

Stoichiometry of cationic nutrients in Phaeozems derived from skarn and Acrisols from other parent materials in lowland forests of Thailand

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ARTICLE INFO

Keywords:

Nutrient rose
Vermic
Earthworms
Termites
Phaeozems
Mollisols
Acrisols
Ultisols

ABSTRACT

Some soils under tropical forests in western Thailand are derived from skarn complexes of hydrothermally metamorphosed granitic, calcareous and ultramafic rocks. We used data from six large, long-term forest ecological research plots to compare the soils derived from skarn with forest soils derived from granites and sedimentary parent materials elsewhere Thailand. The soils derived from skarn are Vermic Phaeozems and have deep, dark, worm-worked topsoils and bimodal particle size distributions of coarse sand and grit in clay or fine loam matrices. They are eutrophic with respect to both labile and non-labile forms of the mineral nutrients. The soils derived from other parent materials are mostly Acrisols. Analyses of variance for the cationic nutrients taken independently clearly distinguished the Phaeozems from the Acrisols. The two groups are also stoichiometrically distinct with respect to the main cationic nutrients, as depicted graphically by nutrient roses and as quantified as $M^{+}:TEB$ ratios. The cationic stoichiometric proportions also differentiated between the Acrisols on different plots and parent materials; and between the Phaeozems in our study and eutrophic soils in lowland forests elsewhere in the lowland tropics, with the Phaeozems having lower exchangeable Ca and Mg contents but higher exchangeable K. Subsoil cationic stoichiometric profiles appear to derive from parent materials, but those of the topsoil may be modified by selective biotic recycling. Nonetheless, inherited lithogenic stoichiometric ratios are still apparent in our topsoils. The forests on skarn in West Thailand are varied and overlap with those on Acrisols and other soils. This confirms earlier findings that climate and disturbance history have more influence than soils on the regional distribution of forest types in Thailand, although soils can be important at more local scales.

1. Introduction

Skarns (calcsilicates) form when siliceous hydrothermal fluids suffuse carbonate or mafic country rocks in contact zones around granite intrusions. They are mineralogically heterogeneous, depending on the compositions of the suffusing fluids and the host rock. Many skarns have porphyritic structures, with coarse quartz or feldspar crystals embedded in fine-grained matrices of intermediate, mafic or ultramafic composition. Skarns are common in contact zones around large granite intrusions, but their outcrops are not extensive. Their location and mode of formation give considerable scope for mineralization, and skarn ore bodies have been prospected and mined for a wide range of resources, including arsenic, copper, gold, molybdenum, tin, tungsten, and rare earth elements. Many studies of soils derived from skarn focus on their potential as pedochemical indicators for mineral prospecting

(Park, Jeon, Kim, & Chon, 2014), or on their contamination during mining (Pfeifer, Haussermann, Lavanchy, & Halter, 2007) and mineral extraction (Requelme, Ramirez, Angelica, & Brabo, 2003).

There are few studies of the pedological and edaphic aspects of soils derived from skarn. The combination of porphyritic quartz and base-rich matrices can give rise to eutrophic soils with high contents of siliceous coarse sand and fine gravel. This mixture gives soils derived from skarn unusual combinations of mineralogical, chemical and physical properties. Soils derived from skarn in Portugal have distinctive clay mineral composition, with substantial contents of pedogenic talc (Stahr, Zarei, Jahr, & Sauer, 2006). Soils derived from skarn in subtropical parts of Bhutan do not contain much coarse sand but are deep red fine loams and clays that are extremely susceptible to dispersion and erosion (Baillie et al., 2004).

Some of the lowland tropical forests of the Huai Kha Khaeng

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Wildlife Sanctuary in Western Thailand are located on a complex of skarn and less metamorphosed calcareous and igneous country rocks (DMR, 1983). However, most forests in Thailand are on deeply and intensely weathered soils derived from a range of igneous and sedimentary parent materials. These soils are brightly colored, intensely leached, acid, dystrophic, and have mainly kaolinitic clay minerals. Most are Acrisols, with some Ferralsols and Alisols (FAO, 2015). Agriculturally-oriented soil analyses emphasize immediately available nutrients, and tend to generalize Acrisols as acid and dystrophic. However, variations in the performance of perennial crops, and edaphically associated floristic and physiognomic patterns in tropical forests indicate that the long-term nutrient status of Acrisols is more variable than first apparent. Acrisols that are derived from different lithologies may be similarly dystrophic with respect to labile nutrients, but can differ substantially in their capacities to replenish the labile nutrient pools from slowly accessible reserves (Ashton & Hall, 1992; Bailey, 1964; Baillie et al., 1987).

The stoichiometric balance between nutrients can be as important as their individual contents. Most previous stoichiometric studies in tropical forest soils have focused on relationships between anionic macronutrients, i.e. C, N and P (Hall, Smith, Lytle, & Liebold, 2005; McGroddy, Danfresne, & Hedin, 2004). Stoichiometry is also important for cations, as the cationic nutrients compete for sites on the non-specific part of the soil exchange complex and for non-specific uptake sites on root surfaces (Schofield & Taylor, 1955; Schuffeln, 1974). The suppression of Ca and K uptakes in many ultramafic soils is as much due to the domination of exchange complexes by Mg as to low absolute contents. Cationic stoichiometric influences have been noted in the floristics, structure and dynamics of dipterocarp forest on Acrisols in Sarawak (Russo, Davies, King, & Tan, 2005; Tan et al., 2009).

We here compare forest soils derived from skarn with those on other parent materials in Thailand. We test whether cation stoichiometry enhances the differentiation between the Phaeozems derived from skarn and the Acrisols; between Acrisols on different plots and parent materials; and between the Phaeozems derived from skarn in Thailand and eutrophic forest soils elsewhere in the tropics.

2. Methods

2.1. Study sites

We characterized the soils of six large long-term inviolate forest ecological research plots in Thailand, including three on the skarn complex in the Huai Kha Khaeng Wildlife Sanctuary in the west of the country. The plots span 12 degrees of latitude (Fig. 1), and a range of lowland tropical climates, with the climate of the most northerly and elevated plot, at Chiang Dao, marginal to lower montane (Table 1). Rainfall ranges from dry and seasonal at Huai Kha Khaeng (ca 1400 mm p.a. and 5–6 dry months dry) to almost perhumid at Khao Chong, with ca 2700 mm p.a. and only two dry months (Bunyavejchewin, Baker, & Ashton, 2002; Williams, Bunyavejchewin, & Baker, 2008). Annual rainfall and duration of the dry season are significant influences on the regional distribution of forest types and also soils in Thailand (Moormann & Rajanasoorthorn, 1972).

