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CHARACTERIZATION AND EFFECT OF BIOCHAR ON NITROGEN AND CARBON DYNAMICS IN SOIL

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ABSTRACT

In the current study the biochar material was produced by the indigenous pyrolysis of prosopis wood material under high temperature and characterized. The impact of biochar on carbon and nutrient dynamics in soil was examined by conducting a laboratory closed incubation experiment. The biochar produced from prosopis was neutral in pH with an exchangeable acidity of 49 mmol kg^{-1}. The cation exchange capacity was 16 cmol kg^{-1}. It had relatively higher potassium (K) content than nitrogen (N) and phosphorus (P). The carbon content was very high (940 g kg^{-1}). One of the major characteristics of biochar that makes it attractive as a soil amendment is its high porous structure, potentially responsible for improved water retention and increased soil surface area. Upon incorporation of different rates of biochar in a soil (pH 8.42) the pH decreased up to 7.92 during incubation; whereas, the cation exchange capacity (CEC) of soil was found significantly increased due to biochar addition. The soil organic carbon (SOC) markedly increased with an increase in rate of application of biochar, which was further increased during the 90 days of incubation. This suggests that the biochar has great potential for carbon sequestration in soil. While marked increase in soil microbial biomass carbon and humic & fulvic acid fraction of SOC was evident during incubation, there was not much change in water soluble organic carbon due to biochar incorporation. The mineral – N, comprising of ammoniacal nitrogen (NH_4-N) and nitrate nitrogen (NO_3-N), concentration has shown significant reduction when different rates of biochar were added to soil. Increase in the rate of application markedly reduced the concentration of both NH_4-N and NO_3-N. During incubation further decrease in the concentration was observed. The results suggest that the carbon and nutrient dynamics in soil affected due to biochar incorporation may have a significant role in the reduction of GHGs (particularly CO_2 and N_2O) emission from soil. Further research on the effect of biochar on GHG emission is in progress.

KEY WORDS: biochar, nitrogen dynamics, carbon dynamics

INTRODUCTION

Biochar is a charred by product of biomass pyrolysis produced from biological wastes, crop residues, animal poultry manure, or any type of organic waste material. Pyrolysis is the chemical breakdown of a substance under extremely high temperatures in the absence of oxygen. Biochar production through pyrolysis is considered a carbon-negative process because the biochar sequesters carbon while simultaneously enhancing the fertility of the soil. Biochar has the capability to both mitigate greenhouse gas emissions and other environmental hazards. It can also be used as a soil amendment and source of alternative energy. The major potential benefits of biochar are carbon sequestration, greenhouse gases (GHG) emission reduction, and enhancement in soil fertility.

Carbon sequestration is the capture and storage of carbon to prevent it from being released to the atmosphere. Studies suggest that biochar sequesters approximately 50% of the carbon available within the biomass feedstock being pyrolyzed, depending upon the feedstock type (Lehmann*, et al.,* 2006). The remaining percentage of carbon is released during pyrolysis and may be captured for energy production. Bruno Glaser *et al.* (2002) reported that large amounts of carbon may be sequestered in the soil for long time periods (hundreds to thousands of years at an estimate), but precise estimates of carbon amounts sequestered as a result of biochar application are scarce. Marris (2006) suggests that a 250-hectare farm could sequester approximately 1,900 tons of CO_2 a year.

Primary greenhouse gases associated with the agriculture sector are nitrous oxide (N_2O) and methane (CH_4). Cropland soils and grazing lands are an important agricultural source of N_2O emissions. Whereas, paddy fields, livestock manure and enteric fermentation are the leading sources of CH_4 emissions. When applied to the soil, biochar can lower greenhouse gas emissions by substantially reducing N_2O emissions. Emissions of N_2O, a greenhouse gas that is approximately 300 times stronger than CO_2 in terms of global warming potential, was reduced by 40 percent (Hamilton, 2007). Laboratory studies suggest that N_2O emissions reduction from biochar-treated soil is dependent on soil moisture and soil aeration (Yanai, *et al.,* 2007). Greenhouse gas emission reductions may be 12% to 84% greater if biochar is land applied instead of combusted for energy purposes (Lehmann, 2007)

Biochar retains nutrients for plant uptake and soil fertility. The infiltration of harmful quantities of nutrients and pesticides into ground water and soil erosion runoff into surface waters can be limited with the use of biochar (Lehmann, 2007).

