PHYSICO-GEOCHEMICAL AND MINERAL COMPOSITION OF NEEM TREE SOILS AND RELATION TO ORGANIC PROPERTIES

WILLIAM C. MAHANEY[1,2], JOAN VOROS[2], RAMANATHAN KRISHNAMANI[3], RONALD G.V. HANCOCK[4], SUSAN AUFREITER[5], MICHAEL W. MILNER[6] and CHRISTOPHER C.R. ALLEN[7]

[1]Quaternary Surveys, Thornhill, Ontario, Canada
[2]Department of Geography, York University, N. York, Ontario, Canada
[3]The Rainforest Initiative and Thesica Foundation, Tamil Nadu, India
[4]Department of Anthropology, McMaster University, Hamilton, Ontario, Canada
[5]The Research Institute, The Hospital for Sick Children, Toronto, Ontario, Canada
[6]MWM Consulting, Toronto, Ontario, Canada
[7]Queen's University Belfast, School of Biological Sciences, Belfast, UK

Mahaney, W.C., Voros, J., Krishnamani, R., Hancock, R.G.V., Aufreiter, S., Milner, M.W. and Allen, C.C.R., 2016. Physico-geochemical and mineral composition of Neem tree soils and relation to organic properties. *Geografiska Annaler: Series A, Physical Geography*. 98, 143–154. DOI:10.1111/geoa.12129

ABSTRACT. The Neem tree, the oil of which has a long history of pesticide, fertilizer and medicinal use in India, has been studied extensively for its organic compounds. Here we present a physical, mineralogical and geochemical database resulting from the analyses of two Neem soil profiles (epipedons) in India. Neem tree derivatives are used in the manufacture of a variety of products, from anti-bacterial drugs and insecticides to fertilizers and animal feeds. A preliminary geochemical and mineralogical analysis of Neem soils is made to explore the potential for chemical links between Neem tree derivatives and soils. Physical soil characteristics, including colour, texture and clay mineralogy, suggest the two pedons formed under different hydrological regimes, and hence, are products of different leaching environments, one well-drained site, the other poorly drained. Geochemically, the two Neem soils exhibit similarities, with elevated concentrations of Th and rare earth elements. These elements are of interest because of their association with phosphates, especially monazite and apatite, and the potential link to fertilizer derivatives. Higher concentrations of trace elements in the soils may be linked to nutritional derivatives and to cell growth in the Neem tree.

Key words: Neem tree, soil–Neem relationships, geochemical processes, soil clay mineral composition

Introduction

The Neem tree (*Azadirachta indica* A. Juss.) is native to India (Fig. 1) and grows in a variety of soils, some nutrient poor, saline rich in arid habitats to more nutrient rich, well leached pedons in subhumid areas (Koul *et al.* 1990; Karnataka Forest Development 1992; Matthews *et al.* 1997; Gurumurthy *et al.* 2007; Brototi and Kaplay 2011) in various countries of the sub-tropics. There is evidence of primate consumption of Neem plant parts (Voros *et al.* 2001) and various derivatives of the Neem tree itself are used in domestic animal feeds (Verma *et al.* 1995). Chemical analysis has determined that the essential amino acids, as well as calcium and phosphorus are principal ingredients of Neem leaves and seed oil (Koul *et al.* 1990; Tiwari 1992). More recent research (Akan *et al.* 2013) has shown heavy metal uptake in Neem roots of Pb, Cr, Ni, Co, Cd and As, all of which exceed the World Health Organization limits for medicinal plants.

Neem derivatives are also used in the treatment of human bacterial, viral and other disorders (Hepburn 1989; Koul *et al.* 1990; Charles and Charles 1992; Hamilton 1992; Siddiqui *et al.* 1992; Garg *et al.* 1993a, 1993b; Biswas and Kaplay 2011), and in the manufacture of fertilizers (Murugan *et al.* 2011), insecticides, contraceptives, toiletries, pharmaceuticals, and lamp fuel (Hepburn 1989; Koul *et al.* 1990; Aldhous 1992; Colin and Pussemier 1992; Stix 1992; Garg *et al.* 1993; Jayaraj and Rabindra 1993; Juneja *et al.* 1994; Upadhyay *et al.* 1994; Jayaraman 1995; Kaushic and Upadhyay 1995; Stark and Walter 1995; Javed *et al.* 2007).

A recent 'Neem Treatise', edited by K. Singh (2009), provides a comprehensive account of research being carried out on the Neem tree. As

DOI:10.1111/geoa.12129

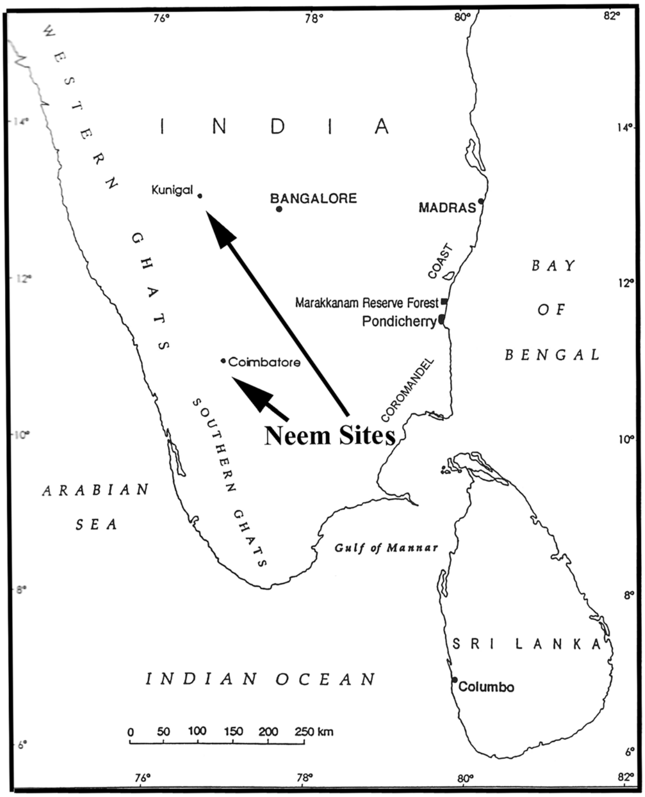

Fig. 1. Location of the Neem soils in the Marakannan.

a reference text, it offers new information on a number of different aspects, including distribution, ethnobotany, agroforestry, propagation by tissue culture, chemical constituents and their bioactivity against microflora and microfauna, disease, fertilizer use, and various therapeutic uses such as malaria and vector control, and ancient veterinary medicines. However, soils have been largely left out of Neem research at a time when knowledge of their properties might shed light on Neem biology.

