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A Pragmatic Method to Estimate Plant Available Water Capacity (PAWC) of Rainfed Cracking Clay Soils (Vertisols) of Maharashtra, Central India

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Abstract : Three Vertisols from Nagpur, Amravati and Akola districts were studied in detail to understand the relation between moisture and soil properties. These soils are deep and during dry periods cracks cut through the slickensides in some soils with subsoil sodicity. A significant positive correlation between available water content (AWC) and smectite content, exchangeable sodium percentage (ESP) and exchangeable magnesium percentage (EMP) indicates the nature of clay and cations in exchange site plays an important role in retaining and releasing moisture. Studies on biophysical factors on water retention and release, and cotton yield in 32 Vertisols indicate that the determination of AWC and PAWC at 33 and 1500 kPa overestimates the soil moisture content because in field conditions soil water in the subsoil do not reach the saturation at 33kPa due to low to very low saturated hydraulic conductivity. A significant positive correlation between PAWC (estimated at 100-1500 kPa for non-sodic and 300-1500 kPa for sodic soils), and yield of cotton indicates that the PAWC estimated by this method can be considered as an important biophysical parameter for evaluation of rain fed Vertisols for growing deep rooted crops in Indian states in general and Vidarbha region of Maharashtra state in particular.

Key words : Plant available water capacity (PAWC), Available water content (AWC), Sodic and non-sodic Vertisols.

In India, cracking clay soils (Vertisols and their intergrades) are one of the major soils supporting agriculture. The revised estimates indicate Vertisols and the associated soils in India occupy 76.4 m ha and 35.5% of which is in the state of Maharashtra (Mandal *et al.*, 2014). The majority of Vertisols distributed in the semiarid and arid part of central India, are rainfed. In many areas under Vertisols,

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cultural operations using handheld or animal-drawn implements are difficult. High ESP in the sub soils disperses the clay and restricts the water movement in the profile. Farmers faced with these difficulties often cultivate them only in the post-rainy season. Thus Vertisols (without soil modifiers, Pal *et al*., 2006) have limitations that restrict their full potential to grow both rainy season and winter crops (NBSS&LUP-ICRISAT, 1991) and this dismal agricultural situation is seen in Amravati and Akola districts of Maharashtra state of central India. Either rainy season or winter crop is grown in Vertisols of the western part of the Amravati district and the adjoining Akola district, whereas both rainy and winter crops are grown in those of Nagpur district with limited irrigation (NBSS&LUP-ICRISAT, 1991).

Vertisols vary in their morphology particularly cracking behaviour and cropping pattern from Nagpur to Akola district within a distance of about 100-200 km (NBSS & LUP-ICRISAT, 1991). Generally cracks are observed up to 40-60 cm depth (*ie*. upto the depth of initiation of slickenside) in Nagpur and eastern part of Amravati districts but in Akola cracks penetrates through the slickenside, thereby depleting the moisture from the subsoil. The diffential crack morphology is due to some intrinsic soil properties such as pH, hydraulic properties, ESP and presence of pedogenic $CaCO_3$, and the nature and content of clay minerals (Balpande *et al*., 1996; Vaidya and Pal, 2002).

The hydraulic properties of Vertisols are impaired due to the formation of pedogenic $CaCO_3$ and the concomitant development of subsoil sodicity even at a low ESP (≥5) (Kadu *et al*., 1993; Balpande *et al*., 1996; Pal *et al*., 2001; Vaidya and Pal, 2002) which affects the yield of crops (Kadu *et al*., 2003). With higher amount of sodium in the exchange complex (with a low electrolyte concentration), the interlayer is hydrated forming a diffuse double layer structure (Wilding and Tessier, 1988). Thus in sodic soils , the water is held at a higher tension and this water is rendered unavailable for plant and thus Kadu *et al.* (2003) suggested that the saturated hydraulic conductivity (sHC) is a more meaningful concept than AWC in Vertisols. This questions the validity of estimating the AWC in Vertisols on the basis of moisture held at 33 kPa and 1500 kPa tensions. Therefore, inclusion of AWC as one of the soil parameters for suitability of deep rooted crops like cotton (Sehgal, 1991; NBSS&LUP, 1994; Mandal *et al*., 2002) is inappropriate. This warrants a pragmatic method to estimate the actual antecedent soil water in terms of AWC and plant available water capacity (PAWC) just after the cessation of rains considering the amount of water that has actually percolated into the Vertisol profile under rainfed conditions. In reality, the yield of deep-rooted crops in Vertisols depends primarily on the amount of rain water stored at depth in the soil profile, and the extent to which this soil water is released during crop growth (Pal *et al.*, 2012). In view of this predicament the present study was undertaken with two objectives, (i) to study the bio-physical factors that influence the soils' water retention and release characteristics which ultimately impairs the productivity and yield of crops, and (ii) to suggest a method to estimate the AWC and PAWC that relate significantly with cotton yield data collected from the farmers' field.

Materials and Methods

Representative Vertisols (without soil modifiers) from the districts of Nagpur (Linga series), Amravati (Asra) and Akola (Paral) of Maharashtra state were selected and studied in detail. All the soils were developed in basaltic alluvium and occur in alluvial plains of 1-2% slopes. The study area falls in a climosequence with the highest rain in Nagpur (1010mm), followed by decreased amount at Amravati (975mm) and Akola (793mm) representing a climosequence from dry sub-humid to semi arid climate. In order to accomplish the above objectives cotton yield data were collected from the farmers, and the soil properties data held by the Division of Soil Resource Studies were utilized supplemented by new data.

Methods

Morphological properties of pedons were studied as per Soil Survey Manual (Soil Survey Division Staff, 1995; Bhattacharyya *et al.*, 2009) and horizon wise samples were collected for laboratory analysis. Both sphenoid and slickensides observed in the field confirm the presence of slickensided B horizon (Bss) and thus classified as Vertisols (Soil Survey Staff, 1999)

The bulk density of soil was determined using core samplers (Richards, 1954). The moisture retention and release behaviour within the available range of 33, 100, 300, 500, 800, 1000 and 1500 kPa were measured on less than 2 mm size sample using pressure plate membrane apparatus as per method outlined by Richards (1954). Plant available water capacity was determined by using the formula suggested by Gardner *et al.* (1984), modified by Coughlan *et al.* (1987).

The particle size distribution was determined as per the International Pipette method after the removal of calcium carbonate, organic matter and free iron oxides. Sand (2000-50μm), silt (50-2μm), total clay (<2μm) and fine clay (<0.2 μm) fractions were separated according to the size segregation procedure of Jackson (1979).The water dispersible clay was determined by the International Pipette method. Saturated hydraulic conductivity (sHC) was determined by constant head permeameter (Richards, 1954). Carbonate clay was estimated by rapid titration, (Piper, 1950) using fine earth sample of less than 2 mm drawn for water dispersible clay. The $CaCO_3$, pH, cation exchange capacity

(CEC), and exchangeable bases were determined following standard methods (Richards, 1954; Jackson, 1973). Extractable Ca and Mg were determined following the method of 1N Na Cl solution extraction (Piper, 1950)

Results and Discussion

Al though we have analytical data for many Vertisols of this area, for brevity one representative shrink-swell pedon from each district is presented below.

Morphological Properties of Soils

All the soils are very deep (>150 cm) and the colour varies from very dark grayish brown (10YR 3/2 M) to dark brown (10YR 3/3M) and structure is subangular blocky. The Vertisols generally had subangular to angular blocky structure. Intersecting slickensides forming parallelopipeds with their long axes tilted at 30-45^0 from the horizontal were prominent in subsoils. All the pedons effervesced with HCl throughout the depth indicating presence of $CaCO_3$. The soils are Vertisols , but their cracks and $CaCO_3$ content differ. Cracks >0.5 cm wide extend down to the zones of sphenoids and wedge-shaped peds with smooth or slickensided surfaces in sub-humid soils, but cracks cut through these zones in semiarid soils. High $CaCO_3$ content indicate that a reduction in mean annual rainfall (MAR) leads to the formation of calcareous and alkaline soils in Akola. Thus, though the soils are Vertisols with comparable clay content, the differences in morphology are due to the modifications related to climatic variations (Pal *et al.*, 2012).

Physical Properties of Soils

The total clay content varies from 59 to 69 per cent, and >50% of this is fine clay (Table 1). The fine clay content ranged from 33 to 65.6 per cent and it gradually increased with depth, indicating clay illuviation in Vertisols (Pal *et al.*, 2006, 2012). Bulk density (dry) of the soils varies from 1.44 to 1.88 with a slight increasing trend with depth. Bulk density of ≥1.4 Mg m^{-3} may pose problem of root penetration. But roots are observed penetrating deep in soils. Higher bulk density was reported for black soils of India (Murthy *et al.*, 1982) and it increased in the soils of drier climates (Bhattacharyya *et al.*, 2007).

The saturated hydraulic conductivity (sHC) is higher (13.9 to 23.2 mm hr^{-1}) in the soils of sub humid region (pedon 1) than that at semi arid climates (pedons 2 and 3). In soils of semi arid climate (Asra and Paral soils) sHC decreased slowly up to the slickenside layers and then rapidly down below (Table 1). Low sHC in subsurface soils indicate poor internal drainage in soils of semiarid area. A significant positive correlation between sHC and exchangeable Ca/Mg (r=0.619) and a significant negative correlation with ESP (r = - 0.870) and EMP (r= - 0.679) indicated that hydraulic properties are impaired initially by Mg^{+2} which is further aggravated by Na^+ due to dispersion of clays (Pal *et al.*, 2006). The dispersed clay blocks

Table 1. *Physical properties of the soils*

Horizon	Depth (cm)	BD (Mg m^{-3})	sHC (mm/hr)	COLE	Partical size distribution (%)				
					Sand (2.0-0.05 mm)	Silt (0.05-0.002)	Total Clay (<0.002) mm	Fine Clay (<0.0002) mm	FC/TC
Pedon 1 : Nagpur (Linga Series : Typic Haplusterts)									
Ap	0-13	1.44	13.9	0.26	1.4	34.5	64.1	48.1	0.75
Bw1	13-35	1.59	15.37	0.27	1.1	33	66	53.8	0.81
Bw2	35-56	1.57	20.76	0.28	1.1	32.5	66.4	56.1	0.84
Bss1	56-76	1.52	14.66	0.28	1	30.9	68.1	50.6	0.75
Bss2	76-106	1.56	14.72	0.29	2	28	70	62.2	0.88
Bss3	106-139	1.48	23.23	0.3	2	28.6	69.5	61.8	0.88
Bss4	139-152+	1.47	15.13	0.3	2.1	28.7	69.3	65.6	0.94
Pedon 2 : Amravathi (Asra Series: Sodic Haplusterts)									
Ap	0-12	1.46	20.84	0.24	1.2	35.3	63.5	33	0.51
Bw1	12—28	1.55	19.89	0.24	0.7	33.5	65.8	44.2	0.67
Bw2	28—54	1.76	16.66	0.25	1.1	36.4	62.5	42.1	0.67
Bss1	54-91	1.68	2.28	0.26	0.7	38.1	61.1	41.9	0.68
Bss2	91-136	1.72	1.31	0.27	0.5	34.7	64.8	44.8	0.72
BC	136-150+	1.88	0.37	0.31	0.5	38.6	60.9	49.5	0.81
Pedon 3 : Akola (Paral series : Sodic Haplusterts)									
Ap	0-16	1.47	24.84	0.27	1.2	33.8	65	33.4	0.51
Bw1	16-39	1.62	21.13	0.28	1	33.1	66	50.2	0.76
Bss	39-75	1.54	3.81	0.26	0.8	36.2	63	37.2	0.59
Bss1	75-118	1.65	0.44	0.29	1	33	66.1	37.3	0.56
Bss2	118-144	1.64	0.39	0.28	0.8	34	65.1	42.5	0.65
Bss3	144-150+	1.59	0.45	0.29	1.1	39.4	59.4	36.7	0.61

both macro and micro-pores of soils, resulting in poor drainage.

The moisture retention and release behaviour data at different tensions within the upper and lower limits of available water (Table 2) indicate that the increase in water content with depth at field capacity is nominal in Pedon 1. In other soils the difference in moisture stored at 1000 and 1500 kPa was very less, particularly in horizons where ESP is >5. Though there is a decrease in moisture retention at different tensions from 33 kPa to 1500 kPa the release of moisture after 800 kPa is not substantial particularly in soils with subsoil sodicity (pedons 2 and 3). The AWC of soils in different horizons varied from 19.0 to 23.6%, 15.2 to 23.8% and 19.0 to 26.3% in pedons 1, 2 and 3, respectively. PAWC (considering water content maximum at 33 kPa) of soils estimated at different horizons increased with depth and the values averaged for 100cm depth is almost comparable among non-sodic Linga soils (259.9 mm) and sodic Asra and Paral soils (Table 2), and it is in contrast to lesser

Table 2. *Water retention of soils at different tensions*

Horizon	33 kPa(%)	100 kPa (%)	300 kPa (%)	500 kPa (%)	800 kPa (%)	1000 kPa (%)	1500 kPa (%)	AWC (%)	PAWC* (mm)
				Pedon 1: Nagpur (Typic Haplusterts)					
Ap	42.0	28.8	28.4	28.2	25.6	22.5	22.4	19.6	
Bw1	41.1	29.1	29.3	28.0	25.9	22.5	22.1	19.0	
Bw2	44.3	29.4	29.6	28.7	26.5	23.6	21.4	22.9	259.9^a
Bss1	45.3	29.9	28.9	28.5	27.0	23.3	22.4	23.0	122.9^b
Bss2	47.6	33.9	31.5	30.2	29.4	24.8	23.9	23.7	
Bss3	47.7	33.8	34.0	32.0	29.3	25.2	24.8	22.9	
Bss4	47.8	33.0	32.5	31.8	30.3	27.0	26.1	21.7	
				Pedon 2 : Amravati (Sodic Haplusterts)					
Ap	34.1	22.5	22.4	22.3	21.3	19.2	18.4	15.8	
Bw1	34.3	23.7	23.1	22.9	21.2	19.7	19.0	15.3	
Bw2	37.9	25.3	24.8	24.7	23.6	20.4	19.2	18.7	217.5^a
Bss1	41.8	27.9	26.8	26.5	24.7	21.5	21.4	20.4	102.6^b
Bss2	45.6	31.4	30.8	28.5	26.0	22.7	21.8	23.8	90.6^c
BC	46.7	31.3	30.8	28.8	26.4	23.6	22.2	24.5	
				Pedon 3 : Akola (Sodic Haplusterts)					
Ap	41.4	27.7	26.8	26.5	24.7	23.6	21.2	20.3	
Bw1	41.4	27.8	27.2	27.7	25.9	24.4	22.4	19.1	
Bw2	45.8	32.4	31.6	30.3	27.8	25.1	22.3	23.5	218.7^a
Bss1	48.4	34.5	33.6	31.5	28.5	26.1	26.0	22.3	126.9^b
Bss2	52.1	36.4	34.8	32.5	29.3	26.5	26.3	25.8	113.8^c
Bss3	51.9	35.6	33.0	31.5	28.8	25.5	25.4	26.3	

*PAWC mm= ^{a}(33-1500kPa), ^{b} =nonsodic (100-1500kPa), ^{c} =sodic (300-1500kPa)

yield of cotton in sodic soils (Kadu *et al*, 2003). Thus Kadu *et al.* (2003) observed that though the Vertisols can hold sufficient water for optimum crop growth, the AWC has no significant correlation with cotton yield due to poor internal drainage in the subsoils.

Chemical Properties of Soils

Soils are moderately to strongly alkaline in reaction. The higher pH (>8.0) in soils of semiarid climate is probably due to higher ESP (Table 3). A positive and significant correlation between pH and ESP (r=0.852 at 1% level) is an indication of this relationship. Organic carbon (OC) content of these soils are low to moderate due to higher rate of decomposition in semi-arid environment (Velayutham *et al*., 2000). Both free carbonates and $CaCO_3$ equivalent on fine earth basis increased with decrease in rainfall was evident from this study (Table 3). Calcareousness in Vertisols is due to the presence of both pedogenic and non-pedogenic $CaCO_3$ (Pal *et al*., 2000a). Since both the forms react with HCl, it is difficult to distinguish one from the other. The CEC of these soils are high and among the extractable cations, Ca^{2+} is dominant followed by Mg^{2+}, Na^+ and K^+ except in Pedon 1 (Table 3). Extractable Ca^{2+} decreases with depth whereas Mg^{+2} increased from subhumid to semi-arid climate. This is due to precipitation of carbonates caused by decrease in rainfall and high evapotranspiration demand (Table 3). A significant positive correlation between sHC and Ca/Mg ratio (r = 0.619) indicate the positive role of Ca^{+2} ion in improving drainage of Vertisols. A significant negative correlation between extractable Mg^{+2} and sHC (r=-0.705) indicates the deterioration of hydraulic properties due to clay dispersion caused by Mg^{+2} ions. ESP increased with depth in semiarid soils but this trend is not observed in soils of the subhumid region. ESP (>5) impairs the hydraulic properties of soils due to deterioration of physical properties of soil (Kadu *et al*., 1993; Balpande *et al*., 1996). A significant positive correlation observed between ESP and water retention at 33 kPa (r = 0.563) and at other tension indicates the capacity of these soils to retain more moisture at high level of ESP.

