

Depletion of Available Potassium Nutrient with Changes in Clay Mineralogy During Pedogenesis of ASS Landscapes

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ABSTRACT

Clay mineralogy of marine-sourced sediments deposited in estuarine floodplains of northern, and east coast Australia is a mix of kaolinite, illite, and smectite clays. The proportions of these clay minerals appear fairly constant through the unoxidised parts of the Holocene-age sulfidic sediment profile. However, in the oxidised upper part of the profile, illite appears to be progressively replaced by smectite. This material, in the case of northern Australian floodplains, has been termed “freshwater sediment”. However, it is clear that this surface sediment has the same marine-source as that for the unoxidised deeper part of the profile. Pedogenesis of clay minerals is shown to involve the destruction of illite and its replacement by smectite, with a concomitant loss of potassium from the acid sulfate soil (ASS) landscape.

Measurement of potassium potential from sulfuric/sulfidic sediment profiles shows that there is a marked decrease in the availability of potassium in the upper oxidised surface sediment. This loss of available potassium affects the growth of the most widely-distributed mangrove, *Avicennia marina*, and also shows in decreased potassium with foliar analysis of sugarcane. The probability of potassium nutrient deficiency is not shown in other standard soil measurements, at least as adopted with sugarcane, and has not been used in ecological studies.

Keywords: acid sulfate soil, potassium potential, available K, pedogenesis, *Avicennia marina*.

INTRODUCTION

Potassium is an essential macronutrient for all plants. Plant-available K includes the K⁺ ions in the soil solution and exchangeable K adsorbed on the soil colloid surfaces. The latter form of K⁺ is readily released to solution by natural equilibrium processes in the soil, or by exchange when extracted with salt solutions. The concept of a nutrient potential was suggested by Schofield (1955) as a measure of the work a plant must do to remove nutrients from the soil. Woodruff (1955a, b) related classical thermodynamics to soil exchangeable K⁺, and Ca²⁺ plus Mg²⁺ release to the soil solution for determining the free energy of K-Ca exchange equilibria in soils. Woodruff (1955a, b) defined the energy of exchange as a measure of the chemical potential of K in the soil relative to the chemical potential of Ca in the same soil. Subsequently, Arnold (1962) showed that the difference in free energy between K and divalent ions, such as Ca and Mg, was well correlated with K uptake by ryegrass and could define the K status of soils, provided other soil factors were examined. The ability of a soil to supply K to plants is characterised by both the total amount of nutrient present (quantity, *Q*) and the energy level at which it is supplied (potential, *P*). The K⁺ potential (ΔG_K ; in J mol⁻¹) is defined as a free energy measure of the soil nutrient availability, expressed as a ratio of the relative activity and exchange between K⁺ and Ca²⁺ plus Mg²⁺:

$$\Delta G_K = RT \ln \left\{ \frac{a_K}{(a_{Ca+Mg})^{1/2}} \right\} \quad 1$$

in which *R* is the molar gas constant, *T* is the absolute temperature, and $a_K/(a_{Ca+Mg})^{1/2}$ is the activity ratio. Details for calculating activities based on the analysed ionic strength are presented in Keene and Melville (1999). Each measured value of ΔG_K (the potential *P*) can be related to its measured exchangeable K (the quantity *Q*) to give a K adsorption isotherm. Just as the soil moisture characteristic relates the free energy of soil water (i.e. moisture potential) to the amount of water held (i.e. soil moisture content), K⁺ potentials are similarly related to the total amount of exchangeable K on the soil colloid, via the K adsorption curve. Hence, the analogous concept of the moisture characteristic is applied to determine the amount of nutrient available to a plant, called the nutrient capacity of the soil. The relationship between quantity and potential (“adsorption curves”) has commonly been used in agricultural soils to predict K availability to crops, and the K⁺ potential may be applied to predict crop

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yield or response to K^+ fertiliser (see Schofield, 1947; Woodruff, 1955a; Beckett, 1964b; Talibudeen and Page, 1978; Goulding, 1986).

The concept of the quantity/potential (Q/P) relationship is applied here in natural and agricultural tidal floodplains to investigate the mineral nutrient K status of contemporary and buried sulfidic/sulfuric soils. The K^+ potential is a means of examining K availability in the Holocene stratigraphy of acid sulfate soils (ASS) and enables some understanding of the pedogenesis and associated vegetation changes of the South Alligator River and McLeods Creek estuarine floodplains.

MATERIALS AND METHODS

Soils were sampled by hand auger and drill core in August 1999 in the sedge and grasslands on the South Alligator River floodplain, northern Australia and in November 1997 in a sugarcane field on the McLeods Creek floodplain, on the right bank of the Tweed River, eastern Australia. Samples were described and had field pH measured at 0.1 m depth intervals and selected for laboratory analysis based on horizon differences. During collection, precautions were taken to avoid contamination and oxidation prior to transport to the laboratory where the soils were oven-dried at 80-85°C for at least 24 h and passed through a 2 mm sieve in preparation for analysis.