MATERIALS AND METHODS

Samples of biochar produced from the pyrolysis of prosopis biomass and characterized. Bulk soil samples were collected from Eastern block field No. 36E of Tamil Nadu Agricultural University. Coimbatore. Some important characteristics of soil and biochar are given in Table 1and 2. The air dried samples were used in the laboratory incubation experiments.

Laboratory incubation experiment

The effect of different levels of biochar on carbon and nutrient dynamics in soil was examined through a laboratory closed incubation experiment. Five hundred grams of air-dried soil (< 2 mm) were weighed in plastic containers. The biochar was added at the rate of 0, 1, 2, 3, 4 and 5% and thoroughly mixed with soil. Whenever necessary required quantity of distilled water was added to achieve a final moisture content equivalent to field capacity (32 g g^{-1}). After adding the biochar the plastic containers were covered with polyethylene bags containing small pin-sized holes to permit aeration. Three replicates of each treatment were prepared, randomly placed and incubated in the laboratory at 25±2°C for 90 days. Based on the weight loss distilled water was added to the container to maintain the moisture content throughout the incubation experiment. At the end of 30, 60 and 90 days samples (≈100 g) were removed from all the treatments and analysed for the pH, NH_4 - N, NO_3 - N (Jackson , 1973) and organic carbon content (Walkley and Black, 1934)) as per the standard methods. Moisture factor was computed and applied to express the results on oven dry basis.

RESULTS AND DISCUSSION

Characterization of Biochar

Some important physical, chemical and biological properties of biochar are presented in Table.1.

TABLE 1. Physical, Chemical and Biological Characteristics of Biochar

S.No.	Characters	Values*
a).Physical Properties		
1.	Bulk Density (Mg m^{-3})	0.45
2.	Particle Density	0.54
3.	Percent Pore space	48
4.	Moisture Content (%)	1.21
5.	Water Holding Capacity (%)	131
6.	Apparent Density (g/cc)	0.516
7.	Absolute Specific Gravity	0.98
8.	Volume Expansion (%)	21
b).Chemical Properties		
9.	pH (1: 2.5 soil water suspension)	7.57
10.	EC (dSm^{-1}) (1: 2.5 soil water extract)	1.30
11.	Cation Exchange Capacity (cmol(+) kg^{-1})	16
12.	Exchangeable Acidity (mmol kg^{-1})	49
13.	Organic Carbon (g kg^{-1})	940
14.	Total Nitrogen (%)	1.12
15.	Total Phosphorus (%)	0.1
16.	Total Potassium (%)	2.9
17.	Sodium (%)	0.38
18.	Calcium(g kg^{-1})	11
19.	Magnesium (g kg^{-1})	0.36
20.	Cellulose (%)	36
21.	Hemicelluloses (%)	31
22.	Lignin (%)	22

* Mean of triplicate samples

Bulk density and particle density of the biochar were 0.45 and 0.54 Mg m^{-3}, with a porespace of 48% respectively. It had high water holding capacity (131%). The pH of the biochar was neutral (7.57). The Electrical Conductivity of the biochar was 1.30 dSm^{-1} with the CEC of 16 cmol(+) kg $^{-1}$. High exchangeable acidity (49 mmol kg $^{-1}$) was observed in the biochar sample. Carbon content was very high a value of 940 g kg^{-1}. Potassium content of the biochar was relatively high (2.9 %) than nitrogen (1.12%) and phosphorus (0.1%). Biochar had relatively lower amount of Mg (0.036%) than Na (0.38%) and Ca (1%). It is important to note that biochar is somewhat depleted in N and slightly depleted in S relative to more thermally stable nutrients. 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. Nitrogen is the most sensitive of all macronutrients to heating; thus, the N content of high-temperature biochar is low (Tyron, 1948). Accordingly, extractable concentrations of NH_4^+ and PO_4 generally decrease with increasing pyrolysis temperature during biochar generation, with a portion of NH_4^+ being oxidized to a small exchangeable NO_3^+ pool at higher temperatures

(Gundale and DeLuca, 2006). The concentration of P is small relative to the large concentration of C, and a significant portion of plant P is incorporated within organic molecules through ester or pyrophosphate bonds (Stevenson and Cole, 1999).This organic P in dead plant tissues is not available for plant uptake without microbial cleavage of these bonds. When plant tissue is heated, organic C begins to volatilize at approximately 100°C, whereas P does not volatilize until approximately 700°C is achieved during pyrolysis (Knoepp *et al.,* 2005). Combustion or charring of organic materials can greatly enhance P availability from plant tissue by disproportionately volatilizing C and by cleaving organic P bonds, resulting in a residue of soluble P salts associated with the charred material.