All six plots are located on the Sibumasu terrane of the Eurasian continental macro-plate (Puttapibhan, 2002), the basement of which is of Paleozoic age. However, most of the plots are on or near the granites (Hutchison, 1986) that were intruded during the Mesozoic. These granites form the mountainous spine of peninsular Southeast Asia (Fig. 1). The three plots at Huai Kha Khaeng Sanctuary in West Thailand are on a rolling pediplain that is underlain by a complex of skarn with granite, granodiorite, limestone and serpentinite. The Khao Chong plot is on the steep spur slopes of a Mesozoic porphyritic granite mountain and includes a concave colluvial toe-slope and a boulder-choked gully (Fig. 2). The Chiang Dao plot is on the steep mid-slope of a Mesozoic porphyritic granite mountain (DMR, 1983). The Mae Ping plot is on an

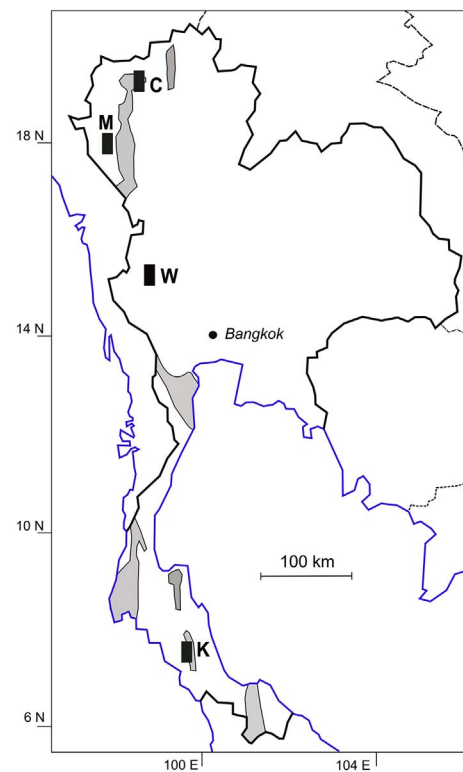


Fig. 1. Forest research plots in Thailand.

C Chiang Dao; K Khao Chong; M Mae Ping; W West Thailand plots (Huai Kha Khaeng, Huai Krading, Kapook Kapieng); Shaded Main granite outcrops.

undulating pediplain on Late Paleozoic - Early Mesozoic limestone (Kurihara et al., 2010). The plain is covered with a thick mantle of decalcified clay. The limestone outcrops as steeply dipping fins on a low rise in the south-western corner, and there is a low ridge of Paleozoic hard interbedded metargillite and quartzite across the southern end of the plot.

2.2. Data collection

Baker (2001) sampled and analyzed soils derived from skarn as part of his ecological study of the forest on the Huai Kha Khaeng 50 ha plot in West Thailand. However, the data for this study come from systematic soil description and sampling in 2004–5 (Table 2). Soil morphology was described by auger at stratified random points along stratified random traverses at densities of 1.5–2 observations per ha. An example of the sampling layout, at the Khao Chong plot, is shown in Fig. 2. Those for the other plots are in Supplementary Figs. S1–S5. Surface litter, wormcasts, termitaria, and snails and their shell fragments were noted at each point, and the upper metre of the soil profile was described by natural horizons for matrix color, mottles, hand texture, consistence, and stones. In addition, soil structure, cutans, porosity, roots, concretions, and faunifacts were described in profile pits located outside the plots.

Auger samples were collected from the main horizons in the pit profiles, and at depths of 0–10 and 40–50 cm at a stratified randomized half of the auger sites (Fig. 2), although the proportion of sites sampled was higher on the 50-ha plot at Huai Kha Khaeng (Supplementary Fig. S1). The samples were analyzed at the Soils Laboratory, Faculty of Agriculture, Kasetsart University, Bangkok: pH electrometrically in 1:2.5 suspensions of fresh soil in water and 1 M KCl; organic C by Walkley-Black dichromate oxidation; total N by micro-Kjeldahl distillation; available P by Bray 2 extraction and colourimetric assay; exchangeable cations by leaching with 1 M neutral ammonium acetate and assay by atomic adsorption spectrometry (AAS); cation exchange

Table 1
Forest research plots, Thailand.

Plot	Fig. 1	Location	Altitude (m)	Total annual rainfall (mm)	Length of dry season (months)	Geology	Topography & slope	Forest
Huai Kha Khaeng	W	15° 38.5' N 99° 21.5' E	500–600	1300–1400	5–6	Skarn complex	Undulating pediplain, < 10%, + low steep hill	Dry seasonal evergreen
Huai Krading	W	15° 39.3' N 99° 21.3' E	550–600	1300–1400	5–6	Skarn complex	Undulating – rolling pediplain, mostly < 10%	Semi-deciduous
Kapook Kapieng	W	15° 38.5' N 99° 22.5' E	600–650	1300–1400	5–6	Skarn complex	Rolling, mostly < 20%	Dry dipterocarp
Chiang Dao	C	19° 16.2' N 99° 50.7' E	820–1010	1700	3–4	Porphyritic granite	Steep, midslope, mostly > 20%	Dry dipterocarp
Khao Chong	K	7° 34.3' N 99° 42.665' E	120–350	2700	2	Porphyritic granite	Steep connecting slope, mostly > 20%, with concave lower slope	Evergreen
Mae Ping	M	17° 39.2' N 98° 45.6' E	690–720	1800	3–4	Decalcified colluvium, quartzite, limestone	Gentle pediplain < 5% with low rocky ridges on W boundary	Dry dipterocarp

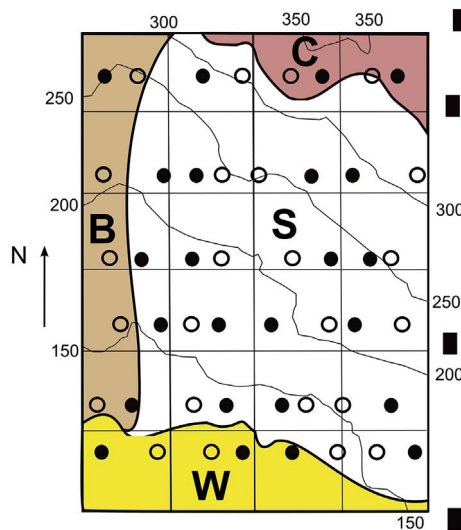


Fig. 2. Soil sampling and soil types on Khao Chong forest research plot, Thailand. Filled circle Sampled & described augering; Open circle Described augering; Rectangle Soil profile; 50 m contours; C Chromic Acrisol on upper slope; S Haplic Acrisol on mid-slope; W Haplic Acrisol (colluvic) on toeslope; B Leptic Entisol in gully.

capacity (CEC) by displacement of the NH_4^+ with excess NaCl and distillation. Total cations and P were extracted by digestion with sulphuric acid and a selenium catalyst, and assayed by AAS or colourimetrically; micronutrient totals were extracted by digestion with nitric and perchloric acids, and assayed by AAS. Particle size distribution was determined hydrometrically after organic matter removal with hydrogen peroxide and dispersion with sodium hexametaphosphate.