In India, the Neem tree may well be said to be used as a pharmacy, in that even small parts of the tree are of medicinal value. For example, a decoction of the bitter bark produces astringent properties used in the treatment of haemorrhoids. Neem leaves are steeped by local populations to treat malaria, intestinal worms and peptic ulcers. Neem leaf juice is used as an infusion or ointment applied externally in the treatment of ulcers, eczema, wounds and boils. Neem twigs are widely used to clean teeth and to prevent gum disease. Neem oil, pressed from seeds, is used as an anti-viral and anti-fungal hair dressing to rid the scalp of lice, and contains spermicidal material. Leprosy has also been treated with Neem oil (Shukla *et al.* 2000; Biswas *et al.* 2002).

The Neem tree's termite-resistant wood tends to discourage the neighbouring construction of termitaria (Delate and Grace 1995). Nevertheless, as shown in Fig. 2, termite mounds are constructed close to the living tree itself. With all these health benefits, it is unfortunate that only of late (Montes-Molina *et al.* 2008; Murugan *et al.* 2011; Shinde and Biswas 2011; Aduloju *et al.* 2013; Mumuni *et al.* 2013; Arora and Srivastava 2014) has attention been paid to soils associated with the Neem tree, although most research has focused on soils vis-à-vis crop production, not on soil chemistry and the distribution of weathered minerals and grain coatings that might influence uptake of chemical elements possibly important in Neem biology. Recent interest among ecologists to focus on AG-BG (above ground–below ground; van Dam and Heil 2011) relationships to better understand aerial → bole → root→ microbe processes failed to

Fig. 2. Neem tree and adjacent termite mound.

focus on soil → microbe → root interactions which might be more closely related to changes in the plant body. A preliminary geochemical and mineralogical analysis of the Neem soils is made here to further explore the potential for chemical links between Neem tree derivatives (AG) and soils (BG).

Field area

The Neem tree soils come from Kunigal (Neem-1) and Coimbatore (Neem-2) and the geodesic distance between sites is 223 km (Fig. 1). Kunigal (13° 1’ 12” N; 77° 1’ 48” E) is 70 km from Bangalore on the Bangalore–Mangalore National Highway (NH 48) at an elevation of 773 m a.s.l. in the Tumkur District, Karnataka State, India. The mean annual precipitation is 1097.3 mm. Coimbatore (11° 1’ 6” N; 76° 58’ 21”) is 300 km from Bangalore on the Salem–Thiruvananthapuram National Highway (NH 47) at an elevation of 411 m a.s.l. The site is located in Coimbatore District, Tamil Nadu State, India. The mean annual precipitation is 640 mm.

India has two monsoons, the southwest and the northeast. The dependable southwest monsoon extends from June to September. The less dependable northeast one (October–December), an extension of the retreating monsoon, is important only for Tamil Nadu, which receives about 50% of its rainfall from this monsoon (*Atlas of India* 1987). The drainage system of the Peninsula exhibits a pronouncedly easterly trend of its main channels, the Western Ghats being the watershed (Wadia 1953). Wide, old valleys of east-flowing rivers are graded almost to their heads.

The greater part of the Peninsula is part of the Deccan Plateau, made up of horizontally bedded lava sheets. Coimbatore, lying just south of the Nilgiri Hills in the southern part of the Deccan, is situated on granitic gneiss (Peninsular gneiss), Indian shield rock (Wadia 1953). Red sandy soils predominate in Tamil Nadu, although in the Coimbatore area there are pockets of mixed red and black soils. Unlike the northern black soils derived from Deccan trap rocks (volcanic origin), southern black soils are derived from ferruginous gneiss and schistose rocks under semi-arid conditions (*Atlas of India* 1987).

Materials and methods

Two samples are examined: Neem-1, a red loamy soil that typifies those found in the southern peninsula; and Neem-2, a black soil, which represents the other important soil group in peninsular India. Soil colours were determined with standard soil colour charts (Oyama and Takehara 1970). Soil horizon nomenclature follows the NSSC (1995).

Air dried samples were sieved to remove mineral matter greater than 2 mm. Particle size separations were made by dry sieving the sands (2 mm–63 μm) following procedures outlined by Day (1965); fine fractions (silt and clay, <63 μm) were calculated by sedimentation.

Following procedures established by Whittig (1965), clay samples (<2 μm) were centrifuged onto ceramic tiles and X-rayed using a Toshiba diffractometer with Ni-filtered CuK alpha radiation to determine mineralogy. Sand analysis by *scanning electron microscope* (*SEM*) and *energy-dispersive spectrometry* (*EDS*) follows procedures outlined by Mahaney (2002) and Vortisch *et al.* (1987).

Geochemical analysis of the samples was performed by instrumental neutron activation analysis (INAA) carried out in the SLOWPOKE Reactor at the University of Toronto (Hancock 1984). Appropriate standards were employed to calibrate the equipment (Harrison and Hancock 2005).

Results

Physical characteristics

The two samples taken from soil epipedons around Neem trees differ from one another in dry colour. The Neem-1 topsoil (Ah horizon) is dark reddish-brown (5YR 3/6); the subsoil (Bt horizon) dark red (10R 3/4), the strong reddish colours suggestive of strong secondary Fe genesis down profile. A cursory microscope analysis of the fine sands indicates that more heavy minerals are concentrated in the topsoil than the subsoil below. The heavy minerals at the surface have probably been concentrated by erosion, with light minerals deflated at an unknown previous time.

Both horizons comprising the Neem-2 soil, inclusive of an Ah horizon with brown (7.5YR 4/6) and subsoil Bt horizon with brown (7.5YR 4/4) colours suggest appreciable secondary Fe but less intense than in Neem-1. In Neem-2, the black surface soil is higher in organics that decrease with depth away from the zone of maximum biologic activity, with organic compounds coating well weathered grains influencing the soil colour to some degree. The presence of white, unstained quartz in fine sand fractions is probably owing to higher pH and lower redox potential. Black sands which are present may be silicates and, as in Neem-1, are more prevalent in the surface horizon.

Preliminary light microscope analysis of all four samples indicates the presence of a wide range of aluminosilicates, magnesium silicates, feldspars, amphiboles, pyroxene, garnets and zircons. SEM analysis has also identified the presence of phosphates, including monazite and apatite. Rutile (titanium dioxide) and variations of ilmenite (Ti and Fe) are present in the samples. Rare, gold-coloured grains are made up of mostly Cu with some Zn and Fe. Arsenic-bearing pyrite shows up in some of the selected grains.

