soluble root derived compounds of tested varieties. Rice varieties are diverse in characters related to N nutrition.

Keywords: Rice, Partial Nitrate Nutrition, Biological nitrification inhibition

INTRODUCTION

Farmers in Sri Lanka spend 10-20 % of the total production cost of rice on N fertilizers yet do not realize the full benefit of fertilization because agronomic nitrogen use efficiency is around 30% (Sirisena *et al*., 2003). It is timely to investigate the plant traits benefitting high N use efficiency (NUE). Supplying N in the form that plant could effectively uptake while minimizing losses would help improving NUE.

Differences have been observed among rice varieties in their response to available N forms (NH_4^+ and NO_3^-) in soil (Kronzucker *et al*., 1999; Ying-Hua *et al*., 2006; Duan *et al*., 2007). Kronzucker *et al*. (1999) demonstrated the presence of NO_3^- enhances NH_3 uptake and translocation from roots to shoots in rice plant. Improvement in nitrogen uptake as a result of the presence of both NH_4^+-N and NO_3^--N in the growth medium is known as partial nitrate nutrition (PNN). Paddy rhizosphere facilitates coexistence of NH_4^+-N and NO_3^--N (Li *et al*., 2008).

Nitrification, conversion of NH_4^+-N to NO_3^--N, is the main transformation yielding NO_3^- in soil. It is carried out by autotrophic and heterotrophic organisms in domains Bacteria and Archaea and determines the NH_4^+ to NO_3^- ratio in soil (Gujer, 2010). High nitrifying environments encourage N loss from the system leading to a number of environmental problems because NO_3^- is susceptible to leaching losses and also serve as the main substrate for denitrification (Subbarao *et al*., 2012; Gujer, 2010). Suppression of nitrification could be useful to improve NUE in high nitrifying environments (Subbarao *et al*., 2012). Secondary metabolites released by roots of *Sorghum bicolor*, *Leymusracemosus*, *Penknisetumglaucum, Arachishypogaea*, and *Brachiariahumidicola* suppressed nitrification as shown in laboratory and field-scale experiments (Ishikawa *et al*., 2003; Gopalakrishnan *et al*., 2007; Subbarao *et al*., 2007). The suppression of nitrification by biologically active plant derived compounds is referred to as biological nitrification inhibition (BNI) (Subbarao *et al*., 2007).

Investigations on BNI potential of rice is still at a preliminary stage (Fillery, 2007). A study conducted to assess the effect of rice root exudates on the activity of *Nitrosomonas europaea* indicate some rice varieties have the potential for BNI (Pariasca Tanaka *et al*., 2010). According to Kong *et al*. (2008), PI312777, an allelopathic rice variety, reduced the number of cultivable ammonia oxidizing bacteria and total phospholipid fatty acids in the rhizosphere compared to a non-allelopathic variety. Briones *et al*. (2002) observed differences in nitrification rates and nitrifying bacterial community composition between different cultivars when growing rice in saturated soils. Nitrification in the rhizosphere might be linked to N nutrition of plant (Fillery, 2007; Li *et al*., 2008). Response of rice varieties to PNN or their ability to suppress nitrification has never been documented in Sri Lanka. Hence, a study was conducted to investigate the plant response for PNN and BNI potential of root derived compounds of selected lowland rice varieties grown in Sri Lanka.

MATERIALS AND METHODS

In the present study 13 rice varieties used in lowland paddy farming were experimented (Table 1). Rice seeds certified for purity were provided by the Department of Agriculture, Sri Lanka. Varieties were first tested for their response to PNN using a hydroponic experiment and selected ten varieties were used to assess the BNI potential. All the experiments were conducted at the Department of Soil Science of Faculty of Agriculture, University of Peradeniya.

Partial nitrate nutrition of rice varieties

Rice seeds were surface sterilized with 1% sodium hypochlorite (NaOCl) for 30 min., rinsed five times and soaked in sterilized water overnight (Bi *et al*., 2007). Then seeds were placed on a sterilized medium of sand saturated with water to pre-germinate. From 3 days after germination (DAG), seedlings were watered with ¼ strength Hoagland's nutrient solution (Hoagland and Arnon, 1950) containing a

50:50 (percent ratio) NH_4^+: NO_3^- mixture to supplement N available in the solution. At 14 DAG healthy and uniformly developed seedlings were transplanted in plastic cups (250 cm^3) with ½ strength Hoagland's nutrient solution (NH_4^+: NO_3^- at 50:50) as two seedlings per cup. Media was renewed at 21 DAG with full strength N-free Hoagland's nutrient solution and three N treatments were imposed with four replicates. The N treatments were; only NH_4^+, only NO_3^-, and both NH_4^+ and NO_3^- (50:50) to supplement N in the growth medium using $(NH_4)_2SO_4$, NH_4NO_3 and KNO_3 as N sources.
A nitrification inhibitor, dicyandiamide (DCD), was used at 7µM concentration in all the treatments to suppress nitrification and to maintain intended NH_4^+: NO_3^- ratios. Growth medium in containers was renewed once every three days throughout the experiment. At 45 DAG plants were harvested, shoots and roots were separated and oven dried to obtain dry biomass.

Biological nitrification inhibition of rice varieties

Isolation of ammonia oxidizing community

A soil sample was collected from 0 -10 cm depth from a paddy field having a crop at panicle initiation stage and soil moisture near field capacity, in the experimental farm of University of Peradeniya in MahaIlluppallama, which is located in the low country dry zone of Sri Lanka. Soil was transferred to the laboratory and $(NH_4)_2SO_4$ was added to soil at 2 mM rate by mixing 100 g of field moist soil with 5 ml of $(NH_4)_2SO_4$ solution, and incubated at room temperature for two days to stimulate the growth of nitrifiers responsive to fertilizers. A sub sample from soil was taken and ammonia oxidizing microbial community was isolated using a culture based approach with P buffer medium (pH 7.8) as described by Weaver *et al*. (2007). To concentrate the number of cells in the growth medium, liquid growth medium containing isolated culture was centrifuged at 12,000 rpm for 5 min and the resulted pellet was dissolved in 50 ml of fresh P buffer medium and incubated for 14 days at 30°C, shaking periodically to aerate the medium (Subbarao *et al*., 2006). Composition of the P buffer medium (g L^{-1}) dissolved in water was: $(NH_4)_2SO_4$ 2.5; KH_2PO_4 0.7; Na_2HPO_4 13.5; $NaHCO_3$ 0.5; $MgSO_4.7H_2O$ 0.1; $CaCl_2.2H_2O$ 0.05; and Fe-EDTA 0.001. The culture was stored at 4°C until use and the potential ammonia oxidation rate of the culture was determined periodically to monitor the activity.

Preparation of plant material

All varieties except for BW267, BW363 and BW272 were used in BNI experiment. Seeds were surface sterilized and transferred to petri dishes lined with Whatman No 1 filter papers and kept until 3 DAG. Healthy uniformly developed seedlings were transferred into test tubes containing 10 ml of sterilized ¼ strength Hoagland's nutrient solution (Hoagland and Arnon, 1950) as two plants per tube and four replicates per variety. Plants were grown at 25-26°C and a photoperiod of 12 h light/12 h darkness. At 14 DAG seedlings in each tube were placed in tubes containing 5 ml of sterilized distill water and shaken for 30 min to collect root wash (RW). After removing the roots sterilized distilled water was added to standardize the concentration of the solution as to compounds from 4 mg fresh roots/ml. Then the roots were pat dried, ground and dissolved in sterilized distilled water to obtain a root extract (RE) solution with a concentration of 10 mg fresh roots/ml. These two extracts (RW and RE) containing plant derived secondary metabolites were used in BNI experiments at concentrations equivalent to root derived compounds extracted from 400 µg of fresh roots per milliliter of media used in bioassay experiments.

Bioassay to test BNI potential

A bioassay was conducted with RW to test its effect on potential ammonia oxidation (PAO) activity of isolated ammonia oxidizing community. 500 µl of 14 d old ammonia oxidizers' culture was mixed with 1ml of RW and incubated for 30 min. Then 9 ml of P buffer medium containing 1.5 mM $(NH_4)_2SO_4$ (PAO medium) was added and the mixture was incubated at 30°C while shaking periodically at 150 rpm for 21 days. Two milliliter subsamples were taken at day one and day 21 of the incubation and analyzed for nitrite colorimetrically using sulfanilamide method (Shinn, 1941). No nitrate production was detected during incubation period. The BNI potential of rice was calculated by dividing PAO with RW from the PAO of control.

BNI potential of root derived compounds in soil

To test whether BNI potential observed in the laboratory bioassay with ammonia oxidizing community agrees with the

Table 1. Rice varieties used in the experiment

Variety	Acronym	Remarks	Seeds source
BW 267 – 3	BW267	Newly improved variety	Regional Rice Research and Development Center, Bombuwela, Sri Lanka.
BW 272 – 6b	BW272	Newly improved variety	
BW 363	BW363	Newly improved variety	
BG 300	BG300	Newly improved variety	Department of Agriculture, Sri Lanka.
BG 352	BG352	Newly improved variety	
BG 358	BG358	Newly improved variety	
BG 94/1	BG94/1	Newly improved variety	
AT 362	AT362	Newly improved variety	
Suduru Samba	SS	Traditional variety	Rice Research and Development Institute, Bathalegoda, Sri Lanka.
SuduHeenati	SH	Traditional variety	
Dahanala	DA	Traditional variety	
Kaluheenati	KH	Traditional variety	
Suwandel	SW	Traditional variety	

effect of root derived compounds on nitrifiers in the presence of other soil organisms, a soil incubation study was conducted. Five grams of soil was mixed with 2 ml of RW and incubated for 2 h. Potential nitrification rate (PNR) of soil nitrifiers was measured using shaken slurry method at 1:10, soil:solution ratio (Weaver *et al*., 2007). The same procedure was repeated with adding 2 ml of RE to soil. A control with 2ml of sterilized distilled water to replace root derived compounds was performed in triplicates. Suppression of nitrification was calculated by dividing PNR with RW or RE from the PNR of control.

Statistical analysis

A two-way ANOVA was performed fitting biomass data from PNN experiment using the Additive Main Effects with Multiplicative Interaction Model (AMMI) to determine the best variety for a given environment using MatModel 3.0 software. Analysis of variance was performed for data generated from the BNI studies using MINITAB® 14.1 statistical software (Minitab Inc.). Means were compared by LSD mean separation ($p < 0.05$).

RESULTS

Rice varieties used in the experiment responded differently to N treatments (Figure 1). Variation in biomass is mostly due to the varietal difference (93 % of treatment effect) and the effect of N treatment on biomass (0.6 %) is not significant (Table 2).

Interestingly, biomass accumulation under different N treatments is variety dependent as revealed by the significance in VxN component in ANOVA. From Interaction Sums of Squares (SS of VxN) 48% is signal and 52% is noise. Varietal effect on plant response to NH_4^+-N was more similar to the response to a mix supply of NH_4^+ and NO_3^- than to only NO_3^--N application (Figure 2).

Genotypes like AT362 and BG94/1 have a positive interaction with NO_3^- treatment (Figure 2). BW267 and BG352 positively respond to NH_4NO_3 and NH_4 in the growth medium. KH, BG358, SH and SS have negligibly small interactions with this contrast in N treatment (Figure 2). Results indicate different rice varieties respond differently to the form of N present in the root environment. Root derived compounds affected nitrifiers differently based on the variety of rice and presence or absence of other soil organisms (Table 3). Three traditional varieties, SS, SH and SW, significantly enhanced the activity of ammonia oxidizing community isolated from soil during laboratory bioassay. However, when nitrifiers were exposed to root wash of the same varieties in the presence of a diverse groups of soil organisms in soil matrix, their activity was less or not different from the control. Root extracts of all varieties obtained by grinding fresh roots and dissolving in distilled water suppressed the potential nitrification at the rate of RE applied, which is nearly compounds from 400 µg fresh roots per milliliter of soil slurry (Figure 3).