2.3. Data depiction and analysis

Differences in mineral nutrient stoichiometry are depicted with nutrient roses (Alvim, 1978; Gemmell, 1974). A frequently used metric to quantify cationic stoichiometry in soils is exchangeable Ca:Mg, as it clearly differentiates mafic from ultramafic soils. A more inclusive measure for acid soils is $\text{M}^+:\text{ECEC}$, where M^+ is the cation of interest and ECEC is the effective cation exchange capacity (= exchangeable $(\text{Ca} + \text{Mg} + \text{K} + \text{Na}) + \text{KCl}$ -extractable Al) (Baillie, Inciong, & Evangelista, 2000). As we have no data for extractable Al, we used the ratio $\text{M}^+:\text{TEB}$ (= total exchangeable bases).

Differences in nutrient contents and stoichiometric ratios were compared by one-way analyses of variance (Anova) and 't' tests for non-paired data. Highly correlated soil attributes were consolidated by factor analysis after removing silt, total N and CEC to avoid linear dependence. After a preliminary scree test, the first five principal

Table 2
Soils data from forest research plots, Thailand.

Plot	Area (ha)	Soils augered	Soils sampled	Sampling depths (cm)
2001				
Huai Kha Khaeng	50	26	26	0–10 10–20 20–30
2004–5				
Huai Kha Khaeng	50	86	60	0–10 40–50
Huai Krading	16	32	16	0–10 40–50
Kapook Kapieng	16	32	16	0–10 40–50
Chiang Dao	16	32	16	0–10 40–50
Khao Chong	24	48	24	0–10 40–50
Mae Ping	16	32	16	0–10 40–50

components were simplified by Varimax rotation. We used SPSS v21 for the statistical analyses.

2.4. Inter-annual variation

The soils of the plots on skarn in West Thailand were described and sampled in 2004 and 2005, by the same operators using the same methods. Preliminary Anova showed no significant inter-annual variations for the morphological and granulometric variables, soil organic matter attributes (Organic C, Total N, and C:N) or for labile (available and exchangeable) nutrients. The data for these variables from the two years were consolidated. However, inter-annual differences for total nutrient contents were significant. The discrepancies probably arose during extraction, rather than in the sampling or assay stages. They precluded consolidation, and the 2004 and 2005 data for total nutrients were treated separately.

3. Results

3.1. Soil morphology

The soils on the Khao Chong, Chiang Dao, and Mae Ping plots are morphologically similar, moderately deep, reddish loams (Table 3 and Supplementary Table S1). Clay contents increase with depth, and there are clayskins on the subsoil blocky structures. The textural fining is associated with increased reddening, from brown or yellow topsoils to redder subsoils. Apart from the soils on limestone at Mae Ping and in

Table 3
Soils of forest research plots, Thailand.

Soil (FAO, 2015)	Plot	Map	Topography	Profile (Supplementary Table S1)
Vermic Phaeozem	Huai Kha Khaeng, Huai Krading, & Kapook Kapieng	Supplementary Figs. S1–S3	Undulating pediplain	1
Skeletal Vermic Phaeozem	Huai Kha Khaeng	Fig. S1	Marble hill	
Humic Acrisol	Chiang Dao	Fig. S4	Steep slope	2
Haplic Acrisol	Khao Chong	Fig. 2	Mid slope	3
Chromic Acrisol	Khao Chong	Fig. 2	Convex upper slope	
Haplic Acrisol (Colluvic)	Khao Chong	Fig. 2	Concave toe-slope	
Leptic Regosol	Khao Chong	Fig. 2	Steep lower slope & gully	
Ferralic Acrisol	Mae Ping	Fig. S5	Colluvial pediplain	4
Skeletal Acrisol	Mae Ping	Fig. S5	Low ridge	5
Eutric Cambisol	Mae Ping	Fig. S5	Low hill	

the gully deposits at Khao Chong, these soils qualify as Acrisols (FAO, 2015). The Acrisols on the lower montane Chiang Dao plot on granite have dark loam topsoils, whereas those at Khao Chong, also on granite, are more varied, with yellowish red stony fine loam topsoils on the rectilinear midslope, reddish fine loam on the convex upper slope, erodible yellowish coarse loam on the concave colluvial toe-slope, and shallow bouldery fill in the gully (Fig. 2). The Mae Ping soils are heterogeneous. Most of the plot is covered by deep, decalcified, uniformly bright red colluvial clay Ferralic Acrisols, with multiple layers of brittle black ferrimanganiferous concretions below one metre. Termites excavate calcareous material from below three metres in places, and there are small dark patches of calcareous soils around termitaria. There are dark brown, slightly calcareous, stony sandy clay Eutrophic Cambisols between the limestone fins in the south-west, and shallow and stony reddish Acrisols over the metasedimentaries in the south of the plot.

The soils derived from skarn on the West Thailand plots are morphologically distinct Vermic Phaeozems. They are mostly gravelly loams with distinctive deep, dark, worm-worked, crumb-structured topsoils and dull brownish red subsoils. Hand textures are bimodal, with quartz grit, fine gravel and coarse sand evenly distributed in a matrix of fine loam or light clay. The combination gives sandy loam and sandy clay loam laboratory textures. There are dark shallow stony Skeletal Vermic Phaeozems on a low hill in the Huai Kha Khaeng 50 ha plot. The white rock is very hard and does not visibly effervesce with hydrochloric acid, but the crumb structures, common earthworms, abundant snails, and soil chemistry indicate that these soils are well-endowed with Ca and are probably derived from siliceous marble or calcsilicate, rather than pure quartzite.

