Nutrient mobility in variable- and permanent-charge soils

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Abstract. Variable-charge (v-c) and permanent-charge (p-c) soils differ fundamentally with regard to many nutrient-cycling processes. Variable-charge soils are more common in the tropics than in temperature zones because their formation requires desilication, which proceeds fastest in warm, moist climates. The dynamics of nutrient mobility tend to be more complex in v-c than in p-c soils. For example, theory predicts that, as pH of v-c soils decreases, cation exchange capacity (CEC) also decreases and anion exchange capacity (AEC) increases. If AEC exceeds CEC, cations such as ammonium and potassium will be more mobile than anions such as nitrate; this is the reverse of the situation in p-c soils, on which most of our knowledge of nutrient cycling is based. Variable-charge surfaces sorb phosphorus, creating plant nutritional problems throughout large areas of the humid tropics. Desilication, the same process that creates v-c surfaces, results also in stable aggregation, creating soils that retain water, yet drain rapidly and resist erosion. The Soil Taxonomy system incorporates information on mineralogy, texture, and organic matter content, and therefore provides insights into patterns of charge chemistry and nutrient cycling across a wide range of soil types.

Introduction

Mobility of nutrient ions in soil is a major factor controlling nutrient cycling in terrestrial ecosystems. Mobility affects the rate at which plant roots can extract nutrients and the rate at which nutrients leach from the system as rainwater percolates through the soil. Although nutrient mobility varies markedly across soil types, simple principles of soil charge chemistry allow important patterns of nutrient mobility to be predicted from the classification of a given soil, in combination with routine data on such variables as pH and soil organic matter (SOM) content. Here, we review factors controlling nutrient mobility and retention in relation to the nature of the electrical charge system of a soil. We give special attention to tropical soils because

these are less familiar to many ecosystem ecologists. We first describe briefly the US Soil Taxonomy so that we can use it to classify soils according to dominance by variable or permanent electrical charge. Next, we discuss the soil-formation processes that result in permanent- or variable-charge soils. With this background, we describe how the two electrical charge systems produce different patterns of nutrient mobility.

Soil classification

Various soil classifications have been developed to confer pattern on the tremendous diversity of soil types. The Soil Taxonomy System (Soil Survey Staff, 1975) classifies soils according to soil temperature and moisture regime and the presence or absence of diagnostic horizons. Implicit in the higher level taxa of the Soil Taxonomy is considerable information on the nature of the secondary (clay) minerals and soil structure. Because all of these factors affect nutrient mobility, the Soil Taxonomy offers a means, not only to deal with the diversity of soil types, but also to predict many aspects of the nutrient cycles that soils support. Although the Soil Taxonomy classifies soils solely in terms of their current properties, the higher taxa (orders) reflect modes of soil genesis. Thus one can infer much from the Soil Taxonomy about the processes that have given rise to a particular soil.

For example, the Hoolehua series, described from the Hawaiian Islands, is classified as an Oxic Ustropept (fine, kaolinitic, isohyperthermic). The ending "ept" indicates that the soil is in the order Inceptisol, young soils with recognizable A, B and C horizons but few other diagnostic horizons. The suborder "Tropept" means the soil is tropical – the mean annual soil temperature is greater than 8 °C, and the difference between mean summer and winter temperature, less than 5 °C. The great group "Ustropept" indicates an ustic moisture regime: a pronounced dry season that does not occur when temperature is most favorable for plant growth. "Isohyperthermic" conveys the additional information that mean annual soil temperature is greater than 22 °C. Subgroup "Oxic" identifies the Hoolehua series as an intergrade between the orders Inceptisol and Oxisol, the latter being strongly aggregated soils markedly lacking in 2:1 silicate clays, and therefore in CEC, except at high pH. The Hoolehua soil, however, is still an Inceptisol – not yet sufficiently weathered to be an Oxisol. "Kaolinitic" identifies unequivocally the major clay mineral. It suggests, for example, that the P-sorption capacity of the soil will be moderate by global standards. The Soil Taxonomy also provides implicit information. The Hoolehua series, for example,

does not contain large amounts of SOM; if it did, it would be classified as a Humitropept.

Excellent introductions to the Soil Taxonomy are available. Sanchez (1976) summarizes features relevant to tropical systems. Birkeland (1984) introduces the system from the point of view of the geomorphologist and quarternary geologist. Buol et al. (1980) have written the standard text, which provides a well-organized, reasonably complete description of the entire system. The primary source is, of course, the Soil Taxonomy monograph itself (Soil Survey Staff, 1975), which is being revised by several international committees.

Electrical charge systems in soils

Soils of the world can be divided broadly into two types based on major factors affecting nutrient mobility. In one type (permanent-charge, or p-c), the electric charge on clay particles results from alteration of the crystal lattice structure of the clay when ions of lower valence substitute for ions of higher valence. The resulting charge deficit is permanent, in the sense that it is a structural feature of the clay particle and persists irrespective of changes in soil pH and soil solution composition. Most of the permanent charge in soils is on surfaces of layer-silicate clays, which compose most of the surface area of p-c soils. These clays include the 2:1 layer-silicates (illite, vermiculite, and smectite), and the 2:2 clays (chlorite). The 1:1 group of kaolin clays have a small amount of permanent charge on their planar surfaces.

In the other type (variable-charge, or v-c), the electric charge results from protonation and deprotonation of surface hydroxyl groups (Gast 1977; Parfitt 1980; Uehara & Gillman 1981; Gillman 1984; Stumm 1986; White & Selazny 1986). Surface hydroxyls occur at the edges of 1:1 layer-silicate clays, such as kaolinite; on less ordered aluminosilicates, such as halloysite; on very poorly ordered aluminosilicates (allophane and imogolite); on crystalline hydroxides and oxides of Al (gibbsite) and Fe (goethite, hematite); and on organic matter. Protonation of these hydroxyls gives positive surface charge and, therefore, anion-exchange capacity (AEC); deprotonation yields cation-exchange capacity (CEC). In addition, surface hydroxyls are readily replaced by phosphate ligands, thus the same surface chemistry that gives rise to CEC in variable-charge soils results also in phosphate sorption (Fox 1978; Mott 1981).

