



# Variable Charge Soil Conference

**4 & 5 March 2026**

Newcastle Exhibition & Convention Centre  
(NEX), Newcastle, NSW, Australia

## Conference Proceedings

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## Wednesday 4 March 2026

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**Nipuni Welivitiya, University of Newcastle, NSW, Australia**



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## Poster Presentations

### POSTER PRESENTATIONS:

Poster 1: Unlocking Acid Soils: How Increasing pH Decreases Potassium Losses in Sandy Soils With Variable Charge

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**Fatima Farhana, The University of Newcastle, NSW, Australia**

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**Kamrun Nahar Mousomi, The University of Newcastle, NSW, Australia**

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**Saifullah Nasif, The University of Newcastle, NSW, Australia**

Poster 5: Environmental Drivers of Humus Form Diversity in the Hyrcanian Forests of Northern Iran

**Akram Haghghat Doust, The University of Newcastle, NSW, Australia**

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**Brett Enman, Earthwise Environmental, NSW, Australia**

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**Dr Roheela Yasmeen, The University of Newcastle, NSW, Australia**

Poster 8: Soil Surface Charge Variation in Agricultural Soils: Effect of Biochar Application in Different Layers

**Dr Santosh Kumar Paul, The University of Newcastle, NSW, Australia**

Poster 9: Soil Surface Charge Dynamics Under PFAS Contamination: Interactive Effects of Biochar and Organic Amendment

**Dr Chuks Kenneth Odoh, Global Centre For Environmental Remediation (GCER), University of Newcastle**

**PLENARY 1:** What Temperate Agriculture Doesn't Teach Us: The Critical Role of Variable Charge Soils in the Tropics

**Dr Leonardus Vergutz, Scientific Office of OCP Nutricrops**

## **What Temperate Agriculture Doesn't Teach Us: The Critical Role of Variable Charge Soils in the Tropics**

Dr Leonardus Vergutz <sup>1</sup>

<sup>1</sup>Scientific Office of OCP Nutricrops

**Abstract Pending**

## **Chemistry and Mineralogy of Variable Charge Soils: Foundations for Sustainable Land Use and Environmental Stewardship**

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### **1. Introduction**

Variable charge soils—including Oxisols, Ultisols, and Andisols—form a major component of agricultural and ecological landscapes across the humid tropics and subtropics. Their pH-dependent surface charge distinguishes them from the permanent-charge soils of temperate regions, underpinning critical aspects of fertility, nutrient dynamics, and environmental behaviour (Sanchez, 2019). These soils occur widely in Southeast Asia, sub-Saharan Africa, Latin America, and the Pacific, supporting millions of smallholder farmers and diverse ecosystems.

### **2. Mineralogical Basis of Variable Surface Charge**

The variable charge properties of these soils arise from their mineralogical makeup. Highly weathered profiles feature low-activity clays such as kaolinite, along with amorphous and poorly crystalline minerals including allophane, imogolite, and short-range-order aluminosilicates (Parfitt, 2009). Crystalline Fe and Al oxides—such as goethite, hematite, and gibbsite—also contribute significantly. Surface charge is generated through protonation and deprotonation of hydroxyl groups at mineral–solution interfaces, in contrast to isomorphic substitution processes typical of permanent-charge soils (Uehara & Gillman, 1981).

### **3. Fertility Constraints and Chemical Challenges**

Variable charge soils generally exhibit low cation exchange capacity (CEC), commonly below 10 cmolc kg<sup>-1</sup> (Brady & Weil, 2016). Strong chemisorption of phosphate onto Fe/Al oxides results in severe phosphorus (P) fixation, reducing fertiliser efficiency and imposing significant costs on farmers (Hinsinger, 2001). Aggregate stability is fragile, relying heavily on organic matter and oxide cementation; heavy rainfall easily disrupts aggregates, causing erosion, crusting, and restricted infiltration. Progressive acidification under high rainfall conditions increases soluble Al<sup>3+</sup> toxicity, constraining root growth and microbial functioning (Fageria et al., 2011).

### **4. Point of Zero Charge (PZC) and Management Implications**

The point of zero charge (PZC) is the pH at which soil surfaces carry no net charge. Below the PZC, soils carry a positive charge and preferentially adsorb anions (e.g., phosphate,

sulfate). Above the PZC, negative charge dominates, enhancing cation retention. Typical PZC values for variable charge soils range from pH 4.0 to 6.5 (Uehara & Gillman, 1981). Under common field pH (4.5–5.5), many surfaces are neutral or positively charged. Liming can shift surface charge towards negative values, increasing CEC and reducing P fixation, while ammonium-based fertilisers may lower pH and intensify P unavailability and Al toxicity.

## **5. Sustainability Opportunities and Soil Improvement Strategies**

Despite their limitations, variable charge soils offer opportunities for sustainable innovation. Organic matter additions—including compost, crop residues, and manure—enhance organo-mineral complexes, increase nutrient retention, improve aggregate stability, and buffer pH (Six et al., 2002). Biochar provides high surface area and adaptable surface chemistry, reducing P fixation and improving long-term carbon storage. Microbial enhancements, such as mycorrhizal fungi and phosphate-solubilising bacteria, can mobilise phosphorus by modifying rhizosphere conditions or competing for oxide binding sites (Hinsinger, 2001).

## **6. Integrated Land and Soil Management Approaches**

Effective use of variable charge soils requires integrated agronomic, ecological, and chemical approaches. Conservation agriculture practices—minimal tillage, soil cover, and crop diversification—help maintain organic matter and structure. Agroforestry systems facilitate nutrient recycling and stabilise soil pH through deep-rooted species (Sanchez, 2019). Precision soil testing incorporating PZC and P sorption indices enables targeted lime and fertiliser applications, reducing environmental risk and enhancing nutrient-use efficiency.

## **7. Broader Environmental and Societal Implications**

The implications of managing variable charge soils extend beyond agriculture. Organo-mineral complexes stabilise substantial quantities of carbon, contributing to climate mitigation (Six et al., 2002). Poorly managed soils, however, lead to dust generation, water contamination, and lower crop nutritional quality. Enhancing soil resilience is therefore central to strengthening food security, environmental protection, and adaptation to climate variability in vulnerable regions.

## **8. Conclusion**

Variable charge soils present both challenges and opportunities. Their distinctive chemistry—dominated by pH-responsive charge and oxide reactivity—demands informed, integrated management strategies. Through organic matter enrichment, biochar application, microbial partnerships, and precision nutrient management, these soils can be transformed into productive and resilient systems that contribute to climate stability and sustainable development.

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Uehara, G., & Gillman, G. (1981). *The mineralogy, chemistry, and physics of tropical soils with variable charge*. Westview Press.

# Pedogenic development of Andisols to Inceptisols and Ultisols along a climosequence in Yangminshan Volcanic National Park of Taiwan

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## INTRODUCTION

Taiwan is located at the convergent boundary between the Eurasian plate and the Philippine Sea plate. The Yangmingshan Volcanic National Park (YMS-NP) is formed by the Pleistocene island-arc volcanic activities related to the Ryukyu arc-trench system, and with its eruptive products covering an area of nearly 200 km<sup>2</sup> in northern Taiwan. Volcanic activity in YMS-NP tailed off after the formation of Shamao Mt. about 0.3 M yrs ago. Volcanic eruptions have caused most of the original sedimentary rock in YMS-NP to be covered by volcanic rocks. The volcanic rocks are largely andesites of different compositions with a small amount of basaltic rock. The chief mineral constituents include grayish-white andesite, black shiny pyroxenes and biotite. Dominant vegetation types are silver grass and kunishi cane at higher elevation, and common machilus and ryukyu pine at lower elevation. The soil moisture and temperature regimes are udic and thermic in the region, respectively.

Weathering of volcanic deposits results in the formation of Andisols in both temperate and tropical environments with sufficient moisture. Andisols form rapidly in humid climates and alter to other Soil Orders as soil age and degree of weathering increase. Several studies along climatic gradients (so-called climosequences) have enhanced our understanding of climatic controls on the formation of poorly crystalline and noncrystalline materials and the development of andic soil properties. Zehetner et al. (2003) found andic properties in both 3 ka-old recent soils as well as in 40 ka-old buried paleosols under temperate climatic conditions in the Andes of Ecuador. Clearly, more research is needed on volcanic deposits of different age in order to get a better insight into the temporal development of Andisols under different climatic regimes. The objective of our studies was to compare soil morphology, physical and chemical properties, as well as clay mineralogy under different soil environments.

## METHODS

Fifty-seven soil pedons were sampled in 9 transects covering the area of YMS-NP, including 21 pedons in two transects on Tatun Mt., 18 pedons in two transects on Chihsing Mt., 4 pedons on Shamao Mt., 4 pedons on Chihteinkang Mt., 4 pedons on Tzutufu Mt., 3 pedons on Meintien Mt., and 3 pedons on Huangtzuei Mt. Three soil pedons were selected on each mountain from high-elevation soils (around 900 m asl), the mid-elevation soils (around 400 m asl) and soil in footslope position (around 200m asl). This approach represents a soil climosequence with a climatic gradient from about 22 °C mean annual temperature (MAT) and 2000 mm mean annual precipitation (MAP) at high elevations to about 16.5 °C

MAT and 5000 mm MAP at low elevations. We analysed many soil characteristics, including phosphate retention,  $Al_o+1/2Fe_o$ ,  $Si_o$  and  $Fe_o/Fe_d$  ratio.

Differences of soil physical and chemical properties at different elevations were attributed to the differences in climatic conditions, stages and processes of weathering. Andisols with melanic epipedon were only found in Shamao Mountain. Soil classification was based on Keys to Soil Taxonomy (USDA).

## RESULTS and discussion

Our studies in YMS-NP indicated that the parent material and elevation gradient (or climate condition) affected the soil characteristics and classification. Phosphate retention,  $Al_o+1/2Fe_o$ ,  $Si_o$  and the  $Fe_o/Fe_d$  ratio, and hence, andic soil properties, significantly increased with elevation. Of the 57 soil pedons collected from this region, three Soil Orders (Andisols, Inceptisols, and Ultisols), three Suborders (Udands, Udepts, and Udults), and five Great Groups (Melanudands, Fulvudands, Hapludands, Dystrudepts and Hapludults) were identified.

Two transects, including representative pedons with the same parent material of andesite and located between Mt. Tatun and a lower marine terrace, were selected to better understand the pedogenic processes and to establish pedogenic indicators of the transition from Andisols to Inceptisols, and then from Inceptisols to Ultisols derived from different landscape positions and climate conditions, especially temperature and precipitation. The results of this study indicated that four kinds of soils have developed along this toposequence, including Acrudoxic Hapludands (elevation >700m), Andic Dystrudepts (elevation 440~700 m), Typic Dystrudepts (elevation 100~400m), and Typic Paleudults (elevation <100m).

The soil transition between Andisols, Inceptisols, and Ultisols are characterized by significant increase in bulk density, reduced amounts of amorphous materials, lower phosphate retention, and increased clay content in the B horizon. The results suggested that six pedogenic indices may be useful for identification of the transitional soils between Andisols and Ultisols in the study area, including soil texture, soil consistence, bulk density, phosphate retention,  $Al_o+1/2Fe_o$  (%) and  $Si_o$  (%) (Table 1).

Table 1. The quantitative indicators of soil characteristics for identification of three Soil Orders in the Yangminshan Volcanic National Park of Taiwan

Soil Order	n <sup>#</sup>	Texture <sup>†</sup>	Consistence <sup>§</sup>	Bulk density (Mg/m <sup>3</sup> )	P <sub>retention</sub> (%)	$Al_o+1/2Fe_o$ (%)	$Si_o$ (%)
Andisols	2	L	very friable	<0.6	>90	>2.5	1.0-1.5
Inceptisols	4	SiCL or CL	very friable, ss & sp	0.8-1.0	40-75	1.5-2.5	0.3-0.4
Ultisols	2	C	firm, s&p	1.35-1.5	ND	<0.7	0.2

<sup>#</sup>: n: number of soil pedons. <sup>†</sup>: L: loam, SiCL: silty clay loam, CL: clay loam, C: clay

<sup>§</sup>: ss: slightly sticky, sp: slightly plastic, s&p: sticky and plastic.

## CONCLUSIONS

At high elevations, higher rainfall, lower evapotranspiration (ET) and cooler temperatures result in greater leaching and favor the accumulation of organic matter and the precipitation of amorphous materials. Under these conditions, andic soil properties are well-expressed and the soils classify as Andisols mostly with umbric but rarely also with melanic epipedons. In contrast, at lower elevations, rainfall decreases and ET increases, the soils experience less leaching and remain relatively warm throughout the year, which promotes organic matter decomposition and in-situ mineral weathering. Under these conditions, the soils do not have

andic properties, kaolinite is the dominant clay mineral, and the soils classify as Inceptisols. The soils at intermediate elevation (400 to 500 m asl) are at the threshold of andic soil properties and classify as Andic Inceptisols. The soils at lowest elevation (<100 m asl) are at the threshold of argillic horizon properties and classify as Ultisols.

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## DYNAMIC AQUEOUS REDOX – MONITORING METHODS AND IMPLICATIONS FOR VARIABLE CHARGE SOILS

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### INTRODUCTION

The relationship between hydrological conditions and reduction–oxidation (redox) dynamics in subsurface media plays a critical role in controlling the chemistry, mobility, and bioavailability of contaminants and nutrients in soil–water systems. In variable-charge soils, where the net surface charge can shift markedly with changes in aqueous pH, ionic strength, and oxidation–reduction potential (ORP), these interactions are particularly complex. Under such conditions, evaluating and predicting the fate and transport of chemical constituents—especially contaminants that pose risks to environmental and human receptors—remains a major challenge.

Spatiotemporal variations in groundwater levels, hydraulic connectivity, flow paths, and residence times—driven by rainfall, irrigation, flooding, drainage, sea-level/groundwater rise, or seasonal water-table oscillations—frequently generate alternating oxic and anoxic conditions along soil profiles and within the vadose zone. These shifts can result in rapid and sustained changes to subsurface redox environments, profoundly influencing geochemical and hydraulic processes that govern contaminant mobility. Rapid transitions between reduced and oxidised states in the subsurface are termed here as Dynamic Aqueous Redox Conditions (DARC). Under DARC, redox-sensitive elements such as iron, manganese, arsenic, chromium, nitrogen, sulphur, and phosphorus may undergo rapid transformations. These transformations can trigger episodic contaminant release, mobilisation, or re-sequestration, depending on prevailing conditions. The rate, magnitude, and persistence of these redox changes depend strongly on the source, chemistry, and flux of infiltrating or receding water. In some systems, redox transitions may occur rapidly and persist for extended periods—seasonally or longer—before returning to baseline conditions. With such changes in redox, shifts in media pH and mineral assemblages can be anticipated which could affect the dissolution and re-precipitation of metal oxides and carbonates that can affect soil stability and nutrient availability for plant uptake. In practice, most long-term fate and transport models do not explicitly account for dynamic soil charge driven by fluctuating redox conditions. As a result, DARC can introduce significant uncertainty where surface binding sites respond dynamically to aqueous chemistry and can lead to under- or over-estimation of contaminant persistence and fate.

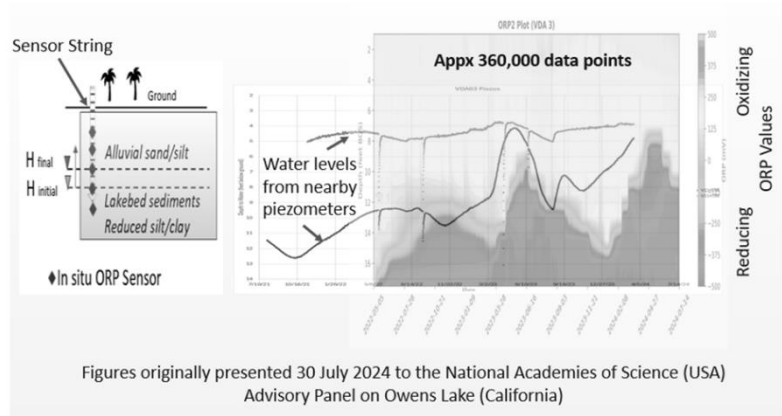
## methods: Monitoring redox dynamics under hydrogeologic forcing

Capturing redox dynamics under field conditions requires high-resolution, in situ monitoring approaches that integrate geochemical and hydrological measurements. These include continuous monitoring of ORP, dissolved oxygen, pH, and temperature using microelectronic sensors, combined with pore-water chemistry and hydrological measurements such as piezometric monitoring using pressure head transducers. While recognising the limitations of bulk ORP measurements in heterogeneous subsurface environments, focused evaluation of hydrogeologically driven redox cycling provides critical insight into dynamic processes. These include dissolution–reprecipitation reactions that alter mineral surface charge density, reactive surface area, and sorption capacity, all of which directly influence contaminant and nutrient behaviour. Such monitoring forms a necessary foundation for subsequent quantitative fate and transport modelling.

This study focuses on the first stage of evaluating DARC through continuous, in situ ORP monitoring. Using an advanced subsurface ORP monitoring technology developed by researchers at Colorado State University (Sale, et al., 2021), originally designed to assess remediation progress at contaminated groundwater sites, we applied this approach to a non-contaminated field setting. The monitoring system consisted of twelve ORP sensing electrodes mounted at approximately 0.2–0.4 metre (m) vertical intervals along an inert narrow pipe, extending from ground surface through the vadose zone and capillary fringe into the shallow saturated zone and to a final depth of about 6 m. The assembly was installed in a narrow-diameter boring and backfilled with native collapsed sediments (clay, silt, and sand), alongside a reference electrode. Sensors were connected to a solar-powered, cellular transmitter, enabling continuous data transmission to a cloud-based platform for analysis.

## RESULTS and discussion

Over a continuous monitoring period exceeding 36 months—one of the longest such datasets reported to date—the system recorded more than 360,000 ORP measurements. Monitoring captured redox dynamics across periods of extreme precipitation, drought, tropical storm events, and sustained high temperatures in the arid desert setting. Stratigraphically, deeper sensors were located within ancient lakebed sediments exhibiting persistently reduced geochemical signatures, while shallower sensors were positioned within overlying unconsolidated dune and alluvial sediments. The resulting dataset clearly demonstrates pronounced vertical and temporal redox variability, consistent with hydrogeologically driven DARC.



**Fig. 1. Data visualised as a redox “heat map” revealed strongly reduced conditions reaching approximately  $-400$  mV and oxidised zones exceeding  $+200$  mV.**

## CONCLUSIONS

The observed redox cycling indicates that DARC may be a common but under-recognised phenomenon, particularly in systems where soil surface charge is highly sensitive to aqueous conditions. These findings underscore the need to integrate redox and hydrogeological monitoring into contaminant behaviour assessments and into the design of resilient management and remediation strategies under dynamic soil–groundwater conditions.

Continuous ORP monitoring provides a valuable indirect or proxy indicator of dynamic soil charge behaviour and associated contaminant mobility. This is critical in variable-charge soils, where fluctuations in binding site availability can drive rapid transitions between contaminant retention and release. Ignoring such dynamics risks mischaracterising contaminant fate, exposure potential, and long-term system behaviour.

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## THE BRAZILIAN SOIL SCIENCE SOCIETY AND THE ADVANCING KNOWLEDGE ON VARIABLE CHARGE SOILS

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### ABSTRACT

Brazil encompasses vast and diverse areas dominated by variable charge soils, positioning the country as a key reference for advancing soil chemistry under tropical and subtropical conditions. Over recent decades, Brazilian research has significantly contributed to the understanding of surface charge behavior, nutrient dynamics, phosphorus interactions, and soil–plant relationships in highly weathered soils.

This presentation highlights the role of the Brazilian Soil Science Society (SBCS) as a scientific and institutional hub that has fostered research, capacity building, and international collaboration in areas of soil science relevant to tropical and subtropical environments. Through its scientific commissions, conferences, publications, and global partnerships, SBCS has promoted the integration of classical soil chemistry with emerging approaches focused on soil quality, environmental sustainability, and ecosystem resilience.

By connecting national research efforts to international networks, SBCS strengthens Brazil's contribution to global soil science and supports the advancement of knowledge on variable charge soils beyond regional boundaries.

**Accredited Testing Laboratories of Scientific Research  
Organization of Samoa (SROS): Analytical Services on Soil  
Samples**

Nofoaga Lisale

Scientific Research Organization Of Samoa

**Abstract Pending**

# PHOSPHORUS DYNAMICS IN HUMID TROPICAL ANDISOLS (HYDRANDEPTS): IMPLICATIONS FOR SOIL MANAGEMENT IN PAPUA NEW GUINEA

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## INTRODUCTION

Variable-charge soils of humid tropical regions commonly contain large reserves of total phosphorus (P) but supply only minute amounts of plant-available P. In Papua New Guinea (PNG), this paradox is most clearly expressed in volcanic ash-derived Andisols, particularly the hydrandepts that dominate the central highlands. These soils underpin predominantly semi-subsistence farming systems with increasing market-oriented (semi-commercial<sup>1</sup>) elements, yet exhibit chronic P deficiency and extremely low fertiliser recovery. This review synthesised global understanding of P cycling in humid tropical environments and deliberately reframes Andisols as the central analytical system rather than a special case. It examined how the prevalence of short-range-order (SRO) minerals and aluminum–humus complexes imposes distinctive constraints on P availability and on the performance of routine soil diagnostic tests. Priority research gaps were identified to support the development of locally grounded, Andisol-specific nutrient management frameworks for sustainable agriculture in Papua New Guinea.

## METHODS

A comprehensive survey of peer-reviewed publications, technical reports, and regional soil studies was undertaken. Literature addressing mineralogical controls on phosphorus sorption, sequential P fractionation, redox-induced transformations, pH-dependent surface charge, and biological mediation of P cycling was synthesized. Empirical studies from PNG were given priority to assess local relevance, including national-scale assessments of phosphorus sorption capacity and investigations of land-use impacts in highland cropping systems. Mechanistic diagnostic approaches such as phosphorus sorption indices and oxalate-extractable aluminum were evaluated alongside conventional chemical extractants including Olsen, Bray, and Colwell P. Comparative evidence from non-volcanic variable-charge soils was incorporated where it aided interpretation.

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<sup>1</sup> Supported by limited agrochemical inputs.

## RESULTS AND DISCUSSION

The synthesis demonstrated that the exceptional P retention of Hydrandepts is driven by the dominance of SRO aluminosilicates such as allophane and imogolite (table 1). These nanoscale minerals exhibit very high specific surface area and abundant hydroxyl groups that bind phosphate rapidly through inner-sphere ligand exchange. Consequently, soil solution P pools remain very small and tightly buffered. Any transient P release produced by mineralisation of organic matter or partial desorption is quickly neutralised by re-adsorption or precipitation as stable Al–P complexes.

**Table 1.** Key drivers of low phosphorus bioavailability in PNG Andisols (Hydrandepts).

<b>Controlling Factor</b>	<b>Dominant Feature in Hydrandepts</b>	<b>Effect on Soil Solution P</b>	<b>Implication for Management</b>
Mineralogy	Abundant short-range-order minerals (allophane, imogolite, ferrihydrite)	Extremely low due to high affinity for phosphate	Need to manage retention intensity
Aluminum chemistry	High oxalate-extractable Al (Alox)	Strong buffering and rapid re-adsorption	Alox as proxy for P fixation classes
Soil acidity	Commonly pH < 5.5	Enhanced positive surface charge and Al–P complex stability	Limited but beneficial responses to liming
Biological turnover	Organic P protected in Al–humus complexes	Slow and tightly neutralized	Importance of mycorrhizae and quality organic inputs

Conventional soil P tests were shown to be poor predictors of crop response in Andisols. Alkaline extractants often dissolve moderately labile or recalcitrant P forms and generate inflated “available” P values, while tests developed for calcareous or permanently charged soils lack sensitivity under acidic, Al-dominated conditions. In contrast, sorption-based parameters (PSI and Smax) provide direct insight into P buffering intensity and are strongly correlated with oxalate-extractable Al, a practical substitute for reactive surface abundance in allophanic systems.

The review further shows that biological factors play a critical but constrained role. Enzymatic access to organic P is limited by physical protection within organo-mineral complexes, and phosphate-solubilizing microorganisms struggle to maintain released P in solution due to immediate fixation. Progressive agricultural intensification in PNG, especially continuous sweetpotato cultivation, has amplified these limitations by reducing organic inputs and by increasing contact between fertilizers and reactive mineral surfaces.

## CONCLUSIONS

Phosphorus behaviour in humid tropical Andisols of PNG is governed by mineralogical and physicochemical processes that differ fundamentally from those of non-volcanic tropical soils. The dominance of Al-rich SRO minerals creates extremely high sorption capacity, strong buffering, and slow P turnover, leading to

chronic P deficiency and unreliable outcomes from routine soil tests. Future sustainable soil management in PNG must therefore rely on Andisol-specific diagnostics and integrated nutrient strategies that enhance phosphorus use efficiency rather than simply increasing fertilizer inputs. Development of simplified, locally calibrated frameworks combining chemical availability with retention potential is identified as a practical pathway to improve crop nutrition and long-term agricultural productivity.

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## Factors affecting dissolved inorganic carbon concentration in the subsoil of an allophanic Andosol

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### INTRODUCTION

Solute transport process in variable-charge soils such as Andosols is distinct from that in other soils particularly in that the cation- and anion-exchange capacities (CEC and AEC) vary with pH and ionic strength (Okamura and Wada, 1983). Studies on laboratory soil columns (Katou et al, 1996) and model calculations (Katou, 2002) have revealed that adsorption of monovalent anions ( $\text{NO}_3^-$  and  $\text{Cl}^-$ ) during invasion of a salt solution into Andosols is largely due to the increase in AEC caused by the increase in the ionic strength, and suggested that under certain simplified conditions ion adsorption may be described as a function of the electrolyte concentration only. In field soils, however, various biological processes provide and/or consume  $\text{H}^+$  and other ions, that complicates adsorption/desorption phenomena. In this study, we focused on the dynamics of dissolved inorganic carbon (DIC) in the subsoil of an allophanic Andosol, which would strongly be controlled by  $\text{CO}_2$  derived from microbial and plant root respiration, and examined the major factors that affect the DIC concentration.

