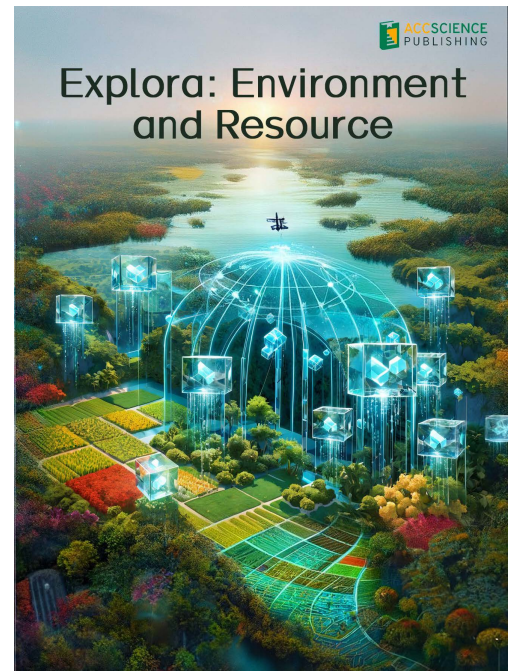


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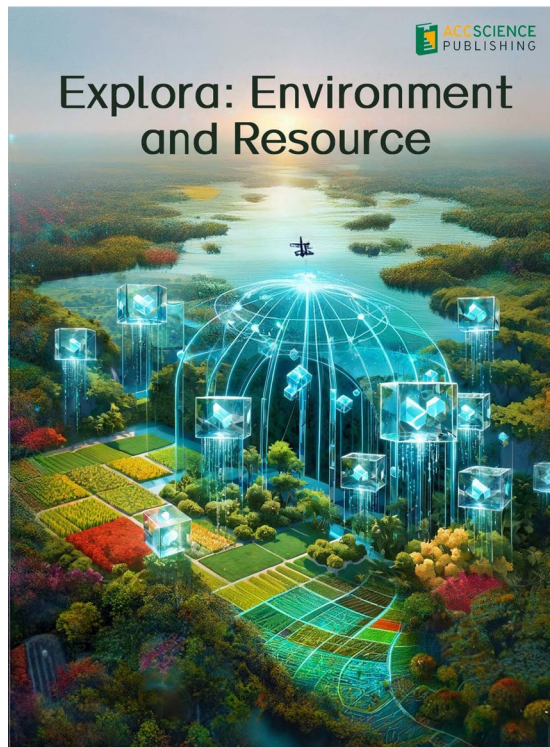
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CONTENTS

REVIEW ARTICLES

- 1 **Titanium: Metal of the future or an emerging environmental contaminant?**
Shailja Sharma, Shiv Bolan, Santanu Mukherjee, Pingfan Zhou, Xiaodong Yang, Jason C. White, Nubia Zuverza-Mena, Tao Zhang, Jianjun Chen, Qing Xu, Xiangying Wei, Shiheng Lyu, Sandun Sandanayake, Meththika Vithanage, Kadambot H.M. Siddique, Nanthi Bolan
- 2 **Different methods and technologies of air pollution mitigation: An overview**
Md Rafiur Rahman, Md Rofiul Islam Rofi

ORIGINAL RESEARCH ARTICLES

- 3 **Diversifying cropping systems to enhance productivity using agroforestry trees: A case study of maize–pigeon pea intercropping in Ghana**
Felix Frimpong, Eric Owusu Danquah, Shadrack Kwadwo Amponsah, Theophilus Frimpong, Joel Adu, Frank Osei Danquah, Natson Eyrarn Amengor, Patricia Amankwaa-Yeboah
- 4 **Nickel foam-supported nickel–cobalt layered double hydroxide/platinum composite electrocatalyst for ammonia oxidation reaction**
Xinyu Zhao, Xinyue Wang, Hongli Cai, Jialu Liu, Jiali Gu, Yingying Zhao, Liang Zhang
- 5 **Impact of zinc oxide and titanium dioxide nanoparticles on growth parameters of chickpeas (*Cicer arietinum* L.)**
Anuradha Navnath Karale, Bhavna Nigam, Indra Jeet Chaudhary
- 6 **The development of the river chief in Nantong and Huzhou: Policy transfer in an authoritarian system**
David P. Dolowitz, Ye Xiong
- 7 **Comparative analysis of chlorination byproduct formation in galvanized iron and high-density polyethylene pipes using low-cost filtration techniques**
Musaab Habib Bangash, Naeem Ejaz, Sadia Nasreen
- 8 **Tuning enzyme concentration and particle size for LDPE biodegradation using lipase and laccase systems**
Muhammad Jimada Aliyu, Benjamin Obinna Uloh, Moses Aderemi Olutoye, Abdulhalim Musa Abubakar
- 9 **Evaluation of yield performance of *Capsicum annuum* (chili) cultivated using a low-cost, sustainable hydroponic system**
Somroop Chakravarti, Arnab Sarkar, Anirban Maity, Bishal Roy, G. M. Al Amin, Moumita Gangopadhyay
- 10 **Adoption of indigenous practices for climate change adaptation by sweet potato farmers in Ebonyi State, Nigeria**
Loveday Chukwudi Njoku, Ngozi Ekunyi Umeh, Chidera Nicholas Akude, Joshua Chibudo Nwabuisi, Abraham Godwin Ominikari, Chibuzo Uzoma Izuogu, Hama Ismail Ibrahim

REVIEW ARTICLE

Titanium: Metal of the future or an emerging environmental contaminant?

Shailja Sharma¹, Shiv Bolan^{2,3,4}, Santanu Mukherjee^{5*}, Pingfan Zhou⁶, Xiaodong Yang⁶, Jason C. White⁷, Nubia Zuverza-Mena⁷, Tao Zhang⁸, Jianjun Chen⁹, Qing Xu⁸, Xiangying Wei¹⁰, Shiheng Lyu¹¹, Sandun Sandanayake¹², Meththika Vithanage^{3,12}, Kadambot H.M. Siddique³, and Nanthi Bolan^{2,3,4*}

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Abstract

Naturally occurring and anthropogenic sources, such as ore (minerals), waste disposal, and mine tailings, can introduce titanium (Ti) into both soils and aquatic environments. Ti is the ninth most abundant element in nature (0.63% w/w) and is found in igneous rocks. Major Ti-bearing minerals include rutile, brookite, anatase, ilmenite, and titanite. Among Ti compounds, Ti dioxide (TiO₂) is of particular environmental and health concern. It is classified as potentially carcinogenic to humans (Group 2B) by the International Agency for Research on Cancer. Ti is increasingly used in aviation and aerospace fields and has important biomedical applications, including in joint replacements and dental implants. TiO₂ nanoparticles (NPs) are one of the most important Ti compounds, entering the environment through various pathways, including biosolid applications, and have been shown to cause deleterious effects on soil microorganisms and, consequently, on soil functioning and health. Excessive Ti uptake can cause toxicity in plants, soil microorganisms, aquatic organisms, animals, and humans. Dust inhalation of TiO₂ NPs by humans may cause chest pain,

coughing, and breathing difficulty, while dermal contact may cause irritation. To control the main anthropogenic input sources of Ti in the environment, it is critical to develop affordable technologies for Ti removal during wastewater treatment. This comprehensive review examines the presence, sources, biogeochemical behavior, and potential risks of Ti in the environment and provides an in-depth outline of the network visualization bibliography to graphically represent the relationships between key publications, research areas, and authors. Additionally, future research priorities are suggested for the sustainable management of Ti contamination.

Keywords: Titanium dioxide; Carcinogen; Biogeochemistry; Human health; Remediation

1. Introduction

Titanium (Ti) is the ninth-most abundant element in nature (0.63% w/w) and is present in most igneous rocks and their associated sediments, although it is primarily found bound to other elements in the Earth's crust.¹⁻³ The main mineral sources of Ti are anatase, rutile, and brookite, each contains approximately 95% Ti dioxide (TiO_2), as well as ilmenite (FeTiO_3) and titanite (CaTiSiO_5), which contain 40 – 65% TiO_2 .^{4,5} The countries with the largest reserves of ilmenite and/or rutile are China, Australia, India, South Africa, Brazil, Madagascar, Norway, Canada, and Mozambique (Table S1).

Two major processing technologies, the sulfate and chloride processes, are used to produce industrial pure TiO_2 for use in pigments or to produce Ti metal from enriched raw materials, including ilmenite and rutile.^{6,7} In the sulfate process, ground ilmenite ore or high- TiO_2 slag is treated with sulfuric acid, while in the chloride process, Ti-enriched materials are converted into Ti chlorides using hydrochloric acid at high temperature. As the chloride process produces high-quality TiO_2 pigments with fewer waste products, this approach has largely replaced the sulfate strategy. This shift from sulfate to chloride processing in TiO_2 pigment production has resulted in increasing demand for high-grade Ti raw materials, including rutile and Ti-enriched slag.⁸

The significance of Ti in various industries, such as aerospace and biomedical applications, has been extensively discussed.⁹⁻¹¹ Ti is light yet strong and corrosion-resistant. These unique properties enabled its wide application in the building and sporting goods industries, as well as in implants in a number of medical procedures. Furthermore, due to its strong resistance to salinity, Ti is used in offshore rigs, propellers and rigging of ships, and desalination units. Ti is capable of osseointegration, indicating that it is readily accepted by bone, and is nonreactive; thus, it is widely used in medical applications, including hip and knee joints, bone screws and plates, and dental implants.¹² TiO_2 is one

of the most important Ti compounds, accounting for the largest application of the metal. Based on the United States Geological Survey (USGS) statistics, there are more than 2.00 billion metric tons of Ti ore in the world, including 0.70 billion metric tons of ilmenite and 0.049 billion metric tons of rutile.¹³⁻¹⁵

Larger-particle TiO_2 , or bulk TiO_2 (>200 nm), is frequently utilized as a pigment in paints and coatings. TiO_2 nanoparticles (NPs), or nano- TiO_2 , are much smaller, typically <100 nm. Natural nanoscale Ti (20 – 300 nm) can be found in a variety of ores and minerals. TiO_2 is primarily available in two sizes, i.e., micrometer (250 – 400 nm) and nanometer (<250 nm) ranges.¹²⁻¹⁴ Due to differences in surface area-to-volume ratios, these various size ranges have distinct physical characteristics. In the food industry, micrometer-sized TiO_2 particles are frequently employed as a food coloring agent to enhance texture, avoid caking, and brighten or whiten food products due to their low toxicity compared to pigmentary and nano- TiO_2 .¹³⁻¹⁵ For applications as a pigment material, TiO_2 particle sizes of 250 nm were found ideal.^{16,17} TiO_2 nanomaterials are the second-most produced nanomaterial worldwide. These materials are bright white pigments that have many applications, such as white paints, sunscreens, infrared reflectors, self-cleaning glass, and food additives. Ti metal alloys are in demand due to their high strength-to-weight ratio and corrosion resistance.¹⁶ Although there are different Ti- and TiO_2 -containing compounds—such as total Ti, soluble ionic Ti, insoluble minerals, TiNPs, TiO_2 NPs—the present review will focus primarily on TiO_2 given its widespread use/applications. A detailed discussion of the applications of TiO_2 as food additives has been provided elsewhere by the authors.¹⁸

The chemistry of Ti is similar to that of silicon and zirconium.¹⁷ The Ti element does not exist alone in nature, as it is mostly chemically bound with oxygen or iron, and chemical processing is applied to synthesize a low-density, high-strength metal.^{3,14} Ti has three

oxidation states: Ti^{2+} , Ti^{3+} (titanous), and Ti^{4+} (titanic). Among them, Ti^{2+} and Ti^{3+} are not stable, while Ti^{4+} is the most stable ionic form, which commonly exists as TiO_2 (Table S2). The major sources of anthropogenic Ti in the environment include the combustion of fossil fuels and the incineration of Ti-containing products (Figure 1). Globally, Ti concentrations in aquatic freshwater systems range from 12 to 926 $\mu g/L$.¹⁹ The mean level of Ti in worldwide river sediments is 0.44% (w/w).^{15,20} In the atmosphere, Ti level ranges from 0.5 to 2.5 ng/m^3 and from 15 to 25 ng/m^3 for regional and urban areas, respectively.²¹ The fate and dynamics of Ti in the environment are controlled by its limited solubility and the low reactivity of Ti minerals.

Ti is not an essential element for humans, animals, or plants, and it is not considered inherently hazardous either.²² However, excessive uptake of Ti can be toxic to humans, animals, soil organisms, and aquatic life. Heringa *et al.*²³ reported a detection limit of 0.3 mg/kg for Ti in human tissues associated with medical applications. As noted above, inhalation of nano- TiO_2 -containing dust may cause tightness and pain in the chest, coughing, and breathing difficulty in humans, while dermal exposure may also result in irritation.²⁴ According to the International Agency for Research on Cancer (IARC), " TiO_2 is probably

carcinogenic to humans (Group 2B) on the basis of sufficient evidence in experimental animals and insufficient evidence from epidemiological studies."^{25(p275)}

Ti enters the human body through ingestion, inhalation, and dermal contact; fortunately, and importantly, most ingested Ti is eliminated from the body. However, the mining of Ti ore and the industrial processing of Ti extraction generate airborne dust, leading to inhalation exposure to high levels of Ti that can be toxic.^{21,26-28} Drinking water guidelines and soil screening levels for Ti have not been established by the US Environmental Protection Agency and the World Health Organization for either industrial or residential land use. In fact, due to the low toxicity of Ti to humans, TiO_2 is being increasingly used to replace lead carbonate and lead oxide as the whiteners in paints. Similarly, water-quality criteria for Ti have not been established for the protection of aquatic species, largely because Ti minerals are almost insoluble and have low bioavailability.