TABLE 2. Characteristics of Experimental soil

S.No.	Characters	Values*
a). Mechanical properties		
1.	Textural class	Sandy clay loam
2.	Sand (%)	30.44
3.	Silt (%)	31
4.	Clay (%)	29
5.	Soil series	Periyanaicken palayam series
6.	USDA classification	*Vertic Ustropept*
b). Physico-chemical properties		
7.	pH (1: 2.5 soil water suspension)	8.42
8.	EC (dSm^{-1}) (1: 2.5 soil water extract)	0.56
9.	Cation Exchange Capacity (cmol(+) kg^{-1})	17.9
10.	Organic carbon (g kg^{-1})	5.10
11.	NH_4- N	93
12.	NO_3- N	56
13.	$NaHCO_3$ - P	5
14.	NH_4OAc- K	183

The structural composition of biochar was cellulose 36%, hemicelluloses 31% and lignin 22%. Similar composition was reported by Demirbas, (2000) for biochar from oak wood. Lignin gives higher yields of charcoal and tar from wood although lignin has threefold higher methoxyl content than wood (Sakakibara, 1983; Demirbas, 2000; Wenzl *et al.,* 1970). Phenolic is derived from lignin by cracking the phenyl-propane units of the macromolecule lattice. Pyrolysis seems to produce the most substituted phenols on a selective basis. Thermal degradation of cellulose proceeds through two types of reaction: a gradual degradation, decomposition and charring on heating at lower temperatures, and a rapid volatilization accompanied by the formation of levoglucosan on pyrolysis at higher temperatures. The degradation of cellulose to a more stable anhydrocellulose, gives higher bio-char yield. High heating rate provides a shorter time for the dehydration reactions and the formation of less reactive anhydrocellulose, which gives a higher yield of char (Zanzi, 2001). The hemicelluloses undergo thermal decomposition very readily. The hemicelluloses reacted more readily than cellulose during heating. Hemicellulose and lignin are depolymerized by steaming at high temperature for a short time (Demirbas and Kucuk, 1994). These data suggest that substantial variation can occur in the chemical properties of biochar due to the temperature that the plant material reaches during charring (Bridle and Pritchard, 2004).

Effect on soil pH and Cation Exchange Capacity

The changes in soil pH due to addition of different levels of biochar during 90 days of incubation are presented in table.3.

TABLE 3. Effect of different levels of biochar application on pH of soil

Treatments	Incubation period (days)				
	0	30	60	90	Mean
T1- Control	8.42	8.41	8.35	8.33	8.38
T2- Soil+ Biochar (1%)	8.38	8.36	8.34	8.30	8.34
T3- Soil+ Biochar (2%)	8.32	8.26	8.24	8.23	8.26
T4- Soil+ Biochar (3%)	8.28	8.20	8.18	8.05	8.18
T5- Soil+ Biochar (4%)	8.24	8.16	8.13	8.01	8.13
T6- Soil+ Biochar (5%)	8.22	8.13	8.06	7.92	8.08
Mean	8.31	8.25	8.22	8.14	8.23
	SEd			CD (0.05)	
Treatment (T)	0.01			0.02 **	
Incubation Period (P)	0.01			0.02 **	
T x P	0.02			0.05 **	

Initially the pH was 8.42. Due to biochar addition the pH was found reduced at all days of incubation. Increase in the rate of application of biochar decreases the soil pH right from its incorporation. At the end of 90 days, the pH was found reduced to 7.92 in soil with the application of biocahr at the rate of 5%. The reduction in soil pH might be due to release of protons (H^+) from the exchange sites of biochar (exchangeable acidity 49 mmol kg $^{-1}$), and due to the proliferation of acid producing soil micro organisms. It is also likely that the production of organic acid during the decomposition of organic matter present in soil and biochar might have also contributed for the reduction in soil pHs. There are few studies that have demonstrated a reduction in pH due to biochar addition in alkaline soils, however, the addition of acid biochar to acidic soils has been observed to reduce soil pH (Cheng *et al.,* 2008)