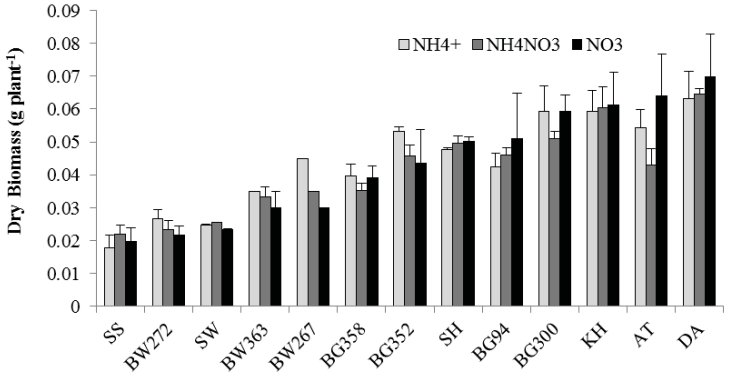

Figure 1. Dry biomass of 45 days old plants of thirteen rice varieties grown under three N treatments (NH_4^+ or NO_3^- or NH_4NO_3 supplying same level of N). Error bars represent standard deviation (n = 4).

Table 2. Summary statistics of AMMI analysis of rice biomass data from PNN experiment (Df – degrees of freedom, SS – Sums of squares, MS – Mean square).

Source	Df	SS	MS	Probability	% Variation explained[2]
Total	112	0.02751	0.00025		
Treatment	38	0.02512	0.00066	0.000***	91%
Variety (V)	12	0.02347	0.00196	0.000***	93.4%
N Treatment (N)	2	0.00015	0.00008	0.102	0.6%
V x N	24	0.00149	0.00006	0.017*	6.0%
IPCA 1	13	0.00100	0.00008	0.010*	67%
Residual	11	0.00050	0.00005	0.194	33%
Error	74	0.00240	0.00003		9%

[1] $P < 0.05$

[2] % variation explained = [SS of the term/ total SS of the respective category] X 100

Table 3. Biological nitrification inhibition (BNI) potential of water soluble root exudates (RW) of 14 days old seedling rice (Values are given as Mean ± Standard Error mean). Values < 1 indicate that potential ammonia oxidation (PAO) of the nitrifiers were suppressed by adding root exudates at the rate of compounds from 400 µg of fresh roots per milliliter of PAO medium compared to control which received distilled water in place of root exudates.

Variety	BNI potential[1] of RW measured on soil nitrifiers isolated and cultured in a laboratory growth media	BNI potential[1] of RW measured on nitrifiers in soil
BG300	1.72 ± 0.15 **b**	1.44 ± 1.18 **ab**
BG352	25.50 ± 16.1 **b**	3.11 ± 0.40 **a**
BG358	1.03 ± 0.02 **b**	0.52 ± 0.06 **b**
BG94/1	1.04 ± 0.01 **b**	1.51 ± 0.17 **ab**
AT362	1.16 ± 0.19 **b**	0.65 ± 0.24 **b**
SS	453.47 ± 6.51 **a**	0.59 ± 0.29 **b**
SH	410.95 ± 2.83 **a**	1.36 ± 0.87 **ab**
DA	1.03 ± 0.01 **b**	0.22 ± 0.04 **b**
KH	1.02 ± 0.04 **b**	0.98 ± 0.06 **b**
SW	435.56 ± 8.37 **a**	1.38 ± 0.67 **ab**

Means in a given column followed by the same letter are not significantly different at $p < 0.05$.

[1] BNI potential = $\frac{\text{(POA of nitrifiers treated with RW)}}{\text{(POA of nitrifiers in control)}}$

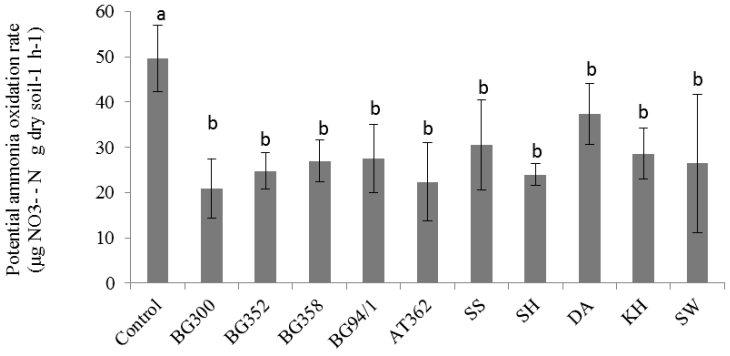

Figure 3. Potential ammonia oxidation (POA) activity of nitrifiers in soil treated with water soluble root tissue extracts (RE) of 14 days old seedlings of ten rice varieties (BG300 – SW) at the rate of compounds from 400 µg of fresh roots per milliliter of PAO medium. The control received distilled water in place of RE. Vertical bars followed by the same letter are not significantly different at $p < 0.05$. Error bars represent the standard deviation (n = 4).

DISCUSSION

Supplying nutrients in the form plants are more responsive to while minimizing nutrient losses from the system would improve fertilizer use efficiency in agricultural systems. The present study evaluates the response of rice to partial nitrate nutrition and potential for suppression of nitrification, which are important traits for the nitrogen nutrition of plants.

Air that leak or exude from roots create an aerobic environment in rice rhizosphere facilitating nitrification to different extents depending on rice variety (Briones *et al*., 2002). Diffusion of NH_4^+-N from the oxygen-limited bulk soil to the rhizosphere and nitrification happening in the vicinity of roots result in an environment with partial nitrate nutrition (Li *et al*., 2008). Hence, rice varieties bred for saturated soil conditions should perform better in hydroponic cultures when N is supplied in mix forms as NH_4^+ and NO_3. However, the results from the present study suggest that the response of rice plants to N form in the root zone vary among varieties. Some varieties show more preference to more NH_4^+ (BW 267 and BG 352); whereas, others perform better under NO_3^- supply (AT 362 and BG 94/1) or indifferent to either N forms (SS, BG 358, KH, etc). Differences among rice varieties in their response to the form N in the growth media has been reported previously (Kronzucker *et al*., 1999; Ying-Hua *et al*., 2006; Duan *et al*., 2007). Nitrification rate in the rhizosphere is retarded if plants are competitive in up-taking NH_4^+ (Verhagen *et al*., 1994). Plants could discourage nitrification in the rhizosphere by secreting allelochemicals directly, suppressing growth of nitrifers and/ or encouraging the growth of fast growing *bacteria* competing for NH_4^+ with nitrifiers (Verhagen *et al*., 1994; Ishikawa *et al*., 2003).

Water-extracted rice root exudates contain amino acids, whose concentration is highest during the first two weeks after seeding than at other growth stages (Bacilio-Jimenez *et al*., 2003). The composition of root wash of rice varieties was not analyzed in the present study. However, a previous research conducted with traditional and improved rice varieties in Sri Lanka confirmed that rice varieties have varying root exudation profiles and some varieties exude more organic compounds like amino acids than others (Dandeniya, 2007). The most common bacterial ammonia oxidizers in agricultural soils including paddy soils belong to genera *Nitrosomonas* and *Nitrosospira* classified as chemolithoautotrophs that use CO_2 as the cellular C source. Presence of fructose, pyruvate and amino acids like organic

compounds in the growth medium could enhance the activity of *Nitrosomonas europaea* serving as cellular C sources in addition to CO_2 (Clark and Schmidt, 1967; Hommes *et al*., 2003). Differences in composition of water soluble root exudates (RW) among rice varieties may have contributed to the variations of the activity of ammonia oxidizers incubated with RW. The bioassay conducted with the nitrifier isolate, which rule out the interference from other soil organisms and the physicochemical effects of soil matrix, indicate RW of the tested varieties could augment the activity of nitrifiers or have no effect than suppressing the activity. However, in the presence of other soil organisms the nitrification was suppressed by the same concentration of RW (Table 2). Root derived organic compounds could act as C and energy sources and stimulate the growth of other fast growing bacteria in the rhizosphere exerting a pressure to slow growing nitrifiers (Verhagen *et al*., 1994). Thus, the mechanism of potential suppression of nitrification by root exudates of BG 358, AT 362, Suduru Samba and Dahanala varieties could be via stimulating the growth of competitors of nitrifiers in the rhizosphere. This needs further investigations. The root tissue extracts (RE) of all tested varieties suppressed soil nitrification; however, the methodology used with RE do not warrant the separation of suppression of nitrifiers due to BNI from competition exerted by soil microorganisms.

One mg ml^{-1} of rhizodeposition is a concentration that is likely to occur in the vicinity of a mass of decaying roots (Uren, 2007). The application rate of root derived compounds in the present study was compounds from 0.4 mg roots ml^{-1} (final concentration in soil slurry) and suppression of nitrifier activity was observed even at this level. Although root derived compounds of some rice varieties suppressed the activity of soil nitrifiers there was no direct relationship between preference of a variety to NH_4^+ as a N source and nitrification suppression potential of tested varieties.

Results from laboratory bioassays on allelopathy are relative and provide information about potential BNI only (Bi *et al*., 2007; Pariasca Tanaka *et al*., 2010). Active plant-derived secondary metabolite concentration in soil is greatly determined by microbial activities, soil physicochemical reactions and plant factors (Gopalakrishnan *et al*., 2009). The response of nitrifiers to plant derived compounds may differ when tested against nitrifiers grown in artificial growth media in laboratory bioassays than from the activity of nitrifiers in soil matrix (Pariasca Tanaka *et al*., 2010) as confirmed by the present study.

The diversity of rice growing systems and rice gene pool in Sri Lanka present great potential to search for traits like biological nitrification inhibition and PNN. The information will be useful in plant breeding programmes to develop varieties with better N use efficiency for environments with excessive nitrification such as rain-fed and upland cultivation systems (Subbarao *et al*., 2012).

CONCLUSION

The response of rice to NH_4^+:NO_3^- ratios in the growth medium is variety specific. Rice varieties differentially suppressed nitrifiers activity. The suppression of soil nitrification by root exudates could be via stimulation of growth of fast growing microorganisms that suppress the slow growing nitrifiers than a direct effect on nitrifiers. There was no direct relationship between BNI potential and the preference of a variety to NH_4^+ among the thirteen rice varieties used in the study.

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HYDRO-CHEMICAL STATUS OF THE *MAHAKANUMULLA* CASCADE IN THE DRY ZONE OF SRI LANKA

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ABSTRACT

The main objectives of this study are to evaluate the hydro-chemical parameters of the tank waters and the trends of nutrient accumulation in Mahakanumulla tank cascade. Water samples were collected from twenty selected tanks of the cascade. In all water samples, dissolved Nitrate (NO_3^-) and Phosphate (PO_4^{3-}), Potassium (K^+), Sulphate (SO_4^{2-}) and Fluoride (F^-), Calcium (Ca^{+2}), Magnesium (Mg^{+2}), Sodium (Na^+), Manganese (Mn^{+2}),pH , Electrical Conductivity (EC), Total Dissolved Solids (TDS), Turbidity and Dissolved Oxygen (DO), Temperature (T^0) were measured using standard techniques. Sodium Adsorption Ratio (SAR) and Hardness of the water samples were also calculated. NO_3^- concentration of all tanks in Mahakanumulla cascade ranged from 2.66 mg L^{-1} (Wellamudawa) to 6.64 mg L^{-1} (Kudagama) and did not exceed the permissible level for irrigation and drinking water. PO_4^{3-} concentration of the water varied from 0.01 mg L^{-1} (Demata wewa) to 0.2 mg L^{-1} (Mahakanumulla). Fairly high K^+ concentrations were detected in all tanks and fell within the range of 2.14- 8.61 mg L^{-1}. Fluoride Content of water samples did not exceed beyond the WHO detection level for drinking and irrigation water. Some of the water quality parameters such as TDS and SAR were higher than the permissible level. It is evident from the ecological point of view, even though NO_3^- and PO_4^{3-} concentrations are below the eutropic level high TDS values along with hardness may create eutropic stage in most of tanks in Mahakanumulla cascade in future.

