

Organically Bound Nutrients in Soils of Small Water Catchments Under Different Forest and Agroecosystems in Northern Thailand

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INTRODUCTION

The hillside area of northern Thailand has been rapidly deforested and intensively used for agriculture during the past few decades. This may have resulted in nutrient depletion because of accelerated soil organic matter (SOM) mineralization, increasing soil erosion, removal of trees and crops, and leaching (Stevenson and Cole, 1999). The mineralization of organic nutrients mainly depends on factors influencing the growth of microorganisms such as temperature, moisture, and pH (Bettany *et al.*, 1973; Stevenson and Cole, 1999). In continuous cropping systems which are regularly fertilized at high rates, nutrient losses may be compensated or nutrient storage may even be increased.

In most ecosystems, the P cycle is almost closed with small short-term losses or gains of P (Magid *et al.*, 1996). The concentrations and the chemical nature of soil P are mainly controlled by the major soil forming factors: parent material, climate, topography, soil biota, and time. The distribution of soil P among various organic and inorganic forms thus reflects the history, present structure, and functioning of the ecosystem. The forms of soil P can be substantially affected by agricultural management practices (Tiessen *et al.*, 1984; Guggenberger *et al.*, 1996a,b; Lilienfein *et al.*, 2000), which often involve dramatic changes in vegetation cover, biomass production, SOM levels, and nutrient cycling rates (Magid *et al.*, 1996).

Hedley *et al.* (1982) developed a sequential extraction technique of soil P to distinguish various inorganic and organic fractions, based on their bioavailability. The application of sequential extraction allows for assessing functional P pools and studying the P dynamics in natural and managed ecosystems (Hedley *et al.*, 1982; Tiessen *et al.*, 1984).

With sequential extraction methods, operationally defined P pools may be characterized. However, sequential extraction does not provide information on the structure of P compounds in soil. The latter requires spectroscopic methods such as ³¹P nuclear magnetic resonance (NMR) spectroscopy which is a useful tool for elucidating the structural composition of P in alkali extracts of soils (Newman and Tate, 1980). Therefore, results of ³¹P NMR can support conclusions based on sequential extractions. The diagnostic property of the studied compounds in ³¹P-NMR spectroscopy is based on the chemical shift of the P nuclei (Robinson *et al.*, 1998). The nuclei of different classes of P species such as orthophosphate monoester P, orthophosphate diester P, phosphonates, pyrophosphates, and inorganic orthophosphate P exhibit distinct chemical shift values, which can be used to determine the proportion of the respective P species relative to the total P in the extract. Liquid state ³¹P-NMR spectroscopy has been applied to characterize P forms as a function of climate, cultivation, fertilizer history or environmental conditions (Hawkes *et al.*, 1984; Condon *et al.*, 1990; Guggenberger *et al.*, 1996a b; Sumann *et al.*, 1998).

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Whereas a range of studies on P partitioning in tropical soils have been published, much less is known on S concentrations and forms (Lilienfein *et al.*, 2000). Most S in soils is strongly bound in stable SOM. Degradation and release of S from the stable SOM fraction as SO_4^{2-} which is the major S source for plants is limited and slow. In contrast, the decomposition of fresh plant residues in soil is relatively rapid (McLaren and Swift, 1977). As land use may affect both the quantity and quality of fresh litter and of stable SOM, a strong impact of land use on S concentrations and forms in soils is expected. A number of methods for fractionation of soil S is currently available (Lowe and DeLong, 1963; Kowalenko, 1978; Tabatabai, 1982). Kowalenko (1993a,b) proposed a fast and versatile method for fractionation of soil S into organic S (C-bonded S and ester $\text{SO}_4\text{-S}$) and inorganic S forms using a combination of KH_2PO_4 extraction and hydroiodic acid reduction of SO_4^{2-} .

The objective of the study was to compare total soil C, N, P, and S concentrations and P and S pools among soils under different land-use (cabbage cultivation, *Pinus* reforestation, secondary forest, and primary forest) in northern Thailand.

MATERIAL AND METHODS

Study site

The study was carried out in the mountain region of Khun Sathan, Na Noi district, northern Thailand, at an elevation of 1,350–1,500 m with slopes up to 50%. The mean annual temperature is 25°C, and the average annual rainfall is about 1,400 mm with the dry season from December to April. The geological parent materials in the area consist of shale, sandstone, and siltstone.