Particle size

Differences in texture exist between the two Neem tree soil samples (Fig. 3). Neem-l consists of sandy clay loam, the Ah horizon with more sand and less clay than the underlying Bt which is very nearly a sandy clay. As shown in Fig. 3, the topsoil is coarser with 67% sand, 12% silt and 21% clay, whereas the lower horizon in the epipedon (Bt horizon) is considerably finer with 49% sand, 16% silt and 35% clay. This sample typifies the red, sandy soils that are found throughout the states of Tamil Nadu, Karnataka and Andhra Pradesh.

The Neem-2 soil is an example of the so-called black soils (cf. black cotton soils) that occur in pockets of Tamil Nadu, the so-called Deccan trap soils which occur in northern Karnataka and northwestern Andhra Pradesh. The trap soils are clayey as shown in Fig. 3, amounting to nearly clay stone in the lower horizon. The particle size readout from Fig. 3 reveals 33% sand, 36% silt and 31% clay in the topsoil (Ah horizon). The subsoil (Bt horizon) yields 28% sand, 27% silt and 45% clay. Silt increases upward in both soils and contains

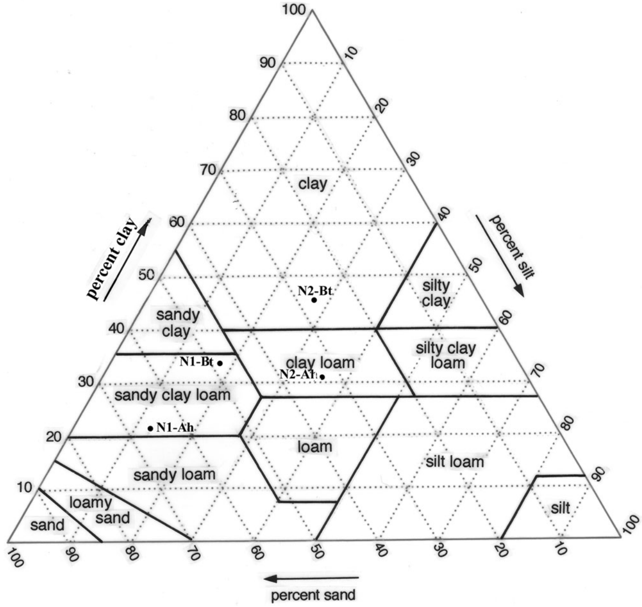

Fig. 3. Ternary diagram showing particle size distributions in profiles Neem-1 and Neem-2. Neem1Ah and Bt horizons fall within the sandy clay loam window showing higher clay in the B horizon. Neem2-Ah yields heavier texture of clay loam, with the Bt horizon heavier still within the clay grade size. Both soils show increasing clay content with depth indicating they classify as Alfisols, probably Tropudalfs (NSSC, 1995). Grain size curves for the four samples are parabolic, suggesting the lower horizons are fluvial, possibly with minor aeolian additions to the surface (Ah horizons).

Table 1. Mineralogy of the <2 μm fraction of the Neem tree soils, Coimbatore and Kunigal, India

Site/horizon	K	MH	I	Ch	S	V	IS	P	Q	O	Mc	Ca	Mi
Neem-1													
Ah (topsoil)	tr	x	x	–	–	–	–	tr	x	x	tr	–	x
Bt (subsoil)	tr	tr	xx	–	–	–	–	–	xx	x	tr	–	x
Neem-2													
Ah (topsoil)	tr	tr	x	tr?	xxx	–	x	x	x	x	x	x	x
Bt (subsoil)	–	–	x	tr?	xxx	–	x	x	x	x	x	x	x

Minerals: K = kaolinite, MH = metahalloysite, I = illite, Ch = chlorite, S = smectite, V = vermiculite, IS = illite smectite, P = plagioclase, Q = quartz, O = orthoclase, Mc = microcline, Ca = calcite, Mi = mica.
Quantities: tr = trace, x = small amount, xx = moderate amount, xxx = abundant amount.

an aeolian component which may explain some of the chemical differences between the Ah and Bt horizons.

Mineralogy

Mineralogical trends were studied to detect differences in leaching conditions between the two Neem sample sites (Table 1). Abundant amounts of smectite and small amounts of illite-smectite occur in Neem-2, and are missing from Neem-1; kaolinite and metahalloysite are more evident in Neem-1. With its 10R and 2.5YR hues, Neem-1 is a well-drained site in a more humid microenvironment. The 10YR 6/1 colour of the clay horizon (subsoil) at Neem-2 appears to be an indication of a poorly drained area where retention of exchangeable cations has led to the formation of smectite. Abundance of illite is slightly greater in Neem-1. Primary mineral weathering appears to be more advanced in the well-drained Neem-1 soil.

Scanning electron microscopy

Selected grains from the sand fraction were subjected to analysis by SEM/EDS to detect microtextures related to transport processes, mineral and coating chemistries. Coatings often archive weathering products (Mahaney *et al.* 2014) that in this instance may relate to fertilization of the Neem tree or to uptake of ions into the tree.

The Ah horizon in Neem-1 contains a number of well weathered and coated grains. The amphibole in Fig. 4(a) shows a thick coating in excess of 1 μm, as the beam at 15 keV barely penetrated to the lithic core underneath. The large adhering grain

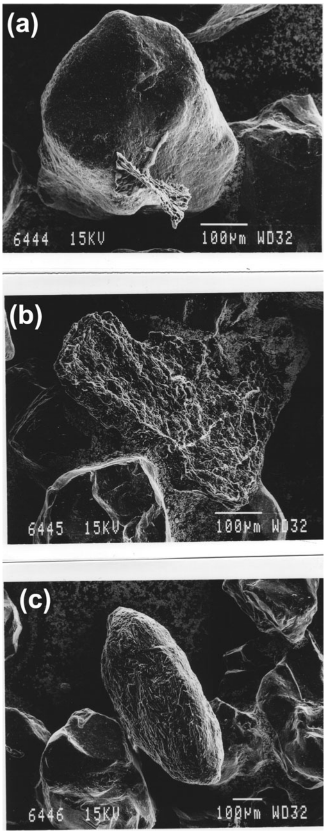

Fig. 4. SEM micrographs, Ah horizon, Neem-1 profile. (a) Subround quartz, thinly coated with Fe and resurfaced with v-shaped percussion cracks with a skeleton of an unidentified organic matter, possibly a microroot well hydrolysed. (b) Apatite grain, well weathered (etched) and representative of ~5% of weathered P-rich grains. (c) Subround hornblende (centre) with a multitude of v-shaped percussion cracks and Fe coating, with subangular quartz to left also carrying v-shaped cracks, and unidentified coated plagioclase grains (centre and upper right).