3.2. Soil nutrient contents

The Acrisols are acid and have low or moderate exchangeable base status. The Acrisols at Chiang Dao are less dystrophic than the others, and have base saturations > 50% in the topsoils and > 20% in the subsoils (Table 4). Combined with the higher altitude and cooler climate, this gives them moderate organic matter contents and higher topsoil available P than in the soils derived from granite at Khao Chong. However, the total contents of K and Mg at Chiang Dao are similar to those in the other Acrisols, and total Ca contents are lower. Total contents of micronutrients, except for Cu, are up to 20-fold greater at Chiang Dao than at Khao Chong, with the contrasts ranked Mn > Fe > Zn.

The subsoils of the deep decalcified colluvial red Ferralic Acrisols at Mae Ping have similar exchangeable base status to those at Chiang Dao, but the topsoils are more dystrophic. The Skeletal Acrisols on the metasediments in the south of the plot have fewer exchangeable cations in the subsoil than the decalcified clay but have moderate total K. This combination of low exchangeable with moderate total K is characteristic of many tropical forest Acrisols on argillaceous parent materials (Baillie et al., 1987).

The Phaeozems derived from skarn are distinctly eutrophic, with

nearly neutral topsoils and only slightly acid subsoils, and base saturations > 75% throughout. The dark worm-worked topsoils are well endowed with total nitrogen, C:N, available P, and exchangeable cations (Table 4). The 2001 data for the Huai Kha Khaeng 50 ha plot showed pronounced, but very localized nutrient spikes, particularly for available P (Baker, 2001). These featured for all three depths sampled at the spike sites, and do not appear to be laboratory artefacts. There were similar but less prominent spikes in the 2004 data. The abundance of snails in the Phaeozems is associated with high contents of exchangeable Ca. The Ca levels are similar to those in the Eutric Cambisol on limestone at Mae Ping, suggesting that the pre-suffusion host rocks were calcareous. The Phaeozem subsoils have available P contents an order of magnitude greater than those of the Acrisols.

The contrasts between the Phaeozems and Acrisols are less clear for total than labile nutrients (Table 5). Total P in the Phaeozems is significantly greater than in the Acrisols, and total K is also high, but is matched in the topsoils and exceeded in the subsoils of the Skeletal Acrisol on the metasedimentary parent material at Mae Ping. Totals Ca contents are moderately high in the Phaeozems, but are matched by the Acrisols on granite at Khao Chong. Both are substantially higher than in the un-replicated Eutric Cambisol on the dolomitic limestone at Mae Ping. The Eutric Cambisol at Mae Ping and the Phaeozems have higher Mg totals than the Acrisols. Total micronutrient contents vary significantly, but not between Phaeozems and Acrisols. Rather, there is a strong regional contrast between the higher contents in the soils of the northern plots (Chiang Dao and Mae Ping) and those further south (West Thailand and Khao Chong).

The first five principal components accounted for 70% of the total variance, and were Varimax-rotated (Supplementary Table S2). The first Varimax factor (26% of total variance) is a cline of labile nutrient fertility, and clearly segregates the Phaeozems from the rest. The second (21%) is granulometric, and clay content is positively associated with totals of some nutrients, especially the micronutrients. There are also strong associations of total Ca and Mg with sand on this factor, which are attributed to the feldspathic coarse sand in the Phaeozems and limestone fragments in the Eutric Cambisol at Mae Ping. The third factor (10%) identifies a weak cline from shallow and stony to deep and stone-free soils, and probably reflects available moisture capacity. This factor is also positively associated with C:N, and negatively with total K and Cu. The significant loadings on the fourth factor (7%) appear to be associated with the proportion of micas in the parent material. The fifth factor (6%) is associated with the regional contrast in micronutrient contents.

Anova showed that differences between the plots were significant for the contents of Ca, Mg and K in both topsoils and subsoils. When the comparisons were restricted to the Acrisols, only P (both available and total), base saturation and Fe failed to show highly significant inter-plot differences at both depths. Exchangeable Ca, organic C, and total Mn were highly significant for topsoils but only marginal in the subsoils (Supplementary Table S3).

Table 4
Labile nutrient means and ANOVA in forest research plot soils, Thailand.