The site was divided into four plots: 1) 20-year-old *Pinus kesiya* (Royle ex Gordon) reforestation (RF), secondary forest (15 years old) mixed with a 15-year-old *Pinus kesiya* (Royle ex Gordon) reforestation (SF), primary forest (PF), and cabbage cultivation (CC) (Figure 1). The reforestation, the secondary forest, and the cabbage cultivation sites were cleared about 30 years ago and had been used for opium production. About 15–20 years ago, all three sites were reforested with *Pinus*. The cabbage cultivation was cleared again about 10 years ago with a few *Pinus* trees remaining and intensively used, with high inputs of pesticides and fertilizers (*e.g.* ammonium sulphate). The soils were derived from shale and were Dystric and Humic Cambisols on lower slopes and Skeletic Umbrisols

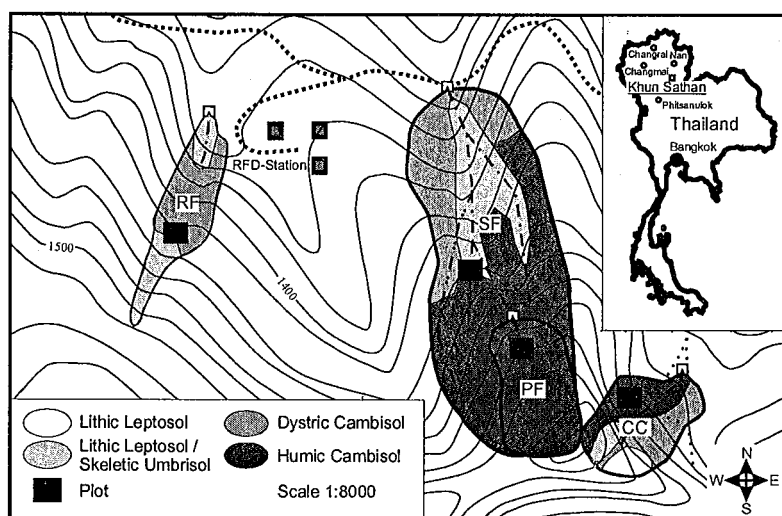


Figure 1: Area and soil map of the study sites at Khun Sathan, northern Thailand (PF: primary forest; SF: secondary forest; RF: *Pinus* reforestation; CC: cabbage cultivation).

and Lithic Leptosols on steeper sloping areas. Under the forest vegetation, organic layers covered the mineral soil surface. The forest floor beneath the primary forest was a mull type (Au horizon only) whereas at the *Pinus* reforestation and the secondary forest a moder was found (additional Oe horizon). At each site, two representative soil profiles were sampled by horizons. Additionally, composite samples of O, A, and B horizons were collected using a radial sampling scheme. All samples were air-dried and the mineral samples were sieved to <2 mm.

Soil analysis

The texture of the soils was analyzed after HCl, hot H₂O, and ultrasonic treatment followed by sieving of sand and determination of silt and clay by the pipette method (Avery and Bascomb, 1974). Soil pH was measured in 0.01 M CaCl₂ at a soil-to-solution ratio of 1:2.5 (w/v). Cation exchange capacity (CEC) was determined with 1 M NH₄OAc (pH 7.0) according to Avery and Bascomb (1974). Total C, N, and S were analyzed with a CHNS-analyzer (Vario EL, Elementar Analysensysteme GmbH, Hanau, Germany). The soils were freed of carbonates. Extraction of oxalate-soluble Al and Fe (Al^{ox} and Fe^{ox}) was carried out with 0.2 M ammonium oxalate at pH 3 (Schwertmann, 1964). Oxalate-soluble Al^{ox} and Fe^{ox} were assumed to represent Al and Fe from humus complexes and short-range ordered mineral phases (Parfitt and Childs, 1988). Dithionite-soluble Fe (Fe^d) was determined by the sodium dithionite-citrate-bicarbonate method (Mehra and Jackson, 1960) and includes Fe from more crystalline oxides and hydroxides (Parfitt and Childs, 1988).

Hedley fractionation for phosphorus

Soil P was determined with a slightly modified sequential extraction according to Tiessen and Moir (1993): resin P was discarded and the samples were extracted with 0.5 M NaHCO₃ followed by 0.1 M NaOH, 1 M HCl, and concentrated HCl; residual P was extracted with 0.5 M H₂SO₄ after heating at 650°C for 5h. Total P was determined in all extracts using an inductively coupled plasma-optical emission spectrometer (ICP-OES, Integra XMP, GBC Scientific Equipment., Dandenong, Victoria, Australia). The alkaline extracts were acidified to pH 1 with HCl and the flocculated organic matter was separated by centrifugation. In the supernatant, inorganic P was measured with the molybdate-blue method (Kuo, 1996).

The NaHCO₃-extractable inorganic and organic P fractions were considered as labile P loosely sorbed on the surfaces of Fe and Al oxides and some microbial P (Bowman and Cole, 1978). The NaOH-extractable P contained secondary inorganic P bound to Fe and Al compounds and clay edges and organic P associated with humic and fulvic acids (Tiessen and Moir, 1993). Therefore, it was considered as moderately labile. Dilute HCl-extractable P was taken as inorganic P associated with Ca (Tiessen and Moir, 1993). The concentrated HCl was intended to remove stable residual inorganic P. Afterwards, the highly recalcitrant P was extracted by 0.5 M H₂SO₄ after combustion at 560°C.