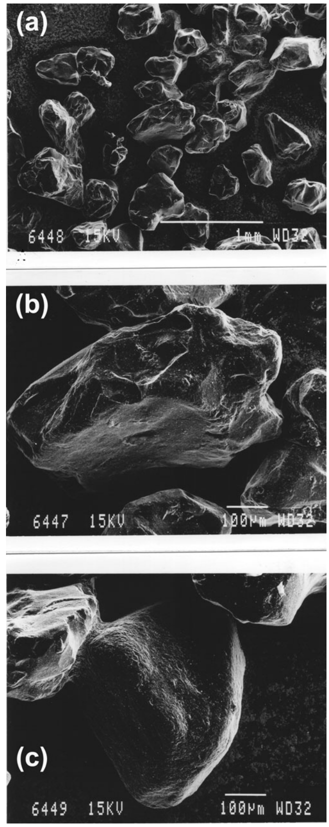

Fig. 5. SEM micrographs, Bt horizon of Neem-1 profile. (a) General frame showing representative grains, many with aeolian characteristics and some with extreme preweathering characteristics and fluvial transport microtextures (v-shaped percussion cracks). (b) Enlargement of the grain in mid centre of (a) shows a preweathered surface (underside) and upper surface with a high frequency of v-shaped percussion microfeatures. (c) Ca-plagioclase grain with a low frequency of adhering particles and thin coating in places and high frequency of v-shaped percussion cracks.

is Ti-Ca amphibole possibly sourced from upper mantle rocks and extremely well weathered. The apatite grain shown in Fig. 4(b) is well weathered, representative of 10–15% of all grains in both the Ah and Bt horizons of Neem-1 and Neem-2, and a source of considerable phosphorus to the soil. Subround quartz (center of Fig. 4c) is representative of 25–35% of all grains encountered in the four samples, and contains a high frequency of v-shaped percussion cracks indicating a long and involved fluvial history. In the upper left of the micrograph a thickly coated quartz grain suggests a long weathering history either in Neem-1 or in some other preweathering locality. To the upper right in the same micrograph, an unidentified plagioclase is well coated.

The Bt horizon in Neem-1 shows several grains representative of angular and subangular grains, mostly quartz and about 25% carrying abrasion fatigue and bulbous edges typical of aeolian-influxed sediment (Mahaney 2002). Some grains are preweathered, meaning they were weathered prior to transport, with fresher surfaces on the same grains a measure of pedogenic alteration after emplacement. The grain in the centre of Fig. 5(a), enlarged in Fig. 5(b), displays a typical preweathered surface (bottom) with partly weathered bulbous edge (top right) and cracked bulbous edge (bottom

Table 2. Selected chemical properties of Neem soils

Site	Horizon	Depth (cm)	pH (1:5)	Salts (mS cm^{-1})
Neem-1	Ah	0–30	6.2	55.9
	Bt	30–60	6.8	38.5
Neem-2	Ah	0–15	7.6	341.1
	Bt	15–40	7.6	308.7

Table 3. Geochemistry of the Neem tree soil samples

Element	Neem-1 Ah	Neem-1 Bt	Neem-2 Ah	Neem-2 Bt
Al (%)	5.7	6.9	5.6	5.9
Ca	0.35	0.28	3.4	3.4
Fe	2.80	2.66	5.50	3.33
K	1.66	1.74	1.39	1.22
Mg	0.5	0.5	1.5	1.4
Na	0.35	0.37	0.37	0.52
Ti	0.33	0.34	1.19	0.38
As (ppm)	1.7	2.6	4.6	4.0
Ba	830	890	920	1150
Br	<0.61	5.5	2.2	5.0
Ce	64.0	34.4	73.7	45.9
Cl	<64	<50	<100	<110
Co	11.3	12.8	18.8	17.4
Cr	81	85	131	106
Cs	2.1	1.7	4.7	2.2
Dy	2.6	2.5	<2.0	<1.9
Eu	0.91	0.79	1.38	1.13
Hf	7.0	5.1	7.4	6.5
I	<6	15	<9	<8
La	35.3	22.7	43.5	30.8
Lu	0.21	0.16	0.32	0.22
Mn	512	629	829	963
Nd	27	19	35	25
Sc	8.68	7.15	17.6	9.91
Sm	4.12	5.12	5.33	3.68
Tb	0.54	0.39	0.74	0.64
Th	15.7	5.8	19.7	7.3
U	2.0	1.8	2.6	2.5
Yb	2.2	1.4	2.9	1.9

right), the bulbous microtexture a signal indicator of wind-blown transport. V-shaped percussion cracks on various grain limbs indicate the grains were water transported at some stage either before or after aeolian emplacement, an interpretation supporting the grain size analysis reported above. The bottom surface is coated with 500 nm of Fe and associated minor elements. A subround coated Ca-plagioclase (Fig. 5c), probably labradorite, is shown with a plethora of adhering particles of mixed mineralogy and v-shaped percussion cracks, the latter again indicative of fluvial transport. The grain to the left of the feldspar is quartz, highlighting a broad plateau with a thick coating (1 μm thick) of Fe and various *rare earth elements* (*REEs*), the latter probably contained in clay minerals.

Chemistry

The pH and total salts (Table 2) were analysed to determine differences between the soil chemistry at the two sites. As expected, the wetter Neem-1 site records lower pH ranging from slightly acid (6.2) in the Ah horizon to near neutrality (6.8) in the Bt horizon. The Neem-2 profile, located in a drier microenvironment yields surface and subsurface slightly alkaline pH values of 7.6, the uniform reaction most likely caused by small moisture differences between the Ah and Bt horizons. The range in total salts reflects the different soil hydrological regimes from site to site, ranging from 56 to 39 mS cm^{-1} in the wetter site and 78–166 mS cm^{-1} in the drier one. As with the pH, total salt variations provide data on the range of H^+ ion concentrations and total salt content preferred by the Neem tree.

