EFFECT OF ACID RAIN ON SOIL BASIC CATIONS IN COASTAL PLAIN SAND PARENT MATERIAL

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A PROJECT WORK SUBMITTED TO THE DEPARTMENT OF SOIL SCIENCE AND LAND MANAGEMENT, FACULTY OF AGRICULTURE, UNIVERSITY OF BENIN CITY IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF BACHELOR OF AGRICULTURE DEGREE (SOIL SCIENCE) OF UNIVERSITY OF BENIN, EDO STATE, NIGERIA

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CERTIFICATION

This is to certify that this Project work titled "**EFFECT OF ACID RAIN ON SOIL BASIC CATIONS IN COASTAL PLAIN SAND PARENT MATERIAL**" was carried out by **God'swill Uchechukwu HYCINTH** with Matriculation Number **AGR1900342**, of the Department of Soil Science and Land Management, Faculty of Agriculture, University of Benin, Benin City, Edo State, Nigeria.

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DEDICATION

This project work is dedicated to God Almighty, for His infinite mercies upon my life, and to my supportive parents, Mr. and Mrs. Hycinth Okenyehike.

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A very special thanks to Almighty God for His love and providence upon my life. I thank my parents, Mr. and Mrs. Hycinth Okenyehike, and my siblings for their love, financial and spiritual support.

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ABSTRACT

Acid rain significantly impacts soil chemistry, particularly the availability of essential basic cations such as calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and potassium (K^+). This study examines the effect of acid rain on soil basic cations within coastal plain sand parent material at three locations in the University of Benin, Edo State, Nigeria.

Soil samples were collected from two depths (0-30 cm and 30-60 cm) in three different locations and were analyzed for some soil physical and chemical properties using standard procedure, while rain water samples were collected from the same locations and were analyzed for pH. The results indicated a general decrease in soil pH with depth, with JSQ showing the highest mean pH (5.65), followed by Hall 2 (5.31) and AGR 305 (5.10). The lowest pH (4.77) was recorded at 30-60 cm in AGR 305, suggesting increased acidification and leaching effects. Exchangeable cation analysis revealed calcium as the dominant cation, with mean values of 0.73 cmol/kg at JSQ, 0.64 cmol/kg at Hall 2, and 0.57 cmol/kg at AGR 305. Magnesium levels ranged from 0.14 to 0.32 cmol/kg, with JSQ (0.26 cmol/kg) near the critical threshold (0.2 cmol/kg), while Hall 2 (0.19 cmol/kg) and AGR 305 (0.18 cmol/kg) indicated possible deficiencies. Sodium and potassium levels remained close to the critical limits across all locations, with potassium at 0.23 cmol/kg in JSQ, 0.17 cmol/kg in Hall 2, and 0.16 cmol/kg in AGR 305.

CHAPTER ONE

1.0 INTRODUCTION

The coastal plain regions, characterized by sandy soils and diverse ecosystems, are increasingly vulnerable to environmental stressors, particularly acid rain. This phenomenon is a direct result of human activities, including industrial emissions and vehicular pollution, which release sulfur oxides (SO_x) and nitrogen oxides (NO_x) into the atmosphere. These pollutants react with water vapor, oxygen, and other chemicals, forming sulfuric and nitric acids. When these acids fall to the ground as precipitation, they can significantly alter the pH of the affected areas, leading to a variety of ecological consequences (Leal *et al*., 2023).

Acid rain poses a serious threat to soil health, particularly in coastal plains where sandy soils have limited buffering capacity. The low nutrient retention of these soils makes them especially susceptible to leaching caused by acidic precipitation. As the pH of the soil decreases, essential nutrients, including basic cations (BCs), are lost more readily. The leaching of these nutrients can severely impact soil fertility and disrupt the delicate balance necessary for healthy plant growth (Akpan-Idiok and Ukwang, 2012).

Basic cations, such as calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), and sodium (Na^+), are crucial for various physiological functions in plants, including nutrient uptake and enzyme activation. When acid rain leaches these cations from the soil, plants may experience nutrient deficiencies, which can lead to reduced growth and lower productivity. Also, the loss of cations can affect soil structure and water retention, further exacerbating the challenges faced by coastal plain ecosystems (Yang *et al*., 2011). Given the increasing frequency and intensity of acid rain events, it is essential to assess its effects on basic cation levels in coastal plain sand.

1.1 Objectives of the Study

The main objective of this study was to determine effect of acid rain on soil basic cations in coastal plain sand parent material. While specific objectives were to determine;

i.) the pH levels of precipitation in each location.

ii.) some physical and chemical characteristics of the soils.

iii.) relationship between soil basic cations and some soil physical and chemical properties.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Acid Rain and Soil Chemistry

Acid rain has been a well-documented environmental issue since the 1960s, primarily due to industrial emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x). These pollutants combine with water vapor in the atmosphere to form sulfuric acid (H_2SO_4) and nitric acid (HNO_3), which, when deposited on the ground, can significantly alter soil chemistry. Soil pH decreases as hydrogen ions (H^+) accumulate in the soil system (Liu *et al.*, 2018). This increase in H^+ concentration leads to the leaching of cations and anions from the soil, with their solubility being influenced by the soil's pH (Bakhshipour *et al.*, 2016).

Despite efforts to reduce industrial emissions in certain regions, the persistent effects of acid rain on soil chemistry remain a significant environmental concern, especially in areas with vulnerable sandy soils. Basic cations such as calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), and sodium (Na^+) are essential to soil fertility and plant health. These cations play crucial roles in soil structure, nutrient cycling, and plant metabolism. Their availability directly influences ecosystem productivity, affecting both natural vegetation and agricultural crops (Wang *et al.*, 2010).

In coastal plain sand, which are often characterized by sandy soils derived from unconsolidated parent materials, acid rain poses a particularly severe threat. These soils typically have low organic matter content and minimal clay content, resulting in a low cation exchange capacity (CEC). This makes them less able to retain and supply essential nutrients like calcium, magnesium, sodium and potassium, rendering them more susceptible to nutrient leaching when acid rain increases the concentration of hydrogen ions (H^+) in the soil. As a result, these soils undergo rapid acidification, depleting essential cations and disrupting the overall soil fertility.

2.2.1 Formation of Acid Rain

Acid rain forms as a result of chemical reactions, primarily driven by anthropogenic activities such as industrial emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x). These gases react in the atmosphere to produce strong acids like sulfuric acid (H_2SO_4) and nitric acid (HNO_3), which can fall as acid rain, fog, or snow, significantly altering soil and water chemistry upon deposition (Leal *et al*., 2023). In coastal plain sand, where natural processes are delicately balanced, the introduction of acid rain can lead to significant soil acidification. This disrupts the cation composition and nutrient availability, ultimately threatening ecosystem health (Liang *et al*., 2020). Coastal plain soils are typically sandy, low in organic matter, and vulnerable to rapid changes in pH, making them especially sensitive to external stressors such as acid rain.

Soil acidity is a reflection of the relative distribution of acidic (H^+, Al^{3+}) and basic (Ca^{2+}, Mg^{2+}, K^+, and Na^+) cations, with the capacity to neutralize acidity largely dependent on the availability of exchangeable calcium (Ca^{2+}) and magnesium (Mg^{2+}) (Tian and Niu, 2015). In these ecosystems, acid rain not only lowers soil pH but also accelerates the leaching of essential base cations, which are crucial for soil fertility and plant growth. As hydrogen ions (H^+) accumulate, they replace these base cations on soil particles, further reducing the soil's cation exchange capacity (CEC) and impairing its ability to retain vital nutrients (Chadwick and Chorover, 2001).

2.2.2 Acid Rain Characteristics and Regional Variations

The intensity and impact of acid rain vary significantly across regions, influenced by factors such as local emissions, climate patterns, and geography. In industrialized areas, high levels of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) from industrial activities and vehicle emissions have led to significant acid deposition. Similarly, in rapidly developing regions like parts of Africa, including Nigeria, acid rain is emerging as a growing environmental concern due to increasing industrialization and urbanization.

In Nigeria, the environmental impact of acid rain is compounded by industrial activities, particularly oil extraction and gas flaring. The U.S. Department of Energy estimates that since 1960, over 4,000 oil spills have occurred in Nigeria, releasing millions of barrels of crude oil into the rivers, streams, and wetlands of the Niger Delta (Mayah, E., 2006). These spills have caused long-term environmental damage, degrading soil quality, water resources, and local biodiversity. Additionally, gas flaring, a common byproduct of oil production, releases acidic gases into the atmosphere, further contributing to acid rain formation (Nduka *et al*., 2021).

As a result, the combined effects of industrial pollution, including acid rain, pose a serious threat to the region's agricultural productivity, degrade biodiversity, and represent a significant public health risk for communities that depend on these ecosystems for their livelihoods (Amaize, 2007).