Sulphur fractionation

The inorganic SO₄-S fraction was analyzed by extracting soluble and adsorbed SO₄²⁻ with KH₂PO₄ (500 mg P l⁻¹). The concentration of SO₄²⁻ was determined by reduction with hydroiodic acid (HI) and quantification of the produced S²⁻ as the bismuth sulphide colouring complex by spectroscopy at 400 nm (Kowalenko, 1993a). Total organic S was estimated as the difference between the total S and inorganic S extracted by KH₂PO₄. The concentrations of HI-reducible S, consisting primarily of ester SO₄-S and inorganic SO₄-S, were determined by direct reduction with the hydroiodic acid reducing mixture. The evolved H₂S was captured in a solution containing the colouring reagents as described above; the concentration of the coloured complex was measured on a spectrophotometer. The difference between HI-reducible S and inorganic SO₄-S (KH₂PO₄-extractable) was considered as ester SO₄-S. C-

bonded S was considered to be the fraction of total organic S minus HI-reducible S, based on the finding of Strickland *et al.* (1987) that C-S (amino acid) or C-SO₃ (sulphonate) linkages are not reduced by HI.

Nuclear magnetic resonance measurements

For liquid-state ¹³C- and ³¹P-NMR measurements, the soils were extracted three times with an extraction solution containing 0.1 M NaOH and 0.4 M NaF at a ratio of soil to extraction solution of 1:5 (w/v). The sample size was adjusted to ensure a minimum yield of 200 mg of organic C (OC) in the extracts. The extraction procedure followed the outline of Schnitzer (1982), modified by Sumann *et al.* (1998). The extracts were dialyzed (molecular weight cut-off, MWCO, 12 000–14 000 daltons) in order to remove salts and freeze-dried.

Liquid-state ³¹P-NMR spectra were obtained using an Avance DRX 500 spectrometer (Bruker Analytik GmbH, Karlsruhe, Germany). About 150 mg of freeze-dried material were dissolved in 3 ml of 0.5 M NaOD in a 10 mm NMR tube. The conditions for ³¹P-NMR were: spectrometer frequency, 202.46 MHz; no ¹H-decoupling; pulse angle, 90°; pulse delay, 0.2 s; acquisition time, 0.1 s; line-broadening factor, 20 Hz. Chemical shifts were measured relative to 85% orthophosphoric acid.

RESULTS AND DISCUSSION

Soil chemical properties

The texture of the soils varied from silt loam to clay. Cation-exchange capacity (CEC) in topsoils was high when compared with strongly weathered tropical soils, reflecting soil mineralogy (mainly high-activity clays) and high SOM concentrations in the A horizons (Table 1).

Organic carbon (OC) and total N (TN) showed similar decreases with soil depth. Organic C ranged from 340 to 490 g kg⁻¹ in organic horizons and from 3 to 74 g kg⁻¹ in the mineral horizons. Total N ranged from 1 g kg⁻¹ in subsoil horizons to 21 g kg⁻¹ in organic horizons. The OC/TN ratio was between 22 and 52 in organic layers and decreased to values of <5 in the deeper subsoil. It is interesting to note that despite fertilization, the OC/TN ratios at the cabbage cultivation site did not significantly differ from those under the *Pinus* reforestation and the primary forest sites. Compared to OC/TN ratios reported for the mineral soil horizons of acidic temperate forest soils (e.g. Stevenson, 1986; Zech *et al.*, 1992), these values were smaller, possibly reflecting the rapid nutrient cycling at the study site.

Phosphorus pools

Total P varied from about 200 mg kg⁻¹ in the subsoil horizons of the primary forest to about 1,200 mg kg⁻¹ in the organic layers and the upper mineral horizons of the *Pinus* reforestation and up to 2,000 mg kg⁻¹ under cabbage cultivation (Table 2). These values are high compared to other tropical soils (e.g. Agbenin and Tiessen, 1995). The relatively rich P status of the cabbage cultivation is assumed to be from addition of inorganic fertilizers. The lowest OC/TP ratios occurred in subsoil horizons, the highest were in the topsoil horizons. Similar to the OC/TN ratios, the OC/TP ratios were below those of temperate forest soils (e.g. Stevenson, 1986; Zech *et al.*, 1992).

