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Role of Clay in Recovery of Organic Matter in Arable Black Soils of India: An Inverse Pyramid Relation

T. BHATTACHARYYA[1]*, D. K. PAL[2] AND S.P. WANI [1]

[1]ICRISAT Development Center, International Crops Research Institute for the Semi-Arid Tropics, Patancheru, Telangana, India
[2] Former Visiting Scientist in ICRISAT
**Present address: Dr Balasaheb Sawant Konkan Krishi Vidyapeeth, Dapoli 415 712, India*

Abstract–*We studied the logic of blanket recommendation of Walkley Black Recovery Factor (WBRF) with a set of ~1000 shrink-swell soil samples with varying clay content, representing two important food growing zones namely the Indo-Gangetic Plains and the Black Soil Region (BSR). Since clay and organic matter form strong clay complexes, we investigated how quantity of clay can influence recovery of organic matter from soils analyzed following standard procedure. Increase in clay content, soil depth and aridity (low rainfall) have similar effect in increasing WBRF due to decreased organic matter recovery. While the relation is a straightforward in low clay soils, the study showed that recovery of organic matter remains unaffected for BSR soil clays > 60% warranting a new initiative for an inter facial research to link pedology and edaphology.*

Key words : WBRF, Soil, Clay, Recovery, Organic matter.

Introduction

There are various methods available to determine soil organic carbon (SOC), which includes wet oxidation method. In this method soil organic matter which contains about 48-58% of organic carbon, is oxidized by chromic acid utilizing the heat of reaction as well as dilution of sulphuric acid (Walkley and Black, 1934; Jackson, 1973). The method claims to estimate organic carbon to an extent of 77% and so as to make it 100%, the determined value is multiplied with the correction factor of 1.29 to get a near true estimate. This factor is known as the Walkley Black Recovery factor (WBRF) which varies among soils, their management regimes and even soil horizon (Tabatabai, 1996).

The qualitative nature of the soil substrate and their quantitative proportion of surface reactivity, referred to as surface charge density (SCD), control the rate of accumulation of organic carbon (OC). The knowledge of its decomposition and recovery while carrying out its determination in the laboratory is important.

Increase in organic C enhances SCD of the soil and the ratio of internal/external exchange sites (Poonia and Niederbudde, 1990). It may be mentioned that in the black soil regions (BSR), the dominant soils in semi-arid tropics (SAT) are black soils (Vertisols and their intergrades, with some inclusions of Entisols in the hills) and associated Alfisols. All these soils are dominated by smectites (Bhattacharyya *et al.*, 1993). The presence of smectites increases SCD, which offers greater potential for carbon sequestration in these soils. Black soils, therefore, may reach a quasi-equilibrium value (QEV) of more than 2% as reported in the representative soils developed in the basaltic alluvium (Bhattacharyya *et al.*, 2014).

While discussing the role of soil colloids in carbon accumulation in soils, Bhattacharyya and Pal (2003) estimated that the total proportion of soil organic pools (i.e., moderately oxidized, strongly oxidized, physically, and chemically sequestered) are controlled by clay minerals to the extent of 18, 20, 20, and 20%, respectively. This suggests that a minimum 78% of the total organic matter in soil is controlled by inorganic substrate (precisely phyllosilicate minerals with higher surface area in the finer fractions). Relatively more (2-3%) SOC content in Indian Mollisols and Australian Vertisols is not uncommon (Bhattacharyya *et al.*, 2006; Dalal and Conter, 2000). The importance of SCD, rainfall, and their combined influence indicates an inverse pyramid relation of content of SOC with US taxonomic soil