The cation exchange capacity (CEC) is an important characteristic of soil which determines nutrients adsorption/ desorption and thus their availability in soil. Initially the soil CEC was 17.9 cmolkg $^{-1}$. During incubation it was increased up to 19.47 cmolkg^{-1} due to the application of biochar (5%). It has been respected that the biochar, a highly porous with high surface area and variable charge organic material, has the potential to increase soil water holding capacity, CEC, surface sorption capacity and base saturation when added to the soil. (Glaser *et al.,* 2002; Bélanger *et al.,* 2004; Keech *et al.,* 2005; Liang *et al.,* 2006).

As biochar ages, the positive exchange sites on biochar surfaces decline and negative charge sites develop (Cheng *et al.,* 2008).The biochemical basis for the increase in CEC is not fully understood, but is likely due to the presence of oxidized functional groups (such as carboxyl groups), whose presence is indicated by high oxygen and carbon ratios on the surface of charred materials following microbial degradation (Liang *et al.,* 2006; Preston and Schmidt 2006) and is further influenced by the high surface area (Gundale and DeLuca, 2006) and high charge density of biochar. Additionally, a high specific surface area was attributable to the presence of biochar, which may contribute to the high CEC found in soils that are rich in biochar. (Liang *et al.,* 2006).

TABLE 4. Effect of different levels of biochar application on CEC (cmol (+) kg^{-1}) of soil

Treatments	Incubation period (days)				
	0	30	60	90	Mean
T1- Control	17.9	17.90	18	17.83	17.93
T2- Soil+ Biochar (1%)	17.9	17.97	18.17	18.57	18.01
T3- Soil+ Biochar (2%)	18.1	18.20	18.50	18.73	18.27
T4- Soil+ Biochar (3%)	18.17	18.43	18.63	18.77	18.41
T5- Soil+ Biochar (4%)	18.23	18.77	18.90	19.03	18.63
T6- Soil+ Biochar (5%)	18.3	18.97	19.17	19.47	18.81
Mean	18.10	18.37	18.56	18.73	18.34
	SEd			CD (0.05)	
Treatment (T)	0.03			0.06 **	
Incubation Period (P)	0.02			0.05 **	
T x P	0.06			0.13 **	

TABLE 5 . Effect of different levels of biochar application on NH_4 – N (mg kg^{-1}) of soil

Treatments	Incubation period (days)				
	0	30	60	90	Mean
T1- Control	93	96	96	91	94
T2- Soil+ Biochar (1%)	91	86	84	82	86
T3- Soil+ Biochar (2%)	89	84	79	77	82
T4- Soil+ Biochar (3%)	84	82	77	70	78
T5- Soil+ Biochar (4%)	79	77	75	68	75
T6- Soil+ Biochar (5%)	75	72	70	65	71
Mean	85	83	80	76	81
		SEd		CD (0.05)	
Treatment (T)		1.74		3.51 **	
Incubation Period (P)		1.42		2.87 **	
T x P		3.49		NS	

Nitrogen Dynamics

Addition of biochar resulted in marked changes in the N (NH_4^+ - N and NO_3 - N) content of soil (Table 5 & 6). Both NH_4^+ - N and NO_3 - N content were found decreased due to biochar application. Initially, the NH_4^+ - N content was 93 mg kg^{-1} and it was decreased significantly at all levels of biochar application, and highest being observed at higher level (5%) of biochar addition. During incubation the rate of reduction was increased. At the end of 90 days, the soil with biochar (5%) had approximately 30% less NH_4^+ - N content that of control.