Plot	Soil	n	pH	OC	TN	C/N	Exchangeable						
							Avail.						
							P	K	Ca	Mg	TEB	CEC	BS
			%	%	mg·kg ⁻¹	cg ⁺ ·kg ⁻¹							
Topsoil													
Huai Kha Khaeng	Vermic Phaeozem	52	6.3 ^a	3.4 ^{ab}	0.17 ^{bc}	20 ^{ab}	68 ^{ab}	0.57 ^{ab}	14.8 ^a	2.6 ^{ab}	18.0 ^a	17.6 ^{abc}	96 ^a
	Skeletal Vermic Phaeozem	8	6.2 ^a	3.8 ^a	0.19 ^b	19 ^b	65 ^{ab}	0.72 ^a	16.6 ^a	3.9 ^a	21.2 ^a	21.5 ^a	81 ^a
Huai Krading	Vermic Phaeozem	16	5.7 ^b	2.5 ^{abc}	0.14 ^{bc}	19 ^{ab}	43 ^{ab}	0.43 ^{bcd}	7.9 ^b	2.4 ^b	10.8 ^b	13.3 ^b	85 ^a
Kapook Kapieng	Vermic Phaeozem	16	6.5 ^a	3.5 ^{ab}	0.16 ^{bc}	22 ^a	109 ^a	0.71 ^a	13.4 ^a	3.0 ^{ab}	17.3 ^a	20.0 ^{ab}	86 ^a
Chiang Dao	Humic Acrisol	16	5.5 ^{bc}	3.5 ^{ab}	0.25 ^a	14 ^{cde}	27 ^b	0.49 ^{bc}	7.2 ^{bc}	2.8 ^{ab}	10.5 ^b	18.6 ^{abc}	57 ^b
Khao Chong	Haplic Acrisol	16	5.0 ^{cd}	2.3 ^{bc}	0.11 ^{cd}	20 ^{ab}	8 ^b	0.29 ^{cde}	3.0 ^{bc}	1.0 ^{cd}	4.3 ^{bc}	9.0 ^{de}	48 ^b
	Chromic Acrisol	2	4.7 ^d	1.8 ^c	0.11 ^{cd}	17 ^{bcd}	6 ^b	0.26 ^{de}	1.5 ^c	1.0 ^{cd}	2.8 ^c	6.4 ^e	42 ^b
	Haplic Acrisol (Colluvic)	5	5.1 ^{cd}	1.3 ^c	0.07 ^d	20 ^{ab}	6 ^b	0.17 ^e	1.5 ^c	0.7 ^d	2.4 ^c	5.9 ^e	30 ^b
Mae Ping	Leptic Regosol	1 ¹	4.9	2.8	0.14	20	12	0.33	3.4 ^{bc}	0.1	3.9	9.2	41
	Ferralic Acrisol	10	5.6 ^{bc}	1.8 ^c	0.15 ^{bc}	14 ^{de}	17 ^b	0.54 ^{ab}	3.2 ^{bc}	2.6 ^{ab}	6.5 ^{bc}	14.8 ^{bc}	45 ^b
	Skeletal Acrisol	5	5.2 ^{bcd}	1.6 ^c	0.17 ^{bc}	10 ^e	38 ^{ab}	0.33 ^{cde}	2.9 ^{bc}	2.1 ^{bc}	5.4 ^{bc}	14.4 ^{bcd}	35 ^b
	Eutric Cambisol	1 ¹	6.6	0.9	0.18	5	10	0.63	11.5	4.4	16.5	20.8	79
All		148		2.9	0.16	18	51	0.51	10.0	2.4	13.0	16.0	74
Anova p		All < 0.001											
Subsoil													
Huai Kha Khaeng	Vermic Phaeozem	49	5.7 ^{ab}	nd	nd	nd	36 ^a	0.32 ^b	4.3 ^b	1.5 ^b	6.2 ^{bc}	nd	nd
	Skeletal Vermic Phaeozem	5	6.0 ^a	nd	nd	nd	26 ^a	1.04 ^a	9.8 ^a	3.3 ^a	14.1 ^a	nd	nd
Huai Krading	Vermic Phaeozem	16 (6) ²	5.2 ^{bc}	0.5 ^{bc}	0.07 ^{cd}	7	15 ^a	0.26 ^b	1.8 ^{bc}	1.3 ^{bc}	3.3 ^{bcd}	4.8 ^{cd}	76 ^a
Kapook Kapieng	Vermic Phaeozem	14 (6) ²	5.8 ^{ab}	0.8 ^{ab}	0.12 ^{bc}	7	35 ^a	0.52 ^b	3.8 ^{bc}	2.4 ^{ab}	6.8 ^b	12.8 ^a	55 ^{ab}
Chiang Dao	Humic Acrisol	16	5.0 ^{bcd}	0.6 ^{bc}	0.08 ^{cd}	7	2 ^a	0.26 ^b	1.2 ^{bc}	1.0 ^{bc}	2.5 ^{cd}	10.3 ^{abc}	24 ^c
Khao Chong	Haplic Acrisol	8	4.2 ^d	0.7 ^{ab}	0.05 ^d	13	3 ^a	0.16 ^b	0.4 ^c	0.2 ^c	0.8 ^d	7.1 ^c	13 ^d
	Chromic Acrisol	2	4.2 ^d	0.4 ^c	0.04 ^d	11	1 ^a	0.13 ^b	0.4 ^c	0.2 ^c	0.8 ^d	8.4 ^{bc}	10 ^d
	Haplic Acrisol (Colluvic)	5	4.2 ^d	0.5 ^c	0.05 ^d	12	4 ^a	0.13 ^b	0.4 ^c	0.3 ^c	0.8 ^d	6.9 ^c	13 ^d
Mae Ping	Ferralic Acrisol	10	4.8 ^{cd}	0.3 ^c	0.04 ^d	11	1 ^a	0.41 ^b	1.5 ^{bc}	1.2 ^{bc}	3.1 ^{bcd}	12.6 ^a	27 ^c
	Skeletal Acrisol	5	4 ^{cd}	0.4 ^c	0.10 ^{bc}	4	1 ^a	0.23 ^b	0.3 ^c	0.7 ^c	1.3 ^d	11.3 ^{ab}	12 ^d
	Eutric Cambisol	1 ¹	6.2	0.8	0.11	7	2	0.23	2.9	2.8	6.0	15.6	38
All		131		0.6	0.07	9	21	0.34	3.0	1.4	4.7	9.1	36
Anova p		All < 0.001						0.023	All < 0.001				

Superscripts indicate significant inter-soil differences (Tukey B, $p < 0.05$) nd = no data.

¹ Single sample - not included in Anova.

² Only 6 subsoil samples from Huai Krading and Kapook Kapieng for Organic C, total N, C:N, CEC and base saturation.

3.3. Mineral nutrient stoichiometry

The stoichiometric roses (Fig. 3) indicate that the topsoils are better-endowed with labile macronutrients, but totals for K and Mg are higher in some subsoils. The roses show that the Phaeozems are markedly more fertile than Acrisols for P and Ca. There are variations between the Acrisols, with Khao Chong having lower K contents than the other plots. Mg is moderate in the Ferralic Acrisol at Mae Ping but low in the other Acrisols. The Acrisols on the metasedimentaries at Mae Ping have low P and Ca but moderate total K. Although the Phaeozems on the three skarn plots are similar for total nutrient contents in the 2005 data, the Kapook Kapieng soils appeared to be somewhat more fertile than the others in the 2004 data.

The differences between the Acrisols for stoichiometric ratios were significant at $p < 0.005$ for topsoil exchangeable K:TEB, but those for topsoil Mg and Ca were marginal ($p < 0.02$) (Table 6). For the subsoils the Ca:TEB ratio had $p < 0.03$, but those for K and Mg were less significant (Supplementary Table S4).

3.4. Phaeozems derived from skarn in Thailand in a pantropical context

We compared the Phaeozems with a range of eutrophic forest soils in other parts of the tropics. Comparisons between legacy soil data are complicated by methodological variations between laboratories and over time. The discrepancies are particularly acute for total nutrients, because of the different extractants used. Most legacy data for exchangeable cations were obtained by leaching with neutral ammonium acetate, and comparisons between them are less problematic.

For our comparisons, we extracted data for eutrophic forest soils in Sarawak (Andriess, 1972), the Solomon Islands (Wall, Hansell, Catt, Ormond, & Varley, 1979), Palawan in the Philippines (Baillie et al., 2000) and Panama (Baillie, Elsenbeer, Barthold, Grimm, & Stallard, 2007) from the World Soil Survey Archive and Catalogue (WOSSAC) at Cranfield University (Hallett, Sakrabani, Keay, & Hannam, 2017). Comparisons for individual nutrients and stoichiometric ratios between lithological groups indicate that the Phaeozems have lower Ca and Mg than the others (Supplementary Tables S5 and S6). The data show that

Table 5
Total nutrient means and ANOVA (2005 data) in forest research plot soils, Thailand.