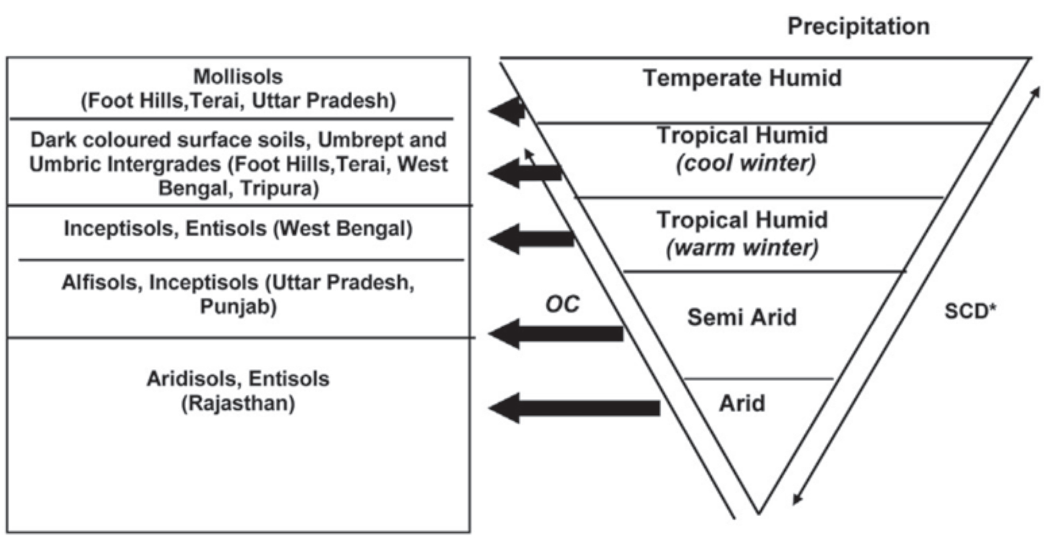

Fig. 1. *Inverse pyramid relation with accumulation of organic carbon (OC) in soils grouped following U.S. Soil Taxonomy as influenced by precipitation, temperature, and substrate quality (* SCD, surface charge density) (source: Bhattacharyya et al., 2014).*

orders (Fig. 1) (Bhattacharyya *et al.*, 2015a).

Recent observations indicate the occurrence of Vertisols and their intergrades (Soil Survey Staff, 2006) in the Indo-Gangetic plains (IGP) (Bhattacharyya *et al.* 2013). These deep to very deep and smectite dominated soils are commonly known as black soils (black cotton soils), which, are characterized by the presence of either slickensides or wedge-shaped peds, ≤ 30% clay and cracks that open or close periodically. Occurrences of vertic intergrades in the IGP are more common than that of the Vertisols (Bhattacharyya *et al.*, 2009).

In order to find out a relation between clay content (in terms of surface areas and SCD of the clay mineral) and the recovery of organic matter, and also to establish an acceptable WBRF as the corrected WBRF (WBRFc) in black soils (collected from each diagnostic horizon) of the different bio-climates of the IGP and BSR, the present study was undertaken with this idea a hope that WBRFc will be used by various soil and other laboratories for soils of similar bio climate and depth ranges in India and elsewhere.

Materials and Methods

Study area

For this study a total of 526 soil samples (303 of IGP and 223 of BSR) were selected in different bioclimatic zones. The IGP covers about 52.01 mha and represents 8 agro-ecological regions (AERs), 14 agro-ecological sub regions (AESRs) (Mandal *et al.,* 2014) and 7 bioclimatic systems. The nature and properties of the alluvium vary in texture from sandy to clayey, calcareous to non-calcareous and acidic to alkaline. In the IGP, rice-wheat cropping system is dominant followed by cotton-wheat, bajra-wheat and maize-wheat.

The BSR is mainly occupied by black soils in the Indian SAT; although their presence has also been reported in the humid and arid bioclimatic systems (Bhattacharyya *et al.,* 1993, 2008, 2009). These soils are spatially associated with red soils and form a major soil group of India and developed in basaltic alluvium under different climates. These soils are potentially good crop production zones in the country and occur in many states and occupy 76.4 mha and cover 30 agro-eco-subregions (Bhattacharyya *et al.*, 2014) and 5 bioclimatic systems. The dominant crops in the BSR are cotton, soybean, followed by sorghum and wheat.

Methods

SOC was determined by Walkley and Black method (Walkley and Black, 1934) which was further refined by Walkley (1947). Essentially, concentrated H_2SO_4 was added to a mixture of soil and aqueous $K_2Cr_2O_7$. The heat of dilution raises the temperature sufficiently to induce a substantial, but not complete oxidation by the acidified dichromate. Residual dichromate was titrated using ferrous sulphate solution. The difference between the sample titrated by ferrous ammonium sulphate [Fe $(NH_4)_2$ $(SO_4)_2$. $6H_2O$] (FAS) and that of the blank titration determined the amount of easily oxidizable organic carbon. The corrected Walkley-Black recovery factor ($WBRF_c$) was estimated using wet (Walkley-Black method) and dry combustion (C/N analyzer) methods as detailed by Bhattacharyya *et al.,* (2015b). Calcium carbonate equivalent in soils was determined following the standard method (Jackson, 1973) to estimate soil inorganic carbon (SIC) which constitutes twelve percent of $CaCO_3$. Prior to analysis, the soil samples were air dried and ground to 100 mesh size.