Relation between water retention and soil parameters with yield of cotton

In rainfed Vertisols, the available water (AWC and PAWC) required for better yield depends on the rain water stored in the profile and the capacity of the soil to release the same during crop growth .This depends on many biophysical properties and among them, sHC, ESP and pedogenic carbonates plays an important role. Kadu *et al*., (2003) observed that in Vertisols with high amount smectite clay along with subsoil sodicity (ESP>5), the water held at 33kPa may not be available to plants, and the AWC estimated on this basis amounts to overestimation. Thus we estimated the AWC and PAWC at different tensions for 32 Vertisols at sites (Table 4) of the three districts and correlated with yield and other soil properties.

The AWC of Vertisols (Table 4) indicates that the soils can hold sufficient water for optimum growth, but correlation between yield of cotton and AWC was poor and non-significant. This indicates that, after the cessation of rain, the water is held at higher tensions in Vertisols. This prompted us to try the PAWC at a combination of different tensions. A significant positive correlation between yield of cotton and PAWC (estimated at 100-1500 kPa for non-sodic and 300-1500 kPa for sodic soils) (Table 5 and Fig. 1) was obtained. This suggests that during the crop growth, estimated amount of water (AWC and PAWC) estimated on the basis of 33 kPa and 1500 kPa, is not released because of prevalence of Na^+ ions on exchange sites in soils of semi arid region (Amaravati and Akola). This is supported

Table 3. *Chemical properties of soils*

Horizon	pH (1:2)	Org.C	$CaCO_3$	$ClayCO_3$	CEC	Exchangeable Cations				Σ of cations	Base saturation (%)	Exch. Na (%)	Exch. Mg (%)	Exch. Ca/Mg
						Ca^{2+}	Mg^{2+}	Na^+	K^+					
		(%)	(%)	(%)	*Cmol(p+)kg^{-1}*	*Cmol(p+)kg^{-1}*	*Cmol(p+)kg^{-1}*	*Cmol(p+)kg^{-1}*	*Cmol(p+)kg^{-1}*					
Pedon 1 : Nagpur (Typic Haplusterts)														
Ap	7.8	0.82	4.67	1.04	60.4	50.57	3.3	0.19	1.02	55.07	91.2	0.31	5.45	15.32
Bw1	7.8	0.67	4.34	1.08	64	50.89	3.08	0.22	0.78	54.96	85.8	0.34	4.8	16.52
Bw2	7.9	0.52	4.66	1.08	64.5	50.43	2.91	0.19	0.67	54.2	84.1	0.3	4.51	17.32
Bss1	7.9	0.54	7.99	1.08	64.5	49.25	3.01	0.22	0.75	53.22	91.3	0.37	4.66	16.36
Bss2	7.9	0.44	5.53	1.09	65.9	49.41	6.27	0.17	0.72	56.57	85.9	0.25	9.52	7.88
Bss3	7.8	0.59	5.55	1.02	64.6	50.88	3.28	0.24	0.79	55.18	85.4	0.37	5.07	15.51
Bss4	7.9	0.59	4.62	1.1	64.1	49.68	5.02	0.22	0.71	55.63	86.7	0.34	7.83	9.9
Pedon 2 :Amravati (Sodic Haplusterts)														
Ap	8.1	0.8	14.24	1.84	52.1	43.82	3.74	0.14	1.04	48.74	93.5	0.27	7.17	11.71
Bw1	8.2	0.65	14.97	1.74	50.9	41.27	7.61	0.62	0.56	50.06	98.4	1.21	14.96	5.42
Bw2	8.4	0.56	14.02	1.89	51.9	39.92	6.5	1.79	0.51	48.73	93.8	3.44	12.51	6.14
Bss1	8.6	0.52	13.12	1.84	53.5	35.66	8.74	3.95	0.51	48.34	91.2	7.37	16.32	4.08
Bss2	8.7	0.48	12.93	1.88	52.6	30.93	9.37	6.77	0.46	47.53	90.4	12.88	17.82	3.3
BC	8.6	0.3	18.13	1.73	52.1	27.98	10.9	8.41	0.49	47.74	91.6	16.15	20.84	2.57
Pedon 3 : Akola (Sodic Haplusterts)														
Ap	8.1	0.94	8.7	1.77	60.5	41.47	6.15	0.26	1.76	49.64	82.7	0.43	10.16	6.74
Bw1	8.4	0.75	10.01	1.75	59.9	39.07	11.5	1.44	0.69	52.73	88	2.4	19.23	3.38
Bw2	8.6	0.68	8.36	1.72	63.4	35.23	10.8	3.48	0.93	50.47	86	5.93	17.1	3.25
Bss1	8.7	0.61	9.65	1.67	70.3	36.09	10.3	5.43	0.89	52.75	82.2	7.72	14.7	3.49
Bss2	8.6	0.56	9.99	1.94	64.2	30.03	14.8	7.21	0.92	52.95	84.1	11.45	23.05	2.02
Bss3	8.7	0.41	14.87	1.94	48.5	22.61	15.7	6.9	0.69	45.89	94.7	14.24	32.38	1.44

Table 4. *Some soil properties and yield of cotton of 32 Vertisols.*

District	Pedon No.	Soil classification	AWC (%)[a]	sHC (mm/hr)[a]	ESP Max [b]	Cotton yield (q/ha) [c]	PAWC (33-1500kPa) (mm m^{-1}) [a]	PAWC (100-1500kPa) (mm m^{-1}) [a]	PAWC (300-1500kPa) (mm m^{-1})[a]	PAWC 100-1500[a] &300-1500[d] kPa(mm m^{-1})
Nagpur	1	Typic Haplustert	20	17.7	1.2	13	257.0	123.5	35.8	123.5
	2	Typic Haplustert	18	7.7	4.7	17	221.3	110.9	26.5	110.9
	3	Typic Haplustert	16	17.8	2.6	13	195.3	86.0	33.1	86.0
	4	Typic Haplustert	20	4.2	11.2	9.5	234.5	115.0	26.6	115.0
	5	Typic Haplustert	20	10.6	3.6	18	234.9	109.3	30.5	109.3
	6	Typic Haplustert	18	14.0	0.5	14	213.3	108.6	33.0	108.6
	7	Typic Calciustert	15	6.2	2.5	9.5	175.5	82.4	25.9	82.4
	8	Typic Haplustert	19	13.5	2.3	10	231.9	107.1	31.1	107.1
	9	Typic Haplustert	22	16.0	0.4	17	259.9	122.9	111.7	122.9
Amravati	10	Sodic Haplustert	18	8.8	15.7	7.5	270.3	198.7	80.4	80.4[d]
	11	Aridic Haplustert	19	18.7	4.3	15	213.7	139.6	70.0	139.6
	12	Aridic Haplustert	13	15.7	0.8	16.6	144.4	89.8	23.2	89.8
	13	Aridic Haplustert	10	9.8	1.3	6.6	130.9	57.6	20.2	57.6
	14	Aridic Haplustert	13	15.5	1.1	15	156.9	100.7	29.4	100.7
	15	Sodic Haplustert	18	7.4	16.8	7.9	284.9	134.5	56.7	56.7[d]
	16	Aridic Haplustert	15	7.8	14.5	6.8	208.8	94.4	46.1	94.4
	17	Aridic Haplustert	15	10.7	2.3	12.5	185.1	95.8	53.7	95.8
	18	Sodic Haplustert	19	1.6	44.1	2.5	271.9	233.1	49.8	49.8[d]
	19	Aridic Haplustert	15	9.9	2.2	12	212.0	169.2	32.5	169.2
	20	Sodic Haplustert	17	0.6	28.7	3.5	268.5	140.1	62.6	62.6[d]
	21	Sodic Haplustert	18	4.2	16	6.5	249.9	109.1	36.0	36.0[d]
	22	Aridic Haplustert	20	7.5	10.6	6	296.3	248.7	123.3	248.7
	23	Aridic Haplustert	19	2.5	1.3	10	223.8	122.7	31.6	122.7
	24	Aridic Haplustert	18	3.4	1.1	11	221.4	120.1	39.8	120.1
	25	Aridic Haplustert	26	2.4	1.4	9.5	273.8	199.2	82.0	199.2
	26	Sodic Haplustert	15	0.9	15.8	6.5	179.4	156.4	5.9	5.9[d]
	27	Sodic Haplustert	8	3.7	23.3	7.5	111.3	95.5	13.1	13.1[d]
	28	Sodic Haplustert	20	2.4	26.2	6	230.9	102.1	42.1	42.1[d]
	29	Sodic Haplustert	19	11.0	12.8	7.5	217.5	102.6	90.5	90.5[d]
Akola	30	Aridic Haplustert	17	3.5	4.2	10	215.9	107.3	39.2	107.3
	31	Sodic Haplustert	18	1.1	19.9	6.4	218.6	115.4	43.5	43.5[d]
	32	Sodic Haplustert	22	10.3	7.7	9.5	218.7	126.9	113.8	113.8[d]

[a]Weighted mean in 0-100 cm depth of soil; [b] maximum value in 0-100 cm depth of soil; [c] seed + lint.; AWC, available water content; [d] PAWC at 300-1500 kPa for sodic soils, ESP:exchangeable sodium percentage; sHC: saturated hydraulic conductivity. Source : Balpande, 1993; Kadu, 1997, Vaidya, 2001.

by a significant negative correlation between yield and ESP (r= - 0.75, significant at 1% level). A significant positive correlation between yield and sHC (r= 0.694 significant at 1% level) indicates that a better hydraulic properties favour the yield of cotton (Table 5).

The subsoil sodicity impaired the hydraulic properties as evident from the significant negative correlation value between ESP and sHC (Table 5). ESP is an important factor which positively contributes to water retention but negatively to water movement (sHC) and yield of crop. In soils with high exchangeable Na$^+$, the water is held at higher tension and thus is unavailable to plants (Kadu *et al*., 2003) Thus the method to estimate PAWC at different tensions for non-sodic and sodic soils is justified and this way a positive correlation between PAWC and cotton yield could be obtained (Fig.1). This suggests that PAWC (determined as shown in this communication) needs to be favoured as an important biophysical parameter in evaluating rainfed Vertisols (without soil modifiers) for deep rooted crops.

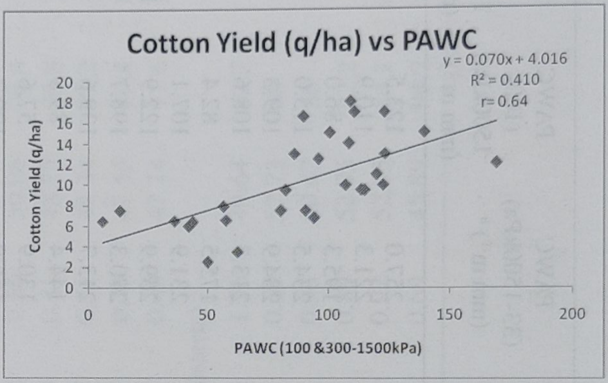

Fig 1. *Relation between yield of cotton and PAWC in Vertisols*

Conclusion

In deep cracking clay soils (Vertisols) hydraulic properties govern the movement

Table 5. Correlation between soil attributes and the yield of cotton

Sl. No.	Parameter A	Parameter B	'r' values
		Based on 32 Vertisols.	
1.	Yield of cotton (q ha^{-1})	AWC ^{a}	0.05
2	Yield of cotton (q ha^{-1})	PAWC^{a} (33-1500 kPa)	-0.21
3	Yield of cotton (q ha^{-1})	PAWC^{a} (100-1500 kPa)	-0.33
4	Yield of cotton	PAWC^{c}	0.653*
5.	Yield of cotton (q ha^{-1})	ESP ^{a}	-0.75*
6.	Yield of cotton (q ha^{-1})	sHC $^{b}_{max}$	0.694*
7.	ESP	sHC	-0.584*
8.	ESP	AWC	0.21

^{a} Weighted mean in 0-100 cm depth of soil; ^{b} maximum value in 0-100 cm depth of soil; ^{c} PAWC estimated at 100-1500 kPa and 300-1500 kPa for non-sodic and sodic soils, respectively. *Significant at 1% level.

of water in soil profile, and the exchangeable Mg^{+2} and Na^{+} ions restrict the release of water. These two factors, especially the ESP, influence the PAWC. Therefore, determination of AWC and PAWC considering moisture at 33 kPa. needs a relook. Instead, a pragmatic approach to estimate these two parameters would be to consider soil water held at 100 kPa for non-sodic soils and at 300 kPa for sodic cracking clay soils that contain no soil modifiers. PAWC estimated this way emerges out as one of the yield influencing parameters for evaluating Vertisols for the suitability of deep rooted crops.

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Leaching Behavior of Chlorothalonil, Chlorpyrifos and Pendimethalin in Soil: Effect of Soil Organic Matter and Clay

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Abstract: *Leaching behavior of chlorothalonil, chlorpyrifos and pendimethalinwas studied in Inceptisolwith normal, partially organic matter removed and clay fraction removed soil samples. In normal soil, the pesticidesadsorbed strongly to soil surfaces leading to low leaching. About 84-87% of the added pesticides were confined to the upper soil layer of depth 0-10 cm. In partially organic matter removed soil (about 50%), about 2.5-6% of the pesticides were found in leachates compared to ~2% in normal soil.Clay fraction controls the mobility behavior of pesticides greatly. In partial clay fraction removed soil (about 79%), the leachates were found to contain 5-25% of the added pesticides. Most pronounced effect of clay on leaching was observed in chlorothalonil. Chlorothalonil leached out faster than other compounds in soils in which clay fraction was removed. The organic matter plays a major role in the leaching behavior of pesticides.*

Key words: Leaching, organic matter, clay, chlorothalonil, chlorpyrifos, pendimethalin, soil column

After green revolution, consumption of pesticides increased tremendously and pesticide pollution is a major concern now a days. Soil acts as a sink for pesticides used in agriculture. The fate of pesticides in soils determines the pollution potential. Those pesticides which are immobile in the soil are less prone to cause pollution of ground water sources compared to mobile pesticides. How long the pesticide remains in the soil depends on how strongly it is bound by soil components and how readily it is degraded. It also depends on the environmental conditions at the time of application, e.g., soil water content (Manuel *et al.*, 2007). Alister *et al*. (2011) reported that soil organic matter, specifically the fulvic acid-humin fractions, affects the

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leaching of herbicides in soil and pesticide leaching was inversely related to soil adsorption, cation exchange capacity, humic substances content and herbicide *pKa.* The importance of organic matter in reducing the mobility of pesticide has also been reported by Ismail *et al.* (2009). Ngan *et al*. (2005) reported lower leaching of chlorothalonil and chlorpyrifos in the soils of Cameron Highlands. Understanding the spatial variability of herbicide sorption to soil is important in determining the bioavailability as well as leaching potential of the chemical across a field (Shaner *et al.* 2008). Sakaliene *et al.* (2007) reported slower mobility of pendimethalin in soils with high clay and low sand contents and faster mobility in soils with high sand content and low organic matter content. Aktar *et al*. (2009) reported that the residues of pendimethalin in column studies were predominantly confined to the upper soil layer (0-6 cm) because of the strong adsorption of chemical on the soil particles. The studies on leaching behaviour of a pesticide are useful for the prediction of the water contamination potential of the chemicals and for taking the proper control measures. Therefore, the present study was undertaken to determine the leaching potential of chlorothalonil, chlorpyrifos and pendimethalin as affected by soil organic matter and clay content.

Materials and Methods

Collection of soil

Surface soil sample (of an Inceptisol) was collected from research farm of Indian Agricultural Research Institute, New Delhi. The soil was air-dried by spreading it on aluminium sheet, ground, sieved through a 2 mm mesh screen and stored in plastic containers for further use. The physical and chemical properties were determined by standard procedures (Page *et al*. 1982 and Jackson, 1979) and are given in table 1.

Partial removal of organic matter and clay fraction from soil

The moist soil was washed with slightly acidic sodium acetate (NaOAc) buffer for efficient dispersion of soil and for the removal of soluble salts and exchangeable cations. The removal of soil organic matter was accomplished by the peroxidation treatment using 30% H_2O_2. H_2O_2 was added in small installments and stirred thoroughly to avoid overflow of the froth. The treatment was continued until the frothing subsided. The organic carbon content in the treated soil was determined by the procedure of Walkley and Black (1934). Clay fractions from the soils were removed by dry sieving method using 0.02 mm sieve. Clay fraction removed soils were stored in plastic containers for use.

Mineralogical characterization of soils

Mineralogical characterization was done by X-ray diffraction analysis. Clays (< 2 μm) were isolated from soil after ultrasonic treatment, without removal of cementing agents and following gravity sedimentation procedure (Jackson, 2005).