Although all soils contain both p-c and v-c surfaces, many soils are

dominated by only one of these charge systems. Variable-charge soils are more common in the tropics than in the temperate zone because v-c minerals develop most rapidly under warm humid conditions. Not all tropical soils are dominated by v-c constituents, however. Both permanent and variable charge occur to at least some extent in all soils, and large areas of the tropics are occupied by nearly pure p-c soils (Sanchez 1976).

Whether a soil is dominantly p-c or v-c depends largely on its mineralogy, which can be inferred from the classification within the Soil Taxonomy. For example, Vertisols and most Mollisols are strongly p-c dominanted, whereas Oxisols, Ultisols, Histosols and Andepts (Andisols) are predominantly v-c. Mineralogy varies within orders such as Alfisol, and more detailed taxonomic information is needed to predict charge chemistry. Thus, at the order level the Soil Taxonomy does not always provide the information needed, but as a rule it is sufficient for at least a preliminary description.

An indication of the power of the Soil Taxonomy can be seen in the fact that Sanchez et al. (1982) were able to develop a system for predicting soil fertility and land-use capability based almost entirely on the same parameters used to classify soils in the Soil Taxonomy. This system successfully predicts many agronomic problems and potential solutions. It works in part because fundamental differences among soils, such as the difference between p-c and v-c mineralogy, are taken into account in the Soil Taxonomy.

Genesis and classification of soils: relation to charge systems

The Soil Taxonomy groups soils of similar mineralogy, partly because they behave similarly and partly because they share similar modes of genesis. Understanding the weathering processes that alter mineralogy thus helps to explain, not only genetic relations among soils, but also the groupings within the Soil Taxonomy.

Desilication and cation loss

By desilication, we mean the progressive lowering of levels of Si in the soil solution as weathering depletes the soil of feldspars and other primary silicate minerals (e.g. Birkeland 1984). With increasing desilication, 2:1 clays become unstable. Existing 2:1 clays dissolve and new 2:1 clays do not form. With more weathering, Si concentrations drop further, and the ratio of gibbsite to kaolinite increases. In the most extremely desilicated soils, even kaolinite is scarce. Indeed, gibbsite plus Fe hydroxides, along with their water of hydration and small amounts of essentially unweatherable primary minerals such as TiO_2, account for as much as 90% of some Hawaiian

Orthoxes (Soil Survey Staff, 1976). It should be noted that desilication is accompanied by a progressive lowering of cation concentrations (alkalis and alkaline earths) in solution. Cation concentrations also determine mineral stability but tend to be more an effect than a cause of the changes in mineral stability.

Loss of Si and cations during weathering is accompanied by a steady decrease in the specific surface area of the clay minerals (Table 1). Permanent-charge 2:1 clays and allophane provide the most surface area; both occur early in their respective weathering sequence. The Al and Fe hydroxides provide the least surface area and are end-members of the weathering sequence. This tendency towards decreasing surface area has both causes and effects that are relevant to nutrient cycling, as discussed later.

The effects of desilication and cation loss can be seen in many tropical landscapes and soil profiles. Where drainage is unimpeded, for example, Si and cations are lost and weathering proceeds towards kaolinite and Al and Fe hydroxides, as just described. Where drainage is impeded, however, or where Si and cations are replenished, 2:1 clays such as smectite accumulate or persist at both the microsite and the landscape level (see Birkeland 1984). For example, Sherman & Uehara (1956) noted that olivine basalt weathered to a smectite (montmorillonite) beneath stones, where water flow and leaching were restricted, but to kaolinite elsewhere in the soil. At the landscape level, one has only to look at large areas of India and Australia where poor drainage prevents depletion of cations and silica and produces smectite-rich soils (Vertisols). Local topography also alters drainage patterns and therefore influences weathering. For example, smectites accumulate deep in the soil profile and at slope bottoms, even in areas otherwise dominated by

Table 1. Cation exchange capacity (CEC), surface area, and surface charge density values for soil minerals. Reprinted from Talibudeen (1981); data compiled originally from various sources.

Mineral type	Surface area $(m^2 g^{-1})$	CEC $(\mu eq\, g^{-1})$	Surface charge density $(\mu eq\, m^{-2})$
Allophanes	500–700	500–1000	0.71–2.0
Hydrous oxides of Fe and Al (pH ~ 8.0)	25–42	5–10	0.12–0.4
Kaolinites	10–20	20–60	1–6
Clay micas (Illites)	90–130	200–400	1.5–4.4
Fithian illite	93	260	2.8
Smectites	750–800	600–1200	0.75–1.6
Wyoming bentonite	750	1000	1.33
Vermiculites	750–800	1200–2000	1.5–2.7
Kenya vermiculite	780	1240	1.6
Llano vermiculite	780	2070	2.7

soils rich in Al and Fe hydroxides (Sanchez 1976). The general principle is that p-c clays form and persist wherever cation and Si concentrations remain high.

Effect of climate

In cold, moist climates, Al and Fe leach faster than Si, resulting often in the formation of a surficial, quartz-rich albic horizon overlying a deeper spodic horizon rich in amorphous Al and Fe precipitates. There is no commonly accepted thermodynamic explanation for the effect of temperature regime on Si versus Al and Fe leaching. Differences in microbial activity could be responsible, if Fe and Al leaching is controlled mainly by levels of organic acids that chelate these elements and produce low pH's. Concentrations of organic acids in soil leachate from forest ecosystems do tend to decrease with increasing site temperature (Johnson et al. 1977), presumably because more intense microbial activity at higher temperatures results in complete decomposition of organic acids to bicarbonate. The bicarbonate, however, lacks chelating ability and is a weaker acid. Thus, given equal rates of production of organic acids from live and decaying vegetation in temperate and tropical climates, Al and Fe would leach more rapidly than Si at colder sites, where microbial activity is less intense.

Effects of parent materials

Weathering of volcanic parent materials produces an unusual sequence of mineralogies. Here the initial weathering products are amorphous aluminosilicates, such as allophane and imogolite, which are purely v-c minerals. Allophane is a gel-like mineral with a very short-range crystal structure (< 5 nm repeat structure (Sposit 1984)) relative to that of layer-silicates and Al and Fe hydroxides. As a result, allophane has a very large specific surface area (Table 1) and is very reactive. Allophane typically converts to halloysite, a hydrated form of kaolinite that contains both p-c and v-c. Often, the halloysite alters to kaolinite.