Characterisation of the samples was further made with pH and electrical conductivity, EC, in $dS\ m^{-1}$ measurements in H_2O extracts. All extracts used a 1:5 soil to solution ratio, and equilibration for 0.5 h on an end-over-end shaker. Potassium exchange characteristics of soil samples were determined by the methods detailed in Keene and Melville (1999). Briefly, samples of soil were equilibrated in triplicate with extracting solutions containing a constant ionic strength background of 0.01 or 0.10 M $CaCl_2$ and increasing amounts of KCl, based on the procedures outlined by Beckett (1964a, b). The concentration of all cations in the extractants were analysed by atomic absorption spectrophotometry (AAS) for all cations. The K^+ potential, ΔG_K , in $J\ mol^{-1}$ for each extract was calculated according to Equation 1.

Exchangeable cation contents in $cmol_c\ kg^{-1}$ were measured in 0.01 M $CaCl_2$ following analysis of the soil solution with no addition of K. The distribution of total carbon and sulfur, mainly as the sulfide mineral pyrite, in the profile was determined gravimetrically following dry combustion and analysis by Leco CNS Analyser. Clay mineralogy of the soil samples was determined by monochromatised $CuK\alpha$ radiation using a Philips X'Pert system, and examined on an "as received" basis for the $<2\ \mu m$ fraction.

RESULTS AND DISCUSSION

In the macrotidal South Alligator River ($<5\ m$ tidal range), marine-sourced estuarine sediments are deposited across the floodplain during the flood peaks of the monsoonal wet season. Subsequently, in the dry season, they have been oxidised because of seasonal water table fluctuations and decreasing tidal influence over the long term. Beneath the plain surface, partly ripe estuarine sediments represent a sedimentary and pedogenic transition from the permanently reduced sulfidic estuarine blue-grey clays of the sulfidic layer to the oxidised floodplain clays of the upper sulfuric layer. Mottles were produced because of the oxidation of pyrite from the underlying mangrove sediments, with the formation of Fe products such as jarosite occurring during pedogenesis. Organic-rich alluvium, the so-called "black soil" of the region, comprises the dark brown to black cracking clays that veneer the floodplain surface and overlie ripe sulfuric sediments. The deepest layer of sediment in this South Alligator River profile is a pale-coloured, weathered sandy clay (probably of Pleistocene age), quite distinct from the overlying Holocene-age, reduced blue-grey, sulfidic clay. This subsoil has a distinctly deficient value of K^+ potential (more negative equilibrium ΔG_K values) shown in Figure 1.

Unoxidised "big swamp" subsoil sediments (Woodroffe et al., 1985), dominated by kaolinite and increased illite contents, exhibited a large availability of K (less negative equilibrium ΔG_K values) shown in Figure 1. There was a general depletion of K throughout the oxidised floodplain clay surface, dominated by smectitic clays with minimal illite present (Figure 1). There is a gradual movement downwards of an oxidation front into the initially reduced sulfidic subsoil which transforms the K-rich, illitic clays to the K-deficient, smectitic floodplain clays of the upper sulfuric layer under acid conditions. The transformation of weathered micas to expansible 2:1 minerals such as smectite is facilitated by a very small activity of K in the soil solution, relative to the activity of replacing cations such as Ca or Mg. The release to the soil solution, of plant-available K from silicate minerals by acid attack during pedogenesis, provides the K necessary to form jarosite in the upper sulfuric horizon.

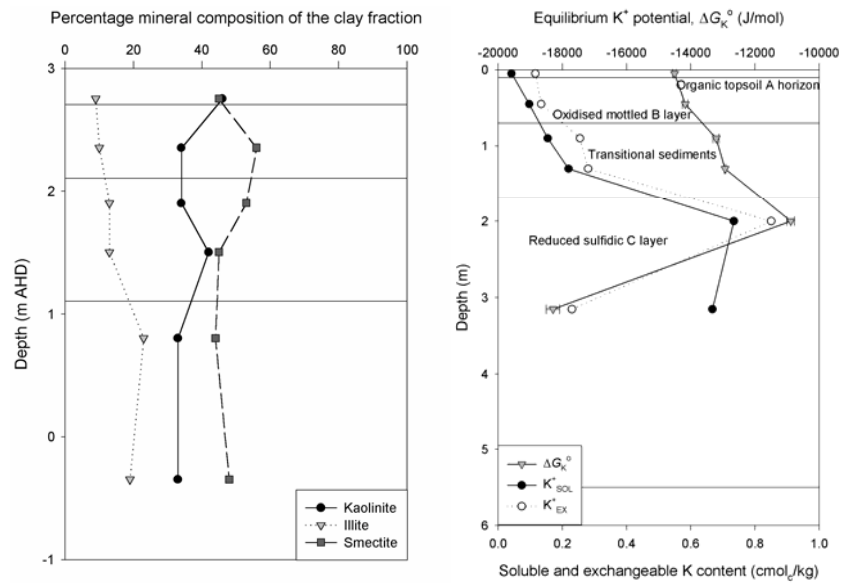


Figure 1 Mineral composition of the clay fraction (left) and equilibrium K⁺ potential, ΔG_K° , in relation to soluble and exchangeable potassium contents (right), for a representative ASS profile on the South Alligator River plain. Reference lines show the boundary between soil layers.