The reduction might be due to adsorption of NH_4^+ onto biochar particles. The CEC (16cmol kg $^{-1}$) of biochar shows that about 2880 of positively charged NH_4^+ can be adsorbed and retained by one kilogram of biochar material. Lehmann *et al.* (2006) have suggested that biochar can adsorb both NH_4^+ and NH_3^- from the soil solution thus reducing solution inorganic N at least temporarily, but perhaps concentrating it for microbial use. Biochar is an N depleted material having a uniquely high C/N ratio (839). It is also possible that some amount of decomposition might have occured when fresh biochar is added to soil (Schneour, 1966; Liang *et al*, 2006), which could induce net immobilization of inorganic N already present in the soil solution. Gundale and DeLuca (2006) reported that the biochar addition to soil caused reduction in ammonification compared to the control due to adsorption and reduce the potential for NH_3 volatilization. The reduction could be due to high C/N ratio of biochar and greater potential for N immobilization (Lehmann et al.,2006). It should be noted, however, that immobilization potential associated with biochar additions to soil would be greatly limited by the recalcitrant nature of biochar (DeLuca and Aplet, 2007).

TABLE 6 . Effect of different levels of biochar application on NO_3 – N (mgkg^{-1}) of soil

Treatments	Incubation period (days)				
	0	30	60	90	Mean
T1- Control	56	58	58	56	57
T2- Soil+ Biochar (1%)	54	51	49	47	50
T3- Soil+ Biochar (2%)	51	47	44	42	46
T4- Soil+ Biochar (3%)	49	44	40	37	43
T5- Soil+ Biochar (4%)	47	42	37	33	40
T6- Soil+ Biochar (5%)	44	40	35	30	37
Mean	50	47	44	41	45
	SEd			CD (0.05)	
Treatment (T)	1.74			3.5 **	
Incubation Period (P)	1.42			2.86 **	
T x P	3.48			NS	

TABLE 7. Effect of different levels of biochar application on soil organic carbon (g kg^{-1}) under incubation

Treatments	Incubation period (days)				
	0	30	60	90	Mean
T1- Control	5.1	5.2	4.7	4.5	4.86
T2- Soil+ Biochar (1%)	5.8	5.9	6.6	6.9	6.30
T3- Soil+ Biochar (2%)	7.4	8.8	10.2	11.5	9.50
T4- Soil+ Biochar (3%)	10	10.6	11.8	12.5	11.21
T5- Soil+ Biochar (4%)	11.7	12.9	13.6	14.7	13.25
T6- Soil+ Biochar (5%)	13.6	15.9	16.8	18.1	16.11
Mean	8.93	9.88	10.63	11.37	10.20
	SEd			CD (0.05)	
Treatment (T)	0.37			0.76**	
Incubation Period (P)	0.31			0.62**	
T x P	0.75			1.52**	

It is also possible that some of the NO_3 – N might have lost through microbial denitrification. Denitrification is a biotic dissimilatory process in which NO_3^- is reduced to N_2 (g) in the absence of O_2. Several intermediates (including NO and N_2O) are formed during this reductive process and are potentially released into the soil atmosphere when conditions are not favourable for complete reduction of NO_3^- to N_2. Biochar has the potential to catalyse the reduction of N_2O to N_2; potentially reducing the emission of this important greenhouse gas to the atmosphere, and thus biochar could directly or indirectly influence denitrification. The process of denitrification requires the presence of substrate (available C) and a terminal electron acceptor, such as NO_3^- (Stevenson and Cole, 1999).

Carbon Dynamics

The application of different rates of biochar had significant effect on soil organic carbon (SOC) content (Table.7). Initially, the experimental soil had only 5.1 g kg^{-1}, due to incorporation of biochar, it SOC content increased and ranged from 5.8 to 13.6gkg^{-1}. Irrespective of treatments, the SOC increased markedly during the incubation, due to biochar application, whereas the SOC was found decreased in control soil (without biochar) after 30 days. At the end of the incubation the control soil had only 4.5 g SOC kg^{-1}, whereas the soils with biochar had SOC ranged between 6.9 and 18.1 g kg^{-1}.The highest SOC was recorded in soil amended with 5% biochar. The high carbon content in biochar might have enriched the soil with organic carbon content. About 33 to 35% increase in SOC was observed from 0th day to 90th day of incubation. During the incubation the SMBC content increased at all treatments up to 60 days and thereafter a declining trend was observed (Table.8). The treatment T_6 (Biochar 5 %) recorded the highest values at 30 (2.57 g kg^{-1}) and 60 days (2.61 g kg^{-1}). At all times the soil microbial biomass carbon (SMBC) contents were more with the higher rates of Biochar application than the lower rates.