Plot	Soil	n	P	K	Ca	Mg	Zn	Mn	Fe	Cu
			%				mg·kg ⁻¹			
Topsoil										
Huai Krading	Vermic	6	0.11 ^a	0.34 ^{cd}	0.71 ^b	0.45 ^a	5.9 ^d	89 ^d	96 ^c	3.3 ^b
Kapook Kapieng	Phaeozem	6	0.10 ^a	0.37 ^c	0.98 ^a	0.54 ^a	7.6 ^{cd}	92 ^d	94 ^c	3.4 ^b
Chiang Dao	Vermic	16	0.05 ^b	0.18 ^{cd}	0.18 ^c	0.11 ^{bc}	31 ^{bc}	514 ^c	11,958 ^{ab}	7.2 ^b
Khao Chong	Phaeozem									
	Acrisol	16	0.04 ^{bc}	0.22 ^{cd}	0.77 ^{ab}	0.12 ^{bc}	5.7 ^d	57 ^d	57 ^c	3.7 ^b
	Chromic Acrisol	2	0.03 ^{bc}	0.26 ^{cd}	0.66 ^b	0.13 ^{bc}	6.7 ^d	69 ^d	80 ^c	5.8 ^b
Mae Ping	Haplic Acrisol	5	0.02 ^c	0.12 ^d	0.79 ^{ab}	0.08 ^{cd}	7.6 ^d	71 ^d	79 ^c	3.2 ^b
	(Colluvic)									
	Leptic Regosol	1 ¹	0.09	0.33	0.72	0.15	6.8 ^d	51	73	4.8
	Ferralic	10	0.03 ^{bc}	0.59 ^b	0.09 ^c	0.06 ^c	64 ^a	1655 ^a	11,551 ^{ab}	11.4 ^b
	Acrisol									
All	Skeletal Acrisol	5	0.04 ^{bc}	0.87 ^a	0.09 ^c	0.05 ^c	45 ^b	1112 ^{ab}	17,791 ^a	21.5 ^a
	Eutric Cambisol	1 ¹	0.04	0.78	0.31	0.97	nd	2448	18,810	14.8
	Anova p	68	0.05	0.39	0.48	0.18	49.7	526	6230	7.2
All < 0.001										
Subsoil										
Huai Krading	Vermic	5	0.08 ^a	0.64 ^{bc}	0.67 ^{ab}	0.45 ^{ab}	6 ^b	89 ^b	95 ^c	3.4 ^d
Kapook Kapieng	Phaeozem	6	0.10 ^a	0.64 ^{bc}	0.79 ^a	0.52 ^a	8 ^b	91 ^b	94 ^c	3.4 ^d
Chiang Dao	Vermic	16	0.03 ^b	0.21 ^d	0.03 ^c	0.12 ^{bd}	40 ^b	282 ^{ab}	19,432 ^b	8.4 ^c
Khao Chong	Phaeozem									
	Acrisol	10	0.02 ^b	0.56 ^c	0.75 ^a	0.45 ^{ab}	6 ^b	53 ^b	73 ^c	4.7 ^d
Mae Ping	Haplic Acrisol	5	0.03 ^b	0.51 ^c	0.51 ^b	0.24 ^{bc}	7 ^b	69 ^b	89 ^c	4.9 ^d
	Chromic Acrisol	10	0.02 ^b	0.91 ^b	0.05 ^c	0.07 ^d	116 ^a	934 ^a	20,485 ^b	20.6 ^b
	Ferralic									
All	Acrisol	5	0.02 ^b	1.85 ^a	0.01 ^c	0.05 ^d	95 ^a	327 ^{ab}	27,962 ^a	47.2 ^a
	Skeletal Acrisol	1 ¹	0.02	1.13	0.08	0.42	1765	2823	33,080	20.4
	Eutric Cambisol	58	0.04	0.66	0.33	0.24	73	348	11,911	12.2
All < 0.001										

Superscripts indicate significant inter-soil differences (Tukey-b at $p < 0.05$) nd = no data.

¹ Single sample - not included in Anova.

the moderate or higher contents of the individual nutrients differ significantly between lithological groups, except for K (Fig. 4 and Supplementary Table S5). All of the cation stoichiometric ratios were significantly different (Supplementary Table S6). Ca predominated in soils derived from skarn and limestone in both topsoils and subsoils, whereas Mg:TEB were significantly higher in soils on mafic parent materials. K:TEB was significantly lower soils on limestone at both depths. The Phaeozem subsoils, had significantly higher K:TEB ratios than the other soils.

4. Discussion

4.1. Soil classification

Soil survey in Thailand has focused on agricultural areas, and there have been only limited surveys in forests. This makes correlation of the soils of the plots with national soil series problematic. We therefore classified the soils according to the World Reference Base (FAO, 2015), and correlated them with Soil Taxonomy (Soil Survey Staff, 2014) in Supplementary Table S7. There are sufficiently large and sharp increases in clay content with depth and clear enough clay skins to qualify most of soils derived from non-skarn parent materials as Acrisols. The dark surface horizons of the Chiang Dao soils qualify them as Humic Acrisols. The upper slope soils at Khao Chong have sufficiently red subsoils to be Chromic Acrisols. The coarse loamy Haplic Acrisols on the concave toeslope at Khao Chong are colluvic. The decalcified red clays at Mae Ping look like Ferralsols, but there are substantial clay increases with depth and visible clay skins, so we designated them as Ferralic Acrisols.

For the soils derived from skarn, the dark, worm-worked upper horizons and Ca contents of satisfy the criteria for the mollic epipedon, and the soils qualify as Phaeozems. The depth of wormcast material is enough for most of them to be Vermic Phaeozems. The dominant pedomorphic role of earthworms is unusual for tropical forests, where they are generally subordinate to termites (Baillie et al., 2000), and as at Chiang Dao (Profile 2 in Supplementary Table S1) and in the distribution of dark calcareous soils around termitaria at Mae Ping.

4.2. Cation stoichiometry in tropical forest soils

The stoichiometric ratios significantly differentiate the Phaeozems from the Acrisols. They also significantly improve differentiation within the pantropical set of eutrophic soils. As well as confirming morphological and other pedo-taxonomic differentiae, stoichiometry has edaphic implications and can indicate potential nutrient imbalances and effective deficiencies that may not be apparent in data for single nutrients. The stoichiometric ratios suggest that cationic imbalances are less likely in Phaeozems derived from skarn than in the other tropical eutrophic soils, in which excessive Ca or Mg may cause K deficiencies.