Results and Discussion

Clay content of black soils in the IGP and that of the BSR varies strikingly. It varies in IGP black soils from 6 to 55% and in BSR from 21 to 78% at different depths (Table 1). Besides, the IGP black soils have the maximum clay content little less than 60% and thus is not falling under fine and very fine at the family level of soil classification (Soil Survey Staff, 2014).

It is known that SCD (determined by nature of clay, surface area, charge characteristics and cation exchange capacity), controls the organic carbon sequestration in soils (Bhattacharyya *et al.*, 2015b). Logically, therefore, the IGP soils with > 30% clay (with vertic properties due to more smectite), and the BSR soils with < 60% and/or > 60% clay, would influence WBRFc. Conversely, these smectites with more clay and SCD should influence the recovery of organic matter. Ideally more organo-clay mineral complexes are formed in the black soils which are stabilized and remain more in the recalcitrant pool than the IGP soils (Chivane and Bhattacharyya 2010; Mandal *et al.*, 2008). Therefore, we arrayed our datasets for the IGP into two groups as < 30% and > 30% clay. Vertisols of BSR have more than 30% clay which demanded two different groups of soils, one containing > 30% and the other with > 60% clay (Table 1). Our purpose was to find out the possible differences in WBRFc in these

Table 1. *Variation of clay content within each two groups of soils in the Indo-Gangetic Plains (IGP) and Black Soil Region (BSR)*

Regions	Clay group (%)	Range of clay (%) in soil depth (cm)			
		0-30	30-50	50-100	100-150
IGP	< 30	10-26	6-29	8-29	4-28
	>30	30-51	33-51	34-55	30-51
BSR	<60	22-59	22-59	23-59	21-59
	>60	61-73	61-75	61-78	60-75

4 different soils grouped according to their clay content. The other variable we introduced was the bioclimatic system which has a major role to play in arriving at the WBRFc.

The trend of graphs (Figs 2- 5) indicate a relatively lower recovery of organic carbon in soils of both the IGP and BSR with high clay content. This trend is more pronounced in black soils and the soils of IGP with > 30% clay. A similar observation was reported fromVenezuelan soils (Chacon *et al.,* 2002). However, the correction factors reported earlier show an increasing trend with increase in clay content (Velmurugan *et al.,* 2009). A closer look at the datasets (Fig. 2 in Velmurugan *et al.*, 2009) indicates Y axis as OC recovery percentage which, as a matter of fact, should be Walkley Black recovery factor. Observations of these authors were made with clays with different nature, and SCD that formed clay- organic complex, which may not be identical to soils under our study.