Table 1. *Salient properties of the test soil*

Properties	Normal soil	Partial OM removed soil	Clay fraction removed soil
pH	8.15	8.35	8.05
Organic carbon (%)	0.36	0.19 (50)	0.29 (19.4)
EC (dS/m)	0.23	0.23	0.21
Particle size distribution (%)			
Sand	54.4	54.4	63.1
Silt	23.3	23.3	31.2
Clay	22.3	22.3	4.7 (79.0)
Textural class		Sandy loam	

(Values in parenthesis indicate the % removal of organic matter and % removal of clay, respectively)

These were successively treated with 30% H_2O_2 and Citrate Bicarbonate Dithionate (CBD)extraction (Mehra and Jackson, 1960) to remove organic matter and sesquioxides, respectively. Clays after the removal of organic matter and sesquioxides were used for semi-quantitative clay mineralogical analysis by XRD. These clays were first saturated with magnesium and potassium and then the samples were mounted on a glass slide (2.5 cm × 4 cm). The Cu-Kα radiation and Ni filter were used in X-ray diffractometer(Model: Philips PW 1710) for measurement of integral width and full width at half maximum (FWHM) at 10 A°peak. Expanding clay minerals change their d-spacing substantially upon glycerol adsorption. Therefore, glycerol solvation was employed to detect 2:1 minerals after the Mg–saturation. To differentiate between vermiculite with other minerals and to get 2nd order peaks, samples treated with K were heated up to 550°C. Minerals were identified by the method of Wilson (1987) and estimated semi-quantitatively (Gjems, 1967). Mica was the dominant clay mineral (51%) followed by kaolinite (28%), vermiculite (13%) and interstratified minerals (8%) with traces of smectite and quartz. X-Ray diffractogram is presented in figure 1.

Pesticides

Analytical grade chlorothalonil (2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile) with 99.2% purity, chlorpyrifos (o,o-diethyl o-(3,5,6-trichloro-2-pyridinyl-phosphorothioate)with 99.5% purity and pendimethalin (N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine)with 98.3% purity were purchased from Sigma-Aldrich.

Purification of solvents/ reagents

AR grade solvents used in the experiment were distilled before use.Anhydrous sodium sulphate was

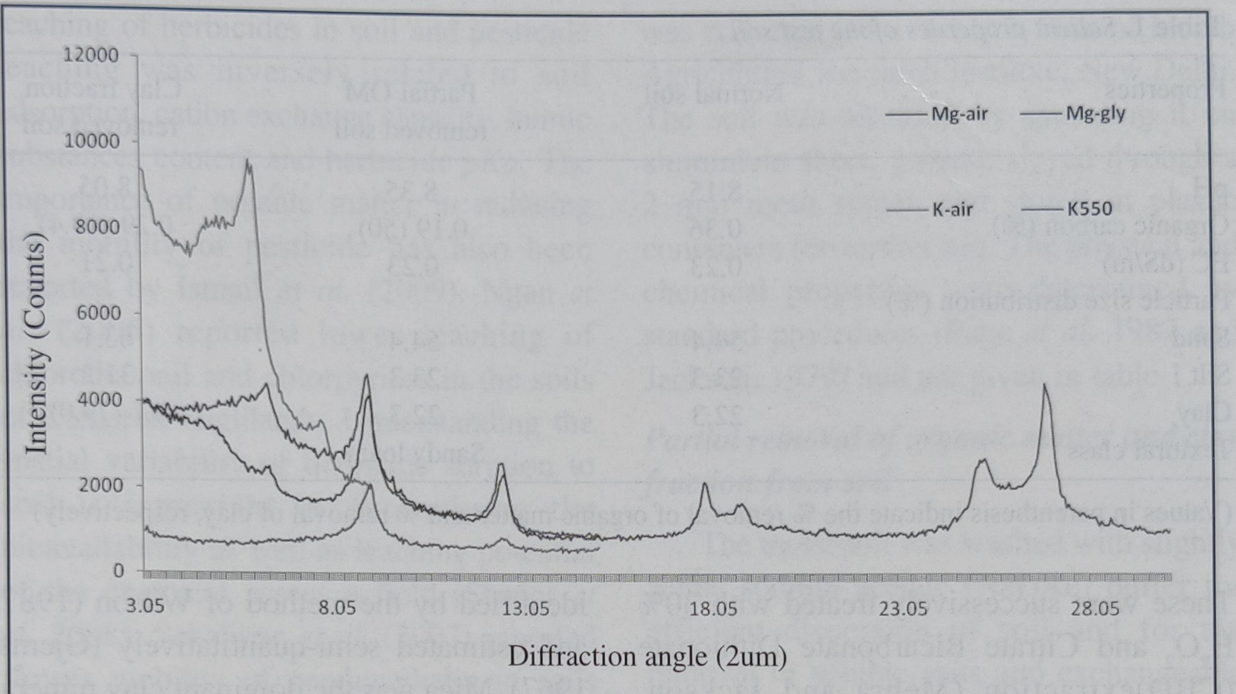

Fig. 1. X-ray diffractogram of clay fraction of Inceptisol from New Delhi

washed with acetone, dried, cooled and stored. Sodium chloride was also washed with acetone, dried in oven at 200 ºC and stored.

Leaching studies in packed soil columns

Soil samples were packed in polythene columns (50 x 2.28 cm) and filled upto 25 cm with Inceptisol normal soil, partially organic matter removed soil and clay fraction removed soil. Small holes were made at the lower ends of the columns to facilitate the collection of leachates. The lower ends of columns were dipped in water overnight to create a saturated condition. Excess water was drained off by hanging vertically. These packed columns were further used for conducting the leaching experiments. The leaching experiments were conducted in duplicate. 5 g of test soil was taken in a beaker and spiked with 5 mL of 10 µg/mL pesticide mixture to get 50 µg each of chlorothalonil, chlorpyrifos and pendimethalin in soil. The solvent was allowed to evaporate off naturally with intermittent stirring with a glass rod. The spiked soil was loaded uniformly at the top of the soil columns. The columns were leached with 200 mL water simulating a rainfall of 400 mm in instalments of 50 mL each. Leachates were collected time to time.

Analysis of leachates and soil cores for pesticides

Leachates samples were extracted by partitioning dichloromethane. The leachate samples were transferred to separatory funnel and diluted with 10% 50 ml NaCl solution. Dichloromethane (30 ml) was added, the contents were shaken for 3 minutes and allowed to stand undisturbed. After separation of layers, the lower dichloromethane layer was drained off in a volumetric flask. The process of extraction was repeated two more times. For removal of traces of moisture, the combined dichloromethane phase was passed through a layer of anhydrous sodium sulphate placed in a glass funnel.The dichloromethane extract was concentrated using rotary evaporator and residues were dissolved in measured quantity of hexane and analyzed in GLC equipped with ECD.

After completion of leaching with 200 mL water, the soil column was cut horizontally into 5 cm cores. The soil from each core was extracted by dipping and shaking method using acetone as solvent. To the soil, 2-3 drops of liquid ammonia was added to release the pesticides. After few minutes, about 50 ml of acetone was added and contents stirred intermittently for 20 minutes using clean glass rod. The supernatant was passed through a Whatman filter paper (Number 1) and collected in a clean conical flask. The process of extraction was repeated two more times using fresh 50 mL acetone each time. During the final extraction, whole amount including soil was transferred. The combined extracts were concentrated to remove acetone, and aqueous phase was diluted with 10% NaCl solution and partitioned with dichloromethane similar to leachate samples. Dichloromethane extract was concentrated to dryness. The residues dissolved in known quantity of distilled hexane and analyzed in GLC. Analysis of the selected pesticides was carried out on Varian CP-3800 gas chromatograph, equipped with electron capture detector (^{63}Ni) and CP-SIL 5CB (25m x 0.25 mm internal diameter, 0.25 µ film thickness) column. Oven was heated to 170°C and held for 1 minute, and then the temperature was increased to 260° @ 10°C per minute and held for 2 minutes. The carrier gas was nitrogen (IOLAR I grade) at a flow rate of 2 ml/min. Under this programming, retention times of chlorothalonil, chlorpyrifos and pendimethalin were 5.23 min, 6.5 min and 7.08 min., respectively.

After analysis with GLC, the residue/ amount was calculated as follows:

$$\underset{(\mu g/g \text{ or mL})}{\text{Concentration}} = \frac{\text{Peak area of sample} \times \text{concentration of standard } (\mu g\ g^{-1}) \times \text{Vol. of extract (mL)}}{\text{Peak area of standard} \times \text{Weight (g)/ volume (mL) of sample processed}}$$

Results and Discussion

Leaching behavior in normal soil

The residues of pesticides, chlorothalonil, chlorpyrifos and pendimethalin in leachates of the tested soils are presented in table 2. It is clear from the data that only less than 2% of the added pesticides were detected in leachates of normal soileven after passage of 200 ml water

Table 2. *Residues in leachates of tested soils*
Amount added : 50 µg of each pesticide

Water added (ml)	Equivalent rainfall (mm)	Residue in leachate (µg)								
		Normal soil			Partial OM removed soil			Clay fraction removed soil		
		CHTNL	CHPFS	PEDMN	CHTNL	CHPFS	PEDMN	CHTNL	CHPFS	PEDMN
50	100	ND	ND	ND	ND	ND	ND	0.595	ND	ND
100	200	ND	ND	ND	0.66	ND	ND	2.12	ND	ND
150	300	0.265	ND	ND	1.03	0.14	0.56	3.17	0.81	1.19
200	400	0.705	0.95	0.95	1.22	1.08	1.05	6.77	1.93	2.10
Total	0.97	0.95	0.95	2.90	1.21	1.60	12.65	2.74	3.29	

CHTNL – chlorothalonil, CHPFS- chlorpyrifos, PEDMN-pendimethalin

(equivalent to 400 mm rainfall). No residue of any of the pesticides was detected in leachate till 100 ml fraction. The chlorothalonil residues were detected in 100-150 ml leachate fraction and chlorpyrifos and pendimethalin residues appeared only in 150-200 ml leachate fraction.

After a passage of 200 ml water (equivalent to 400 mm rainfall), pesticide residues got distributed throughout the column (Table 3). However residues decreased with increasing soil depth. The concentrated band (42.2-43.8 µg, 84.5-87.5% of the added) was present in top 0-10 cm depth and very low amount was detected in lower depths.

The results showed that chlorothalonil, chlorpyrifos and pendimethalin are having low mobility in soil and thus have negligible potential to contaminate ground water. Similar results have also been reported by Ngan *et al.* (2005) for chlorothalonil, Racke (1993) for

Table 3. *Residues of pesticides in soil at different depth in column*

Soil core (depth cm)	Residue in soil(µg)								
	Normal soil			Partial OM removed soil			Clay fraction removed soil		
	CHTNL	CHPFS	PEDMN	CHTNL	CHPFS	PEDMN	CHTNL	CHPFS	PEDMN
0-5 cm	19.265	20.545	24.055	11.72	18.21	19.895	5.725	18.32	17.49
5-10 cm	23.17	21.72	19.70	25.50	21.17	22.00	14.47	20.22	21.13
10-15 cm	5.14	4.26	3.44	8.73	6.14	3.89	10.90	5.94	5.40
15-20 cm	1.22	1.19	1.19	2.06	2.27	1.39	7.58	2.12	3.14
20-25 cm	0.71	0.86	0.43	1.10	1.03	0.43	4.44	1.50	1.38
Total	49.50	48.58	48.80	49.09	48.81	47.59	43.11	48.09	48.53

CHTNL – chlorothalonil, CHPFS- chlorpyrifos, PEDMN-pendimethalin chlorpyrifos and Traub-Eberhard*et al.*, (1994) for pendimethalin. Singh *et al.*, (2013) reported the restricted leaching of lindane in soils with high organic matter content and clay content.

Leaching behavior in partially organic matter removed soil

The removal of organic matter from soil resulted in increased leaching of all the pesticides. The amount in leachate increased from 2% of the added pesticides in normal soil to ~2.5-6.0% in organic matter removed soil after passage of 200 ml water (equivalent to 400 mm rainfall). Among the pesticides, maximum effect was observed in case of chlorothalonil.

Similar to normal soil, the pesticide distributed throughout the column. However, there was more downward movement than normal soil (Fig. 2). Concentrated band of pesticides moved down to 5-15 cm depth in organic matter removed soil column. Pesticides are held up by adsorption which restricts the movement. The H_2O_2 treatment of soil resulted in removal of about 50% of the organic matter thus providing lower number of sites/area for adsorption and consequently more downward movement. Similar effect of organic matter has also been reported by Ismail *et al.,* (2009). Loganayagi and Ramesh (2014) Also reported higher mobility of sulfosulfuron

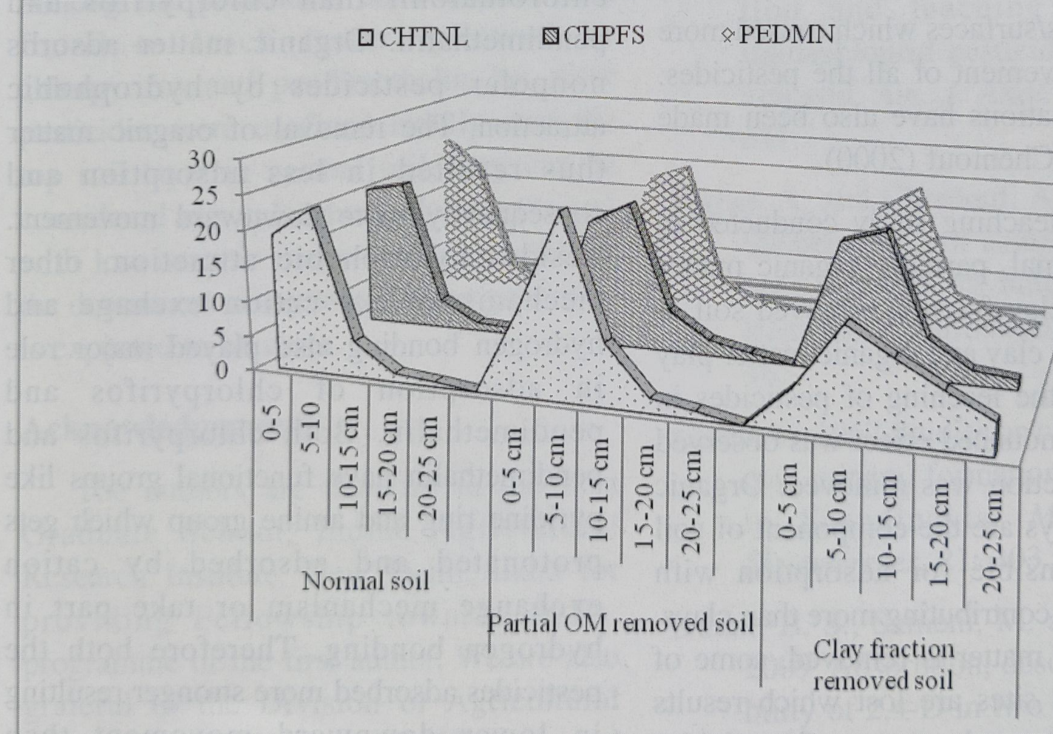

Fig. 2. Distribution of pesticides in soil columns

and and its metabolite aminopyrimidine in soils with low soil organic carbon content.

Leaching behavior in clay fraction removed soil

In clay fraction removed soil column, the amount of pesticides in the leachate was more than the normal soil column amounting to about 5-25% of the added. The analysis of soils at different depths revealed that the pesticides got distributed throughout the column and concentrated band of pesticides moved down to 5-20 cm depth (Fig. 2). The dry sieving of soil with 0.02 mm sieve resulted in removal of about 79 % of clay. However alongwith clay about 19% of the organic matter was also removed. The partial removal of clay fraction resulted in drastic reduction in adsorption sites/surfaces which caused more downward movement of all the pesticides. Similar observations have also been made by Farran and Chentouf (2000).

From the leaching study conducted in Inceptisol normal, partially organic matter removed and clay fraction removed soil, it is revealed that clay and organic matter play major role in the leaching of pesticides in soil. More pronounced effect was observed when clay fraction was removed. Organic matter and clays are the component of soil mainly responsible for adsorption with organic matter contributing more than clays. When organic matter is removed, some of the adsorption sites are lost which results in higher downward movent of pesticides than the normal soil. Similar observations have also been made by Yu and Zhou (2005) who stated that about 34-46% reduction in adsorption capacity of methamidophos was observed after the removal of soil organic matter. Clays have high surface area and exchage sites. Removal of clay fraction by dry sieving resulted in not only removal of clay but also the oganic matter associated with it. Thus loss of adsorption sites was much more than organic matter removed soil where some new sites appeared due to removal of organic matter from clay surfaces. Therefore effect was felt much more in clay fraction removed soil. Amongst the pesticides, the effect of removal of organic matter and clay was more pronounced in the leaching of chlorothalonil than chlorpyrifos and pendimethalin. Organic matter adsorbs nonpolar pesticides by hydrophobic attraction. The removal of oragnic matter thus resulted in less adsorption and consequently more downward movement. Besides hydrophobic attraction, other mechanisms like cation exchage and hydrogen bonding also played major role in adsorption of chlorpyrifos and pendimethalin. Both chlorpyrifos and pendimethalin have functional groups like pyridine ring and amine group which gets protonated and adsorbed by cation exchange mechanism or take part in hydrogen bonding. Therefore both the pesticides adsorbed more stronger resulting in lower downward movement than chlorothalonil. Leaching of pesticides were found to follow the same trend as that of desorption. The effect of clay and organic matter on leaching has earlier been reported by Sakaliene *et al.* (2007). These results are also in conformation with Aktar *et al.* (2009). Lesser leaching of imidachloprid in alluvial soils with less organic matter and sandy texture was also reported by Bajeer *et al.* (2012).