2.3 Soil Chemistry and Cation Exchange Capacity (CEC)

2.3.1 Soil Properties in Coastal Plains Sand

The Coastal Plain Sand (Benin Formation) consist predominantly of continental sand and sandtones (> 90%), with occasional shale intercalations, and a minimum thickness of 1830 meters (Nton and Esua, 2010). These sands are typically coarse-grained, ranging from pebbly to very fine-grained, subangular to well-rounded, poorly sorted, and white due to limonite coatings (Nton and Esua, 2010). Coastal plain soils are mainly characterized by their sandy texture, low organic matter content, and low cation exchange capacity (CEC). These properties make them particularly susceptible to external environmental stressors, such as acid rain. The parent material of coastal plain soils is primarily sand, which has relatively large particles and limited surface area compared to finer-textured soils like clay. This limits the number of available sites for the adsorption and retention of nutrients and minerals (Brady and Weil, 2016). Sandy soils, therefore, have a lower ability to hold onto essential nutrients, making them more vulnerable to nutrient leaching. One of the most significant soil properties is cation exchange capacity (CEC), which refers to the soil's ability to exchange cations such as calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^{+}), and sodium (Na^{+}). These cations play essential roles in plant nutrition, influencing processes such as osmoregulation and enzyme function. CEC is a measure of the number of negatively charged sites in the soil available to bind cations (Rashidi and Seilsepour, 2008). In soils with low CEC, such as those in coastal plains, nutrients are more easily leached away by rainfall or irrigation, as the soil cannot retain them effectively.

Coastal plain soils are also highly weathered, with textures ranging from coarse to fine, and are characterized by acidic conditions, low base saturation, and multiple nutrient deficiencies. In the Southeastern United States, coastal plain soils are classified as Ultisols under USDA Soil Taxonomy. These soils are typically low in fertility due to their sandy texture, acidic pH, kaolinitic clays, low CEC, and low organic carbon content (Akpan-Idiok and Ukwang, 2012).

As acid rain increases, the already low levels of organic matter and clay in coastal plain soils exacerbate their inability to act as buffers against acidity. This further compound the challenges these ecosystems face, resulting in severe disruptions to nutrient cycling and soil fertility.

2.3.2 Cation Exchange Mechanisms

Cation exchange capacity (CEC) is a soil property that allows it to bind positively charged ions (cations). In another words is a measure that expresses the ability of the soil to adsorb cations, and corresponding with plants capability of absorbing nutrients through the roots in ionic form (Jones and Kathrin, 2016).This is a very important property of the soil that affects the stability of structural aggregates, availability of nutrients for plants, regulates pH of the soil, as well as the reaction of the soil affected by fertilization and the addition of other ameliorants (Hazelton *et al.,* 2007).

A key factor in cation exchange is the role of hydrogen ions (H^+). In soils with lower pH, such as those impacted by acid rain, the concentration of H^+ increases. These excess hydrogen ions compete with basic cations, such as calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+) and potassium (K^+), for binding sites on soil particles. As a result, the increased acidity displaces the basic cations from the exchange sites, making them more mobile in the soil solution and more likely to be leached away by rainfall. In coastal plain sand ecosystems, the rapid leaching of cations due to increased acidity can further reduce soil fertility. For example, calcium, which is vital for plant growth and maintaining soil structure by promoting aggregation and reducing erosion, is leached away. This weakens the soil structure, making it more prone to erosion by wind and water, which exacerbates soil degradation (Liu *et al*., 2018).

2.4 Effects of Acid Rain on Soil Chemistry

2.4.1 Soil pH Changes

The primary effect of acid rain on soils is a significant decrease in soil pH, a process known as soil acidification. Research by Yang *et al.* (2011) indicates that acidification leads to nutrient leaching, particularly of calcium and magnesium, while also increasing the solubility and toxicity of metals like aluminum and lead. This can reduce soil fertility, harm plant root systems, and negatively impact plant growth and crop yields (Dai *et al*., 2015).

Acid rain, composed of sulfuric acid (H_2SO_4) and nitric acid (HNO_3), dissociates in the soil, releasing hydrogen ions (H^+) that lower the soil pH. As soil pH decreases, the solubility of toxic elements like aluminum (Al^{3+}) increases, while the availability of essential plant nutrients like calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+) and sodium (Na^+), decreases (Liu *et al.*, 2018). This is particularly concerning for coastal plain soils, which often have low buffering capacity due to their sandy texture and low organic matter content, making them especially vulnerable to acidification.

pH Before-and-After Exposure to Acid Rain

Soil pH plays a critical role in the availability of calcium and other cations. Acid rain introduces hydrogen ions (H^+) into the soil, which displace these cations from the soil's exchange sites, leading to increased nutrient leaching. A study by Jalali and Naderi Peikam (2022) on calcareous sandy loam soils observed significant changes in soil pH before and after exposure to simulated acid rain at various pH levels.

- **Before exposure**: The initial soil pH was 6.8, which is near neutral.
- **After exposure**: After 40 days of exposure to acid rain, the soil pH dropped to 5.1 at the lowest pH treatment (acid rain with pH 4.5). In contrast, soils exposed to neutral pH rain (pH 7.0) saw a more modest decrease, with pH dropping to 6.3.

As soil pH decreases, essential nutrients like calcium, magnesium, potassium, and sodium become less available for plant uptake. These nutrients, typically held on the soil's negatively charged cation exchange sites, are displaced by hydrogen ions (H^+) as the pH drops, making them more susceptible to leaching.

2.4.2 Leaching of Basic Cations

As the concentration of hydrogen ions (H^+) increases in the soil due to acid rain, a series of chemical reactions occurs that leads to the displacement of basic cations from the soil's cation exchange sites. This process, known as cation exchange, is an essential mechanism by which plants acquire nutrients. In healthy, unacidified soils, basic cations like calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and potassium (K^+) are held in place by the negatively charged sites on soil particles, where they can be exchanged with plant roots for uptake. However, when acid rain deposition occurs, the increased concentration of H^+ ions mobilizes heavy metals and aluminum (Al), making them more soluble in the soil (Zheng *et al.*, 2012). The accumulation of H^+ ions displaces basic cations from the exchange sites, enhancing their leaching and further reducing soil fertility (Zhang *et al.*, 2015).

When acid rain introduces large quantities of H^+ ions into the soil solution, these ions effectively “push” the basic cations off the exchange sites, making the cations more mobile and prone to leaching through rainfall or irrigation (Tian and Niu, 2015). This process is particularly pronounced in sandy soils, such as those found in coastal plains, which have a naturally low cation exchange capacity (CEC) and poor water retention abilities. According to Nawaz *et al.* (2012), the leaching of base cations from soils is influenced not only by the pH of acid rain but also by soil properties such as CEC, texture, and the initial concentration of base cations. In coastal plain ecosystems, where soils typically have low CEC and poor water retention, the effects of acid rain induced leaching are particularly severe. This exacerbates nutrient depletion, undermining soil fertility and hindering plant growth.

2.4.3 Impact of Aluminum Toxicity

One of the most significant ecological and agronomic issues associated with soil acidification is the release of soluble aluminum ions (Al^{3+}). Aluminum is a primary factor in reducing crop yields in acid soils (Kochian *et al.*, 2005). As soil pH decreases due to acid rain, aluminum, which is typically insoluble in neutral or alkaline soils, becomes more soluble. This occurs because hydrogen ions (H^+) from acid rain displace aluminum ions from their adsorption sites on soil particles, converting them into soluble Al^{3+}. In acidified soils, the increased concentration of aluminum can have toxic effects on plant roots, severely impairing plant growth and nutrient uptake.

Aluminum toxicity is particularly problematic in coastal plain sand, which are often already deficient in essential nutrients like calcium, magnesium, and potassium, and are more prone to acidification due to their low buffering capacity. As the concentration of soluble Al^{3+} rises, it can damage the integrity of plant root cell membranes, impairing their ability to absorb water and nutrients. In severe cases, the accumulation of soluble aluminum can lead to root death, resulting in poor plant growth and reduced agricultural productivity (Nawaz *et al*., 2012).

2.5 Effects on Basic Cations in Coastal Plain Sand Parent Material

2.5.1 Calcium Depletion and Leaching

Calcium (Ca^{2+}) is a crucial basic cation in soils, playing a key role in maintaining soil structure, facilitating nutrient uptake, and supporting plant growth. In soils, calcium helps bind particles together to form aggregates, which enhance soil porosity, improve water infiltration, and reduce soil erosion. Additionally, calcium contributes to plant health by promoting cell wall integrity, enzyme activation, and stress tolerance (Tooth, J., 2023). However, calcium is highly susceptible to depletion, especially in the presence of acid rain, which accelerates its leaching from soils. This effect is particularly pronounced in sandy soils with low organic matter content.