Ti is both an industrially important metal and a potential environmental contaminant, making it highly relevant to current environmental research priorities. The present article covers a broad variety of subjects, from Ti's natural and human-made origins to its effects on the environment and human health, remediation techniques,

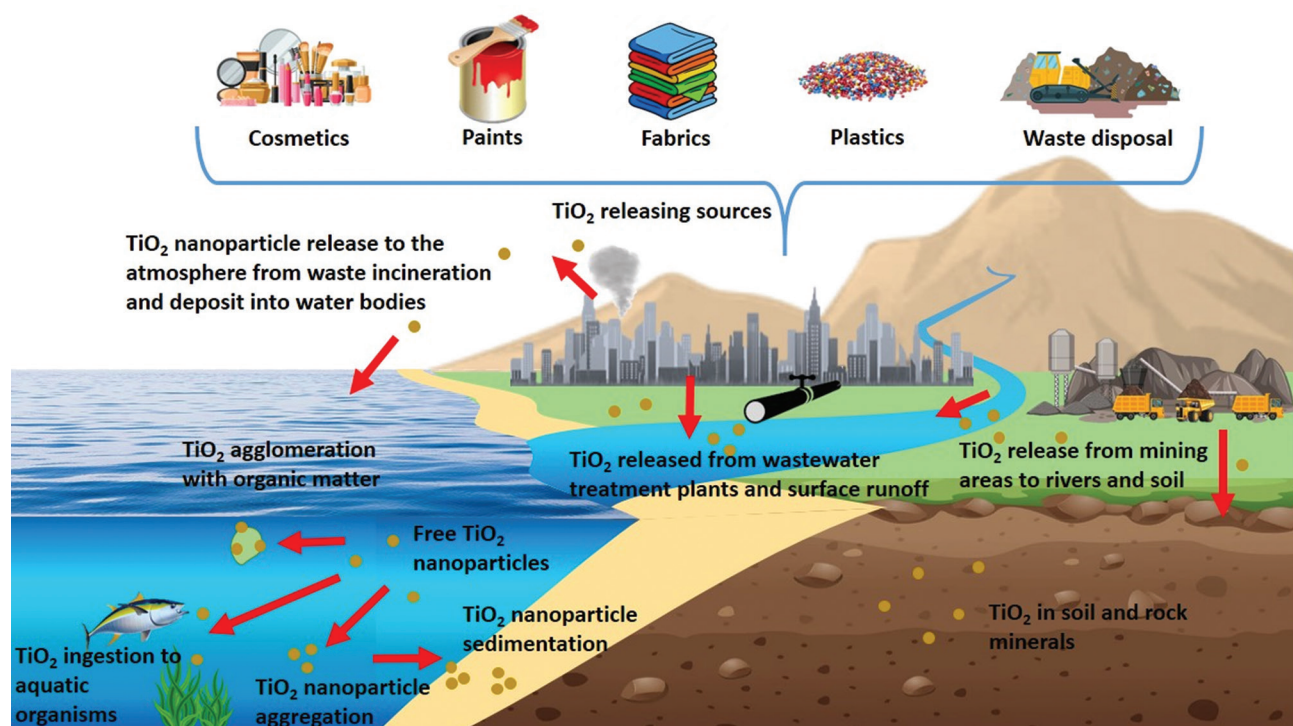


Figure 1. Sources of titanium in terrestrial and aquatic environments. Created with Microsoft PowerPoint 2013 by Sandun Sandanayake and Meththika Vithanage (2025).

Abbreviation: TiO_2 : Titanium dioxide.

and regulatory ramifications. This work also seeks to fill important knowledge gaps regarding the dynamics, ecotoxicity, and remediation of Ti materials, including a critical assessment of the most recent experimental and theoretical results. As noted above, there is limited information available on the accumulation, fate, transport, and ecotoxicity of Ti in terrestrial and aquatic ecosystems, which is concerning given its increased use in a variety of industries that have resulted in the release of Ti into the environment. Similarly, there are few reviews on the remediation of Ti contamination in aquatic and terrestrial ecosystems,²⁹ as well as a dearth of comprehensive information on the specific pathways of Ti contamination, environmental effects, and mitigating techniques. This review seeks to: (i) Identify the sources of Ti inputs and contamination in terrestrial and aquatic ecosystems; (ii) elucidate the dynamics and interactions of Ti in the soil–water–plant continuum; (iii) characterize the effects of Ti accumulation in the environment on ecotoxicity; and (iv) discuss sustainable management strategies to reduce the risks that Ti accumulation in terrestrial and aquatic ecosystems presents.

The following search terms were used in a Web of Science Core Collections literature search: TS = (“Titanium”) AND TS = (“environment” OR “soil” OR “aquatic” OR “terrestrial” OR “sediment” OR “river” OR “lake” OR “marine” OR “ocean” OR “porous media”) AND TS = (“contamination” OR “origin” OR “source” OR “distribution” OR “speciation” OR “biogeochemical” OR “geochemical” OR “geochemistry” OR “biogeochemistry” OR “remediation” OR “toxic” OR “toxicity” OR “availability” OR “bioavailability” OR “management” OR “adsorption” OR “immobilization” OR “passivation” OR “phytoremediation”). The VOSviewer program (version 1.6.20; The Centre for Science and Technology Studies (CWTS), Leiden University, The Netherlands) was used to visualize the 5,819 results that were obtained from this search. This approach is intended to maximize understanding of the research landscape, highlight existing knowledge gaps, and guide future studies in Ti biogeochemistry, environmental impacts, and remediation strategies. Figure S1 presents the number of published papers on Ti in soils and aquatic ecosystems, as well as a keyword co-occurrence map indicating the themes that have been studied most frequently in this field. This figure includes a comprehensive roadmap on the topic, providing a visual representation of the progression and interconnected themes in Ti research.

2. Sources of Ti contamination

Although Ti was discovered in 1791 by the clergyman and geologist William Gregor,³⁰ it was not commercially used

until 1940 when the Kroll process was invented.³¹ Raw ores are reduced with petroleum-derived coke in a fluidized bed reactor at 1,000°C. After the mixture is treated with chlorine gas, TiCl_4 is produced, which is then reduced by liquid magnesium at 800 – 850°C. The resulting material is a porous sponge of Ti that is leached for purification, crushed, and melted in a consumable electrode vacuum arc furnace. To increase uniformity, Ti is remelted to remove inclusions. Other Ti extraction methods include Hunter’s sodium reduction of TiCl_4 and the fused salt electrolysis of TiCl_4 .³²

TiO_2 is manufactured and used in various particle sizes, as discussed earlier. TiO_2 NPs are among the most used forms of the material, having a high refractive index ($n = 2.4$) that makes them ideal in coating applications, cosmetics, food, inks, medicine, plastics, and textiles.³³ The NPs are also used in agriculture for enhancing the rate of photosynthesis, promoting plant growth,³⁴ and controlling plant diseases,³⁵ as well as for photocatalysts in water treatment and air purification.

Such a wide application of Ti has stimulated increased mining and processing of Ti minerals. Based on the USGS, 92% of the world’s consumption of TiO_2 relies on ilmenite.³⁶ Ti material production in China increased from 1.70 million metric tons in 2013 to 3.10 million metric tons in 2023.³⁷ Australia has abundant ilmenite and rutile, producing 790,000 metric tons of Ti minerals. Japan and Russia have limited resources of Ti minerals but produce 35,000 and 27,000 metric tons of Ti sponge, respectively (Table S1). The global implications of Ti contamination, particularly for regions with significant industrial or mining activities, have been discussed elsewhere.^{38–40}

2.1. Ti contamination from geogenic origin

Ti minerals are generally known to be inert in soils and resistant to weathering. As such, Ti concentrations in soils are commonly used to assess the rate of weathering of parental minerals. In contrast to many primary and secondary minerals, the weathering of Ti minerals does occur, albeit rather slowly.⁴¹ For example, neoformed anatase or the slow weathering of bedrock are the sources of rutile, which is most prevalent in soils.⁴² In contrast, the weathering of Ti minerals occurs more quickly in tropical soils. For example, 3.4% of Ti was found in soils from Australia,⁴³ 15% in soils from Norfolk Island,⁴⁴ and 15% in soils from Hawaii.⁴⁵ Due to extensive and prolonged weathering, 2.3% Ti is present in Brazilian soils.⁴⁶ It has been reported that regarding Ti mobility in an Amazonian ferralsol, weathering of Ti minerals proceeds as follows: Ilmenite, pseudorutile, rutile, and anatase. The authors noted that the weathering

process results in absolute Ti losses on the profile scale. Assessment of the mineral reactivity of Ti in soil indicates the movement of Ti at both the centimetric and profile scales, either as a dissolved element or as an organometallic compound. Furthermore, a large amount of Ti is recycled by vegetation, which also increases Ti mobility in soils.⁴⁶ These findings indicate that a soil's Ti content may be largely influenced by the weathering of Ti minerals, except for certain tropical soils.

In addition to Ti minerals, coal is rich in Ti. The Ti concentrations in coal samples collected from Colorado, Pennsylvania, Texas, and Washington, US, ranged from 2,800 to 6,500 mg/kg.⁴⁷ Meanwhile, the Ti concentrations in 37 coal samples collected at Xuzhou-Datun coal mine district, Jiangsu province, China, ranged between 266 and 7,430 mg/kg.⁴⁸ The combustion of coal results in the production of Magnéli-phase Ti oxides—nanoscale Ti suboxides ($\text{Ti}_x\text{O}_{2x-1}$, where $4 \leq x \leq 9$)—whose toxicity hazards on human health are still unknown.⁴⁹ The physicochemical characteristics of TiO_2 NPs have the potential to significantly impact both their toxicity and bioavailability. Researchers have documented that anatase TiO_2 NPs are cytotoxic or genotoxic.^{48,49} Inhalation of TiO_2 NPs is often reported as the primary exposure pathway in the human body during occupational exposure. Additionally, exposure to nano- TiO_2 has been shown to have negative consequences, including oxidative stress in human cells and genetic instability in animals. When exposed to TiO_2 NPs, the two most significant impacts reported in experimental animals (mice and rats) are lung cancer and pulmonary inflammatory reactions.⁴¹⁻⁴³ Zeman *et al.*⁵⁰ reported that when actual dosages were the only factor taken into account, as in certain inhalation experiments, inflammatory reactions resulted in noticeable adverse effects. Through the lung or gastrointestinal tract, TiO_2 NPs enter the systemic circulation and are distributed to the brain, spleen, liver, and kidneys, subsequently exerting localized toxicity.^{46,47}

A limited number of *in vivo* and *in vitro* studies have noted specific reproductive and developmental toxicity in experimental animals or cell cultures.⁴⁶⁻⁴⁸ It is unknown if human exposure to TiO_2 NPs results in similar toxicities. According to research on animals, prolonged exposure (environmental) may cause TiO_2 NPs to accumulate in organs or tissues.⁴⁸ Furthermore, at relatively high doses, TiO_2 NPs induce reactive oxygen species production and cell signal transduction pathway alteration, likely playing a key role in the etiology of TiO_2 -NP carcinogenesis.^{49,51} In general, TiO_2 NPs are more harmful than TiO_2 microparticles. Additional details on Ti toxicity are presented in Supplementary Information 1.

2.2. Ti contamination from anthropogenic activity

Concerns about Ti as an emerging contaminant have been largely focused on anthropogenic activity. Table 1 lists studies describing Ti contamination in the air/dust, mining zones, and sediments.

2.2.1. Ti mining sites and associated contamination of soils and sediments

Interestingly, there is limited information on environmental contamination resulting from mining activity. The Panzhihua region in Sichuan province, China, is the world's largest vanadium-Ti magnetite deposit. Yanguo *et al.*⁵¹ reported that concentrations of heavy metals were higher in the topsoil of the Panzhihua region, with Ti ranging from 0.29% to 0.44%, and Ti in stream sediments ranging from 0.37% to 5.28%. Based on the Muller index of geoaccumulation,⁶⁴ the authors concluded that metal pollution was more serious in the sediment than in the soils. Similarly, high concentrations of Ti, along with other heavy metals, were identified in a Ti mining site in Kwale County, Kenya, where Ti concentrations ranged from 0.47% to 2.8%.⁵² Another study was also conducted in Kwale at a distance of 2.86 km from the Ti mining plant, and the Ti content of the soils ranged from 0.3% to 1.5%.⁵³ Based on the data from Kabata-Pendias and Pendias,⁶⁵ Ti content in surface soils varied from 0.1% to 0.9% with a mean value of 0.35%. Ti soil concentrations higher than a background level could indicate potential risks to sensitive species.

2.2.2. Airborne particulate matter and dust

Airborne particulate matter (PM) is known to be a group 1 carcinogen to humans due to the presence of contaminants, such as polycyclic aromatic hydrocarbons (PAHs) (e.g., benzo(a)pyrene, nitro-PAHs, and quinones) and heavy metals (e.g., vanadium, copper, iron, and nickel). In an industrial suburban station located in Langreo, Spain, Ti in the PM_{10} was 15.3 ng/m³, which was determined to be of anthropogenic origin from the use of coal and coke production.⁵⁴ In China, coal burning is a major contributor to PM. Ti concentration in the fallen dust in arid and semi-arid Northern China was detected at 3,600 mg/kg.⁶⁶ In the dust storms of arid and semi-arid Northwest China, Ti concentrations ranged from 2,558.1 to 3,342.6 mg/kg.⁵⁶ Furthermore, indoor air pollution is a major global public health threat. A study conducted in Columbia and South Carolina, US, showed that the concentration of Ti in house hold dust ranged from 0 to 8,000 mg/kg,⁵⁵ primarily due to anthropogenic releases from paint during home renovations.