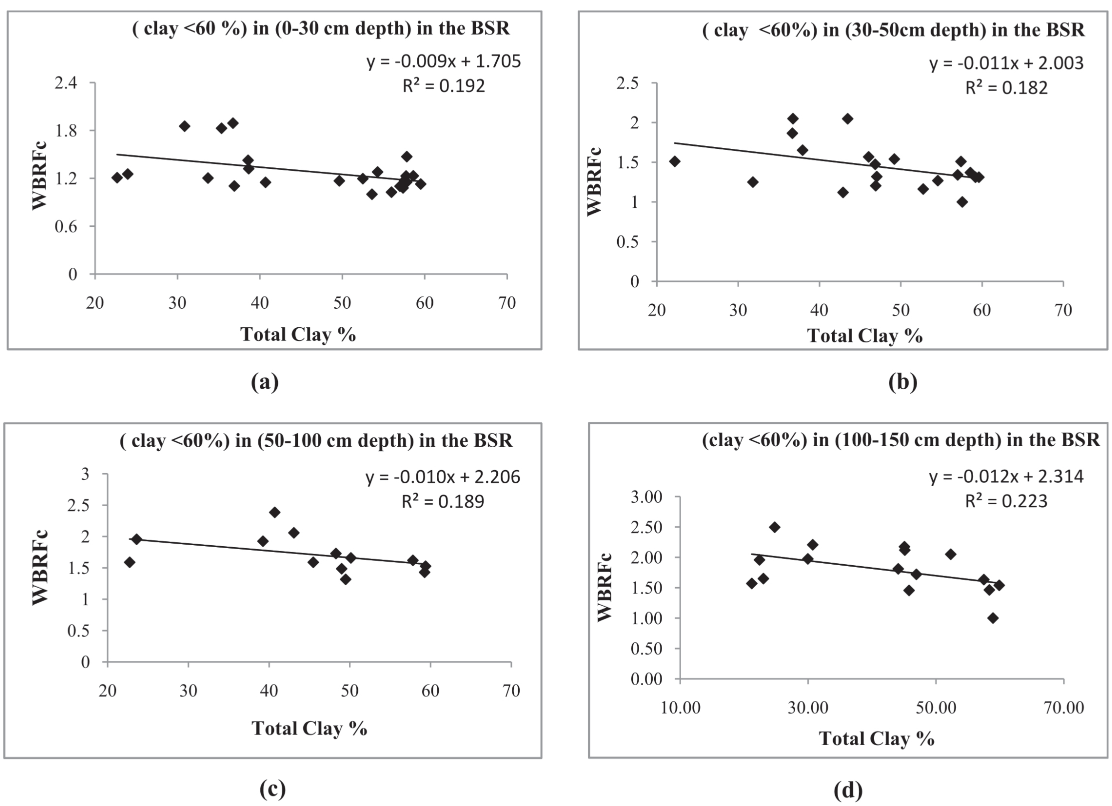

Fig. 2. *Relation between corrected Walkley Black Recovery Factor (WBRF$_c$) and total clay % where (clay 30-60%) in a) 0-30 cm, b) 30-50 cm, c)50-100 cm, d) 100-150 cm soil depth in the black soil regions (BSR)*

We studied soils representing three bioclimatic systems in the IGP (Table 2). Influence of bio-climate in organic matter recovery and WBRFc has been detailed elsewhere (Bhattacharyya *et al.*, 2015b). We discuss in this paper the effect of clay in controlling these two parameters namely organic matter recovery and WBRFc. A general tendency of increased WBRFc with the increase in clay content in IGP black soils is observed (Table 2) with soils low and high clay content with some exceptions. Interestingly, for the black soils an opposite trend was observed. Clay generally increases with pedon depth of black soils due to clay illuviation. Therefore, with the increase in depth increase in WBRFc can also be explained by increased clay content; notwithstanding with the fact of decreased microbial counts in the lower layers ((Bhattacharyya *et al.*, 2015b). Increase in clay content, soil depth and aridity (low rainfall) have therefore similar effect in increased WBRFc due to decreased organic matter recovery (Table 2) (Figures 3, 4).