Calcium Levels After Exposure to Acid Rain

The research by Jalali and Naderi Peikam (2022) documented the effect of acid rain on calcium levels in the soil, showing that calcium leaching increases significantly as the pH of the rain decreases, highlighting a clear relationship between soil acidity and calcium loss.

After exposure:

At pH 2.5 (highly acidic), the calcium loss was 361.8 mg kg^{-1}.

At pH 7.0 (neutral), the calcium loss was 116.5 mg kg^{-1}.

Consequences of Calcium Depletion in Soil

The depletion of calcium due to acid rain exposure can have several negative effects on soil health and plant growth:

- **Soil Structure and Fertility**: Calcium plays a vital role in maintaining soil structure by promoting aggregation and improving porosity. Its loss can degrade soil structure, making the soil more prone to erosion and reducing its ability to retain water and nutrients.
- **Reduced Soil Quality**: As calcium is leached away, the soil may lose important properties, such as cation exchange capacity (CEC), which are essential for supporting plant growth. Over time, this can lead to a decline in soil fertility.
- **Long-term Degradation**: Prolonged exposure to acid rain can result in long-term soil degradation, impairing soil quality and making it harder for plants to access vital nutrients. This ultimately impacts agricultural productivity and ecosystem health

2.5.2 Magnesium Depletion and Leaching

Magnesium (Mg^{2+}) is an essential macronutrient required in large quantities by plants for growth and reproduction. It is a key component of chlorophyll, the molecule responsible for photosynthesis, and plays a crucial role in maintaining plant health, regulating enzymatic processes, and promoting optimal growth (Gransee *et al.*, 2013). Magnesium also enhances agricultural yields and is critical for various metabolic functions. However, in coastal plain sand, magnesium is particularly vulnerable to leaching, especially in the presence of acid rain

Magnesium Levels After Exposure to Acid Rain

Research conducted by Jalali and Naderi Peikam (2022) on calcareous sandy loam soils documented the effect of acid rain on magnesium levels. The study found that magnesium leaching increased significantly as the pH of the acid rain decreased, indicating that more acidic conditions lead to greater magnesium loss.

After exposure:

- At pH 2.5 (strongly acidic), the magnesium loss was 156.1 mg kg^{-1}.
- At pH 7.0 (neutral), the magnesium loss was 64.9 mg kg^{-1}.

Consequences of Magnesium Depletion in Soil

The depletion of magnesium due to acid rain exposure can have several negative impacts on plant health and soil quality:

- **Impaired Photosynthesis**: Magnesium is central to chlorophyll production. Its deficiency reduces a plant's ability to carry out photosynthesis, resulting in reduced energy production and compromised growth potential (Gransee *et al.*, 2013).
- **Chlorosis**: Magnesium-deficient plants often show symptoms of chlorosis, where the leaves yellow due to reduced chlorophyll content. This further impairs the plant's ability to generate energy and reduces overall vitality.
- **Reduced Crop Yields**: In agricultural systems, magnesium deficiency can stunt plant growth, reduce crop yields, and lower plant resilience to environmental stresses such as drought and heat, ultimately affecting food production.

2.5.3 Potassium Depletion and Leaching

Potassium (K^+) plays a critical role in regulating plant water balance, enzyme activation, and stress responses. It is essential for the opening and closing of stomata, which control the exchange of water vapor, oxygen, and carbon dioxide in plant leaves. Proper potassium levels are crucial for maintaining optimal water regulation and gas exchange, both of which are vital for plant health and growth (Kaiser and Rosen, 2018). When potassium is deficient, this balance is disrupted, leading to poor growth, water stress, and reduced crop yields.

In coastal plain regions, potassium depletion is a common issue due to low cation exchange capacity (CEC) and high soil permeability. These soils are more prone to leaching from heavy rainfall or irrigation, which can wash away potassium before plants can absorb it fully. This problem is further exacerbated by acid rain, which accelerates potassium leaching, reducing its availability to plants. This leads to impaired water regulation, reduced stress tolerance, and disruptions in essential metabolic processes (PDA, 2019).

Potassium Levels After Exposure to Acid Rain

The effects of acid rain on potassium leaching were clearly demonstrated in the research by Jalali and Naderi Peikam (2022), which examined calcareous sandy loam soils. The study found that potassium leaching increased significantly as the pH of the acid rain decreased, confirming that more acidic conditions promote potassium depletion from the soil.

After exposure:

At pH 2.5 (strongly acidic), potassium loss was 31.8 mg kg^{-1}.

At pH 7.0 (neutral), potassium loss was 17.5 mg kg^{-1}.

Consequences of Potassium Depletion in Soil

Potassium depletion due to acid rain exposure can have significant negative impacts on plant health and agricultural productivity:

- **Water Stress and Drought Sensitivity**: Potassium is essential for regulating plant water balance by controlling stomatal function. When potassium levels are low, plants are less efficient at managing water loss, making them more vulnerable to water stress, drought, and high salinity—conditions commonly found in coastal areas (PDA, 2019)

- **Impaired Metabolic Functions**: Potassium activates enzymes involved in crucial metabolic processes like photosynthesis, protein synthesis, and nutrient uptake. A deficiency in potassium hampers these processes, resulting in stunted growth and weakened plant vigor.
- **Reduced Crop Yields and Ecosystem Health**: Potassium-deficient plants often show poor growth, chlorosis (yellowing of leaves), and reduced productivity. This is particularly concerning in coastal areas, where diverse plant species are more sensitive to potassium deficiency. As a result, potassium depletion can lead to reduced biodiversity and lower agricultural yields (PDA, 2019).

2.5.4 Sodium Depletion and Leaching

Sodium (Na^+) is generally considered a non-essential cation for most plants, but it still plays a role in osmotic regulation and maintaining ion balance within plant cells. Although sodium is not required in large quantities, it can still influence soil properties and plant health.

Acid rain can influence sodium levels by altering the soil's cation exchange capacity (CEC) and increasing the mobility of sodium ions in the soil. Although sodium is less prone to leaching than other basic cations, such as calcium and magnesium, it can still be displaced from the soil's exchange sites by hydrogen ions (H^+) from acid rain, making it more susceptible to leaching under acidic conditions.

Sodium Levels After Exposure to Acid Rain

While sodium is less impacted by acid rain compared to other cations, its concentration in the soil leachates can still increase when the soil pH drops significantly. The research by Jalali and Naderi Peikam (2022) on soils exposed to varying pH levels demonstrated this effect.

After exposure:

At pH 2.5 (highly acidic), sodium leaching was recorded at 10.2 mg kg^{-1}.

At pH 7.0 (neutral), sodium leaching was much lower at 4.5 mg kg^{-1}.

2.5.5 Effects of Acid rain on Soil Organic Matter

Soil organic matter (SOM) is essential for soil fertility and long-term soil health. Composed of decomposed plant and animal material, as well as microbial by-products, Soil organic matter plays a key role in improving soil structure by binding soil particles together to form aggregates. These aggregates enhance water retention, increase pore space for air and roots, and improve soil aeration. Additionally, Soil organic matter serves as a major reservoir for plant nutrients, storing and gradually releasing essential elements like nitrogen, phosphorus, and sulfur. Under normal conditions, soil acidification caused by acid rain reduces soil organic matter content due to leaching. The more acidic the rain, the more pronounced the inhibition of soil organic matter will be, leading to its depletion (Pham *et al.*, 2020).

Acid rain-induced leaching of basic cations not only depletes essential soil nutrients but also accelerates the decline of soil organic matter. This is because organic matter is closely associated with the cation exchange process. Many organic molecules are bound to cations such as calcium, magnesium, and potassium for stability (Pham *et al.*, 2020). When these cations are leached away, soil organic matter becomes more susceptible to decomposition and leaching, creating a feedback loop where the depletion of soil organic matter further exacerbates soil degradation and fertility loss.

In coastal plain soils, which are typically low in organic content, the impact of acid rain on soil organic matter dynamics can be particularly severe. The reduction in Soil organic matter further weakens soil structure and decreases water-holding capacity, which accelerates nutrient leaching and soil erosion. Over time, this can lead to a rapid decline in soil fertility, adversely affecting agricultural productivity and diminishing the capacity of natural ecosystems to support plant growth.