Table 1. Titanium (Ti) concentrations detected in the air/dust, sediments, and mining zones

Contaminated objects	Contamination sites	Ti concentrations	Locations	References
Mining zones/ near mining zones	Near a mining zone	0.29 – 0.44%	Panzhuhua region, China	51
	Ti mining zone	0.47 – 2.80%	Kwale District, Kenya	52
	2.86 km from Ti mining plant	0.30 – 1.50%	Kinondo area in Kwale, Kenya	53
Air/dust	In the air (PM ₁₀)	15.3 ng/m ³	Langreo, Spain	54
	Home (home dust)	0–8,000 mg/kg with particle size >450 nm	Columbia, South Carolina, US	55
	Dust storms	2,558.1 – 3,342.6 mg/kg	Arid and semiarid Northwest China	56
	Fallen dust in arid and semiarid Northern China	3,600 mg/kg	Arid and semiarid Northern China	57
	Brake pad dust	25,400 mg/kg	Katowice, Poland	58
Sediments	Bay area sediments	1,000 – 21,200 mg/kg with a mean of 5,550 mg/kg	From Thazhankuda to Kodyakkarai coast, India	59
	Marine sediments	530 – 19,539 mg/kg	Periyakalpet to Parangipettai coast of Tamil Nadu, India	60
	River sediments	4,600 – 5,200 mg/kg upstream and 4,700 – 6,100 mg/kg downstream from a coal ash spill site	Dan River, North Carolina, US	61
	River downstream sediments	TiO ₂ NPs ranging 75 – 193 mg/kg	A river downstream of a nano-manufacturer industrial site	62
	River sediments	TiO ₂ NPs ranging 365 – 871 mg/kg	Sava River, Slovenia	63

2.2.3. Sediments

Sediment contamination is mainly due to the release of Ti from mining sites and manufacturing plants. Ti concentrations in the Bay of Bengal coastline from Thazhankuda to Kodyakkarai coast, India, ranged from 1,000 to 21,200 mg/kg, although the cause of the pollution was not specified.⁵⁹ In another study, Ti concentrations in marine sediments from the Periyakalpet to Parangipettai coast of Tamil Nadu, India, ranged from 530 to 19,539 mg/kg.⁶⁰ This area has intensive industrial activities, and the discharge of effluents to the river is a common practice. A coal ash spill in the Dan River in North Carolina, US, resulted in Ti in the sediments of upstream and downstream areas, ranging from 4,600 to 5,200 mg/kg and 4,700 to 6,100 mg/kg, respectively. This type of spill is significant as Ti concentrations in the sediments were similar to those in coal ash.⁶¹

In addition to the bulk form of TiO₂, TiO₂ NPs have been detected in sediments. The concentrations of TiO₂ NPs in the sediment downstream of the Thur River, France, were found to be 75 – 193 mg/kg, which was caused by the release of manufactured TiO₂ NPs from industrial effluent and the wastewater treatment plant.⁶² In the Sava River, Slovenia, TiO₂-NP concentrations ranged from 365 to 871 mg/kg,⁶³ with the main pollution

sources in Vrhovo, Slovenia, are the chemical and glass industries.

2.3. Distinguishing features of natural (geogenic) and anthropogenic origins

As discussed, TiO₂ in the environment originates from either natural or anthropogenic sources. Distinguishing the two origins aids in interpreting toxicity data and the implementation of methods for remediation. However, determining the source is challenging. Particle size distribution was found not to be a significant factor for TiO₂ NPs in sludge-amended soils by del Real *et al.*,⁶⁷ who studied the physical and chemical features of natural and anthropogenic origin TiO₂ NPs. However, the structure of TiO₂ particles and their association with mineral-organic assemblages may provide some insights into their origin. When there were differences in the elemental fingerprints and mass distribution of engineered and geogenic Ti-containing nanomaterials, Bland *et al.*⁶⁸ distinguished sources using binomial logistic regression machine learning models. The nanomaterials were also characterized by single-particle inductively coupled plasma time-of-flight mass spectrometry (SP-ICP-TOFMS); this technique found that most of the geogenic Ti-containing nanomaterials had no elemental association. Consequently, a different strategy was applied

to analyze and categorize individual Ti-containing natural and engineered particles using SP-ICP-TOFMS.⁶⁹ The authors developed quantification techniques based on multielement fingerprints along with element mass ratios—and detection limits of particle types—using decision tree strategies that are independent of Ti's particle size distribution.

3. Distribution and biogeochemistry of Ti in the soils

3.1. Distribution

The weathering of ilmenite and rutile increases TiO₂ concentrations in soils, particularly those in tropical regions. For example, Ti concentrations in the topsoil of the Seville area, Spain, ranged from 1,162 to 8,353 mg/kg.⁷⁰ The authors found that this concentration range was attributed to natural processes rather than traffic and fertilizers. Although healthy, unpolluted soil is an element of the ecosystem, soils are often contaminated by anthropogenic materials that accumulate over extended periods. Agricultural soils subjected to long-term recycled water irrigation in Kano, Nigeria, resulted in Ti concentrations ranging from 4,600 to 14,300 mg/kg.⁷¹ Concentrations of TiO₂ NPs in Stormwater Green Infrastructure (SGI) soils varied between 550 and 1,800 mg/kg in Orange County, California, US.⁷² The SGI is an approach to filter stormwater through growing plants; thus, SGI soils can retain chemicals from the stormwater, including pollutants such as TiO₂ NPs. The mean Ti concentrations in topsoil and sub soils collected from Frydek-Mistek, Czech Republic, were 4,664.4 mg/kg and 4,863 mg/kg, respectively, potentially due to atmospheric deposition resulting from the steel industry, vehicular emissions, tire abrasion, and agricultural operations.⁷³

The TiO₂-bearing rocks from quartzite and quartzitic sandstone quarries in Wiśniówka, Poland had a mean Ti content of 5,036 ± 696 mg/kg in clayey-silty shales and 1,972 ± 682 mg/kg in quartzites/sandstones, while the rocks from Fe-Ti oxide ore in gabbroic complexes in Abu Ghalaga, Egypt, had a mean Ti content of 481,100 mg/kg in ilmenite minerals and 88,800 mg/kg in titanomagnetite minerals (Table 2).⁵

Ti concentrations in soil vary based on the geological characteristics of a particular location (Table 2). The soil Ti content in areas with fewer human activities, such as forest areas (e.g., Amazonian Craton), ranged from 116 – 741 mg/kg (mean: 433 ± 178 mg/kg) in Brazil⁷⁴ while Scandinavian Mountain slopes in Sweden reported a Ti content of 3,660 – 7,830 mg/kg (median: 4,170 mg/kg).⁷⁵ Topsoil in agricultural lands at the Hexi Corridor in China showed a similar Ti content (1,448 – 7,919 mg/kg,

mean: 3,022 ± 1,047 mg/kg); however, agricultural topsoil from various countries in Europe showed higher Ti contents, depending on the parent material of the soils (median values from granite: 5,600 mg/kg, gneiss: 5,700 mg/kg, and schist: 8,000 mg/kg).⁷⁷ Ti contents recorded in the topsoil from urban areas, such as gardens and roadsides, had averages of 1,547 ± 765 mg/kg at Cape Town in South Africa,⁷⁸ 3,087 ± 947 mg/kg at Puning in China,⁸⁵ and 2,308 ± 154 mg/kg at Xining in China.⁸⁰ However, as noted above, human activities can release Ti to the soil environment.⁵ The disposal of Ti-containing industrial wastes contributes to high Ti levels in the nearby soils, as evident in Yerevan in Armenia, where the mean level was 4,115 ± 529 mg/kg due to direct industrial activity.⁸² Surprisingly, the soils and dust near the industrial region of Riyadh in Saudi Arabia recorded low Ti levels of 24 – 240 mg/kg (mean: 117 mg/kg). The soil and dust samples from gold mining areas in Mahd Al Dhahab, Saudi Arabia, had slightly increased Ti content (631 – 987 mg/kg, mean: 809 mg/kg).⁸³ Understanding local Ti concentrations in soil is critical for a variety of applications and responses, ranging from agriculture to environmental management.

3.2. Biogeochemistry

Understanding the biogeochemistry of Ti in soil involves the study of the interaction between Ti and the soil environment. Ti is not an essential element for plant growth, and it is generally considered an inert element in soils, meaning it generally does not play a significant role in biological processes.⁸⁶ As discussed earlier, soil Ti is typically present in the form of minerals or mineral compounds. These Ti-containing minerals are often part of the natural geological composition of soil and rocks. Ilmenite contains both Fe and Ti and is often found in igneous rocks, sediments, and beach sands. When ilmenite weathers and breaks down, it releases Ti into the surrounding soil.⁸⁷ Rutile contributes to the Ti content in soil when metamorphic rocks undergo weathering. Anatase, another form of TiO₂ found in some igneous and metamorphic rocks, is less common than rutile.

Volcanic eruptions can introduce Ti into the soil through the deposition of volcanic ash and lava, which may contain Ti minerals.⁸⁸ Small amounts of Ti are also deposited into the soil from the atmosphere, mainly through dust and aerosol particles that contain Ti. At the same time, some fertilizers and soil amendments may contain traces of Ti, contributing to its presence in soil when these products are used.⁸⁹ The elevated concentrations of Ti in soil due to human activities could exert environmental implications and may require remediation efforts to mitigate potential impacts. Importantly, the pH and redox conditions of the soil affect the solubility and speciation of Ti, although the

Table 2. Titanium (Ti) concentrations and distribution in different soil environments across countries/regions

Country/region	Source/environment	Ti forms	Mass concentration (mg/kg)	References
Canaã dos Carajás, Brazil	Topsoil from undisturbed forest areas in the Amazonian Craton	Ti in soil minerals	116 – 741 (mean: 433±178)	74
Abisco, Sweden	Soil from Scandinavian Mountain slopes	Ti in soil minerals	3,660 – 7,830 (median: 4,170)	75
Hexi Corridor, China	Topsoil from farmlands	Ti in soil minerals	1,448 – 7,919 (mean: 3,022±1,047)	76
Europe (33 countries)	Topsoil from agricultural lands	TiO ₂ in soil derived from granite rocks	1,800 – 55,100 (median: 5,600)	77
		TiO ₂ in soil derived from gneiss rocks	1,400 – 15,700 (median: 5,700)	
		TiO ₂ in soil derived from schist rocks	3,000–19,900 (median: 8,000)	
Cape Town, South Africa	Topsoil from gardens/playgrounds/roadside	Ti in soil minerals	441 – 4,378 (mean: 1,547±765)	78
Puning, China	Topsoil from urban areas	Ti in soil minerals	1,216 – 6,896 (mean: 3,087±947)	79
Xining, China	Topsoil and dust from urban roadside	Ti in urban soil and dust minerals	1,580 – 2,610 (mean: 2,308±154)	80
China Mainland	Topsoil from sediments or alluvial soils	Ti in soil minerals	266 – 24,674 (mean: 3,661)	81
	Magmatic rocks	Ti in rock minerals	16 – 33,950 (mean: 3,749)	
	Sedimentary rocks	Ti in rock minerals	<10 – 29,888 (mean: 2,415)	
	Metamorphic rocks	Ti in rock minerals	<10 – 24,030 (mean: 3,597)	
Yerevan, Armenia	Topsoil from urban and industrial areas	Ti in soil minerals	2,169 – 6,835 (mean: 4,115±529)	82
Riyadh, Saudi Arabia	Industrial activity impacted the topsoil and dust particles	Ti in soil and dust particles	24 – 240 (mean: 117)	83
Mahd Al Dhahab, Saudi Arabia	Gold mining impacted the topsoil and dust particles	Ti in soil and dust particles	631 – 987 (mean: 809)	83
Abu Ghalaga, Egypt	Rocks from Fe-Ti oxide ore in gabbroic complexes	TiO ₂ in the ilmenite minerals	445,100 – 490,700 (mean: 481,100)	5
		TiO ₂ in titano-magnetite minerals	13,800 – 185,000 (mean: 88,800)	
Wiśniówka, Poland	TiO ₂ -bearing rocks from quartzite and quartzitic sandstone quarries	Ti in clayey-silty shales	4,124 – 6,300 (mean: 5,036±696)	84
		Ti in quartzites/sandstones	1,259 – 3,038 (mean: 1,972±682)	
Seville, Spain	Topsoil, <i>Nerium oleander</i> leaves, and <i>Lantana camara</i> leaves	Ti in soil minerals	1,162 – 8,353	70
Kano, Nigeria	Urban agricultural soils	Ti in rock minerals	4,600 – 14,300	71
Orange County and Los Angeles, California, United State	Topsoil from stormwater green infrastructures	Natural and engineered TiO ₂ nanoparticles	1,300 – 2,500	72
Frydek-Mistek, Czech Republic	Topsoiland subsoils from agricultural lands	Ti in rock minerals	Topsoil: 3,134 – 5,560 (mean: 4,664); Subsoils: 3,357 – 6,724 (mean: 4,863)	73

specific effect of pH on the solubility of Ti compounds in various soils is out of the scope of the present review. The chemical speciation of Ti under pH-dependent reactions is discussed in detail in the next section. In solution, Ti(OH)₂²⁺ ions, Ti(OH)₃³⁺ ions, and Ti(OH)₄ exist in different pH ranges; i.e., when pH <1, titanyl ions exist, and with increasing pH, Ti(OH)₄ dominates.⁹⁰ Finally, Ti(OH)₄ precipitates and dehydrates to form stable TiO₂.

The biogeochemistry of Ti in both soil and water is influenced by various factors, including the geological characteristics of an area.⁹¹ Regions with Ti-rich minerals are more likely to demonstrate high Ti concentrations in soil. Soil properties, such as pH, organic matter content, and mineral composition—all that can affect the mobility and solubility of Ti—are also key factors.^{92,93} Acidic soils may release more Ti into solution, while organic matter can complex with

Ti and hinder mobility. Under reducing conditions, Ti becomes more soluble and mobile.⁹⁴ Sedimentation leads to the accumulation of Ti in certain areas. Aquatic organisms accumulate Ti from the water column or sediments; this accumulation may vary depending on the species and their trophic level. Local climate, weather patterns, and seasonal variations can all significantly impact the mobility and behavior of Ti in both soil and water.