For the black soils when all data are

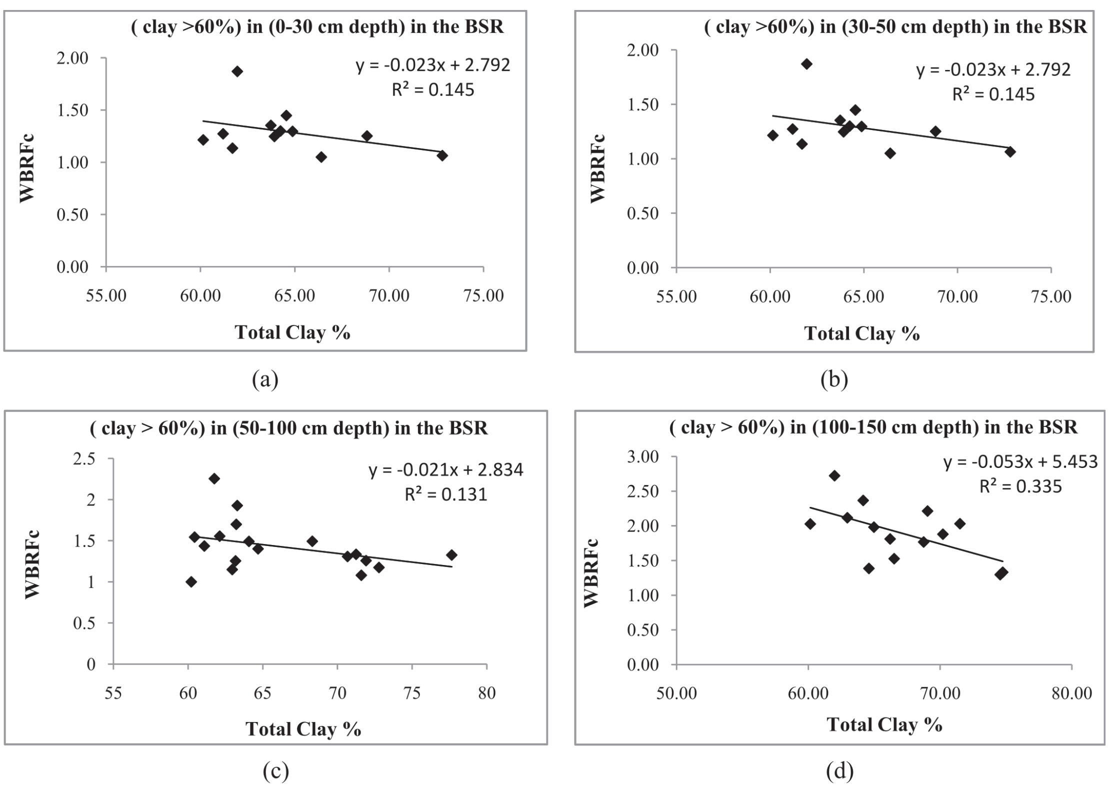

Fig. 3. *Relation between Walkley Black Recovery Factor and total clay % where (clay > 60%) in a) 0-30 cm, b) 30-50 cm, c) 50-100 cm, d) 100-150 cm soil depth in the black soil regions (BSR)*

Table 2. *Corrected Walkley Black Recovery factor ($WBRF_c$) of the Indo-Gangetic Plains*

Clay %	WBRFc (mean)	Soil depth cm	R^2	Clay %	WBRFc (mean)	Soil depth cm (clay %)	R^2
			Humid to per humid (MAR > 2200 mm)				
< 30%	1.12	0-30	0.98	>30%		No examples	
	1.23	30-50	0.98		-		
	1.28	50-100	-		-		
	1.67	100-150	0.43		-		
			Humid to Sub humid (MAR 1000-2200 mm)				
<30%	1.25	0-30	0.11	>30%	1.23	0-30	0.08
	1.42	30-50	0.28		1.46	30-50	-
	1.37	50-100	-		1.58	50-100	0.23
	1.98	100-150	0.44		1.89	100-150	0.29
			Semi arid (MAR < 1000 mm)				
< 30%	1.27	0-30	0.11	>30%	-	0-30	-
	1.50	30-50	0.17		1.53	30-50	1.00
	1.81	50-100	-		1.40	50-100	0.75
	2.10	100-150	-		1.89	100-150	-

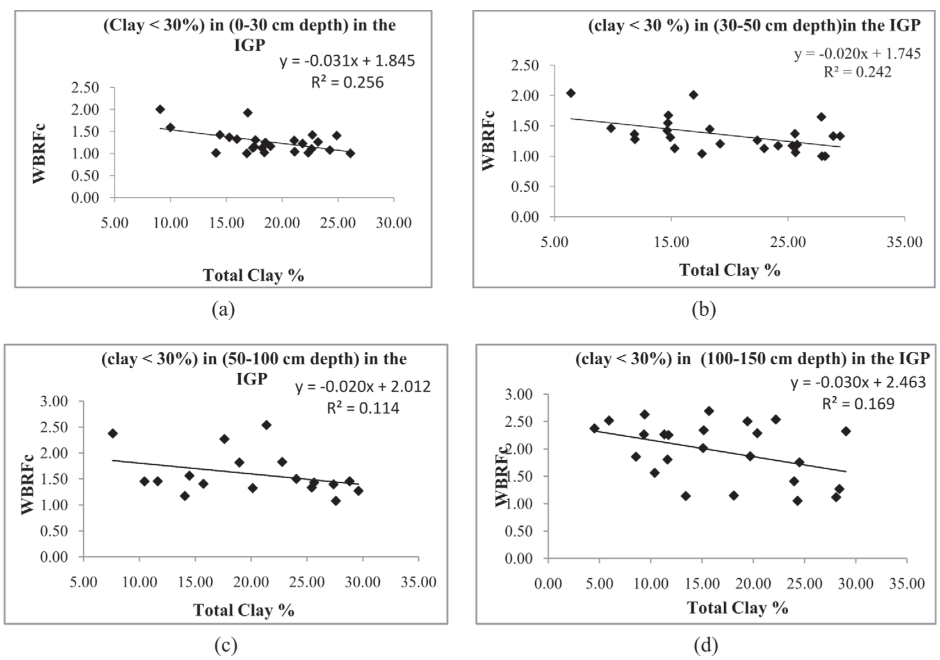

Fig. 4. *Relation between corrected Walkley Black Recovery Factor ($WBRF_c$) and total clay % where (clay < 30%) in a) 0-30 cm, b) 30-50 cm, c) 50-100 cm, d) 100-150 cm soil depth in the Indo-Gangetic plains (IGP)*