Keywords: *Hydro-chemical parameters, Plant nutrients, Tank cascade*

INTRODUCTION

Village tanks in the Dry Zone of Sri Lanka are one of the most important water storage systems on which people depend for their irrigation and domestic purposes. Most of the small tanks are organized as cascading systems within micro- and meso-catchments in the undulating landscape of the dry zone (Sakthvadivel *et al*., 1997; Shinogi, 2001). The cascade system is considered as the main irrigation system in the dry zone of Sri Lanka where the water scarcity is a main limitation for crop production caused by the annual variable low rainfall (<1250 mm) combined with high evaporation rates (6 mm Day^{-1}) (Panabokke, 1996).

In North Central Province of Sri Lanka, located in the Dry Zone, there are 4017 small tanks. Presently 2,095 tanks are functioning (Pannabokke *et al*., 2002). Eutropication, deterioration in water quality, siltation and swallowing of tanks are major problems faced due to various anthropogenic activities (Vijayavera, 2008). Bulk of water in irrigation tanks comes through tank catchment area carrying dissolved materials, organic and inorganic substances (Amarasiri, 1973) during rainy season and very less amount reached through direct precipitation. The contamination and pollution of drinking and irrigable water are main concerns worldwide. Hydro-chemical parameters such as dissolved plant nutrients, other toxic elements, hydrological and biological conditions of water directly affect the water quality.

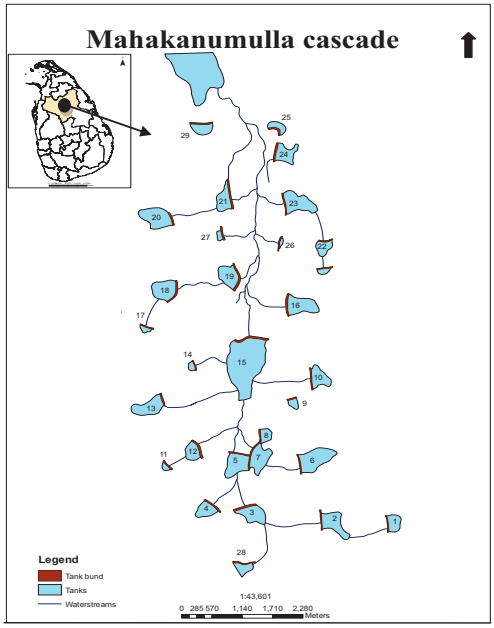
Hydro-chemical properties and their interactions play a significant role in tank ecosystem. Thus, studies addressing the Hydro-chemical status of tank water would help in understanding the functioning of a particular water body in relation to cascade land use types. The proper balance of the hydro-chemical properties of water in tanks is an essential ingredient for successful production of fish and other aquatic resources. The presence or absence of chemical elements might be a limiting factor for the productivity in such water bodies. Also high concentrations of nitrate and phosphate are causative agents for eutropication that lead to algal bloom and the destruction of aquatic ecosystems. Some hydro chemical parameters such as turbidity, pH and temperature play important role in plankton distribution and tank stratification (Vijayavera, 2008).

Mahakanumulla tank cascade located in Anuradhapura district is a branched type tank cascade with a form index of 2.8 (Sakthvadivel *et al*., 1997), having twenty nine connected tanks. Five are located along the main valley and the rest is located along the side or branch valleys finally connecting to *Nachchaduwa* reservoir. The tank beds of 15 of the 29 tanks of *Mahakanumulla* cascade are heavily silted, while the tank beds of 10 are moderately silted (Pannabokke *et al,* 2002). This tank system provides irrigation water for an approximately 324 ha of paddy lands supporting the livelihood of around 1600 families. However, at present the hydro-chemical status of water quality parameters of tank waters of *Mahakanumulla* cascade are not documented. Therefore the main objective of this study is to evaluate hydro-chemical status of the tank waters and also to highlight the trends of nutrient accumulation using newly collected data set.

MATERIALS AND METHODS

Field work was carried out in the *Mahakanumulla* cascade located in *Thirappane* area (Figure 1). Twenty tanks of the

Mahakanumulla cascade were selected for this study based on the accessibility. Two sets of water samples were taken from



1. Palankulama wewa
2. Amana wewa
3. **Ihala amanakkatuwa wewa**
4. **Siwalagala wewa**
5. **Pahala amanakkatuwa**
6. **Walagambahuwa wewa**
7. **Pahala wewa**
8. **Thorapitiya wewa**
9. **Galwaduwagama wewa**
10. Mawathawewa
11. Aiyethiyagama wewa
12. **Marrikkaragama wewa**
13. **Paindikulama wewa**
14. **Achiriya kulama wewa**
15. **Mahakanumulla wewa**
16. **Kudakanumulla wewa**
17. **Thammanagala wewa**
18. **Wagayakulama wewa**
19. **Kudagama wewa**
20. **Etaweerawewa**
21. **Kuchchikulama wewa**
22. **Kuda wewa**
23. **Sembu wewa**
24. **Demata wewa**
25. Weli wewa
26. Tharangollawa wewa
27. ***Wellamudawa wewa***
28. Ihalagama wewa
29. Werappudikulama wewa

Figure 1. Map of Mahakanumulla cascade. Tanks indicated in bold letters were used to collect water samples

Three predetermined locations (4-5m away from tank bund and within ½ m depth) of each tank using clean plastic bottles during the second week of April 2011. Samples were taken as a triplicate. One set was filtered and acidified for metals analysis and few drops of chloroform were added for the other set. The chemical analysis was conducted at the Department of Soil Science, Faculty of Agriculture, University of Peradeniya.

In all water samples, dissolved Nitrate (NO_3^-) and Phosphate (PO_4^{3-}) were determined using Sodium Salicylate (Bremner and Mulvaney, 1982) and Molybdate blue colorimetric procedures (Murphy and Relay, 1962), respectively. Potassium (K^+) determination was done using Flame Emission Spectrophotometer (FES). Sulphate (SO_4^{2-}) was determined by turbidimetric method (Hoeft *et al*., 1973). Whereas Fluoride (F^-) in water samples was analyzed calorimetrically using SPANDS reagent. Calcium (Ca^{+2}), Magnesium (Mg^{+2}), Sodium (Na^+) and Manganese (Mn^{+2}) were determined using Atomic Absorption Spectrophotometer (AAS). Total Dissolved Solids (TDS), pH and the Electrical conductivity (EC) of water samples were measured using multi parameter meter (Model-Hatch sension156). Turbidity of the water samples was measured using portable tubidity meter (Eutech /Turbidimetry/TN 100) and Dissolved oxygen (DO) of the water samples was also measured using DO parameter meter (EUTECH/Cyber scan/DOK100). Temperature (T^0) of the water samples was measured in-situ using Thermometer. Sodium Adsorption Ratio (SAR) and hardness of the water samples were also calculated. The data were analyzed statistically with ANOVA and Turkey's Range test comparison.

RESULTS AND DISCUSSION

Concentrations of major plant nutrients in waters of Mahakanumulla cascade

Concentrations of major plant nutrients in waters of twenty tanks of *Mahakanumulla* cascade are given in Table 01. The NO_3^- concentration ranged from 2.66 mg L^{-1} (*Wellamudawa*) to 6.64 mg L^{-1} (*Kudagama).* The main input sources for NO_3^- are the chemical fertilizers and organic manures added to crop fields in the catchment. In addition, a considerable amount of cattle and buffalo manure and urine which are rich with nitrogen are also added to tanks *thaulla* and subsequently drain off to tank. The NO_3^- concentrations of all tank waters did not exceed the permissible level (50 mg L^{-1}) for irrigation and drinking water (WHO, 2004). This indicates that there is no evidence of NO_3^- pollution in tank waters of *Mahakanumulla* cascade during this period.

Therefore in relation to NO_3^- concentration present at the sampling, water can be considered as safe to be used both for domestic and irrigation purposes. The sampling campaign was carried out during the second week of April. Generally, land preparation for the paddy cultivation is carried out in this area in late April to early May and planting begins in early May (*Yala* season). In this period, fertilizers are applied as basal and top dressings to the fields in the catchment area. The quantity of urea application varies from 40 to 60kg ha^{-1} and Triple Super Phosphate application ranged from 30 to 40 kg ha^{-1}. (Young *et al.*, 2010). Therefore, there is strong possibility that NO_3^- from these sources can be accumulated in the tank water during the growing season.

A progressive accumulation of plant nutrients, toxic and other elements along the entire cascade system was not observed. Scattered distribution of tanks can greatly be attributed for this behavior. However, some increasing trends of the accumulation of nutrients and elements in the linear segments of the tank cascade were observed. For an example, NO_3^-

Table 01. Major plant nutrients in waters of some tanks in *Mahakanumulla* cascade