There is a range of different Ti chemical (polymorphic) forms and speciation stages, such as Ti oxocation (titanyl TiO^{2+}) and Ti(IV) dihydroxideion ($\text{Ti}[\text{OH}]_2^{2+}$), each with a distinct set of features and environmental implications (Table S2). Being aware of Ti speciation is essential for comprehending its behavior, mobility, and potential impact on the environment. In general, in aqueous (acidic) solutions, Ti forms different complexes with hydroxyl groups (the dominance of di/tetra-valent ions). The general formula for these complexes is $[\text{Ti}(\text{OH})_n(\text{H}_2\text{O})_{(6-n)}]^{(4-n)+}$ ($0 \leq n \leq 4$).⁹⁵ Kumar *et al.*⁹⁶ and Migaszewski and Gałuszka⁸⁴ discussed that TiO_2 exists in different polymorphs in nature, including tetragonal anatase, tetragonal rutile, nanocrystalline TiO_2 , and orthorhombic brookite. Amorphous TiO_2 is a non-crystalline type of TiO_2 .⁹⁷ Thermodynamically, rutile is more stable due to its formation under high pressures and temperatures ($>500^\circ\text{C}$), while brookite and anatase are often created under low pressures. This increases the likelihood of anatase and brookite conversion to the rutile form rather than the reverse process. Notably, Ti mobility and solubility usually increase when complexed with organic and inorganic ligands.^{92,93,95}

4. Distribution and biogeochemistry of Ti in the aquatic environment

4.1. Distribution

Sanitary sewer overflows are a major issue in the US, which often leads to the release of contaminants, such as TiO_2 NPs, into water. Sousa *et al.*⁹⁸ reported that TiO_2 NPs are not removed during the sewage treatment process, and the particles enter surface waters along with the treated sewage at estimated concentrations of 20 – 10,000 ng/L. Surface water samples collected from Crane Creek, Stoop Creek, and Gills Creek in Columbia, South Carolina, US, demonstrated TiO_2 -NP concentrations ranging from 1 to 95 mg/L, with a mean of 25 mg/L.⁹⁹ TiO_2 -NP concentrations in the beach shorelines close to the bathing zones in the French Mediterranean ranged from 100 to 900 mg/L; this presence was attributed to the use of sunscreens that contain TiO_2 NPs. TiO_2 -NP concentrations downstream of the Thurriver, France, were found to be 133 – 260 mg/L, which was attributed to the nearby nanomaterial manufacturing industry.⁶² In Taihu Lake, China, TiO_2 -NP

concentrations ranged from 0.1 to 10 mg/L, with a mean level of 21.1 mg/L.¹⁰⁰ Additionally, TiO_2 NP contamination has been reported in other freshwater locations, including forest brooks, agricultural streams, urban streams, and urban watersheds (Table 3).

Ti is detected in aquatic habitats, such as freshwater and marine ecosystems, mostly in the form of TiO_2 NPs.¹⁰⁸ The accumulation of Ti in these water bodies is caused by a complex interaction of natural geological processes and human activities. TiO_2 contents in surface waters have been estimated to range from 2 to 700 ng/L,¹⁰² demonstrating that the distribution of Ti in aquatic environments is not homogeneous and varies from place to place (Table 3). Minerals such as ilmenite, rutile, and anatase in rocks and soils weather and degrade over time, releasing TiO_2 particles into surface water bodies, including rivers, lakes, and oceans. The richness of these minerals in the surrounding geology could have a direct influence on the concentration of Ti in the water bodies, and anthropogenic activities based on these minerals could aggravate the release of Ti into surface waters.¹⁰²

Kiser *et al.*¹¹³ reported that the raw sewage of a wastewater treatment facility in Central Arizona, US, contained Ti as $1 - 30 \times 10^5$ ng/L, and the effluents of the treatment facility still exhibited $5 - 15 \times 10^3$ ng/L of Ti. Aside from wastewater treatment plants, surface water bodies can be directly or indirectly exposed to TiO_2 NPs via landfills, combustion processes, product applications, rainwater deposition, agricultural non-point sources, surface runoff, underground leaching, and accidental release during production and transportation.¹¹⁴ Azimzada *et al.*¹⁰¹ found that the Ti content of river water samples collected from the Netherlands, Germany, Italy, and the US were 5.8 ± 5.6 , 75.1 ± 11.5 , 143 ± 114 , and 524 ± 255 ng/L, respectively, while in Brazil, the levels were reported at $2,262 \pm 423$ ng/L. Similar values were observed in lake water samples from China (6.4 ± 4.8 ng/L) and the United Kingdom (135 ± 45.9 ng/L). Meanwhile, the Tamsui River basin in Taiwan showed high Ti levels ($1,040 \pm 40.0 - 31,700 \pm 600$ ng/L).¹⁰² Importantly, the intensification of industrialization and the application of Ti-nanomaterials are expected to increase NP release and dispersion in river systems.

Due to the protonation–deprotonation equilibria of the surface hydroxyl groups, TiO_2 surfaces present a pH-dependent charge. More specifically, there is a negative charge in higher pH environments and a positive charge in acidic environments.³³ The pH at which the particle's total charge is zero, or the point of zero charge, divides these regimes.^{115,116} Since the Derjaguin–Landau–Verwey–Overbeek force typically controls the aggregation of TiO_2 particles, the strength of the repulsive forces coming

Table 3. Titanium (Ti) concentrations and distribution in aquatic environments across countries/regions

Country/region	Source/environment	Ti forms	Mass concentration	Particle number concentration (particles/L)	References
Arnhem, Netherlands	Ti-based nanoparticles in the Nederrijnriver water	TiO ₂ in nanoparticles	5.8±5.6 ng/L	(1.7±1.2)×10 ⁷	101
Tamsui River basin, Taiwan	TiO ₂ nanoparticles in river water	TiO ₂ in nanoparticles	1,040±40.0 – 31,700±600 ng/L	(4.54±0.56 – 47.9±16.3)×10 ⁴	102
Munich, Germany	Ti-based nanoparticles in the Isar river water	TiO ₂ in nanoparticles	75.1±11.5 ng/L	(1.5±0.2)×10 ⁸	101
Le Chambon-sur-Lignon, France	Ti-based nanoparticles in the Lignon du Velayriver water	TiO ₂ in nanoparticles	332±56.9 ng/L	(1.9±0.3)×10 ⁹	101
Besòsriver basin, Spain	Ti-based nanoparticles in river water	Ti-based nanoparticles	-	(2.32 – 29.8) ×10 ⁷ (mean: 8.0×10 ⁷)	103
Sao Paulo, Brazil	Ti-based nanoparticles in the Rio Passo River water	TiO ₂ in nanoparticles	2,262±423 ng/L	(6.8±1.2)×10 ⁹	101
Venice, Italy	Ti-based nanoparticles in the Rio del Gozzi Canal water	TiO ₂ in nanoparticles	143±114 ng/L	(8.0±1.8)×10 ⁸	101
Durham, US	Ti-based nanoparticles in stream water	TiO ₂ in nanoparticles	524±255 ng/L	(2.9±1.2)×10 ⁹	101
Zhuzhou, China	Terrigenous TiO ₂ in the Xiangjiang River sediments	TiO ₂ in river sediments	7,400–58,700 mg/kg	-	104
Bayannur, China	Ti-based nanoparticles in the Ulansu Lake	Ti-based nanoparticles	6.4±4.8 ng/L	(2.0±1.0)×10 ⁷	101
London, UK	Ti-based nanoparticles in the Long Water lake	Ti-based nanoparticles	135±45.9 ng/L	(1.9±1.2)×10 ⁹	101
Melbourne, Australia	Ti-based nanomaterials in lakes, basins, and wetlands	Ti-based nanomaterials	-	(1.64±0.26 – 25.8±1.0)×10 ⁸	105
	Ti-based nanomaterials in wastewater treatment plant effluents	Ti-based nanomaterials	-	LOD–(3.20±0.12)×10 ⁹	
Vancouver, Canada	Ti-based nanoparticles in the Strait of Georgia (seawater)	TiO ₂ in nanoparticles	15.5 ng/L	(2.3±0.0)×10 ⁸	101
Førde Fjord, Vestland county, Norway	Ti-based nanoparticles in the fjord (seawater)	Ti in nanoparticles	LOD–127 ng/L	-	106
Laizhou Bay, China	Ti-based nanoparticles in seawater	TiO ₂ in nanoparticles	200 – 199,000 ng/L (median: 820 ng/L)	(5.75 – 97.3) ×10 ⁷ (mean: 1.75×10 ⁸)	107
	Ti-based nanoparticles in marine sediments	TiO ₂ in nanoparticles	1.02 – 123 mg/kg (median: 27.3 mg/kg)	(3.70 – 156) ×10 ¹¹ particles/kg (mean: 77.5×10 ¹¹)	
Casablanca, Morocco	Ti-based nanoparticles in the Atlantic Ocean	TiO ₂ in nanoparticles	48.9 ng/L	(5.2±0.0)×10 ⁸	101
Xiamen Bay, China	Ti-based nanomaterials in marine sediments	Ti-based nanomaterials	2,340 – 6,330 mg/kg (mean: 4,360±1,480 mg/kg)	-	108
Pulmoddai, Sri Lanka	Heavy mineral coastal deposits	TiO ₂ in ilmenite minerals	493,400 mg/kg	-	109
South Carolina, US	Ti-based nanoparticles in surface water (Crane Creek, Stoop Creek, and Gills Creek)	TiO ₂ -engineered nanoparticles	95 µg/L	-	99
French Mediterranean coast	Ti-based nanomaterialsin surface water (beach shoreline in bathing zones)	TiO ₂ -based nanomaterials	100 – 9 00 µg/L	-	110

(Cont'd...)

Table 3. (Continued)

Country/region	Source/environment	Ti forms	Mass concentration	Particle number concentration (particles/L)	References
France	Ti-based nanomaterials in the river downstream of a nano-manufacturer industrial site	TiO ₂ -based nanomaterials	133 – 260 µg/L	-	62
Taihu Lake, China	Ti-based nanoparticles in lake water	Ti in nanoparticles	0.1 – 10 µg/L	(2.28 – 2.78) × 10 ⁵	100
Sava River, Slovenia	Ti-based nanoparticles in river water	TiO ₂ in nanoparticles	1.96 – 7.23 µg/L	(0.07 – 7.0) × 10 ⁶	63
Seine River watershed, west of Paris, France	Ti-based nanoparticles in a forested brook	TiO ₂ in nanoparticles	3.5 – 23.4 µg/L	(9 – 900) × 10 ⁸	111
	Ti-based nanoparticles in an agricultural stream		1.4 – 69.6 µg/L		
	Ti-based nanoparticles in an urban stream		0.5 – 5.9 µg/L		
Columbia, South Carolina, US	Ti-based nanoparticles in the surface waters of urban watersheds (Lower Saluda River, Broad River, and Congaree River)	TiO ₂ -engineered nanoparticles	Lower Saluda: 39.2 ± 6.7 µg/L, Broad: 233.4 ± 8.1 µg/L, Congaree: 5,975.7 ± 88.8 µg/L	-	112

Abbreviations: LOD: Limit of detection; UK: United Kingdom; US: United States.

from the overlapping of electrical double layers that develop around the particles is determined by the surface potential and surface charges. The stability ratio values are usually calculated to represent the rate of aggregation in adispersion. Aggregation rates are normalized to those observed in unstable dispersions, where particle diffusion alone controls aggregation, in order to compute the stability ratios.^{117,118}

Due to the dilution effect, Ti levels in marine ecosystems maybe lower than in freshwater systems. Ti levels recorded in coastal seawater samples from Canada and Norway were 10,000 ng/L and 40 – 400 ng/L, respectively, while seawater from Laizhou Bay, China, showed levels of Tiat 200 – 199,000 ng/L (median: 820 ng/L).^{101,106,107} An increase in Ti levels may occur around industrialized coastal areas or in estuaries where rivers deliver larger quantities of Ti from upstream sources. Suspended TiO₂ NPs in rivers and seawater have various surface characteristics and particle sizes, but eventually all will sink into the river and marine sediments due to aggregation with organic substances.¹⁰⁸ Therefore, the Ti concentrations in river and marine sediments could be much higher than the Ti content in the aqueous medium. Sediments in Xiangjiang River, China, showed a high Ti content of 7,400 to 58,700 mg/kg, which was largely due to the weathering of terrigenous minerals in the surrounding environment.¹⁰⁴ Ti in marine sediments was observed in Xiamen Bay, China, at 2,340 – 6,330 mg/kg (mean: 4,360 ± 1,480 mg/kg), while

comparatively low Ti content was present in Laizhou Bay, China (1.02 – 123 mg/kg, median: 27.3 mg/kg).¹⁰⁸ The potential factors for the large differences between Ti concentrations in these two sediments include organic matter contents, abundance of fine fractions of sediment (<63 µm), and pollution from industries and sewage discharges, as well as the occurrence of natural kaolinite minerals in the surrounding regions.

As noted earlier, atmospheric deposition is another natural mechanism for Ti to reach aquatic habitats. Ti particles in the atmosphere can be generated from a range of sources, including natural dust and industrial emissions, such as windblown mineral dust aerosols. In addition, agricultural activities (generate atmospheric dust), airborne PM (PM_{2.5}/PM₁₀), and photochemical reactions of TiO₂-coated material surfaces with atmospheric water vapor and oxygen/irradiation wave lengths are also the sources of TiO₂ in the air.¹¹⁹ These particles accumulate in water bodies, thus increasing the total Ti content.¹⁰⁸ Importantly, the non-homogeneous distribution of the Ti in aquatic environments is controlled by the availability of Ti minerals in the surrounding geology, the presence of industrial activity, and the type of water body, either freshwater or the oceans.

4.2. Biogeochemistry

In aquatic environments, Ti typically exists in the form of suspended PM and is often found associated with

solid particles suspended in water.¹²⁰ TiO₂ can originate from the natural weathering of Ti minerals or industrial processes, such as the production of TiO₂ pigments. In some cases, Ti can form complexes with organic matter in water, resulting in colloidal complexes that may enhance its mobility. Sediments and suspended matter particles can transport Ti within aquatic systems, affecting its distribution and sedimentation processes.¹²¹ Although TiO₂ NPs are known to aggregate rapidly upon contact with solutions lacking electrolytes, it should be noted that this process is influenced by a variety of factors. For example, TiO₂ NPs tend to assemble in seawater within an hour, whereas they are stable in treated wastewater for hours.^{97,122} Furthermore, Gan *et al.*¹²² reported that natural organic matter inhibited the aggregation of TiO₂ NPs. Notably, when using coagulation techniques to extract TiO₂ NPs from water, coagulant types and water quality can significantly impact overall efficacy. Alkalinity, natural organic matter contents, and the type of ionic solutes and their strength are the factors that usually influence water quality parameters. Several groups have documented the application of Ti salts as an excellent coagulant for the purification of natural water and wastewater.¹²²⁻¹²⁴ TiO₂ NPs' remarkable adsorption and photocatalytic degradation properties make them effective for treating environmental pollutants. A suite of contaminants in soil, water, and air could be degraded by TiO₂ NPs due to their potent oxidative potential.¹²⁴ In aquatic environments, the adsorption or redox transformation of pollutants by TiO₂ NPs may decrease the elements' mobility and bioavailability.