Table 3. *Corrected Walkley Black Recovery factor ($WBRF_c$) of the Black Soil Region*

	WBRFc (mean)	Soil depth cm	R^2	Clay %	WBRFc (mean)	Soil depth cm	R^2
			Humid to Sub humid (MAR 1000-2200 mm)				
<60%	1.37	0-30	0.35	>60%	1.06	0-30	-
	1.65	30-50	-		1.51	30-50	0.47
	1.80	50-100	0.24		1.38	50-100	-
	1.92	100-150	-		1.86	100-150	-
			Semi arid (MAR < 1000 mm)				
< 60%	1.32	0-30	0.19	>60%	1.30	0-30	0.29
	1.48	30-50	0.18		1.36	30-50	0.97
	1.81	50-100	-		1.47	50-100	0.29
	2.21	100-150	0.13		1.72	100-150	0.41

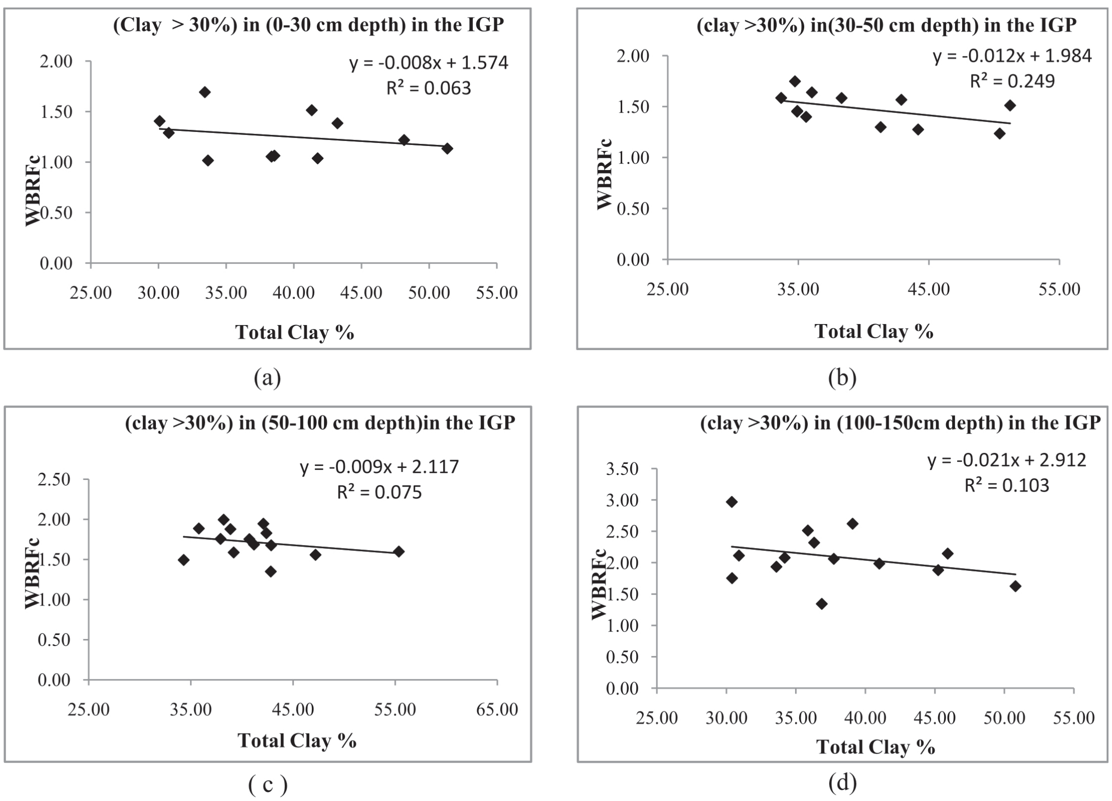

Fig. 5. *Relation between corrected Walkley Black Recovery Factor ($WBRF_c$) and total clay % where (clay > 30%) in a) 0-30 cm, b) 30-50 cm, c) 50-100 cm, d) 100-150 cm soil depth in the Indo-Gangetic Plains (IGP)*