2.6 Ecological Implications of Acid Rain on Coastal Plain Sand Parent Material

2.6.1 Impact on Flora and Fauna

The acidification of soils and the depletion of essential cations caused by acid rain can have profound and cascading effects on the flora and fauna of coastal plain ecosystems. Coastal plain sand, often characterized by sandy soils with low cation exchange capacity (CEC) and poor buffering capacity, are particularly vulnerable to the effects of acid deposition (Liu *et al*., 2018). As the soil becomes more acidic, the availability of essential nutrients such as calcium, magnesium, and potassium decreases, while the concentration of harmful elements like aluminum (Al^{3+}) increases. These changes in soil chemistry directly affect plant health and growth, which in turn impacts the animals and other organisms that rely on plants for food, shelter, and other ecological services. In plant communities, the early signs of stress caused by soil acidification include reduced root growth, chlorosis (yellowing of leaves), stunted growth, and poor nutrient uptake (Gransee *et al*., 2013). Many plant species, particularly those adapted to more neutral or slightly acidic soils, are especially sensitive to these changes. For example, species such as pine trees, which are common in coastal plain sand, may exhibit reduced root development and nutrient deficiencies under acidified conditions. This disrupts the plants' ability to access vital nutrients, leading to lower plant vitality and reproductive success (Gransee *et al*., 2013).

The aboveground parts of ecosystems, such as leaves and twigs, are often the first to show signs of stress from acid rain, as acid deposition occurs when rain, snow, or fog comes into contact with the environment. Previous studies have shown that acid deposition can damage the cuticular structure of plant leaves, reduce mesophyll conductance to CO_2, and limit photosynthesis and transpiration. Additionally, it increases cation leaching and water loss from foliage, all of which contribute to reduced aboveground productivity (Chen *et al*., 2013).

Soil is the final receptor of acid rain in terrestrial ecosystems, and thus, the belowground ecosystem is likely more sensitive to acid rain than the aboveground system (Chen *et al*., 2013). Given the complexity of the belowground environment, observing the effects of acid rain on soil systems is challenging, and its impacts on belowground ecosystems remain less understood than those on aboveground ecosystems (Bokhorst *et al*., 2012). Previous studies have reported that acid rain can alter cation adsorption and solution chemistry in soils, raise cation leaching, increase aluminum toxicity, and change soil microbial community composition and function (Zhang *et al*., 2014). It can also depress the activities of soil organisms such as earthworms (Wang *et al*., 2014). These changes reduce the soil's ability to provide a suitable physicochemical environment and essential nutrients, which may disrupt soil biota and alter community composition and function. Such adjustments may lead to significant changes in key soil ecological processes, such as soil carbon (C) and nitrogen (N) cycling under acid rain stress (Chen *et al*., 2013).

While several studies have noted that various species of soil invertebrates respond to acid rain stress (Felten and Guerold, 2006), how acid rain affects soil fauna community composition and their ecological niches remains underexplored. Further research is needed to bridge the knowledge gaps on this topic, particularly regarding the asymmetric responses of soil fauna with different traits to environmental changes (Bokhorst *et al.*, 2012).

2.6.2 Impact of Acid rain on Coastal Agriculture

Agriculture in coastal plain regions is highly vulnerable to the detrimental effects of acid rain, particularly due to the naturally low fertility of the soils in these areas. Calcium, for example, plays a crucial role in maintaining soil structure and supporting the development of healthy plant roots. Potassium, on the other hand, is essential for regulating water balance and enhancing plant stress tolerance. Crops that require high levels of calcium or potassium, such as tomatoes, potatoes, and various fruit and vegetable plants, are particularly vulnerable to acidification. In the absence of adequate calcium, these crops may exhibit poor root development, which leads to reduced nutrient uptake and stunted growth. Similarly, potassium depletion can impair water regulation in plants, making them more susceptible to drought stress and reducing their resilience to environmental fluctuations (PDA, 2019). Furthermore, acid rain can result in the decline of soil organic matter (SOM), exacerbating nutrient deficiencies and contributing to soil degradation (Pham *et al.*, 2020). As a result, crop yields decrease, and farmers may face increased costs for fertilizers and soil amendments to compensate for nutrient losses.

In addition to nutrient depletion, acid rain also increases the solubility of toxic aluminum (Al^{3+}) ions in acidic soils, posing an additional threat to agriculture. The presence of soluble aluminum in the soil can damage plant roots, impairing their ability to absorb water and nutrients. This is particularly concerning in coastal plain soils, where the low buffering capacity and nutrient leaching can cause significant reductions in crop productivity (Akpan-Idiok and Ukwang, 2012).

In Coastal plain sand regions, acid rain not only leads to decreased agricultural output but also increases risks to food security. Over time, the accumulation of acid rain and the continued depletion of soil nutrients may require farmers to adopt more intensive and costly management practices, such as liming or increased fertilization, to restore soil health and maintain crop yields.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Description of Study Area

The study was conducted at three distinct locations within the University of Benin, Edo State, Nigeria, namely: Hall 2, Junior Staff Quarters (JSQ), and AGR 305 experimental farm. Hall 2 serves as a girls' hostel, accommodating female students and is located at a latitude of 6°23'54.2880" N and longitude of 5°37'9.66950" E, with an altitude of 106 meters above sea level. JSQ primarily functions as a residential area for university staff, featuring a small-scale farming plot utilized for sample collection in this study; its coordinates are 6°23'44.70190" N and 5°37'13.52760" E, with an altitude of 103 meters. Lastly, AGR 305 experimental farm is designated for agricultural activities, situated at a latitude of 6°24'0.54100" N and longitude of 5°37'34.28340" E, at an altitude of 75 meters.

3.1.1 Climate

The average annual temperature and rainfall of the study area is about 27 ^{0}C and 2000 mm respectively, with mean annual relative humidity ranging from 89% in the morning to 75% in the evening (NIFOR, 2013). Rainfall follows a seasonal pattern, with well-marked wet and dry intervals, and exhibits a double peak, which is a result of a short dry period in August. This seasonal variation is driven by the shift in wind patterns: moist southwest monsoon winds from the Atlantic Ocean prevail during the wet season, while dry harmattan winds from the Saharan Desert dominate in the dry season. The wet season lasts from about March to November, with a brief reduction in rainfall during August due to the presence of stratiform clouds that are too thin to produce significant precipitation. The dry season runs from November to early March.

3.2 Sample collection and preparation

3.2.1 Soil Sampling and Preparation

Soil samples were collected at two depth intervals: 0–30 cm and 30–60 cm. Sampling was conducted at three distinct locations within the University of Benin; Hall 2, Junior Staff Quarters (JSQ), and AGR 305 experimental farm, using the soil auger, in three replicates. Materials used for the sample collection include GPS, soil auger, paper tape, polythene bags and permanent makers. The collected soil samples were air-dried, ground and labelled in polythene bags for laboratory analysis. Each location featured three equidistant sampling points, with precise geographic coordinates recorded for each point as shown in Table 1.

3.2.2 Collection of Rainwater

Rain water was collected from each site with a collection jar, covered with plastic to prevent evaporation. The collected rain water was filtered through a Whatman No 1 filter paper and stored in a plastic bottle. This was then used for pH analysis.

3.3 Laboratory analysis

The soil samples were analyzed for various physicochemical parameters to assess the effects of acid rain on soil basic cations.

3.3.1 Determination of pH in Rainwater samples

The collected samples were taken to the soil science laboratory, and their pH were determined using a calibrated electronic pH meter. The pH meter was calibrated using standard buffer solutions of pH 4, 7, and 10 before each set of measurements. For each sample, the pH meter electrode was rinsed with distilled water and then immersed in the sample. The pH reading was recorded after stabilization.

Table 1: Sampling points and locations

Augering points	Coordinates	
	JSQ	
1	6°23'44.70190" N,	5°37'13.52760" E
2	6°23'44.54520" N,	5°37'15.28090" E
3	6°23'42.90010" N,	5°37'15.39470" E
	HALL 2	
1	6°23'54.2880" N,	5°37'9.66950" E
2	6°23'56.47640" N,	5°37'10.2714" E
3	6°23'53.37590" N,	5°37'11.56800" E
	AGR 305 Farm	
1	6°24'0.54100" N,	5°37'34.28340" E
2	6°23'59.14750" N,	5°37'34.28400" E
3	6°24'0.08710" N,	5°37'37.55530" E

JSQ - Junior staff quarter, Hall 2- Female hostel, AGR305- Faculty of agriculture experimental farm.

3.3.2 Soil pH Determination

The determination of soil pH was conducted using an electronic pH meter. Prior to measurement, the pH meter was calibrated using buffer solutions with pH values of 4.0, 7.0, and 10.0. A sample of 10 grams of soil was placed in a beaker, to which 100 milliliters of distilled water was added. The mixture was then stirred vigorously for a duration of 30 minutes, after which the pH was measured using the calibrated pH meter.

3.3.3 Organic Carbon Determination

The determination of the soil organic carbon content was carried out using the Walkley-Black oxidation method (1934). 1 gram oven-dried soil was placed in a 250 ml conical flask, 10 ml of potassium dichromate ($K_2Cr_2O_7$) was added. The mixture was allowed to stand for 30 minutes. Following this, 100 ml distilled water was introduced into the flask, along with 5 drops of ferroin indicator. The solution was then titrated against 0.5N ferrous sulfate ($FeSO_4 \cdot 7H_2O$). A blank titration was performed without soil sample to standardize the potassium dichromate solution.