### METHODS

The study was conducted in an experimental field of NIAES. The annual average precipitation and air temperature during 1991 to 2020 were 1326 mm and 14.3°C, respectively. The soil is an allophanic Andosol with a soil texture of light clay to heavy clay. A total of 11 treatments (Table 1) were set up for the field experiment. Finely-ground basalt (particle size  $\approx 100 \mu\text{m}$ ) and lime (calcium carbonate) were applied at 10 or 0.1 wt%, respectively, of the plow-layer soil as a neutralizer. These amendments were applied only once at the start of the experiment in early June 2023. Chemical fertilizer was applied to all the plots except no-fertilizer (NF) treatment (1). Composted cattle manure was applied to the treatments (6) to (10) with a reduction in chemical fertilizer according to the standard fertilization of Ibaraki prefecture. Soybean and barley were grown every year in summer to autumn and autumn to spring, respectively. Conventional tillage was conducted in all the plots except no-tillage (NT) treatments (9) and (10). Ceramic porous cups were installed at a depth of 62.5 cm in all plots. Soil water was taken once a month after May 2023 using a vacuum pump to measure pH, electrical conductivity (EC), DIC, and major inorganic cation and anion concentrations.

### RESULTS AND DISCUSSION

Our two-year monitoring by now revealed that DIC concentration tended to increase uniformly with soil water pH despite the different treatments, as expected from the theory of dissolution equilibrium between gaseous- and aqueous-phase  $\text{CO}_2$  concentrations (Fig. 1). Nitrification-derived  $\text{NO}_3^-$  was the key to control EC, linearly and positively correlated with EC (Fig. 2a). Conversely,  $\text{SO}_4^{2-}$  was negatively correlated with EC (Fig. 2b), suggesting that divalent anion was adsorbed (partly sorbed, forming inner-sphere complexes) by priority when AEC increased with EC. As liquid-phase  $\text{SO}_4^{2-}$  generally accounts for less than a few percent of total  $\text{SO}_4^{2-}$  in allophanic Andosols, it appears that a slight change in EC made a significant change in liquid-phase  $\text{SO}_4^{2-}$  concentration. Furthermore, we found that relationship between DIC or  $\text{HCO}_3^-$  concentration and EC (Fig. 2c) or pH (Fig. 1) was apparently similar with those

for  $\text{SO}_4^{2-}$  (Fig. 2b). Namely, it appears that adsorption behaviour of  $\text{HCO}_3^-$  in this Andosol was much closer to that of  $\text{SO}_4^{2-}$  than  $\text{NO}_3^-$  although  $\text{HCO}_3^-$  is a monovalent anion.

**Table 1. Treatments for the field experiment combining different amendments and soil/crop managements**

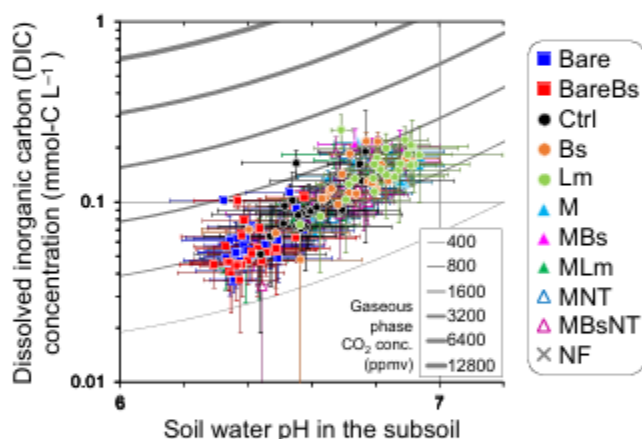
Treatment	Name	Repl. cates	Amendments			Soil & crop management	
			Neutralizer: Basalt (Bs) or Lime (Lm)	Composted cattle manure (M)	Chemical fertilizer (F)	Crop cultivation (crop) or Bare soil (bare)	Conventional tillage (T) or No tillage (NT)
①	Bare	3	-	-	F	bare	T
②	BareBs	3	Bs	-	F	bare	T
③	Ctrl	3	-	-	F	crop	T
④	Bs	3	Bs	-	F	crop	T
⑤	Lm	3	Lm	-	F	crop	T
⑥	M	3	-	M	F	crop	T
⑦	MBs	3	Bs	M	F	crop	T
⑧	MLm	3	Lm	M	F	crop	T
⑨	MNT	3	-	M	F	crop	NT
⑩	MBsNT	3	Bs	M	F	crop	NT
⑪	NF	1	-	-	-	crop	T

## CONCLUSIONS

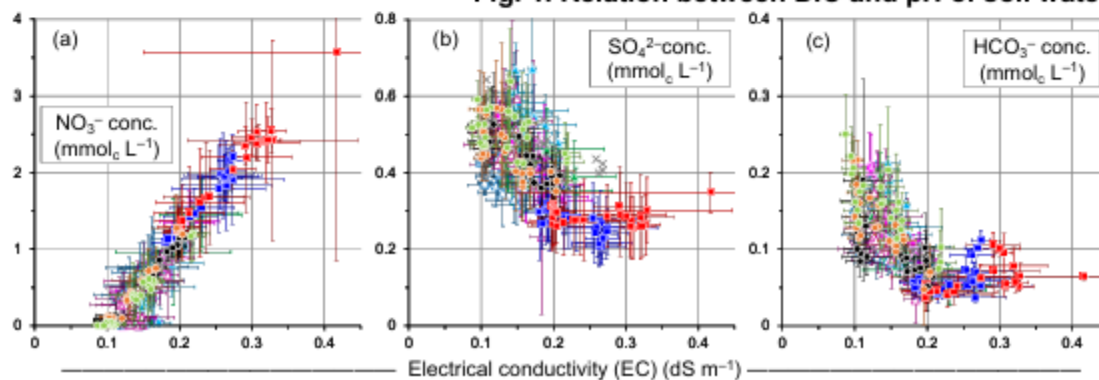
Our results suggest that liquid-phase  $\text{HCO}_3^-$  concentration in this Andosol is largely affected by AEC which is a function of pH and ionic strength, and that unlike  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$  is mostly and strongly adsorbed to the solid phase like  $\text{SO}_4^{2-}$ .

## ACKNOWLEDGMENTS

This study was partly supported by NEDO MS "A-ERW" project.



**Fig. 1. Relation between DIC and pH of soil water**



**Fig. 2. Relation of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$  concentrations to EC in the soil water**

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## **Soil, strategic adaptation and SDGs: The natural science-social science interface**

Steven Ratuva

Interdisciplinary collaboration between different knowledge systems is seen as pivotal in solving some of the major environmental and developmental issues facing the planet and humanity. The presentation will critically examine how soil science and sustainable development discourses and practice can harmonize in helping accelerate adaptation strategies along the lines of the UN Sustainable Development Goals (SDGs). A number of SDGs such as SDG 1 (No poverty), SDG 2 (Zero hunger), SDG 3 (Good health and wellbeing) and SDG 15 (Life on land), amongst others are directly or indirectly linked to the enabling role of soil health. For Pacific Island Countries and Territories (PICTs), soil, a critical component of the broader concept of land, which connects people and the environment, is increasingly being threatened by climate change and other factors. This has contributed to their slow progress in as far as SDGs are concerned. The presentation will examine some of these challenges and provide some potential pathways for accelerating SDGs for PICTs based on partnership between natural science and social science methodologies and modalities.

## **SYNERGISTIC NUTRIENT DYNAMICS AND AGRONOMIC STRATEGIES IN VARIABLE CHARGE SOILS**

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### **INTRODUCTION**

Variable charge soils are predominantly found in tropical and subtropical regions where smallholder farming predominates. These farming systems typically involve both crops and livestock and sometimes agroforestry and typically have low inputs of fertilizers and pesticides, use little mechanisation and produce relatively low yields. Soils are typically acidic (pH < 5.5), P-deficient, have a high P fixation capacity and low CEC. Farming on such soils presents challenges for smallholders because commercial, large scale, farming involves large inputs of lime, phosphate fertilizers, plus other fertilizer and pesticide inputs. In this paper the management of variable charge soils is reviewed and discussed and new developments and low input strategies are outlined.

### **FINDINGS**

Aluminium toxicity is a major limitation to crop production on acid soils. Increasing the pH to precipitate soluble and exchangeable Al results in a large increase in production. Lime needs to be applied to such soils and lime rates should be based on exchangeable Al plus the Al tolerance of the particular crop. Maintenance lime applications are required over time since soil acidification is a natural process which is accelerated by agricultural activity.

The soils not only have a low P status but have a high P-fixation ability for applied P because of the dominance of crystalline and amorphous Al and Fe oxides and hydroxides. In order to minimize P fixation, banding P close to the crop row (rather than broadcasting) can be practiced because this minimizes contact between the applied fertilizer P and the soil surfaces. Liming is beneficial to P use by the crop because it eliminates Al toxicity (a symptom of which is inhibited uptake and translocation of P). Where highly reactive phosphate rock is available it can be used in place of more expensive manufactured soluble P fertilizers. Phosphate rock dissolution is favoured under acid soil conditions and phosphate rock should be applied several months before lime.

In order to produce high yields, N fertilizer inputs are required. It is important to synchronize crop needs with soil N supply from both mineralization and inorganic and organic fertilizer N additions. This maximizes N use by the crop and thus minimizes N losses by leaching and gaseous emissions. There is a characteristic flush of N mineralization in tropical soils at the onset of the rainy season (due to rewetting of dry soil) and it is important to have a crop present to use this soil mineral N. Combining organic and mineral N fertilizers generally gives higher long-term yields than either applied alone. The use of acid tolerant legumes inoculated with suitable *rhizobium* strains can minimize the need for fertilizer N. The bulk of the N fixed by grain legumes is removed in the harvested grain so there is little or no return of N to the soil. Leguminous green manure crops can add substantial amounts of N to the soil. Techniques such as intercropping and alley cropping with legumes can be important in minimizing fertilizer N requirements. Many variable charge soils have a net positive charge in the subsoil and therefore can retain nitrate as it leaches down the profile. Nonetheless, nitrate held below 1m

depth is not normally plant-available so steps to minimize nitrate leaching are as important in variable charge as permanent charge soils.

The application of organic residues (animal manures, composts, plant cuttings and debris) is important because those high in N and P supply these nutrients to the soil as well as other nutrients and also help in maintaining soil organic matter content. Application of organic residues also has a liming effect but high rates of addition are required (e.g. 20-50 t ha<sup>-1</sup>) to raise pH substantially. One solution is to apply organic material through strip tillage (e.g. in a band 15 cm wide down plant rows) so that the application rate over the entire field is low. This will also concentrate added N and P and other nutrients close to the crop root system. Regardless of whether the pH is increased significantly, or not, soluble humic substances and organic acid anions released during organic residue decomposition can complex with Al in soil solution thus greatly reducing the concentration of phytotoxic monomeric Al<sup>3+</sup> in solution, thus increasing crop yields.

Maintaining/increasing soil organic matter content is important for maintaining a high CEC (and the ability of the soil to retain exchangeable cations), good physical properties and nutrient turnover through the organic phase generated by soil biota. Strategies to maintain soil organic matter content involve increasing organic matter inputs (applying organic residues retaining crop residues and stubble, growing green manure crops and then incorporating them) and decreasing organic matter decomposition (minimizing tillage operations). Practices that prevent the ground being bare such as double cropping and using cover crops in rotation are also important since they reduce runoff and erosion with the accompanying loss of organic matter-rich surface soil. Much recent research has concentrated on application of biochar to soils. While it has beneficial effects on soil chemical and microbial soil properties its main benefit is in sequestering carbon into the soil since it is a highly stable carbonaceous material. It is unlikely to be routinely applied unless funding comes from outside such as by Government Policy incentives including accessing global C markets.

Much research has concentrated on breeding Al tolerant crop cultivars for acid soils. Similarly, other research has concentrated on breeding P-use efficient crops that can grow at low available soil P levels. However, in acid soils tolerance to high soluble Al (and sometimes Mn) and low available P and Ca are all required and plants need to be adapted to local climatic conditions. Breeding programmes therefore need to be integrated and existing landraces adapted to local acid soil and climatic conditions are an important genetic resource for plant breeding programmes.

## CONCLUSIONS

It was concluded that management of variable charge soils requires a combination of many soil and agronomic practices and the integration of these will result in sustainable agricultural systems on these soils.

# VARIABLE CHARGE, CATIONS AND CARBON DIOXIDE REMOVAL DURING SOIL REJUVENATION

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## INTRODUCTION

Globally, a large proportion of the world's soils—particularly those in tropical and subtropical regions—have variable surface charge, arising from the dominance of iron and aluminium oxides, hydroxides, and 1:1 layer silicates such as kaolinite. These soils, including the Oxisols, Ultisols and Andisols, especially in warm, humid regions, possess surface charge that varies with pH and ionic strength, profoundly influencing nutrient retention, cation exchange, and reactions with CO<sub>2</sub>.

Following exposure of primary minerals at the Earth's surface, weathering initially enhances fertility through the accumulation of secondary aluminosilicates and organic matter, producing near-neutral pH and high organic matter content, cation exchange capacity and base saturation. However, with prolonged weathering, low activity clays and oxidic minerals form and the soils become strongly acidic with pH-dependent (variable) charge and diminishing nutrient reserves.

Weathering is driven largely by carbonic acid (dissolved CO<sub>2</sub>), leading to generation of bicarbonate, capturing the carbon in inorganic form. The bicarbonate may precipitate as carbonate in the soil, or leach to groundwater, rivers and the sea, where it accumulates and is converted to carbonate. As weathering slows over time, so does the removal of CO<sub>2</sub> via weathering.

In recent years, great interest has emerged in accelerating this CO<sub>2</sub> removal process and rejuvenating soils by applying crushed alkaline rock, i.e. 'enhanced rock weathering' (ERW). Modelling has suggested that a substantial portion of the CO<sub>2</sub> removal required to meet net zero CO<sub>2</sub> emission targets could be met by ERW (Beerling et al., 2020). However, such modelling has generally ignored soil processes. This study investigates how **variable charge characteristics**, soil pH, and exchangeable cations interact to influence the **capture of inorganic carbon** following the addition of crushed silicate rock. By linking charge behaviour to mineral dissolution and CO<sub>2</sub> sequestration dynamics, the work contributes to a deeper understanding of soil rejuvenation processes in landscapes dominated by variable charge systems—an issue central to both soil fertility restoration and climate mitigation.

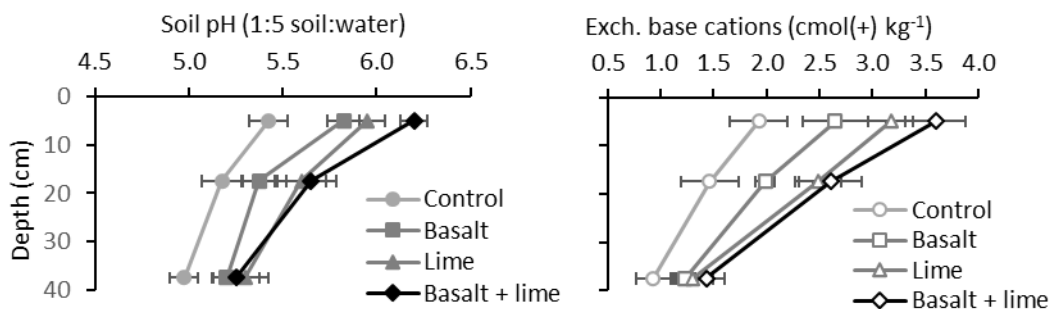
## METHODS

To examine the processes occurring upon addition of crushed alkaline rock to soil, a factorial field experiment was established in sugarcane in North Queensland, with basalt applied annually at 0 or 50 t ha<sup>-1</sup> in 2018-2024 and lime applied annually at 2.5 t ha<sup>-1</sup> in 2022-2024. A wet tropical site was chosen as hot wet conditions were considered highly suitable for CO<sub>2</sub> removal via ERW. Weathering was measured by the release of cations from the rock. CO<sub>2</sub>

removal was measured by the generation of inorganic carbon, calculated as the increase in soil inorganic carbon content plus the export of bicarbonate in deep drainage (Holden et al., 2024). Soil exchangeable cations were measured using 0.1M BaCl<sub>2</sub>/NH<sub>4</sub>Cl extraction. To examine the effects of climate and soil properties, geochemical modelling with PHREEQC (Green et al., 2024) was used to simulate weathering of applied basalt (50 t/ha) and the resultant CO<sub>2</sub> removal and changes in soil properties (0.5-m deep profile) in 5 scenarios, with initial pH ranging from 4.5 to 8.5, over 15 years.

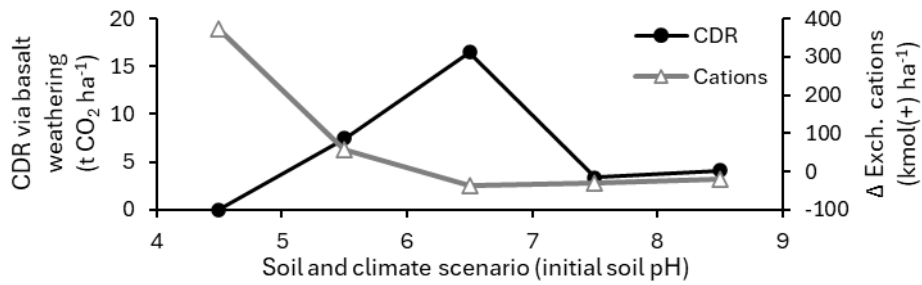
## RESULTS and discussion

The field experiment showed CO<sub>2</sub> capture via ERW was severely attenuated by soil acidity and variable charge. Weathering of the added rock increased soil pH and cation exchange capacity (Fig. 1), with a close linear relationship between pH and the sum of exchangeable base cations over all the data ( $r^2=0.962$ ). The protons released from soil surfaces, which were replaced by base cations released from the weathering rock, were the main causal agent of weathering at low pH. At higher pH, replaced protons may have combined with any bicarbonate generated via carbonic acid weathering, returning the carbon to the atmosphere as CO<sub>2</sub>. Across all pH values, nitric acid and organic acids were also significant weathering agents. Thus, CO<sub>2</sub> capture via weathering of the added basalt was only 0.02-0.05 t CO<sub>2</sub> ha<sup>-1</sup> y<sup>-1</sup>, much lower than the potential determined from base cation release via weathering. While addition of crushed alkaline rocks increased soil pH, charge and exchangeable base content, it had very little effect on the carbon balance or export of acidity or alkalinity from the soil. If higher pH were reached, variable charge might reach a maximum and carbonate might accumulate in the soil, but that did not occur under agricultural management in this wet climate.



**Fig. 1. Effect of basalt and lime addition on soil pH and exchangeable cations in a field experiment.**

The geochemical modelling showed that CO<sub>2</sub> removal via weathering was attenuated by variable charge and pH buffering capacity across a broad range of agricultural soil and climate conditions. CO<sub>2</sub> removal was greatest in the scenario with an initial pH of 6.5 and was inversely related to the increase in exchangeable base cations over the acidic-neutral pH range (Fig. 2).



**Fig. 2. Modelled effect of different soil and climate scenarios on CO<sub>2</sub> removal (CDR) and change in exchangeable base cations following addition of basalt.**

## CONCLUSIONS

Soil variable charge has an important role in preventing or negating CO<sub>2</sub> removal via ERW, resulting in actual rates being much lower than potential values in the literature. It will therefore be essential to consider soil variable charge when assessing the feasibility of wide-scale deployment of ERW for CO<sub>2</sub> removal and soil rejuvenation.

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# Phosphorus Retention in Variable Charge Soils: Implications for Taro Productivity in Fiji

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The Pacific Community (SPC)

## 1. Background and Rationale

Taro (*Colocasia esculenta* L.) is Fiji's third most important economic crop and a culturally significant staple across the Pacific. However, national exports have declined over the past decade, partly due to soil fertility decline under continuous cultivation. Among the key constraints, phosphorus (P) deficiency has emerged as a primary limiting factor in taro productivity.

Many taro-growing regions in Fiji are dominated by highly weathered tropical soils characterised by kaolinitic clays, abundant aluminium (Al) and iron (Fe) hydrous oxides, and strongly developed variable charge surfaces. Unlike permanent-charge temperate soils, these soils exhibit pH-dependent surface charge and a high affinity for phosphate ions due to ligand exchange reactions. Consequently, applied P fertiliser is rapidly adsorbed or fixed, reducing plant-available phosphorus and fertiliser efficiency.

Traditional fertiliser recommendations in Fiji have been largely island-wide and uniform, without accounting for site-specific P fixation capacity. This blanket approach does not reflect spatial variability in P retention driven by mineralogical differences, resulting in suboptimal productivity.

## 2. Objectives

This study aimed to: (i) quantify soil phosphorus status and P-retention capacity across taro farms in Taveuni, Fiji; (ii) evaluate the adequacy of current fertiliser practices; (iii) estimate site-specific P requirements to achieve optimal Olsen P levels; and (iv) demonstrate the importance of variable charge mineralogy in guiding fertiliser recommendations.

## 3. Materials and Methods

A combined grower and soil survey was conducted across 63 taro farms in Taveuni, Fiji. Farms were categorised according to measured P-retention capacity: high retention soils (>60%), medium retention soils (30–60%), and low retention soils (<30%).

Soil analyses included soil pH (water), Olsen P, total nitrogen, exchangeable potassium, and phosphorus retention index. Grower interviews documented fertiliser application rates and nutrient management practices.

## **4. Results**

Soils were moderately acidic (mean pH 5.6–5.8). Mean Olsen P values ranged from 6–7.9 mg P/kg across retention classes, substantially below the estimated optimum of approximately 20 mg P/kg required for taro production. Total nitrogen (0.8–1.0%) and exchangeable potassium (0.4 me/100 g) were moderate, indicating phosphorus as the primary limiting nutrient.

Semi-commercial and commercial growers applied only 17 and 26 kg P/ha, respectively—far below requirements needed to overcome strong P fixation.

To increase Olsen P from approximately 7 to 20 mg P/kg, estimated requirements ranged from 169 kg P/ha in low P-retention soils to 377 kg P/ha in high P-retention soils. These differences demonstrate the dominant influence of variable charge mineralogy on fertiliser efficiency.

## **5. Discussion**

In highly weathered tropical soils, Fe and Al oxides provide abundant positively charged surfaces under moderately acidic conditions. Phosphate ions are strongly adsorbed via ligand exchange, forming inner-sphere complexes that are not readily reversible. Consequently, phosphorus dynamics differ fundamentally from permanent-charge temperate soils.

The findings confirm that blanket fertiliser recommendations are inadequate for variable charge systems. Effective management must include site-specific soil testing, quantification of P retention capacity, targeted placement (banding), split applications, and potential amendments to reduce fixation losses.

Given the limited buffering capacity of many Pacific island soils, integrating mineralogical understanding into agronomic recommendations is essential for improving productivity, fertiliser efficiency, and food security.

## **6. Conclusions**

Taro-growing soils in Taveuni exhibit high phosphorus fixation due to variable charge mineralogy. Current fertiliser rates are insufficient to achieve agronomic targets. Phosphorus requirements vary more than two-fold across retention classes, underscoring the need for soil test-based, site-specific nutrient management.

Sustainable taro productivity in Fiji and comparable Pacific systems depends on integrating soil mineralogy into fertiliser policy and extension frameworks. Soil mineralogy must guide agronomy in variable charge environments.

## **Navigating Chemical Fate in Variable Charge Soils: Interactions, Mobility, and Risk Management in a Changing Environment Conditions**

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### **Introduction**

Variable-charge soils dominate much of the humid tropics and subtropics, including Ferralsols/Acrisols and basaltic ash-derived Andisols such as found in Japan, New Zealand, Samoa, Fiji and other Pacific Rim nations. These soils contain allophane, imogolite, ferrihydrite and Fe/Al oxyhydroxides that generate highly pH-dependent surface charge and exceptional reactivity. Foundational work by Naidu and colleagues on Australian, Samoan and Fijian volcanic soils demonstrated strong phosphate fixation, high metal sorption and sensitivity to pH/redox fluctuations. In contrast, temperate regions are dominated by permanent-charge soils, and this continental transition critically shapes nutrient mobility, pesticide fate and contaminant export to sensitive systems such as the Murray River and the Great Barrier Reef.

### **Charge Development and Soil Reactivity**

Permanent-charge soils maintain constant negative charge, supporting cation retention but allowing anion mobility. Variable-charge soils exhibit reversible protonation–deprotonation, shifting between positive and negative charge depending on pH, ionic strength and redox conditions. Basaltic ash-derived Andisols have extremely high surface area and ligand-exchange capacity, making them among the most chemically reactive soils worldwide.

### *Fate of Organic Contaminants*

Organic contaminants include non-ionic pesticides (R–H, R–X), weak-acid herbicides (R–COOH), weak-base pesticides (R–NH<sub>2</sub>), pharmaceuticals, metabolites and other organics such as PFAS and legacy organic contaminants. Hydrophobic non-ionic pesticides sorb mainly to organic matter. Ionisable pesticides exhibit strong pH-dependent behaviour: weak acids such as 2,4-D, picloram, dicamba and glyphosate are retained at low pH when neutral but become mobile as anions at higher pH; weak bases behave oppositely. Andisols display strong affinity for anions at moderate pH.

PFAS show amphiphilic behaviour, with sorption enhanced under acidic conditions but reduced by competition with  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$ . Redox-driven dissolution of Fe/Al oxides weakens sorption and increases mobility.