Allophanic soils develop from most volcanic parent materials, especially those rich in mafic materials, and from sedimentary and metamorphic rocks whose component particles derive from volcanic rock. The only requirements may be abundant Al and Si in the parent material and abundant, freely draining moisture to remove base metal cations. Allophanic soils rarely, if ever, form from granitic parent materials or from those largely lacking in Al and Fe (e.g. quartzics, limestones). Allophane is thought to be absent in desert and semi-desert environments, although volcanic soils

(Andisols, in the revised Soil Taxonomy) occur in arid areas (Wright 1965; Wada 1977).

Ultra-mafic rocks contain little Al and thus weather to nearly pure v-c soils (Oxisols) much sooner than do other parent materials. The Nipe soils series of the Greater Antilles, for example, derives from serpentinite and, though not particularly old, contains almost exclusively Fe (and some Al) hydroxides in the clay size-fraction (Beinroth 1982). The iron content may be an especially important factor. Minerals in ultra-mafic rocks contain large amounts of Fe(II), oxidation of which disrupts their crystal structure and causes rapid breakdown of the rocks (Birkeland 1984).

Effects of charge chemistry on nutrient cycling

Exchange capacity of variable-charge soils

The surface charge of a v-c soil changes markedly with changes in the pH and composition of the soil solution. Beginning with a now classic paper by Parks & de Bruyn (1962), equations that describe these relationships have been derived. The following equation (after Uehara & Gillman 1980; Singh & Uehara 1986) is used widely:

$$\sigma = (2\mu\varepsilon RT/\pi)^{1/2} \sinh[1.15z(PZC - pH)]$$

where σ = net surface charge density (C/m^2, C = coulombs), μ = electrolyte concentration (kmol/m^3), ε = dielectric constant of water (C^{2}J^{-1} m^{-1}), R = gas constant (J kmol^{-1}deg^{-1}), T = absolute temperature (deg), z = counter-ion valence (dimensionless), and PZC = pH at the point of zero charge.

A v-c soil is electrically neutral (i.e. at its isoelectric point) when pH equals PZC. Not only is net charge zero, but total charge (positive plus negative) is minimal (Fig. 1). The PZC for pure Al and Fe hydroxides is at a pH of about 8, so these minerals have net positive charge unless pH exceeds 8. The PZC of Si-OH (silanol) surfaces and of organic matter, on the other hand, is at a pH of about 2 (Sposito 1984). (By definition, p-c minerals lack a PZC because the surface charge is permanent.) Because soils contain a mixture of Al, Fe, Si and organic hydroxyls, bulk soil PZC's tend to range between pH 3.5 and 5 (Parfitt 1980; Uehara & Gillman 1981).

The net charge of a soil, and thus its ion-exchange capacity, depend on both the amounts of clay minerals present and the charge density (charge per unit surface area). Thus
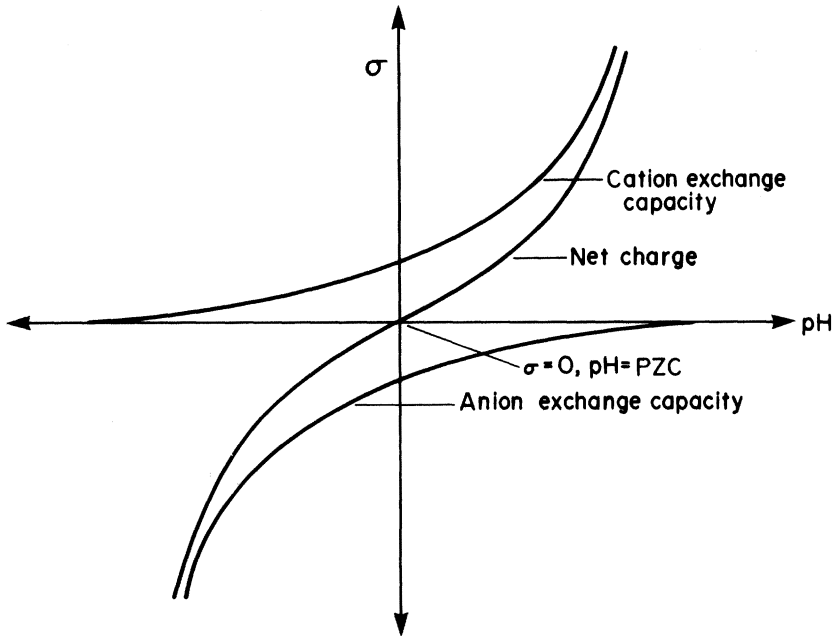
Fig. 1. Effect of pH on cation and anion exchange capacity and net charge of a variable-charge material. σ = net surface charge density, PZC = point of zero charge.

$$\phi = 0.01036 S\sigma$$

where ϕ = net charge (mmol($+/-$)/g, S = specific surface area (m²/g), and σ = net surface charge density (C/m²). Table 1 lists CEC, specific surface area and charge density of typical soil clay minerals. Interestingly, clay minerals differ little in their charge density (charge per unit area of surface). It is, rather, the differences in specific surface area, and of course PZC, that create the large differences in ion-exchange capacity among clay types.

Soil pH values tend to remain near the PZC because total charge (the sum of absolute values of negative and positive charge) is minimal when the soil pH is at the PZC (Fig. 1) and the soil is therefore at its chemically most stable state. In fact, highly weathered tropical soils generally are acid only so long as organic matter is abundant. Where both silicate clays and SOM are scarce – for example, in Oxisol subsurface horizons – pH's greater than 6 are common.