Tanks	NO_3^- (mg L^{-1})	PO_4^{3-} (mg L^{-1})	K^+ (mg L^{-1})	Ca^{+2} (mg L^{-1})	Mg^{+2} (mg L^{-1})	SO_4^{-2} (mg L^{-1})
Siwalagala	$3.20^{ghi}\pm0.02$	$0.08^{cdef}\pm0.01$	$4.50^{l}\pm0.1$	$15.69^{l}\pm0.08$	$3.93^{l}\pm0.47$	$1.87^{cdef}\pm0.05$
Ihala Amanakkatuwa	$3.45^{fgh}\pm0.01$	$0.07^{cdefg}\pm0.01$	$5.16^{l}\pm0.15$	$18.53^{l}\pm0.06$	$9.47^{d}\pm0.07$	$2.07^{cd}\pm0.46$
Pahalaamanakkatuwa	$4.38^{cd}\pm0.04$	$0.11^{bc}\pm0.01$	$6.70^{f}\pm0.1$	$29.72^{c}\pm0.34$	$8.21^{e}\pm0.04$	$4.16^{a}\pm0.41$
Walagambahu	$3.03^{ij}\pm0.12$	$0.04^{efgh}\pm0.01$	$5.40^{hi}\pm0.1$	$19.75^{h}\pm0.12$	$7.22^{fg}\pm0.07$	$1.32^{fg}\pm0.05$
Pahala wewa	$3.14^{hij}\pm0.06$	$0.03^{gh}\pm0.01$	$8.30^{d}\pm0.10$	$25.85^{e}\pm0.08$	$6.71^{g}\pm0.07$	$1.25^{fgh}\pm0.03$
Thorapitiya	$3.23^{ghi}\pm0.03$	$0.04^{efgh}\pm0.01$	$4.70^{j}\pm0.1$	$22.50^{f}\pm0.14$	$4.36^{l}\pm0.17$	$0.31^{i}\pm0.02$
Galwaduwagama	$3.73^{f}\pm0.15$	$0.02^{h}\pm0.005$	$7.20^{e}\pm0.1$	$15.64^{l}\pm0.06$	$1.65^{kl}\pm0.51$	$0.83^{ghi}\pm0.001$
Marikkaragama	$4.67^{c}\pm0.09$	$0.07^{cdefg}\pm0.01$	$6.80^{f}\pm0.05$	$10.19^{m}\pm0.11$	$5.87^{gh}\pm0.08$	$0.80^{ghi}\pm0.12$
Paindikulama	$3.49^{fg}\pm0.14$	$0.06^{defgh}\pm0.01$	$5.36^{hi}\pm0.05$	$10.13^{m}\pm0.12$	$3.65^{l}\pm0.07$	$1.36^{efg}\pm0.14$
Mahakanumulla	$5.78^{b}\pm0.11$	$0.20^{a}\pm0.03$	$8.63^{c}\pm0.15$	$41.32^{b}\pm0.34$	$10.03^{cd}\pm0.53$	$1.59^{cdef}\pm0.52$
Kudakanumulla	$3.21^{ghi}\pm0.07$	$0.14^{b}\pm0.01$	$6.06^{g}\pm0.11$	$43.56^{a}\pm0.06$	$16.20^{a}\pm0.54$	$1.45^{defg}\pm0.11$
Thammanagala	$3.05^{ij}\pm0.06$	$0.02^{h}\pm0.005$	$5.56^{h}\pm0.15$	$2.75^{o}\pm0.11$	$2.55^{l}\pm0.12$	$2.02^{cde}\pm0.30$
Wagayakulama	$4.05^{e}\pm0.06$	$0.08^{cde}\pm0.005$	$8.10^{d}\pm0.10$	$16.17^{kl}\pm0.06$	$7.79^{ef}\pm0.05$	$3.00^{b}\pm0.06$
Kudagama	$6.64^{a}\pm0.17$	$0.10^{bcd}\pm0.02$	$12.70^{a}\pm0.10$	$27.48^{d}\pm0.06$	$10.36^{c}\pm0.09$	$0.88^{ghi}\pm0.20$
Etaweerawewa	$4.25^{de}\pm0.09$	$0.08^{cdef}\pm0.01$	$9.30^{b}\pm0.10$	$17.80^{l}\pm0.13$	$1.66^{kl}\pm0.11$	$0.57^{hi}\pm0.06$
Kuttikulama	$3.26^{ghi}\pm0.11$	$0.05^{efgh}\pm0.005$	$7.20^{e}\pm0.10$	$21.31^{g}\pm0.22$	$12.64^{b}\pm0.14$	$2.22^{c}\pm0.06$
Kudawewa	$2.82^{jk}\pm0.13$	$0.02^{h}\pm0.01$	$5.50^{h}\pm0.1$	$16.33^{k}\pm0.06$	$6.67^{g}\pm0.38$	$1.19^{fgh}\pm0.26$
Sembu wewa	$3.71^{f}\pm0.14$	$0.05^{efgh}\pm0.005$	$8.10^{d}\pm0.1$	$1.64^{p}\pm0.41$	$1.70^{kl}\pm0.24$	$0.61^{hi}\pm0.11$
Demata wewa	$4.10^{de}\pm0.02$	$0.01^{h}\pm0.005$	$8.80^{c}\pm0.10$	$7.92^{n}\pm0.05$	$2.12^{jk}\pm0.06$	$1.81^{cdef}\pm0.14$
Wellamudawa	$2.66^{k}\pm0.11$	$0.03^{fgh}\pm0.01$	$5.30^{hi}\pm0.10$	$27.26^{d}\pm0.11$	$1.15^{l}\pm0.11$	$0.57^{hi}\pm0.11$

concentration increased steadily from 3.05 mg L^{-1} to 4.05 mg L^{-1} and finally to 6.64 mg L^{-1} (Figure 2) of waters in one linear segment of tank cascade containing three tanks (*Thammannagala*, *Wagayakulama* and *Kudagama* tanks). Similarly another liner segment of tank cascade (*Siwalagala, Pahala amannakkatuwa* and *Mahakanumulla*) also showed increasing trend of NO_3^- concentration from first to third tank (Figure 03).

PO_4^{3-} concentration of the water ranged from 0.01 mg L^{-1} (*Demata wewa*) to 0.2 mgL^{-1} (*Mahakanumulla* tank) at a very narrow range (Table 01). Phosphorous is one of major nutrients responsible for biological productivity and also its excessive accumulation in water can cause eutropication. The PO_4^{3-} concentrations of six tanks were greater than the EPA suggested critical value (0.08 mgL^{-1}) for the development of eutropication (EPA, 1976). This relatively high PO_4^{3-} concentration in water may be attributed to the input of phosphates from sediments transported from the catchment area due to the surface runoff.

However, none of the water samples exceeded the PO_4^{3-} level beyond the WHO standard (2 mg L^{-1}) for drinking and irrigation water. The highest K^+ concentration was observed in *Kudagama* tank (12.70 mg L^{-1}) and the lowest was recorded in *Siwalagala* tank (4.50 mg L^{-1}) (Table 01). The K^+ contents were significantly different across the studied tanks ($p < 0.05$) and their concentrations exceeded the WHO standard (2 mg L^{-1}). The relatively high K^+ contents in irrigation water may be due to K released from organic matter specially decomposed rice straw and fertilizer (Amarasiri and Wickramasingha, 1988). That may be the reason for elevated K^+ content in water than Mg^{+2}. The highest Ca^{+2} and Mg^{+2} were observed in the *Kudakanumulla* tank (43.56 mg L^{-1} and 16.20 mg L^{-1}, respectively). The lowest Ca^{+2} concentration was examined in *Sembukulama* (1.64 mg L^{-1}) tank and the lowest Mg^{+2} was recorded in *Wellamudawa* tank (Table 01). According to the standards established for drinking water in Sri Lanka, maximum desirable and permissible levels for Ca^{+2} are 100 mg L^{-1} and 240 mg L^{-1}, respectively (SLS, 1983). For Mg^{+2} these levels are 30 mg L^{-1} and 150 mg L^{-1}, respectively. According to the results, neither Ca^{+2} nor Mg^{+2} of the water samples exceeded the maximum permissible levels. The SO_4^{-2} concentration was ranged from 0.31 mg L^{-1} *(Thorapitiya* tank) to 4.16 mg L^{-1} (*Pahala Amanakkatuwa* tank) (Table 01). According to the Sri Lankan standards the maximum desirable level for SO_4^{2-} in water is 200 mg L^{-1} and maximum permissible level is 400 mg L^{-1} (SLS, 1983).

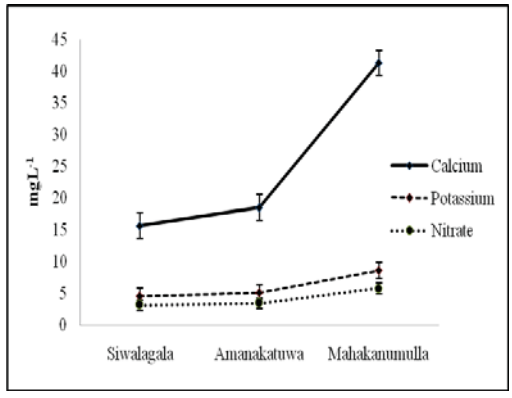


Figure 2. Nutrient transfer along *Siwalagala,Amanakatuw--a and Mahakanumulla* tanks

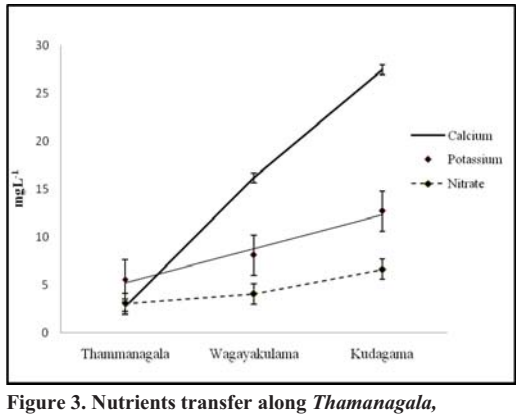


Figure 3. Nutrients transfer along *Thamanagala, Wagayakulama and Kudagama* tanks

None of water samples exceeded the SO_4^{-2} concentration beyond the maximum permissible level of 400 mg L^{-1} of water.

Other elements in waters of *Mahakanumulla* cascade

Highest F^- level was recorded (1.27 mg L^{-1}) in *Walagambahu* tank and lowest was recorded in *Etaweera wewa* (0.22 mg L^{-1}) (Table 02). According to Sri Lankan standards for potable water, Maximum desirable level for F^- in water is 0.6 mg L^{-1} and maximum permissible level is 1.5 mg L^{-1} which is same as WHO standards. None of the water samples exceeded level beyond these standards. According to WHO (2004) and Sri Lankan standards for potable water (SLS, 1983).

Concentrations of selected elements in tank waters of *Mahakanumulla* cascade are given in the Table 02. The desirable range of F for drinking is specified as 0.5 to 1.5 mg L^{-1}. According to the results, only 04 tanks out of 20 tanks studied were within the desirable range thus fit for drinking purpose. Waters of sixteen tanks were observed with the F concentration below 0.5 mg L^{-1}. The F^- concentration below 0.5 mg L^{-1} causes tooth decay (Dharmagunawardhane and Dissanayake, 1993).

Heavy metals can be considered as one of the most hazardous environmental pollutants. The most common adverse effect of heavy metals is the contamination of soil, pollution of ground and surface water sources. Apart from acute health effects, main problems associated with heavy metal pollution are the persistence and the potential of bioaccumulation and biomagnifications which could cause severe damage to some organisms. Elevated levels of heavy metals in drinking and irrigating water are one of the major problems in both industrial and agricultural countries.

The accumulation of Mn^{+2} can cause direct toxicological effects, as it can influence the concentration of other elements, including toxic heavy metals in surface water. Manganese can be absorbed into soil and the extent of adsorption depending on the organic matter content and the cation exchange capacity of the soil. Moreover, it can be bio-accumulated in organisms such as phytoplankton, algae and some fish spp. Bio magnification in food chains is not expected to be very significant (ATSDR, 2000).

Manganese occurs naturally in many surface water and groundwater sources and in soils that may erode into these waters. The highest Mn^{+2} content was detected in the *Kudakanumulla* tank (0.025 mg L^{-1}) and the lowest was recorded in *Punchchikulama* tank (0.001 mg L^{-1}) (Table 02). None of the water samples exceeded the WHO permissible level for drinking water quality and the Sri Lankan standards established for drinking water by the SLS 614:1983 (0.5 mg L^{-1}). The highest Cu^{+2} content was recorded in both *Sembukulama* and *Kuttikulama* (0.005 mg L^{-1}). The highest contents were noted in *Walagambahu*, *Siwalagala*, and *Punchchikulama* and *Wagayakulama* tanks (0.001 mg L^{-1}) (Table 02). None of water sample exceeded the WHO permissible level for drinking water quality which is 1.5 mg L^{-1}.