3.3.4 Total Nitrogen Determination

The total nitrogen content in the soil was determined using the Kjeldahl digestion method.

Digestion Stage

A 1 gram sample of air-dried, ground soil was placed in a 250 ml Kjeldahl flask. To this, copper sulfate ($CuSO_4$), potassium sulfate (K_2SO_4), and a pinch of selenium were added. Following this, 5 ml of concentrated sulfuric acid (H_2SO_4) was introduced. The mixture was then heated on a heating mantle at 400°C until it became clear, after which it was allowed to cool. Once removed from heat, approximately 100 ml of distilled water was added, and the contents were filtered through Whatman 42 filter paper into a 100 ml volumetric flask. The solution was then brought to volume and shaken thoroughly for proper mixing.

Distillation Stage

A 10 ml aliquot of the digested solution was transferred into a 50 ml Kjeldahl flask, followed by the addition of 25 ml distilled water and 5 ml sodium hydroxide (NaOH) as an excess base. The mixture was heated, and a distillate of 25 ml was collected in a separate 50 ml flask containing a standard acid indicator. The ammonium nitrogen (NH_4^+) content was determined by titrating the distillate with 0.01N standard hydrochloric acid (HCl), observing a color change from green to pink.

3.3.5 Particle Size Distribution

The particle size distribution of the soils were analyzed using the Bouyoucos hydrometer method (1962). 51 grams air-dried soil (sieved to < 2 mm) was placed in a 250 ml plastic container. 50 ml of sodium hexametaphosphate solution was added, followed by 100 ml of distilled water. The mixture was vigorously mixed for approximately one minute using a glass rod and allowed to stand for 30 minutes. After settling, the suspension was transferred to a multi mix machine, where it was shaken at high speed for 15 minutes. The resulting mixture was then poured into a sedimentation cylinder and diluted to the 1 liter mark with distilled water. The suspension was stirred with a plunger to set the particles in motion, and the first hydrometer reading was recorded after 40 seconds, along with the temperature reading. The second hydrometer reading was taken two hours later. The first hydrometer reading was used to determine the sand and silt content, while the second hydrometer reading was used to determine the clay content. These readings were then used to calculate the percentages of sand, silt, and clay in the soil sample. It was calculated using the formula:

% Sand = 100 - (corrected 40sec. Hydrometer reading) x 100

Weight of sample used 1

$$\% \text{ Clay} = \frac{\text{(corrected 2hrs hydrometer reading)}}{\text{Weight of sample used}} \times \frac{100}{1}$$

% Silt = 100 - (%sand + %clay)

3.3.6 Available Phosphorus Determination

The determination of available phosphorus in the soil was performed using the colorimetric method of Bray and Kurtz method (1945), after extraction with Bray P-1 extracting solution. 5 grams of soil was placed into an extraction cup, followed by the addition of 10 ml of Bray-1 solution. The mixture was stirred using a mechanical shaker for 5 minutes and then filtered into a reagent bottle using Whatman filter paper. 10 ml aliquot of the filtered solution was pipetted into a 5 ml volumetric flask, to which 6 ml distilled water was added. Following this, 2 ml of color-developing reagent was incorporated and mixed thoroughly. To facilitate color development, 1 ml of ascorbic acid solution was added, and the mixture was allowed to sit for approximately 10 minutes. The resulting solution was then analyzed at a wavelength of 650 nm using a visible range spectrophotometer. A calibration graph plotting absorbance against ppm standard mono potassium phosphate was constructed for quantification.

3.3.7 Exchangeable Cations (Ca, Mg, K, Na)

The determination of exchangeable cations was conducted using the ammonium acetate method. 10g soil was weighed and placed into a 250 ml soil bottle. To this, 100 ml 1N ammonium acetate (NH_4OAc) was added, and the mixture was shaken in a mechanical shaker for one hour. The solution was then filtered through Whatman No. 42 filter paper into a 100 ml volumetric flask, which was subsequently filled to the 100 ml mark with ammonium acetate solution and stored in a plastic reagent bottle. Potassium (K) and sodium (Na) concentrations were measured using an eyelet flame photometer, while calcium (Ca) and magnesium (Mg) levels were analyzed using a Unican series atomic absorption spectrophotometer (AAS). To ensure accurate readings within the measurable range of both instruments, the soil extracts were diluted as necessary.

3.3.8 Exchangeable Acidity

5 grams of prepared soil was placed into a shaking bottle. 50 ml of 1N potassium chloride (KCl) was added, and the mixture was shaken for one hour using a mechanical shaker. The resulting solution was then filtered using a whatman-42 filter paper into a 100 ml volumetric flask. The acidity was titrated with 0.05N sodium hydroxide (NaOH), using phenolphthalein as indicator until the pink color endpoint, was reached.

3.3.9 Exchangeable Aluminium

10g prepared soil sample was weighed into a 50 ml centrifuge tube, and 25 ml of 1 M KCl solution was added. The mixture was shaken for 30 minutes and then centrifuged at 3,000 rpm for 10 minutes. The supernatant was decanted and filtered through a 0.45-µm membrane filter. The filtered extract was then analyzed for aluminum using atomic absorption spectroscopy (AAS). The exchangeable aluminum content was calculated and expressed in cmol(+)/kg soil.

3.4 Statistical analysis

Data obtained from the laboratory were subjected to One-way analysis of variance (ANOVA), and the Least Significant Difference (LSD) at 5% level of probability was used to separate the means of physical and chemical properties.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Particle size distribution

The particle size distribution of the soil samples, as presented in Table 2, revealed significant variations in sand, silt, and clay content across depths (0-30 cm and 30-60 cm) and locations (USQ, AGR 305, and HALL 2). These variations are crucial in understanding soil physical properties, influencing water holding capacity, aeration, and nutrient availability (Hillel, 1998).

Sand content, which generally dominates surface soils, decreased significantly with depth. This decrease was statistically significant, as indicated by the LSD value for depth (1.396). This aligns with typical soil profiles where finer particles accumulate in lower horizons due to gravitational sorting and illuviation (Brady and Weil, 2008). Location also influenced sand content, with JSQ (883.88 g/kg) and AGR 305 (885.33 g/kg) recording higher mean values than HALL 2 (881.33 g/kg). The LSD value for location (1.710) confirms that there was significant difference, suggesting variations in parent material or depositional history across the locations (Jenny, 1941).

Silt content also decreased with depth. HALL 2 recorded the highest silt content at depth 0-30cm (61.35 g/kg), while AGR 305 had the lowest overall mean (53.33 g/kg). Both depth and location significantly influenced silt content, as reflected in the LSD values of 1.296 for depth and 1.587 for location. Silt particles, being intermediate in size, are susceptible to both erosion and translocation, contributing to the observed variability (Foth and Turk, 1972). Clay content exhibited an opposite trend to sand and silt, increasing significantly with depth. This accumulation of clay in the subsoil suggests the presence of an argillic horizon formed through illuviation processes where clay particles are transported from the upper horizons and deposited in lower ones

Table 2: Effect of depth distribution on particle sizes (g kg^{-1}) in acid rain environment

	Sand			Silt			Clay		
Depth(cm)	JSQ	AGR305	Hall 2	JSQ	AGR305	Hall 2	JSQ	AGR305	Hall2
0-30	886.00	888.67	886.33	58.67	57.00	61.33	55.33	54.67	52.33
30-60	881.67	882.00	876.33	51.67	49.67	49.00	66.67	69.67	74.67
Mean	883.83	885.33	881.33	55.17	53.33	55.17	61.00	62.17	63.50
LSD(0.05)									
Depth		1.396			1.296			1.990	
LSD (0.05)									
Location		1.710			1.587			ns	
Interaction		2.418			2.245			3.446	

ns - not significant at 0.05 level of probability, JSQ - Junior staff quarter, Hall 2- Female hostel, AGR305- Faculty of agriculture experimental farm.

(Buol *et al*., 2011). However, there were no significant differences in clay content across locations ("ns"), indicating that location had little effect on clay distribution. The accumulation of clay in the subsoil suggests the presence of an argillic horizon formed through illuviation processes where clay particles are deposited in lower soil layers. (Kafle, 2022).

4.2 Rain water pH Analysis

As shown in Table 3, rainwater obtained from AGR 305 farm had the lowest pH value of 4.83, making it the most acidic. Rain water obtained from Hall 2 ad JSQ follows as the second and third, it terms of acidity, having a pH of 4.91, ad 5.61 respectively.

Table 3: pH levels of rainwater harvested from each location.