Improper disposal of waste materials that contain Ti can result in leaching to soil and groundwater. This occurs when industrial wastes, construction debris, or discarded consumer products with Ti are not managed and disposed of properly. Some agricultural practices involve the use of Ti-based materials, such as TiO₂, as a whitening agent in animal feed. Runoff from agricultural fields carries these materials into nearby water bodies or soil. Additionally, stormwater runoff from urban areas may also transport these particles into water bodies. Notably, accidental spills of Ti-containing materials can result in the sudden release of Ti into the environment, including soil and water.¹²⁵

4.3. Bioavailability and toxicity of Ti

4.3.1. Microorganism and plant-Ti interactions

The toxicity of NPs to plants and microorganisms depends not only on their concentration but also on the particle size. A number of published papers investigated the impact of Ti on soil microorganisms and reported that TiO₂ can inhibit the growth of essential soil microorganisms.^{126,127}

Simonin *et al.*¹²⁸ added 1 – 500 mg/kg nano scale TiO₂ to the soil for 90 days and observed significant shifts in several bacterial groups, leading to compromised nitrification and other nitrogen cycling processes. Meanwhile, Moll *et al.*¹²⁹ showed that although prokaryotic organisms were impacted by TiO₂ exposure in the soil, fungal groups remained unaffected. Bellani *et al.*¹²⁶ reported dose-dependent impacts of nanoscale TiO₂ on bacterial diversity and observed that 800 mg/kg induced changes, but 80 mg/kg had little impact on bacterial diversity and populations. Conversely, Kaur *et al.*¹²⁷ exposed soils to 1 – 20 mg/L TiO₂ and reported dose-dependent impacts, with stimulated microfloral growth and activity at low doses but inhibitory effects at high concentrations (>15 mg/L). Interestingly, contradictory results were obtained by Zhang *et al.*,¹³⁰ who exposed soils to 1,000 mg/kg TiO₂ and Fe₃O₄ NPs. The authors observed changes in soil pH and available nutrient fractions, but there was no impact on the populations of soil bacteria or fungi.

The existing literature on plant-Ti interactions falls into three general categories, including phytotoxicity, growth promotion/disease suppression, and the biosynthesis of nanoscale TiO₂ for other purposes (Tables 4, S3 and S4). The number of papers published in the former two categories is roughly equivalent, with the vast majority being focused on nanoscale TiO₂; the literature on biosynthesis is more limited (Figure 2).

With regard to phytotoxicity, a number of mechanisms have been proposed for TiO₂-induced toxicity (Figures 3 and S2). Doronila and Fox¹³¹ reported on the regrowth of native plant species on a TiO₂ residue pond in Australia, and observed that by 5 years, species richness and metal contents were largely equivalent to the control sites. Experimentally, Asliand Neumann¹³² exposed corn to TiO₂ colloidal suspensions under laboratory hydroponic or soil conditions. They noted a reduction in plant water flow, potentially resulting from apoplastic inhibition; however, shoot production recovered after extended exposure. Besides, Ghosh *et al.*¹³³ observed increased lipid peroxidation and DNA damage in TiO₂ (4 mM)-exposed onion and tobacco. Similarly, Song *et al.*¹³⁴ observed a dose-dependent toxicity in *Lemna minor* L. upon anatase TiO₂ NP exposure, with concentrations above 200 mg/L causing progressively greater impact.

Alternatively, Larue *et al.*¹³⁶ reported minimal physiological impact on wheat and canola from TiO₂ NP exposure, despite Ti accumulation occurring in both species. Song *et al.*¹³⁷ demonstrated minimal phytotoxicity of nanoscale TiO₂ to three plant species as measured by a range of parameters; the authors suggested that particle agglomeration under environmentally relevant conditions

Table 4. Selected studies on plant–titanium (Ti) interactions and corresponding treatment technologies

Plant species	Concentration (mg/L, unless otherwise stated)	Treatment technology	Effects	References
Multiple native species	Not stated	Native species growth on a TiO ₂ residue containment pond was measured 5 years after exposure	Normal native plant species rehabilitation on site	131
<i>Zea mays</i>	300 – 1,000	Laboratory Ti exposure in water to maize roots; impacts on water transport and leaf response were measured	Exposure caused reduced water transport; impacted leaf function from physical inhibition of apoplastic flow	132
<i>Allium cepa</i> , <i>Nicotiana tabacum</i>	0 – 10 mM	Genotoxicity evaluated by comet assay and DNA laddering	Micronuclei, chromosomal aberrations, and reduced root growth linked to lipid peroxidation	133
<i>Lemna minor</i>	1 – 2,000	Exposure in media to nanoparticles (NPs) or bulk TiO ₂ for 7 days. Plant growth, chlorophyll, and antioxidant defense enzymes were measured	Particle size- and dose-dependent effects; growth stimulation at low doses but toxicity at high doses	134
<i>Brassica napus</i> , <i>Triticum aestivum</i> , <i>Arabidopsis thaliana</i>	10	Hydroponic exposure. Germination, root elongation, dry biomass, and evapotranspiration were measured. Particle uptake evaluated by electron microscopy and X-ray techniques	Ti accumulated in plants, but no impacts on germination or growth	136
<i>Brassica campestris ssp. Napus</i> , <i>Lactuca sativa</i> , <i>Phaseolus vulgaris</i>	0 – 5,000	Hydroponic exposure. Germination, root elongation, chlorophyll and stress enzymes measured	Ti accumulated in plants but little phytotoxicity evident	137
<i>Lactuca sativa</i> , <i>Lycopersicon lycopersicum</i> , <i>Brassica oleracea</i> , <i>Glycine max</i> , <i>Daucus carota</i> , <i>Lolium perenne</i> , <i>Z. mays</i> , <i>Cucumis sativus</i> , <i>Avena sativa</i> , <i>Allium cepa</i>	250 – 1,000	Seed germination, cotyledon development, and root length	Eight of 10 species responded to exposure; many with enhanced germination and growth at lower concentrations. Nonlinear dose-response evident	138
<i>Panicum virgatum</i>	0 – 2.5%	TiO ₂ NPs' impact on plant growth, development, and expression of microRNAs measured	Dose-dependent toxicity as measured by inhibited root development and altered microRNA expression	139
<i>Aristolochia debilis</i>	10	Transfer of NPs within the terrestrial food chain assessed. Eggs of the swallowtail butterfly were hatched on the leaves of <i>A. debilis</i> grown in the presence of TiO ₂	TiO ₂ detected in plant vasculature; particles transferred from the plant to the larvae, and with release to the environment via larval excretion	140
<i>Glycine max</i>	250 – 1,000	Impact of exposure on seed germination, growth, content of reactive oxygen species, lipid peroxidation, and activity of antioxidant enzymes in roots	No impact on germination; some root damage due to the physical adsorption of aggregated TiO ₂	141
<i>Vallisneria natans</i>	5 – 20	Exposure to nanoscale and bulk TiO ₂ NPs; impact on plant health and epiphytic microbial community assessed	Exposure damaged plant leaf cells and disrupted the epiphytic community (increasing some groups, decreasing others)	142
<i>Z. mays</i>	100 – 1,000 mg/kg	Maize growth, photosynthetic activity, and biochemical response were determined, as was Ti uptake. Impacts on soil microbiome and enzyme activity were assessed	Plant growth, biomass, and photosynthetic activity. Some lipid peroxidation occurred at higher doses. Evidence of some disruption of soil health	143

limited the effective dose. Meanwhile, Andersen *et al.*¹³⁸ developed a modified standard phytotoxicity assay and noted that eight of 10 plant species exhibited negative effects upon exposure to 250 – 1,000 mg/L TiO₂. Similarly, Boykov *et al.*¹³⁹ reported that TiO₂ NPs significantly reduced

switchgrass root development and altered microRNA expression. In an interesting demonstration of trophic transfer, Kubo-Irie *et al.*¹⁴⁰ observed that swallowtail butterflies that fed on *Aristolochia debilis* exposed to 10 mg/L TiO₂ NPs accumulated Ti, with subsequent transfer to the

environment from excretion. More recently, de Melo *et al.*¹⁴¹ observed that exposure of soybean to 250 – 1,000 mg/L

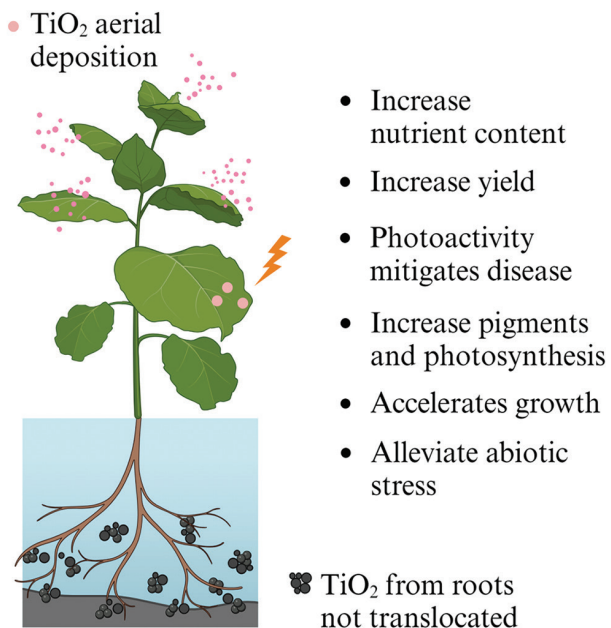


Figure 2. Schematic highlighting the overall beneficial effects on plants exposed to TiO₂ nanoparticles. Created with BioRender.com. Zuverza-Mena, N. and White, J. (2025) <https://BioRender.com/lwvj7lx>.

TiO₂ NPs led to significant root tissue damage, largely through particle adsorption and direct physical interaction. Similarly, Alklaf *et al.*¹⁴² reported that exposure of the aquatic plant *Vallisneria natans* to 5 – 20 mg/L anatase for 30 days resulted in damaged leaf cells, altered epiphytic species composition, and reduced interaction intensity among the epiphytic genera in the microbiome. Bakshi and Kumar¹⁴³ reported that exposure of corn grown in soil to TiO₂ NPs at concentrations of 100 – 1,000 mg/kg had little impact on growth or photosynthesis. However, oxidative stress and Ti uptake were observed at the high dose range. Similar observations were reported for green pea (*Pisum sativum* L.) at 10 – 100 mg/L TiO₂ NPs.¹⁴⁴

5. Risk management of Ti in the contaminated environment

5.1. Remediation of Ti-contaminated soil

The investigation of Ti removal from the environment is limited due to the generally perceived low biological toxicity of the element.¹⁴⁵ However, with the escalating utilization of Ti-containing products and the emergence of negative incidents, such as the European Food Safety Authority (EFSA)'s prohibition on the use of nano/micro TiO₂ in food and the genotoxicity of TiO₂ indicated by meta-analyses,^{146,147} it has become imperative to regulate

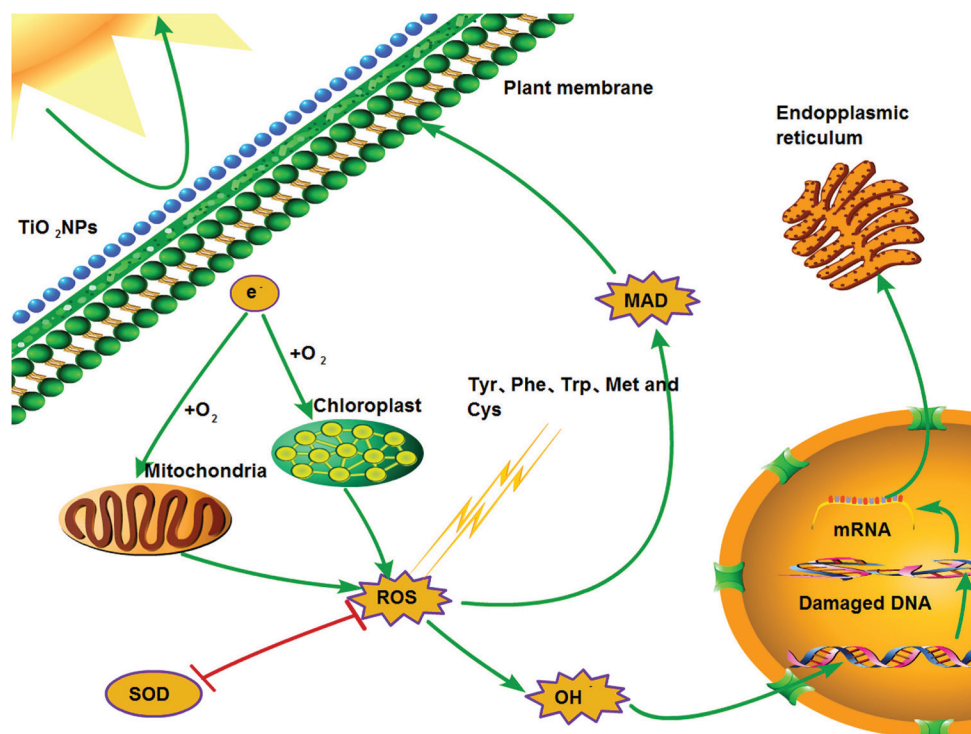


Figure 3. TiO₂ nanoparticles (NPs) interactions/mechanisms of toxicity with plant cells. Reprinted with permission from Hou *et al.*¹³⁵; Copyright 2019 Elsevier. Abbreviations: Cys: Cysteine; Met: Methionine; mRNA: Messenger RNA; OH: Hydroxyl group; Phe: Phenylalanine; ROS: Reactive oxygen species; SOD: Superoxide dismutase; Trp: Tryptophan; Tyr: Tyrosine.

the accumulation rate of Ti in the environment and mitigate associated environmental risks.¹⁴⁸

The National Institute for Occupational Safety and Health (NIOSH) classifies TiO₂ as a potential occupational carcinogen. However, in response to growing concerns over TiO₂ NPs' toxicity and the evidence of TiO₂ carcinogenic qualities in animal studies revealed by IARC, France has started a classification process under European Regulation (EC) No.1272/2008.^{118,149} According to the Toxic Enforcement and Safe Drinking Water Act administered by the Office of Environmental Health Hazard Assessment of the California Environmental Protection Agency, the list of chemicals known to cause cancer, created in 1986 under Proposition 65, was revised on September 2, 2011.^{118,150} This list was expanded to include respirable TiO₂ airborne particles.¹⁵¹ The US Food and Drug Administration has allowed TiO₂ as a food additive as long as its content is less than 1% of the food's weight. Similarly, as long as acceptable manufacturing procedures are adhered to, the EFSA also permits TiO₂ as a food additive with no maximum limit.³³ According to time-weighted average concentrations, the USNIOSH recommends exposure limits of 2.4 mg/m³ for "fine TiO₂" (including pigmentary TiO₂) and 0.3 mg/m³ for "ultrafine TiO₂" (including nano-TiO₂) for up to 10 h/day over a 40-h workweek.^{149,150} Additional detailed discussions on regulatory measures regarding the use of TiO₂ in consumer products are beyond the scope of the present review.