Geochemistry

In Table 3, the elements are presented in two groupings. The major and minor elements come first, followed by the trace elements, both in alphabetical order. The REEs are scattered among the other trace elements. Geochemical differences between the two pairs of Neem soils support the clay mineralogy trends. Higher concentrations of Ca in Neem-2 favour the production of smectite. A number of other elements, including Fe, Mg, Mn, As (arseno-pyrite), Co, Cr, Cs and Sc, are also present in higher concentrations in the Neem-2 soils. However, K is elevated in the samples of Neem-1, pointing to greater amounts of illite in these samples.

Bromine, in addition to being concentrated in the termitaria, is almost equally concentrated in the lower horizons of the two Neem profiles. This may confirm the physical evidence, along with measurable I in the subsoil of Neem-1, that the lower horizons are organic enriched, relative to the surface horizons.

Aluminium occurs uniformly throughout the samples, while Ti and Fe (from ilmenite?) are anomalously concentrated in the topsoil (Ah horizon) of Neem-2.

There is an interesting group of elements, Th and the rare earths, that appear to be preferentially concentrated in the surface horizons. The variable concentrations of these elements may confirm the presence of monazite in the Neem samples (see below).

Table 4. **Rare earth elements, Neem soils, India.**

Sample	Ce	Dy	Eu	La	Lu	Nd	Sm	Th	Yb
Neem-1 Ah	64.0	2.6	0.91	35.3	0.21	27	4.12	0.54	2.2
Neem-1 Bt	34.4	2.5	0.79	22.7	0.16	19	5.12	0.39	1.4
Neem-2 Ah	73.7	<2.0	1.38	43.5	0.32	35	5.33	0.74	2.9
Neem-2 Bt	45.9	<1.9	1.13	30.8	0.22	25	3.68	0.64	1.9

Phosphorus, an essential element for living organisms, may be a component in fertilizers derived from the Neem tree. Phosphorus has been identified as a principal constituent of Neem leaves and seed oil (Koul *et al.* 1990; Tiwari 1992), but until now has not been directly linked with the Neem soil samples. Concentrations of P are not measured by INAA, but results outlined above suggest P may derive from apatite and monazite minerals in the Neem profiles. Monazite is a phosphate of REEs (La through Lu in Table 4) and thorium (Th). The REEs and Th occur in obviously elevated concentrations in the Neem topsoils (Fig. 6).

Of the remaining chemical elements, Hf occurs in slightly higher concentrations in the topsoil Neem samples, confirming the presence of quartz in the <2 mm fraction of the surface samples and supporting the XRD for the <2 μm fraction reported in Table 1.

Discussion

The Neem tree (*Azadirachta indica*), native to tropical Southeast Asia, is fast growing, resistant to drought and generally found in nutrient-poor soil but with variable leaching histories as discussed above. Neem trees have been planted over large areas of India primarily to help purify air as the plant is known to take up heavy metals (Akan *et al.* 2013). Seeds on the ground are collected for oil extraction, for use in lamps countrywide. The Neem tree is well adapted to a wide range of climates and elevations up to 1500 m (Matthews *et al.* 1997) and thrives in hot weather with maximum shade temperatures up to 49°C. Neem trees grow in almost all types of soil texture ranging from clay-rich to sandy as indicated in this study, and under alkaline and acidic conditions. The tree is said to improve soil fertility and water-holding capacity as it is known to take up Ca which modifies the soil pH toward neutrality, as shown in the soil chemistry results.

The high concentrations of clay size material in Neem soils suggest that closer scrutiny of adsorbed cations is needed to identify organic and inorganic substances bound to these clays. The variable presence of REEs in the soil clay fractions suggests both silicate and monazite (P-rich) sources. Moreover, regarding potential pharmaceuticals from Neem plant extracts, future research might be directed toward endophytic fungi and bacteria, symbiotic with the tree and subsequently adsorbed to certain clay minerals resident in local soils, as Neem bark will inevitably decay to form a significant organic component in the soil. The soil clay mineralogy in Neem-2 contains abundant smectite, a 2:1 (Si:Al = 2:1) clay with high adsorptive characteristics known to include microbes (Boyd and Mortland 1990; Kostka *et al.* 2002; White 2005). Kaolinite, a 1:1 clay mineral, more prevalent in Neem-1 than Neem-2, is a non-expandable clay species but known in other localities to contain adsorbed organics including microbes and enzymes (Boyd and Mortland 1990). The clay mineral data reported here suggest that expanded geological/pedological/geochemical/biochemical/ microbiological analyses of Neem soils may yield important pharmaceutical results.

With some 80% of the world's biological diversity lying in the tropical and sub-tropical regions of the world (Fullick 2002), the Neem tree is listed as providing one of the most important herbal medicines in South Asia. The potential reward of studying associated soils is enormous but largely ignored in the great range of research carried out on the tree. Despite the fact that many plant species have been tested for pharmaceutical properties, the distinctive properties of their associated soils have not been researched for similar components. Moreover, the limited research on Neem soils is fragmentary at best and limited to only physical and some minor chemical properties when a greater emphasis on mineralogy and chemistry offers the prospect of pharmaceutical discovery.

Phosphorus, an essential element for plant growth, has been identified as a major component of Neem leaves and seed oil (Koul *et al.* 1990; Tiwari 1992), and is contained in fertilizers derived from the Neem Tree which may show promise for increased agricultural production. While concentrations of P are not directly measured by INAA, the presence of elevated Ce indicates monazite, a P-rich mineral, and our SEM investigations indicate P is likely derived from apatite and monazite minerals documented in the local soils. However, our data provide only an approximation of the frequency of occurrence of P-rich minerals, which is less than 10%, and release of P from these minerals depends upon weathering rates under the present

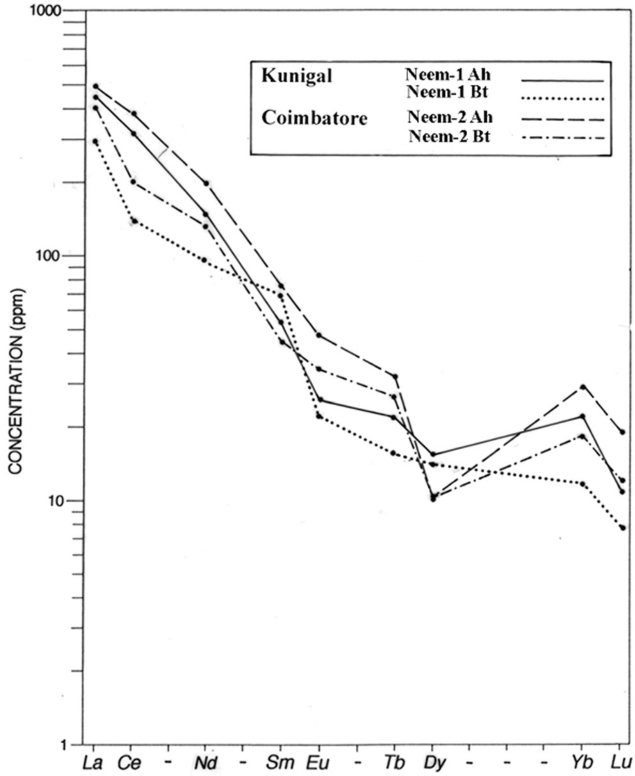

Fig. 6. Rare-earth element profile of the four Neem soils.

climate. With warming and increased precipitation trends outlined by Chaturvedi *et al.* (2012), a future increased release of P is expected which may affect projected agricultural projections (Khan *et al.* 2009; FAO 2012).