Soil organic matter is the only major soil component other than silicate clays with a low PZC. Thus SOM offsets the effects of desilication, maintaining a low PZC and, therefore, at least some CEC in highly weathered v-c soils (Gillman 1985). The inverse correlation between PZC and SOM con-

tent can be strong (Fig. 2). We know of no data for the PZC of SOM per se; however, titration curves for Douglas-fir 02-horizon material converged but did not actually cross even at pH of less than 2.5 (D. Turner & P. Sollins, unpublished), indicating that R-OH$_2^+$ groups do not form and thus that the organic material does not provide AEC even at very low pH's. (Wada (1977)
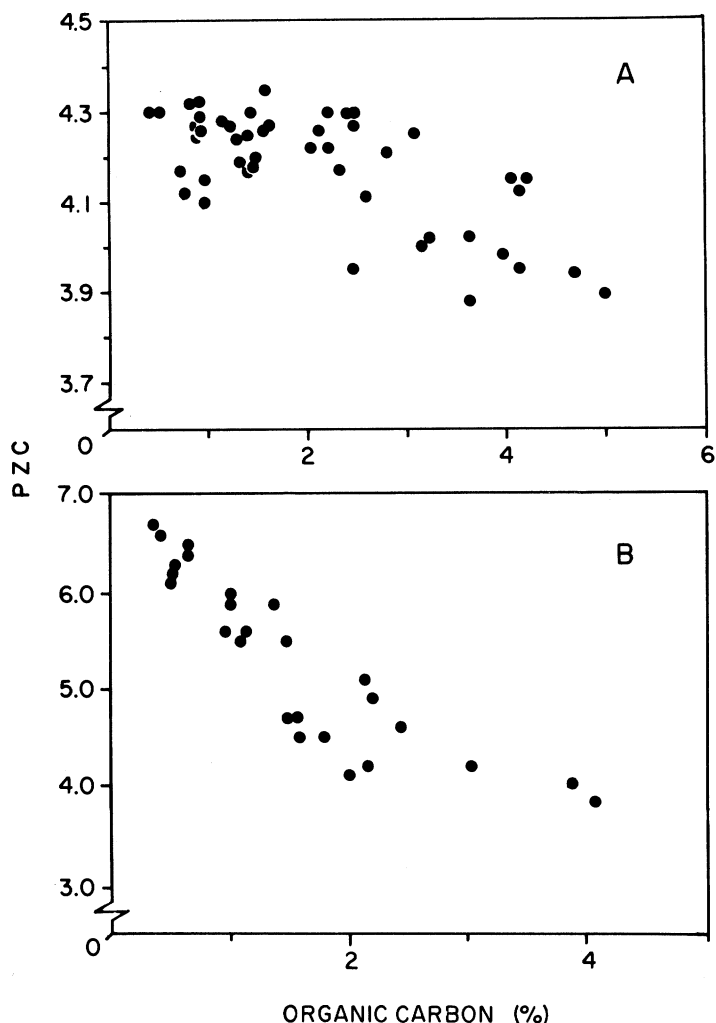
Fig. 2. Relation between point of zero charge (PZC) and soil organic carbon. (*A*) Samples spanning four depths and 13 locations in an Oxic Dystropept at La Selva, Costa Rica (P. Sollins and E. Hidalgo, unpublished data). NaCl used as background electrolyte. (*B*) Samples taken at four depths from six Oxisols in Queensland, Australia and at two depths from a basalt-derived soil in Guangdong Province, China (G.P. Gillman, unpublished data). CaCl$_2$ used as background electrolyte.

notes similarly that Al-OH groups in Al-humus complexes differ from Al-OH groups in allophane in that the former do not develop positive charge.) Presumably both silicate clays and organic matter keep the PZC low in less weathered v-c soils, but to what degree each is responsible is unknown.

Surface complexation in variable-charge soils

Ion exchange, as described above, is but a special case of the more general phenomenon of surface complexation, in which "a surface functional group reacts with a molecule dissolved in a surrounding fluid" (Sposito 1984). Again v-c and p-c clays behave differently. To discuss differences, it helps to distinguish mechanisms of surface complexation by bonding mechanism and stability. Unfortunately, dozens of terms are used to describe these different bonding mechanisms, including specific and non-specific adsorption, chemisorption, fixation, ion exchange, and ligand exchange.

From a practical standpoint, it may be helpful to distinguish between only two types of surface complexes – outer sphere and inner sphere. In outer-sphere complexes, the ion is separated from the particle surface by water molecules. Bonding depends solely on the presence of opposite charge on the particle surface. Chloride, nitrate and many cations (K^+, Mg^{2+}, Na^+) form only outer-sphere complexes (Sposito 1984). Permanent positive surface charge does occur, but outer-sphere anion complexation is important mainly in v-c soils with pH below the PZC. In v-c soils, outer-sphere anion complexation is, of course, highly pH dependent (Fig. 3).

Inner-sphere complexes are stronger than outer-sphere because, in the former, water molecules do not interpose between the ion and the particle surface. The bond strength of inner-sphere complexes can vary considerably, however (Mott 1981; Sposito 1984; Stumm 1986). Phosphate and silicate actually replace the surface hydroxyls of v-c minerals and bond covalently with the underlying Al, Fe, or Si atoms. As a result, phosphate and silicate surface complexation is only weakly pH dependent (Fig. 3). Sulfate bonds more weakly than phosphate or silicate but much more strongly than nitrate or chloride. The nature of the bond with sulfate is unclear (Marsh et al. 1987; Zhang et al. 1987). On the one hand, sulfate forms complexes with pure oxide surfaces such as goethite only when the pH is below the PZC and the surface has net positive charge (Fig. 3). On the other hand, sulfate is not readily displaced by anions such as nitrate and chloride. Overall, the anion-displacement sequence reflects bond strength: phosphate displaces silicate and sulfate; silicate displaces sulfate better than it does phosphate; sulfate tends to displace neither phosphate nor silicate.
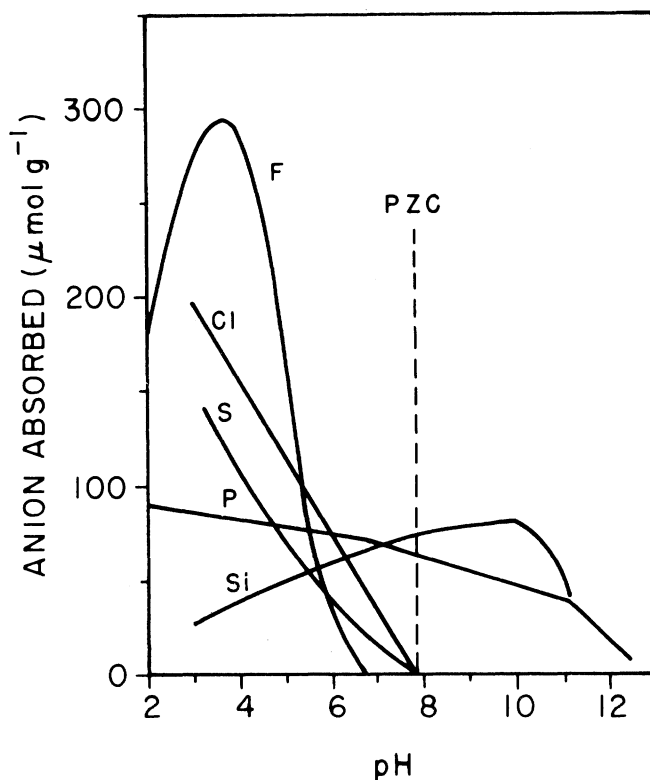
Fig. 3. Effect of pH on surface complexation of fluoride, chloride, silicate, phosphate, and sulfate on goethite (from Mott 1981). Note that fluoride, sulfate and chloride do not sorb at pH > PZC.