The leaching study conducted in Inceptisol before and after removal of organic matter and clay fraction suggests that organic matter and clays play major role in retaining the pesticides in top soil thus restricting their downward movement. In soil the major factor which affected leaching behavior of pesticides is clay. Among the pesticides, chlorothalonil was found to leach faster followed by chlorpyrifos and pendimethalin. As these pesticides were confined mainly onto the top soil layer in normal soil, they can be considered as non leachers. However in soil with low oragnic matter and clay content, the downward movement of these pesticides is expected to be more.

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Textural Control on the Weathering of Basic Igneous Rocks: A Micro-morphological Approach

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Abstract: *The micro-morphological studies on the rock weathering suggest that basalt shows strong mechanical fracturing during the early stages of weathering. In basalts labradorites are slightly to moderately altered while augites are moderately to strongly altered. In their most advanced stage of weathering the labradorites and augites are highly or even completely altered thereby indicating higher to highest degree of alteration. In the initial stages of weathering of dolerite; labradorites and augites still retain their identity with labradorite showing nuclei of alteration at their centers. However during the more advanced stage of weathering the plagioclases (labradorites) and augites rarely show preservation of diminishing cores of fresh rocks. Formation of enormous clays and related minerals indicate that the dolerite has been strongly to completely altered. During an early stage of weathering of gabbro, labradorite is seen to be altered rapidly than augite. However, in the most advanced stage of weathering the augite is highly altered than labradorite. Camptonite (basic lamprophyre) in its early stages of weathering is not much altered although the minerals are seen to be intensely fractured. However in the most advanced stages of weathering of camptonite the groundmass is seen to be highly altered while labradorite and augite crystals have become highly dirty with the formation of clayey material indicating strong to complete alteration. It is seen that rocks with high amount of glass (e.g. basalt and camptonite) weather more rapidly than the rocks with low glass content and the fine- grained rocks weather more slowly than the coarse-grained rocks. Gabbro shows effects of both mechanical and chemical weathering. In case of the fine-grained rocks like basalt, as they contain plenty of glass, there is a little scope of expansion and contraction of minerals due to their tiny crystals.*

Key words *:* Rock weathering, Basic rocks, Lithological control, Micromorphology, India.

Introduction

Micromorphology refers to microscopic observations, usually in thin sections. Micromorphology methods are useful since these help identify fabrics and composition of soils and weathered materials, which may be used to distinguish one soil from another (Stoops, 2003). Micromorphology is also used in conjunction with modeling to reconstruct climate (Matviishina, 1982; Lacka *et al.*, 2007; Grigor'eva *et al.*, 2012;

Beverley *et al.,* 2014). There are both qualitative and quantitative methods of this technique (Kemp, 1999; Sheldon, 2003). Micromorphology is the description, interpretation, and measurement of components, features and fabrics in the weathered rocks, soils and palaeosols, at the microscopic level (Bullock *et al.,* 1985). Soils and saprolites, which result from the chemical weathering of the parent rocks often register variations of environmental changes in time and space. Soil chronosequences register pedogenic change over time-scales ranging from years to millions of years and they help in testing rival theories of pedogenesis. The heterogeneity of such alteration mantles resulting from the complex interplay between various physical and chemical conditions makes it difficult to interpret the weathering history. Micromorphology is a powerful tool to discriminate different processes through the identification of parageneses by *in situ* approach. For unlocking the mineralogical record in soils, palaeosols and saprolites an integrated approach based on micro- and nano-morphological observations, combined with spatially resolved chemical, isotopic and mineralogical analyses is required. Micromorphology is also considered as a proxy for climate change to establish climatic control on the rock weathering in the geologic past as well in the Holocene (Mehrjardi *et al.,* 2009; Rellinia *et al.,* 2013). These studies help in demonstrating some of the pathways of formation of clay minerals in response to specific climatic conditions. An advantage of micromorphology is that it is a low-cost methodology that requires only preparation of standard petrographic thin sections and access to microscope (Driese and McKay, 2004). In India although micromorphology of soils and palaeosols has been studied in considerable detail (Bronger, 1994; Achyuthan, 2004; Srivastava and Parkash, 2002; Srivastava *et al.,* 2010) the micromorphological studies of weathered rocks are seriously overlooked. In the present paper the textural control on the weathering of basic igneous rocks have been attempted which brings about the different weathering features during weathering under similar climatic conditions.

The weathered rocks are the most ubiquitous features of the earth's surface and the breaking down of the minerals in the process of weathering is governed not only by their chemical composition but also by their physical properties. Besides chemical composition and the crystal structures of minerals, parameters like crystal size, crystal shape, crystal perfection also control the rate of mechanical breakdown and chemical alteration of the minerals (Sayyed, 1996). Minerals with bigger crystals weather at a slower rate than the smaller crystals. In view of this the micro-morphological studies of the minerals of fresh and unaltered rocks along with their weathering products were undertaken. For the petrographic studies, the thin sections of the representative rocks both fresh and their weathered products were prepared. In case of the weathered and friable materials necessary firm cementing were done by penetrating biding substance i.e. Canada balsam in to the material before it is mounted on a glass slide.

Basalt weathering

The basalts are fine grained volcanic rocks showing inequigranular texture: the most common being the intergranular and intersertal texture. The fresh unaltered basalts under microscope shows clusters of subhedral plagioclase lathes embedded in fine crystalline, cryptocrystalline or glassy groundmass. The subhedral plagioclase laths showing lamellar twinning and seen to occur in clusters of crystals, thereby imparting triangular or polygonal patterns leading to the development of intergranular or intersertal texture. During the early stages of weathering, basalt shows well preserved rock structure wherein many minerals are partly or completely altered. Moreover, development of pores and spaces and formation of secondary materials including coatings are seen. In the earlier stages of weathering the basalts are subjected to strong mechanical fracturing with development of granular, intergranular and intragranular fractures. The degree of alteration of micro-phenocrysts of plagioclase during the early stage of basaltic weathering varies from slightly to moderately altered. However the groundmass plagioclase are moderately or strongly altered. During the early stages of basaltic weathering the augites are seen to be altered along the crystal borders, cleavages and fracture planes. The pattern of alteration shown by augite crystals occurring as micro-phenocrysts and in groundmass is of pellicular, linear or reticulate (Fig. 1) types (FitzPatrick, 1984). On the basis of degree of alteration, the augites from the basalts under study, are found to be either moderately or strongly altered. It is, also observed that the augite micro-phenocrysts are comparatively less affected than the tiny augite crystals in the groundmass. Pellicular alteration pattern is prominently observed in the groundmass augites, while reticulate and linear patterns of alteration have been exhibited by augite micro-phenocrysts.

The basaltic rocks in their most advanced stage of weathering show partial preservation of rock texture. The rock is

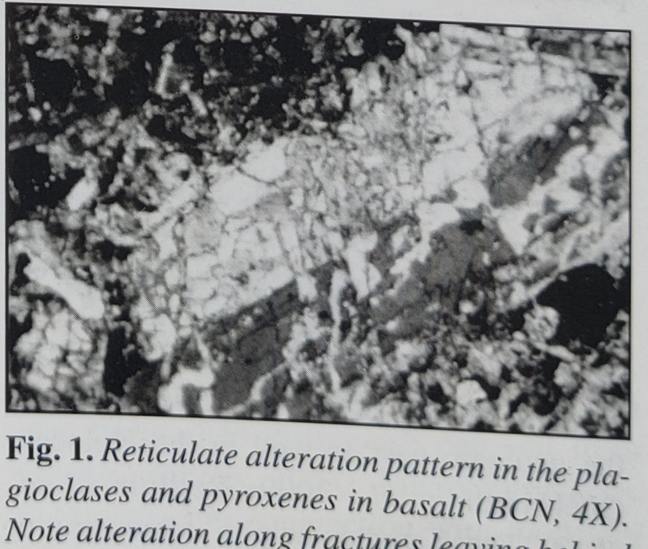

Fig. 1. *Reticulate alteration pattern in the plagioclases and pyroxenes in basalt (BCN, 4X). Note alteration along fractures leaving behind diminishing cores of fresh plagioclase.*

highly altered and the fragments that escaped chemical weathering show intense mechanical fracturing and staining by iron oxide. The plagioclases and augites are highly to completely altered thereby indicating pretty high degree of alteration of the basaltic rocks. The groundmass constituted of fine plagioclases and augite crystals, the crypto-crystalline glassy materials is totally altered to clays imparting cloudy and dirty appearance. Very dark, more or less rounded grains of opaque minerals are seen floating in the highly altered groundmass.

Dolerite weathering

The dolerites are composed chiefly of plagioclases and pyroxenes. Pyroxenes are mainly augite, and the plagioclases are represented by labradorite (An60-An65). In addition to these two minerals, the opaques constitute appreciable portion of the doleritic rock, the most common being ilmenite and magnetite. The plagioclases and augites respectively occur in the form of laths and tabular crystals constituting both the groundmass and micro-phenocrysts. The labradorite in dolerites is commonly zoned and generally occurs as clear colourless crystals while the augites in dolerite show uniform optical characters with occasional simple twinning and hour-glass structure in a few of the thin sections. The dolerites distinctly show differences in their physical and chemical characteristics both at the initial and advanced stages of weathering. The dolerite minerals during their initial stages of weathering have developed those features that show release of stresses and strain energy within the rock with incorporation of water. The features include fissures and fractures developed on account of mechanical fracturing, formation of clays and related minerals along cleavages (Fig. 2), fractures and crystal borders. During the initial stages of weathering the dolerite rock still shows well preserved rock structure without much obliteration of original igneous textures and mineralogy. The doleritic minerals, namely, labradorite and augite still possess their identity in terms of their physical and chemical characteristics. However, linear, pellicular and reticulate alteration patterns (FitzPatrick, 1984) have been noticed in these minerals. Labradorite show nuclei of alteration at their centers and as a result the fresh minerals of dolerite became cloudy, dirty and clogged with clods at several places.

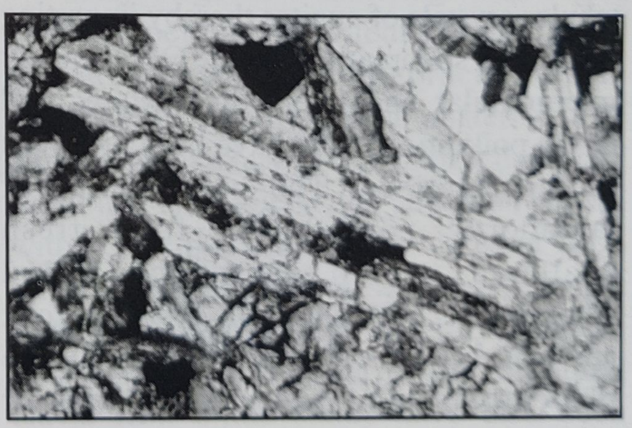

Fig. 2. *Highly mechanically fractured plagioclases and pyroxenes in dolerite showing linear alteration pattern (BCN, 10X).*

The more advanced stage of chemical weathering of dolerite the highly altered plagioclases and augites have totally lost their crystallographic/mineralogical characteristics due to their intense alteration. Preservation of diminishing cores, in both augites and plagioclases, is rarely seen. The weathered product is highly oxidized and seen to be stained with iron oxides. Formation of clays and related minerals is enormous, especially along the cleavages, fractures and crystal borders. It is, thus, seen that the dolerites have been strongly altered (75-97.5%) to completely altered (more than 97.5%) during their most advanced stage of weathering.

Gabbro weathering

The gabbroic rock is medium to coarse grained and holocrystalline rocks showing inequigranular texture, the most dominant being the ophitic texture. The gabbro is composed of subhedral laths of plagioclases completely or partially enclosed within the tabular crystals of augites thereby imparting ophitic to subophitic texture. Occasionally intergranular and intersertal textures and rarely poikilitic texture have been observed in thin sections. The plagioclases of labradortic composition from fresh unaltered gabbro appear clear and colourless. The augites of gabbroic rock are pale brown coloured showing feeble pleochroism and occur as tabular or prismatic plates. In addition gabbro shows the presence of appreciable amounts of opaques, the dominant being ilmenite and magnetite which occur in the form of skeletal grains floating within the plagioclases and augites. Gabbro shows well preserved rock structure during its early stage of weathering. The minerals are partially or completely altered. Pores and spaces are seen. Secondary minerals are found and iron oxide staining and/or coating are seen along the cleavage or fracture planes and crystal borders. Similarly the minerals are seen to be highly mechanically fractured with the development of granular, intergranular and intragranular fractures (Fig. 3). Both the plagioclases and augites show reticulate network of fractures (FitzPatrick, 1984) along which the intensity of chemical alteration is very high. The effects of alteration are also seen in the central parts of augite and labradorite crystals. During the early stages of weathering the laths of plagioclases appear turbid and dull with stable nuclei of alteration (Fig. 4). The plagioclases are seen to alter mainly along fracture, cleavages and other weak lines thereby exhibiting linear pattern of mineral alteration. The pellicular pattern of alteration observed in augite has left relatively unaltered core at the center with the formation of alteration rind (Fig. 5) especially in prismatic sections. The longitudinal sections of augite show linear alteration pattern. On the basis of degree of alteration of augite and labradorite the gabbros are fresh or nearly fresh or slightly altered during their early stages of weathering. Between labradorite and augite, labradorite is seen to be altered

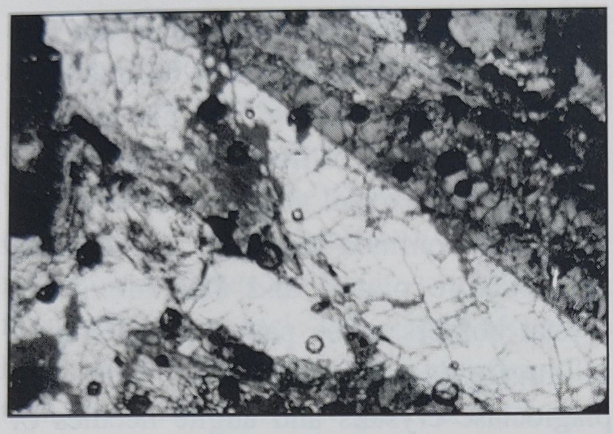

Fig. 3. *Highly mechanically fractured plagioclases and pyroxenes in gabbro (BCN, 4X). Note: Granular nature of fractures, alteration of minerals along cleavages, fractures and borders.*

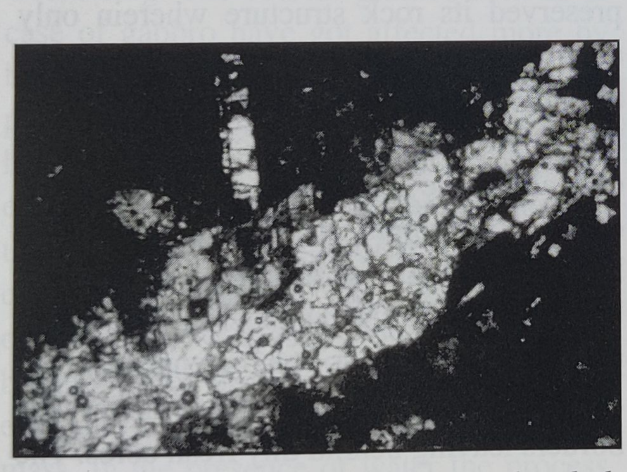

Fig. 4. *Highly mechanically fractured and altered plagioclases in gabbro (BCN, 6.3X). Note: Several nuclei of alteration in plagioclases, alteration along fractures and cleavages.*

rapidly than augite during the early stages of the weathering. However, in the most advanced stage of weathering the augite is seen to alter rapidly than labradorite. This has been associated with the chemical composition of mineral, especially the calcium content. The calcic core of labradorite thus gets altered rapidly initially.

Fig. 5. *Basal section of augite in gabbro showing dark alteration rind around it and also at its center (IPL, 4X). Note: The presence of yellowish green chlorite and greenish clay*

In the most advanced stage of gabbroic weathering, the augites and labradorite have been seen to be altered simultaneously and equally, the degree of chemical alteration being much more when compared with the early stage of weathering. The augite exhibits pellicular, reticulate and linear alteration patterns with practically no diminishing cores of fresh material. The labradorite crystals also exhibit a dominant linear and feeble pellicular alteration pattern with very small diminishing cores of fresh mineral (Fig. 6). Both these minerals appear dirty and cloudy with the formation of greyish brown to dark brown coloured clays. Iron oxide stains have also been profusely observed along the cleavage of the minerals. The augites show very thick alteration rinds composed chiefly of iron

Fig. 6. *Highly mechanically fractured and chemically altered plagioclase in gabbro showing diminishing cores of unaltered material ((BCN, 6.3X). Note: Totally alterd plagioclase and pyroxene grains.*

oxide and clays. The opaques, on the other hand do not show much change in their physical and chemical properties, both during the early and the most advanced stages of weathering. On the basis of the degree of alteration the gabbro is moderately to strongly altered.

Camptonite weathering

Camptonite showing porphyritic texture has well developed large augite phenocrysts set in a fine grained brownish groundmass composed chiefly of tiny laths of plagioclase, granules of iron oxide and fine needles of augite. In addition to these three minerals, euhedral crystals of olivine have also been recorded in some thin sections. The camptonite thus shows dominance of mafic minerals. Camptonite in its early stages of weathering shows some effects of chemical alteration and mechanical fracturing, however, the minerals are not much altered but are seen to be intensely fractured. The augite crystals exhibit reticulate network of fractures (FitzPatrick, 1984). The chemical alteration of augite is seen to be confined largely to its cleavages and fracture planes and also along the crystal borders. The pattern of alteration in augite is of linear type. The tiny plagioclase crystals and augite needles of groundmass are seen to be altered more than the augite phenocrysts.