Table 02: Average concentrations of other elements in waters of some tanks in *Mahakanumulla* cascade (Averages with different superscript letters are significantly different at P<0.05)

Tanks	F^- (mg L^{-1})	Mn^{+2} (mg L^{-1})	Cu^{+2} (mg L^{-1})	Na^+ (mg L^{-1})
Siwalagala	$0.09^{bc}\pm0.08$	$0.010^{e}\pm0.003$	$0.001^{ef}\pm0.005$	$7.60^{b}\pm0.26$
Amanakkatuwa	$1.04^{b}\pm0.08$	$0.005^{hi}\pm0.005$	$0.002^{cdef}\pm0.005$	$7.20^{b}\pm0.10$
Pahalaamanakkatuwa	$0.86^{c}\pm0.06$	$0.004^{i}\pm0.005$	$0.003^{bcd}\pm0.005$	$6.20^{c}\pm0.70$
Walagambahu	$1.27^{a}\pm0.02$	$0.003^{a}\pm0.001$	$0.001^{f}\pm0.0005$	$4.25^{h}\pm0.08$
Punchikulama	$0.31^{fg}\pm0.03$	$0.007^{gh}\pm0.002$	$0.001^{f}\pm0.005$	$6.10^{cd}\pm0.10$
Thorapitiya	$0.71^{d}\pm0.05$	$0.022^{d}\pm0.001$	$0.003^{bcde}\pm0.005$	$5.80^{cde}\pm0.10$
Galwaduwagama	$0.47^{e}\pm0.06$	$0.002^{ij}\pm0.0005$	$0.002^{cdef}\pm0.005$	$4.70^{gh}\pm0.10$
Marikkaragama	$0.25^{g}\pm0.01$	$0.001^{jk}\pm0.001$	$0.003^{bcd}\pm0.005$	$6.33^{c}\pm0.15$
Paindikulama	$0.25^{g}\pm0.01$	$0.001^{k}\pm0.001$	$0.002^{cdef}\pm0.005$	$6.33^{c}\pm0.15$
Mahakanumulla	$0.40^{ef}\pm0.03$	$0.001^{jk}\pm0.001$	$0.002^{cdef}\pm0.001$	$8.93^{a}\pm0.35$
Kudakanumulla	$0.32^{fg}\pm0.02$	$0.025^{b}\pm0.0005$	$0.002^{def}\pm0.001$	$7.06^{b}\pm0.15$
Thammanagala	$0.26^{g}\pm0.02$	$0.008^{fg}\pm0.0001$	$0.002^{cdef}\pm0.005$	$5.20^{efg}\pm0.10$
Wagayakulama	$0.23^{g}\pm0.01$	$0.001^{jk}\pm0.0005$	$0.001^{ef}\pm0.005$	$4.70^{gh}\pm0.10$
Kudagama	$0.28^{fg}\pm0.001$	$0.001^{jk}\pm0.005$	$0.003^{bcd}\pm0.005$	$4.83^{fgh}\pm0.05$
Etaweerawewa	$0.22^{g}\pm0.01$	$0.002^{jk}\pm0.005$	$0.004^{abc}\pm0.001$	$5.40^{defg}\pm0.20$
Kuttikulama	$0.32^{fg}\pm0.04$	$0.001^{jk}\pm0.01$	$0.005^{ab}\pm0.001$	$5.46^{def}\pm0.28$
Kudawewa	$0.29^{fg}\pm0.01$	$0.023^{c}\pm0.005$	$0.002^{cdef}\pm0.005$	$5.70^{cde}\pm0.10$
Sembu wewa	$0.23^{g}\pm0.01$	$0.002^{ij}\pm0.002$	$0.005^{a}\pm0.005$	$5.2^{efg}\pm0.10$
Dematawewa	$0.27^{g}\pm0.01$	$0.009^{f}\pm0.0006$	$0.002^{cdef}\pm0.001$	$4.80^{fgh}\pm0.10$
Wellamudawa	$0.23^{g}\pm0.005$	$0.001^{jk}\pm0.0002$	$0.002^{cdef}\pm0.005$	$5.63^{cde}\pm0.30$

Other water quality parameters in *Mahakanumulla* cascade

The average values of the water quality parameters are given in Table 03. The highest Na^+ concentration was observed in *Mahakanumulla* tank as 8.93 mgL^{-1} and the lowest was recorded in *Walagambahu* tank as 4.25 mg L^{-1} (Table 02). EPA suggested values for drinking water is 20 mg L^{-1}. But in this cascade, none of tank water samples exceeded the EPA suggested value. pH of all the water samples varied from 7.06 - 8.29 (Table 03). Highest was recorded in *Marrikaragama* while lowest was observed in *Amanakkatuwa* tank. According to the WHO guidelines for irrigation, these pH values are within the suitable range (6.5-8.5). Turbidity is a measure of the degree to which the water loses its transparency due to the presence of suspended particulates. The WHO has established that the turbidity of drinking water required not to be more than 5 NTU (Naptheometer Turbidity Unit) and should ideally be below 1 NTU. Turbidity of the studied cascaded was ranged from 2.67-27.83 NTU (Table 03). Dissolved oxygen analysis measures the amount of gaseous oxygen dissolved in an aqueous solution. Oxygen enters into water by diffusion from the surrounding air by aeration and as a result of the photosynthesis of aquatic plants. Dissolved oxygen content of water ranged from 2.86 mg L^{-1} (*Ihalaamanakkatuwa)* to 9.64 mg L^{-1}*(Paindikulama tank)*. Conductivity increases with the increase of cation and anion in the water. The highest conductivity was observed in the *Wellamudawa* tank (878.00 µS cm^{-1}) and the lowest value was observed in the *Galwaduwagama* tank (98.20 µS cm^{-1}) (Table 03). The desirable range suggested by WHO is 250 µS cm^{-1}. Most of the tanks exceeded this limit while few lies below the limit.

The TDS values were varied from 37.47 mg L^{-1} to 384.67 mg L^{-1}. Highest was recorded in *Wellamudawa* tank and lowest was observed in *Etaweerawewa* (Table 03). Beeton (1965) suggested that the separation of oligotropic and eutropic tanks on the basis of TDS values. Oligotropic tanks have less than 100 mg $L^{-1}$and eutropic tanks have more than 100 mg L^{-1}. All the tanks except four tanks TDS values were higher than 100 mg L^{-1}. Therefore in ecological point of view, there is a strong possibility that these tanks in *Mahakanumulla* cascade are moving towards eutropic stage in future.

Concentration of Ca^{+2}, Mg^{+2} and Na^+ ions was used to calculate the Sodium Adsorption Ratio (SAR) of the water samples. SAR is a parameter used to determine the sodium hazard of the water which is represented by the ratio of the Na^+ concentration to the squire root of the summation of Ca^{+2} and Mg^{+2} ions concentration. The SAR of water varied from 1.11 to 4.05 (Table 03). All tanks except *Thammanagala* and *Sembu wewa*, showed SAR values which were below the WHO standard (3.00). Total hardness of the water is reflected by the concentrations of Ca and Mg ions present in the water. Hard water which contains high Ca^{+2} and Mg^{+2} ions is generally not harmful to the human health but some studies have shown a weak inverse relationship between water hardness and cardiovascular disease in men. Moreover, the hardness of water can cause serious problems in industrial settings (Rebeca, 1957). According to the WHO standards, hardness of water is classified into four groups namely; soft (0-60 mg L^{-1}), moderately hard (61-120 mg L^{-1}), hard (121-180 mg L^{-1}) and very hard (>180 mg L^{-1}) water.

Table 03: Average values of water quality parameters in waters of some tanks in *Mahakanumulla* cascade. (Averages with different superscript letters are significantly different at P<0.05)

Tanks	pH	T (^{0}C)	Turbidity (NTU)	DO (mg L^{-1})	EC (µS cm^{-1})	TDS (mg L^{-1})	SAR	Hardness) (mg L^{-1})
Siwalagala	7.43^{bcdef}±0.01	32.30^{cde}±0.10	11.48^{e}±0.88	6.26^{b}±0.005	289.67^{ghij}±8.02	120.93^{fgh}±3.72	2.42^{c}±0.10	55.73^{l}±1.79
IhalaAmanakkatuwa	7.06^{i}±0.005	31.63^{def}±0.05	3.87^{jkl}±0.78	2.86^{ij}±0.40	605.00^{bcde}±16.46	269.67^{abcde}±5.69	1.42^{g}±0.02	86.10^{fg}±0.38
Pahalaamanakkatuwa	7.16^{ghi}±0.005	31.50^{efg}±0.10	5.55^{hij}±0.48	3.45^{gh}±0.02	662.33^{abcd}±0.58	281.33^{abc}±1.15	1.50^{g}±0.04	108.78^{cd}±1.02
Walagambahu	7.22^{ghi}±0.01	32.50^{cd}±0.01	2.67^{l}±0.12	4.13^{de}±0.18	713.67^{abc}±4.62	299.00^{abc}±1.00	1.62^{efg}±0.80	79.70^{g}±2.05
Punchikulama	7.27^{defghi}±0.04	29.27^{ij}±0.55	5.64^{ghij}±0.40	3.32^{ghi}±0.13	574.33^{bcdef}±1.15	253.67^{bcde}±0.58	1.51^{fg}±0.02	92.81^{e}±0.28
Thorapitiya	7.22^{fghi}±0.01	31.60^{def}±0.10	5.73^{ghi}±0.15	4.07^{ef}±0.10	384.67^{efgh}±1.53	159.07^{defg}±0.74	1.58^{fg}±0.02	74.56^{gh}±0.56
Galwaduwagama	7.36^{bcdef}±0.01	34.60^{a}±0.40	6.89^{fgh}±0.02	5.50^{c}±0.04	98.20^{j}±4.67	38.00^{h}±2.00	1.60^{fg}±0.06	46.03^{l}±2.07
Marikkaragama	8.29^{a}±0.26	29.64^{jk}±0.05	19.64^{c}±0.05	5.48^{c}±0.07	453.00^{defgh}±2.00	186.70^{cdef}±1.44	2.23^{cde}±0.05	50.13^{kl}±0.30
Paindikulama	7.43^{bcde}±0.05	24.52^{ijk}±0.06	4.52^{ijk}±0.06	9.64^{a}±0.27	368.00^{fghi}±1.00	150.37^{efgh}±3.84	2.33^{cd}±0.09	40.66^{m}±0.57
Mahakanumulla	7.46^{bcd}±0.05	33.90^{b}±0.26	7.82^{f}±0.10	4.53^{c}±0.12	663.67^{abcd}±2.08	272.33^{abcd}±0.58	2.36^{c}±0.08	145.63^{b}±2.87
Kudakanumulla	7.23^{efghi}±0.05	28.86^{ab}±0.15	13.87^{d}±0.24	4.28^{de}±0.06	519.33^{cdefg}±17.67	212.67^{cdef}±7.57	1.29^{g}±0.03	176.94^{a}±2.22
Thammanagala	7.43^{bcde}±0.005	29.36^{ij}±0.32	3.65^{kl}±0.19	4.49^{de}±0.06	126.07^{ij}±7.56	55.50^{gh}±3.53	3.19^{b}±0.05	17.59^{o}±0.76
Wagayakulama	7.14^{hi}±0.02	30.66^{gh}±0.32	27.83^{a}±0.40	3.67^{fg}±0.08	626.67^{bcde}±62.07	290.00^{abc}±2.65	1.35^{g}±0.03	73.14^{h}±0.33
Kudagama	7.55^{bc}±0.01	23.84^{jkl}±0.01	3.84^{jkl}±0.01	3.34^{ghi}±0.02	814.67^{ab}±1.53	357.00^{ab}±1.00	1.11^{g}±0.01	112.21^{c}±0.40
Etaweerawewa	7.56^{b}±0.05	25.78^{ghi}±0.13	5.78^{ghi}±0.13	5.11^{c}±0.06	89.60^{j}±6.45	37.47^{h}±2.95	1.73^{defg}±0.05	51.47^{k}±0.70
Kuttikulama	7.30^{defgh}±0.02	31.06^{fgh}±0.15	2.68^{l}±0.20	3.34^{ghi}±0.11	767.67^{ab}±1.53	335.33^{ab}±2.31	1.32^{g}±0.07	106.36^{d}±1.03
Kudawewa	7.2^{ghi}±0.02	28.23^{k}±0.20	7.42^{fg}±0.87	3.17^{hij}±0.15	273.67^{hij}±47.62	201.68^{cdef}±172.04	1.68^{efg}±0.04	68.84^{i}±1.48
Sembu wewa	7.35^{cdefg}±0.02	32.70^{c}±0.62	22.40^{b}±0.10	4.19^{de}±0.06	103.50^{j}±1.5	41.53^{gh}±0.76	4.05^{a}±0.35	11.24^{p}±1.98
Dematawewa	7.26^{defghi}±0.01	29.36^{jk}±0.32	7.62^{f}±0.05	3.61^{g}±0.08	461.00^{defgh}±1.00	205.00^{cdef}±1.00	2.14^{cdef}±0.03	28.70^{n}±0.35
Wellamudawa	7.08^{i}±0.03	30.23^{hi}±0.11	11.88^{e}±0.26	2.92^{ij}±0.04	878.00a±5.00	384.67^{a}±3.79	1.49^{g}±0.08	72.98^{h}±0.20

Waters in eight tanks belongs to soft water category, waters in ten tanks were in the category of moderately hard waters and two tanks (*Mahakanumulla* and *Kudakanumulla*) were in hard water category. Even though the hard water is not harmful to the health, it may adversely affect to the industry where boilers are used extensively with this water.