While REEs are commonly used in the electronics and high-tech industries, some of these elements have links to pharmaceuticals and medicine. Cerium, for example, is used as an additive to some anti-emetic pharmaceuticals[1] and other rare earths may eventually prove of value in nutrition and human physiology. Based on US Geological Survey data, only 3% of imported REEs in the US were used in pharmaceutical production.[2] Certain REEs, including Nd, La, Ce, at various concentrations, are known to have positive effects on the cell growth of *Cistanche deserticola* and in the production of phenylethanoid glycosides, with a mix of La, Ce, Pr and Sm producing the strongest effect (Ouyang *et al.* 2003). *C. deserticola* is a member of the Orobanchaceae family of plants, commonly known as desert-broomrape, common to semi-desert areas similar to environments where the Neem tree grows well. While no link has been established between local soils and the Neem tree, it is possible that REEs, after uptake from soil, play a biological role in these plants, the correlation of which should be the subject of future research.

The toxicology of REEs has been investigated in relation to other heavy metals (Cd, Pb, Cr etc.) that have similar biomolecular binding energies (Hirano and Suzuki 1996) but recent research is lacking. Because the binding properties of REEs are similar to other heavy metals it is likely that REEs may affect toxicity and metabolism in living systems in a similar way. Thus far, of the lanthanides in group III of the periodic table, the focus has been on Ce which is known to have a concentration approximately 100 times that of Cd (its weight ratio normalized to La is 4.25; Parker 1967), considered one of the most toxic heavy metals. Aside from its possible toxicity, Ce has been shown to have

[1] http://avalonraremetals.com/rare_earth_metal/rare_earths/cerium/

[2] US Geological Survey, Mineral Commodity Summaries, January 2009 (http://minerals.usgs.gov/minerals/pubs/).

antiseptic properties and is useful in the treatment of burns (Monafo *et al.* 1976). The Ce concentrations reported in our database, however, do not appear to offer detrimental toxic effects.

Conclusions

Clay mineralogy, soil colour and texture suggest that the two Neem soils discussed here have different leaching histories, with Neem-1 better leached than Neem-2. The Neem-1 profile appears to be an example of a well-drained site, whereas Neem-2 is less leached, with retention of exchangeable cations and the formation of smectite, a 2:1 (Si:Al = 2:1) clay mineral with great adsorptive qualities and possible medicinal effects.

Despite differences in leaching regimes, the two Neem soils exhibit geochemical similarities. Since Neem tree derivatives are used in the manufacture of fertilizers, the suggestion of elevated concentrations of phosphates in Neem soils is noteworthy. Cursory SEM analysis identifies the presence of monazite and apatite in the samples, although the relative abundances remain undetermined. Concentrations of phosphorus are not available for the sample suite, but other geochemical trends show that Th and a number of the REEs associated with monazite and apatite are found in elevated amounts, especially in topsoil samples. Elevated Th may be important with medicinal benefits at low concentrations and health risks with higher doses (Mahaney *et al.* 1997; Georges-Ivo-Ekosse and Jumbam 2010).

Also of potential interest are the higher concentrations of essential macro and trace elements Ca, K, Mg, Na and Mn in the Neem soils. Bromine is concentrated in the B horizons, possibly as a residue of former leaching events, with an origin in surface organics. Elevated nutrient status of the soils is interesting because Neem tree derivatives are used in domestic animal feeds. On this basis, more detailed analysis of Neem soils is warranted to probe clay mineral and geochemical links with Neem bacterial and fungal species that may play a role in Neem tree physiology and in the production of pharmaceutically useful organics. While no bacterial and fungal filamentous forms were seen with the SEM conducted here, a more robust analysis of grain coatings at higher magnification might prove rewarding, as would metagenomic studies of microbial communities in the sediments surrounding the Neem tree with the possible presence of endophyte-derived organic components in the soil.

Acknowledgements

This work was funded by Quaternary Surveys, Toronto and by minor research grants from York University to WCM. This research was carried out whilst JV was funded by an Ontario Graduate Scholarship.

William C. Mahaney, Quaternary Surveys, 26 Thornhill Ave., Thornhill, Ontario, Canada L4J 1J4, Department of Geography, York University, 4700 Keele St., N. York, Ontario, Canada M3J 1P3
Email: arkose41@gmail.com

Joan Voros, Department of Geography, York University, 4700 Keele St., N. York, Ontario, Canada M3J 1P3

Ramanathan Krishnamani, The Rainforest Initiative, 11/1, Kongu Nagar (East), Ramanathapuram PO, Coimbatore 641 045, Tamil Nadu, India

Ronald G.V. Hancock, Department of Anthropology, McMaster University, Hamilton, Ontario, Canada L8S 4K1

Susan Aufreiter, The Research Institute, The Hospital for Sick Children, University Avenue, Toronto, Ontario, Canada M5G 1X8

Michael W. Milner, MWM Consulting, 182 Gough St., Toronto, Ontario, Canada M4K3P1

Christopher C.R. Allen, Queen's University Belfast, School of Biological Sciences, Belfast BT7 1NN, UK

References

Aduloju, M.O., Adelana, F.Y. and Shuaib, O.M., 2013. Studies on the potentials of *Neem* and *Albizia* pruning as soil amendment. *Global Journal of Bio-Science and Biotechnology*, 2 (4), 467–470.

Akan, J.C., Inuwa, L.B., Chellube, Z.M. and Lawan, B., 2013. Heavy metals in leaf, stem bark of Neem tree (*Azadirachta indica*) and roadside dust in Maiduguri Metropolis, Borno State, Nigeria. *Environment and Pollution*, 2 (1), 88–95.