In the most advanced stages of weathering, the camptonite has partially preserved its rock structure wherein only augite phenocrysts can be very well identified. The groundmass is seen to be highly altered. The plagioclase and augite crystals in the groundmass have lost their optical characters and became dull and highly dirty with the formation of brackish brown coloured clayey material. The augite phenocrysts have also been intensely altered along cleavages, fracture planes and crystal borders leaving behind tiny fresh cores. The augite crystals show dominance of reticulate and pellicular alteration pattern. Thus the degree of mineral alteration during the most advance stage of chemical weathering is very high and hence camptonites are strongly to completely altered.

Conclusions

The finely crystalline rocks weather more slowly than the coarser ones as the intergranular surface area decreases with increasing grain size which therefore requires more energy to disintegrate finer grained rocks (Birkeland, 1984). However this is not always true as the rocks like basalts and camptonite which contain large quantities of glassy or non-crystalline materials weather at faster rate than the finely crystalline rocks. Thus the rocks with high amount of glass weather more rapidly than the rocks with low glass content and the rocks with finer grain size weather more slowly than the rocks with coarser grain size. The crystal size and glass content of the rock defines the type and nature of weathering. The coarser grained rock as in case of gabbro have got affected more by both mechanical and chemical weathering processes. The igneous minerals, as they have different co-efficient of expansion, expand and contract at different rates on their exposure to repetitive heating and cooling processes. This leads to the development of cracks along their crystal borders which provide channel ways for an easy entry of percolating water into rock mass. In the presence of water the process of chemical alteration gets accelerated as it requires little energy for mineral decomposition. In case of the fine grained rocks like basalts, as they contain plenty of glass, there is a little scope of expansion and contraction of minerals due to their tiny crystals. This, however, leads to the development of rind on the rock surface on account of the chemical alteration. The alteration layer gradually migrates deeper down into the rock with passage of time; ultimately developing into several sets of weathering layers representing advancing weathering fronts towards the central portion of the rock leaving more advanced weathering layers behind.

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Spectral, Chemical and Physical Characterisation of Mustard Stalk Biochar as Affected by Temperature

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Abstract: *Conversion of agricultural residue to biochar and its application to soil has been accepted as a novel approach to sequester carbon, improve soil fertility and reduce environmental pollution. Application and impact of biochar depends on its intrinsic properties which in turn depend on the pyrolysis conditions. Mustard stalk was pyrolysed at 400 °C (MSB4), 500 °C (MSB5), and 600 °C (MSB6) through slow pyrolysis process to examine the effect of temperature on biochar properties. Mass recoveries of biochars decreased while pH, EC, calcium carbonate equivalent (CCE), ash content, bulk density and particle density increased with increase in pyrolysis temperature. MSB4, MSB5, and MSB6 had pH 8.7, 10.1 and 11.0, respectively and the EC values of the biochar were 2.41dS m^{-1}, 3.25 dS m^{-1} and 4.76 dS m^{-1} in the same order. The CCE of the biochar increased from 19.06 for MSB4 to 34.38 for MSB6. The C recovery efficiency of biochar was around 50%. Though the total P content in biochar increased with increase in pyrolysis temperature, the water and acid soluble P content decreased. The major inorganic minerals present in the biochar identified by X-ray diffraction analysis were quartz (SiO_2), sylvite (KCl) and calcite ($CaCO_3$). Infrared spectroscopy analysis of biochars samples indicated the presence of CO_3^{2-}, aromatic C=O ring and hydroxyl group (^-OH). The scanning electron micrograph clearly indicates the presence of highly porous structure in biochar. The low temperature mustard stalk biochar could be used as a good source of P and K in P and K deficient soil, and high temperature biochar (MSB6) is recommended as a liming material for reclamation of acid soil.*

Key words : Mustard stalk biochar, pyrolysis temperature, nutrient content, XRD, Spectral Characters

Biochar or black carbon gained importance since the identification of the so-called *terra preta* by the late Wim Sombroek in the Amazon River basin area, Brazil. Black carbon is a term reserved for the spectrum of chemical–thermal solid conversion products preparedfrom carbonaceous materials, which could be

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biomass or fossil fuels (Masiello *et al.,* 2002) and biochar is a recent term intently used for the materials produced from different residues and waste products in relation to carbon sequestration and soil management issues (Lehmann *et al.,* 2006). Recently the strong attention of researchers in biochar is based on some interesting aspect of it. Firstly, it sequester carbon in soil, stabilize native soil carbon thus negatively impacting global climate change. Secondly, biochar increased nutrient availability due to its capacity to hold nutrient against loss in soil and high nutrient concentration as a result of some fundamental properties (Lehmann and Joseph, 2002). Biochar has also been investigated as an adsorbent for various environment pollutant including heavy metals and pesticides (Ahmad *et al.,* 2014). The uses of biochar for specific purpose primarily depend on its intrinsic properties. The raw biomass feedstock and the pyrolysis condition is the regulating agent for determining specific properties to the resulting biochar, like ash content, its elemental content compositionand concentration, density, and hardness (Spokas *et al.,* 2012). Biochar can be prepared from a series of materials like wood chip, agricultural waste, compost, sewage sludge and many other carbonaceous materials via through slow to intermediate pyrolysis process. In literature pyrolysis temperature varied from 200-900 °C with heating rate ranging from 2.5 to 20 °C min^{-1}. The feedstock nature is more important in determining biochar character than pyrolysis temperature for various livestock manure based biochar in a slow pyrolysis process (Cantrell *et al.,* 2012) while the pyrolysis temperature is important in shaping biochar character than rate of heating for mustard biochar (Karaosmanoglu *et al.,* 2000).

Rapeseed and Mustard is the second most important oilseed crop in terms of production and area coverage after soybean in India among other nine oilseeds (MoA, 2013). It occupies 6.1 M ha with oilseed production to the tune of 6.89 Mt. The 50% of mustard stalks are available as surplus besides their major uses as domestic fuel, out of their total stalk generation of 12.4 Mt. In this context, conversion of mustard stalk into biochar will be an option for its sustainable use in agriculture and allied sector. The prospect of mustard stalk biochar (MSB) is promising as biofuels due to increased carbon content and less polluting possibility than lignite coal (Karaosmanoglu *et al.,* 2000). The detail characteristics of MSB are very important to decide its potential use in agriculture and energy sector for environmental studies. Therefore, the effect of pyrolysis temperature on characteristics and nutrient values of MSB was studied.

Materials and Methods

Mustard stalk, collected from the IARI field was cut into small pieces of 4-5 cm and sundried for couple of days to get constant weight and devoid of extra moisture. Biochar was prepared at 400ºC (MSB4), 500 ºC (MSB5), and 600 ºC (MSB6) in an electrically operated temperature (3 ºC per minute) controlled biochar machine under nitrogen atmosphere. The machine was allowed to cool down under natural cooling process. Biochars were ground with the help of wooden pastel and mortar and passed through 2 mm sieve and 0.5 mm sieve for subsequent analysis.

The pH and EC of biochar in water was determined at 1:20 (w/v) ratio after continuous shaking over 1 h. Calcium carbonate equivalent (CCE) of the biochar was determined by the AOAC method 955.01 which was recommended for determining ash alkalinity with required modification (AOAC, 1999). In brief, 1 g biochar was boiled in 50 ml 0.5 N HCl for five minutes in a 250 ml conical flux. After cooling, the suspension was filtered with whatman no 42 and the filtrate was titrated with 0.25 N standard NaOH solution using phenolphthalein as an indicator and CCE was calculated.

Biochar bulk density (Core method), particle density (water pycnometry) and saturated water holding capacity (Keen Rackzowski box) was measured. Water soluble ions were determined by suspending 0.2 g of biochar in 100 ml MilliQ water for overnight following one hour shaking. Filtrate obtained for determining CCE was used to measure acid soluble ions. Two hundred milligram of biochar and mustard stalk were digested in Microwave digester following total elemental analysis in ICP-MS (Perkiln Elmer, Germany). Total content of carbon (C) and nitrogen (N) in mustard stalk and biochars were determined directly by dry combustion on CHN analyzer.

The biochar samples were subjected to X-ray diffractogram using Ni-filtered Cu-Kα radiation at a scanning speed of 1.5°2θ/min in a Philips diffractometer, (Model 1710), while operating at 40 kV and 20 mA. Fourier transformed infrared spectroscopy (FTIR) of the powdered samples was carried out by using the Bruker: ALPHA, FTIR/ATR system (Typically 24 scans, Resolution- 4cm^{-1}). Samples were scanned in the region of 4000-400 cm^{-1}. Scanning electron microscopy (SEM) performed with Zeiss EVOMA 10 Scanning Electron Microscope after 24 mm coating the samples by alloy of palladium and gold. Energy-dispersive X-ray spectra (EDX) were also collected to analyze elemental composition of biochar surface in qualitative basis.

Results and Discussions

Physical and chemical characteristics

Mass recovery of the mustard stalk biochar prepared at 400 ºC, 500 ºC, and 600 ºC were 34.21%, 31.03%, and 28.63%, respectively. In contrast to the mass recovery, total ash content of biochar increased with increasing temperature

(Table 1). This contrasting phenomenon can be explained by the fact that higher temperatures increase the loss of carbon, oxygen and hydrogen in the form of CH_4, H_2 and CO from the mustard stalk residue and greater condensation of aliphatic compounds into aromatic structure with minimal loss of mineral elements constituting ash throughout the temperature range (Chen *et al.*, 2008). The pH and EC of the biochar samples increased gradually with increase in temperature (Table 1). MSB4, MSB5, and MSB6 indicated pH 8.7, 10.1, and 11.0, respectively. The higher EC value of the biochar (2.41 to 4.76 dS m^{-1}) could create problem if it is applied to soil at higher rates (20-40 tones ha^{-1}) (Lehmann and Joseph, 2002). The increasing trend was also observed for CCE of the biochar (19.06 for MSB4 to 34.38 for MSB6 (Table 1). The increased ash content of biochar is the reason behind higher pH, EC and CCE of biochars produced at higher temperature. Bulk density and particle density of biochar increased while saturated water holding capacity decreased with increased pyrolysis temperature. Higher temperature caused loss of volatile carbon which is mainly comprised of aliphatic hydrophilic functional group and generation of aromatic hydrophobic carbon, groups in biochar. This resulted in repellence of higher temperature biochar for water to adsorb resulting low saturated water content (Keiluweit *et al.*, 2010; Uchimiya *et al.*, 2010).

Nutrient content

Total C and N content of the mustard biochar was more over the stalk, which was

Table 1. *Mass recoveries, physical and chemical properties of mustard stalkbiochars.*

	Temperature (°C)	Mass Recovery Rate (%)	Ash Content (%)	pH	EC (dS m^{-1})	CCE	Bulk Density (g cc^{-1})	Particle Density (g cc^{-1})	Saturated water holding capacity (%)
MTR			5.91±0.16						
MTB4	400	34.21	15.07±0.11	8.47±0.0	2.41±0.01	19.06±0.44	0.135	0.40	568±13
MTB5	500	31.03	17.08±0.02	10.12±0.10	3.25±0.01	25.00±0.88	0.140	0.53	576±21
MTB6	600	28.63	19.73±0.07	11.04±0.01	4.76±0.06	34.38±0.88	0.152	0.65	520±12

Values are given as mean ± standard deviation for duplicate measurements.

used as feedstock (Table 2). The C and N in biochar increased with increase in pyrolysis temperature. The C recovery efficiency ((biochar C/residue C) was found to be around 50%. The increase in C content in biochar with increment in temperature is probably be due to the loss of H and O in greater proportion than C due to dehydration and pyrolysis. At pyrolysis temperature of 600 °C, polyaromatic graphene sheets with high C concentration begin to grow at the expense of the amorphous-C matrix which forms below 300 °C (Amonette and Joseph, 2002). The total contents of P, K, Ca and Mg in biochar also increased due to increment in pyrolysis temperature (Table 2). The P, K, Ca and Mg enrichment (% nutrient in biochar/% nutrient in residue) in the biochar was 2.25 and 3.17, 2.32 and 3.29, 2.35 and 3.25, 2.39 and 3.33, respectively. Despite the increase in total P content, the water soluble P content decreased with increase in pyrolysis temperature (Table 3). In biochar the water soluble P constitutes about 1-3% of total P. The acid soluble P followed the similar pattern as water soluble P though acid soluble P content was around 10 times higher. Higher water and acid soluble P in the low-temperature biochars is due to loss of carbon and the presence of less crystallized P associated minerals. With increasing temperature, crystallinity of P associated minerals increases that might reduce solubility of P in water as well as in acid solution (Zheng *et al.,* 2013). Approximately 65-70% of the total K in the biochar was soluble in water and acid and with increasing temperature these forms of K increased. The higher amount of water and acid soluble K in biochar is due to greater solubility of the K associated minerals formed during pyrolysis. The major K minerals in biochar formed was identified as sylvite (Fig. 1) having higher solubility in water. Similar observations were also reported for rice husk biochar (Prakongkep *et al.,* 2013). The water solubility of Ca and Mg in MSB4, MSB5, and MSB6 was 14%, 16% and 17% and 26%, 25% and 23% of the total Ca and Mg present in biochar. The less content of water and acid soluble Ca and Mg confirm the presence of calcite and dolomite mineral which are less soluble in water while highly soluble in dilute acid solution. The acid

Table 2. *Elemental compositions of mustard stalkbiochars. (%)*

	C	N	P	K	Ca	Mg
MTR	38.49±0.29	0.74±0.03	0.24±0.02	1.03±0.03	0.52±0.04	0.18±0.01
MTB4	58.41±0.20	1.37±0.02	0.54±0.03	2.39±0.14	1.22±0.02	0.43±0.03
MTB5	62.77±0.13	1.44±0.03	0.68±0.03	2.96±0.06	1.42±0.02	0.52±0.03
MTB6	66.54±0.08	1.51±0.02	0.76±0.02	3.39±0.11	1.69±0.04	0.60±0.04

Values are given as mean ± standard deviation for duplicate measurements.

Table 3. *Water and acid solubility of K, Ca, Mg and P in mustard stalkbiochars.*

	Water Soluble (g kg^{-1})				Acid Soluble (g kg^{-1})			
	K	Ca	Mg	P	K	Ca	Mg	P
MTB4	16±0.55	1.68±0.09	1.13±0.08	0.18±0.01	16±0.87	9.4±0.23	3.10±0.21	1.90±0.12
MTB5	19±0.63	2.30±0.10	1.30±0.01	0.12±0.00	21±0.47	11±0.35	3.71±0.13	1.46±0.02
MTB6	23±0.82	2.95±0.05	1.39±0.02	0.08±0.01	24±0.60	14±0.25	4.92±0.40	0.71±0.10

Values are given as mean ± standard deviation for duplicate measurements.

soluble Ca and Mg content in biochars were around 65-80 % of the total content.

Spectral characteristics

The X-ray diffraction pattern of MSB4, MSB5 and MSB6 varied significantly (Fig. 1). The diffractograms were analysed according to previous publication (Yuan *et al.,* 2011; Wu *et al.,* 2012). The major inorganic mineral present in the biochar are quartz (SiO_2), sylvite (KCl), calcite ($CaCO_3$). The Peak at 2θ=20.3 correspond to 4.3Å indicates the presence of quartz in MSB4 and MSB5, while in MSB6, quartz peak appears at 2θ=26.5, 3.35Å. The presence of sylvite mineral was confirmed by the peak at 2θ= 28.3 and 40.4. Calcite present in the biochars were identified by the peaks at 2θ= 29.4, 39.3, 43.1, 47.1 and 48.5. The sharp peak at 2θ=26.5, 28.3 and 29.4 corresponding to quartz, sylvite and calcite indicates the increase in the crystalinity of these mineral with increasein pyrolysis temperature of 600

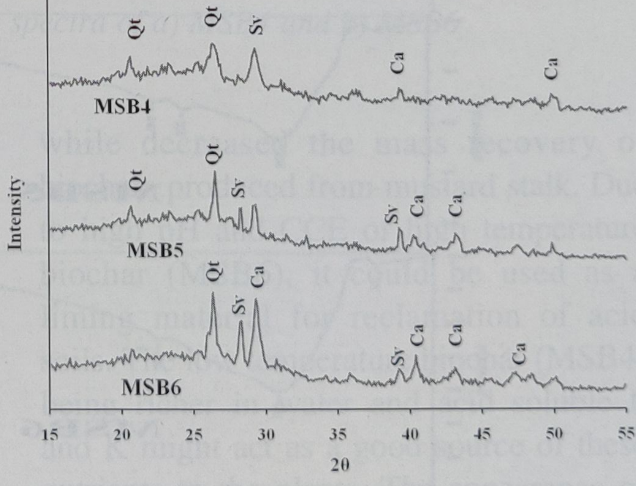

Fig. 1. X-ray diffraction profiles of biochars. *Qt=Quartz, Sv=Sylvite,. Ca=Calcite*

°C (Yuan *et al.*, 2011).