In the environment, the most prevalent oxidation state of Ti is the Ti(IV) ion, which shares similar characteristics with aluminum(III) and iron(III) ions, including the ionic radius.²⁴ Therefore, the removal of metal elements, such as aluminum and iron, can serve as a reference for Ti removal (Figure 4 and Table S5). In soil, Ti predominantly exists in a stable form, with limited concentrations in its available state and restricted uptake of NPs by plants, thereby making phytoremediation the primary approach for remediating elemental Ti and nano-Ti.^{34,152} More details are discussed in Supplementary Information 2.

6. Conclusion and future research directions

Although Ti is found naturally in certain mineral forms, such as rutile, brookite, anatase, ilmenite, and titanite, paints, nanomaterials, and wastes from mining and industrial processing are the primary anthropogenic sources of Ti accumulation in terrestrial and aquatic ecosystems. In general, Ti comes from terrestrial environments, such as ore. However, low mineral solubility and relatively strong adsorption onto soils and sediments

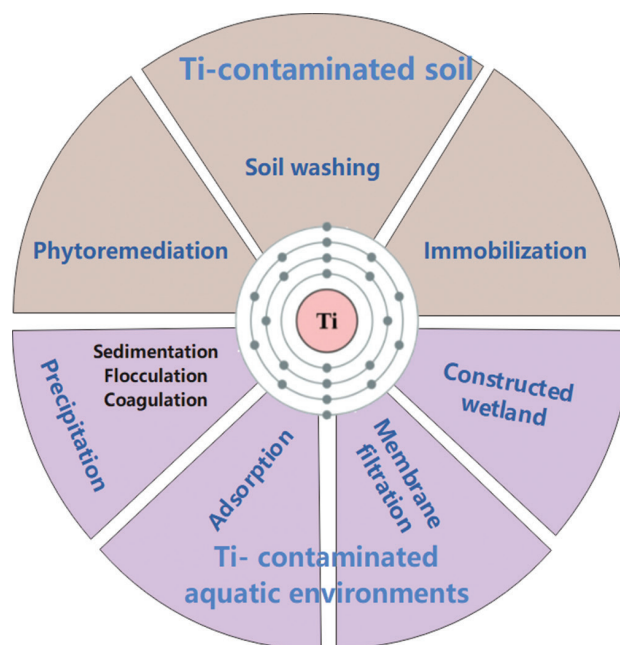


Figure 4. Technologies for the removal of titanium (Ti) from aquatic and soil environments. Created with Edraw Max by Xiaodong Yang (2025) <https://www.edrawsoft.cn/viewer/public/s/max/578fc91242b811f0aadcfda6796e95fb>.

limit the mobility of Ti in soil and groundwater sources; conversely, Ti's solubility and mobility are increased when it complexes with both inorganic and organic ligands. The current review summarizes the sources, biogeochemistry, and its effects on the environment and human health, as well as suggests future research areas of concern. This work also addresses Ti contamination's potential advantages or disadvantages in comparison to other materials, although there is a clear focus on negative impacts. Ti is considered a non-essential element for plant, animal, and human nutrition and is not toxic at low levels of uptake. However, excessive Ti uptake can cause toxicity to plants, soil organisms, aquatic life, animals, and humans. For example, dust inhalation of TiO₂ NPs by humans has resulted in chest pain, coughing, and breathing difficulty. There are several methods for remediating Ti-enriched aquatic and terrestrial environments, including ion exchange, flocculation, adsorption, phytoremediation, reverse osmosis, and nanofiltration.

Increased mining and processing, along with the wide application of Ti, have raised concerns about its pollution in the environment. TiO₂ particles are traditionally known to have low solubility and toxicity, and have been used as negative controls in many *in vivo* and *in vitro* toxicological analyses. Thus, Ti is not only a metal likely to see increased use but also potentially an emerging contaminant in the

environment. Research has demonstrated that TiO₂ NPs can have adverse effects on human health and ecosystems, as they accumulate in the environment and pose risks to various organisms. Given the importance and brief overview of Ti's application throughout history, its natural occurrence, anthropogenic sources, environmental effects, mitigation techniques, and existing knowledge gaps regarding the long-term environmental fate of TiO₂ NPs, the following research directions are suggested:

- (i) Processes of biogeochemical transformation: In both terrestrial and aquatic environments, Ti can be found in a variety of forms, such as free ionic species and inorganic and organic complexes. The interactions of Ti with soil and sediment components, as well as the transformation and bioavailability of Ti, are influenced by soil properties (e.g., pH, organic matter, and clay content), aquatic conditions (e.g., salinity and dissolved organic carbon), and environmental variables (e.g., moisture content and temperature). Additional mechanistic studies are needed to gain a comprehensive understanding of the underlying processes that ultimately control the environmental fate and disposition of Ti.
- (ii) Ecotoxicological assessment: While soluble Ti species in aquatic systems and soil solutions are generally less harmful to living organisms, excessive accumulation of TiO₂ NPs in soil and aquatic environments can be harmful to organisms. Therefore, it is necessary to employ biomonitoring techniques to track the ecotoxicity of TiO₂ NPs in both terrestrial and aquatic environments. An analysis of gaps in current policies is needed to identify how these shortcomings can be addressed to effectively manage environmental risks, i.e., the detailed discussions of regulatory requirements for Ti contamination. Discussions on regulatory measures regarding the use of TiO₂ in consumer products are also necessary. Increasing scrutiny may result in stricter regulations aimed at mitigating its environmental impact, especially as concerns grow over its toxicity and accumulation in ecosystems.
- (iii) Ti-contaminated soil and aquatic system remediation: To reduce the input of TiO₂ NPs into terrestrial and aquatic ecosystems through irrigation with recycled water and the application of biosolids, it is imperative to assess source control strategies. To accomplish risk-based remediation, *in situ* Ti stabilization techniques in contaminated soils and sediments—utilizing innovative and

effective adsorbents, such as biochar—and long-term monitoring of the release and remobilization of Ti are essential. The challenges associated with implementing conventional remediation techniques (e.g., cost, scalability, or regional feasibility) need to be discussed in detail. Furthermore, experimental methodologies for studying the long-term environmental fate of TiO₂ NPs, along with merging approaches such as machine learning for Ti removal from aquatic systems, need to be studied. Finally, long-term environmental effects and field-based toxicity data must be taken into account in future studies to bridge the knowledge gaps in these areas.

- (iv) Costs of remediation: It is imperative to critically evaluate the feasibility and cost-effectiveness of existing remediation techniques, such as phytoremediation and nanofiltration methods. Additionally, a comparison of the strengths and limitations of these methods, along with their applicability to real-world contamination scenarios, needs to be considered.

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REVIEW ARTICLE

Different methods and technologies of air pollution mitigation: An overview

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Abstract

Air pollution represents a critical dimension of environmental contamination and poses severe risks to human health and ecological systems. While environmental pollution can manifest in various forms—such as air, water, and soil pollution—air pollution remains the most pervasive and damaging. Rapid industrialization and the proliferation of pollution-intensive technologies have significantly contributed to the degradation of air quality. This review provides an overview of existing research focused on strategies for controlling and mitigating air pollution. Emphasis is placed on technological interventions, regulatory measures, and innovative approaches being explored to reduce airborne pollutants. The study also addresses current research gaps and proposes future approaches for air pollution mitigation measures.

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1. Introduction

Air pollution remains one of the most concerning environmental issues in modern society, contributing considerably to worldwide illness loads and environmental degradation. According to the World Health Organization, air pollution causes approximately 7 million premature deaths each year, with low- or middle-income countries bearing the greatest burden due to rising urbanization and insufficient regulatory restrictions.¹ Pollutants, including particulate matter (PM)_{2.5} and PM₁₀, nitrogen oxides (NO_x), sulfur dioxide (SO₂), and volatile organic compounds (VOCs), are increasingly prevalent due to both anthropogenic and natural sources. PM_{2.5} (PM with a diameter of <2.5 μm) can carry hazardous chemicals deep into the lungs, where they may enter the human bloodstream and cause significant health issues.²

A defining challenge of the Anthropocene is the catastrophic impact of air pollution on both health and economic growth.² According to the Global Burden of Disease research, various kinds of pollution caused 9 million deaths in 2015, with air pollution accounting for 6.5 million of them.² Furthermore, air pollution reduces gross domestic product in low- and middle-income nations by 2% every year.² If air pollutants are not effectively managed, they will continue to endanger human health.²

One of the most effective strategies for mitigating air pollution is reducing emissions.³ The effectiveness of air pollution control primarily depends on the political climate,

governmental transparency, and the nation's economic standing.³ Local issues can be addressed more effectively when there is a targeted approach supported by flexible policies.³ In developed nations such as the United States (US), industrialization has contributed to deteriorating air quality. In China, rapid technological advancement and urbanization have driven recent initiatives to reduce air pollution. Several studies indicate that technological improvements remain the most effective approach. Additional mitigation techniques include photocatalysis, strict enforcement of environmental regulations, smart city planning, the use of alternative vehicle fuels, radical-induced oxidation, renewable energy adoption, stainless steel catalysts, green infrastructure, and energy-based biofiltration. In particular, biofiltration, a technique in which off-gases containing inorganic air toxics or biodegradable VOCs are vented through a biologically active medium, has proven effective in controlling air pollution.⁴

As expected, coal continues to serve as a major source of electricity worldwide. Improving air quality requires better emission management, which can be supported by technological solutions.⁵ Photocatalysis, for example, has been demonstrated as an effective strategy for removing environmental contaminants from the atmosphere.⁶ In this process, powerful oxidizing and reducing agents are photochemically generated on a catalyst's surface, leading to the degradation of contaminants, particularly organic compounds.⁶ When treating air pollution in indoor or semi-enclosed spaces, photolysis, also known as visible light-driven photocatalysis, is recommended.⁷ However, nitrate compounds have been less responsive to efforts aiming at lowering NO_x emissions, which often increase during wintertime pollution episodes that cause haze.⁸ Weak deposition has been identified as the primary factor contributing to this seasonal rise in nitrate.⁸

Urban design also plays a significant role in reducing air pollution, as hotspots are not always directly associated with high traffic density.⁹ The Google ranking-inspired General Information Report approach can assist in ranking cities based on their environmental conditions.¹⁰ In addition, sensor modules are valuable tools for mitigating air pollution.⁹ These devices continuously monitor air pollutants such as PM, nitrogen dioxide (NO₂), SO₂, carbon monoxide (CO), ozone, and VOCs. By providing real-time data, they facilitate early detection of hazardous air quality conditions. Sensor modules can be strategically installed near traffic signals or toll booths.⁹ Furthermore, plant leaves can absorb PM, thereby lowering ambient concentrations.¹¹ Improving energy efficiency in the non-power sector can further reduce SO₂, NO_x, PM, and carbon dioxide (CO₂) emissions.¹²

The shipping industry is another contributor to air pollution, as oil combustion produces black smoke and emits high concentrations of NO_x, CO, CO₂, and other pollutants.¹³ In response, the global maritime and port sectors are developing new technologies, such as advanced engine systems and improved fuel quality.¹³ Biofuels, derived from organic matter, offer a promising alternative to conventional fossil fuels. They can reduce overall energy consumption and emissions.¹⁴ Different types of biofuels each offer specific advantages, such as enhanced atomization and low viscosity. Moreover, various renewable energy resources have the potential to replace fossil fuels, whereas hybrid power systems integrating multiple renewable sources can supply electricity more efficiently and significantly reduce carbon emissions.

This study aims to examine the technologies and techniques currently employed for air pollution mitigation, analyzing their mechanisms, applications, and overall effectiveness. It also seeks to identify research gaps and limitations in current air pollution control strategies, highlighting critical areas that require further investigation. In addition, the study assesses the effectiveness of various mitigation solutions across diverse environmental and socioeconomic contexts to understand their adaptability and real-world impact. Based on these findings, recommendations for future research are proposed to support the development of more effective and sustainable air quality management strategies.

2. Methodology

This study adopts a qualitative research approach through a comprehensive literature review to examine various methods and technologies for mitigating air pollution. The methodology involves collecting, analyzing, and synthesizing data from previously published research articles, industrial reports, environmental assessments, and relevant case studies. Sources were selected from peer-reviewed journals, reports by governmental and non-governmental organizations, and recognized environmental databases.

The literature review specifically focused on identifying the types and mechanisms of air pollution control, as well as distinguishing between active and passive control methods and technologies. Data collection was conducted through searches of electronic databases such as Google Scholar, ScienceDirect, ResearchGate, and other academic repositories, using keywords including "air pollution," "air pollution control," "environment pollution," "CO," "PM," "VOCs," and "electrification." Articles published between 2000 and 2023 were prioritized to ensure relevance and currency of information.