Aldhous, P., 1992. Neem chemical: the pieces fall in place. *Science*, 258, 893.

Arora, K. and Srivastava, A., 2014. Variation in nitrification inhibition activity of Neem leaves collected from different locations of Lucknow (India). *International Journal of Plant and Soil Science*, 3 (5), 457–466.

Atlas of India, 1987. Oxford University Press, Delhi.

Biswas, B. and Kaplay, R.D., 2011. *Azadirachta indica* (neem): its economic utility and chances for commercial planned plantation in Nanded district. *International Journal of Pharmacy*, 1–2, 100–104.

Biswas, K., Chattopadhyay, I., Banerjee, R.K. and Bandyopadhyay, R., 2002. Biological activities and medicinal properties of neem (*Azadirachta indica*). *Current Science*, 82, 1336–1345.

Boyd, S.A. and Mortland, M.M., 1990. Enzyme interactions with clays and clay-organic matter complexes. In: Bollag, J.-M. and Stotzky, G. (eds), *Soil Biochemistry*, vol. 6. CRC Press, Boca Raton, Florida. 1–28.

Brototi, B. and Kaplay, R.D., 2011. *Azadirachta indica* (Neem): its economic utility and chances for commercial planned plantation in Nanded District. *International Journal of Pharmacy*, 1 (2), 100–104.

Charles, V. and Charles, S.X., 1992. The use and efficacy of *Azadirachta indica* ADR ('Neem') and *Curcuma longa* ('Turmeric') in scabies. A pilot study. *Tropical & Geographical Medicine*, 44 (1–2), 178–181.

Chaturvedi, R.K., Joshi, J., Jayaraman, M., Bala, G. and Ravindranath, N.H., 2012. Multi-model climate change projections for India under representative concentration pathways. *Current Science*, 103 (7), 1–12.

Colin, J.E. and Pussemier, L.D., 1992. The Neem *Azadirachta indica* as a means to control soil nematodes and its application in vegetable cultures in Benin. *Tropicultura*, 10 (3), 89–92.

Day, P., 1965. Particle fractionation and particle size analysis. In: Black, C.A. (ed.), *Methods of Soil Analysis*. American Society of Agronomy, Madison, WI. 545–567.

Delate, K.M. and Grace, J.K., 1995. Susceptibility of Neem to attack by the Formosan subterranean termite, *Coptotermes formosanus* Shir. (Isopt., Rhinotermitidae). *Journal of Applied Entomology*, 119 (2), 93–95.

FAO, 2012. *World Agriculture Towards 2030/2050: The 2012 Revision*. Alexandratos, N. and Bruinsma, J. (eds). Global Perspective Studies Team, FAO Agricultural Development Economics Division, Rome, 129 p.

Fullick, A., 2002. The spice of life. *New Scientist*, 176, 1–4 December.

Garg, G.P., Nigam, S.K. and Ogle, C.W., 1993a. The gastric antiulcer effects of the leaves of the neem tree. *Planta Medica*, 59 (3), 215–217.

Garg, S., Taluja, V., Upadhyay, S.S. and Talwar, G.P., 1993b. Studies on the contraceptive efficacy of Praneem polyherbal cream. *Contraception*, 48 (6), 591–596.

Georges-Ivo Ekosse, E. and Jumbam, N.D., 2010. Geophagic clays: their mineralogy, chemistry and possible human health effects. *African Journal Biotechnology*, 9, 6755–6767.

Gurumurthy, B.R., Nataraja, S.P., Rudramurthy, H.V. and Shivanna, M.B., 2007. Influence of soil salinity on relative biomass and critical limits of growth in selected tree species. *Karnataka Journal of Agricultural Science*, 20 (1), 133–134.

Hamilton, D.P., 1992. The wonders of the Neem tree – revealed! *Science*, 255, 275.

Hancock, R.G.V., 1984. On the source of clay used for Cologne Roman pottery. *Archaeometry*, 26, 210–217.

Harrison, T.P. and Hancock, R.G.V., 2005. Geochemical analysis and sociocultural complexity: a case study from Early Iron Age Megiddo, (Israel). *Archaeometry*, 47 (4), 705–722.

Hepburn, G., 1989. Pesticides and drugs from the Neem tree. *The Ecologist*, 19 (1), 31–32.

Hirano, S. and Suzuki, K.T., 1996. Exposure, metabolism, and toxicity of rare earths and related compounds. *Environmental Health Perspectives*, 104 (Suppl. 1), 85–95.

Javed, N., Gowen, S.R., Inam-ul-Haq, M. and Anwar, S.A., 2007. Protective and curative effect of Neem (*Azadirachta indica*) formulations on the development of root-knot nematode *Meloidogyne javanica* in roots of tomato plants. *Crop Protection*, 26, 530–534.

Jayaraj, S. and Rabindra, R.J., 1993. The local view on the role of plant protection in sustainable agriculture in India. Ciba Foundation Symposium 177, 168–180, discussion 180–184.

Jayaraman, K.S., 1995. Neem unsheaths contraceptive potential. *Nature*, 377, 95.

Juneja, S.C., Pfeifer, T., Willliams, R.S. and Chegini, N., 1994. Neem oil inhibits two-cell embryo development and trophectoderm attachment and proliferation in vitro. *Journal of Assisted Reproduction & Genetics*, 11 (8), 419–427.

Karnataka Forest Department, 1992. *Trees in Society in Rural Karnataka, India*. Overseas Development Administration, Karnataka Forest Department, Karnataka. 42–43.

Kaushic, C. and Upadhyay, S., 1995. Mode of long-term antifertility effect of intrauterine Neem treatment (IUNT). *Contraception*, 51 (3), 203–207.

Khan, Kumar, S., Hussain, M.Z. and Kalra, N., 2009. Climate change, climate variability and Indian agriculture: impacts vulnerability and adaptation strategies. In: Singh, S.N. (ed.), *Climate Change and Crops*. Singer, Berlin, 384 p.

Kostka, J.E., Dalton, D.D., Skelton, H, Dollhopf, S. and Stucki, J.W., 2002. Growth of iron (III)-reducing bacteria on clay minerals as the sole electron acceptor and comparison of growth yields on a variety of oxidized iron forms. *Applied and Environmental Microbiology*, 68 (12), 6256–6262.

Koul, O., Isman, M.B. and Ketkar, C.M., 1990. Properties and uses of neem, *Azadirachta indica*. *Canadian Journal of Botany*, 68, 1–11.