The IR spectra of the biochar (Fig. 2) indicated the presence of relatively similar functional groups on the surfaces. The peaks at 873 cm^{-1}, 877cm^{-1}, and 875 cm^{-1} in MSB4, MSB5, and MSB6 indicates the presence of CO_3^{2-} which was also confirmed by the presence of calcite in the biochars by X-ray diffraction analysis. The characteristic peaks of the aromatic C=O ring stretching appear in MSB4 and MSB6 at 1423 and 1425 cm^{-1}. The band at 1378 cm^{-1} in MSB5 isattributed to δ(C=H) vibration in alkanes and alkyl groups (Caglar *et al.*, 2000). The broad peaks seen for all the samples at around 3200-3420 cm^{-1} indicate the presence of hydroxyl group ($^{-}$OH) stretching (Liu *et al.*, 2013).

The morphology of biochar changed dramatically due to increase in pyrolysis temperature from 400 °C to 600 °C (Fig. 3). The micrograph clearly indicates the presence of highly porous structure comprised of inter connecting macro and micro pores inherited from the original mustard stalk. Capillary movement of soil solution through these pores dissolves the minerals in these pores by the process of diffusion and mass flow. The minerals that had been identified using conventional XRD were also detected as discrete crystals or in mixtures by SEM with EDS (Fig. 4). In MSB6 the intense and clear peak of the elements like P, K and Ca was

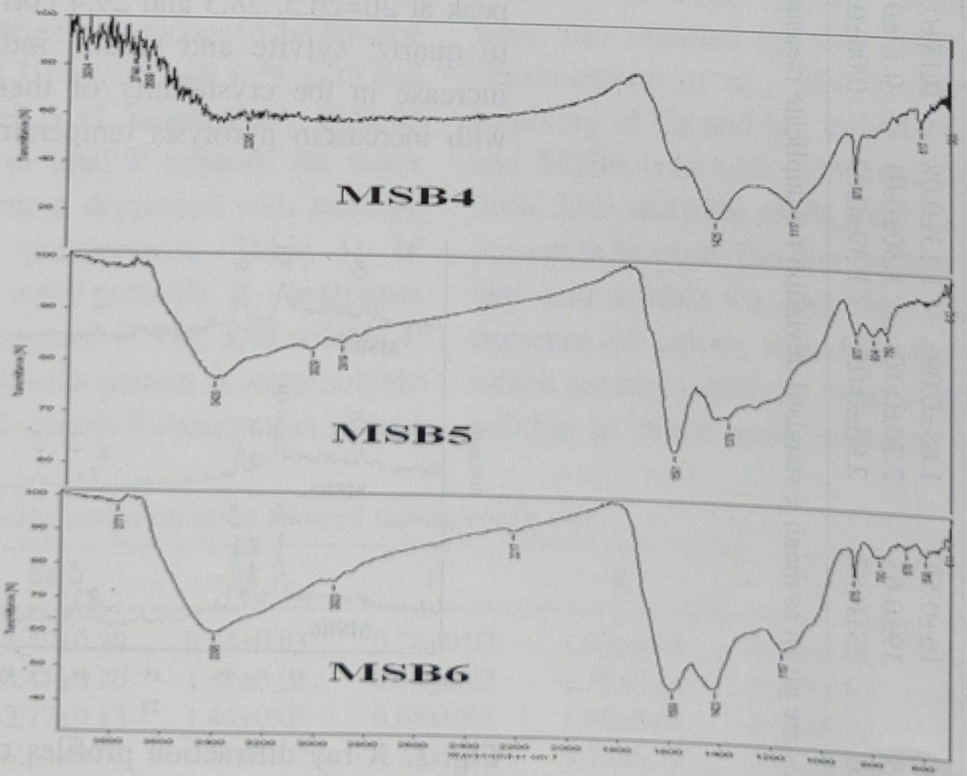

Fig. 2. *FTIR spectra of biochars*

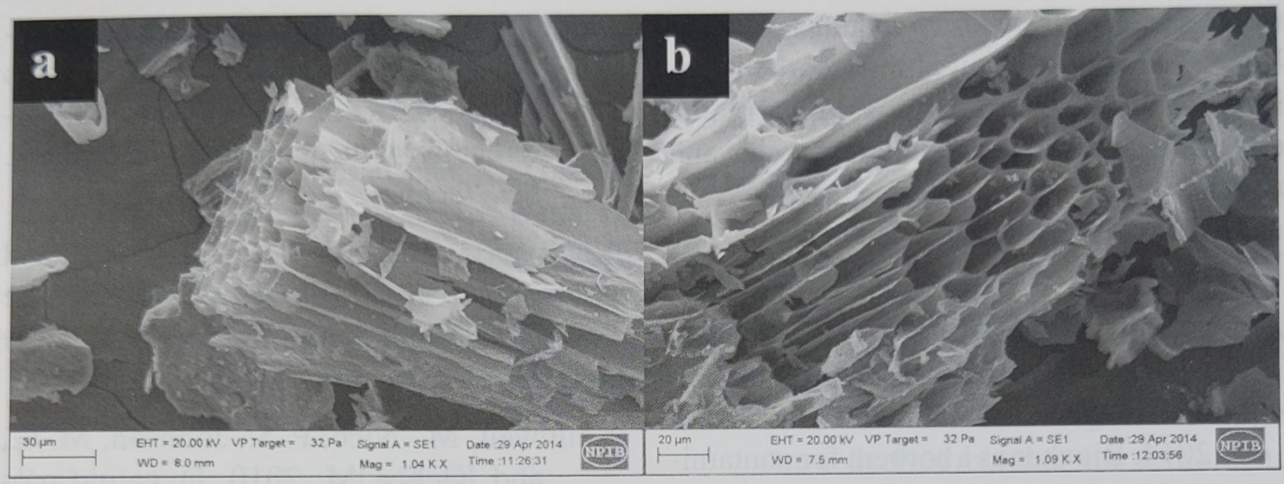

Fig. 3. *Scanning electron microscopic image of a) MSB4 and b) MSB6*

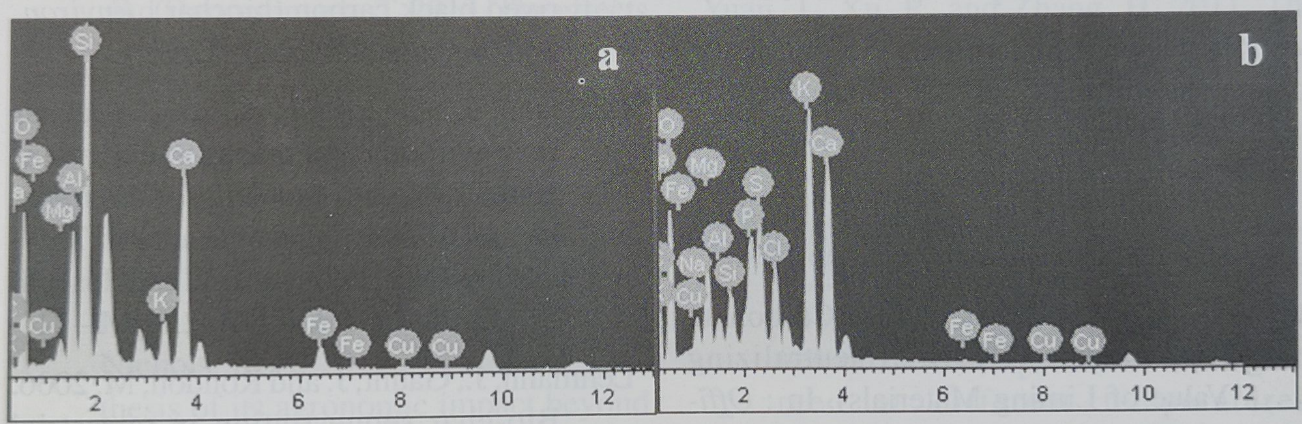

Fig. 4. *Electron dispersive x-ray spectra of a) MSB4 and b) MSB6*

noticed over MSB4. This increase in these mineral in the biochar matrix is also reflected by the increase in concentration as measured by total elemental concentration via chemical analysis.

Conclusions

The increase in pyrolysis temperature from 400 °C to 600 °C considerably enhanced the pH, EC, CCE and ash content while decreased the mass recovery of biochars produced from mustard stalk. Due to high pH and CCE of high temperature biochar (MSB6), it could be used as a liming material for reclamation of acid soils. The low temperature biochar (MSB4) being richer in water and acid soluble P and K might act as a good source of these nutrients to the plants. The appearance of CO_3^{2-}, aromatic C=O ring, hydroxyl group

($^{-}$OH) and high porosity in mustard stalk biochar make it a suitable adsorbent for immobilization of organic and inorganic contaminates from contaminated water and soil.

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Weathering of Silicate Minerals by Humic Acids : II. Nature of Cation Solubilisation from Hornblende and Biotite and Characteristics of the Residual Products

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Abstract : The present study aims at understanding how humic acids (HAs) (extracted from Entisol, Alfisol and Mollisol) affect and transform primary silicate minerals, viz., hornblende (inosilicate) and biotite (phyllosilicate), and aid in nutrient release therefrom. The focus is on the kinetics of dissolution and the alterations brought about in the products formed after treatment with HA. The kinetic curves exhibit alternate crests and troughs pointing to alternate solubilisation and precipitation. Structural difference between the two primary silicates lead to differential release of cations. The contrast between the minerals is more pronounced when the altered products are compared. While hornblende shows drastic changes including reduction in $Fe^{2+/3+}$ and Ca^{2+} and enrichment in Si^{4+}, Al^{3+} and Mg^{2+}, biotite is almost minimally altered. XRD(X ray diffraction) studies indicate the disappearance/attenuation of many prominent bands of hornblende in the weathered residues with several new crystalline phases. Biotite, however, is only slightly altered with the formation of a few new phases. IR studies suggest deposition of HA on the surfaces of both biotite and hornblende but such deposition is far more prominent with hornblende.

Key words : Weathering, silicates, hornblende, biotite, humic acids, cation, solubilisation.

In an earlier publication (Das *et al.*, 2013), we described the weathering of olivine (nesosilicate) and tourmaline (cyclosilicate) by humic acids (HAs) particularly the nature of cation solubilisation and characteristics of the residual products. Here, we are extending such studies to representative minerals of two other groups of silicates, *viz.,* hornblende (inosilicate) and biotite (phyllosilicate). Mention may be made that scanty information is available on the weathering of primary minerals with HAs and that too is mostly limited to olivine and feldspars.

Mineral dissolution by biological molecules is a well-established fact (Barker *et al.*, 1997). Hees and Lundström (2000) calculated that most of the Al and Fe are organically bound and organics enhance

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mineral dissolution rates significantly (Rasmussen *et al*., 1994; Cama and Ganor, 2006). Polyfunctional acids including HAs are known to be extremely effective in promoting silicate dissolution (Ochs *et al*., 1993; Welch and Ullman, 1993; Franklin *et al*., 1994; Zhang and Bloom, 1999; Kawano and Obokata, 2007). The mechanism of dissolution (Welch and Ullman, 1992) is a combination of proton-promoted dissolution (Stumm and Furrer, 1987; Stumm and Wieland, 1990), ligand-promoted dissolution and a mixed proton/ligand interaction (Furrer and Stumm, 1986; Welch and Ullman, 1996). Ligand-mediated mechanism involves the adsorption of ligands to specific sites on the mineral surface (Barker *et al*., 1997) with the formation of metal-organic complex (Wit *et al*., 2001); the rate is proportional to the concentration of surface-ligand complexes (Bennett, 1991; Ochs *et al*., 1993) whose detachment (rate-limiting step) leaches the metal cation into the solution. Dissolution is mostly incongruent but this depends on the nature of the reacting acid and the mineral (Song and Huang, 1988; Tan, 1989; Zhang and Bloom, 1999). Some researchers proposed that hyper coordinated Si-organic complexes can form in biologically relevant fluids (Kubicki and Heaney, 2003). Working with low molecular weight organic acids, Barman *et al.* (1992) suggested that it is the crystal structure that primarily governs the accessibility of the ligand ions to the cations and determines relative solubilities of the cations from a mineral. It is interesting to note here that the weathered biotite was found to be extremely fragmented while weathered hornblende contained new crystalline phases in it (Varadachari *et al*., 1994a).

Materials and Methods

Characterisation of minerals

Hornblende (inosilicate) and biotite (phyllosilicate) provided by the Geological Survey of India, Kolkata were used in this study. The minerals were powdered and dry-sieved to the 80-150 mesh B.S. size fractions, then washed and dried at 80°C. X-ray diffraction (XRD), infrared spectroscopy (IR) and chemical analysis of the minerals and their weathered products were done as described by Das *et al.* (2013).

Extraction and characterisation of humic acids

The HAs were extracted from surface soils (0-15 cm) of an Entisol (Fine loamy, mixed, hyperthermic, Aeric Fluvaquent; deltaic new alluvium; Baruipur, W. Bengal), Alfisol (Fine loamy, kaolinitic, hyperthermic, Ultic Paleustalf; ferruginous soil; Vishnupur, W. Bengal) and Mollisol (Coarse loamy, mixed, cryic, Typic Hapludoll; mountain soil; Auli, Uttarakhand). The method of extraction, fractionation, purification and characterisation of HAs was carried out as described by Das *et al.* (2013).

Elimination of interference by humic acids in the chemical analysis of cations

Spectrophotometric methods for the determination of cations in solution in the presence of HA had to be slightly modified because HA interferes in colour development procedures. Modifications adopted herein are described by Das *et al.* (2013).

Kinetics studies

Kinetics of solubilisation of cations from the minerals by HAs were studied in the following manner (Das *et al.*, 2013). To 200 mg of mineral sample in plastic bottles, 20 ml of 1000 ppm HA was pipetted in. The pH of HA was varied from 6-9. The suspensions were shaken intermittently (8h/day) up to 49 days. At the end of the reaction period, which was 7, 14, 21, 28, 35, 42 and 49 days, the solutions were filtered, washed, made to volume and analysed for the major cations.

Studies on residual products

Weathered products of reaction were prepared as follows (Das *et al.*, 2013). To 2 g mineral sample in a plastic bottle, 50 ml of 1000 ppm HA was added and the solutions agitated on a shaker intermittently (5h/day) for three consecutive months. The residues were then filtered, washed and dried in an oven at 80°C. These were analysed for the major cations as described for untreated minerals.

Results and Discussion

Compositional analysis and XRD studies affirm that the mineral specimen hornblende (Tables 1 and 4) conforms to hornblende of the amphibole group and biotite falls within the field outlined by annite (Deer *et al.*, 1985).

Table 1. *Chemical composition of the silicate minerals*

% Oxide	Hornblende	Biotite
SiO_2	43.66	35.94
$FeO+Fe_2O_3$	13.19	24.90
Al_2O_3	13.89	18.16
TiO_2	1.08	3.17
MnO_2	N.D.	N.D.
CaO	14.00	N.D.
MgO	11.19	5.31
Na_2O	N.D.	0.55
K_2O	0.13	10.41
H_2O^-	2.31	0.14
H_2O^+	1.48	3.00

Elemental analysis data of HAs on dry ash-free basis were 55.20% C, 5.05% H, 4.36% N and 35.39% O for Entisol HA; 54.90% C, 6.51% H, 5.64% N and 32.95% O for Alfisol HA; 57.47 % C, 5.91% H, 4.83% N and 31.79% O for Mollisol HA. The E_4/E_6 ratios of the HA samples were 4.29, 3.27 and 4.23 for Entisol, Alfisol and Mollisol HAs respectively. The NaOH titratable acidity values were 2.50, 2.60 and 3.50 meq/g and the total acidity values were 5.90, 6.66 and 8.50 meq/g for Entisol, Alfisol and Mollisol HAs, respectively. The IR spectrum of HAs show absorptions at 3750, 3400, 2900, 2370, 1600, 1200, 1000 and 660 cm^{-1} (Das *et al.*, 2013).

Order of cation solubilisation from the minerals

Dissolution curves (Fig. 1) of hornblende are remarkable for their alternate crest-trough pattern. The general nature of the kinetics curves shows similar patterns for all cations, viz., $Fe^{2+/3+}$, Al^{3+}, Ca^{2+} Mg^{2+} and Si^{4+}. Highest release is observed with $Fe^{2+/3+}$ for all the HAs. This is followed by Al^{3+} and Ca^{2+} in case of Entisol and Mollisol HA but this order is reversed with Alfisol HA. The release of Si^{4+} as well as Mg^{2+} is very poor with all the three HAs. The effect of variation in pH on kinetics is almost insignificant. The order of solubilisation appears to be related to the complexing abilities of HAs with the cations and their respective positions in the crystal lattice (Barman *et al.*, 1992; Varadachari *et al.*, 1994b).

Cation solubilisation from biotite (Fig. 1) is also indicative of repetitive cycles of dissolution and precipitation. Here also, the most solubilised cation is $Fe^{2+/3+}$ followed by $Al^{3+} \geq Mg^{2+}$ for Entisol HA and $Mg^{2+} > Al^{3+}$ for Alfisol HA. Si^{4+} release is very low and follows linear kinetics; release of K^+ and Mg^{2+} are also small. Mollisol HA is quite different in that it complexed Al^{3+} in preference to all other cations from biotite.