In many tropical soils recently cleared from forest vegetation, a substantial proportion of soil P is present in organic form. In the studied subhumid tropical ecosystems, organic P (NaHCO₃-P and NaOH-P) comprised up to 50% of the total soil P, NaOH-P being the dominant fraction representing more than 85% of the total organic P pool. These values are in a good agreement with the results for forest-derived tropical soils under humid environments (Udo and Ogunwale, 1977; Sattell and Morris, 1992).

Table 1. Means and standard deviation of selected chemical properties of the studied soils

| | N | OC -----g kg ⁻¹ ----- | TN ----- | OC/TN mmolc kg ⁻¹ | CEC CaCl ₂ | pH | Feo -----mg kg ⁻¹ ----- | Fed | Alo | Ald |
|----------------------------|----|-------------------------------------|-------------|---------------------------------|--------------------------|---------|---------------------------------------|--------|---------|---------|
| Reforestation | | | | | | | | | | |
| Organic layer | 7 | 426±39 | 11±2.3 | 42±17 | 96±15 | 4.8±0.3 | | | | |
| Topsoil | 5 | 40±6.3 | 3.6±0.3 | 11±0.4 | 154±60 | 4.8±0.4 | 6.2±0.3 | 25±6.0 | 3.8±0.5 | 4.6±1.1 |
| Subsoil | 9 | 8.6±2.9 | 1.3±0.3 | 6.6±0.8 | 103±34 | 4.6±0.6 | 4.2±1.3 | 29±8.5 | 2.2±0.6 | 4.9±1.4 |
| Secondary forest | | | | | | | | | | |
| Organic layer | 6 | 428±42 | 15±4.6 | 30±7.0 | 99±18 | 5.6±0.5 | | | | |
| Topsoil | 5 | 53±8.6 | 4.3±0.8 | 12±0.5 | 209±86 | 4.6±0.5 | 7.8±1.8 | 29±10 | 4.5±0.9 | 7.0±2.2 |
| Subsoil | 7 | 21±11 | 2.0±0.9 | 10±1.4 | 137±78 | 4.3±0.3 | 5.8±1.9 | 31±12 | 3.1±1.3 | 6.1±1.9 |
| Primary forest | | | | | | | | | | |
| Organic layer | 6 | 467±18 | 17±2.1 | 28±4.4 | 105±33 | 5.1±0.4 | | | | |
| Topsoil | 5 | 65±8.8 | 4.8±0.6 | 14±0.5 | 253±114 | 3.8±0.1 | 13±1.4 | 38±6.7 | 6.3±0.7 | 9.6±1.3 |
| Subsoil | 15 | 10±6.5 | 1.2±0.5 | 7.8±2.4 | 110±2.4 | 4.2±0.2 | 5.1±3.7 | 35±11 | 2.5±1.5 | 5.8±2.2 |
| Cabbage cultivation | | | | | | | | | | |
| Topsoil | 6 | 41±7.0 | 3.4±0.4 | 12±0.8 | 181±33 | 4.7±0.4 | 7.2±0.7 | 22±6.8 | 4.4±1.2 | 5.6±0.4 |
| Subsoil | 10 | 15±9.9 | 1.6±0.6 | 8.4±2.9 | 126±44 | 4.4±0.2 | 6.5±1.1 | 25±9.0 | 4.4±1.7 | 5.4±0.7 |
| All sites | | | | | | | | | | |
| Total | 80 | 124±179 | 5.1±5.5 | 15±12 | 134±69 | 4.6±0.6 | 6.4±3.0 | 30±10 | 3.6±1.7 | 5.9±2.0 |

TS, total S; OC, organic carbon; TN, total N; CEC, cation exchange capacity; Feo, acid oxalate-extractable Fe; Fed, dithionite-extractable Fe; Alo, acid oxalate-extractable Al; Ald, dithionite-extractable Al.

The ratio of organic C to organic P (OC/P) was used to estimate the mineralization potential of organic P in the soils under investigation. The OC/P ratios of these soils ranged from 13 to 253. Since the OC/P ratios of these soils were below 200 (an exception is the topsoil of the primary forest), mineralization of organic P would readily occur (Dalal, 1977), leading to an increase in the level of available inorganic P, provided the P thus released is not fixed in unavailable forms by Fe and Al oxides and hydroxides or silicate clays.

The P concentrations in and the distribution among the various inorganic P fractions at the sites are shown in Table 2. The labile ($\text{NaHCO}_3\text{-P}$) and moderately labile (NaOH-P) inorganic P fractions constitute between 0.4–11% (7 to 108 mg kg^{-1}) of the total P at the forest plots and 18–30% (220 to 624 mg kg^{-1}) at the cabbage cultivation. The inorganic P associated with Ca (1 M HCl-P) ranged from 0.5 to 63 mg kg^{-1} and comprised up to 6% of the total soil P under forest and up to 14% of the total P under cabbage. The recalcitrant P fractions (both concentrated HCl-P and $0.5\text{ M H}_2\text{SO}_4\text{-P}$) ranged between 93 and 487 mg kg^{-1} representing between 23 and 86% of the total P. These values show that in the studied clayey tropical soils, the refractory inorganic P fractions (1 M HCl-P , concentrated HCl-P and $0.5\text{ M H}_2\text{SO}_4\text{-P}$) were the major inorganic P pool at the forest plots, while the plant available or labile and moderately labile inorganic P fractions were generally small and made up only 22% of the total inorganic P pool. The results are in good agreement with those of Neufeldt *et al.* (2000) for Oxisols of Brazil.