### *Nutrients and Inorganic Contaminants*

Phosphate forms strong ligand-exchange complexes with Fe/Al oxides and allophane, giving volcanic ash soils—including Samoa, Fiji, NZ and Japan—exceptional P-fixation capacity, as demonstrated in Naidu's early work. In contrast, permanent-charge soils of such as that in South Australia show limited P sorption, contributing to eutrophication in the Murray River. Nitrate is mobile across all soils: in temperate systems it leaches into groundwater, while in northern horticultural belts it rapidly enters waterways, contributing to Great Barrier Reef nutrient loading. Heavy metal transport involves specific and non-specific interactions; Naidu & Kookana showed strong retention of Cd in variable-charge soils, though redox shifts can remobilise As and Cr.

### *Experimental and Modelling Approaches*

Surface-charge behaviour is quantified using zeta potential, FTIR and potentiometric titration. Flow-through columns and microcosms simulate realistic pH–redox–ionic strength cycles. Reactive-transport modelling integrates mechanistic data to predict catchment-scale movement of nutrients and contaminants.

### *Management Implications*

Environmental and human-health risk assessments must incorporate soil type, as mineralogy and charge behaviour fundamentally determine chemical mobility. Variable-charge soils retain phosphate but allow nitrate export, and erosion/acidification can release stored P, increasing nutrient delivery to the Great Barrier Reef. Permanent-charge soils in the Murray Basin allow rapid phosphate transport and deep nitrate leaching. Fertiliser strategies must therefore reflect mineralogy, with volcanic ash soils requiring specialised P management. PFAS and ionisable pesticide mobility depends on pH, redox state and competing anions, underscoring the need for soil-type-specific regulation.

## **Conclusions**

Soil charge characteristics control nutrient and contaminant behaviour across Australia and the Pacific. From Samoan and Fijian basaltic ash soils to Ferralsols and temperate clays, differences in surface chemistry drive variability in nutrient leakage, pesticide fate and certain organic contaminants including PFAS transport. Mechanistic understanding is essential for improved regulatory frameworks and for protecting the Great Barrier Reef, the Murray River and other sensitive ecosystems.

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# Speciation and Bioavailability of metals and metalloids in mixed waste organic output (MWOO) and MWOO amended soils

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## INTRODUCTION

Mechanical and biological treatment of mixed solid waste produces mixed waste organic outputs (MWOO) that can improve soil properties but concerns about contaminant metals and metalloids restrict their use (Wilson, Bayat and Wilson, 2014). Since total concentrations provide limited insight into ecological risk, bioavailability assessed through sequential extraction offers a clearer measure (Illera *et al.*, 2000; He, Yang and Stoffella, 2005; Barral and Paradelo, 2011). Studies show soluble and exchangeable fractions in mature MWOO usually constitute <10% of total metals (Soumare *et al.*, 2002; Castaldi, Santona and Melis, 2006), but minor research has examined MWOO or MWOO-amended soils in Australia. This study therefore investigated how MWOO affects metal speciation and availability in two acidic NSW agricultural soils (sandy loam and clay) over 18 months, chosen because acidic soils pose greater risks of leaching and bioavailability (Smith, 2009a).

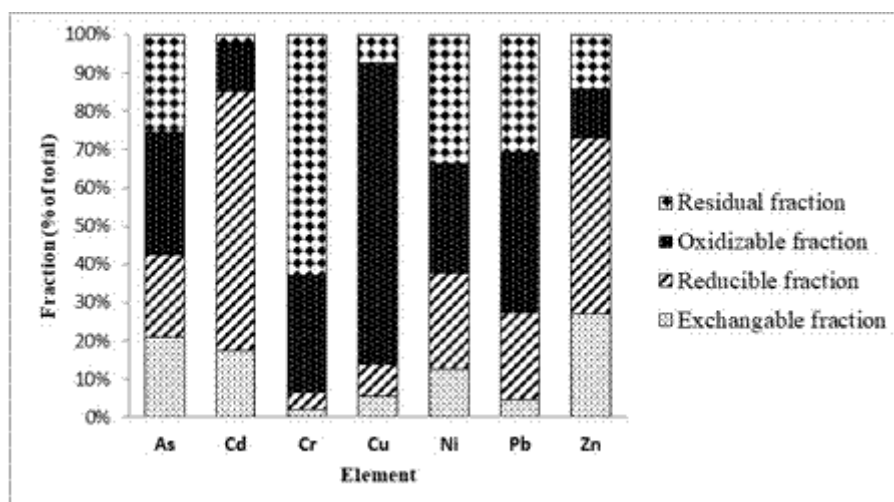
## METHODS

The study assessed the impact of mixed waste organic output (MWOO) on soil properties using sandy loam and clay soils collected from Kirby Farm, University of New England, in a controlled glasshouse column experiment over 18 months. MWOO was sourced from a Sydney AWT plant, air-dried, homogenised, and applied at varying rates (20, 50, 140 t/ha), either surface-applied or incorporated, with replicated treatments and unamended controls. Soil columns were maintained under controlled temperature, humidity, and moisture, and destructively sampled at multiple depths and time intervals. Physico-chemical analyses included pH, EC, particle size, carbon, nitrogen, phosphorus, and total metals/metalloids via aqua regia digestion and ICP-OES, with QA/QC using certified reference materials. Sequential extraction followed a modified BCR method to partition metals into exchangeable, reducible, oxidisable, and residual fractions, analysed by ICP-MS. Statistical analyses (t-tests, ANOVA, Tukey's HSD) were conducted in R to evaluate treatment and temporal effects, with significance set at  $p < 0.05$ .

## RESULTS and discussion

The study showed that MWOO application significantly increased total concentrations of Cu, Pb, and Zn in sandy loam soil and Pb in clay, with these changes persisting over 18 months, while As, Cr, and Ni remained largely unaffected in terms of total concentration. Sequential extraction of metals and metalloids in MWOO (refer to Figure 1) and MWOO amended soils were conducted which revealed that most metals were bound in the residual fraction,

particularly Cr and As, but MWOO addition shifted Cu, Pb, Zn, and Ni into more labile fractions exchangeable, reducible, and oxidisable especially in sandy loam, reflecting their higher concentrations in MWOO relative to background soils. Pb displayed strong affinity for Mn oxides, increasing in the reducible fraction in both soils, while Zn recorded the greatest increase in exchangeable form (up to 20% in sandy loam), though absolute concentrations remained below plant toxicity thresholds. As remained largely immobile, with only minor increases in exchangeable form in sandy loam due to pH effects, and Cr and Cu were stable and mostly unavailable, while Ni showed only transient changes. Overall, MWOO altered metal speciation more than total concentrations, with sandy loam soils more sensitive than clay, underscoring the importance of soil texture, background contamination, and fractionation analysis in assessing environmental risk and bioavailability.



**Fig 1. Percentage of various metals in MWOO fractions detected by BCR sequential extraction**

## CONCLUSIONS

MWOO application increased Cu, Pb, and Zn in sandy loam and Pb in clay soils, with most metals remaining in residual, relatively unavailable fractions. However, MWOO shifted portions of Cu, Pb, Zn, and Ni into more labile forms especially in sandy loam while As and Cr stayed largely immobile. Zn showed the greatest rise in exchangeable fraction (up to 20%), though concentrations stayed below risk thresholds. Overall, sandy soils were more sensitive than clay, and risks are greatest when MWOO with high contaminant loads is applied repeatedly or at high rates, particularly under changing soil conditions that could mobilize reducible or oxidisable fractions.

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## **Developing a Restoration Model for Lead Mining Contaminated Soils in Zambia: Would Zambian Contaminated sites provide a framework for restoration of Lead Contaminated Sites in Sub Saharan Africa**

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Mining is an essential driver of economic development across the Sub-Saharan Africa. Some studies have enumerated and mapped 469 mines in SSA as mining and pollution hotspots in the DRC, Zambia, Zimbabwe, Nigeria, Ghana, and Guinea. While SSA has witnessed expansion in the mining sector, with over 200 significant mines and numerous artisanal and small-scale mines (ASMs) becoming operational in the last two decades, this has led to a rise in environmental degradation in the form of mining-generated wastelands and degraded landscapes as well as pollution of various ecosystems. Legacy mining and smelting have rendered pollution a persistent environmental and public health threat in the region. There is need to understand the spatial distribution, mineralogical characteristics and potential food chain pathways across the contaminated sites especially the lead contaminated sites which is currently missing. In order to do this, this study was undertaken across selected sites in the Zambia's Kabwe lead contaminated sites in form of soil survey complemented with soil incubation with different types of biochars used as soil enhancers (Pb immobilization). The different types of biochar were produced from wood shavings, maize cobs and cow dung, treated under different pyrolysis conditions ( $T^\circ$  and residence time). The study revealed that soil Pb concentrations in the soils from lead contaminated sites ranged from 82.9 mg kg<sup>-1</sup> to 3,911.1 mg kg<sup>-1</sup>. Mineralogical analysis of the studied Pb-contaminated soil identified galena (PbS) as the predominant Pb-bearing phase. Further, sieve analysis indicated that Pb is predominantly concentrated in finer soil fractions, suggesting increasing environmental risk through enhanced mobility in the soil-plant system. Soil properties were differentially influenced by different biochars after 4 months of incubation. Overall wood shavings-derived biochars significantly increased soil pH in comparison with maize cobs and cow dung. However, regardless of the type of feedstock, a steady reduction of pH was observed with the incubation time, with stable values recorded from the third month. A similar trend was observed for CEC. Biochar efficiency in modulating soil properties was influenced by pyrolysis conditions, as positive effects noted with increased pyrolysis temperature and residence time.

# Global Prediction of Multi-Metal Soil Contamination Risk Using Explainable and Physics-Guided Machine Learning: Insights from Spatial Hotspots, Nonlinear Controls, and Federated Learning Limitations in Variable Charge Soils

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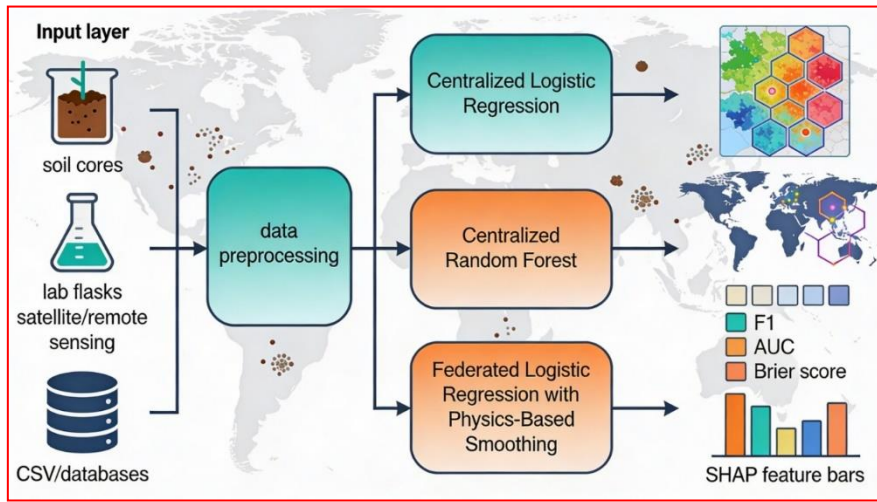
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## INTRODUCTION

Soil contamination caused by toxic metals has become a serious problem across the world. It affects food safety, soil health, the environment, and human life for a long time. Due to fast industrial growth, mining activities, heavy use of fertilizers and chemicals in agriculture, and unplanned urban development, harmful metals like arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), and lead (Pb) are increasing in soils in many regions [9], [18]. This problem becomes more difficult in variable charge soils, where the movement and holding of metals depend on many connected factors such as soil pH, clay type, iron and aluminium oxides, organic matter, redox conditions, water flow, and climate. In these soils, even small changes in environmental conditions can cause big changes in how metals attach to or release from soil particles, which makes risk prediction very hard [1][2].

## METHODS

To understand the problem in a proper way, we used three types of models so we can compare simple and strong methods under global differences. First, we used Centralized Logistic Regression as a basic linear baseline model. It is easy to train and easy to understand, but it may not capture the complex nonlinear behaviour seen in variable charge soils. Second, we used Centralized Random Forest, which is a nonlinear tree-based model.

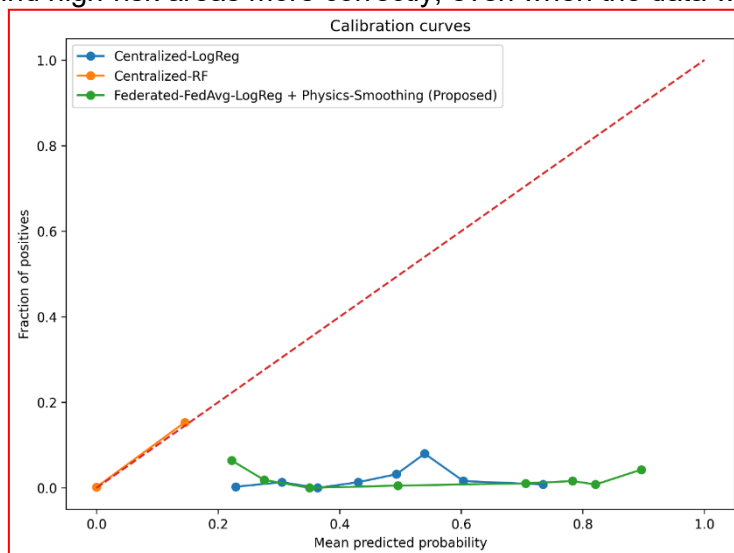


**Figure 1. Soil Risk Prediction Framework**

Figure 1 shows the overall working of our global soil risk prediction system in a clear Framework.

### RESULTS and discussion

From the experiments, the Random Forest model worked much better than the simple linear models. This shows that soil contamination is not caused by just one or two simple reasons, but by many factors acting together. Random Forest can understand these combined effects, so it was able to find high-risk areas more correctly, even when the data were very uneven.



**Fig. 2. Comparison of How Well Different Models Estimate Arsenic (As) Risk**

Figure 2 shows how accurately the risk probabilities predicted by different models reflect the actual occurrence of arsenic contamination.

**Table 1. Performance Comparison Between Existing and Proposed Approaches for Soil Contamination Risk Prediction.**

Parameters	Existing system (Centralized LogReg)	Proposed system (Centralized RF)
Accuracy	0.5843	0.9887
F1-score	0.0701	0.6667

AUC-ROC	0.6321	0.9439
AUC Impro vs Existing ( $\Delta$ AUC)	0.0000	+0.3118

Table 1 shows a clear numerical comparison between the earlier method and the proposed approach for predicting soil contamination risk at the global level.

## CONCLUSIONS

From this research, we can clearly see that predicting soil pollution risk for the whole world is not an easy job. The results show that we cannot depend on only one method or one model. We need to use explainable machine learning, hotspot maps, and simple soil science ideas together. The nonlinear model, especially Random Forest, worked much better than simple linear models because soil pollution is affected by many factors at the same time.

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# ROLE OF ORGANIC MATTER ON SURFACE CHARGE AND ADSORPTION OF PFOS IN SOILS

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## INTRODUCTION

Soil organic matter (SOM) is widely recognised as a major sink for long-chain per- and polyfluoroalkyl substances (PFAS), with sorption generally increasing with chain length and often exceeding that of mineral phases (Umeh et al., 2021). Sorption behaviour varies across SOM fractions, with long-chain PFAS preferentially associating with condensed, humin-like domains, while shorter-chain PFAS are more closely associated with humic and fulvic fractions where surface charge effects and cation bridging are more influential (Wang et al., 2022). In soils with variable charge characteristics, SOM contributes significantly to surface charge development and provides key sorption domains for PFAS through hydrophobic and electrostatic interactions. This study investigates the role of soil organic matter in controlling surface charge behaviour and the sorption capacity of perfluorooctane sulfonate (PFOS) in a range of Australian soils.

## MATERIALS AND METHODS

Six surface soils (0–15 cm) were collected from selected sites across Australia (Table 1). The soils were used without further modification or purification. Analytical-grade chemicals and PFAS standards were obtained from Sigma-Aldrich (Australia). Soil physicochemical properties, including total organic carbon (TOC), pH, electrical conductivity (EC), cation exchange capacity (CEC), particle size distribution, and mineralogical composition, were characterised.

**Table 1 Soil properties**

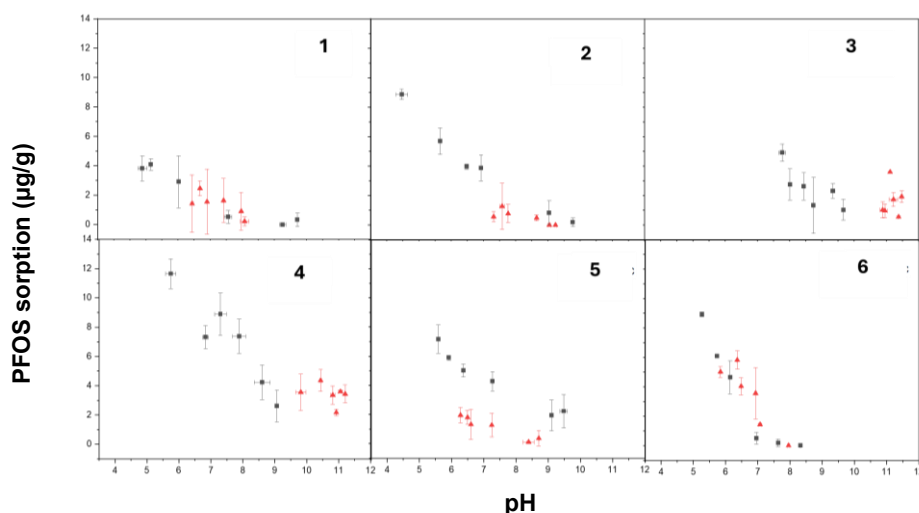
Soil ID	1	2	3	4	5	6
<b>Location</b>	NSW	NSW	WA	SA	QLD	QLD
<b>TOC (%)</b>	1.29	2.8	0.15	1.7	3.27	7.5
<b>pH<sub>water</sub></b>	6.6	6.69	9.12	6 8.7	6	5.1
<b>EC (µs/cm)</b>	190.5	101.4	110.15	- 2	75.5	87
<b>CEC (meq100 g<sup>-1</sup>)</b>	9.7			5.8	38.7	6.37
<b>Sand (%)</b>	63.8				53	61.9
<b>Silt (%)</b>	23.8				16.1	16.8
<b>Clay (%)</b>	12.4			6.7	30.9	21.2

<b>Major mineral compound</b>	Quartz, Oligoclase, Albite, Sodalite	-	-	-	Montmorillonite, Kaolinite, Montmorillonite- Kaolinite interstratifications, Feldspar	Kaolinite, Gibbsite, Quartz
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Oven-dried soils were adjusted to six pH values ranging from 4 to 9. Changes in mineral composition and organic matter content were determined using X-ray diffraction (XRD), thermogravimetric analysis (TGA), and LECO carbon analysis. Batch adsorption experiments were conducted to quantify PFOS sorption onto soils across the pH range. Surface charge characteristics of the pH-adjusted soils were determined using ion adsorption methods (Naidu et al., 1994). To isolate the role of organic matter, pH-adjusted soils (~100 g) were combusted at 300–600 °C to remove organic matter. Adsorption experiments were repeated using the combusted soils, followed by post-sorption characterisation to confirm PFOS presence and pH-dependent sorption behaviour.

## RESULTS AND DISCUSSION

PFOS sorption before and after removal of soil organic matter under varying pH conditions is shown in Figure 1. Across all six soils, PFOS sorption decreased with increasing pH, indicating strong pH dependence of PFOS–soil interactions. In unmodified soils, higher PFOS sorption at lower pH is attributed to enhanced electrostatic attraction between anionic PFOS and protonated soil surface sites. Increasing pH resulted in progressive surface deprotonation and increased electrostatic repulsion, reducing PFOS sorption. Removal of organic carbon led to a marked reduction in PFOS sorption, particularly in soils 4 and 5, highlighting the dominant role of SOM in PFOS retention. Following organic matter removal, soils exhibited a narrower pH buffering range, reflecting reduced charge buffering capacity. The persistence of pH effects after combustion indicates that mineral surface interactions also contribute to PFOS sorption, although to a lesser extent than hydrophobic interactions associated with SOM. Variability among soils reflects differences in organic carbon content, mineralogy, and variable-charge characteristics.



**Figure 1 PFOS sorbed by soils before and after removal of organic carbon by combustion (square- original soil; triangle – soil after removal of organic carbon)**

## CONCLUSIONS

This study demonstrates that soil organic matter plays a critical role in PFOS sorption by contributing both sorption domains and variable surface charge. Removal of organic matter significantly reduced PFOS sorption capacity, while the continued influence of pH indicates

that electrostatic interactions also contribute to PFOS retention in soils. These findings highlight the importance of considering organic matter content and variable-charge behaviour when assessing PFOS mobility and risk in soils.

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## CHARGE VARIABILITY OF SOILS INFLUENCING THE SORPTION PROCESS OF GLYPHOSATE

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### INTRODUCTION

Herbicides are widely used agrochemicals for weed control in both agricultural and non-agricultural settings worldwide. Although many herbicides are considered non-persistent, increasing evidence indicates their continued presence in a wide range of soils following application. Once introduced into soil, herbicide behaviour and fate are governed by soil physicochemical properties, organic matter content, and soil–chemical interactions. Among these processes, sorption plays a central role in controlling herbicide mobility, bioavailability, degradation, and leaching potential. Consequently, understanding the sorption behaviour of glyphosate—one of the most widely used herbicides—is essential for accurately predicting its environmental fate, particularly in soils exhibiting variable surface charge characteristics.

### METHODOLOGY

Six contrasting Australian soils were comprehensively characterised using conventional wet chemical analyses in combination with advanced solid-state techniques, including X-ray diffraction, thermogravimetric analysis, surface area and porosity measurements, and scanning electron microscopy. Time-dependent sorption kinetics of glyphosate were investigated under controlled laboratory conditions over a 72-h period.

### RESULTS

Glyphosate exhibited rapid initial sorption across all soils, with 70–90% of total adsorption occurring within the first 2 h, followed by a slower approach to pseudo-equilibrium within 24 h. Sorption capacity varied substantially (87.3–101.2 mg kg<sup>-1</sup>)

and was strongly controlled by soil pH, variable surface charge, clay mineralogy, and the abundance of Fe and Al oxides. Kinetic modelling indicated that the pseudo-second-order model best described glyphosate sorption ( $R^2 > 0.99$ ), consistent with chemisorption mechanisms involving ligand exchange and surface complexation on oxide-rich, variable-charge minerals. Elovich and intra-particle diffusion models further highlighted the role of heterogeneous surface sites and diffusion-limited processes. Soils representative of tropical and island environments, characterised by acidic pH and high oxide content, exhibited greater glyphosate retention, whereas alkaline, calcareous soils with limited variable-charge surfaces showed reduced sorption affinity.

## CONCLUSION

The findings demonstrate that charge variability is a dominant control on glyphosate sorption behaviour, particularly in oxide-rich soils typical of tropical and island regions. Integrating solid-state characterisation with time-resolved kinetic analysis provides a mechanistic basis for predicting herbicide fate in variable-charge soil systems. These insights are critical for improving risk assessment, land management, and agrochemical stewardship in environmentally sensitive tropical and island settings.

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# HEAVY METAL (PB) ACCUMULATION IN METALLOPHYTES AS INFLUENCED BY THE VARIATIONS IN RHIZOSPHERIC AND NON-RHIZOSPHERIC SOILS PHYSICO-CHEMICAL CHARACTERISTICS

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## INTRODUCTION

The activities in the rhizosphere have been described as major factors determining the behaviour of different plant species under heavy metal stress. For instance, some plant species called excluders are able to prevent the accumulation of metals in their biomass whereas hyperaccumulators take up these metals due to variation in their rhizospheric compositions or activities. Different plant species therefore use various strategies to enhance metal dissolution in the soil so as to increase metal uptake. According to Wang *et al.* (2003) enhanced metal uptake by hyperaccumulators is mostly achieved through the secretion of root exudates such as phytosiderophores, organic acids, and protons. The quality and type of exudation by different plant root determine the response of hyperaccumulating and non-hyperaccumulating plants to different metal concentrations (Rakesh *et al.*, 2013). These exudates in turn increase the Dissolved Organic matter (DOM) functional groups in the soil which in turn form ligands with metals, thereby enhancing the mobility and bioavailability of heavy metals in soil (Wenzel *et al.*, 2013). The objectives of this study were; (a) to investigate the differences in the physicochemical characteristics of rhizospheric soil of plant species growing on contaminated soil and the non-rhizospheric soil. (B) to identify different functional groups present at each plant rhizosphere using Fourier transform infrared spectroscopy (FTIR).

## METHODS

Seven plant species were collected in triplicates from Pb contaminated site. Namely: *Imperata cylindrica*, *Cynodon dactylon*, *Eleusine indica*, *Gomphrena celosoides*, *Sporobolus pyramidalis*, *Chromolaena odorata* and *Rhynchospora corymbosa*. They were collected along with the soil adhering to their roots. The rhizospheric soil from each plant root was separated gently to prevent damage and removal of roots. Electrical conductivity (EC) and pH of the soil samples (1:5 v/v) using a Eutech Instrument Cyberscan Pc 300 pH, conductivity/TDS/Temp meter. Concentrations of inorganics [macronutrients (P, K, Ca and Mg) and micronutrients (Fe, Mn Cu, Ni and Zn) as well as heavy metals (Pb, Cd, Cr and As), in soil and plant digests were determined using inductively coupled plasma emission spectrometry (ICP–OES, Thermo-Fisher, ICAP, 6300 series). Total C and S were determined using CHNS Analyzer Vario EL (Elemental Germany). Dissolved organic carbon (DOC) was determined using TOC Analyzer (TOC Vcph, Shimadzu, Japan). All analyses were carried out in triplicates. Heavy metals were determined in six operationally defined fractions; water soluble (F1), exchangeable (F2), carbonate bound (F3), Fe-Mn oxides bound (F4), organically bound (F5) and the residual form (F6). FTIR analysis was carried out for the identification of inorganic and organic functional

groups of different rhizopheric and non-rhizopheric soils collected from different metallophytes using FTIR Bruker Vertex 70. Potassium bromide (KBr) was used as standard.