Locations	pH
JSQ	5.61
Hall 2	4.91
AGR 305	4.83

JSQ - Junior staff quarter, Hall 2- Female hostel, AGR305- Faculty of agriculture experimental farm

4.3 Soil pH Analysis

Soil pH is a crucial indicator of soil acidity or alkalinity, influencing nutrient availability and microbial activity (Brady and Weil, 2017). As shown in Table 4, JSQ exhibited the highest mean pH value of 5.65, with a notable decrease from 5.97 at the 0-30 cm depth to 5.25 at the 30-60 cm depth. This decrease in pH with depth is a common phenomenon and can be attributed to several factors, including the leaching of basic cations (e.g., Ca2+, Mg2+) from the topsoil to lower layers (Foth and James, 1973).

In contrast, HALL 2 recorded a mean pH of 5.31, with values decreasing from 5.64 at the surface to 4.97 in the subsoil. AGR 305 had the lowest mean pH value of 5.10, with a decrease from 5.42 at 0-30 cm to 4.77 at 30-60 cm. This trend further emphasizes the increasing acidity with depth across all locations. The lower pH values observed in AGR 305 may suggest a higher degree of leaching or lower organic matter content compared to the other sites. Soil acidity can be exacerbated by factors such as acid rain, the use of certain fertilizers, and the decomposition of organic matter (Reuss and Johnson, 1986).

4.4 Organic carbon content

Organic carbon (OC) content is a vital component of soil organic matter (SOM), which plays a critical role in soil structure, water retention, nutrient cycling, and carbon sequestration (Lal, 2004). The organic carbon content of the soil samples varied significantly across different locations and depths. JSQ exhibited an organic carbon content of 15.80 g/kg at the 0-30 cm depth, which decreased to 10.18 g/kg at the 30-60 cm depth, resulting in a mean value of 12.99 g/kg. This decline suggests that organic matter is more concentrated in the surface layer, likely due to the

Table 4: Effect of depth distribution on soil basic cations and other parameters in acid rain environment

Depth	pH in H20	OC	Total N	Av. P	Ca	Mg	Na	K+	Al3+	H+
(cm)		(g/kg)	(g/kg)	(mg/kg)	(Cmol/kg)					
					JSQ					
0-30	5.97	15.80	0.83	14.20	0.80	0.32	0.16	0.28	0.06	0.12
30-60	5.25	10.18	0.63	8.87	0.65	0.21	0.12	0.19	0.10	0.18
Mean	5.65a	12.99	0.75	11.54	0.73	0.26	0.14	0.23	0.08	0.15
LSD depth	0.18	0.977	0.035	0.687	0.044	0.028	0.012	0.029	0.029	0.04
					HALL 2					
0-30	5.64	16.07	0.76	13.37	0.75	0.24	0.14	0.22	0.11	0.16
30-60	4.97	10.57	0.61	8.89	0.53	0.14	0.10	0.13	0.19	0.32
Mean	5.31	13.32	0.64	11.18	0.64	0.19	0.12	0.17	0.15	0.24
LSD depth	0.18	0.977	0.035	0.687	0.044	0.028	0.012	0.029	0.029	0.04
					AGR 305					
0-30	5.42	14.63	0.70	12.43	0.60	0.22	0.13	0.19	0.10	0.17
30-60	4.77	9.33	0.59	8.96	0.53	0.15	0.10	0.13	0.15	0.25
Mean	5.10	11.98	0.65	10.70	0.57	0.18	0.11	0.16	0.13	0.21
LSD depth	0.18	0.977	0.035	0.687	0.044	0.028	0.012	0.029	0.029	0.04

OC- Organic Carbon, Basic cations- (Ca^{2+}, Na^{+}, K^{+}, Mg^{2+}), JSQ - Junior staff quarter, Hall 2- Female hostel, AGR305- Faculty of agriculture experimental farm accumulation of plant residues and microbial activity. Plant litter, root exudates, and other organic inputs contribute significantly to topsoil organic matter (Swift, 2001). HALL 2 recorded an organic carbon content of 16.07 g/kg at the surface depth, decreasing to 10.57 g/kg in the subsoil, with a mean value of 13.32 g/kg. Similar to JSQ, HALL 2 shows a significant reduction in organic carbon with depth, indicating that topsoil is richer in organic matter compared to deeper layers. In contrast, AGR 305 had the lowest organic carbon content among the three locations, with values of 14.63 g/kg at 0-30 cm and 9.33 g/kg at 30-60 cm, leading to a mean value of 11.98 g/kg. The lower OC content in AGR 305 could be attributed to various factors, including differences in vegetation, land management practices, or soil texture. For example, intensive tillage can lead to the oxidation and loss of soil organic matter (Six *et al.,* 2002).

4.5 Total Nitrogen Content

Nitrogen is a key component of proteins, nucleic acids, and chlorophyll, making it an indispensable nutrient for plant development (Marschner, 2012). JSQ exhibited the highest total nitrogen levels, with values of 0.83% at the 0-30 cm depth and 0.63% at the 30-60 cm depth, resulting in a mean total nitrogen content of 0.75%. This indicates that the surface soil at JSQ is relatively rich in nitrogen, likely due to organic matter decomposition and biological nitrogen fixation (Paul, 2016). In comparison, HALL 2 recorded total nitrogen levels of 0.76% at the surface and 0.61% at depth, leading to a mean value of 0.64%. While this location also shows a decrease in nitrogen content with depth, it is notably lower than that of JSQ. AGR 305 had the lowest total nitrogen content among the three locations, with values of 0.70% at 0-30 cm and 0.59% at 30-60 cm, resulting in a mean of 0.65%. The differences in total nitrogen content across all the locations could be due to differences in land use, vegetation, management practices (e.g., fertilization, crop rotation), and soil properties (e.g., texture, organic matter content) (Dass *et al.,* 2018).

The mean values indicate that JSQ has the highest total nitrogen content, followed by AGR 305 and then HALL 2. The consistent decrease in nitrogen content with depth across all locations is a common observation due to the accumulation of organic matter and higher biological activity in topsoil (Richter and Markewitz, 2001).

4.6 Available phosphorus

Phosphorus is another essential macronutrient required for plant growth, particularly for root development, energy transfer, and DNA synthesis (Marschner, 1997; Kaur *et al*., 2021). JSQ exhibited the highest levels of available phosphorus, with values of 14.20 mg/kg at the 0-30 cm depth and a decrease to 8.87 mg/kg at the 30-60 cm depth, resulting in a mean available phosphorus content of 11.54 mg/kg. This trend suggests that surface soils at JSQ are relatively enriched with phosphorus, likely due to organic matter decomposition and release of root exudates. There is abundant evidence that roots of many species exude compounds which have the ability to solubilize sources of phosphorus (Attiwill and Adams, 1993). Root exudates, such as organic acids, can dissolve insoluble phosphorus forms, making them accessible to plants.

HALL 2 recorded available phosphorus levels of 13.37 mg/kg at the surface and a slight decrease to 8.89 mg/kg in the subsoil, leading to a mean value of 11.18 mg/kg. While HALL 2 also shows a decline in phosphorus content with depth, it remains lower than that of JSQ. AGR 305 had the lowest available phosphorus content among the three locations, with values of 12.43 mg/kg at 0-30 cm and 8.96 mg/kg at 30-60 cm, resulting in a mean of 10.70 mg/kg. The lower available phosphorus in AGR 305 could be related to factors such as soil pH, mineralogy, and the presence of phosphorus-fixing cations (e.g., iron, aluminum) (Havlin *et al.,* 2016).

4.7 Total Exchangeable cations (Ca, Mg, Na, K)

Exchangeable cation ratios (Ca, Mg, Na, K) were assessed at JSQ, Hall2, and AGR305 farm locations at soil depths of 0-30cm and 30-60cm. The observed ratio ranges were 0.53-0.80 for Calcium (Ca), 0.14-0.32 for Magnesium (Mg), 0.10-0.16 for Sodium (Na), and 0.13-0.28 for Potassium (K). Across all locations and depths, the exchangeable cation ratios were primarily dominated by Calcium. This dominance of Calcium in the exchange complex is a common characteristic of many soils, reflecting its abundance in the soil solution and strong affinity for negatively charged soil colloids (Brady and Weil, 2017). Based on these ratios for the JSQ location, the calculated mean exchangeable cation values were: 0.73 for Ca, 0.26 for Mg, 0.14 for Na, and 0.23 for K. For the Hall2 location, the calculated mean exchangeable cation values were: 0.64 for Ca, 0.19 for Mg, 0.12 for Na, and 0.17 for K. Lastly, for the AGR305 farm location, the calculated mean exchangeable cation values were: 0.57 for Ca, 0.18 for Mg, 0.11 for Na, and 0.16 for K.