Our comparisons stress the lithology of the source rocks, and assume that cation stoichiometric profiles are largely inherited from the composition and weathering of the soil parent material. However, as soils are increasingly leached and the primary minerals are progressively weathered, selective plant uptake and recycling may modify soil nutrient balances. Labile stocks of limiting nutrients are hypothesized to become increasingly concentrated in topsoils and to occupy increasing proportions of topsoil exchange complexes (Jobbagy & Jackson, 2001). K is the cationic nutrient for which these trends are most apparent on a

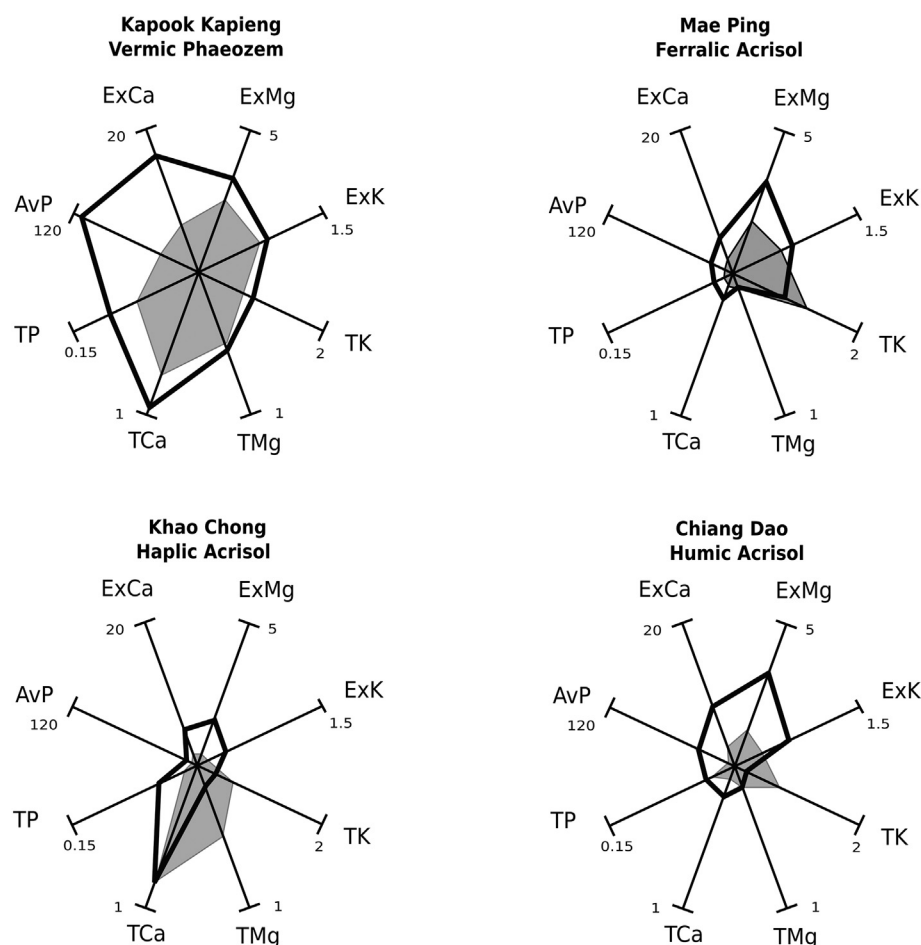


Fig. 3. Macronutrient stoichiometric roses for soils of forest research plots, Thailand.

T Total (2005 data only); Ex Exchangeable; Av Available; Clear polygon Topsoil (0–10 cm); Shaded polygon Subsoil (40–50 cm).

Table 6
Anova of exchangeable cation stoichiometric ratios in forest research plot soils, Thailand.

Plot	Soil	Exchangeable Ca/TEB		Exchangeable Mg/TEB		Exchangeable K/TEB	
		Topsoil	Subsoil	Topsoil	Subsoil	Topsoil	Subsoil
Huai Kha Khaeng	Vermic Phaeozem	0.82 ^a	0.68 ^a	0.15 ^a	0.27 ^a	0.03 ^a	0.06 ^a
	Skeletal Vermic Phaeozem	0.76 ^{ab}	0.67 ^a	0.20 ^{ab}	0.26 ^a	0.04 ^a	0.07 ^a
Huai Krading	Vermic Phaeozem	0.71 ^{ab}	0.50 ^{ab}	0.23 ^{ab}	0.39 ^{abc}	0.05 ^{ab}	0.11 ^{ab}
	Vermic Phaeozem	0.75 ^{ab}	0.55 ^{ab}	0.18 ^a	0.37 ^{abc}	0.04 ^a	0.08 ^a
Chiang Dao	Humic Acrisol	0.66 ^{bc}	0.40 ^{bc}	0.29 ^{bc}	0.46 ^{bc}	0.05 ^{ab}	0.14 ^{ab}
Khao Chong	Haplic Acrisol	0.63 ^{bc}	0.46 ^{ab}	0.28 ^{bc}	0.28 ^{ab}	0.09 ^c	0.38 ^c
Mae Ping	Ferralic Acrisol	0.48 ^c	0.45 ^b	0.42 ^d	0.40 ^{abc}	0.09 ^c	0.16 ^c
	Skeletal Acrisol	0.52 ^c	0.25 ^c	0.40 ^d	0.52 ^c	0.07 ^{bc}	0.23 ^{bc}
	Eutric Cambisol	0.70	0.48	0.26	0.48	0.04	0.04

Superscripts indicate significant inter-soil differences (Tukey-b at $p < 0.05$).

global scale. Most of the soils in this study have saprolite within 1.5 m and are not deeply weathered. Nonetheless, they do show more labile nutrients in topsoils than subsoils. However, the stoichiometric ratios show that K:TEB tends to be lower, not higher, in the topsoils than

subsoils. This suggests either that the lithogenic influence persists and overrides selective biotic accumulation, or that K is not limiting. The Ferralic Acrisols at Mae Ping are the only really deep sola in the study, and even they have lower K:TEB in the topsoils than subsoils.