## RESULTS and discussion

Results showed that non-rhizopheric soils (Topsoil and Subsoil) had the highest values of electrical conductivity (EC; 2660 and 5520  $\mu\text{s}$ ) and Pb concentrations (51390.0 and 64080.0 mg/kg) compared to rhizopheric/vegetated soils with EC that ranged from 276 $\mu\text{s}$  to 3160 $\mu\text{s}$  and Pb concentrations from 3289.0 to 44850.0 mg/kg (Table 1). Though, the pH was generally low (5.0 – 5.54) in all the soil samples but lower pH values were recorded for rhizopheric soils with *Eleucine indica* soil. Rhizopheric soils also had more nutrients, DOM and pronounced peaks of carbohydrates functional groups (C-O; 1100 -1000 and O-H; 3700 - 3600) compared to non-rhizopheric soils (Fig 1). The DOM in different rhizopheric soils however varied with the highest in the rhizosphere of *S. pyramidalis* though not statistically different from those of *E. indica*, *I. cylindrical* and *R. corymbosa* while the lowest was found in *C. dactylon* soil. Variations were also observed in the Pb fractions with the highest concentration in organic and residual fractions of rhizopheric and non-rhizopheric soils respectively. Lower concentration of Pb was however found in the soluble and exchangeable fractions of rhizopheric soils compared to non-rhizopheric soils. *Eleucine indica* accumulated the highest Pb concentrations both in the shoot (8030 mg/kg) and root (16380 mg/kg) followed by that of *G. celosoides* having 6800 and 4644mg/kg in shoot and root respectively while *C. odorata* which had the highest values of pH, P, Ca and Mg and lowest amount of Pb and EC in the rhizopheric soil. Reduction in EC coupled with nutrients and DOM availability in the rhizopheric soils increased Pb uptake by plants and in turn reduced total Pb concentration in the rhizopheric soils.

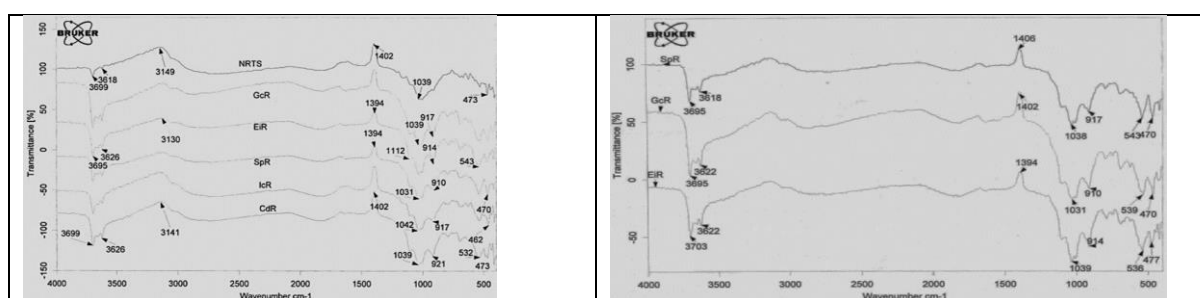


Fig 1. FTIR results showing different peaks in rhizopheric and non-rhizospheric soils

**Table 1. Physico-chemical parameters of rhizopheric and non rhizopheric soil samples from lead-acid battery wastes contaminated site**

Soil samples	pH	Ec $\mu\text{s}$	C (%)	S	Mg	Ca	Fe (mg/kg)	Mn	Ni	P
Top soil	5.5 <sup>a</sup>	5520.0 <sup>a</sup>	0.2 <sup>g</sup>	1.4 <sup>a</sup>	1143.0 <sup>b</sup>	718.6 <sup>c</sup>	25190.0 <sup>a</sup>	252.0 <sup>c</sup>	27.0 <sup>a</sup>	48.6 <sup>i</sup>
Ic soil	5.3 <sup>c</sup>	3160.0 <sup>b</sup>	0.2 <sup>g</sup>	0.1 <sup>b</sup>	820.9 <sup>f</sup>	451.1 <sup>i</sup>	22560.0 <sup>d</sup>	164.8 <sup>f</sup>	12.8 <sup>c</sup>	95.9 <sup>e</sup>
Cd soil	5.2 <sup>d</sup>	1349.0 <sup>d</sup>	0.3 <sup>f</sup>	0.1 <sup>b</sup>	1058.0 <sup>c</sup>	470.3 <sup>h</sup>	17790.0 <sup>g</sup>	77.9 <sup>e</sup>	9.3 <sup>e</sup>	71.3 <sup>g</sup>
Ei soil	5.0 <sup>e</sup>	630.0 <sup>f</sup>	0.4 <sup>e</sup>	0.0 <sup>c</sup>	1089.0 <sup>bc</sup>	494.9 <sup>g</sup>	25000.0 <sup>b</sup>	276.3 <sup>c</sup>	27.1 <sup>a</sup>	179.4 <sup>c</sup>
Gc soil	5.2 <sup>d</sup>	674.0 <sup>e</sup>	1.5 <sup>a</sup>	0.0 <sup>c</sup>	1461.0 <sup>a</sup>	736.0 <sup>b</sup>	24320.0 <sup>c</sup>	309.3 <sup>b</sup>	22.4 <sup>b</sup>	216.5 <sup>b</sup>
Sp soil	5.5 <sup>a</sup>	511.0 <sup>g</sup>	0.9 <sup>c</sup>	0.0 <sup>c</sup>	900.6 <sup>d</sup>	626.7 <sup>e</sup>	18670.0 <sup>f</sup>	207.7 <sup>d</sup>	10.6 <sup>de</sup>	113.1 <sup>d</sup>
Co soil	5.5 <sup>a</sup>	224.0 <sup>i</sup>	1.1 <sup>b</sup>	0.0 <sup>c</sup>	1491.0 <sup>a</sup>	1018.0 <sup>a</sup>	17170.0 <sup>h</sup>	390.7 <sup>a</sup>	5.6 <sup>f</sup>	345.0 <sup>a</sup>
Rc soil	5.2 <sup>d</sup>	276.0 <sup>h</sup>	0.8 <sup>d</sup>	0.0 <sup>c</sup>	959.8 <sup>d</sup>	535.5 <sup>f</sup>	22265.0 <sup>e</sup>	254.8 <sup>c</sup>	11.0 <sup>d</sup>	74.5 <sup>f</sup>
Subsoil	5.4 <sup>b</sup>	2660.0 <sup>c</sup>	0.3 <sup>f</sup>	0.1 <sup>b</sup>	859.8 <sup>e</sup>	638.9 <sup>d</sup>	16210.0 <sup>i</sup>	154.8 <sup>e</sup>	13.0 <sup>c</sup>	64.5 <sup>h</sup>

NB: Ic = *Imperata cylindrical*; Cd = *Cynodon dactylon*; Ei = *Eleucine indica*; Gc = *Gomphrena celosoides*; Sp = *Sporobolus pyramidalis*; Co = *Chromolaena odorata*; Rc = *Rhynchospora corymbosa*. The values are the means of three replicates and means followed by the same letter are not significantly different from each other at P<0.05 using Tukey and DMRT

## CONCLUSIONS

Significant differences were observed in the rhizopheric and non-rhizopheric soils from this contaminated site

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## **Pacific Food Systems**

### **Is interconnectedness of people to land, water, and culture**

Siosiu M Halavatau

*‘Tongan culture and traditions are deeply rooted in a philosophy of living in harmony with the environment, viewing the land and sea not as resources but as sacred, interconnected entities’.* HM King Tupou VI

#### **ABSTRACT**

Our lives in the Pacific Islands are results of interconnectedness of people, land (soil), water, and culture. In ecosystem science- these are ecosystem services provided by nature for benefits of human. They come in 4 categories: (i) Provisional services - these are products provided by nature like food, fibre, firewood, biodiversity, clean water, and even medicines; (ii) Regulatory services - benefits from moderation of natural processes like climate regulation; water purification; erosion control; pollination: and disease control; (iii) Cultural services - non-material benefits like recreation, ecotourism, aesthetic values, etc; and (iv) Supporting services- necessary for all services, like nutrient cycling, soil formation, photosynthesis, and habitat provisions for biodiversity.

Currently the ecosystem services demand is high and supply is threatened. Many times, the provisioning ecosystem services demand threatened the already declining supporting and regulatory services

Because of this plus farmers and technicians looking at issues as isolated entities but not interconnected, we are now seeing results of these as ecosystem disservices like habitat losses because of inappropriate land uses and overuse of pesticides removing natural enemies resulting in pest outbreaks.

The demand on supply services has resulted in downward spiral of soil productivity. Underpinning this downward spiral is soil organic carbon degradation and the high P-fixing capacity of the mostly volcanic ash soils of the islands. These are directly linked to the variable charge nature of these soils.

Our connectedness to land, soil, water and culture must determine our strategies. The multidimensional ways people see and understand ecosystems must be taken onboard: intrinsic, instrumental, and relational values of natural environment. To make an impact we need to integrate our indigenous and reductionist modern knowledge in developing appropriate technologies to address the problems in our food systems.

## **AI-DRIVEN HYPOTHESES FOR ADVANCING CARBON STABILISATION IN VARIABLE CHARGE TROPICAL SOILS**

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### **INTRODUCTION**

Variable charge soils occupy large areas of the tropics and subtropics and play a central role in the global carbon cycle. However, the mechanisms governing carbon stabilisation in these systems remain less well understood than in temperate soils. Current evidence suggests that the stabilisation of soil organic carbon (SOC) is strongly controlled by its association with mineral surfaces, with soil pH exerting major influence on the formation of mineral–organic interactions. Despite this, the relative importance of different stabilisation pathways in tropical environments is still debated, and opportunities for management to enhance carbon sequestration remain underexplored.

To address these knowledge gaps, this contribution uses artificial intelligence to generate a series of novel research hypotheses informed by soil science, biogeochemistry, microbiology and complex systems thinking (Minasny et al., 2025). These hypotheses highlight the need to move beyond examining individual mineral effects in isolation. Instead, they emphasise the synergistic and antagonistic relationships among iron oxides, aluminium oxides and clays that jointly determine SOC persistence in variable charge soils.

### **METHODS**

AI-assisted hypothesis development involved an iterative process integrating literature mining, pattern detection and conceptual modelling. The resulting hypotheses were reviewed and refined to align with known mineralogical, microbiological and physicochemical processes relevant to tropical soils.

This study also incorporated methodological advances in digital soil mapping, including the fusion of digital soil mapping, remote sensing, spectroscopy and machine-learning prediction.

### **RESULTS and discussion**

The AI-assisted analysis generated several novel hypotheses that together propose new mechanisms and intervention pathways for enhancing carbon sequestration in variable charge soils. Some of the include

(a) Synergistic mineral controls on SOC

Interactions among iron oxides, aluminium oxides and kaolinite are hypothesised to exert stronger control on carbon stabilisation than individual mineral concentrations alone (Jia et al., 2024).

#### (b) Bio-engineered mineral weathering pathways

Selectively assembled microbial consortia may accelerate the weathering of primary minerals and promote the formation of reactive Fe and Al oxides. This increase in mineral surface area could improve SOC stabilisation.

#### (c) Depth-stratified sequestration management

Different minerals dominate SOC stabilisation at different depths. Management tailored to horizon-specific mineral assemblages may therefore maximise total sequestration. Surface layers may benefit from amendments promoting poorly crystalline Fe oxides, whereas deeper horizons may require practices enhancing organic matter interaction with kaolinite- and hematite-rich subsoils.

#### (e) Land-use optimisation guided by mineral mapping

Spatial patterns of minerals such as goethite, gibbsite, kaolinite and hematite may serve as a basis for allocating land uses that maximise carbon storage. Areas with mineralogical profiles linked to high sequestration potential could be prioritised for agroforestry or pasture-forest mosaics.

In parallel, digital soil mapping methodologies offer practical pathways for identifying where these interventions would be most effective. Digital soil mapping, remote sensing, Vis–NIR spectroscopy and machine-learning models can be combined to predict mineral abundance and carbon sequestration potential, as demonstrated by Rodríguez-Albarracín et al. (2023). This integrated framework provides a scalable approach for prioritising zones for soil carbon enhancement across complex tropical landscapes.

## CONCLUSIONS

The AI-derived hypotheses highlight new pathways for advancing understanding of SOC stabilisation in variable charge tropical soils. They emphasise the need to consider multi-mineral interactions, depth-dependent processes and engineered biological approaches. Integrating these hypotheses with large-scale mapping technologies provides a promising framework for identifying carbon sequestration opportunities across tropical landscapes. The study by Rodríguez-Albarracín et al. (2023), which combines Vis–NIR spectroscopy, carbon saturation modelling and machine learning to map mineral abundance and sequestration potential in Brazil, illustrates the practical feasibility of this approach.

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# MINERALS AND MANAGEMENT: NOVEL INSIGHTS INTO VARIABLE CHARGE SOIL ORGANIC MATTER FRACTIONS ACROSS PACIFIC ISLAND LANDSCAPES

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## INTRODUCTION

The basaltic and volcanic ash-influenced soils of Hawai'i serve as an excellent model system for examining soil processes in variable-charge environments. Pacific Island landscapes span steep gradients in topography and rainfall and encompass a continuum of soil-forming conditions, resulting in a wide diversity of soils with distinct physicochemical properties. These interacting soil-forming factors create a valuable context for examining how mineral composition, soil organic matter, and soil moisture regimes shape soil behavior. Andisols and Oxisols, two soil orders representing opposite ends of the soil development spectrum, exhibit contrasting inherent properties. The study of these soils offers insight into how variable-charge minerals govern aggregation, carbon stabilization, and nutrient-contaminant interactions. Understanding these processes is fundamental to assessing soil resilience, productivity, and vulnerability under changing land use and climate regimes.

### Soil Order Characteristics

Hawaiian Andisols, geologically young soils derived from volcanic tephra, contain high concentrations of amorphous mineral phases such as allophane, imogolite, and ferrihydrite, that exhibit high specific surface area and reactivity. These minerals impart pH-dependent charge and are intimately associated with organic matter. Andisols contain up to 25% organic carbon, have low bulk density, and high phosphate retention. In contrast, the highly weathered Oxisols of the older main islands contain appreciable concentrations of kaolins and metal (hydr)oxides, resulting in low effective cation exchange capacity. Despite their contrasting stages in development, both soil orders share a key feature: the presence of pH-dependent surface charge.

### Soil Aggregation and Physical Behavior

In these variable charge soils, the balance of charges among organic matter, oxides, and clay minerals, combined with pronounced wetting and drying cycles, promote unique flocculation processes. As a result, soils rich in pedogenic oxides and/or poorly- and non-crystalline minerals contain stable aggregates that resist standard dispersion methods. These aggregates, sometimes referred to as "pseudo-sands", enhance macroporosity in finely textured soils and physically protect soil organic carbon. Carbon is a central

component of soil organic matter, which plays a key role in regulating soil structure. As a result, it influences water movement and retention, as well as the transport of nutrients and contaminants.

## METHODS

Our ongoing work investigates how land use and weathering intensity (i.e., soil moisture regime) influence dynamic soil health properties and soil organic matter fractions in Hawaiian Andisols and Oxisols. Sites included croplands, pastures, and forests in both Ustic (seasonally dry) and Udic/Perudic (humid) moisture regimes. We measured a suite of soil health indicators including bulk density, total organic carbon, pH, and microbial respiration and applied size and density fractionation to isolate light-particulate (LPOM;  $< 1.85 \text{ g/cm}^3$ ), coarse-heavy associated (CHAOM;  $> 1.85 \text{ g/cm}^3$  &  $> 53 \text{ }\mu\text{m}$ ), and mineral-associated organic matter (MAOM;  $> 1.85 \text{ g/cm}^3$  &  $< 53 \text{ }\mu\text{m}$ ).

## RESULTS and DISCUSSION

Soil health properties varied substantially by soil order, land use, and moisture regime. Bulk density was highest in croplands compared to forests and pastures, with Andisols ( $0.59 \pm 0.05 \text{ g/cm}^3$ ) consistently lower than Oxisols ( $0.94 \pm 0.03 \text{ g/cm}^3$ ) due to their high amorphous mineral and organic matter content. Total organic carbon was generally lowest in croplands and highest in forests, except in Ustic Andisols (Ustands), where pastures had the highest carbon content ( $p < 0.05$ ).

The CHAOM fraction typically represents a small portion of C content ( $< 5\%$ ) in temperate soils but contained up to 35% of total organic carbon in Hawaiian Andisols. This substantial contribution to the soil carbon balance suggests that stable micro- and macroaggregates were isolated within CHAOM, indicating its importance as a carbon reservoir in variable charge soils. Across moisture regimes, Andisol CHAOM-carbon was consistently higher in pastures compared to forests and croplands, highlighting the role of management in maintaining aggregate stability. Preliminary analyses of Oxisols revealed similar trends, with pastures storing more CHAOM-carbon than forests and croplands, particularly in humid Perox and Udox environments.

## CONCLUSIONS

The insights emerging from this study have important implications for soil conservation, climate mitigation, and agricultural resilience across Pacific Island systems and other volcanic regions. Our analysis demonstrates that variable charge soils in Hawai'i exhibit distinct carbon stabilization pathways shaped by mineralogical composition, moisture regime, and land use. The strong influence of land management on CHAOM-carbon underscores how management decisions interact with inherent mineralogical traits to promote aggregate stability and physically protect soil carbon. Together, these findings provide a mechanistic foundation for informing soil stewardship and guiding land management in volcanic island environments.

# UNDERSTANDING BRAZILIAN SOILS WITH VARIABLE CHARGE: HISTORY AND DEVELOPMENT OF SUSTAINABLE TECHNOLOGIES TO ENSURE FOOD SECURITY

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## INTRODUCTION

Brazilian soils are predominantly highly weathered and composed of low-activity clays. The main soil groups are Ferralsols and Acrisols, followed by Plinthosols, Lixisols, and Nitisols. Until the mid-20<sup>th</sup> century, Brazil relied on food imports. However, it overcame the challenges of variable-charge soils – once considered to have low agricultural potential – and became a leading example of science-based technological development. By adapting cropping systems to local soils and tropical climate conditions, the country became one of the world's top five food producers. Much of this output comes from the Cerrado biome, where the so-called "Cerrado revolution" transformed extensive areas of variable-charge, naturally low-fertility soils into an agricultural powerhouse. Sound agricultural decisions depend on robust soil knowledge. This paper reviews the history and technological advances that have supported food production in Brazil.

## METHODS

This review, based on the technical and scientific literature, highlights the main technologies that enabled food production on variable-charge soils in Brazil. The text does not claim to be comprehensive but aims to highlight advances in agriculture and challenges.

## RESULTS and discussion

### History

Many pioneers helped establish Brazil as a leading agricultural powerhouse, including Ana Primavesi, who advanced a holistic, systemic view of agriculture through agroecology; Bernardo Van Raij, whose research revolutionized understanding of the electrochemical properties of Brazilian soils; Alfredo S. Lopes, a pioneer in soil fertility surveys that enabled accurate nutritional diagnoses and fertilization recommendations for *Cerrado* soils; Djalma M. G. Sousa, whose work focused on correcting soil acidity and improving phosphate fertilization in *Cerrado* soils; Johanna Döbereiner, whose research focused on biological nitrogen fixation; and Marcelo N. Camargo and Paulo T. K. Jacomine, whose contributions to soil survey and classification led to the development of the Brazilian Soil Classification System. The legacy of these and other scientists (see the Brazilian Society of Soil Science – SBCS) has strengthened many postgraduate programs in the country (USP/Esalq, UFV, UFLA, UFRGS, UFRRJ,

UFMS, UFRPE) and supported the development of public policies and territorial management systems. Founded in 1947, SBCS is one of the oldest scientific societies in Brazil.

### **Development**

Decades of research and investment in technology, proper soil management, soil acidity correction, rational fertilizer use, and plant breeding, together with innovative strategies such as biological nitrogen fixation (BNF) in legumes, have made Brazil an important player in global food security, as recognized by organizations such as the UN/FAO. These advances have been driven by institutions such as the Agronomic Institute of Campinas (IAC), EMBRAPA, state research organizations, and universities. In the 1990s, management systems based on conservation agriculture (CA) became widespread in southern Brazil. No-till farming, a conservation practice originating in England and the USA, was adapted and scaled up, evolving into a comprehensive management system. The no-till farming system (Sistema Plantio Direto, SPD) has become a widely disseminated Brazilian concept and the basis for Conservation and Regenerative Agriculture in the country. Integrated Crop-Livestock-Forestry systems (ILPF, ILP, and IPF), which combine different production components in the same area, offer another strategy to maximize productivity, reduce risks, conserve water, soil, and biodiversity, and enhance resilience to climate change. At the same time, agroecology and organic agriculture have gained ground, especially among small producers, and are closely linked to markets that value nutritional quality and sustainability.

### **Challenges**

Agriculture in the Brazilian Cerrado has advanced substantially thanks to scientific knowledge and technologies developed since the first soil fertility surveys in the region in the mid-1970s (Lopes & Guilherme, 2016). However, livestock farming remains predominant in this biome, and much pastureland is degraded by compaction and erosion, resulting in low productivity. To address this problem, the government launched the National Program for the Conversion of Degraded Pastures into Sustainable Agricultural and Forestry Production Systems, a key initiative to conserve biodiversity, reduce deforestation, and meet environmental commitments (ABC+ Plan, Green Path, Brazilian Government). Brazil spans about 8.5 million km<sup>2</sup> and includes several biomes (Amazon, Caatinga, Cerrado, Atlantic Forest, Pampa, and Pantanal), for which detailed information on soil properties and distribution remains limited. Closing this gap requires a better understanding of soil–landscape relationships, multidisciplinary training for soil scientists (*e.g.*, digital soil mapping, pedometrics, and remote sensing), and expanded information in national soil databases. Essential initiatives in this context include the Brazilian Soil Spectral Library and the Soil Spectral Service (BraSpecS) (Demattê et al., 2019, 2022). Territorial planning and management depend on accurate knowledge of soil distribution. Micro-watershed-scale surveys are essential to support land-use policies, mitigate the impacts of environmental disasters (such as droughts, floods, and fires), and prepare the country to face climate extremes. Without this knowledge, the capacity for prevention and adaptation is compromised. Detailed soil surveys are therefore crucial for agricultural planning and management, as well as for ecosystem conservation (Demattê et al., 2022).

## **CONCLUSIONS**

Key technologies and practices adapted to Brazilian soils include: i) soil acidity correction through liming and phosphogypsum use; ii) build-up and maintenance fertilization following the 4R nutrient stewardship framework; iii) no-till farming; iv) biological nitrogen fixation; v) integrated crop-livestock-forestry systems; vi) adapted, resilient, high-yielding crop varieties and cultivars for acidic soils; vii) biofertilizers and regenerative agriculture; and viii) double- and triple-cropping in the same area within a year, maximizing land-use efficiency and significantly increasing food production. Despite remarkable progress, Brazilian agriculture faces regional inequalities in agrarian structure and biome characteristics, which can be

addressed only through soil surveys and public policies that advance sustainable soil management and prevent adverse environmental impacts from deforestation and wildfire practices.

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**SAFEGUARDING VARIABLE CHARGE SOILS IN WEST AFRICA:  
ADDRESSING PESTICIDE POLLUTION THROUGH MANAGEMENT,  
MONITORING AND CAPACITY BUILDING**

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Food and Agriculture Organisation of the United Nations

**Abstract Pending**

# Spatial Distribution and Stewardship-Oriented Management of Phosphorus in Long-Term Phosphate-Fertilized Soils of Bangladesh

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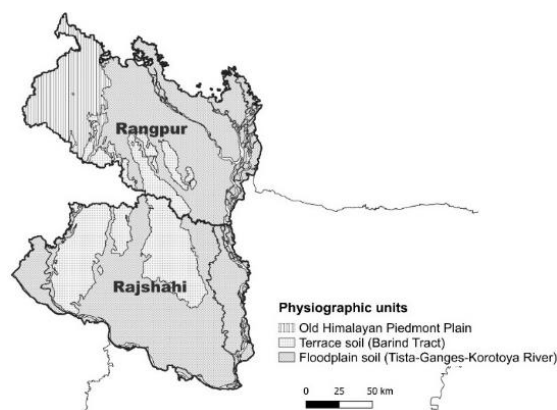
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## INTRODUCTION

Degradation of natural soil fertility due to imbalance fertilizer application is a major concern in the intensively cropped soils of Bangladesh. The apparent balance of phosphorus (P) in Bangladesh soils is estimated to be near zero (Hasan et al., 2020). Hence, efficient P management in the farm soils is a key step in crop production, to avoid irrational applications that may enhance environmental risk. A collaborative research program was adopted in Bangladesh funded by OCP via the leadership of crcCARE, Australia to formulate strategies to enhance P use efficiency and promote soil health. As a part of the program, this paper discussed the distribution of P in the North western region of the country as it was affected by various soil factors.

### **Database Preparation on Soil Phosphorus and Other Nutrients**

Initially, the project aimed at generating database on soil nutrient status in the agricultural soils of Bangladesh. To accomplish the objective, nutrient and other edaphic data were recorded with the help of the Land and Soil Resources Utilization Guides prepared by the Soil Resources Development Institute (SRDI), Bangladesh. The database included detail information of 1142 farm soils across the north west part of the country, namely, Rajshahi and Rangpur Divisions. The study area included i) Recent Floodplain soils of the Tista, Ganges and Karotoya Rivers, ii) highly weathered Pliocene Terrace soil (Barind Tract), and iii) the Old Himalayan Piedmont Plain (Fig. 1). Data were analyzed statistically to compare the means of the soil properties.