Table 2. Hedley fractionation of P forms of the mineral soil from representative soil profiles of different land use systems.

| System/Fractions | | NaHCO_3 | | NaOH | | $\text{HCl}_{1\text{M}}$ | HCl_{conc} | H_2SO_4 | P_o | P_i | P_{tot} | OC/P _o | P_i/P_o |
|---------------------------------|-------|------------------|--------------|---------------|--------------|--------------------------|----------------------------|-------------------------|--------------|--------------|-------------------------|-------------------|-------------------------|
| Horizon | | P_i | P_o | P_i | P_o | | | | | | | | |
| ----- mg kg ⁻¹ ----- | | | | | | | | | | | | | |
| Primary forest | | | | | | | | | | | | | |
| O | | | | | | | | | | | 322 | | |
| A | 10.8 | nn | 49 | 264 | | 3.7 | 169 | 56 | 264 | 279 | 543 | 253 | 1.1 |
| BA | 1.1 | nn | 15 | 100 | | 0.6 | 128 | 50 | 100 | 193 | 293 | 213 | 1.9 |
| Bw1 | nn | nn | 12 | 71 | | 0.5 | 122 | 35 | 71 | 169 | 241 | 130 | 2.4 |
| Bw2 | nn | nn | 11 | 49 | | 0.6 | 135 | 52 | 49 | 198 | 247 | 109 | 4.0 |
| Bw3 | nn | nn | 11 | 42 | | 0.6 | 130 | 44 | 42 | 185 | 227 | 107 | 4.4 |
| Bw4 | nn | nn | 9 | 23 | | 0.5 | 114 | 40 | 23 | 163 | 186 | 123 | 7.1 |
| Bg1 | nn | nn | 7 | 34 | | 0.5 | 95 | 40 | 34 | 142 | 176 | 74 | 4.1 |
| Bg2 | 0.1 | nn | 7 | 40 | | 0.5 | 62 | 31 | 40 | 100 | 140 | 116 | 2.5 |
| Secondary forest | | | | | | | | | | | | | |
| Oi | | | | | | | | | | | 353 | | |
| Oe | | | | | | | | | | | 332 | | |
| A | 6.9 | nn | 30 | 237 | | 10.8 | 306 | 66 | 237 | 412 | 649 | 198 | 1.7 |
| CA | 3.0 | nn | 17 | 166 | | 4.1 | 143 | 49 | 166 | 213 | 378 | 161 | 1.3 |
| C | 2.2 | nn | 8 | 90 | | 2.0 | 97 | 28 | 90 | 135 | 225 | 147 | 1.5 |
| Reforestation | | | | | | | | | | | | | |
| Oi | | | | | | | | | | | 416 | | |
| Oe | | | | | | | | | | | 486 | | |
| A | 16.3 | 51.3 | 92 | 418 | | 63.1 | 380 | 107 | 469 | 658 | 1128 | 88 | 1.4 |
| Bw | 1.7 | nn | 36 | 147 | | 11.9 | 223 | 56 | 147 | 326 | 473 | 66 | 2.2 |
| CB | 1.6 | nn | 46 | 124 | | 9.7 | 299 | 89 | 124 | 444 | 568 | 59 | 3.6 |
| C | 1.2 | nn | 44 | 116 | | 9.9 | 291 | 82 | 116 | 428 | 544 | 60 | 3.7 |
| Cabbage cultivation | | | | | | | | | | | | | |
| A | 173.0 | 70.2 | 451 | 636 | | 288.6 | 351 | 84 | 706 | 1348 | 2054 | 63 | 1.9 |
| AB | 29.8 | 42.5 | 190 | 560 | | 104.0 | 236 | 54 | 603 | 613 | 1216 | 34 | 1.0 |
| Bw1 | 36.5 | 36.6 | 247 | 557 | | 129.9 | 252 | 56 | 594 | 721 | 1315 | 18 | 1.2 |
| Bw2 | 78.1 | 23.3 | 486 | 533 | | 161.8 | 370 | 83 | 556 | 1179 | 1735 | 13 | 2.1 |