The findings were thematically categorized to highlight key concerns related to air pollution control technologies. Where applicable, comparative data and statistics were tabulated or referenced to support critical analysis.

3. Technical strategies

Effective air pollution control requires an integrated combination of technological, regulatory, and societal approaches. These strategies aim either to prevent pollutant formation at the source or to capture and treat emissions before they are released into the atmosphere. Control measures vary depending on the type of pollutant, source characteristics, and applicable environmental regulations. This section provides an overview of key methods and technologies for air pollution control, drawing on data from previous research.

Electrostatic precipitators (ESPs) are widely used in power plants and industrial facilities to remove PM, dust, and smoke. They operate by applying high-voltage electric fields to charge airborne particles, which are then attracted to oppositely charged collector plates. The particles accumulate on the plates and are periodically removed. Baghouse filters, also known as fabric filters, are highly effective in capturing fine particulates such as PM_{2.5} and PM₁₀, as well as heavy metals. Contaminated air passes through fabric filter bags that trap particles, allowing clean air to exit. Accumulated dust is periodically removed, making this system particularly efficient in industries such as cement, steel, and chemicals. Cyclone separators are typically used to eliminate coarse particle debris. In a cylindrical chamber, centrifugal force drives heavier particles toward the walls, separating them from the air stream. Cyclones are often used as pre-cleaners before more efficient filtration systems. Wet scrubbers are versatile devices capable of removing PM, SO₂, ammonia (NH₃), and certain VOCs. In these systems, polluted gas comes into contact with a scrubbing liquid—usually water (H₂O) or a chemical solution—that absorbs or reacts with the pollutants. The cleaned gas is released into the atmosphere, and the resulting liquid waste is treated separately. Activated carbon adsorption is widely used for removing VOCs, odors, and mercury. The high surface area and porosity of activated carbon granules enable pollutants to adhere to their surfaces. Spent carbon can be regenerated or replaced, making this method suitable for both indoor air purification and industrial exhaust treatment. Selective catalytic reduction (SCR) is commonly used to control NO_x emissions, especially in power plants and heavy-duty vehicles. In this process, NO_x gases react with NH₃ in the presence of a catalyst, producing harmless nitrogen and H₂O. Biofiltration is an environmentally friendly technique for treating air containing VOCs, hydrogen sulfide (H₂S),

and other odorous compounds. Polluted air is passed through a biologically active medium, such as compost or soil, where microorganisms degrade the organic pollutants. This method is particularly useful in wastewater treatment plants and food-processing industries. Finally, low-NO_x burners and combustion modification techniques aim to minimize NO_x formation during combustion. By altering conditions such as temperature, air-to-fuel ratio, and burner design, these approaches reduce NO_x emissions and are commonly applied in industrial boilers and furnaces.

Numerous methods and technologies are available for controlling air pollution. The most effective approaches, along with supporting data, are presented in the subsequent subsections.

3.1. Emission control technology improvements

Coal remains the primary fuel source for many power stations. While combustion of coal generates power, it also releases substantial amounts of pollutants, including SO₂, nitrous oxide (N₂O), PM, and mercury. Coal-fired power plants are major emitters of SO₂ and NO₂.⁵ PM is primarily released from coal ash generated during combustion.⁵ The quality of the coal plays a significant role in determining emission levels.⁵ Advancements in pollution control technologies can substantially reduce the concentration of pollutants emitted into the atmosphere. These technologies must be both cost-effective and efficient in removing pollutants. [Table 1](#) summarizes findings from previous studies on various air pollution control techniques, including their pollutant removal efficiencies, costs, and applicability.

3.2. Photocatalyst immobilization methods

Photocatalysis, especially using semiconductor materials such as titanium dioxide (TiO₂), offers a sustainable approach to air pollution mitigation by degrading pollutants such as NO_x, VOCs, and other hazardous air contaminants under ultraviolet or visible light. However, practical deployment of photocatalysts requires immobilization onto a substrate to prevent catalyst loss and facilitate continuous operation.⁶ Free (powdered) photocatalysts possess high surface area and reactivity but are impractical for large-scale, real-world applications due to challenges in recovery, particle agglomeration, and the risk of secondary pollution. Immobilization overcomes these limitations by anchoring the photocatalyst to a solid matrix or support, thereby improving durability and reusability.

The main photocatalyst immobilization techniques include ([Table 2](#)):

- Sol-gel method: A solution of metal alkoxides is hydrolyzed and polymerized to form a gel that

Table 1. Summary of techniques for air pollution control⁵

Techniques	SO ₂ (%)	NO _x (%)	Mercury (%)	Particulate matter (%)	Cost (\$/kW)	Applicability
Advanced dry scrubber	90–95	–	0–90	–	50–150	Pilot to commercial scale; it depends on the type of coal
Activated carbon injection with an electrostatic spray adsorption process	–	–	50–90	99	3–8	Pilot scale; retrofit and new plants with FF and ESP
Combined mercury and SO ₂ sorbents	40–85	–	Up to 90	–	30–60	Pilot scale; integrated with ESP or FF unit
WFGD with mercury oxidation process	95	–	>80	90% for >10 μm (up to 39.6% for PM _{2.5})	160–275	Pilot scale testing
Wet scrubbers with a wet electrostatic precipitator	99	–	80	90–99	10–20	Commercial level; integrated with existing wet scrubbers
Activated coke	90–98	15–80	90–99	80–85	150–200	New plants and retrofits
SCR with WFGD	95	90–95	40–90	90% for >10 μm (up to 39.6% for PM _{2.5})	SCR: 50–140; WFGD: 160–275	Commercial level
Electrocatalytic oxidation	98	90	90	86	200 (for 500 MW)	Demonstration level: new plants and retrofits

Abbreviations: SO₂: Sulfur dioxide; NO_x: Nitrogen dioxide; WFGD: Wet flue gas desulfurization; SCR: Selective catalytic reduction; FF: Fabric filter; ESP: Electrostatic precipitator; PM: Particulate matter.

Table 2. Factors influencing photocatalyst immobilization method selection⁶

Criteria	Consideration
Substrate type	Porous ceramics, glass, metals
Operating environment	Indoor versus outdoor, ultraviolet versus visible light
Pollutant target	Nitrogen oxides, volatile organic compounds, and particulate matter
Durability requirements	Resistance to weathering, abrasion
Reactor design	Batch versus continuous flow

embeds the photocatalyst onto a substrate (e.g., glass or ceramics). Advantages include excellent coating uniformity, strong substrate adhesion, and pore structure control that enables high surface area. The highest reported NO_x removal rate using this method is 16 mg/m² min.⁶ Limitations include the potential for cracking during drying and the complexity of its multi-step process

- **Thermal spraying:** The photocatalyst is deposited onto a surface by spraying at high temperatures, causing partial melting and strong adhesion. Variants include plasma spraying, flame spraying, and high-velocity oxy-fuel. Advantages are high durability and suitability for coating large and irregular surfaces. The highest reported VOCs removal rate is 107 mg/m²•min. Limitations include possible thermal degradation of photocatalyst (especially TiO₂) and reduced surface area and porosity
- **Dip coating:** The substrate is immersed in a suspension of photocatalyst, then withdrawn, dried, and calcined.

Advantages include simplicity, scalability, and potential good adhesion depending on the substrate. Limitations are the difficulty in controlling coating thickness and the need for multiple application cycles

- **Spin coating:** A small amount of catalyst suspension is dropped onto a substrate, which is then rapidly spun to distribute the liquid uniformly. Advantages include high uniformity and production of thin films ideal for optical applications. Limitations are its restriction to flat, small substrates and the poor mechanical strength of the resulting film
- **Chemical vapor deposition:** Volatile precursors decompose or react on a heated substrate to form a thin film. Advantages include strong adhesion, high purity, and good crystallinity. Limitations are high cost, operational complexity, and potential substrate damage from elevated temperatures
- **Electrophoretic deposition:** Charged photocatalyst particles are deposited onto a conductive substrate under an electric field. Advantages are rapid, efficient deposition and suitability for complex geometries. Limitations include the requirement for a conductive substrate and the need for post-deposition sintering.

3.3. Radical-induced oxidation

To remediate air pollutants present in flue gas, additional oxidants can be introduced as radical precursors. Various types of reactive radicals are used in this process, such as hydroxyl radicals, sulfate radicals, chlorine radicals, and ozone. These radicals can be generated and applied through different catalytic and photochemical pathways, such as homogeneous catalysis, heterogeneous catalysis,

thermal catalysis, photolysis, photocatalysis, and electrical catalysis. For sulfate radical-based processes, both single-catalyst and synergistic-catalyst approaches are possible, with the latter often achieving higher removal efficiencies due to enhanced reaction pathways. Table 3 summarizes the reported pollutant removal efficiencies for SO₂, NO_x, and mercury using different types of radicals.

3.4. Expansion of renewable energy use

The primary source of CO₂ emissions is the combustion of fossil fuels. Reducing fossil fuel use is therefore essential for mitigating air pollution. Transitioning to renewable energy offers multiple benefits, including lowering the demand for fossil fuels, ensuring a sustainable clean fuel resource, and reducing greenhouse gas emissions.

Previous research has examined hybrid power systems, such as one combining a lead–acid battery with renewable regeneration, and another applied in coastal regions of Bangladesh. Both systems demonstrated effective results in achieving sustainable electrification.¹ From these studies, it was observed that CO₂ emissions decreased from 67% to 64%. For instance, while a 1% increase in renewable energy can reduce air pollution management costs in China by 17–35%, the same increase yields a reduction of more than two-thirds in India. Increasing renewable energy capacity not only lowers CO₂ emissions but also contributes to controlling NO_x and PM levels in China; however, it is less effective in reducing SO₂ emissions.¹⁵

3.5. Catalytic methods for air pollution control

Catalysis, which encompasses catalytic oxidation and catalytic reduction, is an effective and energy-efficient approach to air pollution mitigation that produces no secondary pollutants.¹⁶ It has substantial emission-reduction potential, making it an essential component of global air pollution control strategies.¹⁶ Stainless steel catalysts have properties that make them suitable for installation near diesel engines to control emissions. For example, Co–Ba–K/ZrO₂/AISI 314 foam catalysts can be manufactured and utilized to remove both soot and NO_x.¹⁶ Catalytic combustion is particularly effective¹⁶ for oxidizing VOCs into CO₂ and H₂O at relatively lower temperatures

(200–500°C). Stainless steel is affordable, widely available, and its elemental compositions make it an effective support for VOC oxidation.

For NO_x control, SCR with NH₃ is the most effective method for tail gas denitrification. N₂O, which has a global warming potential approximately 300 times greater than CO₂, can be decomposed using monolithic stainless-steel supports, which have been widely applied in N₂O abatement.¹⁶

3.6. Biofiltration

Biofiltration is a low-cost biological process for air pollution control that requires minimal maintenance¹⁷ and produces fewer hazardous byproducts compared to many physicochemical techniques.¹⁷ It is also recognized for its potential to reduce atmospheric CO₂ levels. It entails passing polluted air through a bed of solid media, often maintained at a specific moisture level, where microorganisms degrade methanotrophs, ammonia-oxidizing bacteria, oligotrophic bacteria, fungi, and algae. Bacteria play the primary role in contaminant removal during biofiltration, whereas fungi aid in the degradation of complex compounds.¹⁷

Biofiltration can remove H₂S, odor, and VOCs, as well as carbon disulfide, when combined with biotrickling filtration.¹⁷ The efficiency of the process depends largely on the concentration and activity of microorganisms, as well as environmental factors such as temperature, pH, and moisture content.¹⁷

3.7. NH₃ emission reduction strategies

According to the GEOS-Chem model, decreasing VOCs and NO_x by 30% during winter leads to only an 8.6% reduction in PM levels. In contrast, NH₃ reduction is the most effective strategy for lowering PM_{2.5} nitrate concentrations, especially during winter haze events. Even small reductions in NH₃ emissions are beneficial.

A 50% reduction in NH₃ emissions can lower nitrate-containing PM_{2.5} by 25% and decrease haze days by 31%. Such a reduction also lowers total PM_{2.5} by 13% in winter, 18% on winter haze days, and 14% annually. Agriculture is a major source of NH₃ emissions, which can be reduced through measures such as optimized fertilizer application and improved manure management practices.

3.8. Traffic management and urban planning

Two primary strategies can be applied to mitigate urban air pollution: improving traffic systems and enhancing urban planning efficiency.