**Fig. 1. Location of the study area in Rajshahi and Rangpur Divison, Bangladesh.**

### **Status of Phosphorus and Soil Properties in the North-west Bangladesh**

The highly weathered Terrace soil and the Piedmont Plain soils showed strongly acidic to slightly alkaline pH (3.6 - 7.9), while the pH of many Floodplain soils was strongly alkaline (8.9) probably due to the presence of calcareous materials in the Floodplain soils (Table 1). The average soil organic carbon (SOC) and available P contents were higher in the Piedmont Plain soils, which indicates that organic-P was the main P contributor in this soil as evidenced by Egashira et al. (2003). Conversely, the contents of SOC and P were markedly lower in Terrace soil, while the range of DTPA iron (Fe) (6 - 623 mg/kg) was much higher (Table 1).

**Table 1. Mean soil nutrients in the Physiographic units of North-west Bangladesh.**

Soil parameters		Terrace soil (n=256)	Floodplain soil (n=741)	Piedmont Plain soil (n=143)
Soil pH	Mean	5.58	5.95	5.10
	Range	4.40-7.90	3.90-8.98	3.63-6.68
SOC (%)	Mean	1.02	1.06	1.19
	Range	0.34-2.15	0.10-2.43	0.36-2.40
Available P (mg/kg)	Mean	15.48	18.44	22.31
	Range	1.0-80.2	1.02-84.5	3.72-79.5
Exch. Calcium (Ca) (meq/100g)	Mean	4.25	7.09	2.68
	Range	0.16-18.9	0.16-60.6	0.12-13.8
DTPA iron (Fe) (mg/kg)	Mean	146	113	165
	Range	6.32-623.0	1.00 - 498.3	1.21- 571.0

The low P content in the Terrace soils has been attributed to high P fixation, strong acidity, low SOC and cation exchange capacity, and intense leaching (Hussain, 1998). P sorption is stronger in the highly weathered soils by the oxides having variable charge (Wang et al., 2009). The larger content of exchangeable Ca implies increased P-fixation by Ca-bearing minerals in the Floodplain soils. However, very high upper limits of soil P (79-84 mg/kg) in the studied soils were alarming and indicated risk of groundwater contamination. A high level of soil P depicts the rapid escalation in P fertilizer application in recent years (IFA, 2025). Major interventions are crucial for the rational use of P fertilizers in crops for sustaining soil health.

## 4 R Stewardship

A central outcome of the project is the translation of spatial phosphorus information into actionable nutrient management guidance under the 4R nutrient stewardship framework—applying the right fertilizer source, at the right rate, at the right time and in the right place. By aligning fertilizer practices with soil-specific P retention and release behaviour, the project aims to improve P use efficiency, reduce excessive fertilizer application, minimise P losses to surface and groundwater, and lower the environmental and climate footprint associated with fertilizer production and use.

## CONCLUSIONS

Soil P in the North west Bangladesh is affected by variable environmental factors. The project provides a scientific basis for developing soil-specific fertilizer recommendations, standard operating procedures for P assessment, and national guidelines to support sustainable intensification of agriculture in Bangladesh. The outcomes will benefit farmers, extension agencies and policymakers by enhancing crop productivity, maintaining soil health, reducing environmental risks and contributing to long-term food security in one of the world's most densely populated agrarian systems.

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# SOIL CHARGE VARIABILITY AND AGRICULTURAL FERTILITY RESPONSES IN A TROPICAL ENVIRONMENT: THE CASE OF GUINEA-BISSAU

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## INTRODUCTION

In Guinea-Bissau, agriculture has developed on tropical soils with variable charge, where each plot seemed to have a will of its own sometimes generous, sometimes stingy in nutrient delivery. These soils, typically poor in organic matter (often below 2%), with limited cation exchange capacity and prone to leaching, have conditioned the availability of essential elements for crops, presenting a true test of persistence for local farmers (Uehara and Gillman, 1981; Sanchez, 2019). In low-input contexts, edaphic instability has manifested as a silent yet relentless obstacle to productivity and the sustainability of agricultural systems.

## METHODS

This study adopted a technical-analytical approach, combining field observations conducted across various agroecological zones with analysis of secondary data from regional edaphic studies and scientific literature on variable-charge soils in tropical climates. Parameters evaluated included soil texture, pH, organic matter content, adopted management practices, and crop responses, following methodologies widely described for highly weathered soils (Sanchez, 2019; Brady and Weil, 2017). This approach sought to give voice to the land, understanding its behavior and how it shapes productivity.

## RESULTS AND DISCUSSION

Results revealed significant variations in soil pH, ranging from 4.5 to 6.2, directly influencing the surface charge of colloids and the availability of nutrients such as calcium, magnesium, and phosphorus reflecting the delicate balance that sustains plant life (Uehara and Gillman, 1981). Plots with organic matter content above 2.5% exhibited a 20–35% increase in nutrient retention capacity, as if the soil had regained its generosity, confirming patterns observed in other tropical systems (Brady and Weil, 2017).

Mineral fertilization proved irregular, with nitrogen losses exceeding 40% in bare soils during the rainy season, demonstrating the vulnerability of systems lacking vegetative cover. In contrast, plots combining organic fertilization with conservation practices recorded productivity gains of 15–30%, confirming the role of organic matter as a true guardian of fertility in variable-charge soils (Sanchez, 2019).

## **CONCLUSIONS**

Soil charge variability has emerged as a crucial determinant of productive instability in Guinea-Bissau, reminding us that the land does not always yield without effort. Integrated soil fertility management strategies increasing organic matter content, adapting fertilization to local conditions, and adopting conservation practices have proven essential to mitigate nutrient losses and strengthen productive resilience, in line with evidence from other tropical soils (Uehara and Gillman, 1981; Sanchez, 2019).

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## **AN EUROPEAN PERSPECTIVE OF SUSTAINABLE SOIL MANAGEMENT WHEN DEALING WITH VARIABLE CHARGE SOILS**

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### **INTRODUCTION**

Despite variable charge soils are most common in tropical and subtropical regions, they are also present in Europe, particularly in soils developed on volcanic material and some in less weathered areas. These soils are characterized by a high content of iron and aluminium oxides, as well as organic matter, which gives them their variable charge property. Examples include subtypes of Andisols (derived from volcanic ash), Spodosols, Histosols, Alfisols and Ultisols, that may exhibit variable charge properties due to their mineralogy. Spodosols are found throughout northern Europe, especially in Scandinavia, they are acidic, sandy and have lower fertility (Gustafsson et al., 1995). Their variable charge is primarily caused by large amounts of organic matter, iron (Fe), and aluminium (Al) oxides that have leached from the upper horizons and accumulated in deeper layers. Andisols occur in European volcanic areas such as Iceland and parts of southern Europe (McDaniel et al., 2012). Their variable charge comes from the presence of minerals like allophane and imogolite. A significant portion of European soils have pH values below 5.5 and are considered acidic (Soil Atlas of Europe, 2005). These are common in northern and central Europe, particularly on parent material like granites and sandstones. In these soils, the variable charge is influenced by the surface hydroxyl groups of phyllosilicates (e.g., kaolinite) and oxides of iron and aluminium. Histosols contain a high percentage of organic material that develops a pH-dependent charge from its carboxyl, phenolic, and amino functional groups. Histosols can be found in peatlands and bogs throughout Europe, but mostly in the Northern latitudes. Younger soils such as Inceptisols that are widely spread in the continent represent less-weathered soils that can exhibit too variable charge characteristics.

### **METHODS**

Studying variable charge soils involves a combination of laboratory and theoretical methods to understand the pH-dependent nature of their surface charge. These methods are crucial for accurately characterizing soil properties, predicting nutrient and pollutant behavior, and developing effective management strategies. In Europe, the history of research on variable charge soils was intertwined with the broader development of soil science, but it was historically overshadowed by the study of soils with permanent charges, which dominate the temperate climate zones where early research was concentrated. The recognition and specific study of variable charge properties in European soils emerged later as soil science became more nuanced and global in its scope.

## RESULTS AND DISCUSSION

The management of variable charge soils in Europe is complex due to the pH-dependent nature of their surface charge. These soils can have a low cation exchange capacity (CEC) at low pH, leading to aluminum toxicity and nutrient leaching. However, they can also develop an anion exchange capacity (AEC) under acidic conditions, allowing them to retain anions like nitrates and sulfates. Effective management strategies focus on adjusting soil pH, increasing organic matter content, and carefully managing nutrient applications (Rowell, 2008; Van Ranst et al., 2017).

**Adjusting soil pH:** As the surface charge is highly dependent on pH, managing the soil's pH is a primary strategy for addressing nutrient availability and toxicity issues.

*Liming:* The most common practice for acidic soils is the application of lime (calcium carbonate) to increase soil pH. Raising the pH increases the soil's CEC, improves its capacity to retain base cations like calcium ( $Ca^{2+}$ ), magnesium ( $Mg^{2+}$ ), and potassium ( $K^+$ ). Liming also reduces the availability of toxic aluminum ( $Al^{3+}$ ) and manganese ( $Mn^{2+}$ ).

*Fertilizer selection:* Using nitrogen fertilizers that leave a less acidifying residue can help stabilize soil pH. However, the overuse of certain nitrogen fertilizers can accelerate soil acidification.

**Increasing soil organic matter:** Organic matter has a high variable charge and plays a crucial role in buffering soil pH and improving nutrient retention.

*Manure and compost:* Applying organic materials like manure and compost increases the overall cation exchange capacity of the soil, improving its ability to hold onto nutrients. This is especially important for soils with very low CEC due to low clay content, such as Spodosols.

*Cover crops:* Planting cover crops can protect the soil from erosion, increase soil organic matter, and improve soil structure.

*Conservation tillage:* Practices that minimize soil disturbance, such as conservation tillage, help to preserve and increase soil organic matter.

**Nutrient and water management:** Careful management of nutrients and water is essential to optimize soil fertility and minimize environmental impact in variable charge soils.

*Fertilizer efficiency:* By adjusting the soil pH, farmers can increase the efficiency of applied fertilizers. Soil testing, which includes measuring buffer pH, helps determine the appropriate liming and fertilizer rates needed to reach the desired pH level.

*Nutrient dynamics:* In highly weathered soils with a positive net charge in the subsoil, the ability to retain anions like nitrates ( $NO_3^-$ ) and sulfates ( $SO_4^{2-}$ ) is enhanced. This can influence the timing and rate of fertilizer applications to reduce nutrient leaching.

*Water management:* Practices that help regulate soil water, such as improving drainage or increasing water infiltration, can influence the movement of ions and the potential for landslides in susceptible variable charge soils.

## CONCLUSIONS

The European Union's agricultural and environmental strategies promote broader sustainable practices that benefit variable charge soils.

- **EU Soil Strategy for 2030:** This initiative aims to promote sustainable soil management through various actions, including free soil testing, restoring peatlands, and developing a "soil passport" to track soil health.
- **Agri-environment-climate commitments (AECMs):** Under EU rural development programs, farmers receive support for voluntarily adopting environmentally friendly practices that protect soil health and prevent degradation.
- **Conservation tillage and cover crops:** These practices, often encouraged by EU policies, enhance soil structure, increase organic matter, and reduce erosion, which are all beneficial for managing variable charge soils.
- **Soil Monitoring and Resilience Law** approved by the European Parliament in October 2025. This is one of the most important pieces of legislation to protect and manage sustainably the European soils.

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## STATUS OF ENVIRONMENTAL CONTAMINATION IN NIGERIA

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### INTRODUCTION

Nigeria is one of the countries in the western part of Africa. It is the most populated African nation with about 200 million people of diverse ethnicity, cultures and religions. It covers land area of about 923,770 km<sup>2</sup> and is positioned between 4° and 14°, latitude, North of the Equator, and amid longitudes 2° 2' and 14° 30' East of the Greenwich Meridian. It is bordered/bounded by the Republics of Niger and Chad to the north, the Atlantic Ocean to the south, the Republic of Cameroon to the east, and the Republic of Benin to the west (Hasan, 2016). Nigeria is made up of 36 states including Federal Capital Territory which is the seat of Government. It is blessed with abundant natural resources such as petroleum and natural gas which account for over 90% of her export revenue (Shittu, 2017). The oil exploration, production, transportation and refinement in Nigeria however, contribute greatly to various environmental and ecological problems facing the country most especially in the Niger Delta region of Nigeria. These result from oil spillage and gas flaring. Apart from oil exploration, environmental degradation in Nigeria could also be linked with improper waste disposal, uncontrolled/unguided mining and industrial activities. Perfect examples are the illegal mining activities in Zamfara State of Nigeria and improper disposal of lead acid battery wastes in Ibadan. Unfortunately, enforcement of environmental regulations is still very poor in Nigeria as industries continue to discharge untreated wastes into the environment.

### TYPES, SOURCES AND EXTENT OF ENVIRONMENTAL POLLUTION IN NIGERIA

The major source of land and water contamination in Nigeria is oil. As reported by the Nigerian National Oil Spill Detection and Response Agency (NOSDRA), about 1,150 oil spill sites were abandoned by oil companies within the Niger delta in the beginning of 2008. The Nigerian National Petroleum Corporation places the quantity of petroleum jettisoned into the environment yearly at 2,300 cubic meters with an average of 300 individual spills annually (Adelana et al., 2011). United Nations Development Program and Shell Petroleum Company also listed some spillage incidents from the period of 1979 to 2004 in the Niger delta (UNDP, 2006). Oil spillage releases hydrocarbon and heavy metals into the environment and as a result of oil pollution, an estimated 5 to 10% of Nigerian mangrove ecosystems have been wiped out while, rainforest which previously occupied some 7,400 km<sup>2</sup> of land has disappeared (Adelana et al., 2011). Agricultural productivities are also affected through contamination of the groundwater and soils. Though, mining in Nigeria is still in developmental stage but artisanal mining and processing of gold in small scale is taking place in some states such as Oyo, Osun,

Kebbi, Zamfara and Plateau etc. The activity has also resulted in pollution of the environment. For instance, illegal mining activities in Zamfara, northern Nigeria was reported to have resulted in lead contamination of the environment with Pb concentration as high as 60,000 mg/kg killing hundreds of people mostly children in 2010 in the villages and compounds where gold ore that contains Pb as an impurity are processed (JEU, 2010; NNP 2011). This has also resulted in contamination of farmlands and various water sources in the affected villages.

Industrial and municipal wastes are other sources of pollution in Nigeria. The improper disposal and ineffective management of municipal and industrial wastes create major environmental and aesthetic challenges in most of Nigeria's urban areas through unguided urbanization and industrialization. This emanated from lack of appropriate environmental protection policies to guide indiscriminate siting of industries, waste treatment and disposal. Typical examples are as found in Ibadan Metropolis, Oyo State, Nigeria where several hectares of agricultural land in about five villages (Lalupon, Kumapayi, Erunmu, Ile-igbon and Olodo) were contaminated with high levels of heavy metals as a result of indiscriminate disposal of lead-acid battery wastes (Adejumo *et al.*, 2011). These culminated in the degradation of the environment and devastating ecological and human disasters.

### ***Environmental policies in Nigeria and the roles of Government***

As a result of different issues of environmental pollution, the need to combine industrial development with environmental protection arose. Environmental laws, were enacted and environmental enforcement programmes developed through establishment of Ministries of environments and agencies both at the national and state levels. National Environmental Standards and Regulation Enforcement Agency (NESREA) was established to curb the menace of environmental pollution both at the state and federal levels. For quick intervention, ecological funds is made available by the Government to help in attending to different environmental issues. There are different policies also put in place by the Ministry of Environment on the industrial wastes and effluent control. These include: Polluter pay policy, industrial compliance policy on waste treatment and disposal. Other efforts being made by government and non-government organizations within and outside the country to curb environmental pollution in Nigeria, include, the international interventions on Zamfara and Niger delta cleanup program. Medicins Sans Frontiers (MSF) in collaboration with the Zamfara State Ministry of Health (ZMoH) helped in the medical treatment of affected patients while restoration of lead contaminated soil is still ongoing by Zamfara State Ministry of Environment and Solid Minerals (ZMoE) in collaboration with Blacksmith Institute (BI) of New York and another US firm, TerraGraphics Environmental Engineering (TG). To reduce the rate of oil incidents along the Nigerian Coast particularly as a result of vandalisation, the Federal Government through an act of the National Assembly created the Niger Delta Development Commission (NDDC) and other agencies such as: Department of Petroleum Resources (DPR), National Maritime Authority, National Oil Spill Detection and Response Agency (NOSDRA). Scientifically, the use of biological remediation has

also been implemented to restore contaminated soil and water (Adejumo et al., 2011). Recently, in conjunction with UNEP and Shell, Nigerian Government is embarking on a full and total cleanup project of ogoniland which is being projected to last for 30 years.

## CONCLUSIONS

Environmental contamination in Nigeria arises mainly from oil exploration, mining and industrial activities. Many hectares of land have been degraded and unproductive. Available remediation strategies being employed are expensive and not environment friendly. There must therefore be a sustainable method of remediation, awareness creation, policy enactment and enforcement.

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## **Dynamic nature of variable charge soils as related to ions adsorption and nutrients cycling**

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### **INTRODUCTION**

In humid, subtropical and tropical regions of the world, soils are developed under intensive weathering as a result of high temperatures, intensive rainfall and leaching conditions. The clay fraction mineralogy of the soils at the advanced stage of weathering is usually dominated by kaolinite, gibbsite, goethite, hematite (Qafoku et al., 2004). These soils carry positive and negative charges on their surfaces. The magnitude and sign of the variable charge change with the aqueous phase pH and ionic strength (Yu, 1997). Therefore, they are termed “variable charge soils (VCS)”. Due to the differences in clay mineral composition and surface charge properties between permanent and variable charge soils, both cations and anions can get adsorbed on the surfaces of VCS (Yu, 1997; Qafoku et al., 2004). Changes in surface charge will affect the adsorption of cations and anions by VCS, and thus nutrients cycling and their bioavailability.

### **DEVELOPMENT OF VARIABLE CHARGE PROPERTIES**

The amount of positive charge increases with decreasing soil pH, while soil negative charge change oppositely in VCS. The mineral constituents and thus surface charge of the soils in tropical and subtropical regions change with soil development. Soil samples of three profiles derived from the basalts of 10, 1330 and 2290 kilo annum (ka) in age were collected from Hainan Province, China. In a young soil derived from 10-ka-basalt, the dominant clay minerals were smectite, halloysite and mixed-layer clay minerals of kaolinite and smectite. The clay minerals in the two older soils derived from 1330 and 2290 ka-basalt were dominated by kaolinite, halloysite and gibbsite. The subsoil cation exchange capacity (CEC) decreased from 18.6 cmol<sub>c</sub>/kg for the 10-ka soil to 9.3 cmol<sub>c</sub>/kg for the 1330-ka soil and 5.4 cmol<sub>c</sub>/kg for the 2290-ka soil. As the degree of soil development increases, the number of negative charges on the soil surface decreases, and the ability to absorb cationic nutrients weakens, leading to the easy leaching loss of these nutrients from the soils.

### **INTERACTION BETWEEN OPPOSITELY CHARGED PARTICLES**

#### **Interaction between Fe/Al oxides and phyllosilicates**

Positively charged Fe/Al oxides and negatively charged phyllosilicate co-exist in VCS. The overlapping of diffuse layers on these oppositely charged particles is believed to occur when VCS is subjected to strong leaching, resulting in leaching loss of counter ions from the diffusion layers, which is confirmed by a series of simulating experiments. When VCS of Ultisols and Oxisols are electro-dialyzed, the cations and anions are removed from soil surfaces in the electric field, and the overlapping of the diffuse layers on oppositely charged particles in the soils is promoted, which leads to a decrease of soil effective CEC due to charge neutralization. Overlapping of diffusion layers is a reversible process. The overlapping process of diffusion layers will accelerate the leaching loss of nutrient ions. After the overlapping of diffusion layers occurs, when fertilization increases the concentration of nutrient ions in soil solution, the salt adsorption will occur in the soils. Although the fertility of VCS is generally low, fertilization can

easily improve the nutrient status of the soils. The interaction between oppositely charged particles will increase the stability of soil aggregates, which is beneficial for the ecological function of microorganisms.

### **Interaction between variable charge soils and bacteria**

Bacteria are a type of biological colloids with a net negative charge and abundant functional groups on their surfaces. The adhesion of bacteria to VCS involves two mechanisms: electrostatic interactions and the formation of surface chemical bonds. The adhesion of bacteria can increase negative charge of VCS and thus the retention of cationic nutrients such  $K^+$ ,  $Mg^{2+}$  and  $NH_4^+$ . The functional groups on bacteria compete adsorption sites on VCS with phosphate, thus inhibit phosphate adsorption by the soils and increase P bioavailability in the soils (Hong et al., 2021). During the formation of chemical bonds of bacteria on the soils, the functional groups on bacteria replace surface hydroxyls on Fe/Al oxides and release them to soil solution. Therefore, the adhesion of bacteria to VCS can increase soil pH, decrease the content of active Al in the soils and alleviate the toxicity of aluminium to plant roots, which is beneficial for the restoration of degraded land and ecosystems.

### **ADSORPTION OF LOW-MOLECULAR-WEIGHT ORGANIC ANIONS**

Low molecular weight (LMW) organic acids are ubiquitous in soils, especially in the rhizosphere. LMW organic acids are mainly plant exudates and plant residue at different stages of decomposition. The anions of LMW organic acids can be adsorbed onto VCS mainly through the specific adsorption mechanism and thus alter surface charge of the soils. The adsorption of LMW organic anions decreases positive charge and increases negative charge on VCS, and thus enhances the adsorption of  $K^+$ , while decreases the adsorption of  $NO_3^-$ . LMW organic anions can compete for adsorption sites with phosphate and sulfate and thus increase the bioavailability of P and S in the soils.

### **BIOCHAR-INDUCED CHANGES OF SURFACE CHEMICAL PROPERTIES**

Biochar is a carbon-rich, trendy yet ancient soil amendment, produced by slow thermochemical pyrolysis of biomass materials. Biochar incorporation into VCS can increase soil CEC, which is responsible for increasing the retention ability of the soil for nutrient cations of  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$  and  $NH_4^+$ . Biochar can also increase P bioavailability through increasing soil pH and competing for adsorption sites with phosphate. The physical structure of biochar, with a large number of pores of different sizes, makes it an excellent habitat for soil inoculants and organisms. Biochar alters the dynamics of soil microbial communities.

Biochar incorporation can increase pH buffering capacity and thus inhibit the acidification of variable charge soils through protonation of organic anions on the biochar. Biochar contains alkaline materials and can be used as an amendment to ameliorate soil acidity, decrease soil exchangeable acidity and increase soil exchangeable base cations. Therefore, biochar can alleviate Al toxicity to plant roots, improve crop growth and thus increase crop yields.

### **CONCLUSIONS**

Intensive weathering and leaching led to low CEC and retention ability for nutrient cations, while high immobilized ability for phosphate of VCS. However, bacteria adhesion, LMW organic anion adsorption and biochar incorporation can increase CEC and retention ability for nutrient cations, and P bioavailability. Biochar can inhibit soil acidification, ameliorate soil acidity and increase crop yields. The interactions of VCS with microorganisms, organic matter and biochar can enhance the stability and resilience of the ecosystem.

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# INTEGRATING SOIL PRODUCTIVITY, NUTRIENT BALANCE, 4R STEWARDSHIP, AND CRITICAL ZONE SUSTAINABILITY TO SUPPORT OPTIMAL CROP PRODUCTION IN TAMIL NADU, INDIA

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## **Background and Rationale**

Sustaining agricultural productivity while protecting soil, water, and atmospheric resources remains a major challenge in intensively managed agro-ecosystems across the tropics and subtropics. In India, this challenge is particularly acute due to long-term reliance on fertiliser-intensive production systems, policy-driven nutrient subsidies, declining soil organic matter, and increasing pressures on land and water resources. Tamil Nadu, one of India's most agriculturally advanced states, exemplifies these challenges. Despite limited cultivable land and increasing climate variability, the state continues to maintain high cropping intensity, supported largely by fertiliser inputs and irrigation-driven intensification.

Soil productivity in Tamil Nadu is increasingly constrained not simply by nutrient scarcity, but by nutrient imbalance, declining nutrient-use efficiency (NUE), and degradation of soil – water–crop interactions within the Critical Zone. The Critical Zone - encompassing soil, water, biota, and atmospheric interfaces - regulates nutrient cycling, crop productivity, groundwater quality, and greenhouse gas emissions. Agricultural practices that neglect Critical Zone processes often result in nitrate leaching, nitrous oxide (N<sub>2</sub>O) emissions, soil acidification, salinisation, and micronutrient depletion.

This extended abstract presents outcomes from Phase-1 of an Australia–India Strategic Research Fund project co-funded by OCP Group (Morocco) and coordinated by crc CARE. The project integrates soil productivity enhancement with Critical Zone sustainability to support optimal crop production across Tamil Nadu. Phase-1 focuses on developing a spatially explicit understanding of cropping patterns, fertiliser use, soil health status, nutrient imbalance, and soil degradation pathways as the foundation for subsequent intervention – oriented research.

## **Study Area, Soil Charge Characteristics, and Analytical Framework**

Tamil Nadu encompasses seven major agro-climatic zones - Cauvery Delta, North Eastern, North Western, Western, Southern, High Rainfall, and Hilly Zones - representing wide variation in rainfall, soil types, cropping systems, and management intensity. These zones range from intensively irrigated rice-based deltaic landscapes to semi-arid rainfed systems, plantation - dominated high rainfall regions, and ecologically sensitive hill ecosystems.

The study sites include soils exhibiting both permanent-charge and variable-charge behaviour, reflecting the mineralogical diversity of the region. Permanent-charge soils, typically associated with 2:1 clay minerals in selected alluvial and black soil regions, provide relatively stable cation retention but are prone to nutrient imbalance under sustained fertiliser loading. In contrast, variable-charge soils, widespread across Tamil Nadu and enriched in iron and aluminium oxides and kaolinitic clays, exhibit pH-dependent surface charge that strongly governs phosphorus fixation, nutrient mobility, and fertiliser response. Recognition of this distinction is critical for interpreting nutrient dynamics and designing soil-specific nutrient stewardship strategies.