Pi, inorganic P; Po, organic P; Ptot, total P; OC, organic carbon

³¹P-NMR spectroscopy

The ³¹P-NMR spectra of soil extracts from topsoils of the four different land use systems (Figure 2) revealed the presence of seven different ³¹P spin environments, namely phosphonates (~19 mg kg⁻¹), inorganic orthophosphate P (~6.2 mg kg⁻¹), orthophosphate monoester-P (4.1 to 5.6 mg kg⁻¹), teichoic acid-P (1.0 to 2.0 mg kg⁻¹), orthophosphate diester-P (~0.2 mg kg⁻¹), pyrophosphate-P (~-4.8 mg kg⁻¹), and unknown P species (-2.5 to -1 mg kg⁻¹). The monoester-P fraction probably indicated hydrolysis products of plant-derived phospholipids such as inositol phosphate and choline phosphate (Anderson, 1980). At the cabbage cultivation site, monoester-P might additionally result from the input of inorganic P due to fertilization and annual burning. Increasing soil concentrations of orthophosphate is assumed to increase monoester-P in soil (Guggenberger *et al.*, 1996b).

The diester-P fraction contains, among other compounds, nucleic acids, and phospholipids. The fraction is considered to represent a labile P fraction (Stevenson, 1986; Tate and Salcedo, 1988). Phosphonates and teichoic acids may be derived from lysis products of microorganisms (Condon *et al.*, 1990; Bedrock *et al.*, 1994).

As in previous studies dealing with the identification of P forms, monoester-P was usually the dominant P form in surface soils (e.g. Hawkes *et al.*, 1984; Dai *et al.*, 1996; Gressel *et al.*, 1996). Compared with the forested sites, the proportions of diester-P were smaller in the extracts of the cabbage cultivation (Figure 2). This probably reflected an enhanced mineralization of the more labile diester-P form due to cultivation practices, as well as the input of fertilizer resulting in higher proportions of monoester-P (Condon *et al.*, 1990). A detailed discussion of P forms in the studied soils is given in Möller *et al.* (2000).

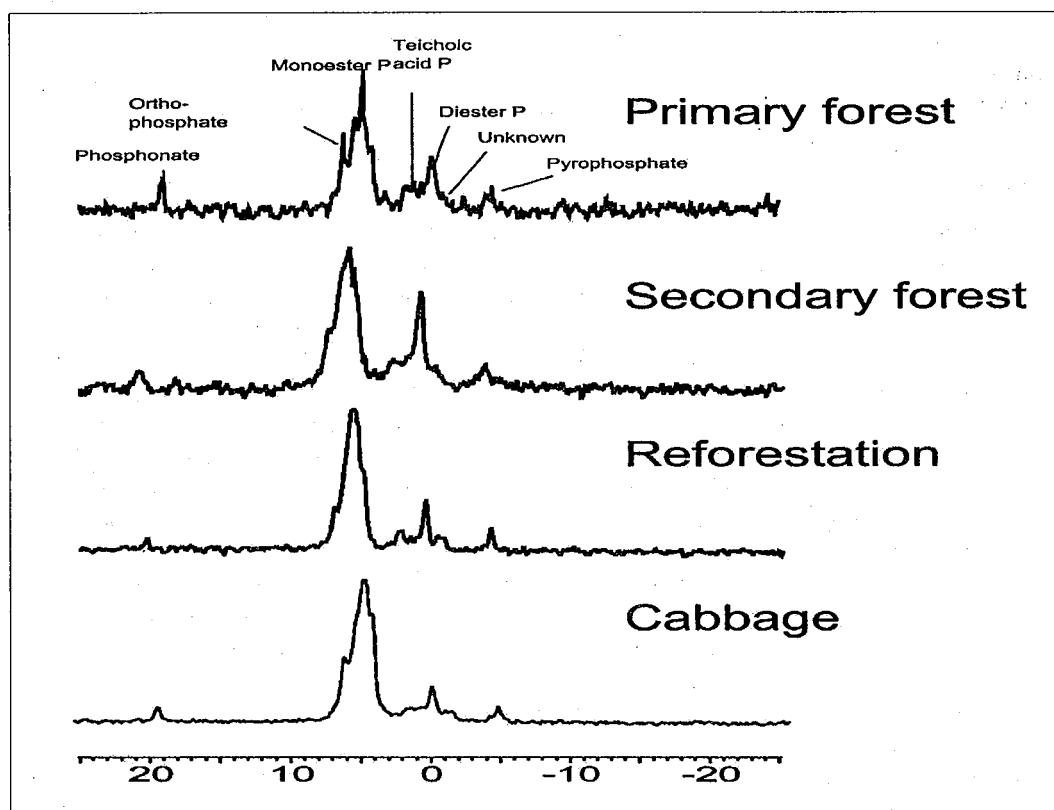


Figure 2: ³¹P-NMR spectra of the topsoil horizons in different land use systems.