The affinity of HAs to form strong complexes with $Fe^{2+/3+}$ causes higher dissolution (Schnitzer and Kodama, 1976; Barman *et al.*, 1992). The very low release of Si^{4+} is due to the great stability of Si-O bonds (energy of formation 3127 Kcal/mol for inosilicates and 3123 Kcal/mol for phyllosilicates) compared to that of the Fe-O, Al-O, Ca-O and Mg-O bonds (Keller, 1954).

Relative stabilities of the minerals

In the hornblende structure, Ca^{2+} ions are exposed to attack by HA as they serve to link units, each comprising two bands of silica tetrahedral. The Mg^{2+}/Fe^{2+} ions are sandwiched between the silica tetrahedral bands (Bragg, 1937) and are, therefore, better protected. After Ca^{2+} ions are removed, the two silica units get separated and HA can access the Mg^{2+}/Fe^{2+} ions. Although Fe^{2+} is present in a similar position as Mg^{2+}, the strong complexation of Fe^{2+} by HA increases the degree of dissolution. The HAs have very low capacity to dissolve Si^{4+} since it is well protected in Si_4O_{11} chains. Al^{3+} ion is mostly present as a substitute for Si^{4+} in the tetrahedral chain and for Mg^{2+} in the octahedral positions and is released more than Si^{4+} due to its preferential complexation with HA.

Each individual sheet in biotite structure comprises an octahedral layer of Mg^{2+}/ $Fe^{2+/3+}$ sandwiched between two layers of silica tetrahedral units wherein Al^{3+} substitutes for Si^{4+}; K^+ ions between adjacent sheets neutralise the residual charge (Grim, 1968). HA may be envisaged to percolate from the edges and slowly find access into the octahedral sheet and towards the interior (Murakami *et al.*, 2003). Al^{3+} is solubilised by tunneling of octahedral

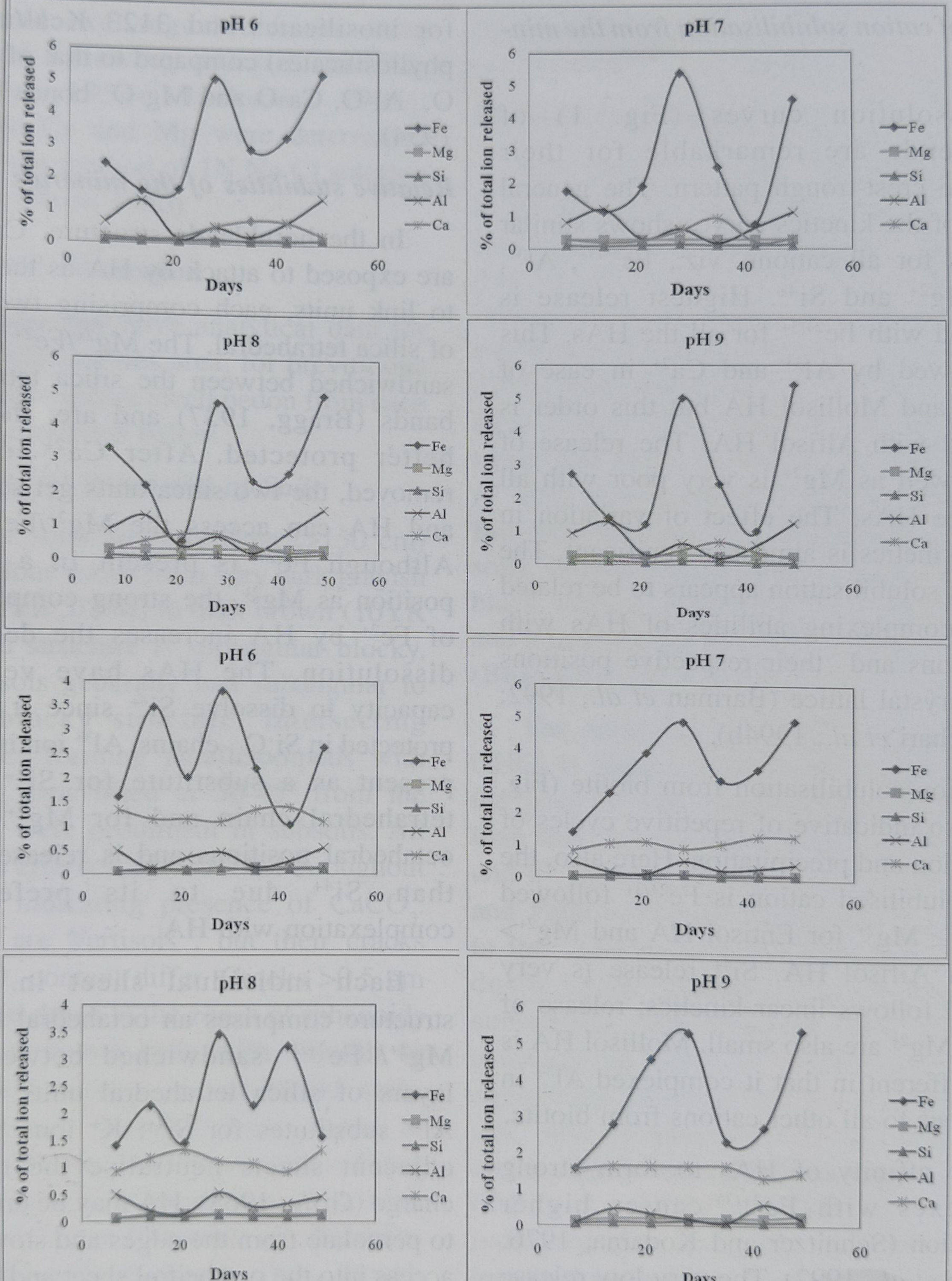

Fig. 1. (A) *Release of cations from (a) hornblende by Entisol (first four figures) and (b) hornblende by Alfisol (last four figures)*

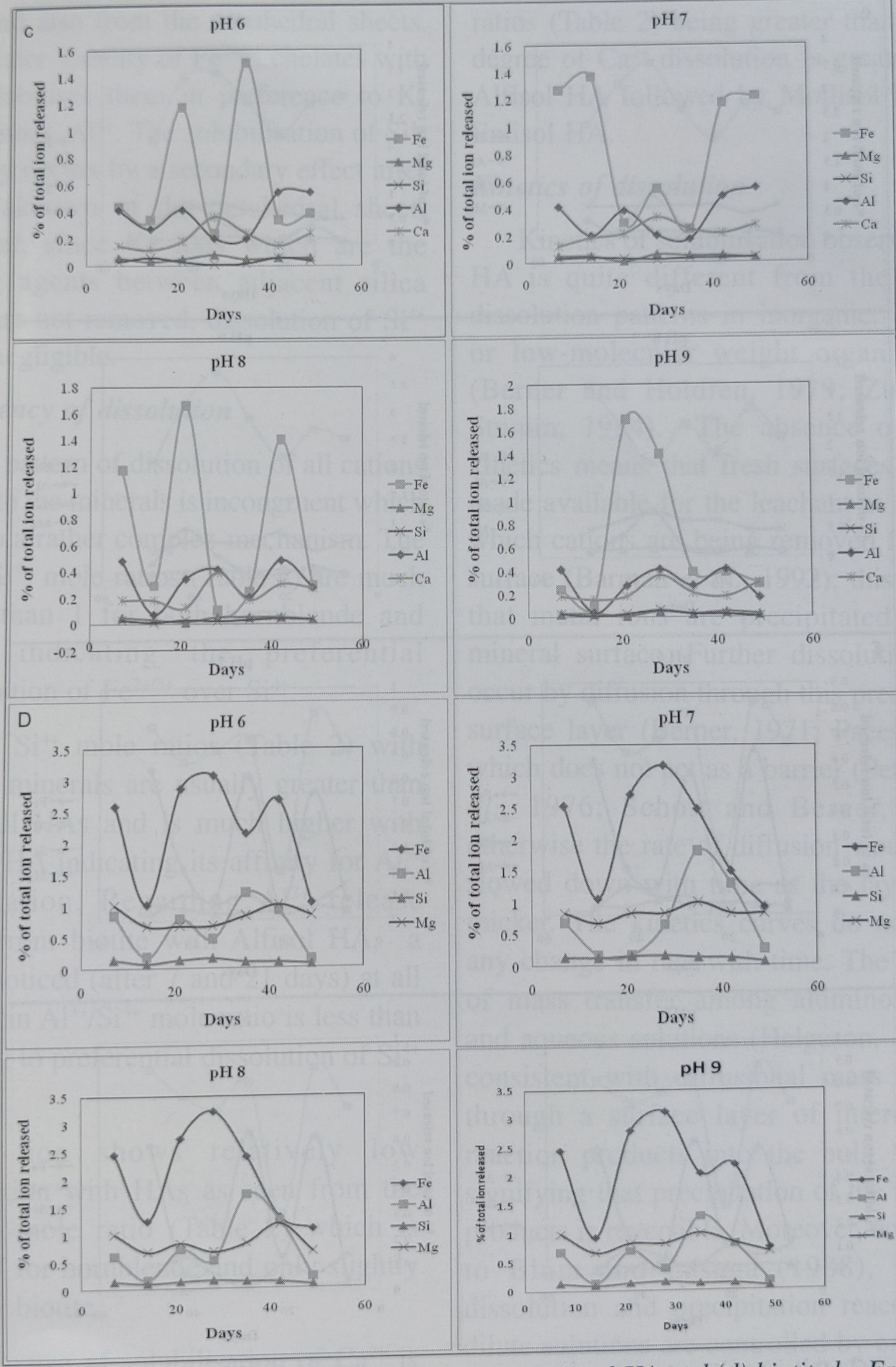

Fig. 1. (B) *Release of cations from (c) hornblende by Mollisol HA and (d) biotite by Entisol HA*

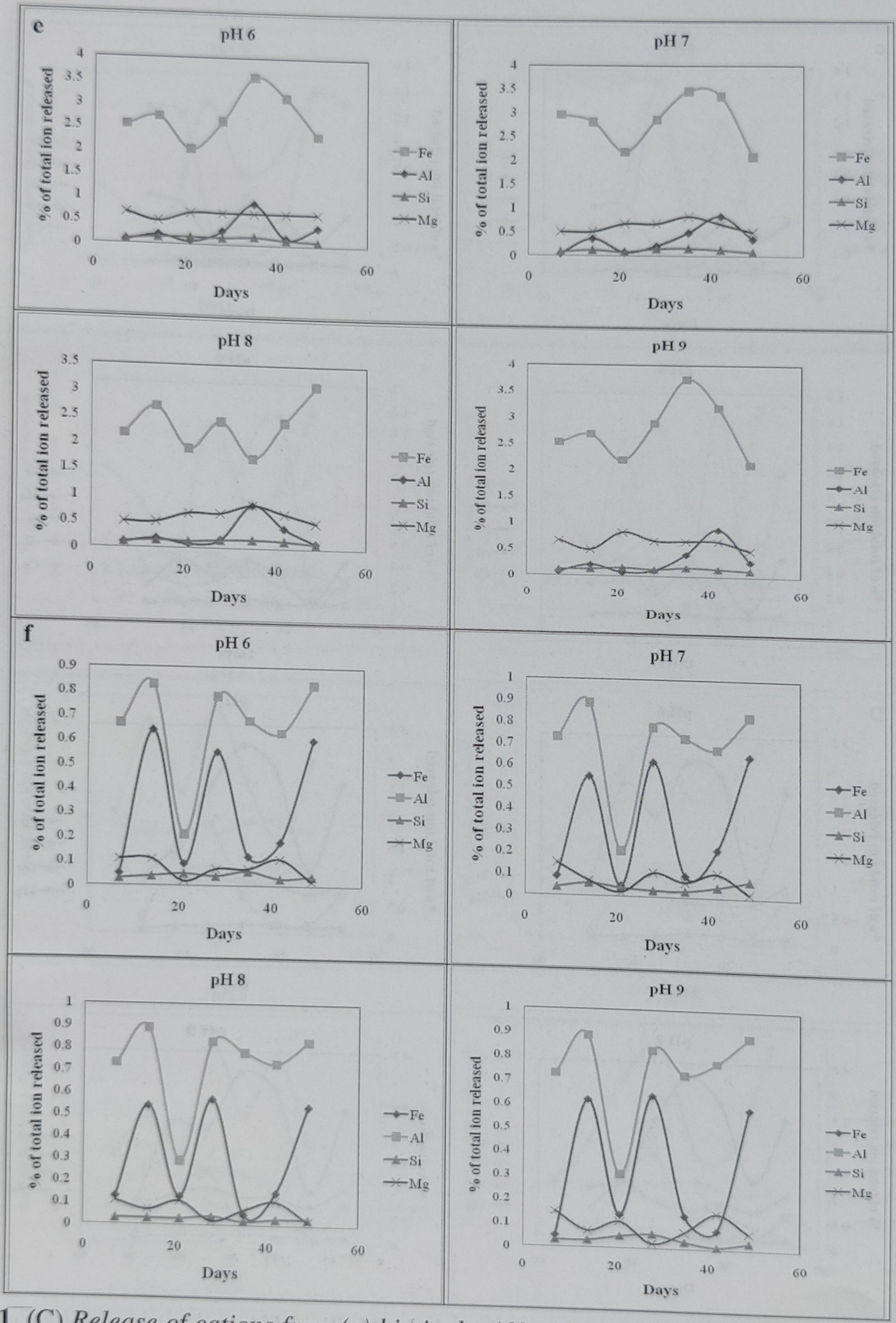

Fig. 1. (C) *Release of cations from (e) biotite by Alfisol HA and (f) biotite by Mollisol HA*

layer and also from the tetrahedral sheets. The greater stability of $Fe^{2+/3+}$ chelates with HA solubilises them in preference to K^+ and at times, Al^{3+}. The solubilisation of Si^{4+} probably occurs by a secondary effect after the breakdown of the octahedral sheet. However, since K^+ ions which are the binding agents between adjacent silica sheets are not removed, dissolution of Si^{4+} is also negligible.

Congruency of dissolution

The pattern of dissolution of all cations from both the minerals is incongruent which points to a rather complex mechanism. The $Fe^{2+/3+}/Si^{4+}$ mole ratios (Table 2) are much greater than 1 for both hornblende and biotite indicating the preferential solubilisation of $Fe^{2+/3+}$ over Si^{4+}.

Al^{3+}/Si^{4+} mole ratios (Table 2) with both the minerals are usually greater than 1 with all HAs and is much higher with Mollisol HA indicating its affinity for Al^{3+} complexation. Regarding Al^{3+} release kinetics from biotite with Alfisol HA, a stage is noticed (after 7 and 21 days) at all pH wherein Al^{3+}/Si^{4+} mole ratio is less than 1 pointing to preferential dissolution of Si^{4+} over Al^{3+}.

Mg^{2+} ion shows relatively low complexation with HAs as seen from the Mg^{2+}/Si^{4+} mole ratio (Table 2) which is close to 1 for hornblende and only slightly higher for biotite.

The degree of solubilisation of Ca^{2+} is higher than that of Si^{4+} with Ca^{2+}/Si^{4+} mole ratios (Table 2) being greater than 1; the degree of Ca^{2+} dissolution is greatest with Alfisol HA followed by Mollisol HA and Entisol HA.