Similar to SMBC, the water soluble organic carbon (WSOC) was also found markedly influenced by the Biochar application (Table .9). Initially the soil had a concentration of only 0.14 g kg^{-1}. The WSOC concentration in soil ranged from 0.14 to 0.27 g kg^{-1}, 0.26 to 0.40 g kg^{-1}, 0.23 to 0.37 g kg^{-1} and 0.21 to 0.34 g kg^{-1} at 0, 30, 60 and 90 days of incubation, respectively. The acid fraction of organic C (Humic acid and Fulvic acid) in soil as influenced by varied levels of Biochar and incubation are presented in Table.10. Increase in the level of Biochar increased the concentration of both humic acid and fulvic acid content in soil. The interaction between treatment and incubation period was significant. This indicates that large amount of carbon was sequestered in soil due to biochar application.

TABLE 8. Effect of Biochar on soil microbial biomass carbon (g kg^{-1}) content during incubation

Treatments	Incubation period (days)				
	0	30	60	90	Mean
T_1- Control	0.45	0.54	0.63	0.36	0.5
T_2- Soil+ Biochar (1%)	0.49	0.95	0.99	0.72	0.89
T_3- Soil+ Biochar (2%)	0.52	1.31	1.35	1.08	1.25
T_4- Soil+ Biochar (3%)	0.52	1.76	1.8	1.53	1.69
T_5- Soil+ Biochar (4%)	0.55	2.21	2.3	2.03	2.14
T_6- Soil+ Biochar (5%)	0.56	2.57	2.61	2.3	2.5
Mean	0.56	1.55	1.61	1.34	1.49
		SEd		CD (0.05)	
Treatment (T)		0.49		0.98**	
Incubation Period (P)		0.40		0.80**	
T x P		0.98		NS	

TABLE 9. Effect of Biochar on soil water soluble organic carbon (g kg^{-1}) content during incubation

Treatments	Incubation period (days)				
	0	30	60	90	Mean
T_1- Control	0.14	0.26	0.23	0.21	0.21
T_2- Soil+ Biochar (1%)	0.17	0.28	0.26	0.26	0.24
T_3- Soil+ Biochar (2%)	0.21	0.33	0.30	0.28	0.28
T_4- Soil+ Biochar (3%)	0.22	0.35	0.33	0.30	0.31
T_5- Soil+ Biochar (4%)	0.25	0.37	0.35	0.33	0.33
T_6- Soil+ Biochar (5%)	0.27	0.40	0.37	0.35	0.36
Mean	0.23	0.33	0.31	0.29	0.29
	SEd			CD (0.05)	
Treatment (T)	0.01			0.03**	
Incubation Period (P)	0.01			0.03**	
T x P	0.03			0.07	

TABLE 10. Effect of Biochar on acid fraction of organic carbon (g kg^{-1}) content during incubation

Treatments	Incubation period (days)									
	Humic acid					Fulvic acid				
	0	30	60	90	Mean	0	30	60	90	Mean
T_1- Control	2.6	2.7	3	2.9	2.8	0.8	0.9	1.1	1	0.9
T_2- Soil+ Biochar (1%)	2.9	4.1	4.8	4.4	4.3	1	1.2	1.4	1.5	1.2
T_3- Soil+ Biochar (2%)	3.2	4.6	6.1	5.8	5.1	1.3	1.5	1.7	1.9	1.6
T_4- Soil+ Biochar (3%)	3.4	5.7	6.9	6.5	5.9	1.6	1.8	2.1	2.4	2
T_5- Soil+ Biochar (4%)	3.8	6.2	7.4	7.1	6.5	1.7	2.3	2.7	3	2.5
T_6- Soil+ Biochar (5%)	3.9	7.5	8.2	7.9	7.5	1.9	2.6	2.8	3.1	2.7
Mean	4.8	5.1	5.7	6.1	5.3	1.5	1.7	1.9	2.1	1.8
		SEd		CD (0.05)			SEd			CD (0.05)
Treatment (T)		0.89		1.79**			1.27			2.56**
Incubation Period (P)		0.72		1.46**			1.04			2.09**
T x P		1.78		3.58**			2.54			5.13

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