Sulphur pools

Total S

The highest total S concentration was found in the organic horizons of the primary forest. It ranged from 1,794 to 2,705 mg kg⁻¹. Under *Pinus* reforestation, the concentrations were lower ranging between 1,283 and 1,732 mg kg⁻¹ (Figure 3). The organic layers of the secondary forest showed the highest variability in S concentrations ranging between 1,447 and 2,410 mg kg⁻¹. The high variations in S concentrations can be attributed to the input of litter with different quality, caused by the alternating vegetation at the secondary forest site comprising planted *Pinus* and natural succession trees. The overall results were similar to those reported by David *et al.* (1982) and Zhang *et al.* (1999) who found 1,306–2,353 and 1,641–2,202 mg S kg⁻¹ in organic horizons of temperate forests, respectively.

The total S concentration decreased with soil depth following the OC concentrations. In the mineral topsoil, S concentrations ranged between 403 and 802 mg kg⁻¹ with the highest values in the topsoil of the primary forest (Figure 3). The only exception was the C horizon of one profile under secondary forest with 2,140 mg S kg⁻¹. The values are higher than those reported by Acquaye and Kang (1987) for topsoils in Ghana (44–281 mg S kg⁻¹) and Neptune *et al.* (1975) for topsoils in Brazil (59–398 mg S kg⁻¹). However, they are similar to those reported for topsoils in Puerto Rico (353–1231 mg S kg⁻¹, Stanko-Golden and Fitzgerald, 1991) and Ethiopia (520–1041 mg S kg⁻¹, Solomon *et al.*, 2000). The S concentrations in the subsoil horizons (149–494 mg kg⁻¹) were slightly higher or within the range of those reported in the literature for soils from various climates (Tabatabai and Bremner, 1972; Johnson and Henderson, 1979; Zucker und Zech, 1985; Houle and Carigan, 1992).

The TN:S and OC:S ratios of all samples averaged 7.8 and 252 in the organic layer, 7.7 and 93 in the surface horizons, and 4.7 and 38 in the subsoil horizons, respectively (Figure 3). These values are again in good agreement with the results reported for a range of temperate and tropical soils (Tabatabai and Bremner, 1972; Ghani *et al.*, 1991; Stevenson and Cole, 1999; Solomon *et al.*, 2000).

Organic S

Among the different S forms, organic S dominates in the studied soils comprising between 75 and 99% of total S. Exceptions were a few B horizons that contained less than 75% of organic S. The dominating role of organic S forms in soil is in agreement with the literature. Organic S concentrations were higher than those reported in the literature for tropical soils and similar to those of temperate soils (Tabatabai and Bremner, 1972; Ghani *et al.*, 1991; Stevenson and Cole, 1999; Solomon *et al.*, 2000).

The major organic S form was C-bonded S contributing 81–99% to total S in the organic layers and 35–83% in the mineral soil. Its contribution decreased with soil depth. These results are common observations for many soils (Ghani *et al.*, 1991; Haynes and Williams, 1992; Houle and Carigan, 1992; Solomon *et al.*, 2000). Stanko-Golden and Fitzgerald (1991) pointed out that the C-bonded S pool in tropical soils is mainly derived from leaves and other photosynthetic tissues and amino acid S remetabolized by soil microorganisms.

The third major component of organic S, ester SO₄-S, is generated predominately by the soil microflora that metabolizes organic residues in the presence of adequate S sources (Sagger *et al.*, 1998). In the study, ester SO₄-S played only a minor role compared with C-bonded S. The maximum ester SO₄-S concentrations were observed in the A horizons (128 ± 49 mg kg⁻¹), the microbially most active zone in soil. Less ester SO₄-S was found in the organic layers (91.5 ± 81.5 mg S kg⁻¹ or 1–12% of organic S). Its concentration decreased in the upper subsoil and remained almost constant in the lower subsoil (64 ± 34 mg S kg⁻¹). Ghani *et al.* (1991) reported in their study on New Zealand soils, that the concentration of C-bonded S in soil was the best predictor of mineralized S and that the bulk of the mineralized S was derived from the C-bonded S pool.