Kinetics of dissolution

Kinetics of solubilisation observed with HA is quite different from the known dissolution patterns in inorganic, aqueous or low-molecular weight organic acids (Berner and Holdren, 1979; Zutic and Stumm, 1984). The absence of linear kinetics means that fresh surfaces are not made available for the leachant at a rate at which cations are being removed from the surface (Barman *et al.*, 1992); this implies that metal ions are precipitated on the mineral surface. Further dissolution may occur by diffusion through this precipitated surface layer (Berner, 1971; Paces, 1973) which does not act as a barrier (Petrovic *et al.*, 1976; Schott and Berner, 1983), otherwise the rate of diffusion would have slowed down with time as the layer grew thicker. The kinetics curves do not show any change in rate with time. The kinetics of mass transfer among aluminosilicates and aqueous solutions (Helgeson, 1971) is consistent with diffusional mass transfer through a surface layer of intermediate reaction products into the bulk solution signifying that precipitation of the reaction products is reversible. Moreover, according to Blum and Lasaga (1988), silicate dissolution and precipitation reactions in dilute solutions are controlled by exchange and adsorption of the dissolved species on

Table 2. *Mole ratio of cations/ Si^{4+} solubilised from minerals by various HAs*

Mole ratio	HA	pH	Hornblende							Biotite						
			Days							Days						
			7	14	21	28	35	42	49	7	14	21	28	35	42	49
Fe$^{2+/3+}$/Si^{4+}	Entisol	6	21.80	18.75	15.37	33.96	29.59	30.00	35.78	18.03	13.50	21.35	19.80	20.52	30.00	16.48
		7	17.89	12.04	17.21	39.77	23.58	6.61	36.98	19.27	9.10	18.54	19.35	23.08	16.73	15.58
		8	34.67	29.82	5.47	35.33	21.68	30.11	36.51	17.49	11.87	21.33	22.08	21.18	13.52	14.54
		9	26.20	12.97	16.04	37.20	20.29	11.99	7.29	19.12	10.74	20.77	20.94	17.53	18.39	10.04
	Alfisol	6	22.63	35.26	24.70	31.61	22.94	13.59	23.55	24.23	18.17	12.27	17.84	19.90	26.18	25.96
		7	19.02	24.09	39.23	37.52	34.89	30.80	40.16	34.02	22.25	24.23	17.96	19.84	24.81	23.08
		8	22.83	21.87	17.00	25.64	19.44	33.44	13.46	19.75	17.99	14.55	15.18	10.12	16.42	29.67
		9	21.54	25.94	47.92	40.15	21.20	28.22	40.76	21.42	20.19	13.53	21.92	21.78	22.08	17.96
	Mollisol	6	17.90	5.54	47.70	19.58	59.50	5.54	9.94	1.73	20.77	2.47	10.38	4.32	2.08	19.91
		7	51.69	31.82	9.55	29.13	7.83	38.16	28.41	4.33	18.17	4.33	15.23	2.31	5.19	18.17
		8	47.70	23.87	54.09	5.30	7.95	32.95	11.93	2.08	9.51	1.38	20.77	3.46	3.96	8.65
		9	9.94	15.92	54.09	23.06	12.72	15.89	23.87	1.73	17.31	1.48	15.23	2.16	6.06	15.93
Al^{3+}/ Si^{4+}	Entisol	6	5.99	15.35	1.38	3.46	2.36	6.17	9.51	5.90	2.38	5.82	2.96	11.48	10.19	2.08
		7	8.24	12.75	2.71	4.43	1.61	5.78	9.02	5.16	1.34	1.07	3.97	16.98	14.56	4.36
		8	9.19	17.53	3.67	4.97	1.57	9.18	10.98	4.31	1.50	5.60	3.57	15.17	12.99	2.80
		9	9.09	11.83	3.66	4.73	1.70	7.17	17.35	5.28	1.50	5.20	2.62	11.20	6.81	2.10
	Alfisol	6	6.68	1.08	4.19	3.73	1.56	3.67	4.89	0.78	1.31	0.40	2.00	4.92	1.31	4.37
		7	6.92	1.89	1.52	4.15	3.16	3.08	3.82	0.54	2.91	0.91	1.34	2.82	6.21	3.96
		8	0.98	1.31	4.75	1.10	2.34	5.33	1.10	0.85	1.19	0.64	0.99	4.87	2.67	1.09
		9	1.20	4.41	3.55	1.46	0.80	6.27	1.54	0.55	1.55	0.40	0.85	2.41	6.06	2.62
	Mollisol	6	16.62	4.40	16.62	16.62	8.31	8.80	13.76	24.46	29.70	5.99	13.98	24.46	20.97	29.70
		7	16.62	4.75	12.39	11.08	5.54	15.51	12.58	24.46	29.70	9.78	22.37	34.94	24.46	27.95
		8	19.39	5.54	11.08	22.15	6.65	11.08	11.01	19.57	14.85	5.59	26.21	24.46	12.98	11.18
		9	16.60	6.65	8.81	6.65	8.81	16.60	13.85	22.71	22.37	3.99	20.96	11.35	20.97	22.36
Ca^{2+}/ Si^{4+}	Entisol	6	1.79	1.71	1.82	3.67	7.52	6.25	2.00				Nil			
		7	3.01	2.11	2.23	4.01	8.85	1.78	2.40							
		8	2.57	7.35	7.51	5.56	3.61	2.29	1.82							
		9	1.91	2.28	2.59	3.28	5.72	4.68	2.67							
	Alfisol	6	18.65	11.52	13.96	8.98	13.87	18.70	9.80							
		7	11.36	10.02	11.52	7.18	12.29	12.02	10.82							
		8	15.23	12.02	15.46	8.37	9.80	9.76	11.27							
		9	21.33	15.47	17.45	12.85	15.13	13.87	11.13							

Table 2. *Continued ...*

Mole ratio	HA	pH	Hornblende							Biotite						
			Days							Days						
			7	14	21	28	35	42	49	7	14	21	28	35	42	49
	Mollisol	6	6.00	1.90	7.25	29.49	9.74	9.74	2.40							
		7	4.75	4.14	6.79	17.99	7.79	6.79	6.28							
		8	7.25	14.49	3.80	21.32	5.80	7.00	11.00							
		9	7.25	23.99	5.80	5.90	6.79	7.25	24.49							
Mg^{2+}/Si^{4+}	Entisol	6	2.50	3.22	2.56	1.88	2.82	2.51	1.88	6.85	8.72	4.84	4.19	7.86	10.96	13.10
		7	2.82	2.97	2.51	2.05	2.62	2.51	2.26	6.25	5.59	5.61	5.00	9.13	9.17	13.75
		8	2.89	3.76	2.82	2.09	2.56	3.22	2.04	6.99	6.23	6.40	4.45	7.24	12.00	8.72
		9	2.68	2.56	3.64	2.05	2.30	3.32	3.76	7.64	7.52	6.11	5.50	8.43	6.88	8.72
	Alfisol	6	0.97	0.70	0.85	0.57	1.44	1.88	1.25	6.23	3.29	3.96	4.45	3.63	5.45	5.48
		7	0.94	0.64	1.41	1.06	1.57	1.25	1.13	5.67	3.91	7.27	4.11	4.74	4.84	5.48
		8	1.13	1.41	1.61	1.02	1.25	1.45	1.17	4.21	3.29	4.96	4.11	4.82	4.45	4.70
		9	1.88	1.92	2.17	1.60	1.88	2.17	2.09	5.45	3.65	5.00	4.84	3.76	4.45	4.11
	Mollisol	6	2.55	0.45	1.84	6.51	1.84	1.02	1.59	3.56	2.85	0.47	1.75	1.10	3.56	0.66
		7	1.84	1.05	0.34	3.40	1.47	1.47	0.65	3.95	1.10	0.66	3.56	2.19	2.04	0.33
		8	1.84	2.27	0.34	2.45	1.47	1.05	1.13	3.56	2.19	3.56	0.66	2.92	3.56	0.82
		9	1.13	4.53	0.34	0.74	0.91	1.84	2.27	4.93	2.19	2.04	0.41	2.19	3.95	2.19

the silicate surfaces. The weathering of hornblende is, thus, a stoichiometric dissolution-reprecipitation reaction (Velbel 1989).

In the presence of organic ligands, the dissolution of silicates is controlled by the formation of surface complexes with metal ions (Kononova *et al.*, 1964; Hansley and Briggs, 1994). Chelation appears to be the dominant factor of cation release (Ponomareva, 1969; Schalscha *et al.*, 1967; Tan, 1980) with some contributions by proton promoted mineral weathering and specific adsorption onto the mineral surfaces (Stumm and Furrer, 1987; Stumm and Wieland, 1990).

From the above discussion, it appears that it is not a single factor rather a combination of many factors that influences the dissolution of cations by HA. The cation initially gets complexed by HA and then comes into solution; this process continues till the limit of solubilisation is crossed, i.e., the point up to which it can no longer be retained in a soluble form by HA. As this critical point is crossed, precipitation begins and again continues up to the limit which serves as the threshold for redissolution. The cycle of dissolution-precipitation repeats itself a number of times at definite intervals during the experimentation. For every cation in a mineral being reacted by a particular HA, there is a definite threshold of dissolution and precipitation which may be slightly influenced by pH changes.

Study of Residues

Chemical analysis

There has been only slight change in pH after reaction of the minerals with HA, indicating that the cations dissolved from the minerals are not in solution as otherwise this would have contributed to a rise in pH. Therefore, it appears that these cations must have precipitated on the mineral surface after complexation with HA, as suggested by the kinetics curves.

Analysis of the weathered residues (Table 3) indicate that hornblende has undergone significant changes with enrichment of Si^{4+}, Mg^{2+} and Al^{3+} and loss in $Fe^{2+/3+}$ and Ca^{2+}. The greatest decrease in $Fe^{2+/3+}$ content is brought about by Alfisol HA whereas the greatest reduction in Ca^{2+} is effected by Entisol and Mollisol HAs. The deposition of Si^{4+} is highest with Entisol HA and that for Mg^{2+} with both Entisol and Mollisol HAs. In contrast to hornblende, the mineral biotite has undergone only minor changes in its chemical composition. There are small reductions in $Fe^{2+/3+}$, Si^{4+} and K^+ and some enrichment in Al^{3+} contents. Increase in both adsorbed water (H_2O^-) and structural water (H_2O^+) is observed with biotite while only structural water increases with hornblende.

Table 3. *Percent change in ionic constituents on weathering*

Humic acid	Mineral		%Si	% change	%Fe	% change	%Al	% change	%Ca	% change	%Mg	% change	%K	% change
	Hornblende	O	20.38		10.25		7.36		10.00		6.80			
Entisol		W	24.00	+17.8	8.50	-17.1	7.00	-4.9	4.75	-52.5	8.40	+25.0		
Alfisol		W	22.75	+11.6	4.75	-53.5	8.04	+9.2	8.25	-17.5	9.40	+14.1		
Mollisol		W	21.50	+5.5	9.00	-12.2	7.67	+4.2	5.25	-47.5	9.10	+35.2		
	Biotite	O	16.77		19.38		9.60				3.20		8.64	
Entisol		W	16.40	-2.2	17.40	-10.0	11.00	+14.6			3.00	-6.3	8.30	-3.9
Alfisol		W	15.25	-9.1	17.00	-12.3	11.30	+17.2			4.10	+26.6	8.00	-7.4
Mollisol		W	16.50	-1.6	17.50	-9.7	10.90	+13.5			3.10	-4.4	8.40	-4.6

O : Original mineral W : Weathered mineral % Change (-) : indicates deposition

XRD studies

Some of the prominent diffraction bands of hornblende (Table 4) are either significantly weakened or even disappeared after treatment with HAs. A number of bands of hornblende attributed to the presence of Ca^{2+}, calcium silicate hydrate (JCPDS 1967, 1972, 1979) and calcium silicate hydroxide (JCPDS 1987), are missing in the weathered residues, whereas a number of new bands assigned to calcium aluminium oxide hydrate and calcium aluminium silicate hydrate (JCPDS 1972, 1974, 1979) have emerged. The likely reason is that Ca^{2+} is taken out of the hornblende structure by complexation with HA and thereafter partially precipitated on the surface of the weathered residues; chemical analysis supports this inference. Precipitations of aluminium hydroxide and aluminium silicate (JCPDS 1972, 1980, 1984), magnesium aluminium silicate hydroxide, magnesium aluminium iron hydroxide silicate (chlorite), magnesium aluminum silicate hydroxide hydrate (JCPDS 1972, 1974, 1980) are indicated.

The XRD pattern of biotite (Table 4) remained nearly unchanged on weathering, particularly on treatment with Alfisol and Mollisol HAs. A few new bands detected in the residues are attributed to potassium aluminium silicate hydroxide (illite), potassium aluminium silicate hydrate and potassium magnesium silicate hydroxide (JCPDS 1983, 1984).

IR spectroscopic studies

With hornblende, vibrations at 3400 cm^{-1} are detectable in the original mineral as well as in the weathered residues. This may either be characteristic hornblende vibration or of H-bonded –OH. The presence of this band along with another around 2360 cm^{-1} indicates HA deposits on the surface of the mineral. This inference is corroborated by the disappearance of 1000 cm^{-1} band of Si-O-Si (Lazarev, 1972) characteristic of silicates, in the weathered residues. Absorptions around 950 and 460 cm^{-1} attributable to vibrations of O_t (Farmer, 1974) and to lattice vibrations (Farmer and Russel, 1964) respectively are observed in all the weathered residues.

IR spectra of the weathered residues of biotite, on the other hand, have retained most of the absorptions of the original mineral. The most prominent feature in the weathered residues is the presence of absorptions around 3754 cm^{-1} and 2370 cm^{-1} which are attributed to deposition of HA on biotite surface as suggested by compositional data. Other absorptions include 3590 cm^{-1} attributed to H-bonded OH, 700 and 460 cm^{-1} attributed to lattice vibrations (Farmer and Russel, 1964) and at 550-400 cm^{-1} due to Fe-O (Stubican and Roy, 1961). In contrast to hornblende, the Si-O-Si vibrations around 1000 cm^{-1} (Lazarev, 1972) are observed here implying that there is no significant HA deposition on the biotite surface.

Table 4. *XRD data of hornblende and biotite and its residues*

Hornblende								Biotite							
Original		Weathered by Entisol HA		Weathered by Alfisol HA		Weathered by Mollisol HA		Original		Weathered by Entisol HA		Weathered by Alfisol HA		Weathered by Mollisol HA	
d (A^0)	I	d (A^0)	I	d (A^0)	I	d (A^0)	I	d (A^0)	I	d (A^0)	I	d (A^0)	I	d (A^0)	I
9.36	4	5.18	5	6.97	7	19.51	12	10.41	7	10.02	40	10.04	100	10.39	9
8.66	7	2.95	3	6.75	5	10.8	11	10.04	100	5.07	4	5.03	5	10.0	100
8.4	100	2.57	5	4.04	3	8.12	9	5.02	3	3.5	15	3.49	2	6.98	1
6.48	6	2.45	3	3.69	8	4.55	20	4.57	1	3.35	33	3.35	61	5.03	2
5.52	4	2.34	8	3.56	3	3.89	6	4.1	1	2.96	3	2.73	1	3.53	1
5.14	4	2.24	3	3.28	13	3.29	7	3.35	80	2.64	5	2.64	5	3.37	11
4.72	6	2.08	3	3.01	5	3.21	37	3.04	1	2.6	4	2.51	12	3.35	33
4.57	8	2.03	100	2.9	3	3.14	17	2.67	1	2.51	9	2.45	1	2.64	3
4.36	4	1.8	3	2.63	5	2.97	4	2.51	13	2.34	24	2.34	3	2.51	5
3.98	6			2.54	6	2.72	11	2.34	4	2.16	3	2.14	1	2.45	1
3.75	7			2.34	30	2.34	11	2.27	1	2.09	5	2.03	22	2.34	3
3.36	7			2.17	3	2.14	7	2.2	3	2.03	100	2.01	8	2.27	1
3.24	13			2.09	5	2.1	4	2.07	1	1.99	2	1.92	1	2.19	1
3.2	19			2.07	3	2.03	100	2.03	11	1.79	2	1.71	1	2.08	1
3.13	84			2.03	100	1.84	12	2.01	11	1.73	2	1.68	4	2.03	11
3.06	6			1.98	1	1.82	2	1.91	1	1.67	5			2.01	3
2.93	6			1.84	3	1.74	3	1.68	4	1.64	2			1.96	1
2.83	13			1.71	1	1.69	8	1.63	1	1.55	2			1.91	1
2.67	8			1.55	5	1.62	3	1.6	1					1.75	1
2.6	81					1.57	2							1.68	1
2.48	3													1.6	1
2.44	6													1.59	1
2.42	2													1.55	1
2.39	10														
2.34	10														
2.26	5														
2.2	2														
2.1	3														
2.07	2														
2.03	58														
2.0	16														
1.93	7														

Table 4. *Continued...*

Hornblende								Biotite							
Original		Weathered by Entisol HA		Weathered by Alfisol HA		Weathered by Mollisol HA		Original		Weathered by Entisol HA		Weathered by Alfisol HA		Weathered by Mollisol HA	
d (A^{0})	I	d (A^{0})	I	d (A^{0})	I	d (A^{0})	I	d (A^{0})	I	d (A^{0})	I	d (A^{0})	I	d (A^{0})	I
1.86	4														
1.83	7														
1.79	5														
1.74	7														
1.65	5														
1.58	8														

Conclusions

The solubilisation pattern of various cations from hornblende and biotite by HAs of diverse origin is typified by the appearance of alternate peaks and troughs and is, therefore, distinct from the known dissolution characteristics of minerals by low molecular weight organic acids. Variation in pH has little effect on the nature of dissolution. With hornblende, the general order of cation solubilisation is $Fe^{2+/3+} > Al^{3+} \geq Ca^{2+} > Mg^{2+} > Si^{4+}$. The order of cation release from biotite by Entisol HA is $Fe^{2+/3+} > Al^{3+} \geq Mg^{2+} > Si^{4+}$; however, with Alfisol HA the order of Mg^{2+} and Al^{3+} is reversed whereas with Mollisol HA, the order of $Fe^{2+/3+}$ and Al^{3+} dissolution is reversed. The release of K^+ from biotite is negligible. In general, $Fe^{2+/3}$ is liberated the most due to its preferential chelation with HAs. The pattern of dissolution of both the minerals is incongruent.

Altered products of weathering indicate that while hornblende has been severely attacked, biotite has been minimally weathered. A relative enrichment in Si^{4+}, Mg^{2+} and Al^{3+} with reduction in $Fe^{2+/3+}$ and Ca^{2+} is observed in hornblende with all the HAs. Slight reduction in Si^{4+}, $Fe^{2+/3+}$, Mg^{2+}, K^+ and a relative enrichment in Al^{3+} content is observed with biotite on treatment with HAs. Many of the major bands of hornblende have either disappeared from the diffractogram or are much reduced in intensity in the weathered residues. It is evidenced that Ca^{2+} has been removed from hornblende by complexation with HA and thereafter precipitated on the surface of the weathered residues in new chemical forms. Precipitation of certain Al^{3+} and Mg^{2+} compounds are also indicated from chemical analysis data. The XRD pattern of biotite remains unaltered in the weathered residues. Precipitation of K^+ and Al^{3+} are indicated. The deposition of HA on the surface of both the minerals are suggested by IR spectra. However, vibrations due to Si-O-Si are not observed in the weathered hornblende residues indicating that the HA deposits are thicker on hornblende surface than on biotite.

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