(Anions that form only outer-sphere complexes tend not to displace those that form inner-sphere complexes.)

Note that inner-sphere complexation of oxyanions at a surface lowers the PZC of that surface (Hingston et al. 1967; Wann & Uehara 1978), presumably because hydroxyls of oxyanions protonate less readily than the original surface hydroxyls. This provides a potential mechanism for managing soil PZC, as discussed later.

Effects of charge chemistry on phosphorus cycling
Effects of P availability on crop production are well known. Tropical agronomists regard P deficiency as one of the most pervasive agronomic problems of the humid tropics, along with soil acidity and attendant Al toxicity (Fox 1980; Uehara & Gillman 1981). Phosphorus availability may also control primary production in some mature tropical forests (Vitousek 1984). Differences in P availability result from differences in the tendency for

P to become "fixed" on adsorptive sites in the soil instead of remaining free in solution, available for plant uptake. Again, distinguishing between p-c and v-c soils (keeping in mind that all soils contain a mixture of both) helps us understand these differences in P dynamics. Phosphorus mobility in p-c soils is regulated largely by pH, but this is not the case in v-c soils. As Fox (1978) points out,

> A cherished assumption of many temperate zone agronomists is that many problems of highly weathered soils could be solved by raising soil pH ... within the pH range where much agriculture is performed, (however,) modifying soil pH has little influence on P solubility ...

Instead, P mobility in v-c soils is regulated mainly by exchange of the orthophosphate ligand with surface hydroxyl groups on v-c minerals. The principles of charge and surface chemistry already discussed relate P sorption to the amounts and types of clay minerals present in a soil. Overall, the amount of v-c (hydroxylated) surface correlates well with P-sorption capacity. High surface-area allophanic soils, such as Andepts, sorb the most P; oxidic soils sorb somewhat less; kaolinite- and halloysite-dominated soils sorb intermediate amounts; and the p-c soils (dominated by 2:1 clays) sorb the least (Sanchez 1976).

Phosphorus sorption is of great agronomic significance because it can result in very low P availability despite high levels of total inorganic P. The problem can be difficult to correct by fertilization because the P is adsorbed almost as fast as it is added (Sanchez 1976; Fox 1978; Uehara & Gillman 1981). Liming, a solution to P deficiency in p-c soils, may have little effect on P availability in v-c soils; the large buffer capacity of some v-c soils can make raising the pH difficult, and even a substantial rise in pH may have little effect on P availability (Fig. 3).

Goldberg & Sposito (1984a, b) have offered a mechanistic model of surface orthophosphate complexation that includes effects on surface protonation and deprotonation and thus deals explicitly with the effect of solution pH on P sorption. Their model includes surface-phase activity coefficients with values that depend on the sign and magnitude of the surface charge. The model successfully predicted P sorption as a function of pH in 41 v-c soils, based on constants developed for reference Al and Fe oxides. They noted that P-sorption curves for allophanic soils probably will not fit their model, because allophane enters into precipitation, rather than complexation, reactions with phosphate. In addition, their model does not include effects on P sorption of SOM sorbed on the mineral surfaces, so it

cannot be used to predict, for example, effects of SOM depletion on P dynamics. Nonetheless, the model does illustrate that equations derived from simple assumptions about physicochemical mechanisms can successfully predict soils characteristics that affect nutrient cycling.

Soil charge chemistry and soil structure

Variable charge also gives rise to unique soil physical structure. As desilication proceeds, net charge and the resulting repulsive forces decrease (El-Swaify 1980; Sposito 1984, chapter 6). Thus the highly weathered v-c soils of the humid tropics (e.g. Oxisols and some Ultisols and Tropepts) aggregate much more stably than do p-c soils. (The less weathered, allophanic v-c soils such as Andepts also form very stable aggregates, as discussed below.) Such soils behave both as sandy soils, draining rapidly to field capacity (less than one day), and as clayey soils, retaining more than 25% moisture at -15 bar matric potential (Tsuji et al. 1975; Uehara & Gillman 1981). A large amount of very fine pore space can produce abundant anaerobic microsites, providing a favorable environment for anaerobic processes such as denitrification. A very well-aggregated Oxic Dystropept at La Selva, Costa Rica, has in fact yielded some of the highest denitrification rates yet found in unfertilized soils (Robertson & Tiedje, in review). This same soil resists erosion and leaching by passing water rapidly along preferred paths between aggregates (Sollins & Radulovich, in press).

Effects of pH on soil structure are to be expected in v-c soils. In theory, increase in surface charge with increasing pH should cause particles to repel each other more strongly and thus aggregate less stably. Tama & El-Swaify (1978) found that aggregation decreased abruptly as pH rose above 5 in a Typic Torrox, but the management implications of this have received little attention.