Considering a critical ratio level of 0.2 for Ca, Mg, Na, and K, the JSQ, Hall2, and AGR305 locations show values greater than the critical level for Calcium. This suggests adequate Calcium availability at all sites, which is important as Calcium plays a vital role in plant cell wall development and enzyme activation (Marschner, 2012). For Magnesium, the JSQ (0.26) and Hall2 (0.19) locations are around the critical ratio level. Magnesium is essential for chlorophyll production, and levels near the critical threshold could indicate a potential deficiency, particularly at Hall2 (Marschner, 2012). For Sodium, the Hall2 (0.12) and AGR305 (0.11) locations are around the critical ratio level. While not necessarily problematic, elevated Sodium levels can lead to soil dispersion and structural issues if they increase further (US Salinity Laboratory Staff, 1954). Finally, for

Potassium, the JSQ, Hall2, and AGR305 locations are also around the critical ratio level.

Potassium is crucial for osmotic regulation and enzyme activation in plants (Mengel and Kirkby, 2001). The closeness to the critical level at all sites suggests potential limitations in Potassium availability, which might require management strategies like fertilization.

4.8. Correlation coefficient between some soil physical-chemical properties and the exchangeable cations

This section explores the correlation coefficients (r) between selected soil physical-chemical properties and exchangeable cations (Table 5). Aluminum (Al3+) exhibited significant negative correlations with Available Phosphorus (Av. P) (r = -0.621), Exchangeable Calcium (EX Ca) (r = -0.744), Potassium (K+) (r = -0.836), Magnesium (EX Mg) (r = -0.828), Sodium (Ex Na) (r = -0.845), Total Nitrogen (TN) (r = -0.615), Organic Carbon (Org C) (r = -0.532), pH (r = -0.768), Sand (r = -0.677), and Silt (r = -0.572), but positively significantly correlated with Clay content (r = 0.634) at the 5% level of probability. These negative correlations with essential nutrients and pH are consistent with the established chemistry of aluminum in soils, where Al3+ dominance in acidic conditions leads to reduced nutrient availability (Lindsay, 1979). The negative correlations with TN and Org C may reflect Al3+'s impact on microbial activity and organic matter decomposition, while the relationships with particle size fractions might be indirect, reflecting underlying mineralogy and weathering processes (Sposito, 2008). The positive correlation with clay is expected as clay minerals are a primary aluminum source and contribute to higher cation exchange capacity. Available P, in turn, positively correlated with EX Ca (r = 0.755), K+ (r = 0.833), EX Mg (r = 0.818), Ex Na (r = 0.812), TN (r = 0.915), Org C (r = 0.928), pH (r = 0.843), Sand (r = 0.717), and Silt (r = 0.884), highlighting the interconnectedness of nutrient availability and the influence of calcium, magnesium, and potassium on phosphate solubility and plant uptake (Havlin *et al.*, 2016). However, Av. P negatively correlated with Clay content (r = -0.860), which could be attributed to phosphorus fixation by strongly weathered clay minerals or other pedogenic factors. EX Ca demonstrated positive correlations with K+ (r = 0.935), EX Mg (r = 0.916), Ex Na (r = 0.856), TN (r = 0.834), pH (r = 0.881), and Silt (r = 0.752), reflecting the similar behavior of these cations in soil systems. Conversely, EX Ca negatively correlated with Clay content (r = -0.70), potentially due to specific clay mineralogy or other influencing factors. Interestingly, H+ positively correlated with EX Ca (r = 0.754) but also negatively correlated with EX Ca (r = -0.883). Finally, Clay content negatively correlated with pH (r = -0.785), Sand (r = -0.903), and Silt (r = -0.956), which is expected due to the inverse relationship between clay and coarser fractions in particle size distribution (Sposito, 2008).

-Table 5: Correlation coefficient between some soil physical-chemical properties and the exchangeable cations

Property	Al3+	Av.P	EX Ca	H+	K+	EX Mg	Ex Na	TN	Org C	Clay	pH	Sand	Silt
Al3+													
Av.P	-0.621	-											
EX Ca	-0.744	0.755	-										
H+	0.945*	-0.736	0.754	-									
K+	-0.836	0.833	0.935	-0.883	-								
EX Mg	-0.828*	0.818	0.916	-0.861	0.982	-							
Ex Na	-0.845*	0.812	0.856	-0.831	0.889	0.876	-						
TN	-0.615	0.915	0.834	-0.705	0.874	0.852	0.837	-					
Org C	-0.532	0.928	0.713	-0.631	0.751	0.734	0.746	0.919	-				
Clay	0.634*	-0.860	-0.710	0.753	-0.726	-0.709	-0.727	-0.794	-0.864	-			
pH	-0.768	0.843	0.881	-0.774	0.885	0.874	0.947	0.846	0.795	-0.785	-		
Sand	-0.677	0.717	0.551	-0.771	0.624	0.605	0.615	0.632	0.697	-0.903	0.591	-	
Silt	-0.572	0.884	0.752	-0.699	0.741	0.724	0.734	0.831	0.897	-0.956	0.825	0.753	-

EX Mg- Exchangeable magnesium, EX Na- Exchangeable sodium, Org C- Organic carbon, EX Ca- Exchangeable calcium, T-Total nitrogen, Av P- Available phosphorus

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1. CONCLUSION

This study highlights the significant impact of acid rain on the basic cations in coastal plain sand, revealing its detrimental effects on soil fertility, plant growth, and ecosystem health. Increased concentration of hydrogen ions (H^+) from acid rain accelerates the leaching of essential cations such as calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and potassium (K^+), leading to nutrient deficiencies and soil degradation. Coastal plain sand, which are naturally low in cation exchange capacity (CEC) and organic content, are particularly vulnerable to these processes, amplifying the risk of long-term soil fertility loss and reduced agricultural productivity. Additionally, the mobilization of toxic aluminum (Al^{3+}) in acidified soils further impairs plant health by damaging root systems and hindering nutrient uptake, contributing to stunted plant growth and lower crop yields.

5.2 RECOMMENDATIONS

Based on these findings and results, I recommend:

1. The application of lime (calcium carbonate) or other soil amendments to help neutralize acidity and restore critical cations such as calcium and magnesium.
2. Enhancing soil organic matter (SOM) content through organic amendments like compost or mulch to help improve the cation exchange capacity (CEC) of coastal plain sand, providing better buffering against acidity and reducing the rate of nutrient leaching.
3. Adoption of cleaner technologies in industrial practices, so as to decrease air pollution

4. Planting vegetation that is more tolerant of acidic soils to help prevent erosion and enhance the natural buffering capacity of soils.

REFERENCES

Akpan-Idiok, A. U., and Ukwang, E. E. (2012). Characterization and classification of coastal plain soils in Calabar, Nigeria. *Journal of Agriculture, Biotechnology and Ecology*, 5(3), 19–33.

Amaize, E. (2007). Crises from the creeks. *Saturday Vanguard Newspapers*, pp. 11–13.

Attiwill, P. M., and Adams, M. A. (1993). Nutrient cycling in forests. *New Phytologist,* 124(4), 561–582.

Bakhshipour, Z., Asadi, A., Huat, B. B. K., Sridharan, A., and Kawasaki, S. (2016). Effect of acid rain on geotechnical properties of residual soils. *Soils and Foundations*, 56(6), 1008–1020.

Bouyoucos, G.J. (1962). Hydrometer Method Improved for Making Particle Size Analysis of Soils. *Agronomy Journal*, 54, 464-465.

Brady, N. C., and Weil, R. R. (2008). *The nature and properties of soils* (14th ed.). Pearson Education.

Brady, N. C., and Weil, R. R. (2017). *The nature and properties of soils* (15th ed.). Pearson.

Bray, R.H., and Kurtz, L.T. (1945). Determination of Total, Organic, and Available Forms of Phosphorus in Soils. *Soil Science*, 59, 39-45.

Buol, S. W., Hole, F. D., McCracken, R. J., and Southard, R. J. (2011). *Soil genesis, morphology, and classification* (6th ed.). John Wiley and Sons.

Chadwick, O. A., and Chorover, J. (2001). The chemistry of pedogenic thresholds. *Geochimica et Cosmochimica Acta*, 65(7), 1079–1092.

Chen, D., Lan, Z., Bai, X., Grace, J. B., and Bai, Y. (2015). Evidence that acidification-induced declines in plant diversity and productivity are mediated by changes in below-ground communities and soil properties in a semi-arid steppe. *Journal of Ecology*, 103(6), 1702–1711.

Dai, P., Cong, P., Wang, P., Dong, J., Dong, Z., and Song, W. (2021). Alleviating soil acidification and increasing the organic carbon pool by long-term organic fertilizer on tobacco planting soil. *Agronomy*, 11(11), 2135.

