

**THE ROLE OF SILICON IN SURFACE CHARGE
CHARACTERISTICS, PHOSPHORUS SORPTION
CAPACITY AND ALUMINIUM TOXICITY OF
VARIABLE CHARGE SOILS**

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Declaration

I certify that the substance of this thesis has not already been submitted for any degree and is not currently being submitted for any other degree or qualification.

I certify that any help and support received in preparing and completing this thesis, and all sources used, have been acknowledged in this thesis.

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Abstract

Silicon (Si) is the second most abundant element in the Earth's crust, and it has been widely demonstrated that it is a beneficial nutrient for stimulating the growth and development of many higher plants. The potential effects are associated with the ameliorating/mitigating effects of Si on both abiotic and biotic stresses, which occur through the interactions between plants and external media, such as climate and soil conditions. However, Si solubility (monosilicic acid) in soils, which is an important factor determining these effects, is often low due to leaching or desilication during soil development under tropical climate conditions, and this is particularly the case with variable charge soils (VCS). Variable charge soils are often acidic, and typically have soil fertility constraints of aluminium toxicity, high phosphorus fixation and low cation retention. Silicon repletion by the application of Si amendments is one management option for improving the fertility of these soils.

The overall objectives of this study were: a) to investigate the role of Si in ameliorating/amending major constraints of VCS from north Queensland and New South Wales (NSW), and b) to apply the results to other relevant VCS, particularly in the uplands of Vietnam where VCS have similar characteristics to those investigated in this study and where Si amendments are available, yet their use is not widespread because of a lack of awareness of their potential benefits.

Both inorganic Si [monosilicic acid (Mono-Si), calcium silicate (Ca-Si), acidulated calcium silicate (Ac-Ca-Si), magnesium silicate (Mg-Si), acidulated magnesium silicate (Ac-Mg-Si) and fused magnesium phosphate (FMP)] and organic amendments [mulched sugarcane trash (sugarcane) and *Tithonia diversifolia* (*Tithonia*)] were used for investigating the role of Si in surface charge characteristics, phosphorus sorption capacity and aluminium toxicity of selected VCS from north Queensland (a Redoxic Hydrosol, an Aquic Grey Vertosol and a Red Ferrosol) and from NSW (Red Ferrosols located in Dorrigo and in Alstonville). All experiments were incubated at 40°C for 7 days and/or 30 days. The charge fingerprint procedure was used to determine surface charge characteristics of the soils. Phosphorus sorption capacity of the soils was measured using a simple phosphorus sorption index known as the phosphorus buffer index (PBI). Silicon-induced amelioration of aluminium toxicity of the Red Ferrosol from Alstonville was investigated using a short-term bioassay of mungbean seedlings grown in the soil solution.

All investigated soils were acidic and low in cation exchange capacity (CEC). In particular, the Red Ferrosols from both north Queensland and NSW were extremely acidic, very low in CEC and very high in PBI. The Red Ferrosol (Pingin Soil Series) from Palmerston, north Queensland, was the only soil dominated by net variable charge, and this soil exhibited the lowest CEC and the highest PBI. Differences in the statistical significance and magnitude of the effects between investigated soils are attributed to variations of mineralogical composition, which is mainly controlled by Fe and Al hydrous oxides contained in the soils. Within Red Ferrosols from both sites (Dorrigo, NSW and Palmerston, north Queensland) subsoil layers (20 - 40 cm) were more acidic and had lower CEC and higher PBI than topsoil's (0 - 20 cm). Net positive charge, a 'geric' property, occurred in the subsoil layer (20 - 40 cm) of the Red Ferrosol from Palmerston, north Queensland; this property also occurs in the subsoil layer of many Ferralsols in the uplands of Vietnam. The differences in characteristics between soil layers within a given soil are mainly due to differences of total organic carbon contents.

All studied amendments increased surface negative charge (and, accordingly, the CEC of the soils) through either an increase in soil pH by the accompanying basic elements (Ca or Mg) and anions (e.g. CO_3^{2-}), or a decrease in the point of zero charge (PZC or pH_0) by specific adsorption of silicate anions resulting in the reversal of positively charged to negatively charged surfaces in the VCS. The beneficial effect of FMP amendment on surface charge characteristics was more pronounced than that of the other inorganic silicate amendments. This is due to the simultaneous addition of Ca, Mg, P and Si; all of these have synergistic influences on surface charge characteristics. Organic amendments (sugarcane and *Tithonia*, both at $125 \text{ kg Si ha}^{-1}$) had a significant effect on enhancing surface negative charge and reducing surface positive charge of the soils. The effects caused by *Tithonia* addition were much greater than those of the sugarcane and inorganic silicate amendments, even with Si applied ($250 \text{ kg Si ha}^{-1}$) at double the rate of that as *Tithonia*. This is accounted for by the large amounts of Ca, Mg, P and organic matter (OM) applied, together with Si, from *Tithonia*. Therefore, *Tithonia* has an optimum effect. Since the P sorption capacities of the soils are strongly negatively correlated with the development of negative charge surface, the greater the increase in CEC caused by a given amendment, the lesser the P sorption capacity.