Phase-1 adopted a zone-wise analytical framework integrating agricultural statistics, Season and Crop Reports, ICAR datasets, and inputs from Tamil Nadu Agricultural University. Indicators analysed included land-use intensity, cropping dominance, fertiliser consumption (N, P<sub>2</sub>O<sub>5</sub>, K<sub>2</sub>O), soil organic carbon status, macro- and micronutrient constraints, and degradation indicators. These were synthesised into a Soil Health Index (SHI) to enable cross-zone comparison of soil condition and resilience (ICAR 2023; Kumar *et al.*, 2025).

### **Cropping Intensity, Fertiliser Use, and Nutrient Imbalance**

Tamil Nadu agriculture is characterized by high land-use intensity, with a net sown area of approximately 47.6 lakh ha and a gross cropped area of 61.2 lakh ha, resulting in a cropping intensity of 1.29 (DES, GoTN, 2025). The Cauvery Delta Zone accounts for the largest share of cropped area and is dominated by irrigated rice systems. Other zones exhibit varying degrees of specialisation, including pulses and oilseeds in rainfed regions, sugarcane and banana in irrigated western tracts, and plantation crops in high rainfall and hill zones.

Fertiliser use closely mirrors cropping patterns and irrigation intensity. Nitrogen application is highest in irrigated rice-based systems, often exceeding agronomic requirements, while phosphorus and potassium use remain imbalanced. Rainfed zones exhibit low fertiliser inputs constrained by moisture availability, whereas high rainfall and hill zones show elevated potassium use to offset leaching losses. These contrasting patterns highlight the limitations of uniform fertiliser recommendations and reinforce the need for soil- and zone-specific nutrient strategies.

### **Soil Health Status and Critical Zone Implications**

Soil health assessment reveals distinct degradation pathways across agro-climatic zones. Intensively irrigated zones show declining soil organic carbon, widespread micronutrient deficiencies (notably zinc), and emerging salinity risks. Rainfed zones suffer from low organic matter, nutrient depletion, and poor soil moisture retention, reducing fertiliser-use efficiency. High rainfall and hill zones retain higher organic carbon but face challenges associated with acidity, erosion, and nutrient leaching (DES, GoTN, 2025).

The Soil Health Index ranged from 0.46 to 0.74 across zones, identifying several regions as moderately degraded to degraded. These outcomes demonstrate that soil productivity is

governed not solely by fertiliser quantity, but by interactions among nutrient balance, soil charge behaviour, land-use intensity, hydrological fluxes, and Critical Zone processes regulating nutrient retention and loss.

#### **4R Nutrient Stewardship as an Integrating Framework**

Phase-1 findings strongly reinforce the relevance of the 4R Nutrient Stewardship framework—Right source, Right rate, Right time, and Right place—as an operational pathway for improving nutrient-use efficiency while safeguarding Critical Zone integrity. Excessive nitrogen application at suboptimal timing and placement in irrigated systems drives nitrate leaching and N<sub>2</sub>O emissions, while poorly synchronised nutrient supply in rainfed systems leads to low recovery and yield instability. In variable-charge soils, fertiliser source and placement play a critical role in phosphorus fixation and nutrient availability.

Embedding 4R principles within zone-specific Integrated Nutrient Management strategies provides a scientifically defensible mechanism to correct N:P:K imbalance, align fertiliser practices with soil charge characteristics, and reduce environmental externalities. Subsequent glasshouse and field experiments under this programme are explicitly designed to translate these diagnostics into actionable 4R-based recommendations.

#### **Conclusions and Way Forward**

Phase-1 outcomes demonstrate that sustaining agricultural productivity in Tamil Nadu requires a transition from uniform, input-intensive fertilisation towards 4R-aligned, soil charge-aware, and Critical Zone-informed nutrient management frameworks. Explicit recognition of contrasts between permanent-charge and variable-charge soils, combined with agro-climatic zoning, provides a robust basis for improving nutrient-use efficiency while protecting soil and environmental resources.

The integrated framework presented here directly informs subsequent experimental and technology-enabled interventions under the OCP-supported programme, supporting the development of scalable, site-specific solutions that enhance crop productivity, soil health, and long-term agro-ecosystem resilience.

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# KEY INDICATOR TOOLS FOR EARLY WARNING SHALLOW SLOPE FAILURE USING SOIL CHEMICAL PROPERTIES SIGNATURES AND SOIL CHROMATICITY

**Prof Rashidi Othman**

## **Abstract:**

Slope instability is a significant geotechnical and environmental concern in regions dominated by variable charge soils, particularly in tropical and subtropical landscapes. These soils—commonly rich in iron and aluminium oxides and characterized by pH-dependent surface charges—exhibit unique physicochemical behaviour that influences soil cohesion, structure, and hydrology. Under conditions of high rainfall, land use change, and seismic activity, the dynamic charge properties of these soils contribute to rapid loss of structural integrity and increased susceptibility to landslides, earthflows, and other forms of mass movement.

This keynote will explore the underlying mechanisms driving slope instability in variable soil chemical properties and chromaticity, with an emphasis on the role of heavy metal composition, surface charge reversal, colloidal dispersion, and loss of aggregate strength, as well as interactions between soil reflectance colorimeter values and soil texture. Drawing on field observations, laboratory analyses, and multivariate data analysis, it will highlight how climatic variability, design and construction errors, and anthropogenic disturbance exacerbate slope failure risks. Case studies from Southeast Asia, specifically Malaysia, will be used to predict real-world impacts and responses. Finally, the address will consider mitigation strategies—such as design patterns, construction and plant materials, and soil conditioning—designed to enhance slope stability and resilience in vulnerable terrains.

## **ANALYTICAL TECHNIQUES AND CHALLENGES IN VARIABLE CHARGE SOIL CHARACTERISATION**

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### **INTRODUCTION**

Variable soil charge responds dynamically to pH and other environmental factors and is a defining feature of highly weathered tropical and subtropical soils rich in kaolinite, Fe–Al oxides, and organic matter. Although Australia contains both permanent- and variable-charge soils, prolonged weathering has resulted in the widespread dominance of variable-charge systems across much of the continent. Characterising soil charge behaviour and its response to changing environmental conditions is fundamental to soil utilisation and management (Cao et al. 2024). Soil surface charge governs key processes, including nutrient retention and availability, nutrient interactions, soil mineral chemistry, and the transport, fate, and bioavailability of pollutants. Accurate quantification of soil charge across different soil types is therefore essential for optimising agronomic practices, nutrient management strategies, and environmental risk assessment. A range of analytical techniques (Cao et al. 2024; Nguyen and Truong 2020) has been developed to quantify soil charge behaviour, including the  $\Delta$ pH method, zeta potential and electrophoretic mobility analysis, potentiometric and salt titrations, ion exchange capacity measurements (CEC/AEC), and complementary spectroscopic and microscopic approaches. However, measured charge values are strongly method-dependent and sensitive to environmental and experimental conditions (Wen et al. 2020; Yu 1997). This study reviews existing analytical techniques and the key challenges associated with variable charge soil characterisation.

### **METHODS**

Soil charge characterisation is evaluated using  $\Delta$ pH methods (water versus salt solutions), electrophoretic mobility and zeta potential analysis, potentiometric and salt titrations, and ion exchange capacity measurements (CEC and AEC). Complementary spectroscopic (FTIR, XPS, NMR) and microscopic (XRD, SEM-EDS, TEM) techniques are considered to elucidate surface chemistry and charge-bearing mineralogy. Key methodological limitations, environmental controls, and emerging innovations in soil charge determination are also considered.

### **RESULTS and discussion**

Variable charge soil characterisation relies on a suite of complementary analytical techniques that collectively capture surface charge sign, magnitude, reversibility, and reactivity across mineralogically heterogeneous systems. Methods such as  $\Delta$ pH and zeta potential provide rapid insights into apparent charge behaviour, whereas potentiometric and salt titrations allow more quantitative assessment of pH-dependent charge development. Ion exchange measurements reflect nutrient retention capacity, while spectroscopic, microscopic, and selective dissolution techniques identify the chemical and mineralogical origins of charge.

However, soil charge expression is strongly regulated by environmental factors including pH, electrolyte composition, moisture, organic matter, and temperature, resulting in pronounced spatial and temporal variability. Methodological assumptions, equilibrium constraints, and the lack of standardised protocols further limit cross-study comparability and interpretation.

**Table 1. Analytical Techniques and Key Challenges in Variable Soil Charge Characterisation**

Aspect	Method / Factor	Key Information Provided	Main Limitations / Challenges
<b>ΔpH Method</b>	pH (H <sub>2</sub> O vs salt)	Net charge sign, PZC estimation	Sensitive to electrolyte; response to H <sup>+</sup> and OH <sup>-</sup> only
<b>Zeta Potential / Electrophoretic Mobility</b>	Electrokinetic measurements	Effective surface charge, interfacial behavior	Represents shear-plane rather than intrinsic surface charge; aggregation and solution chemistry effects
<b>Potentiometric Titration</b>	Acid–base titration	Variable charge density, surface reactions	Time-consuming; model-dependent
<b>Salt titration / Back-titration</b>	Electrolyte adsorption–desorption	Net surface charge and charge reversibility	Assumes equilibrium conditions; sensitive to electrolyte selection
<b>Ion Exchange (CEC/AEC)</b>	Exchangeable ions	Nutrient retention capacity	Strongly influenced by extractant, pH, and competing ions
<b>Spectroscopy and Microscopy</b>	Surface functional group and mineralogy	Chemical origin of charge and charge-bearing phases	Semi-quantitative for charge
<b>Selective dissolution techniques</b>	DCB, oxalate, pyrophosphate extractions	Quantification of Fe/Al oxides and organo-mineral complexes	Operationally defined; partial phase overlap
<b>Environmental Factors</b>	pH, moisture, OM, electrolytes, temperature	Dynamic and reversible charge response	Field variability difficult to reproduce in laboratory systems
<b>System-level challenges</b>	Soil type, mineralogy, kinetics	Spatial and temporal variability	Lack of standardisation and cross-study comparability

## CONCLUSIONS

No single analytical method adequately represents intrinsic soil surface charge due to the dynamic nature of OM dissolution, reactive oxide surfaces, soil mineralogy, and other environmental factors. Integrated, multi-method approaches are therefore essential to reliably quantify soil charge behaviour under both laboratory and field conditions. Future advances in variable-charge soil characterisation will integrate high-resolution surface analytics, in-situ sensing, molecular modelling, and AI-based data fusion to improve the prediction of charge dynamics under realistic environmental conditions.

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# Synchrotron Insights into Redox-Driven Fe–Mn Mineral Transformations and Trace Element Mobility in Variable-Charge Soils

*Nilo Karimian*

## 1. Introduction

Variable-charge soils, particularly highly weathered red soils dominated by iron (Fe) and manganese (Mn) oxides, are inherently reactive environments in which surface charge, mineral stability, and contaminant behaviour are strongly governed by pH and redox conditions. In tropical, subtropical, and island landscapes, fluctuations in oxygen availability, hydrology, and organic matter inputs drive continuous Fe–Mn mineral transformations, fundamentally regulating nutrient cycling and trace element mobility. Unlike permanent-charge clay systems, these soils exhibit pH-dependent surface charge arising from Fe- and Al-oxide minerals and kaolinitic clays, making their sorption behaviour highly dynamic and sensitive to environmental perturbations.

In red soils, acid sulfate soils, and mine-impacted environments, episodic flooding, seasonal drying, irrigation cycles, and climate-driven extreme rainfall events create recurring redox oscillations. Because Fe–Mn oxides and sulfide/sulfate phases are redox-sensitive and highly surface-reactive, even subtle changes in redox potential can induce mineral dissolution, recrystallisation, and phase transformation. Understanding these coupled processes is critical for predicting contaminant risk and nutrient behaviour in variable-charge systems.

## 2. Redox-Driven Mineral Transformations

Under circumneutral to acidic conditions typical of many weathered red soils, Fe- and Mn-bearing minerals undergo structural reorganisation in response to redox shifts. A key mechanism involves interaction between aqueous Fe(II) and Mn(II)—generated either abiotically or through microbial reduction—and existing oxide phases. Rather than complete dissolution, Fe(II) and Mn(II) may adsorb to mineral surfaces and initiate electron transfer reactions that promote atom exchange within crystal lattices. These processes restructure oxide frameworks, modify crystallinity, and alter reactive site density.

Such redox-driven restructuring can either destabilise trace element binding domains or promote their re-sequestration into newly formed or reorganised mineral phases. In variable-charge soils, where surface protonation behaviour governs sorption, these structural modifications directly influence point of zero charge (PZC), sorption envelopes, and contaminant attenuation capacity.

### **3. Synchrotron-Based Analytical Approach**

To resolve nanoscale mineral transformations and associated trace element redistribution, advanced synchrotron-based X-ray absorption spectroscopy (XANES/EXAFS) was employed alongside stable isotope tracing. XANES analysis enabled determination of Fe and Mn oxidation state evolution, while EXAFS provided insight into short-range coordination environments and mineral phase transitions. Stable isotope tracing quantified atom-exchange processes between aqueous and solid phases, demonstrating mineral restructuring without complete dissolution.

By integrating spectroscopy and isotopic tools, this study directly links electron-transfer reactions and lattice exchange mechanisms to macroscopic geochemical behaviour in redox-reactive soils.

### **4. Implications for Trace Elements and Nutrient Cycling**

Redox-induced transformations of Fe–Mn oxides strongly influence the environmental fate of arsenic (As), antimony (Sb), and phosphorus (P). Reductive dissolution may release previously sorbed species into porewaters, whereas re-oxidation can generate newly reactive oxide surfaces that facilitate re-immobilisation. The balance between release and re-sequestration is governed by transformation kinetics, mineral crystallinity, and evolving surface reactivity.

These processes are especially significant in tropical and island systems, where intense rainfall and fluctuating water tables amplify redox variability and where nutrient retention capacity is critical for agricultural productivity. Incorporating redox-driven mineral evolution into risk assessment frameworks is therefore essential for sustainable management of variable-charge soils under climate variability.

### **5. Conclusions**

Variable-charge soils are intrinsically sensitive to redox perturbations due to the dominance of Fe–Mn oxides. Fe(II)- and Mn(II)-mediated atom exchange can restructure oxide minerals without complete dissolution, altering surface reactivity and trace element hosting environments. Synchrotron spectroscopy combined with stable isotope tracing provides mechanistic insight into these transformations, enabling improved prediction of contaminant mobility and nutrient availability in redox-fluctuating environments. Such understanding is fundamental for climate-resilient management of highly weathered red soils.

# DATA FUSION OF LOW-COST PROXIMAL SENSORS FOR THE PREDICTION OF ORGANIC CARBON IN Ultisols and Oxisols: NIXPRO COLOR SENSOR AND KT10 K METER

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## INTRODUCTION

Highly weathered tropical soils are characterized by low soil organic carbon (SOC), strong Fe-oxide pigmentation, and limited nutrient retention, making rapid, cost-efficient SOC assessment essential for soil monitoring and land management. This study quantified the relationships between SOC and individual sensor outputs, specifically NixPro-derived color indices and KT10 magnetic susceptibility ( $\kappa$ ) values, and evaluated the predictive capacity of two low-cost proximal sensors, the NixPro color sensor and the KT10  $\kappa$  meter, and further tested whether combining their outputs through data fusion could improve SOC estimation.

## METHODS

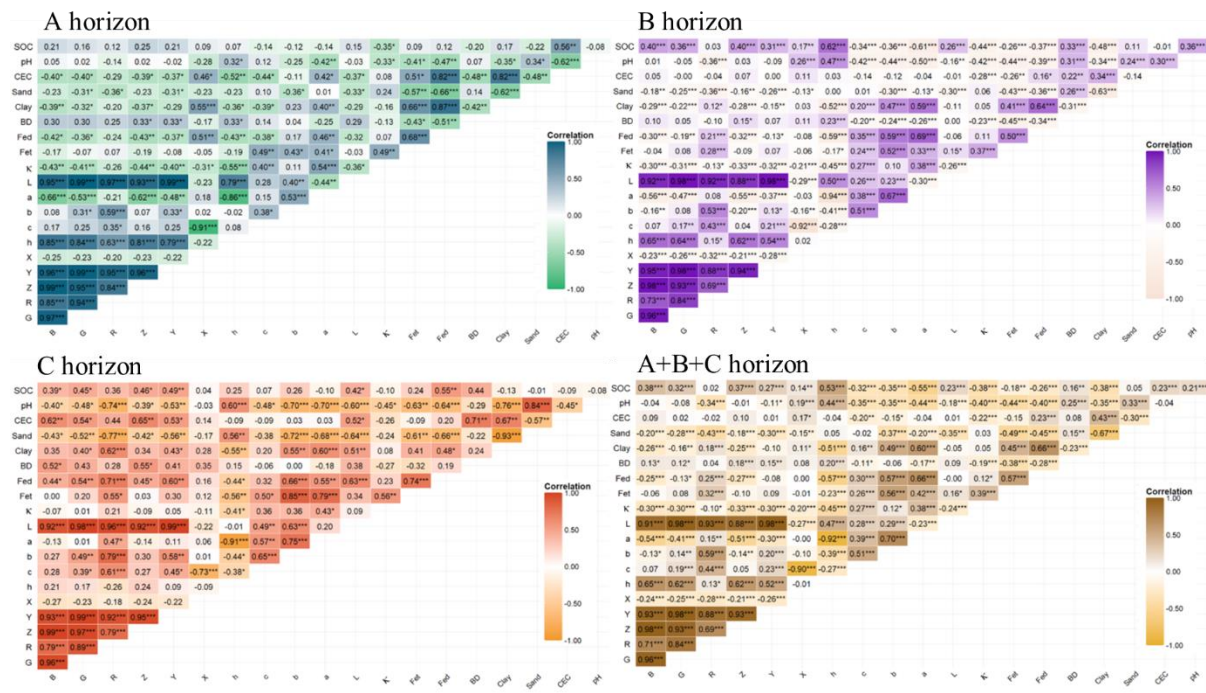
A total of 363 soil samples across A, B, and C horizons of Ultisols and Oxisols in Taiwan were analyzed for SOC by wet-oxidation, colorimetric indices (CIELab\*, CIELCh\*, RGB, XYZ), and  $\kappa$ . Pearson's correlation analysis was performed to evaluate SOC-predictor (colorimetric indices and  $\kappa$ ) relationships and to assess multicollinearity among variables. Model development included partial least squares regression (PLSR) and support vector machine (SVM), with calibration and validation performed using 10-fold cross-validation, repeated 5 times to improve reliability and minimize overfitting.

## RESULTS AND DISCUSSION

Correlation analysis demonstrated strong depth-dependent behaviour with SOC in A horizon showed no measurable chromatic or reflectance response, suggesting that Fe-oxide coatings masked the optical contribution of organic matter (Fig. 1). In B horizons, however, SOC was positively correlated with brightness and reflectance indices, including  $L^*$ , X, Y, Z, G, and B ( $p < 0.001$ ), indicating that even small increases in SOC enhanced surface reflectance within this Fe-rich subsurface layer. Corresponding negative correlations with  $a^*$ ,  $b^*$ , and  $c^*$  ( $p < 0.001$ ) showed clear pigment dilution by SOC. In C horizons, SOC effects were weaker but still detectable, evidenced by low-strength correlations with  $L^*$ , Y, Z, G, and B ( $p < 0.05$ – $0.01$ ). Across all horizons, SOC was also strongly associated with chromatic indices at the whole-profile scale: SOC was positively correlated with  $h^\circ$  and negatively correlated with  $a^*$ ,  $b^*$ , and  $c^*$  (all  $p < 0.001$ ), indicating reduced red–yellow pigmentation and lower chroma intensity as SOC increased. These whole-profile chromatic trends were driven almost entirely by the B horizon, as neither the A nor C horizons showed significant SOC–chromatic relationships. In A, B, C, and A+B+C horizons, SOC was negatively related to  $\kappa$  ( $p < 0.05$  to  $0.001$ ), while  $\kappa$  remained positively correlated with free iron ( $Fe_d$ ) and total iron ( $Fe_t$ ) ( $p < 0.05$ – $0.001$ ), confirming that  $\kappa$  primarily reflected Fe-oxide mineralogy rather than SOC distribution. Predictive modelling showed that the SVM with fused NixPro color sensor + KT10  $\kappa$  meter inputs achieved the highest SOC prediction accuracy in the B horizon ( $R^2 = 0.70$ , RMSE = 0.52, RPD = 1.80, LCCC = 0.81; Table 1). These results confirm that multisensor SVM offers a highly effective and scalable tool for SOC estimation in these types of variable charge soils.

## CONCLUSIONS

Low-cost NixPro color and KT10  $\kappa$  meter showed strong, depth-dependent relationships with SOC, with the B horizon providing the clearest and most predictable sensor response. Multisensor fusion with SVM greatly improved SOC estimation, confirming its value as a rapid, cost-efficient tool for monitoring carbon in highly weathered tropical soils.



**Fig. 1. Correlation among selected basic soil properties, color indices, and magnetic susceptibility of highly weathered tropical soils.**

**Table 1. Model performance for SOC prediction using NixPro color sensor and combined NixPro color sensor + KT10  $\kappa$  meter data with PLSR and SVM algorithms.**

Predictor variable	Algorithm	R <sup>2</sup>	RMSE	RPD	LCCC
<b>A horizon (n = 43)</b>					
NixPro color sensor	PLSR	0.06	1.21	1.04	0.11
	SVM	0.44	0.98	1.29	0.49
NixPro color sensor + KT10 $\kappa$ meter	PLSR	0.14	1.15	1.09	0.25
	SVM	0.33	1.03	1.22	0.46
<b>B horizon (n = 293)</b>					
NixPro color sensor	PLSR	0.43	0.70	1.33	0.60
	SVM	0.62	0.59	1.59	0.74
NixPro color sensor + KT10 $\kappa$ meter	PLSR	0.45	0.69	1.35	0.62
	SVM	0.70	0.52	1.80	0.81
<b>C horizon (n = 27)</b>					
NixPro color sensor	PLSR	0.24	0.67	1.17	0.39
	SVM	0.17	0.74	1.05	0.13
NixPro color sensor + KT10 $\kappa$ meter	PLSR	0.24	0.67	1.17	0.39
	SVM	0.23	0.73	1.08	0.16
<b>A + B + C horizons (n = 363)</b>					
NixPro color sensor	PLSR	0.39	0.78	1.28	0.56
	SVM	0.56	0.68	1.47	0.68
NixPro color sensor + KT10 $\kappa$ meter	PLSR	0.41	0.77	1.30	0.58
	SVM	0.63	0.62	1.61	0.75

## IMPACT OF VARIABLE-CHARGE SOILS ON THE ANALYSIS OF PESTICIDE RESIDUES IN SOIL

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### INTRODUCTION

Variable-charge soils possess pH-dependent surface functional groups on iron (Fe) and aluminium (Al) oxides, clays, and soil organic matter. These reactive surfaces regulate critical environmental processes, including nutrient retention, contaminant mobility, and the fate of agrochemicals (Sparks, 2003). Many pesticides are weak acids, weak bases, or amphoteric compounds, and both the pesticide ionisation state and the soil charge strongly influence their interactions with soil surfaces. Under acidic conditions, where variable-charge soils typically exhibit net positive charges, anionic pesticides may undergo strong iron-incorporating bonding, while charge-neutral and polar pesticides can participate in ligand exchange or form inner-sphere complexes with Fe and Al oxides. Additionally, negatively charged pesticide species are attracted to positively charged mineral surfaces at low pH, resulting in outer-sphere complexation; however, these interactions get weakened as soils approach or exceed their point of zero charge. Hydrogen bonding and van der Waals interactions also contribute significantly to pesticide retention, particularly for neutral or weakly polar pesticides interacting with organic matter or the edge sites of clays such as kaolinite and allophane. At low pH, protonated pesticide species may form cation bridges with negatively charged organic functional groups or clay surfaces. Conversely, at higher pH, deprotonated pesticides can complex with dissolved Al or Fe released from oxide surfaces, thereby forming secondary organometallic species that are difficult to extract. These interactions can result in elevated sorption, the formation of bound (non-extractable) residues, and the suppression or enhancement of recoveries during analytical extraction. The pH-dependent electrochemistry and sorptive complexity of variable-charge soils therefore, introduce considerable uncertainty into pesticide residue analysis. Careful consideration of these soil properties is necessary to achieve accurate and reproducible quantification in environmental monitoring and risk assessment.

### ANALYTICAL CHALLENGES FOR RESIDUE ANALYSIS

Due to interactions among pesticides in variable-charge soils, the extraction of pesticide residues from soils is often tricky. Extraction efficiency in variable-charge soils is highly sensitive to pH, solvent polarity, ionic strength, and other factors. Alkaline solvents, such as potassium hydroxide and sodium tetraborate, either alone or in combination with polar organic solvents (e.g., methanol), are commonly employed to enhance the extraction of polar pesticides by generating a net negative surface charge in variable-charge soils, thereby reducing electrostatic sorption and promoting desorption. For nonpolar pesticides, the

QuEChERS method using water-acetonitrile separation is widely applied for extraction. Other extraction methods, such as Solid-Liquid Extraction, SPE, and DSPE have also been investigated. However, variable-charge soils often release dissolved organic matter (González-Pradas et al., 2005), aluminium and iron ions, and colloidal particles into extracts, with the extent of release varying with the extraction method used. This increases the risk of matrix effects in instrumental analysis. These co-extracted components pose challenges for detection and quantification. Therefore, additional steps are required during extraction to reduce or compensate for these interferences. Reagents such as phosphate buffers, EDTA, and Alkaline extractants are often required to disrupt metal–ligand interactions and enhance desorption (Gros et al., 2017). Cleanup with dichloromethane, Primary Secondary Amines (PSA), Graphitised Carbon black (GCB), is also performed to address matrix interferences. In mass spectrometry, matrix-induced ion suppression or enhancement is compensated for using either matrix-matched calibration or isotopically labelled internal standards for accurate quantification (Niessen, 2006). Without such optimisation, conventional multiresidue methods may significantly underestimate actual pesticide concentrations in oxide-rich soils.