pooled, cutting across the bioclimatic systems, a general trend of decrease of WBRFc with increased clay content is observed (Figs 1 and 2). However, when the data are analyzed separately the trend is reversed. It appears that after a threshold clay content (> 60%) in BSR black soils, the clay content may not have any influence in recovery of organic matter because high amount of clay with much higher surface area and SCD are likely to impart resistance to OC decomposition (Mandal *et al.*, 2008) and this causes the stabilization of the WBRFc. This observation from a large dataset suggests that this threshold limit for the recovery of organic matter may work for highly clayey black soils, in particular and other soils, in general. Earlier an inverse pyramid relation was reported for soil taxonomy vis-à-vis bioclimate and surface charge density to comment on both organic and inorganic carbon sequestration (Bhattacharyya *et al.*, 2014) (Fig. 1). The present study shows that climatic parameters (such as rainfall) and percent recovery of organic matter from soils are inversely related to clay content as it (clay) influence WBRFc as well as surface charge density. The figure 6 shows schematically the relative proportion of four different types of soils containing clay of varied quantity. Interestingly, black soils in BSR containing > 60% forms least proportion so far as sample size is concerned. It was

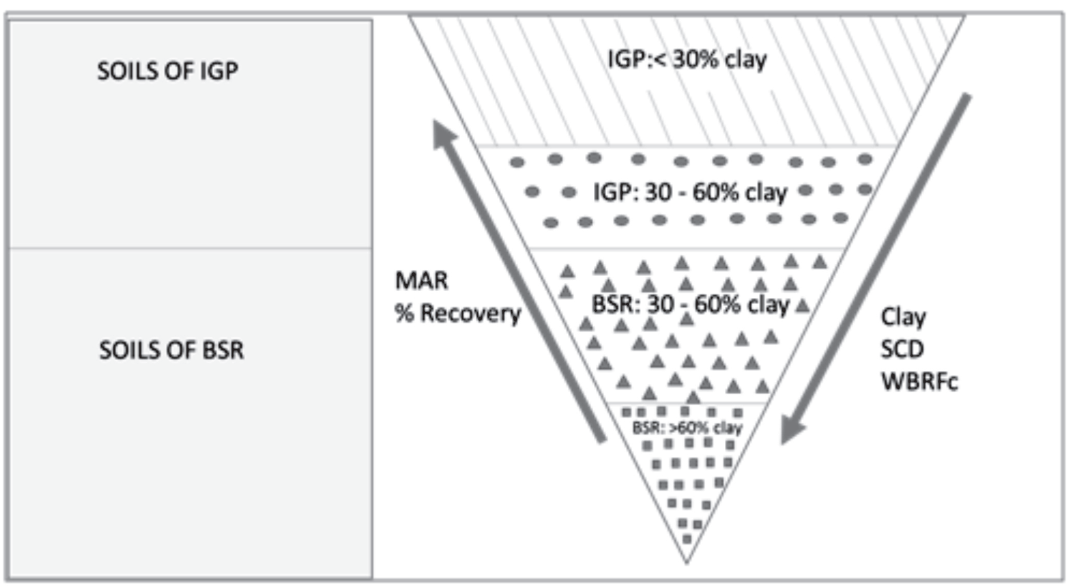

Fig. 6. *Schematic diagram showing an inverse pyramid relation between climate, soil properties and Walkley Black Recovery Factor (WBRF$_c$) (Most of the black soils in IGP contain < 30% clay and a little less is occupied by those containing 30-60% clay; for BSR most of the black soils fall within the range of 30-60% clay and few with > 60% clay category)*

noticed that recovery rate in these soils do not follow the trend observed for other types of soils. The quality of clay minerals with smectites as the dominant minerals may be the reason for holding organic matter more tenaciously. The charge characteristics of the smectites of these type of soils and the other soils might open up a new vistas of clay research looking for an interface between pedology (soil taxonomy, mineralogy) and edaphology (soil organic matter estimation and linking it to amount of nitrogen for plant growth).

Conclusions

Studies over the last 50 years showed that the fundamental assumption upon which the recovery per cent of about 77 per cent by WB method to determine SOC was based, is arbitrary. Among other factors substrate quality has often been addressed but never demonstrated with affirmity. The present study shows that WBRFc is controlled by clay content and this relation ceases to exist for soils with > 60% clay content.

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