Mahaney, W.C., 2002. *Atlas of Sand Grain Surface Textures and Applications*. Oxford University Press, Oxford, UK, 237 p.

Mahaney, W.C., Barendregt, R.W., Hamilton, T.S., Hancock, R.G.V., Tessler, D. and Costa, P.J.M., 2014. Stratigraphy of the Gorges Moraine System, Mount Kenya: palaeosol and paleoclimate record. *Journal Geological Society*, doi: 10.1144/jgs2012-079.

Mahaney, W.C., Milner, M.W., Aufreiter, S., Hancock, R.G.V., Wrangham, R. and Campbell, S., 1997. Soils consumed by chimpanzees of the Kanyawara Community in the Kibale Forest, Uganda. *International Journal of Primatology*, 26, 1375–1398.

Matthews, B.W., Ram, J. and Takahashi, M.K., 1997. Neem tree establishment and soil response to the use of polypropylene ground cover cloth on a Hawaiian Andisol. *Journal of Hawaiian and Pacific Agriculture*, 8, 1–12.

Monafo, W.W., Tandon, S.N., Ayvazian, V.H., Tuchschmidt, J., Skinner, A.M. and Dietz, F., 1976. Cerium nitrate: a new antiseptic for extensive burns. *Surgery*, 80, 465–473.

Montes-Molina, J.A., Luna-Guido, M., Ceballos-Ramirez, J.M., Fernádez-Luqueño, F., Espinoza-Paz, N., Rincón-Rosales, R., Dendooven, L. and Gutierrez-Miceli, F.A., 2008. Effect of pest-controlling Neem and mata-raton on bean growth, soil N and soil CO_2 emissions. *Agronomy for Sustainable Development*, 28, 187–194.

Mumuni, A., Salifu, A.B., Opare-Atakora, D., Haruna, M., Baba, I.I.Y, Dzomeku, I.K., Brandenburg, R.L and

Jordan, D.L., 2013. Field efficacy of Neem (*Azadirachta indica*) for managing soil arthropods and Cercospora leaf spots damage for increased yield in peanut. *Plant Protection Science*, 49 (2), 65–72.

Murugan, R., Chitraputhirapillai, S., von Fragstein Und Niemsdorff, P. and Nanjappan, K., 2011. Effects of combined application of biofertilizers with Neem cake on soil fertility, grain yield and protein content of Black Gram (*Vigna mungo* (L.) Hepper). *World Journal of Agricultural Sciences*, 7, 583–590.

National Soil Survey Center (NSSC), 1995. *Soil Survey Laboratory Information Manual*. Soil Survey Investigations Report No. 45, version 1.00. USDA, Lincoln, Nebraska, U.S., 305 p.

Ouyang, J., Wang, X., Zhao, B., Yuan, X. and Wang, Y., 2003. Effects of rare earth elements on the growth of *Cistanche deserticola* cells and the production of phenylethanoid glycosides. *Journal of Biotechnology*, 102, 129–134.

Oyama, M. and Takehara, H., 1970. *Standard Soil Color Charts*. Japan Research Council for Agriculture, Forestry and Fisheries, Tokyo, Japan.

Parker, R.L., 1967. *Data of Geochemistry*. USGS Prof. Paper 440-D. US Government Printing Office, Washington, D.C., 19 p.

Shinde, G.N. and Biswas, B., 2011. An environ-economic backbone in the economic resurgence of barren and semi-arid regions; *Azadirachta indica*. *Journal of Natural Products and Plant Resources*, 1 (2), 8–13.

Shukla, R., Sharma, S.B., Puri, D., Prabhu, K.M. and Murthy, P.S., 2000. Medicinal plants for treatment of diabetes mellitus. *Indian Journal of Clinical Biochemistry*, 15 (Suppl. 1), 169–177.

Siddiqui, S., Faizi, S., Siddiqui, B.S. and Faize, G., 1992. Constituents of *Azadirachta indica*: isolation and structure elucidation of a new antibacterial tetranortriterpenoid, mahmoodin, and a new protolimonoid, naheedin. *Journal of Natural Products*, 55 (3), 303–310.

Singh, K.K., 2009. *Neem – a Treatise*. K. International Pvt Ltd, Bangalore, India.

Stark, J.D. and Walter, J.F., 1995. Neem oil and Neem oil components affect the efficacy of commercial Neem insecticides. *Journal of Agricultural & Food Chemistry*, 43 (2), 507–512.

Stix, G., 1992. Village pharmacy: the Neem tree yields products from pesticides to soap. *Scientific American*, 266, 132.

Tiwari, D.N., 1992. *Monograph on Neem (Azadirachta indica A. Juss.)*. International Book Distributors, Dehra Dun, India. 147–191.

Upadhyay, S.S., Dhawan, S., Sharma, M.G. and Talwar, G.P., 1994. Long-term contraceptive effects of intrauterine neem treatment (IUNT) in bonnet monkeys: an alternative to intrauterine contraceptive devices (IUND). *Contraception*, 49 (2), 161–169.

Van Dam, N.M. and Heil, M., 2011. Multitrophic interactions below and above ground: en route to the next level. *Journal of Ecology*, 99, 77–88.

Verma, A.K., Sastry, V.R.B. and Agrawal, D.K., 1995. Feeding of water washed neem (*Azadirachta indica*) seed kernel cake to growing goats. *Small Ruminant Research*, 15 (2), 105–111.

Voros, J., Mahaney, W.C., Milner, M.W., Krishnamani, R., Aufreiter, S. and Hancock, R.G.V., 2001. Geophagy by The Bonnet Macaques (*Macaca radiata*) of Southern India: a preliminary analysis. *Primates*, 42, 327–344.

Vortisch, W, Mahaney, W.C. and Fecher, K., 1987. Lithology and weathering in a paleosol sequence on Mt. Kenya, East Africa. *Geologica et Paleontologica*, 21, 245–255.

Wadia, D.N., 1953. *Geology of India*. Macmillan and Co., London, 531 p and maps.

White, R.E., 2005. *Principles and Practice of Soil Science: The Soil as a Natural Resource*. Wiley, New York.

Whittig, L.D., 1965. X-ray diffraction techniques for mineral identification and mineralogical composition. In: Black, C.A. (ed.), *Methods of Soil Analysis*. American Society of Agronomy, Madison, WI. 671–696.

Manuscript received 26 Jul., 2015; revised and accepted 11 Feb., 2016