### **ADVANCEMENTS IN ANALYTICAL METHODS**

Since 2010, analytical methods for pesticide residue determination in soils have diversified beyond mass-spectrometry-based workflows to include immunochemical, spectroscopic, and sensor-based techniques. (Han et al., 2025). Tandem mass spectrometry remains the dominant platform due to its excellent sensitivity, selectivity, and multiresidue capability; however, fluorescence and UV detection are still widely employed for cost-effective routine monitoring, especially when paired with derivatisation strategies for chromophore-lacking or highly polar compounds. Gas chromatography continues to serve as a robust analytical technique for volatile and semi-volatile pesticide while ion chromatography coupled to either conductivity detection or mass spectrometry provides superior performance for highly polar herbicides and ionic species (Schäfer et al., 2025). Emerging technologies, including biosensors, surface-enhanced Raman spectroscopy, and electrochemical detection systems, show promise for rapid screening and on-site analysis (Wang et al., 2016) however, these methods currently lack the analytical sensitivity, selectivity, and robustness required for regulatory-grade residue quantification.

### **CONCLUSIONS**

The accurate determination of pesticide residues in variable-charge soils remains challenging due to pH-dependent interactions that reduce extraction efficiency and introduce matrix interferences. Although significant advancements have been made in extraction protocols (QuEChERS, alkaline extractants, chelating agents with clean-up steps) and detection platforms (LC-MS/MS, GC-MS/MS), conventional methods developed for temperate soils require substantial modification for variable-charge environments. Emerging technologies show promise for rapid screening but lack the sensitivity for regulatory quantification. Developing robust, universally applicable protocols tailored to variable-charge soils is essential for accurate environmental monitoring and risk assessment in tropical and subtropical agricultural regions.

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## UNLOCKING ACID SOILS: HOW INCREASING pH DECREASES POTASSIUM LOSSES IN SANDY SOILS WITH VARIABLE CHARGE

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### INTRODUCTION

Widespread soil acidification in agricultural soils with pH-dependent charge may be increasing K leaching in southern Australia due to decreases in cation exchange capacity. This study aims to quantify the relationship between increasing the pH of acid soils and the amount of K leaching on a sandy loam and loamy sand.

### METHODS

A column experiment was carried out with a loamy sand (4 % clay) and sandy loam (13 % clay). Treatments consisted of a factorial combination of K rates (0, 34 and 68 mg K/column, equivalent to 0, 30, 60 kg K ha<sup>-1</sup> applied as KCl) and three pHCaCl<sub>2</sub> levels (control (4.5-4.8), pH 5.5, 6.5).

### RESULTS

With increasing soil pH, there was more than 3-fold increase in effective cation exchange capacity (ECEC) and the extra K<sup>+</sup> retained in both the unlimed soils increased by 37%, whereas fertilized soils exhibited 63-80% increase over the same pH ranges. The calculated extra K retained (relative to pH 4.5) showed that pH increase from 4.5 to 5.5 led to gains of 4.1–35.4 kg ha<sup>-1</sup>, while further increase to pH 6.5 resulted in 9.6–38.4 kg ha<sup>-1</sup> of additional K retained, depending on the K level in the loamy sand. However, in the sandy loam, extra K retained (relative to pH 4.8) showed that pH increase from 4.5 to 5.5 led to gains of 0.9–31 kg ha<sup>-1</sup>, while further increase to pH 6.5 resulted in 5.2–56.9 kg ha<sup>-1</sup> of additional K retained, depending on the K level applied. In the loamy sand, CEC at pH 4.5 was 0.61 cmol/kg, but increased to 1.99 cmol/kg at pH 5.5 and further to 2.4 cmol/kg at pH 6.5. In the sandy loam, at pH 4.8, CEC was 1.22 cmol/kg, which increased to 3.8 cmol/kg at pH 5.5 and further to 4.81 cmol/kg at pH 6.5. Also, at the highest rate of K (68 mg K/column) application in the loamy sand, increasing pH to 5.5 or 6.5, reduced K loss by 58% and 57%, respectively. In the sandy loam, at pH 5.5 and 6.5, K leaching was reduced by 51% and 38% at 68 mg K/column, respectively. At the highest K application (68 mg K/column) in both the loamy sand and sandy loam, there was delay in the peak of the K breakthrough until 4.75 pore volumes (PV) at pH 6.5. In contrast, at pH 4.5 and 4.8, the K leaching peaked was at 2.75 to 3 PV at 68 mg K/column application.

## CONCLUSIONS

The variable charge characteristics of acid soils need to be considered as a factor in K nutrient management on sandy soils. More K were retained following liming which was related to the more than 3-fold increase in ECEC of two acid soils. These findings highlight the importance of integrating liming with K fertilization in soil fertility management programmes, particularly in sandy and sandy loam soils with low inherent K content. The loss of K through leaching on acid soils could be reduced or delayed by raising the pHCaCl<sub>2</sub> to 5.5 or higher.

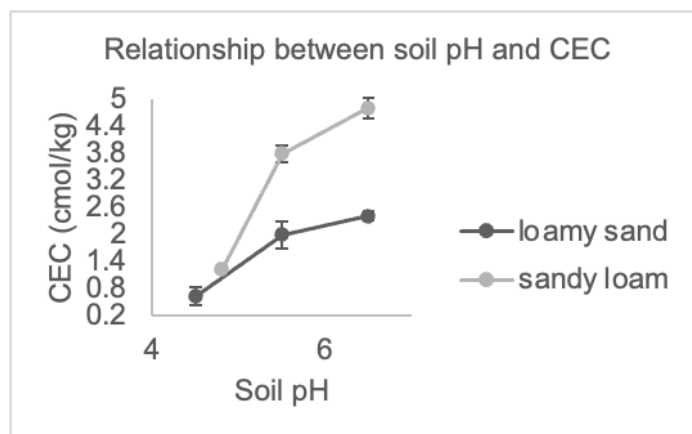


Figure 1: Relationship between soil pH and CEC. Values are means of four replicates. Vertical bars represent the standard error of the mean.

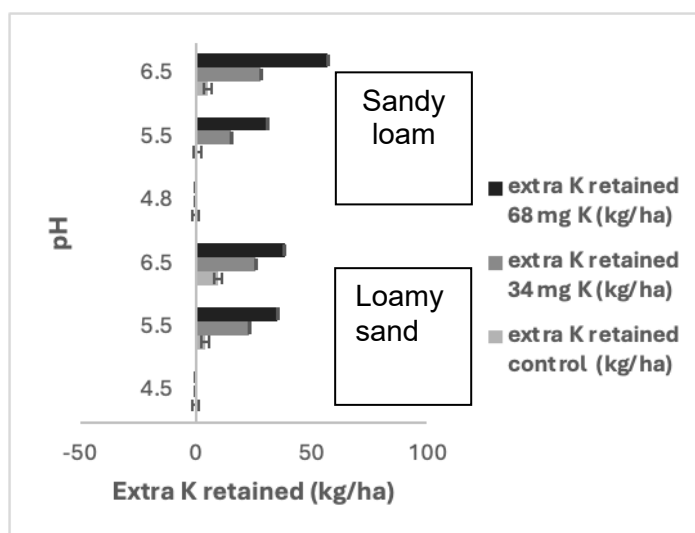


Figure 2: Relationship between pH and extra K retained in soils as exchangeable K.

## ACKNOWLEDGEMENTS

This research was conducted as a PhD study through financial support of the Grains Research and Development Corporation (GRDC) as part of the project: Increasing profit from N, P and K fertilizer inputs into the evolving cropping sequences in the Western Region (UMU1801-006RTX, UWA1801-002RTX). My special thanks to the farmers at Goomalling and West Brookton for granting me permission to collect soil samples at their farms.

# NUTRIENT–TRACE ELEMENT INTERACTIONS IN AGRICULTURAL SOILS OF BANGLADESH: IMPLICATIONS FOR SOIL FERTILITY, 4R NUTRIENT STEWARDSHIP AND ENVIRONMENTAL RISK

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## INTRODUCTION

Increasing concern has been directed toward trace elements (TE) contamination in agricultural soils due to its potential risks to human health, soil health, crop productivity and environmental integrity (Xu et al. 2022). Globally, rapid industrialisation and urbanisation, combined with intensive agricultural practices and the use of low-quality agrochemicals, have contributed to elevated concentrations of trace elements in farming systems (Meena et al. 2025). Numerous studies report enrichment of elements such as Cr, Zn, As, and Pb in agricultural soils, in some cases exceeding permissible thresholds (Ahogle et al. 2023). The mobility and bioavailability of TEs are strongly influenced by soil physicochemical properties and nutrient status, yet these interactions remain insufficiently understood in intensively managed cropping systems. In particular, inappropriate nutrient management can inadvertently enhance trace-element mobility or uptake by crops. Understanding nutrient–trace element interactions within the context of 4R nutrient stewardship (Right source, Right rate, Right time, Right place) is therefore critical for maintaining soil fertility while minimising environmental and human-health risks.

This study examines how soil physicochemical properties and nutrient status influence trace-element dynamics in rice-growing soils of Bangladesh, with implications for risk-informed and sustainable nutrient management.

## METHODS

Soil samples were collected from agricultural rice-growing areas across Bangladesh. Soil physicochemical properties including pH, organic matter (OM) content, Electrical conductivity (EC), and cation exchange capacity (CEC) were analysed using standard methods. Concentrations of trace elements and nutrients in soils were digested using aqua regia followed by quantified using both ICP-MS and ICP-OES. Data quality was ensured through a rigorous QA/QC program incorporating certified reference soil material (NIST SRM 2711a, Montana II Soil).

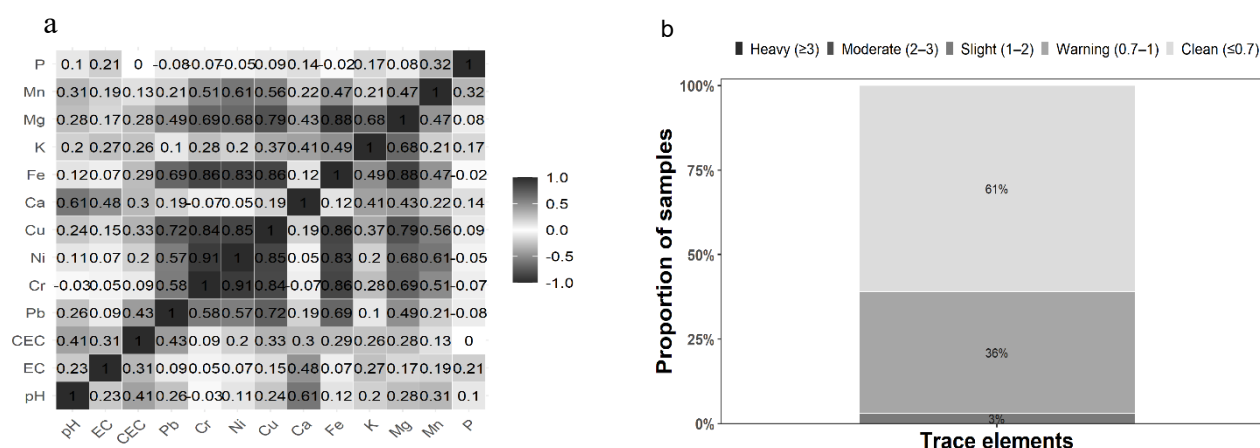
Overall soil contamination was assessed using the Nemerow Pollution Index ( $P_n$ ), which integrates both mean contamination levels and maximum single-factor pollution indices, providing a balanced assessment of multi-element contamination risk (Ali et al. 2019).

## RESULTS and discussion

### Interaction of Soil Nutrients and Soil Properties with Trace elements

Strong inter-correlations were observed among several trace metals (Pb, Cr, Ni, Cu), with the strongest association between Cr and Ni ( $r = 0.91$ ). Soil pH showed a negative correlation with Cr, indicating reduced metal solubility at higher pH (Figure 1a). Phosphorus was negatively correlated with several trace elements (Cr, Ni, Pb, Fe), highlighting metal–phosphate interactions and adsorption onto iron oxides. Soil fertility indicators (CEC, Ca, Mg, K) formed a distinct correlated group, while Fe and Mn showed strong associations reflecting coupled redox behaviour.

These results indicate two dominant controlling systems: (i) a trace-element geochemical cluster, and (ii) a nutrient–CEC fertility cluster, with pH acting as a key regulator. From a management perspective, the findings reinforce the importance of 4R nutrient management, where inappropriate nutrient source, rate, timing, or placement could alter trace-element mobility and bioavailability in variable-charge soils.



**Fig. 1. (a) Correlation matrix of trace elements, nutrients, and soil properties and (b) soil contamination levels based on the Nemerow Pollution Index ( $P_n$ ).**

### Nemerow pollution index

Based on the Nemerow Pollution Index, 61% of samples were classified as clean ( $P_n \leq 0.7$ ), 36% at the warning level (0.7–1), and only 3% as slightly polluted (1–2), with no samples exceeding moderate pollution thresholds. Overall,  $P_n$  values ranged from 0.24 to 1.13, indicating generally low contamination levels across the study area (Figure 1b).

### CONCLUSIONS

The study demonstrates that nutrient status and soil physicochemical properties exert strong controls on trace-element behaviour in Bangladeshi agricultural soils. Correlation patterns reveal two principal regulatory systems—a metal-oxide-dominated geochemical cluster and a nutrient-CEC fertility cluster—mediated by soil pH. While overall contamination levels are low, the results underscore the importance of adopting 4R nutrient stewardship as a practical framework to optimise soil fertility while minimising trace-element risks in intensively managed, variable-charge soil systems.

## ACKNOWLEDGMENTS

The author gratefully acknowledges PhD fellowship and tuition fee support from the Science and Technology Fellowship Trust, Bangladesh along with research funding provided by OCP through the crcCARE project.

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# SOIL CONTROLS ON LEGACY CADMIUM BIOAVAILABILITY IN LONG-TERM PHOSPHATE-FERTILISED SYSTEMS: A 4R NUTRIENT STEWARDSHIP PERSPECTIVE

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## INTRODUCTION

Cadmium (Cd) is a persistent, non-biodegradable toxic heavy metal classified as a Group 1 human carcinogen by the International Agency for Research on Cancer. Human exposure to Cd occurs predominantly through dietary intake and is associated with adverse effects on kidney function, liver health, and reproductive systems. In several rice-consuming regions, including Bangladesh, Cd concentrations in marketed rice have exceeded recommended safety thresholds, raising concerns regarding long-term human health risks. Historically, the long-term and repeated use of phosphatic fertilisers derived from Cd-rich phosphate rock has been a major source of Cd accumulation in agricultural soils. While modern fertiliser manufacturing and regulatory controls have largely eliminated Cd from contemporary phosphate fertilisers in many countries, the **legacy Cd accumulated in soils from past fertiliser use remains a significant and ongoing concern**. Importantly, current fertiliser applications may no longer contribute additional Cd loading, yet legacy Cd continues to persist, interact with soil constituents, and bioaccumulate in crops. Once present in soil systems, Cd mobility, retention, and bioavailability are governed by key soil physicochemical properties, including pH, redox potential (Eh), electrical conductivity (EC), cation exchange capacity (CEC), organic matter content (OM), and the presence of Fe, Mn, and S minerals. In long-term fertilised soils, total and bioavailable Cd concentrations may increase over time, increasing the potential for plant uptake and food-chain transfer. Phosphorus management plays a complex role, influencing Cd solubility, speciation, and plant translocation under varying soil conditions. In this context, **4R Nutrient Stewardship (right source, right rate, right time, and right place)** is critical for managing legacy Cd risks in agricultural soils. Appropriate fertiliser selection, application rate, timing, and placement can minimise Cd mobilisation, limit plant uptake, and reduce dietary exposure without compromising crop productivity or food security. This research was aimed to see how soil properties and phosphorus influence the legacy Cd translocation and bioavailability in long-termed fertilized rice farming soil and if it causes any possible human health threat. It will also support the 4R nutrient stewardship principles by choosing Cd free P fertilizer, application rate, timing, and proper placement that can limit Cd accumulation and uptake by plant.

## METHODS

Paired soil and ripened rice grain samples were collected from long-term fertilised paddy fields in the Moulvibazar district, Bangladesh. Soil and grain macro- and trace elements were analysed after aqua regia and HNO<sub>3</sub> digestion using ICP-MS and ICP-OES. Soil pH, electrical conductivity (EC), cation exchange capacity (CEC), organic matter (OM), and CaCl<sub>2</sub>-extractable Cd were determined using standard methods. Quality control was ensured using NIST reference materials (1568a and 2711a). Cadmium transfer and bioavailability factors, daily dietary intake, and target hazard quotient were calculated to assess Cd mobility, plant uptake, and non-carcinogenic human health risk.

## RESULTS and discussion

The correlation table (Table 1) showing all the soil properties are positively correlated with the total soil P, bioavailable P, and grain Cd. The increase of soil pH enhanced the grain Cd and its translocation but reduced its bioavailability and bioaccumulation. Besides, soil P increased the Cd bioavailability and translocation in plant. All the soil properties including soil total P are negatively correlated with the Cd bioaccumulation in soil. Soil bioavailable P increase Cd translocation in plant and decrease its bioaccumulation in soil.

**Table 1. Correlations among soil properties and phosphorus influencing Cd bioavailability, translocation and bioaccumulation.**

	<i>pH</i>	<i>EC</i>	<i>CEC</i>	<i>OM</i>	<i>Soil P</i>	<i>Soil Cd</i>	<i>Grain Cd</i>	<i>Bio. P</i>	<i>Bio. Cd</i>	<i>TF Cd</i>	<i>BAF Cd</i>
<i>pH</i>	1.00										
<i>EC</i>	0.10	1.00									
<i>CEC</i>	-0.06	0.08	1.00								
<i>OM</i>	-0.15	0.27	0.46	1.00							
<i>Soil P</i>	0.08	0.27	0.45	0.16	1.00						
<i>Soil Cd</i>	-0.06	0.41	0.46	0.45	0.68	1.00					
<i>Grain Cd</i>	0.10	0.15	0.15	0.14	0.47	0.49	1.00				
<i>Bio. P</i>	0.16	0.56	0.15	0.19	0.39	0.34	0.21	1.00			
<i>Bio. Cd</i>	-0.32	-0.17	0.17	0.32	0.17	0.47	0.34	0.00	1.00		
<i>TF Cd</i>	0.13	-0.05	-0.25	-0.12	0.14	-0.07	0.70	0.08	0.07	1.00	
<i>BAF Cd</i>	-0.27	-0.44	-0.40	-0.14	-0.37	-0.48	-0.03	-0.22	0.42	0.42	1.00

The mean and range of daily Cd intake is 0. The mean and range of daily Cd intake is 0.02 µg/kg/bw which is below the tolerable limit of 0.83 µg/kg (Chen et al. 2018). The mean target hazard quotient value also found THQ <1 meaning no possible threat of non-carcinogenic risk due to the consumption of Cd (Sarkar et al. 2023).

## CONCLUSIONS

The findings highlight that while modern fertiliser practices may no longer introduce additional Cd into agricultural soils, legacy Cd derived from historical phosphatic fertiliser use remains a critical risk pathway. Soil pH and phosphorus availability strongly influence Cd bioavailability and plant translocation, underscoring the importance of 4R Nutrient Stewardship in managing long-term contamination risks. Strategic fertiliser source selection, coupled with optimised

application rate, timing, and placement, offers a practical and scalable approach to limiting Cd uptake by crops while safeguarding food security and soil health.

#### **ACKNOWLEDGEMENTS:**

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# THE INFLUENCE OF SOIL CHARGE VARIABILITY ON DROUGHT-PRONE SOILS

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## INTRODUCTION

Drought is some of the most significant environmental stressors affecting agricultural and natural soils worldwide. Drought alters soil physical and chemical properties compounding water stress. As soil dries, matric potential becomes increasingly negative, making water less accessible to plants, while ion concentrations in the remaining soil solution can rise by orders of magnitude (Chaves et al., 2003). Rapid rewetting of dry surfaces often triggers aggregate slaking and clay dispersion, leading to surface sealing that reduces subsequent water entry (Lado et al., 2004). While much attention has focused on soil texture and organic matter content, the role of surface charge variability particularly pH-dependent charge in shaping drought outcomes remains underdiscussed. Charge variability is usually observed in highly weathered and volcanic-influenced soils include edge sites of kaolinite, Fe/Al (hydr)oxides (e.g., goethite, hematite, gibbsite), and short-range-order aluminosilicates such as allophane and imogolite (Uehara & Gillman, 1981). Variable-charge minerals exhibit charge densities that respond dynamically not only to pH but also to ionic strength and specific ion adsorption, altering electrostatic interactions, aggregation–dispersion equilibria, and the effective CEC/AEC expressed by the soil. These dependencies are particularly consequential under drought, when concentration effects and pH micro-gradients can shift surface speciation and thereby modify soil physical and chemical functioning during drying and subsequent rewetting.

## ROLE OF CHARGE VARIABILITY IN DROUGHT AFFECTED SOILS

During drought, rising ionic strength compresses the electrical double layer around particles, reducing electrostatic repulsion and promoting flocculation when divalent cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  form bridges between negatively charged surfaces. In

variable-charge soils, this effect is strongly pH-sensitive. Above the point of zero charge (PZC), increased negative charge enhances cation bridging and aggregation; below the PZC, reduced or positive charge weakens aggregation. To this end, the drought-rewetting cycle poses risks; if drought-concentrated salts are diluted by low-ionic-strength rainfall or if pH shifts occur, previously flocculated clay can disperse rapidly, migrate into pores, and form surface seals that drastically reduce hydraulic conductivity (Ben-Hur et al., 2009). This aggregation–dispersion dynamic directly influences pore-size distribution. Stable macroaggregates maintain large pores that facilitate rapid infiltration, allowing soils to capture episodic rainfall efficiently during drought, while smaller pores store plant-available water. Surface crusting following rewetting reduces infiltration for subsequent rainfall, compounding drought impacts.

Nutrient retention is equally sensitive to charge dynamics. Cation exchange capacity (CEC) typically increases with pH, while anion exchange capacity (AEC) often increases as pH falls. During drought, localized pH changes and rising ionic strength shift exchange capacities and suppress nutrient buffering. Upon rewetting, pulses of dissolved organic matter and soluble salts transiently alter surface charge and can displace adsorbed nutrients, increasing leaching risk. Soils with low organic matter may exhibit poor nutrient retention during these cycles, exacerbating plant stress even when water becomes available. Thus, organic matter plays a pivotal role in drought management. Variable-charge minerals especially Fe and Al oxides form strong bonds with organic matter through ligand exchange and electrostatic attraction (Torn et al., 1997). This binding enhances aggregate stability and helps aggregates resist collapse during drying-rewetting cycles.

## **CONCLUSION**

Charge variability i.e., the pH- and ionic-strength-dependent nature of surface charge in oxide- and kaolinite-rich soils influences drought responses. Drought intensifies ionic strength and can shift pH, directly altering surface charge and governing aggregation, infiltration, water retention, and nutrient availability. Variable-charge soils with low organic matter are especially vulnerable to dispersion and sealing during drought-rewetting cycles. Management strategies including liming, gypsum application, organic matter building, compaction control, and surface cover must target charge dynamics to improve drought resilience.

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# ENVIRONMENTAL DRIVERS OF HUMUS FORM DIVERSITY IN THE HYRCANIAN FORESTS OF NORTHERN IRAN

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## INTRODUCTION

Humus plays a fundamental role in soil fertility and stability (Hu et al., 2021). Its formation is governed by biotic and abiotic factors (Ponge et al., 2014), yet studies on humus forms in Iran's Hyrcanian forests are lacking. This research investigates humus variability and its environmental drivers to support sustainable forest management.

## METHODS

The study was conducted in the Bahramnia Forest, eastern Hyrcanian region, northern Iran. 104 plots (20×20 m) were established across three forest types along an elevation gradient (150–1000 m). Humus forms were classified using the European Humus Form Classification (Zanella et al., 2011). Topography was recorded, and soil samples were analyzed for pH, SOC, and TN. One-way ANOVA was used.

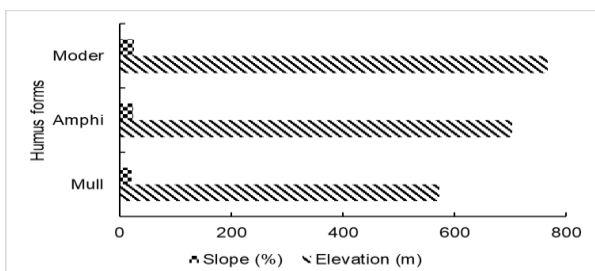
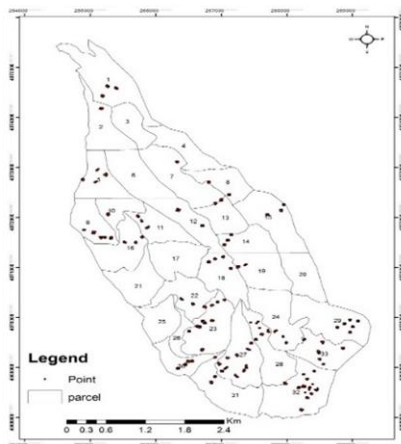


Fig. 1. Study area map and sampling design

# RESULTS and discussion

Mull was the dominant humus form across the study area (59% of samples). Humus composition differed significantly among forest types ( $p < 0.001$ ): Mull occurred in all *Carpinus betulus* stands (100%), was frequent in mixed *Parrotia-Carpinus* stands (65%), and declined in *Fagus orientalis* forests (22%). Amphi reached its peak in *Fagus orientalis* stands (42%), whereas Moder was most abundant in mixed stands (32%) (Fig. 2). Elevation and slope significantly influenced humus distribution, with Amphi and Moder increasing at higher elevations, likely due to reduced decomposition rates (Fig. 3). Organic layer thickness also varied significantly, with thicker layers observed in mixed beech stands and at higher altitudes (Fig. 4). In contrast, soil physicochemical properties (SOC, TN, pH, moisture) did not differ significantly among forest types or humus forms (Table 1). This may be attributed to the dominant influence of broader environmental factors such as parent material and microtopography, coupled with rapid organic matter turnover in this ecosystem.