Allophanic soils (Andepts), which occur in volcanically active areas, hold the record for fine pore space among all soils; Hydrandepts, for example, retain more than 100% moisture content (by weight) at -15 bar (Warkentin & Maeda 1980). Allophane is extremely reactive because of its large surface area (see Table 1). Its P-sorption capacity is unrivalled (e.g. Uehara & Gillman 1981), and SOM can accumulate in allophanic soils in extraordinary amounts – often more than 30% by weight (Broadbent et al. 1964; Zunino et al. 1982). Allophane flows and coalesces around crystalline and organic soil particles, perhaps preventing access by microorganisms. Thus part of the capacity of allphanic soils to retard SOM decomposition probably results from P unavailability (Ino & Monsi 1964; Munevar & Wollum 1977).

Effects of charge chemistry at the ecosystem level

Interactions among the various factors controlling nutrient mobility can be extremely complex. For example, vegetation removal often stimulates nitrification, which can in turn lower soil pH. A causal-loop diagram (Fig. 4) helps to illustrate the resulting chain of effects in a v-c soil. As H^+ ions are produced by nitrifiers, not only are cations – including ammonium – displaced from negatively charged exchange sites by H^+ (as occurs in p-c soils), but also v-c surfaces are protonated and lose part of their CEC. The soil thus loses its ability to retain any cations (including H^+) in outer-sphere complexes. The cations remain instead in solution, where they may be taken up by plants, heterotrophs, or nitrifiers, or leach from the system.

If pH continues to drop, AEC will increase and eventually exceed CEC, resulting in a soil in which ammonium is more mobile than nitrate – the inverse of p-c soils, on which most of our knowledge of N cycling is based. More nitrate is retained as AEC increases, in part offsetting increased ammonium loss. In practice, however, the nitrate is retained mainly in the subsoil, where low levels of organic matter result in high PZC's. Nitrate adsorption capacities from 2–9 cmol/kg have been reported (Kinjo & Pratt 1971; Espinoza et al. 1975; Singh & Kanehiro 1969). Although even 1 cmol/ kg extrapolates to some 1100 kg N/ha for each meter of subsoil depth, actual
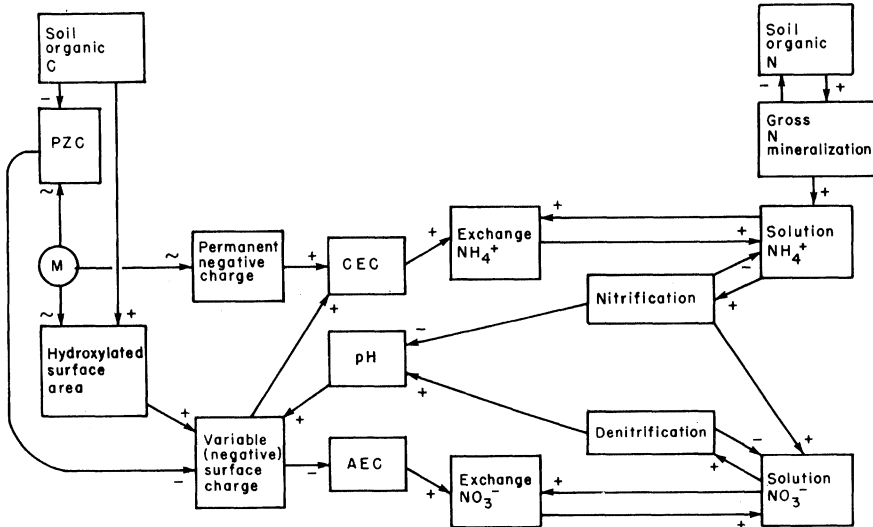

Fig. 4. Causal loop model for interactions between nitrification and ion-exchange capacity in a variable-charge soil. The symbols " $+$, $-$, $\sim$ " indicate a positive, negative, or variable effect of the parameter at the root of the arrow on the parameter at the point of the arrow. M = mineralogy, PZC = point of zero charge, AEC = anion exchange capacity.

values reported are 2–15 mg/kg, about 30 to 180 kg N/ha (Bartholomew 1977; Matson et al. 1987). Recycling of this pool by deep-rooted vegetation has been suggested (Bartholomew 1977; Fox 1980; Aweto 1981), but not demonstrated.

Additional mechanisms can offset effects of nitrification on pH, however. For example, nitrification will not lower soil pH if the nitrate is assimilated or denitrified, because both these processes consume H^+. Nitrate retention may well stimulate denitrification, which appears to be nitrate-limited in many tropical ecosystems with v-c soils (Robertson & Tiedje, in review). If disturbance drives the pH of a v-c soil below its PZC, allowing ammonium to leach readily and stimulating denitrification, the potential for N loss could be extremely large.

A vegetation-removal experiment at La Selva, Costa Rica illustrates some of the complex interactions between changing soil pH and soil-charge properties. The soil at this site is a highly weathered Oxic Dystropept with a PZC near 4.0 (based on titration in NaCl). Within several weeks after vegetation was cleared and carried off-site, soil suspension pH (0–15 cm depth) dropped from 4.6 to 3.8 (Fig. 5), probably because of nitrification. At soil pH of 3.8, the pH rose when KCl was added to a soil suspension, indicating that the soil had more AEC than CEC. (Soil pH will be higher in KCl than in water [Δ pH > 0] when there is more exchangeable OH^- than H^+.) The pH in water rose again at week 39 with the onset of the rainy season. As the water pH rose above about 4.0 (the measured PZC), Δ pH once again became negative. Such patterns provide evidence of the fragile nature of nutrient-retention capacity of a weathered v-c soil.

Apart from direct pH effects, long-term management practices can also affect the PZC of v-c (but not p-c) soils. Adding silicate minerals or phosphate can substantially lower the PZC of bulk soil. Gillman & Fox (1980), for example, found good relationships between CEC and extractable P (in boiling HCl) in an Andept and two Oxisols fertilized with superphosphate. The CEC of an Acrohumox increased by about 50% after incubation of the soil with crushed basaltic cinders for one year, again presumably because PZC of the bulk soil had been lowered (Gillman 1980).