CONCLUSIONS

It can be concluded that NO_3^- concentration of the all tanks in *Mahakanumulla* cascade, did not exceed the permissible level for irrigation and drinking water. Six tanks showed the higher PO_4^{3-} concentrations than the critical value that favors the eutropication. However, none of the water samples exceeded the PO_4^{3-} level beyond the WHO detection level for drinking and irrigation water. Fairly high K^+ concentration was detected in all tanks falling within the range of 2.14- 8. 61 mg L^{-1}, where the permissible level is 2 mg L^{-1} according to WHO standards. The fluoride content of water samples did not exceed beyond the WHO detection level for drinking and irrigation water. It is evident from the ecological point of view, even though NO_3^- and PO_4^{3-} concentrations are below the eutropic level that higher TDS values along with hardness may create eutropic stage in most of tanks in *Mahakanumulla* cascade in future.

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ASSESSING THE QUALITY OF BIOCHAR PRODUCED FROM COCONUT HUSK WASTE

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ABSTRACT

Biochar is an organic amendment with the potential for restoring carbon in the long-run and improving fertility in agricultural soils. The quality of biochar produced from coconut-husk based materials with retort method was evaluated by analyzing physical and chemical properties and assessing its effect on plant growth. Pyrolysis efficiency of coconut-husk biochar (CB) production was 37±4%. Feedstock materials resulted 40% of <2 mm size biochar particles. Ash, low-temperature volatile matter and apparent fixed carbon contents of CB were 16±0.2 %, 16±1.2 % and 68±1.4%, respectively. Exchangeable K, available P, pH, EC and CEC of CB were 30281±3 mg kg^{-1}, 174±17 mg kg^{-1}, 10.24±0.01, 5.57±0.02 dSm^{-1} and 21.9±0.0 $cmol_{(+)}$ kg^{-1}, respectively. The retort method adopted produced CB with a consistent quality. Lettuce seed germination was suppressed at CB application rates to sand above 1% (w/w). CB improved maize growth in an Ultisol at 1% application rate. Quality of CB was comparable to that of sawdust biochar. Coconut husk waste is suitable to produce biochar with moderate quality and CB has the potential to be used as a soil amendment in crop production systems.

Keywords: Biochar, Coconut husk waste, Soil fertility

INTRODUCTION

Sri Lanka produces over 0.5 million tons of coconut husk wastes annually. Coconut husk waste is the waste material produced during coir extraction from coconut husk and constitutes a mixture of dust (i.e. coir pith), bits and coir fiber of various lengths. As estimated in 1999, about 70,000 tons of dry coir dust is generated annually as a byproduct of fiber-extraction industry (Wickramasinghe, 1999). More than 85 % of the carbon in coconut husk waste present as lignin and cellulose, and C:N ratio could vary from 75 to 186 (Abad *et al*., 2002; Rajan *et al*., 2005). Coconut husk waste is known to have high levels of soluble salts resulting in electrical conductivity values in saturated extract ranging from 0.39 to 5.97 dS m^{-1} (Abad *et al*., 2002). Due to these characters coconut husk waste decompose very slowly. Hence, accumulation of mounds of husk waste has become a serious concern for fiber extraction industries. Leaching of sodium and potassium salts from mounds of husk waste could pollute ground water. Ignite the waste material and dispose the ash is not a viable solution because of emission of fugitive gases during the process and generation of considerable amount of ash. High moisture content in husk waste limits its use as a fuel. Mounds of coconut husk wastes limit effective use of space, while increasing potential threats of fire and health hazards, and pollution of environment at dumping sites (Wickramasinghe, 1999). Hence, fiber extraction industry is urged to search for a viable solution to handle waste. Present study explores the possibility of producing biochar from coconut husk waste as a value added product.

Biochar is an organic amendment obtained from thermal decomposition (pyrolysis) of biomass at relatively low temperature and under oxygen limited conditions. It has the greatest potential for the long term sequestration of carbon as it can remain stable in soil for many hundreds of years (Lehmann, 2007). Additions of biochar to soil have shown definite increases in cation exchange capacity and availability of nutrients (Glaser *et al.,* 2002; Lehmann *et al*., 2003).The elemental composition, fixed carbon, volatile matter, and ash content of biochar depend on the feedstock used and the duration and temperature of pyrolysis (Demirbas 2004; Keiluweit *et. al.*, 2010; Enders *et al*., 2012). Since pyrolysis conditions greatly affect physical and chemical properties of biochar, it is important to assess the reproducibility of biochar under a given process by testing specific properties on a batch by batch basis.

The present study was conducted with the objectives of evaluating the quality of biochar produced from coconut husk wastes generated from fiber extraction industry and its potential use as a soil amendment. The quality consistency of the biochar produced using the method adopted in this study was also assessed.

MATERIALS AND METHODS

Biochar production

Coconut Husk waste samples were collected from Growrite Substrate (Pvt) Ltd, Ratmalane estate, Amunugama, Nikadalupotha, Sri Lanka. The coconut husk, the raw material of their production, was treated with $Ca(NO_3)_2$ and H_2O_2 for the maintenance of electrical conductivity of husk based products. The particle size of starting material for the biochar was not uniform and had fiber, bits and coir pith. Production of biochar was undertaken at the Department of Soil Science and Plant Nutrition of Rubber Research Institute, Agalawatta, Sri Lanka. Retort method described in Dharmakeerthi *et al*. (2012) was used to produce biochar. Inside temperature of the furnace was maintained approximately at 600°C until the end of the production process, which took approximately 2 h. The end point of the production of biochar generally was identified by the finishing time of syngas production. Four batches of biochar were produced following the same procedure to check the quality consistency of the product.

Biochar produced from sawdust of *Alstonia macrophylla* as the feedstock material using the same method was used as a reference biochar during characterization (Mariaselvam *et al.*, 2013; Chathurika *et al.*, 2013). The moisture content of raw material and produced biochar was measured by oven dry method by heating samples at 105^{o}C for 18 hours (Enders *et. al.*, 2012). The pyrolysis efficiency was calculated as the percent weight conserved during pyrolysis.

Characterization of biochar

All the laboratory analyses were conducted at the Department of Soil Science, Faculty of Agriculture, University of Peradeniya. Coconut husk waste based biochar (CB) was air dried and separated into two fractions based on particle size and used in further analyses. A 4 kg composite sample was prepared by drawing one kilogram sub samples each from the four batches and sieved through 2 mm sieve and hereafter referred to as composite husk-biochar (CMB). The particles greater than 2mm size leftover from each batch was pooled and was crushed using mortar and pestle with gentle force and sieved through 2mm sieve again to compare with originally < 2mm particles. This crushed biochar is referred to as crushed husk biochar (CCB) hereafter. Further, a subsample of biochar from each batch was sieved through 2 mm sieve and stored separately (CB 1 to CB4). In the present study, 2 mm was used as the upper-limit particle size for quality evaluation considering implications of results on commercially producing and marketing CB as a soil amendment. Characterization was done for the composite sample (CMB), crushed and sieved sample (CCB), biochar that produced as four batches separately (CB1 to CB4), and reference saw-dust biochar (SDB) in replicate.

Electrical conductivity and pH of biochar were determined in 1:5 distilled water suspension. CEC was measured using ammonium as the index ion (Sumner and Miller, 1996). Available phosphorus and potassium in biochar were extracted with 0.5M $NaHCO_3$ (pH 8.5) and ammonium acetate (pH 7.0), respectively, and measured using spectrometry. Biochar samples were prepared for total elemental analysis (P, K, Mg, Ca, and Na) using modified dry ash method as described by Enders and Lehmann (2012). Water holding capacity of the oven dried biochar was measured by weight gain method. In brief, two grams of oven dried biochar was placed on a moisten filter paper and saturated with water. The setup was allowed to free-drain. Once the free draining ceased gravimetric water content in biochar was determined and expressed as the water holding capacity (WHC) of biochar. Particle size distribution of air dried biochar was determined by sieving through a mechanical sieve set (0.125, 0.375, 0.605, 0.855, 1.500, 2.675, and 3.350 mm) at 60 amplitude for 5 minutes (Gee, 1986). Specific surface area of biochar was calculated as described by Fooladmand, *et al*. (2011). Ash content, low temperature volatile matter content and moisture content were determined by dry combustion method using muffle furnace (Enders *et. al.*, 2012). Apparent fixed carbon level of biochar was calculated as:

$$Apparent\ fixed\ C = \frac{(w2 - w3) \times 100}{w1}$$

Where; w1 is the dry weight of biochar after heating at 105 ^{0}C for 18 h, w2 is the weight of biochar after heating at 350 ^{0}C for 2 h, and w3 is the weight of biochar (ash) after heating at 600 ^{0}C for 20 h.

Effect of biochar on plant growth

The effect of biochar on lettuce (*Lactuca sativa* L.) seed germination was assessed in a laboratory bioassay. Sand passed through 2-mm sieve was rinsed with 1 % sulfuric acid and then twice with tap water, and oven dried at 105^{o}C for one hour. Dry sand was mixed with biochar at the rates of 0.5, 1.0 and 2.0 % (w/w dry weight basis) and filled into petri-dishes (9 cm diameter) in three replicates. Plates filled with sand only (0.0% biochar) served as the control. The pH (1:2.5, sand: distilled water) and EC (1:5, sand: distilled water) of replicated subsamples of the sand-biochar mixtures were measured. Randomly selected lettuce seeds were placed on sand medium as 20 seeds per petri-dish. Water was added to bring moisture level close to saturation initially and incubated at room temperature. Observations on seed germination were made until 7 days after seeding. Speed of germination was calculated following the method suggested by Enoniytan (2013) :

$$\text{Speed of germination} = \frac{\text{X1}}{\text{Y1}} + \frac{\text{X2} - \text{X1}}{\text{Y2}} + \cdots \frac{\text{Xn} - \text{X(n} - 1)}{\text{Yn}}$$

Where X1, X2 and Xn are number of seeds germinated on the first, second and nth day, respectively, and Y1, Y2 and Yn are number of days from sowing to the first, second and nth count, respectively. The speed of germination is expressed as number of seeds germinated per day.