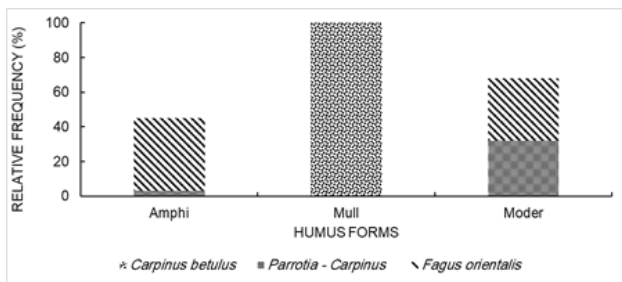


Fig. 2. Humus form distribution

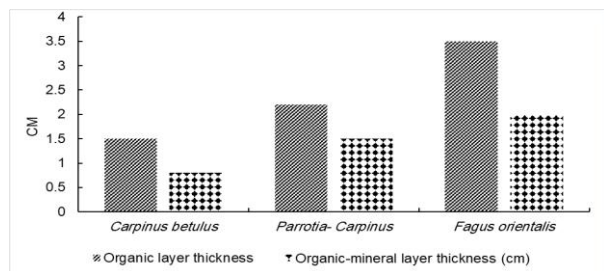


Fig. 3. Elevation/slope effects

Fig. 4. Variability in organic layer thickness among forest types

Table 1. Soil physicochemical properties across forest types and humus forms (mean  $\pm$  SD)

Soil Parameter	df	Mean Square	F-value	p-value
Organic Carbon (SOC)	2	5.518	2.043	0.139
Total Nitrogen (TN)	2	0.019	1.67	0.197
pH	2	0.099	0.95	0.391

## CONCLUSIONS

This study confirmed the applicability of the EHF in the Hyrcanian forests. The Mull form was predominant at lower elevations, particularly under hornbeam and beech-hornbeam stands, reflecting favourable litter quality and high biological activity. With increasing elevation and slope, Amphi and Moder forms became more abundant, corresponding to lower temperatures and reduced decomposition rates. Although soil properties did not vary significantly among forest types, humus forms proved to be a sensitive and practical indicator for assessing soil ecological status and informing sustainable forest management in this region.

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# REFINING BENZO(A)PYRENE RISK ASSESSMENT IN URBAN VARIABLE CHARGE FILL SOILS: A MULTIPLE LINES OF EVIDENCE APPROACH.

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## INTRODUCTION

Urban recreational reserves across eastern Australia commonly contain heterogeneous historical fill derived from coal ash, coke residues and demolition materials. Generic Tier 1 Health Investigation Levels (HILs) under the NEPM (2013) frequently trigger exceedances for benzo(a)pyrene (BaP) in such environments, often resulting in conservative remediation or disposal decisions. This study examined the behaviour, mobility and bioavailability of BaP in historical urban fill underlying an intensively used public open space (sporting fields, children's play, dog walking), with the objective of determining whether exceedances of generic HIL-C open-space criteria represented a true human health risk (HHR) in a variable charge soil context.

## METHODS

Thirteen soil samples were collected from six boreholes (0–1 m below ground level) across a proposed construction footprint of approximately 32 × 36 m within a public recreational reserve in eastern Australia. Samples were analysed at a NATA-accredited laboratory for:

- PAHs (including BaP and BaP toxic equivalence (TEQ))
- Heavy metals
- TRH (with silica gel clean-up where required)
- TCLP leachability testing

Statistical evaluation using USEPA ProUCL (v5.2) was undertaken to derive the 95% Upper Confidence Limit (UCL) of BaP(TEQ). PAH fingerprinting, following the methods described by Mulvey and McKay (2006), was conducted to determine contaminant origin. A Tier 2 investigation was undertaken to derive a site-specific HIL-C criteria in accordance with NEPC (2013) Schedule B7, incorporating:

- Conservative oral bioavailability (BA<sub>o</sub>)
- Site-specific dermal absorption factor (DAF)
- Public open space exposure assumptions.

## RESULTS AND DISCUSSION

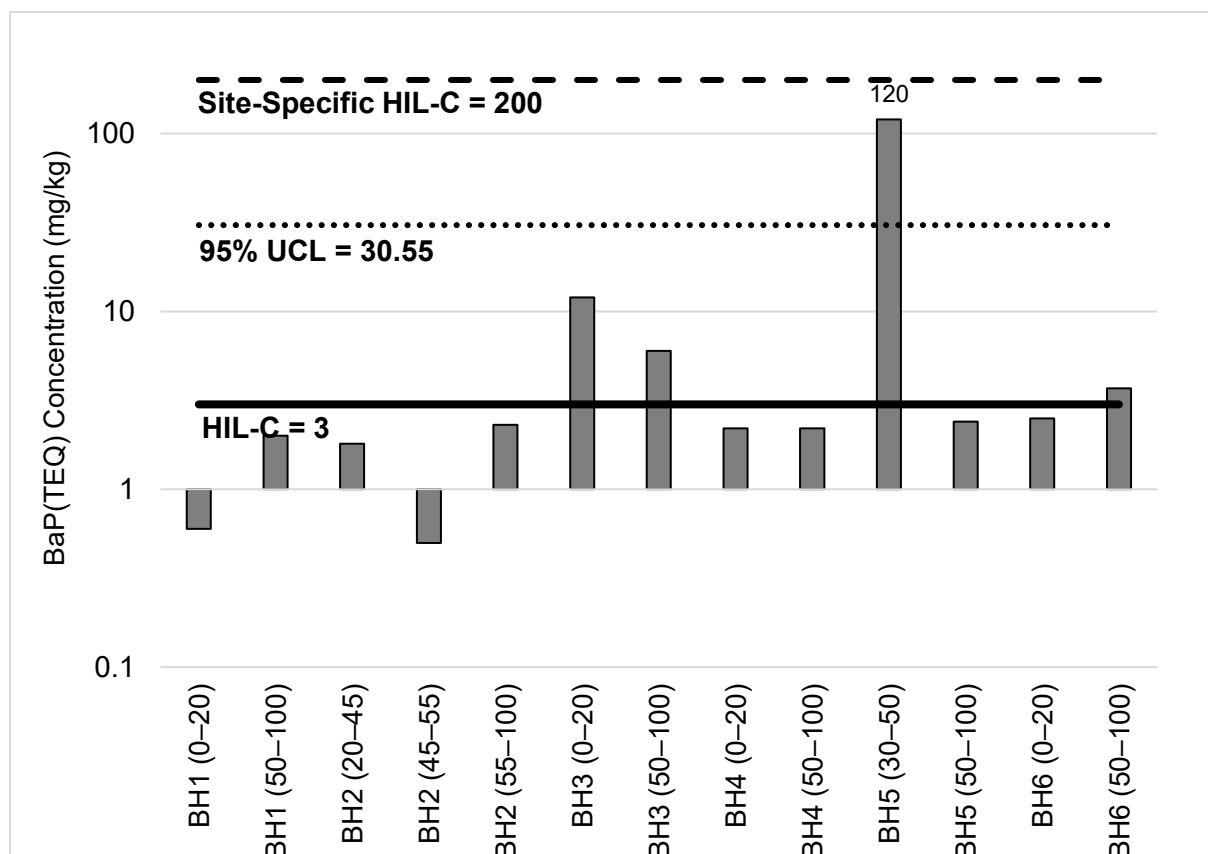
BaP(TEQ) concentrations exceeded the generic Tier 1 HIL-C (3 mg/kg) in several samples, with a maximum concentration of 120 mg/kg in fill material at 0.3–0.5 m depth (Figure 1). Total PAHs reached 1,200 mg/kg in isolated fill horizons.

Despite exceedances of the generic HIL-C, TCLP leachate concentrations for BaP were <0.0001 mg/L, indicating negligible mobility. Calculated oral bioavailability derived from mass transfer modelling was <0.08%. PAH fingerprinting demonstrated strong correlation with coal ash and coke residues rather than recent petroleum sources. Data distribution was lognormal, with a 95% UCL for BaP(TEQ) of 30.55 mg/kg. Using conservative assumptions

( $BA_o = 5\%$ ;  $DAF = 2.6\%$ ), a site-specific BaP(TEQ) HIL-C of 200 mg/kg (young child exposure) and 700 mg/kg (adult exposure) was derived.

All measured concentrations were substantially below the derived site-specific HIL-C (200 mg/kg), and the 95% UCL (30.55 mg/kg) also remained well below the refined threshold (Figure 1).

The findings demonstrate strong sorptive binding of BaP within ash-derived matrices in variable charge fill soils, limiting both mobility and bioavailability. Despite frequent soil–human contact in this recreational setting, exposure pathways are incomplete or negligible under current and proposed land use.



**Figure 1. BaP(TEQ) concentrations in surface and subsurface soils compared with the generic HIL-C (3 mg/kg), the derived site-specific HIL-C (200 mg/kg), and the 95% Upper Confidence Limit (UCL = 30.55 mg/kg) for public open space.**

## CONCLUSIONS

Generic Tier 1 HIL-C exceedances for BaP in historical urban fill do not necessarily equate to unacceptable human health risk. A multiple lines of evidence approach incorporating leachability, source fingerprinting, statistical evaluation and site-specific exposure modelling can substantially refine risk characterisation.

This case study highlights the importance of understanding contaminant–soil interactions in variable charge environments, particularly where reactive oxide and carbonaceous surfaces govern sorption behaviour. Adoption of site-specific criteria avoided unnecessary soil removal from a heavily used public recreational reserve and supported proportionate risk management decisions.

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# Sources, Speciation and Environmental Behaviour of PFAS in Variable-Charge Soils

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**Keywords:** PFAS; Variable-charge soils; Iron and aluminium oxides; Sorption mechanisms; Bioavailability; Groundwater risk

## 1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are persistent synthetic fluorinated compounds extensively used in aqueous film-forming foams, surface treatments, industrial processes, wastewater sludge applications, and consumer products. Their environmental persistence and mobility have resulted in widespread soil contamination globally (Naidu et al., 2025).

While PFAS–soil interaction studies have largely focused on temperate, permanently charged clay systems, comparatively limited attention has been directed to variable-charge soils enriched in iron (Fe) and aluminium (Al) oxides (Campos-Pereira et al., 2023). These soils exhibit pH-dependent surface charge behaviour that significantly alters PFAS sorption, transport, and bioavailability (Oliver et al., 2019). Understanding these mechanisms is particularly important for tropical, subtropical, and island environments where such soils dominate.

## 2. Sources and Entry Pathways

PFAS enter soils through multiple anthropogenic pathways including application of firefighting foams, land application of biosolids, irrigation with contaminated groundwater, atmospheric deposition, and landfill leachate migration. In high rainfall and coastal systems, shallow groundwater tables increase vulnerability to vertical and lateral migration (Umeh and Naidu, 2025).

## 3. Physicochemical Controls

PFAS behaviour is strongly influenced by molecular structure and soil properties (Xu et al., 2023). Short-chain PFAS exhibit higher solubility and mobility, whereas long-chain PFAS display stronger retention through hydrophobic and electrostatic interactions. Soil organic carbon contributes to sorption, but mineralogical composition plays a dominant role in variable-charge soils (Kookana et al., 2022).

## 4. Variable-Charge Soil Interactions

Variable-charge soils (e.g., Ferralsols, Oxisols, Ultisols) are dominated by Fe and Al oxides such as goethite, hematite, and gibbsite. These minerals exhibit pH-dependent surface charge and strong surface reactivity.

Under acidic to moderately acidic conditions, oxide surfaces often carry net positive charge, promoting electrostatic attraction of anionic PFAS. Sorption mechanisms include electrostatic attraction, ligand exchange, surface complexation, and mineral–organic interactions. These controls differ fundamentally from permanently charged clay systems (Wisawapipat et al., 2010).

### **5. Mobility and Groundwater Risk**

Despite enhanced sorption potential in oxide-rich soils, mobility remains influenced by pH shifts, competitive adsorption (e.g., phosphate), ionic strength, and extreme rainfall events. Short-chain PFAS remain highly mobile and pose persistent groundwater contamination risks, particularly under climate-driven hydrological variability (Campos-Pereira et al., 2020).

### **6. Bioavailability and Plant Uptake**

Short-chain PFAS demonstrate greater plant uptake potential. Rhizosphere processes can modify pH and surface charge, potentially enhancing desorption. Understanding dynamic interactions in agricultural systems developed on variable-charge soils is essential for managing food-chain risks (Odoh et al., 2020).

### **7. Implications for Risk Assessment and Remediation**

Risk-based frameworks should incorporate mineralogical composition, point of zero charge (PZC), oxide content, and seasonal pH dynamics. Remediation strategies must account for pH-dependent surface charge behaviour and competitive adsorption processes to ensure effective contaminant stabilization or removal.

### **8. Research Gaps**

Further research is required to quantify sorption processes in oxide-dominated systems, model long-term desorption kinetics, evaluate competitive interactions with nutrients, and integrate mineralogical parameters into predictive transport models under tropical rainfall regimes.

### **9. Conclusions**

PFAS behaviour in variable-charge soils is governed by complex electrochemical and mineralogical controls distinct from temperate clay systems. Incorporating these mechanisms into risk assessment and remediation frameworks is critical for managing contamination in tropical and island environments where such soils predominate.

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## SOIL SURFACE CHARGE VARIATION IN AGRICULTURAL SOILS: EFFECT OF BIOCHAR APPLICATION IN DIFFERENT LAYERS

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### INTRODUCTION

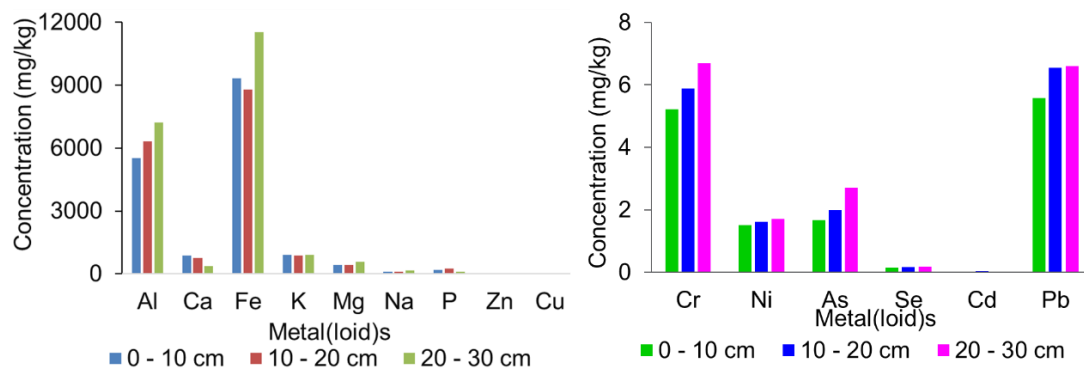
Nutrients management is always an important part of agricultural crop production. Various factors including surface charge, pH and ionic strength significantly affects on plant available nutrients in agricultural soils (Barrow & Hartemink, 2023; Sollins et al., 1988). In addition, heavy metals mobility and sorption by soils also depends on various factors like pH, surface charge etc. (Appel & Ma, 2002). Soils surface charge greatly varied with pH changes. Application of biochar (as a nutrients supplements) can increase soils pH which might changes soil surface charge and ultimately affects on plant nutrients availability and crop yield. Last few decades, biochar from various sources have been used in agricultural field as a source of plant nutrients and remediation of contaminants from the soils (Cheng et al., 2020; Das & Ghosh, 2023; Jassal et al., 2015; Tang et al., 2013). This study investigates the role of biosolid derived biochar application in controlling soil surface charge behaviour in different layers of agricultural soils.

### MATERIALS AND METHODS

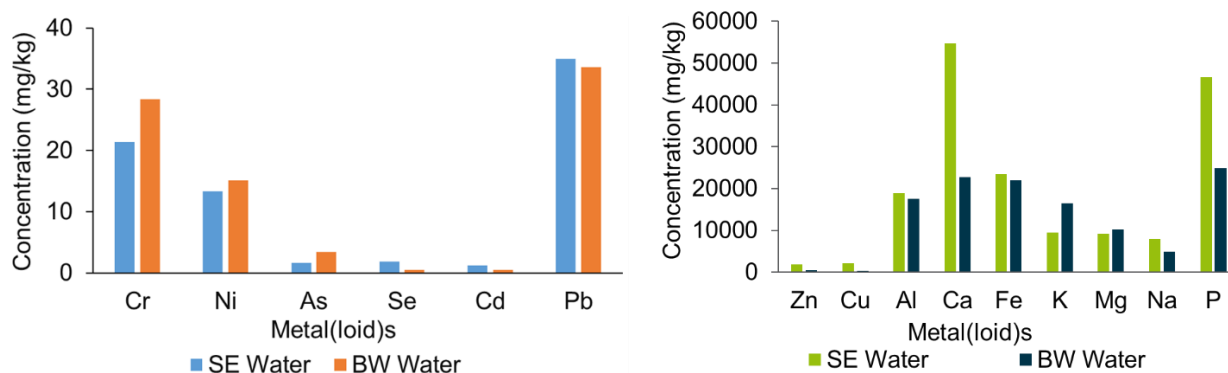
Two different biosolid derived biochar and agricultural soils from different layers were used without further modification or purification. Physicochemical properties of soils and biochar were characterised using analytical-grade chemicals from Sigma-Aldrich, Australia (Table 1). Biochar from different sources were mixed separately (5% volumetric basis) with soils collected from two different layers and repack into column following sand on the bottom layer, untreated soil in the 20-30 cm depth and biochar treated soils following 10-20 and 0-10 cm respectively and allow them for nine months in wet condition for weathering. The soils were collected separately from different layers and plant nutrients, heavy metals contents and physicochemical properties including surface charge were calculated (Figure 1 & 2).

**Table 1. Physicochemical properties of soils and biochar**

Sample name	Moisture (%)	pH	EC ( $\mu\text{s}/\text{cm}$ )
Soil (0-10 cm)	4.40	5.74	102.80
Soil (10-20 cm)	7.74	6.00	114.41
Soil (20-30 cm)	11.25	6.26	134.67
SE-Water Biochar	2.86	10.58	481.01
Barwon Water Biochar	23.26	9.38	444.83



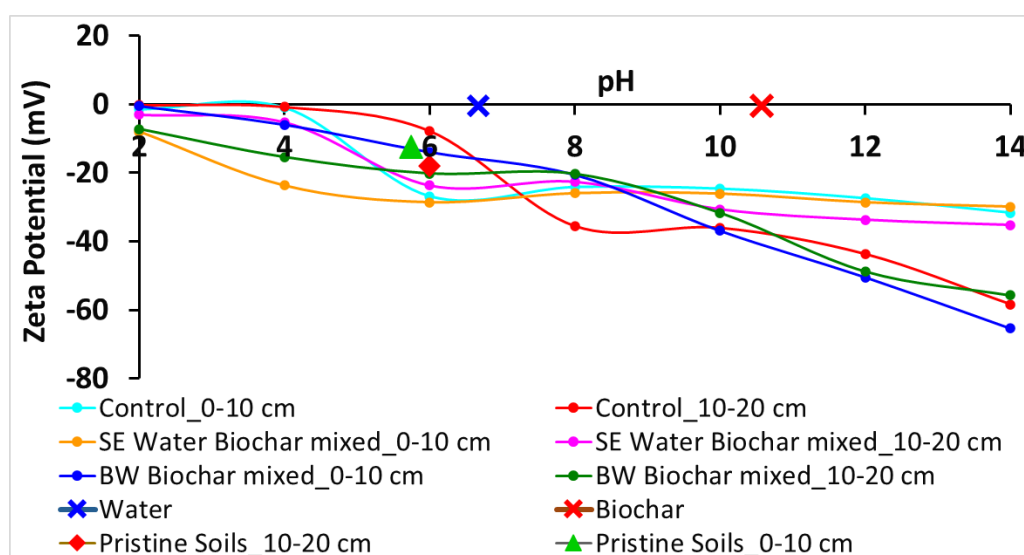
**Figure 1. Metal(loid)s concentration in different layers of soil samples**



**Figure 2. Metal(loid)s concentration in different layers of soil samples**

## RESULTS AND DISCUSSION

The zeta potential of raw and biochar treated soils with various pH conditions are presented in Figure 2. Both control and biochar treated soils from different layers revealed negative charge at pH 2, which gradually increased with pH, though SE Water supplied biochar treated soils showed relatively lower negative charge compared with Barwon Water supplied biochar treated soils for both soil layers. Pristine soils of two different layers (0-10 & 10-20 cm), biochar and water revealed their own pH as 5.74, 6.00, 10.58 and 6.67 and zeta potential at their own pH were recorded as -12.34, -18.01, -0.36 and -0.31 respectively.



**Figure 3. Zeta potential of pristine and biochar treated soils from different layers**

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# SOIL SURFACE CHARGE DYNAMICS UNDER PFAS CONTAMINATION: INTERACTIVE EFFECTS OF BIOCHAR AND ORGANIC AMENDMENTS

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## Introduction

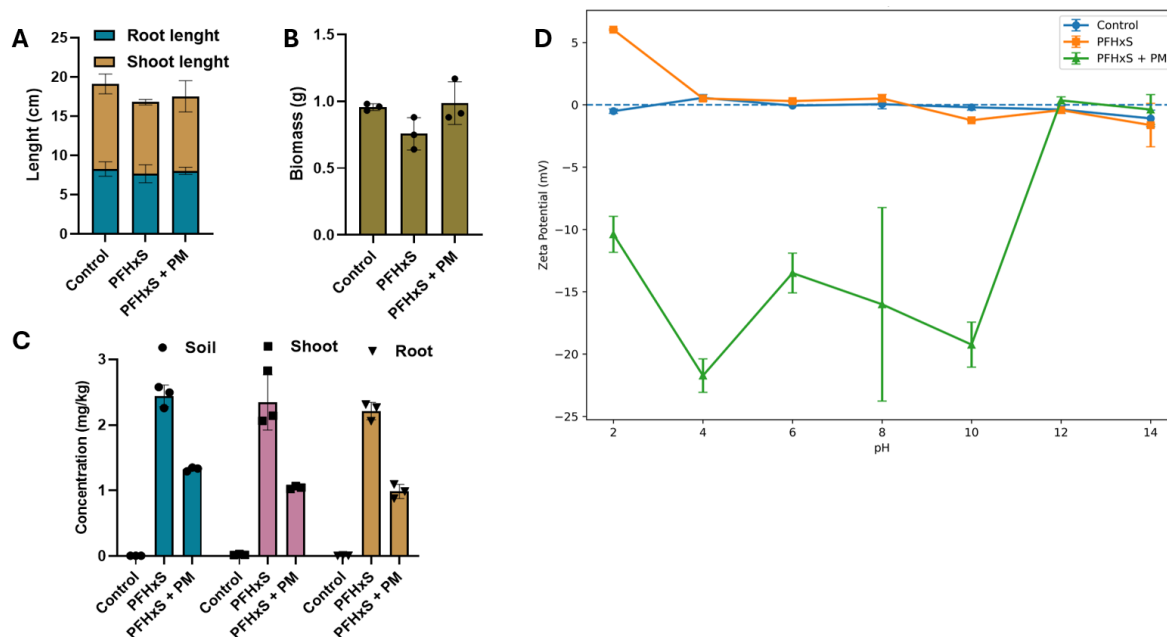
Perfluorohexane sulfonic acid (PFHxS) is frequently detected in agricultural soils, posing substantial risks to food production and human health given its high persistence and accumulative nature. The bioavailability of PFHxS in soil is determined by its mobile fraction within soil porewater and significantly influenced by soil properties. The soil surface charges (SSC) can influence bioavailability of PFHxS as electrostatic interaction plays important role in PFHxS retention in soils. Using Zeta potential ( $\zeta$ -potential), we measured the electrokinetic potential at the shear plane of particles, to examines surface charges in PFHxS-contaminated soil amended with potting mix (PM). The phytotoxicity response and uptake dynamics were also investigated.

## Materials and Method

Soil samples were spiked with 5 mg/kg of PFHxS and blended with potting mix and grown with lettuce for 8 weeks. After harvesting, the root and shoot lengths, plant biomass, were measured. PFHxS was extracted from soil and plant tissues using deionized water, acetonitrile,  $\text{MgSO}_4$ , and NaCl, followed by evaporating the filtrates and reconstituting them with 1 ml of methanol for analysis. For zeta potential analysis, 20 mg of soil was weighed into 20 ml of MQ water (0.1% w/v). The pH was adjusted ranging 2–14 and the suspension were shaken overnight at 120 rpm and sonicated for 15 minutes. The suspension was then analyzed using a zeta/nano particle analyzer. Zeta potential values (mV) were measured in duplicate with mean values and standard deviations reported.

## Result and Discussion

Figures A–D integrate plant performance, contaminant dynamics, and soil electrokinetics. The control soil exhibited consistently negative  $\zeta$ -potentials across the pH range, reflecting a stable clay–organic colloidal system. PFHxS spiking markedly altered this electrokinetic equilibrium, increasing the magnitude and variability of negative  $\zeta$ -potential, indicative of an enhanced electrostatic repulsion within the soil matrix. This shift promoted greater PFHxS persistence in porewater, elevating plant exposure. Correspondingly, root elongation, shoot growth, and biomass declined significantly (Figures A and B), concurrent with increased PFHxS accumulation in plant tissues (Figure C). These results demonstrate that electrokinetic alteration could directly amplifies phytoavailability and toxicity. Pot Mix (PM) further reduced PFHxS mobility by providing organic binding sites that promoted retention and lowered bioavailability (Figure D).



## Conclusion

Collectively, these results establish soil electrokinetic regulation as a primary mechanistic driver of PFHxS bioavailability, plant accumulation, and phytotoxic expression.

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