Conclusions

Based on the available theory, we expect the interactions between biological processes and nutrient mobility to be potentially more complex and dynamic in v-c than in p-c soils.
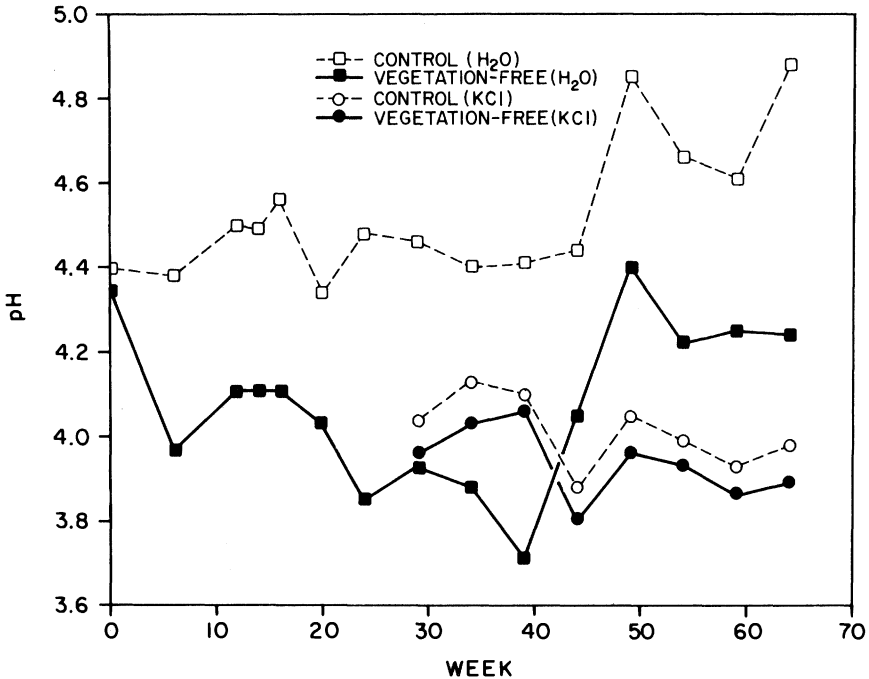
Fig. 5. Soil pH (0–15 cm depth) in water and in KCl after clearing vegetation from an Oxic Humitropept at La Selva, Costa Rica. The dry season began about week 16 and ended about week 39. KCl pH was not measured until week 20. (M. Huston, G.P. Robertson, P. Sollins & E. Hidalgo, unpublished data).

- In v-c soils, any process that affects soil pH will alter surface charge, and thus ion exchange capacity and mobility; in p-c soils, surface charge is relatively unaffected by soil solution composition.
- In v-c soils any process that affects the PZC of the mineral surfaces will alter ion exchange capacity. For example, theory predicts that adding oxyanions, such as sulfate, phosphate, or silicate, should affect cation retention more strongly in v-c than in p-c soils.
- Soil pH affects soil structure more in v-c than in p-c soils.
- Only v-c soils ever develop significant AEC.

Many patterns of nutrient mobility are predictable from soil charge and surface chemistry. Within broad limits, these characteristics can be inferred from soil classification within the Soil Taxonomy. Ecosystem scientists would do well to take more advantage of soil classification principles in studying nutrient cycles. Too many reports provide only the barest details of soil properties, often including no information on classification, mineralogy and charge status.

Variable-charge soils still have not received the attention they deserve, despite their distinct properties and large extent globally. Unusually stable physical structure and potentially fragile nutrient supplies that are markedly sensitive to changes in pH stand out as distinct features of v-c soils. More attention to the differences between v-c and p-c soils, along with better integration of soil science into ecosystem studies, could increase our ability to predict nutrient cycling patterns throughout the world.

Acknowledgements

References

Aweto AO (1981) Secondary succession and soil fertility restoration in southwestern Nigeria. II. Soil fertility restoration. Journal of Ecology 69: 609–614

Bartholomew WV (1977) Soil nitrogen changes in farming systems in the humid tropics. In: Ayanaba A & Dart PJ (Eds) Biological Nitrogen Fixation in Farming Systems of the Tropics (pp 27–42) John Wiley and Sons, Chichester, England

Beinroth FH (1981) A study of highly weathered soils of Puerto Rico. 1. Morphology, formation and classification. Geoderma 27: 1–73

Birkeland PW (1984) Soils and Geomorphology, Revised edition. Oxford University Press, New York, New York, USA

Broadbent FE, Jackman RM & McNicoll J (1964) Mineralization of C and N in some New Zealand allophanic soils. Soil Science 98: 118–132

Buol SW, Hole FD & McCracken RJ (1980) Soil Genesis and Classification, second edition. Iowa State University Press, Ames, Iowa, USA

El-Swaify SA (1980) Physical and mechanical properties of Oxisols. In: Theng BKG (Ed) Soils with Variable Charge (pp 303–324) New Zealand Society of Soil Science, Lower Hutt, New Zealand

Espinoza W, Gast RG & Adams RS Jr (1975) Charge characteristics and nitrate retention by two andepts from south-central Chile. Soil Science Society of America Proceedings 39: 842–846

Fox RL (1978) Studies on phosphorus nutrition in the tropics. In: Andrew CS & Kamprath EJ (Eds) Mineral Nutrition of Legumes in Tropical and Subtropical Soils (pp 169–187)

CSIRO, Brisbane, Australia

Fox RL (1980) Soils with variable charge: agronomic and fertility aspects. In: Theng BKG (Ed) Soils with Variable Charge (pp 195–224) New Zeland Society of Soil Science, Lower Hutt, New Zealand

Gast RG (1977) Surface and colloid chemistry. In: Dixon JB & Weed SB (Eds) Minerals in Soil Environments (pp 27–73) American Society of Agronomy, Madison, Wisconsin, USA

Gillman GP (1980) The effect of crushed basalt scoira on the cation exchange properties of a highly weathered soil. Soil Science Society of America Journal 44: 465–468

Gillman GP (1984) Using variable charge characteristics to understand the exchangeable cation status of oxic soils. Australian Journal of Soil Research 22: 71–80

Gillman GP (1985) Influence of organic matter and phosphate content on the point of zero charge of variable charge components in oxidic soils. Australian Journal of Soil Research 23: 643–646

Gillman GP & Fox RL (1980) Increases in cation exchange capacity of variable charge soils following superphosphate applications. Soil Science Society of America Journal 44: 934–938