The effect of biochar on plant growth was tested in a greenhouse pot experiment conducted with maize (*Zea maize* L.) as the indicator crop. An Ultisol sampled at 0-10 cm depth from a vegetable field, intensively cultivated for more than 20 years, in Nuwara Eliya was used in the study (pH – 4.84 EC – 0.37 dSm^{-1}, CEC – 15 $cmol_{(+)}$ kg^{-1}, available P 108 mg kg^{-1}, exchangeable K – 2973 mg kg^{-1}, organic matter 2.43 %). Soil was treated with biochar as 0.5 % SDB, 0.5 % CMB and 1 % CMB. After considering the available nutrients added through biochar the amounts of nutrients to match the recommendation by the Department of Agriculture for maize was calculated (equivalent to nutrients added from Urea:TSP:MOP at 75:100:50 kg ha^{-1} as basal dressing), and biochar treated soils were amended with respective levels of fertilizers. A soil treated with fertilizers only and an un-amended soil (no fertilizers and no biochar) were included as treatments in the experiment. Pots filled with soil in five replicates per treatment and arranged in a complete randomized design and were incubated for three days and

seeded with pre-germinated seeds of maize (variety Sampath). Two seedlings per pot were maintained for one month and soil moisture level was kept close to field capacity throughout the period. At one month after seeding plants were uprooted and growth parameters were recorded and soil from pots were air-dried and analyzed for pH, EC, available P and exchangeable K.

Statistical analysis

Significant effects of treatments on measured parameters of biochar were tested by general linear procedure (GLM) in Analysis of Variance (ANOVA) using SAS statistical package (version 9.1). The effect of biochar application on plant growth and soil were also tested by ANOVA and mean comparison was performed with Duncan's multiple range test at $P < 0.05$ probability level.

RESULTS

Quality consistency of biochar produced from retort method

Biochar production from coconut husk waste resulted in a product with considerable consistency in composition as indicated by the low coefficient of variance (CV) of measurements (Table 1). The average pyrolysis efficiency of biochar produced from coconut husk waste was 37 ± 4 %. Properties of biochar produced in four batches showed statistically significant differences but values varied in a narrow range as indicated by CV less than 20 % (Table 2 and 3). Particle size distribution was comparable among the four batches (Figure 1). Retort method at RRI is reproducible for biochar production with coconut husk waste.

Biochar characterization

Saw dust biochar (SDB) was used to compare the biochar produced from coconut husk waste. Particle >2mm was crushed and sieved through 2mm sieve(CCB) to compare with naturally <2mm particles (CMB). Fixed Carbon of SDB was significantly higher than CMB and CCB (Figure 2). Volatile matter content of three type of biochar did not have any significant differences. CMB had the highest ash content. The CEC of SDB, CCB and CMB were comparable and all three types of biochar were alkaline in nature (Table 4). CCB had the highest EC but the values do not fall into saline range. Available P and K contents of coconut husk based biochar were significantly higher than SDB (Table 4). Total elemental composition of CCB and CMB were comparable (Table 5). Water holding capacities significantly differed across three biochar types with SDB having the highest (600 %) followed by CMB (387%) and CCB (332%).

Effect of biochar on plant growth

Cumulative germination percentage of lettuce seeds were significantly affected by the rate of biochar application and biochar type (Table 6). At 0.5 % rate CB resulted in higher or comparable germination percentage of lettuce seeds to SDB. Lettuce seed germination was inhibited by CB when the application rate was increased to 1 % and above; whereas, SDB at the same rates resulted in comparable results to the control indicating no suppression on germination. Germination speed gradually declined with increased application rate of CB but no significant effect of application rate on germination speed was observed for SDB. Coconut husk waste based biochar and sawdust based biochar resulted in comparable germination speeds at 0.5 % application rate and the values did not differ significantly from the control.

Table 1. Ash content, volatile matter content and apparent fixed carbon contents of < 2mm particle size fraction of four batches of biochar produced from coconut husk waste (CB1 to CB4) in dry weight basis. Values are given as mean ± standard deviation (n= 2). Means followed by the same letter in the columns are not significantly different ($p < 0.05$).

Batch	Ash content (%)	Low temperature Volatile matter (%)	Apparent Fixed Carbon (%)
CB1	14.9 ±0.78 b	16.36±0.37 a	68.74±0.41 b
CB2	15.09±0.24 b	16.19±1.25 a	68.73±1.01 b
CB3	17.03±0.42 a	15.85±1.48 a	67.13±1.90 b
CB4	16.75±0.62 a	6.95±3.21 b	76.30±2.60 a
CV	3.47	13.62	2.42
P	0.037	0.018	0.0188

CV= Coefficient of variance *p*= probability value

Table 2. Chemical properties naturally <2mm size fraction of four batches of biochar produced from coconut husk waste (CB1 to CB4). Values are given as mean ± standard deviation (n= 2) on dry weight basis. Means followed by the same letter in the columns are not significantly different ($p<0.05$)

Batch	CEC cmol(+)kg^{-1}	EC (dSm^{-1})	pH	Exchangeable K (mg kg^{-1})	Available P (mg kg^{-1})
CB1	16± 1	5.14 ±0.26 ab	10.4 ± 0.01 b	29817± 2536	248 ± 8 b
CB2	21 ± 1	4.02 ± 0.23 b	10.35 ±0.00 c	36119± 11340	258 ± 2 b
CB3	23 ± 4	5.87 ± 0.87 a	10.44±0.01 a	33095 ± 1898	323 ± 7 a
CB4	25± 1	5.81 ± 0.84 a	10.34 ±0.04 c	25552 ± 2307	317 ± 26 a
CV	11.32	12.07	0.19	19.24	5.10
P	0.089	0.023	0.0006	0.434	0.013

CV= Coefficient of variance *p*= probability value

Table 3. Physical properties of naturally <2mm size fraction of four batches of biochar produced from coconut husk waste (CB1 to CB4). Values are given as mean ± standard deviation (n= 2). Means followed by the same letter in the columns are not significantly different ($p < 0.05$)

Batch	Amount of particles naturally<2mm size (%)	Water holding capacity(%dry weight basis)	Specific surface area(m^2g^{-1})
CB1	44 ± 2 a	397 ± 9 a	3.40 ± 0.08 a
CB2	41 ± 3 a	384 ± 1 ab	3.24 ± 0.09 ab
CB3	40 ± 1 a	362 ± 6 b	3.19 ±0.03 b
CB4	42 ± 1 a	377 ± 16 ab	3.18 ± 0.02 b
CV	5.02	2.53	1.92
P	0.47	0.09	0.08

CV= Coefficient of variance *p*= probability value

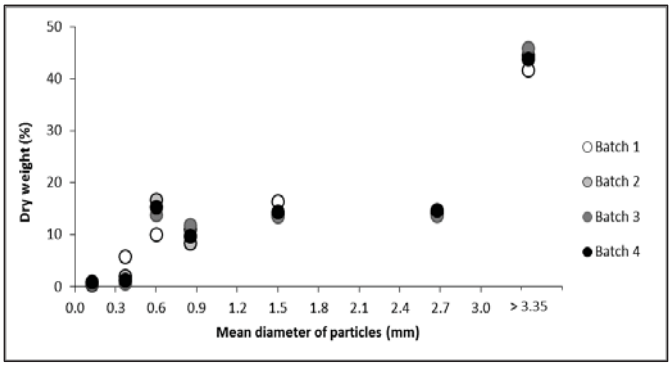

Figure 1. Particle size distribution of four batches of biochar produced from coconut husk waste.

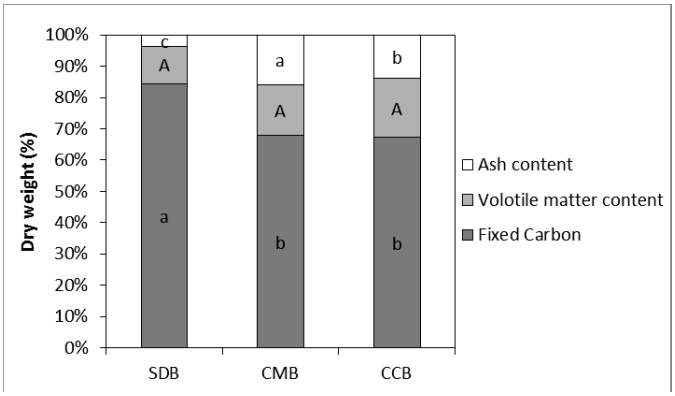

Figure 2. Ash content, volatile matter content and apparent fixed carbon % in dry weight basis of biochar. SDB – Sawdust biochar, CMB – composite coconut husk biochar, CCB – crushed and sieved coconut husk biochar. For a given property the vertical bars having same letter are not significantly different ($p < 0.05$).

Table 4. Chemical properties of < 2 mm particles of biochar used in the study. SDB - Saw dust biochar, CMB - Composite sample of originally < 2mm particles of four batches of biochar produced from coconut husk waste, and CCB – Composite sample of crushed and sieved originally >2 mm particles of four batches of biochar produced from coconut husk waste. Values are given as mean ± standard deviation (n= 3). Means followed by the same letter in the columns are not significantly different ($p<0.05$).

Biochar	CEC ($cmol_{(+)}\ kg^{-1}$)	EC ($dS\ m^{-1}$)	pH	Available P ($mg\ kg^{-1}$)	Exchangeable K ($mg\ kg^{-1}$)
SDB	18.12± 3.34 a	5.05 ± 0.20 b	9.52 ± 0.01 c	17.6±4.1 c	3855±50 c
CMB	21.87 ± 0.00 a	5.57 ± 0.02 b	10.24 ± 0.01 b	174.3±17.4 b	29221± 1221 b
CCB	21.16 ± 2.72 a	11.31 ± 0.32 a	10.36 ± 0.03 a	267.7±6.5 a	36420 ± 763 a
CV	12.2	2.966	0.1863	7.164	10.5746
P	0.396	0.0002	0.0001	0.0004	0.0017

CV= Coefficient of variance *p*= probability value
* EC and pH were measured in 1:5, biochar:water suspension.

Table 5. Total nutrient contents in biochar. CMB – composite coconut husk biochar, CCB – crushed and sieved coconut husk biochar. Values are given as mean ± standard deviation (n= 2). Means followed by the same letter in the columns are not significantly different (p<0.05)

Biochar	Total nutrients (mg kg^{-1} Dry biochar)				
	K	P	Na	Ca	Mg
CMB	30281± 3252	851 ± 136	17950 ± 277	5616 ± 99	12598 ± 418
CCB	41223 ± 3253	872 ± 17	23199 ± 603	3959± 213	8477 ± 686
CV	4.276	9.745	3.029	1.678	1.797
P	0.1226	0.4179	0.774	0.2215	0.1514

CV= Coefficient of variance p= probability value

Biochar produced from sawdust and coconut husk waste applied to soil at 0.5% and 1 % rates, respectively, resulted in comparable effects on maize plant growth (Table 7 and Figure 3). Since biochar contained considerable amount of potassium and phosphorous in plant available forms the fertilizer requirement to supply the recommended level of nutrients to maize was less when biochar was applied. Although residual phosphorous levels in soils were comparable among treatments the residual potassium level in fertilizer only treatment was significantly less than the control and soils amended with biochar (Table 7). Soils that received only fertilizers had significantly low pH values than biochar added treatments and the control. Biochar application at 1 % rate is equivalent to 28 tons ha^{-1} if broadcast in the field assuming a soil bulk density of 1.4 g cm^{-3} and rooting depth of 20 cm.