Soils dominated by permanent negative charges (the Hydrosol and the Vertosol) exhibited high total Si and Si availability, and low Fe/Al hydrous oxides content and responded to the amendments less than the Ferrosols that were dominated by variable negative charges, and

exhibited low Si contents and high Fe/Al hydrous oxides. The amendments also produced greater effects in the subsoil than the topsoil, particularly in the case of the Palmerston Ferrosol where a net positive charge occurred in the unamended subsoil. However, although Fe/Al hydrous oxides were strongly correlated with surface charge characteristics and P sorption capacity of the soils, inorganic silicate amendments had little effect on these properties. The importance *per se* of Si derived from *Tithonia* on soil characteristics was not clearly verified in this study. This was due to the additional effect of organic functional groups contained in *Tithonia* that confounded the effect of Si on soil properties.

Silicon applied at a high rate more effectively increased surface negative charge and decreased P sorption capacity of the Red Ferrosol from Alstonville, NSW (0 - 30 cm) than at a low rate. Between the two incubation periods (7-DAI and 30-DAI), faster effects were found for the amendments with high soluble Si content (i.e., Mono-Si and Ac-Mg-Si) than those with low soluble Si content (Ca-Si, Ac-Ca-Si and Mg-Si). Since the acidulated silicate amendments (Ac-Mg-Si and Ac-Ca-Si) had a higher Si solubility than their non-acidulated equivalents (Mg-Si and Ca-Si, respectively), they exhibited greater effects than the non-acidulated forms. All investigated inorganic silicate and organic amendments significantly ameliorated Al toxicity of the soil, thereby enhancing relative root elongation of mungbean seedlings grown in soil solutions. The order of magnitude of the ameliorative effects from these amendments was as follows: *Tithonia* > FMP > Ac-Mg-Si > Ca-Si = Ac-Ca-Si > Mg-Si > Mono-Si > sugarcane. The ameliorative effect can be attributed to different mechanisms, including: a) an increase of soil solution pH reducing Al toxicity; b) Si interference with Al uptake into the root and co-deposition of Al and Si in plants; and c) indirect effects due to the supply of essential nutrients from the amendments.

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Abbreviations

7-DAI	7 days after incubation
30-DAI	30 days after incubation
$\Delta\text{CEC}_{4.5-5.5}$	Difference CEC_T between soil pH 5.5 and 4.5
ΔpH	Delta pH [pH(1:5, 1 M KCl) – pH(1:5, H ₂ O)]
Ac-Ca-Si	Acidulated calcium silicate
Ac-Mg-Si	Acidulated magnesium silicate
AEC	Anion exchange capacity of soil
Al_{CBD}	Citrate bicarbonate dithionite extractable aluminium
$\text{Al}_{\text{Cryst.}}$	Crystalline aluminium
Al_{Ox}	Acid oxalate extractable aluminium
BD	Bulk density of soil
Ca-P	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$
CAS	Chromeazurol S dye
Ca-Si	Calcium silicate
CEC_B	Basic cation exchange capacity of soil
CEC_T	Total cation exchange capacity of soil
DOC	Dissolved organic carbon
ECR	Eriochrome cyanine R dye
FC	Field capacity of soil

Fe _{CBD}	Citrate bicarbonate dithionite extractable iron
Fe _{Cryst.}	Crystalline iron
Fe _{Ox}	Acid oxalate extractable iron
FMP	Fused magnesium phosphate
HAS	Hydroxyaluminosilicates
HEM	Hematoxylin dye
IEP	Iso-electric point
IS	Ionic strength
MIR	Mid-infrared reflectance
Mono-Si	Monosilicic acid (H ₄ SiO ₄) solution
Mg-Si	Magnesium silicate
NPC	Net permanent charge of soil
NV	Neutralizing value
NVC	Net variable charge of soil
OM	Organic matter
P _{avail}	Phosphorus availability (0.01 M CaCl ₂ extraction)
P _{Colwell}	Colwell extractable phosphorus
P _{Olsen}	Olsen extractable phosphorus
PBI _{Colwell}	Phosphorus buffer index (calculated with Colwell extractable phosphorus)
PBI _{Olsen}	Phosphorus buffer index (calculated with Olsen extractable phosphorus)
pH ₀	pH value at which the variable net surface charge resulting from the adsorption of potential determining ions H ⁺ and OH ⁻ is zero
pHBC	pH buffer capacity
PZC	Point of zero charge
PZNC	Point of zero net charge
RCF	Relative centrifugal force
RE	Root elongation
RRE	Relative root elongation
Si _{avail}	Silicon availability (0.01 M CaCl ₂ extraction)

Si _{ox}	Acid oxalate extractable silicon
TNC	Total net charge of soil
TOC	Total organic carbon
VCS	Variable charge soils