Goldberg S & Sposito G (1984a) A chemical model of phosphate adsorption by soils. I. Reference oxide minerals. Soil Science Society of America Journal 48: 772–778

Goldberg S & Sposito G (1984b) A chemical model of phosphate adsorption by soils. II. Noncalcareous soils. Soil Science Society of America Journal 48: 779–783

Hingston FJ, Atkinson RJ, Posner AM & Quirk JP (1967) Specific adsorption of anions. Nature 215: 1459–1461

Ino Y & Monsi M (1964) On the decomposition rate of soil organic matter in humic allophane soils of Mt. Kirigamine. Botanical Magazine (Tokyo) 77: 168–175

Johnson DW, Cole DW, Gessel SP, Singer MJ & Minden RV (1977) Carbonic acid leaching in a tropical, temperate, subalpine, and northern forest soil. Arctic and Alpine Research 9: 329–343

Kinjo T & Pratt PF (1971) Nitrate adsorption. Soil Science Society of America Proceedings 33: 722–732

Marsh KB, Tillman RW & Syers JK (1987) Charge relationships of sulfate sorption by soils. Soil Science Society America Journal 51: 318–323

Matson PA, Vitousek PM, Ewel JJ, Mazzarino MJ & Robertson GP (1987) Nitrogen cycling following land clearing in a premontane wet tropical forest near Turrialba, Costa Rica. Ecology 68: 491–502

Mott CJB (1981) Anion and ligand exchange. In: Greenland DJ & Hayes MHB (Eds) The Chemistry of Soil Processes (pp 179–219) John Wiley and Sons, Chichester, England

Munevar F & Wollum AG (1977) Effects of the addition of phosphorus and inorganic nitrogen on the carbon and nitrogen mineralization of some Andepts from Colombia. Soil Science Society of America Journal 41: 540–545

Parfitt RL (1980) Chemical properties of variable charge soils. In: Theng BKG (Ed) Soils with Variable Charge (pp 167–194) New Zealand Society of Soil Science, Lower Hutt, New Zealand

Parks GA & de Bruyn PL (1962) The zero point of charge of oxides. Journal of Physical Chemistry 66: 967–973

Robertson GP & Tiedje JM. Denitrification in a lowland tropical rainforest. Nature (in review)

Sanchez PA (1976) Properties and Management of Soils in the Tropics. John Wiley and Sons, New York, USA

Sanchez PA, Cuoto W & Buol SW (1982) The fertility capability soil classification system: interpretation, applicability and modification. Geoderma 27: 283–309

Sherman GD & Uehara G (1956) The weathering of olivine basalt in Hawaii and its pedogenic significance. Soil Science Society of America Proceedings 20: 337–340

Singh BR & Kanehiro Y (1969) Adsorption of nitrate in amorphous and kaolinitic Hawaiian soils. Soil Science Society of America Proceedings 33: 681–683

Singh U & Uehara G (1986) Electrochemistry of the double-layer: principles and applications to soils. In: Sparks DL (Ed) Soil Physical Chemistry (pp 1–38) CRC Press, Boca Raton, Florida, USA

Soil Survey Staff (1975) Soil Taxonomy: a basic system of soil classification for making and interpreting soil surveys. United States Department of Agriculture Handbook 436

Soil Survey Staff (1976) Soil survey investigations. Report No. 29. USDA Soil Conservation Service, Washington, DC

Sollins P & Radulovich R. Effects of soil physical structure on solute transport in a weathered tropical soil. Soil Science Society America Journal (in review)

Sposito G (1984) The Surface Chemistry of Soils. Oxford University Press, New York, New York, USA

Stumm W (1986) Coordinative interactions between soil solids and water – an aquatic chemist's point of view. Geoderma 38: 19–30

Talibudeen O (1981) Cation exchange in soils. In: Greenland DJ & Hayes MHB (Eds) The Chemistry of Soil Processes (pp 115–177) John Wiley and Sons, Chichester, England

Tama K & El-Swaify SA (1978) Charge, colloidal, and structural stability relationships in oxidic soils. In: Emerson W, Bond RD & Dexter AR (Eds) Modification of Soil Structure (pp 41–52) John Wiley and Sons, Chichester, England

Tsuji GY, Watanabe RT & Sakai WS (1975) Influence of soil microstructure on water characteristics of selected Hawaiian soils. Soil Science Society of America Proceedings 39: 28–33

Uehara G & Gillman G (1980) Charge characteristics of soils with variable and permanent charge minerals: I. Theory. Soil Science Society of America Journal 44: 250–252

Uehara G & Gillman G (1981) The Mineralogy, Chemistry, and Physics of Tropical Soils with Variable Charge Clays. Westview Press, Boulder, Colorado, USA

Vitousek PM (1984) Litterfall, nutrient cycling, and nutrient limitation in tropical forests. Ecology 65: 285–298

Wada K (1977) Allophane and imogolite. In: Dixon JB & Weed SB (Eds) Minerals in Soil Environments (pp 603–638) Soil Science Society of America, Madison, Wisconsin, USA

Wann SS & Uehara G (1978) Surface charge manipulation in constant surface potential soil colloids. I. Relation to sorbed phosphorus. Soil Science Society of America Journal 42: 565–570

Warkentin BP & Maeda T (1980) Physical and mechanical characteristics of Andisols. In: Theng BKG (Ed) Soils with Variable Charge (pp 281–301) New Zealand Society of Soil Science, Lower Hutt, New Zealand

White GN & Zelazny LW (1986) Charge properties of soil colloids. In: Sparks DL (Ed) Soil Physical Chemistry (pp 39–81) CRC Press, Boca Raton, Florida, USA

Wright CA (1965) The volcanic ash soils of Chile. Report 2017. FAO, Rome, Italy

Zhang GY, Zhang N & Yu TR (1987) Adsorption of sulfate and fluoride by variable-charge soils. Journal of Soil Science 38: 29–38

Zunino H, Borie F, Aguiler S, Martin JP & Haider K (1982) Decomposition of ^{14}C-labelled glucose, plant and microbial products and phenols in volcanic-ash derived soils of Chile. Soil Biology and Biochemistry 14: 37–43