Table 6. Cumulative germination % of seeds in day 3 and 7 with 0.5%, 1% and 2% (w/w) application rate of biochar. CB1 to CB4 – originally < 2mm particles of biochar produced from coconut husk waste in four batches, SDB - <2 mm particles of sawdust biochar. Values are given as mean ± standard deviation (n= 3). Means followed by the same letter in a column for a given biochar application rate are not significantly different (p<0.05)

Biochar application rate	Biochar type	Cumulative germination %		Germination speed (Seeds day^{-1})
		Day 3	Day 7	
0.0 %		82±8 a	90 ± 0 a	5.7 ± 0.3a
0.5 %	CB1	80 ±10 a	88 ±0 ab	5.6±0.5 a
	CB2	80 ± 5 a	90 ±5 a	5.6±0.3 a
	CB3	78± 8 a	90±5 a	5.6±0.2 a
	CB4	78 ± 12 a	87 ±8 ab	5.5±0.6 a
	SDB	72 ± 6 a	80 ±5 b	5.0±0.4 a
1.0 %	CB1	53 ±13 b	75±5 b	4.2±0.3 b
	CB2	43 ± 8 cb	72 ± 8 b	3.7±0.4 b
	CB3	78 ± 3 a	87 ± 3 a	5.5±0.2 b
	CB4	33 ± 6 c	57 ± 3 c	2.9±0.3 c
	SDB	77 ± 3 a	88 ± 6 a	5.4±0.1 a
2.0 %	CB1	32 ±10 b	45 ± 0 c	2.5±0.4 b
	CB2	32 ± 8 b	58 ± 12 cb	2.9±0.6 b
	CB3	33 ± 12 b	62 ± 13 b	3.0±0.6 b
	CB4	33 ± 6 b	47 ± 10 cb	2.6±0.5 b
	SDB	72 ± 6 a	80 ± 0 a	5.0±0.2 a

Table 7. Properties and nutrient availability of soil treated with fertilizers and two rates (0.5 and 1%) of biochar (CMB – composite coconut husk biochar, SDB – sawdust biochar) after growing maize for one month, and plant performance under different treatments. Control – untreated soil. Values are given as mean ± standard deviation (n= 5). Means followed by the same letter in a column are not significantly different (p<0.05)

Treatment	Soil parameters				Plant performance	
	pH	EC (µS cm^{-1})	Available P (mg kg^{-1})	Available K (mg kg^{-1})	Shoot length (cm)	Root length (cm)
Control	4.84 ± 0.007 b	37.1 ± 2.05 b	99.7 ± 6.0 a	392 ±18 a	56.0 ± 3.5 c	31.6 ± 5.8 c
Fertilizer only	4.36 ± 0.064 d	32.6 ± 1.62 cd	87.1 ± 9.8 a	67 ± 3 c	80.6 ± 7.2 a	41.3 ± 5.8 ab
0.5 % SDB + Fertilizer*	4.56 ± 0.035 c	31.2 ± 1.13 d	90.4 ± 0.3 a	287 ± 14 b	73.9 ± 1.1 ab	44.7 ± 6.3 a
0.5 % CMB + Fertilizer*	4.78 ±0.007 b	36.7 ± 0.99 bc	76.3 ± 11.7 a	392 ±18 a	71.7 ± 6.8 b	35.3 ± 4.3 bc
1.0 % CMB + Fertilizer*	4.93 ± 0.000 a	47.6 ± 0.49 a	97.4 ± 7.5 a	287 ± 13 b	77.7 ± 7.2 ab	48.2 ± 8.7 a

*Fertilizer levels were adjusted to provide equivalent levels of available nutrients across treatments

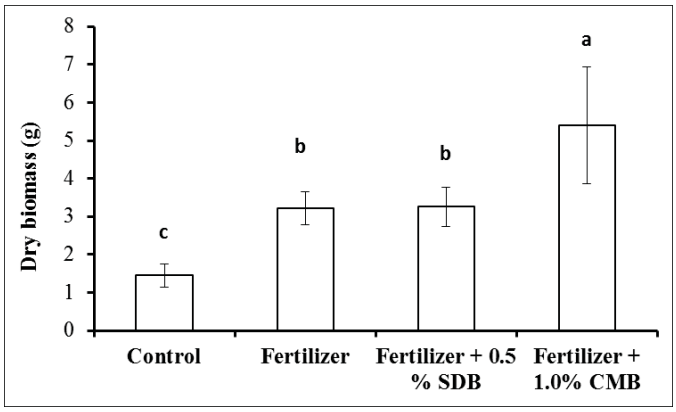

Figure. 3. Total dry biomass of one month old maize plants grown with inorganic fertilizers and biochar (Control – no amendments, 0.5 % SDB – sawdust biochar applied at 0.5 % wt rate, 1.0% CMB – Coconut husk biochar applied at 1.0 % wt rate). Error bars represent standard deviation. Vertical bars having same letter are not significantly different ($p < 0.05$).

DISCUSSION

Biochar is considered as an organic amendment with the potential for long term restoration of carbon and maintenance of soil fertility in agricultural soils (Lehmann, 2007). Depending on the feedstock material used to produce biochar and the production conditions such as heating rate, temperature and availability of air, the properties of biochar changes (Cetin et al., 2004; Enders et al., 2012). The agronomic utility of biochar is largely determined by the nature of soil constraints and properties of biochar itself (Cetin et al., 2004; Enders et al., 2012). The mass recovery of biochar, which is expressed as the pyrolysis efficiency, varies with the nature of feedstock material and generally decline with increasing pyrolysis temperature (Demirbas, 2004; Enders et al., 2012). Average mass recovery observed during biochar production at 600^{0}C from oak, pine, hazelnut, corn, and digested dairy manure ranged from 20 to 30 %; whereas, the values were above 50% for poultry manure and paper feedstocks (Enders et al., 2012). Mass recovery from coconut husk waste feedstock is thus, moderate. High liginin content in coconut husk waste may have contributed to high mass recovery. Demirbas (2004) observed feedstocks with high lignin contents produce the highest biochar yields when pyrolysis is done at moderate temperatures (500 ^{0}C). Enders et al. (2012) observed ash content is more influenced by feedstock material; whereas, volatile matter and fixed carbon depend more on pyrolysis temperature. It has been observed that high-ash feedstock (biochar with > 20% w/wbiochar) such as poultry manure, paper mill and digested dairy manure contain high levels of carbonates, indicating a significant contribution from inorganic carbon to the total carbon in biochar. In a previous study a negative correlation has been observed between the fixed carbon yield and the ash content of biochar suggesting high ash content may be contributing to low stable biochar content in a biochar system (Enders et al., 2012).

In the present study, biochar was produced via slow pyrolysis (heating rate: 5-7oC min-1) in a retort reactor, where individual particles remain almost immobile. These reactors only allow the discharge of biochar after it has been cooled, hence has the potential to keep the total carbon content at a higher level. When biochar makes contact with air during production process before cooling, a part of carbon is lost due to oxidation and amount of white color ash content would increase (Enders et al., 2012). Cellulose, hemi-cellulose and lignin have higher distinctive thermal decomposition behaviors depend on heating rate, thus heating rate affect biochar composition at the end (Lehmann et al. 2009; Kwapinski et al., 2010). Rajan et al., (2005) report coconut coir fiber contain about 45 % of lignin and 43 % of cellulose by dry weight. Though coefficient of variance remained low for parameters measured to evaluate the reproducibility of biochar from coconut husk waste significant differences existed among the four batches. This may be attributed to the variability in distribution of cellulose, hemicellulose and lignin of the feedstock material (Abad et al., 2002; Kwapinski et al., 2010) than to variability in particle sizes because the particle size distribution of four biochar batches remained same. By comparing properties of biochar made from sawdust and coconut husk waste, present study confirm biochar composition depend on the nature of feedstock when produced under same pyrolysis condition.

The formation of surface functional groups and adsorption sites on biochar can influence its CEC (Liang et al., 2006). It is interesting to see that even though sawdust and coconut husk wastes are different as starting materials, these results biochar with comparable CEC. The cation retention ability of the biochar in present study is moderate when compared to the values reported in literature (Liang et al., 2006). Water holding capacity of CB remained lower than SDB may be because of comparatively high volatile matter content and less fixed carbon in CB, and differences in surface chemistry. Coconut husk waste is known to have high levels of soluble salts resulting in EC ranging from 0.39 to 5.97 dS m-1 and high available phosphorous and potassium contents (Abad et al., 2002). Electrical conductivity of coconut husk biochar is

in the range of 4 to 6 dS m-1 implying no risk of salt loading to soil (Shenbagavalli and Mahimairaja, 2012). Biochar with high available nutrient contents tend to have high EC values as observed with SDB and CB. The nutrient content of biochar depends on feedstock and, it varies with pyrolysis temperature (Demirbas, 2004; Keiluweit et. al., 2010; Enders et. al., 2012).

During the pyrolysis or oxidation process that generates biochar, heating causes some nutrients to volatilize, especially at the surface of the material, while other nutrients become concentrated in the remaining Biochar (Shenbagavalli and Mahimairaja, 2012). It is known that smaller feedstock particles increase the heating rate during biochar production (Demirbas, 2004). This may have contributed to the observed high potassium and phosphorous availability and high EC values in CMB compared to CCB because CMB is the originally < 2mm particles and CCB is the particles >2mm being crushed and sieved. Interestingly, total elemental concentrations did not differ significantly among CCB and CMB. Further, coconut-husk material was not homogenous in size as there were coconut pith (coir dust), fiber, pericarp skin, etc. and the contribution from each of these initial particles to the CCB and CMB fractions should be different. Since production of biochar from coconut husk waste generated only 40 % (w/w) of particles < 2 mm in size, it is worth to consider whether larger particles can be crushed and sieved to increase the biochar yield without deteriorating the quality. Comparison of CMB and CCB suggest mixing <2 mm particles with crushed and sieved particles would be acceptable. Crushing larger CB particles would be economically effective than trying to cut the feedstock to reduce the particle size.

Agronomic use of biochar to improve soil fertility depends on biochar properties as well as nature of soil constraints (Enders et al., 2012; Revell et al., 2012). It is reported that short-term emissions of volatile compounds from biochar may suppress or induce seed germination depending on composition of volatiles and plant species (Spokas, 2010; Artiola et al, 2012; Bargmann et al., 2013). Increasing concentration of soluble salts and changes in pH of growth media as a result of biochar application are also known to suppress seed germination (Artiola et al., 2012; Revell et al., 2012). Since soluble salts increase with increasing biochar application rate, seed germination may have partially suppressed at biochar applications at ≥1% in the present study as indicated by the reduction in germination speed and cumulative germination percentage. The impact of salts and volatile compounds originate from biochar on seed germination may be high because bioassay was conducted with biochar amended sand and not in soil. To avoid negative impact of the liming properties of biochar on seed germination Free et al. (2010) incubated biochar in soil for 3 weeks before seeding. Although CMB application rate 0.5% seems best with lettuce seed germination, the highest - growth in maize was observed at 1 % CMB and it exceeded the -growth under inorganic fertilizer only treatment.

The soil used in the present study was acidic and application of biochar significantly increased soil pH while application of only inorganic fertilizers further reduced pH. Since nutrient inputs to soil was equivalent across treatments the improved plant growth can be attributed to the improvements in other soil properties such as increase in pH, microbial activity. Potassium and phosphorous fertilizer usage was reduced with the application of coconut husk based biochar without affecting crop growth. Similar advantage has been observed with the use of SDB in greenhouse and field experiments with maize previously (Mariaselvam, 2013; Chathurika, 2013).

CONCLUSION

Coconut husk waste can be used as a feedstock material to produce biochar in retort method. The composition of feedstock could contribute to batch to batch variation of biochar properties when pyrolysis conditions are the same. Since the properties of originally <2 mm particle size of coconut husk biochar is comparable to crushed and sieved biochar particles of >2mm size, the two fractions can be combined to improve the economical yield of biochar produced from coconut husk waste without sacrificing the quality of biochar. With physical and chemical characters compared with saw dust biochar, which is being tested at the field previously, coconut husk biochar is acceptable as a soil amendment at rates not exceeding 1 %. It is important to study the effect of coconut husk waste based biochar on soil fertility parameters using a range of soils because agronomic use of biochar depends on soil fertility constraints.

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