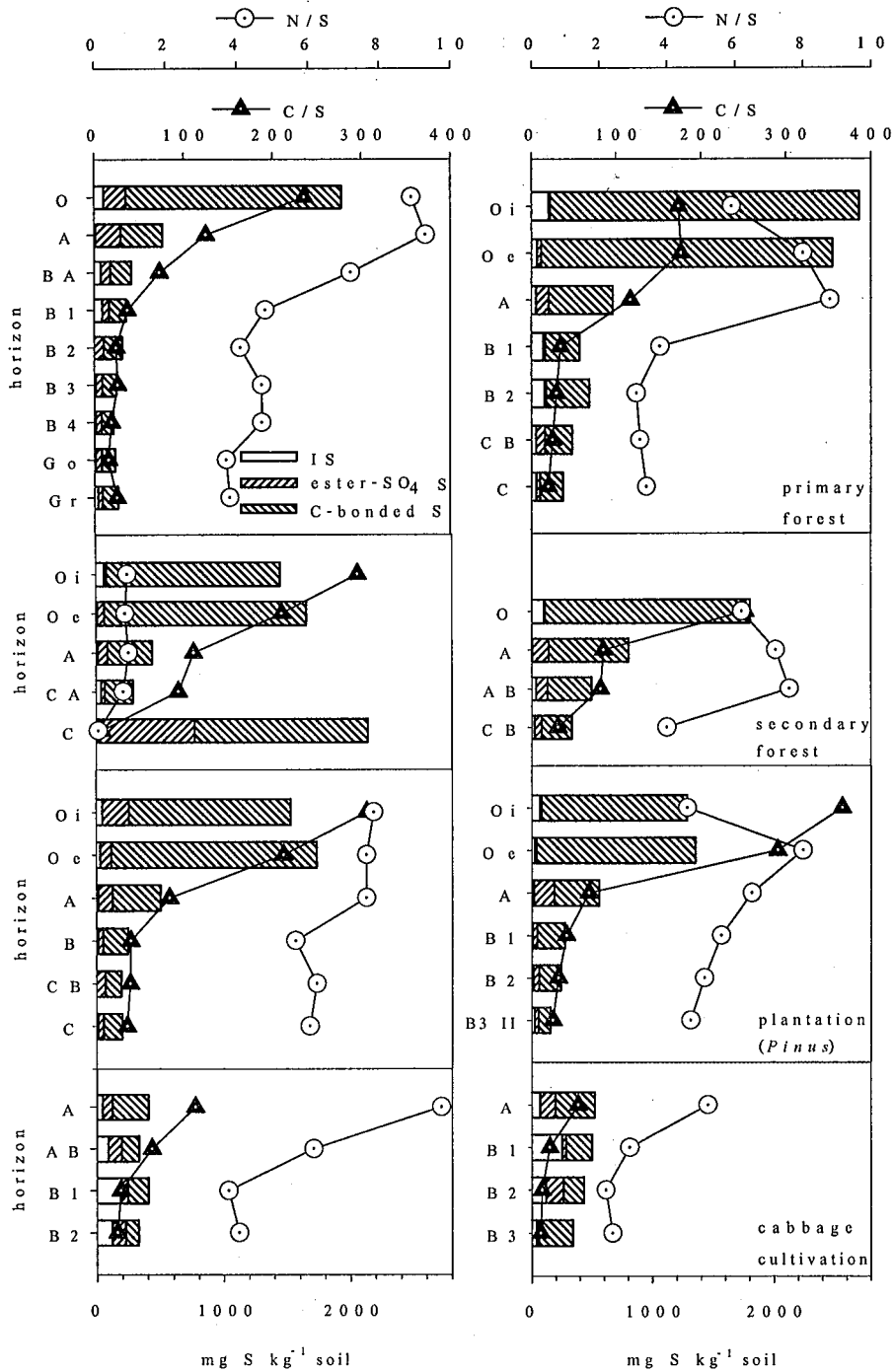


Figure 3:Depth distribution of S fractions, TN/S, and OC/S rations in bulk soil of different land use systems in northern Thailand (IS is inorganic S).

Inorganic S

Tropical systems frequently show a high rate of organic matter decomposition and recycling of nutrients, therefore only low SO_4^{2-} concentrations are found in soil solution. Most of the released S is directly remobilized by the soil microflora. Furthermore, the released SO_4^{2-} may be quickly taken up by plants or leached to greater soil depth. In the study, inorganic S concentrations ranged from 3.5 mg kg^{-1} in the subsoil of the reforestation plot to 192 mg kg^{-1} in the organic layer of the secondary forest and 252 mg kg^{-1} in the subsoil of the cabbage cultivation.

CONCLUSIONS

The study examined the distribution and nature of nutrient pools in differently managed tropical soils of northern Thailand. The results showed higher N, P, and S concentrations in these soils than in many tropical lowland soils. The dominating P species at all sites was inorganic P while the monoester P was the dominant organic P form.

The cabbage cultivation plot showed the highest P concentration because of a high input of fertilizer while the highest S concentrations were found in the organic horizons under forest. The dominant organic S fraction was C-bonded S which provides the largest part of the rapidly mineralized S.

The results further demonstrate that P concentrations and forms in the catchment are mainly controlled by the fertilizer regime while the S concentrations mainly depend on the vegetation type.

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