During the oxidation of the sulfide minerals, the acidity generated reacts with and changes the host clay minerals from K-rich illitic clays to K-poorer smectitic clays. The oxidation product jarosite that forms above the oxidation front acts as a powerful temporary sink for K. As this jarosite subsequently hydrolyses to goethite the K is released to enable its upward leaching and export from the profile. Drainage systems and agricultural practices that export increased amounts of K can exacerbate the natural K deficiency that is likely to exist in these ASS landscapes. As well, the addition of large concentrations of divalent ions, such as with agricultural lime in a Na- or Al-dominated ASS could increase the exchangeable Ca and Mg concentration and thereby decrease the K⁺ potential (Beckett, 1964b; Tinker, 1964).

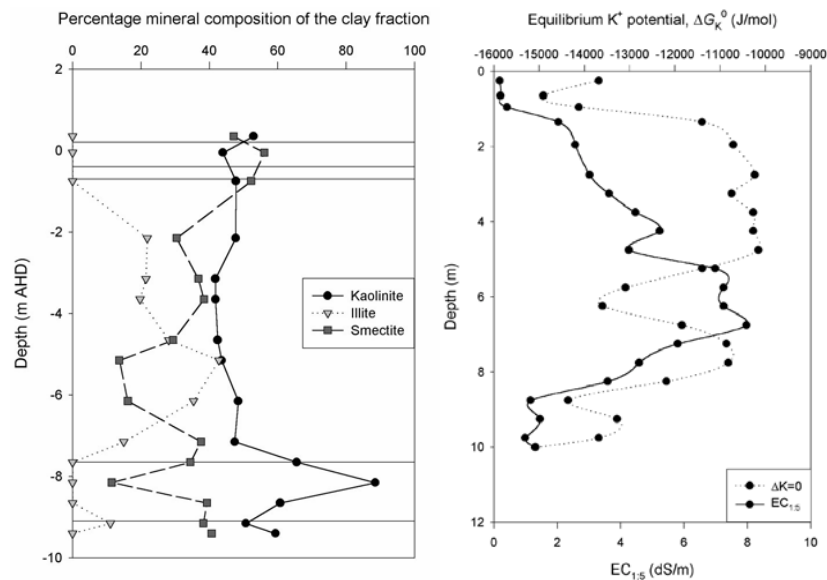


Figure 2 Mineral composition of the clay fraction (left) and equilibrium K⁺ potential, ΔG_K° , in relation to electrical conductivity (right), for a representative ASS profile on the McLeods Creek floodplain. Reference lines show the boundary between soil layers.

Results from the K adsorption curves for the McLeods Creek ASS profile under sugarcane cultivation showed that the oxidised upper sulfuric sediments had decreased equilibrium values of ΔG_K (Figure 2). The pyrite oxidation and associated acidification depleted K from the ASS of the McLeods Creek estuarine floodplain surface, and resulted in changes to the clay mineral structure with the dominance of kaolinite and minimal illite fractions (Figure 2). Leaching and uptake by sugarcane of K from the sulfuric layer can decrease

the K level and contribute to the decrease in K availability. Potassium deficiency was associated with the formation of the sulfide mineral oxidation product jarosite, which acts as an infinite sink for K in the upper sulfuric horizon, and reduces the amount of K that is readily available for sugarcane growth. This contrasted with the sulfidic sediments of the subsoil, which exhibited considerably less negative ΔG_K° values and revealed a significantly greater availability of K shown in Figure 2. Here, the illitic clay fraction was considerably larger than the upper sulfuric sediment. The highly weathered Pleistocene sediment at the base of the McLeods Creek profile (Figure 2) also shows the depletion of illitic clay and K deficiency but there, the clay is predominantly kaolinitic. This is similar to the highly weathered, kaolinitic clays of the South Alligator River floodplain basal sediments which also show a reduction in potassium availability (Figure 1).

CONCLUSIONS

Based on the clay mineralogy and equilibrium potassium potentials presented above we propose that the pedogenesis of acid sulfate soil profiles is the likely cause of changes in potassium nutrient availability in these landscapes. Under acid conditions, the weathering of illitic clays of the sulfidic layer releases exchangeable K to the soil solution, transforming illite into the smectitic clays of the upper sulfuric layer and depleting K from the clays of the floodplain surface by the formation of jarosite, and by leaching and plant uptake of K. These pedogenic changes in clay mineralogy are accompanied by natural hydrological and oxidation processes in an estuarine environment with markedly wet and dry seasons that cause upward leaching and export of K from ASS landscapes. This has consequences for plant growth under natural and agriculturally-modified conditions.

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