4.3. Soils and forest in Thailand

As soils and forest both vary with climate, the distinction between climatic and edaphic influences on the regional distribution of forest types is problematic. The total annual rainfall and the length and intensity of the dry season appear to be the main determinants of the regional distributions of forest types in Thailand (Kasao-ard, 1989; Ogawa, Yoda, & Kira, 1961). The predominant influence of rainfall on regional variations on the floristics and structures of tropical forests has also been noted in the neotropics (Gentry, 1982) and Borneo (Slik et al., 2003). Nonetheless, significant edaphic effects on meso-scale variations within the regional macroclimatic pattern have been reported in Thailand (Baker, Bunyavejchewin, Oliver, & Ashton, 2005; Bunyavejchewin, 1985; Bunyavejchewin et al., 2003; Sakurai, Tanaka, Ishidya, & Kanzaki, 1998) and Borneo (Ashton & Hall, 1992; Baillie et al., 1987). The clearest example of edaphic effects on forest floristics in the study plots is at Mae Ping. The Dry Dipterocarp forest on the 16 ha of the plot is very diverse, and > 100 woody species achieve stem diameter > 1 cm at 1.3 m above ground level. The proportions of the main species vary on the different soils, with *Shorea siamensis* predominant on the Eutrophic Cambisols on limestone, *Shorea obtusa* on the Skeletal Acrisols on metasedimentaries, and *Dipterocarpus tuberculatus* on the Ferralic Cambisols. The proportion of *Shorea siamensis* increases in the patches of calcareous soils around termitaria.

Although the three skarn plots in Western Thailand are within a few

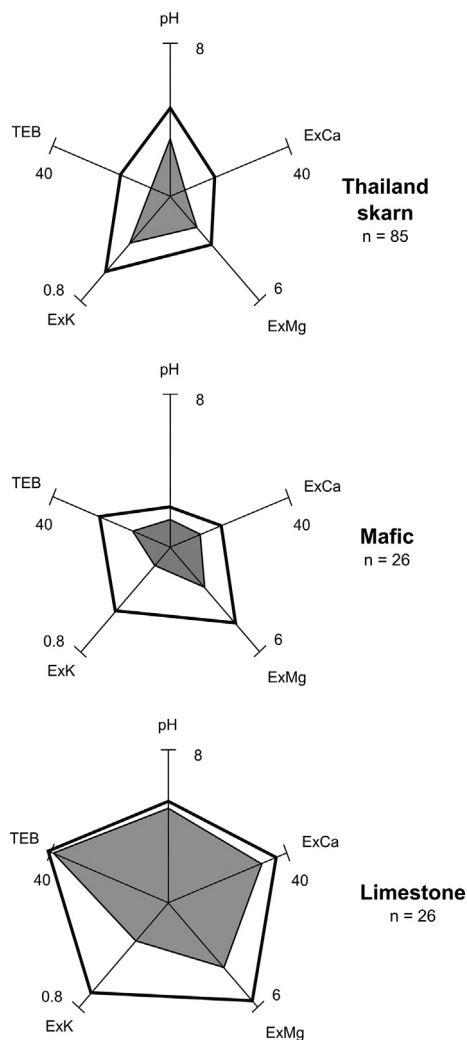


Fig. 4. Macronutrient stoichiometric roses for skarn soils in West Thailand and eutrophic forest soils elsewhere in the tropics.

Clear polygon Topsoil (0–10 cm); Shaded polygon Subsoil (40–50 cm).

kilometers of each other, and have similar climates, parent materials, and soils, they support different forests (Table 1). Analyses of the floristics and stem size profile of the forest on the Huai Kha Khaeng 50 ha plot indicate that it is late successional, and that it was subject to major disturbance in the past few centuries. The disturbance was either caused by, or accompanied by, intense ground fires. Disturbance history appears to be the dominant influence on the distribution of forests at Huai Kha Khaeng (Baker, 2001; Bunyavejchewin, LaFrankie, Baker, Davies, & Ashton, 2009).

The Acrisols in this study are similar to, but slightly more fertile than, those of other Asian dipterocarp forest soils (Adzmi et al., 2009; Baillie, Gunatilleke, Seneviratne, Gunatilleke, & Ashton, 2006; Tan et al., 2009). The Phaeozems have higher cation totals than the eutrophic red clays on the Bukit Mersing basalt in Sarawak but are similar for total P (Ashton & Hall, 1992). The general mineral nutrient fertility levels of the Phaeozems are similar to those on andesitic-basaltic parent materials in Palawan, Philippines (Baillie et al., 2000) and on Barro Colorado Island, Panama (Baillie et al., 2007). However, they are stoichiometrically distinct, with high Ca, and moderate Mg, K and Fe in the Phaeozems in West Thailand, compared with high Mg and Fe in the Barro Colorado soils.

5. Conclusion

Cation stoichiometry supplements and complements conventional taxonomic differentiation of forest soils in Thailand. Stoichiometric ratios enhance the characterization of soil nutrient status, and highlight possible nutrient imbalances. As stoichiometry involves no additional laboratory analyses and resources, it is a potentially useful additional data analysis for the routine edaphic characterization of tropical forest soils.

Acknowledgements

We are grateful to many colleagues for assistance in the fieldwork and data processing, particularly the forest inventory teams at Huai Kha Khaeng and Khao Chong. All of the plots are maintained by the National Parks Wildlife and Plant Conservation Department of the Royal Government of Thailand. The 50 ha plot at Huai Kha Khaeng and the Khao Chong plot are part of the Center for Tropical Forest Science (CTFS) pantropical network and receive financial assistance from the Arnold Arboretum of Harvard University (USA), Smithsonian Tropical Research Institute (USA), National Institute for Environmental Studies (Japan), National Science Foundation (USA) (Grant DEB.0075334) US-AID (USA), Rockefeller Foundation (USA), and the John D. and Catherine T. McArthur Foundation, (USA). The plots at Huai Krading, Kapook Kapieng, Mae Ping and Chiang Dao are wholly resourced by the Royal Government of Thailand. PJB's fieldwork was supported by grants from the Lockwood Fellowship, National Science Foundation, and Sigma Xi. IB's fieldwork was funded by a Bullard Fellowship from Harvard Forest and a travel grant from CTFS. We acknowledge the use of the Ecosystem Services Databank and Visualisation for Terrestrial Informatics facility at Cranfield University, supported by NERC, UK (NE/L012774/1).

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at <https://doi.org/10.1016/j.geoder.2017.11.002>. These data include the Google maps of the most important areas described in this article.

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Stoichiometry of cationic nutrients in Phaeozems derived from skarn and Acrisols from other parent materials in lowland forests of Thailand

Baillie, Ian C.; Bunyavejchewin, Sarayudh; Kaewfoo, Manop; Baker, Patrick J.; Hallett, Stephen H.

2017-11-07

Elsevier

<http://dx.doi.org/10.1016/j.geodrs.2017.11.002>

Baillie IC, Bunyavejchewin S, Kaewfoo M, Baker PJ, Hallett SH, Stoichiometry of cationic nutrients in Phaeozems derived from skarn and Acrisols from other parent materials in lowland forests of Thailand, *Geoderma*, Volume 12, March 2018, pp. 1-9