Dass, P., Samal, A., Mandal, B., and Adhya, T. K. (2018). Soil organic carbon and nitrogen stocks in different land uses of a tropical Alfisol. *Geoderma*, 319, 109–117.

Felten, V., and Guérold, F. (2006). Short-term physiological responses to a severe acid stress in three macroinvertebrate species: A comparative study. *Chemosphere*, 63(9), 1427–1435.

Foth, H. D., and James, D. W. (1973). *Fundamentals of soil science*. John Wiley and Sons.

Foth, H. D., and Turk, L. M. (1972). *Fundamentals of soil science* (5th ed.). John Wiley and Sons.

Gransee, A., and Führs, H. (2013). Magnesium mobility in soils as a challenge for soil and plant analysis, magnesium fertilization, and root uptake under adverse growth conditions. *Plant and Soil*, 368, 5–21.

Havlin, J. L., Beaton, J. D., Tisdale, S. L., and Nelson, W. L. (2016). *Soil fertility and fertilizers*. Pearson Education.

Hazelton, P. A., and Murphy, B. W. (2007). *Interpreting soil test results: What do all the numbers mean?* CSIRO Publishing.

Hillel, D. (1998). *Environmental soil physics*. Academic Press.

Hogan, G. D. (1992). Physiological effects of direct impact of acidic deposition on foliage. *Agriculture, Ecosystems and Environment*, 38(1), 29–48.

Jalali, M., and Naderi Peikam, E. (2022). Measuring and simulating the effect of acid rain on cations leaching from calcareous soil of Western Iran. *Arabian Journal of Geosciences*, 15(13), 397.

Jenny, H. (1941). *Factors of soil formation: A system of quantitative pedology*. McGraw-Hill.

Jenny, H. (1980). *The soil resource: Origin and behavior*. Springer-Verlag.

Jones, C., and Kathrin, O. R. (2016). *Plant nutrition and soil fertility*. Montana State University.

Kafle, G. (2022). Diagnostic horizons of soils in the world. *Academia Letters*, Article 5757.

Kaiser, D. E., and Rosen, C. J. (2018). *Potassium for crop production*. University of Minnesota Extension.

Kaur, G., Shukla, V., Meena, V., Kumar, A., Tyagi, D., Singh, J., Kandoth, P. K., Mantri, S., Rouached, H., and Pandey, A. K. (2021). Physiological and molecular responses to combinatorial iron and phosphate deficiencies in hexaploid wheat seedlings. *Genomics*, 113, 3935–3950.

Kochian, L. V., Pineros, M. A., and Hoekenga, O. A. (2005). The physiology, genetics, and molecular biology of plant aluminum resistance and toxicity. *Plant and Soil*, 274(1), 175–195.

Lal, R. (2004). Soil carbon sequestration impacts on global climate change and food security. *Science*, 304(5677), 1623–1627.

Leal, R. A., Silva, T. A., Mergulhão, T. J. C., Monteiro, E. C. B., and Takaki, G. M. C. (2023). Factors and consequences of acid rain incidence. *Environmental Science and Pollution Research,* 30(15), 10923–10937.

Lindsay, W. L. (1979). *Chemical equilibria in soils*. John Wiley and Sons.

Liu, X., Zhao, W. R., Meng, M. J., Fu, Z. Y., Xu, L. H., Zha, Y., Yue, J. M., Zhang, S. F., and Zhang, J. C. (2018). Comparative effects of simulated acid rain of different ratios of SO_4^{2-} to NO_3^- on fine root in subtropical plantation of China. *Science of the Total Environment*, 618, 336–346.

Marschner, H. (1997). Functions of mineral nutrients, macronutrients. In *Mineral nutrition of higher plants*. Academic Press.

Marschner, H. (2012). *Mineral nutrition of higher plants* (3rd ed.). Academic Press.

Mayah, E. (2006). Inside the militant colony. *Saturday Sun Newspaper*, pp. 4–5, 50.

Mengel, K., and Kirkby, E. A. (2001). Principles of plant nutrition (5th ed.). Kluwer Academic Publishers.

Mitchell, C. C., and Mylavarapu, R. (2014). Soil test correlation and calibration for recommendations. In F. J. Sikora and K. P. Moore (Eds.), *Soil test methods from the Southeastern United States* (pp. 11–18).

Nawaz, R., Parkpian, P., Garivait, H., Anurakpongsatorn, P., Delaune, R. D., and Jugsujinda, A. (2012). Impacts of acid rain on base cations, aluminum, and acidity development in highly weathered soils of Thailand. *Communications in Soil Science and Plant Analysis*, 43(10), 1382–1400.

Nduka, J. K. C., Orisakwe, O. E., Ezenweke, L. O., Ezenwa, T. E., Chendo, M. N., and Ezeabasili, N. G. (2021). Acid rain phenomenon in the Niger Delta region of Nigeria: Economic, biodiversity, and public health concern. *Environmental Health Perspectives*, 129(11), 117–123.

Nigerian Institute for Oil Palm Research (NIFOR) Meteorological station (2008).

Nton, M. E., and Esua, T. B. (2010). Sequence stratigraphy of EMI field, offshore eastern Niger Delta, SPDC of Nigeria. *European Journal of Scientific Research*, 44, 115–132.

Paul, E. A. (2016). *Soil microbiology and sustainable crop production*. CABI.

PDA. (2019). *Introduction to potash use* (Leaflet). Published June 2019.

Pham, H. T., Nguyen, A. T., Nguyen, T. T., and Hens, L. (2020). Stakeholder Delphi-perception analysis on impacts and responses of acid rain on agricultural ecosystems in the Vietnamese upland. *Environmental Development and Sustainability*, 22, 4467–4493.

Rashidi, M., and Seilsepour, M. (2008). Modeling of soil cation exchange capacity based on soil organic carbon. *ARPN Journal of Agricultural and Biological Science*, 3(4), 41–45.

Reuss, J. O., and Johnson, D. W. (1986). *Acid deposition and the acidification of soils and waters*. Springer-Verlag.

Six, J., Conant, R. T., Paul, E. A., and Paustian, K. (2002). Stabilization of soil organic matter by microbially derived secondary minerals. *Soil Science Society of America Journal*, 66(6), 1930–1935.

Sposito, G. (2008). *The chemistry of soils*. Oxford University Press.

Swift, M. J. (2001). *Organic matter and soil fertility*. Kluwer Academic Publishers.

Tian, Q., and Niu, J. (2015). The impact of acid rain on soil cation exchange and forest ecosystems in subtropical China. *Science of the Total Environment*, 537, 58–66.

Tooth, J. (2023, December 9). Why calcium is critical for soil, plant, and animal health. *Farmers Weekly*, pp. 1.

US Salinity Laboratory Staff. (1954). *Diagnosis and improvement of saline and alkali soils*. USDA.

Walkley, A., and Black, I.A. (1934). An Examination of the Degtjareff Method for Determining Soil Organic Matter and a Proposed Modification of the Chromic Acid Titration Method. *Soil Science*, 37, 29-38.

Wang, C. Y., Guo, P., Han, G. M., Feng, X. G., Zhang, P., and Tian, X. J. (2010). Effect of simulated acid rain on the litter decomposition of Quercus acutissima and Pinus massoniana in forest soil microcosms and the relationship with soil enzyme activities. *Science of the Total Environment*, 408, 2706–2713.

Wang, L., Chen, Z., Shang, H., Wang, J., and Zhang, P.-Y. (2014). Impact of simulated acid rain on soil microbial community function in Masson pine seedlings. *Electronic Journal of Biotechnology*, 17(5).

Wei, H., Liu, Y., Zhang, J., Li, S., Zhong, X., and Xiang, H. (2021). Leaching of simulated acid rain deteriorates soil physiochemical and mechanical properties in three agricultural soils. *Catena*, 206, 105485.

Xu, Z. J., Liu, G., Yu, J. D., and Liu, W. (2002). Effects of acid rain on aggregate and its cementing components of red soil by simulated experiments. *Journal of Soil and Water Conservation*, 16(1), 9–11.

Yang, S., Li, J., Yang, B., Liao, B., Zhang, J., and Shu, W. (2011). Effectiveness of amendments on re-acidification and heavy metal immobilization in an extremely acidic mine soil. *J. Environ. Monit.* , 13(7), 1876.

Zhang, J. E., Yu, J., Ouyang, Y., and Xu, H. (2014). Impact of simulated acid rain on trace metals and aluminum leaching in Latosol from Guangdong Province, China. *Soil and Sediment Contamination: An International Journal*, 23, 725–735.

Zheng, S. A., Zheng, X., and Chen, C. (2012). Leaching behavior of heavy metals and transformation of their speciation in polluted soil receiving simulated acid rain. *PLoS ONE*, 7, e49664.