Traffic systems can be improved by establishing low-emission zones and enforcing strict penalties for traffic

Table 3. Summary of multi-pollutant removal efficiencies using different radicals⁷

Radical type	SO ₂ removal efficiency (%)	NO _x removal efficiency (%)	Mercury removal efficiency (%)
Hydroxyl radical	99–100	75–100	75–98
Sulfate radical	99–100	72–100	85–99
Chlorine radical	99–100	77–98	90–95
Ozone	97–100	91–97	82–91

law violations, which can moderately reduce air pollution.⁹ Studies show that heavy-duty diesel vehicles are responsible for 40–60% of NO_x emissions and 70–90% of CO₂ emissions from black smoke.⁹ One-way traffic flow has been found to be more effective in reducing emissions.⁹ Reducing the number of heavy diesel vehicles and improving road pavement quality can further limit air pollution.⁹

The adoption of electric vehicles and advancements in engine technology can mitigate transport-related emissions.⁹ Between these two options, electric vehicles are considered the most effective;⁹ VOC emissions are reduced by 98% and NO_x emissions by 34% compared to conventional vehicles.⁹ Strict regulatory enforcement remains critical to further reduce transportation-related pollution.⁹

Urban planning also plays a significant role in air quality management. Effective city layouts should facilitate natural ventilation into open spaces. Building height is an important factor in dispersing pollutants.⁹ Weather conditions, such as wind speed, sunlight, temperature, and humidity, should be considered in planning. Urban greenery, such as roadside tree planting, promotes pollutant deposition and can facilitate beneficial chemical reactions that further reduce air pollution.⁹

3.9. XGBoost and grid ranking for pollution source identification

Research on XGBoost and grid ranking methods has not adequately captured air quality dynamics across entire regions, despite broad geographic coverage. The General Information Report approach is comparable to the Google PageRank algorithm, which ranks web pages based on their impact.¹⁰ XGBoost, a non-linear machine learning algorithm, incorporates variable relevance mechanisms to enhance predictive performance.^{10,11} This approach can identify the pollution sources that have the greatest influence on other areas, enabling targeted interventions to mitigate air pollution.¹⁰ For example, studies have shown that XGBoost can be applied in various fields, including environmental monitoring, and can guide governments to prioritize air pollution prevention in high-impact regions, such as southern Oregon, which has been identified as significantly affecting air quality in northern parts of the US.¹⁰

3.10. Cloud computing-based air pollution monitoring systems

Cloud-based air pollution monitoring systems store air pollution data in a centralized database. In this approach,⁹ sensor modules are installed at toll collection centers and traffic light intersections. When a vehicle passes these points, the system measures its emissions and uploads the

data to the cloud. If emissions exceed permissible limits, both the local police and the vehicle owner are notified. The system can also verify inspection compliance, such as insurance expiry dates and smoke test results.⁹

High traffic volumes in street canyons can significantly elevate pollution concentrations. Green infrastructure can help improve air quality in areas where planting space is limited. Options include green walls, green screens, and green roofs. The effectiveness of green infrastructure interventions depends on the design of the street canyon.⁹ Roadside vegetation can reduce PM concentrations by up to 60% and NO₂ levels by up to 40%.⁹ Where planting space is available, trees are an excellent long-term solution; in more constrained areas, smaller potted plants and rooftop gardens can also contribute to localized air quality improvements.

3.11. Energy intensity improvements and electrification

Improving energy intensity can reduce SO₂ emissions by 26–44%, NO_x emissions by 19–44%, PM emissions by 25–46%, and CO₂ emissions by 18–50%. Electrification can lower SO₂ emissions by 19–25%, NO_x emissions by 4–28%, PM emissions by 20–29%, and CO₂ emissions by 11–12%.¹⁴

Among industrial sub-sectors, the non-ferrous industry demonstrates the largest spectrum of co-benefits, with reduction rates ranging from 20.9% to 55.8% for SO₂ emissions, 17.5% to 44.6% for NO_x emissions, 24.5% to 47.8% for PM emissions, and 24.0% to 58.3% for CO₂ emissions.¹⁵ The paper sector achieves substantial reductions in NO_x (7.9–38.1%) and CO₂ (9.6–41.3%), but lower reductions in SO₂ and PM emissions.¹² According to Qian *et al.*,¹² the average direct co-benefits are highest in the non-ferrous industry and lowest in the non-power sector. In the non-ferrous industry, average reduction rates are 43.7% for SO₂, 44.2% for NO_x, 46.4% for PM, and 49.6% for CO₂.¹² In contrast, the non-power sector achieves reductions of 25.5% for SO₂, 24.1% for NO_x, 32.5% for PM, and 18.5% for CO₂, which remain significant.

Coal power plants, due to their higher energy intensity, provide smaller co-benefits to the non-power sector,¹² with reductions of 6.1% for SO₂, 3.6% for NO_x, 6.0% for PM, and 2.5% for CO₂. NO_x reduction rates vary the most across industries.¹² Petroleum and non-metallic sectors achieve the highest NO_x reductions¹²—19.3% and 27.6%, respectively—when 30% of fossil fuels are replaced with electricity.¹² In other industries, NO_x reductions are below 12% under the same conditions.¹² CO₂ reduction rates are relatively similar across sectors when electricity substitutes 12–30% of fossil fuel use.¹²

3.12. Plastic waste disposal and recycling

Plastic is recognized as a significant contributor to air pollution. Most plastic products are single-use and cannot be reused. While biodegradable plastics have been developed as eco-friendly alternatives, their limited availability reduces their overall impact. Several strategies exist for plastic waste disposal. At present, a large proportion of plastic waste is sent to landfills, which has negative environmental impacts. Thermal treatment offers an alternative, as the heat generated during waste incineration can be utilized for other purposes.¹³ Recycling is another viable option; however, it is constrained by factors such as polymer impurities and economic feasibility. Contamination of the plastic stream can disrupt the recycling process, and when economic returns are minimal, recycling becomes impractical.¹³

3.13. Air pollution predictor system development

Air pollution affects regions worldwide, and the ability to predict pollutant concentrations is essential for timely countermeasures. Several predictive systems have been developed, with advanced models increasingly built on deep learning frameworks.¹⁸ One such approach employs recurrent neural networks in combination with particle swarm optimization algorithms.¹⁸ The prediction process generally involves several steps. First, air quality data are collected from multiple monitoring stations. Second, the data are processed and prepared for analysis. Third, the dataset is divided into training and testing subsets according to established principles. The predictive model is then trained to interpret patterns from the collected data and generate forecasts.¹⁸ Although data are typically collected over 30 days, using 25 days of data for model input has been demonstrated to yield optimal results.¹⁸

3.14. Fuel quality improvements

China produces the largest number of automobiles globally and is also among the world's most heavily polluted countries.¹⁹ Faulty vehicles and low-quality gasoline are major contributors to urban air pollution.¹⁹ Implementing strict fuel standards is a viable strategy for reducing pollutant emissions. For example, improvements in gasoline quality in China have resulted in a 12.9% reduction in pollutant emissions and an estimated financial benefit of USD 26 billion.¹⁹ Under the new standards, the sulfur content of fuel is significantly reduced.⁹ Biofuels also offer a promising solution for reducing air pollution.¹⁴ Each type of biofuel provides specific benefits; for instance, oils derived from lemon peel and orange peel have been identified as suitable biofuel feedstocks.¹⁴ Research indicates that blending 20% biofuel with conventional diesel can be used effectively in traditional diesel engines without major modifications.¹⁴

3.15. Sensor and monitoring systems

Low-cost sensors provide a practical approach for evaluating air pollutants in urban settings. However, they can sometimes produce inaccurate readings due to environmental factors. The integration of machine learning and advanced computational techniques can help overcome these limitations. In addition, calibration methods can be used to ensure accurate operation under extreme weather conditions. Intelligent calibration systems allow sensors to function reliably even in challenging environments, such as those with heavy smoke.²⁰ Calibration results have shown that these sensors can measure aerosol mass accurately. Two primary types of calibrators are used: (i) White-box calibrators and (ii) black-box calibrators.²⁰

Black-box calibrators generally outperform white-box calibrators, although their performance may vary depending on environmental conditions.²⁰ Advanced monitoring systems can be developed by integrating wireless sensor network technology with building information modeling.²¹ Previous research has demonstrated that the integration of these two technologies provides accurate monitoring, as shown in tests conducted over distances of up to 250 m.²¹ However, signal strength was decreased by 15–20% when the receiver was rotated by 90° and by 30–40% when penetrating thick walls.²¹

4. Non-technical strategies

4.1. Public awareness and education

Public awareness campaigns play an important role in encouraging behaviors that reduce air pollution, such as reducing private vehicle use, promoting public transportation, preventing open burning, and supporting clean energy initiatives. These campaigns should focus on educating individuals about the sources and health effects of air pollution while fostering community-level action.

Several case studies illustrate the impact of awareness initiatives. For example, Mahajan *et al.*²² reported that involving approximately 400 citizens in air quality monitoring increased awareness of PM_{2.5} and NO₂ exposure risks and led to a 21% reduction in car usage among participants in European urban areas. Similarly, a survey of 800 citizens in Isfahan by Jökar *et al.*²³ found that higher environmental awareness significantly predicted pro-environmental behavior ($p < 0.01$), with educational interventions improving willingness to adopt cleaner practices by 30%. In Spain, Sánchez-García *et al.*²⁴ found that among 1200 respondents, 68% were willing to pay for policies aimed at reducing traffic-related air pollution. The average willingness to pay was EUR 3.95/month per person, highlighting the connection between awareness and economic support for pollution control policies.

4.2. Government policy and regulation

Governments can implement regulatory frameworks that set emission limits, monitor air quality, enforce pollution control standards, and promote cleaner technologies. Examples include establishing ambient air quality standards, incentivizing the installation of pollution control equipment, phasing out high-emission vehicles, and promoting renewable energy adoption. Successful policy implementation typically requires a combination of legal enforcement, financial incentives, and regular monitoring. Selected case studies are outlined below.

In a study by Jin *et al.*,²⁵ implementation of the 2013 Air Pollution Action Plan led to a 33–47% reduction in $PM_{2.5}$ concentrations in key Chinese cities, resulting in an average life expectancy gain of 0.4 years in urban areas. Industrial regulations and vehicle emissions control policies achieved 30–60% reductions in SO_2 and NO_x emissions over 5 years. Amann *et al.*²⁶ reported that integrating air pollution and climate policies (e.g., EURO vehicle standards, low-emission zones) reduced premature deaths by approximately 500,000 annually across European nations. Nasir *et al.*²⁷ demonstrated that regulatory enforcement in the cement and textile sectors reduced PM emissions by 15–25% in pilot cities, with industries receiving incentives for pollution control equipment demonstrating 50% higher compliance than non-incentivized facilities. According to Mir *et al.*,²⁸ integrated strategies combining cleaner transportation and renewable energy promotion could yield a 16% reduction in CO_2 emissions, an 18% decrease in $PM_{2.5}$, and annual health cost savings of approximately USD 800 million. Meanwhile, Li *et al.*²⁰ reported that upgrading fuel standards (2010–2015) reduced $PM_{2.5}$ levels in urban centers by an average of $12.5 \mu g/m^3$.

5. Discussion

The increasing threat of air pollution, as outlined in earlier sections, underscores the urgent and growing need for integrated, multidimensional control strategies. The comprehensive analysis of existing technologies and non-technical approaches reveals a wide spectrum of methods that are currently applied worldwide to mitigate the impacts of air pollutants—ranging from traditional engineering-based solutions to innovative, sustainable, and community-driven practices. The effectiveness of these strategies, however, is not uniform. Success depends largely on a region's geographical, climatic, socioeconomic, and regulatory context. For instance, countries with robust regulatory frameworks and strong economies can often deploy high-cost, technologically advanced solutions, while developing regions may need to rely on cost-effective, scalable alternatives.

Recent studies emphasize the critical importance of integrated approaches that combine PM control technologies—such as ESPs, baghouse filters, and cyclone separators—with advanced gaseous pollutant treatment systems such as SCR, wet scrubbers, and chemical absorbers.^{28–32} Evidence supports that no single technology, regardless of sophistication, can adequately address the complex and multifaceted nature of air pollution. Instead, hybrid strategies that merge end-of-pipe control (targeting pollutants after formation) with preventive measures (minimizing pollutant formation at the source) have proven more effective in achieving significant reductions in air pollutant concentrations across urban, industrial, and rural settings.

Furthermore, sustainable and low-cost alternatives such as biofiltration systems and activated carbon adsorption show significant promise. These methods are not only effective in pollutant removal but also align with environmental sustainability goals, owing to their low energy consumption and minimal secondary pollution. For example, biofilters, which use microorganisms to degrade VOCs and odorous substances, have been successfully deployed in multiple industrial zones across Southeast Asia. Previous studies⁹ have demonstrated that biofilters can significantly reduce VOC levels and odor emissions, making them particularly appealing for application in regions with limited financial and technical resources.

In addition to technological interventions, non-technical strategies play a crucial role in comprehensive air quality management. This review reinforces the findings of past research,³¹ who argue that public awareness campaigns, community education programs, and behavioral change initiatives can meaningfully contribute to emission reductions at the community level. These efforts foster a sense of environmental responsibility among citizens, which in turn supports broader pollution control objectives. However, the long-term effectiveness of such initiatives hinges on several key factors, including consistent enforcement of environmental regulations, the availability of institutional support, and public perceptions of both the seriousness of air pollution and the benefits of mitigation.

Moreover, the regulatory and policy frameworks discussed earlier in this review align with key international environmental governance instruments, such as the World Health Organization's Air Quality Guidelines, the United Nations Sustainable Development Goals, and various regional climate action plans. These frameworks advocate the use of adaptive policy tools, market-based economic incentives, and the integration of technological

innovation into national and local governance systems. The importance of aligning national efforts with international best practices emerges as a recurrent theme in the reviewed literature, further supporting the call for cohesive and harmonized policy actions.

In summary, the evidence presented in this discussion demonstrates that while a wide array of air pollution control technologies and strategies is currently available, their ultimate success is largely dependent on thoughtful integration, strong policy support, active public engagement, and a nuanced understanding of the local context. The findings of this review not only corroborate previous research but also extend it by offering a synthesized, holistic perspective that bridges conventional engineering solutions with emerging sustainable practices. In addition, it identifies critical areas where further research, policy innovation, and cross-sector collaboration are necessary to address existing gaps and enhance the overall effectiveness of air pollution mitigation efforts.

6. Conclusion

Air pollution remains an important environmental and public health concern, with multiple factors contributing to degraded air quality in both urban and industrial settings. This study has reviewed several key technologies for air pollution control, including ESPs, wet scrubbers, bag filters, and SCR systems, as well as alternative methods such as biofiltration and activated carbon adsorption. In addition, non-technical strategies, such as public awareness and regulatory policies, were highlighted as essential complements to technological interventions. Despite these developments, significant gaps remain. Many existing technologies are either cost-prohibitive or limited in scope, particularly when addressing mixed pollutant loads. The impact of public awareness campaigns is often hampered by inadequate educational outreach and inconsistent implementation. Similarly, regulatory policies, while in place in many regions, frequently lack the enforcement mechanisms necessary to achieve meaningful results. Future progress should focus on improving the efficiency and affordability of control technologies to facilitate broader adoption, especially in developing countries. There is also a pressing need for integrative frameworks that combine technological, behavioral, and policy-based approaches in a context-sensitive manner. Strengthening monitoring systems, promoting community participation, and reinforcing regulatory compliance mechanisms can amplify the overall impact of air pollution control measures.

Overall, this study underscores the importance of a multidimensional approach to air quality management

and emphasizes the importance of continual innovation and adaptation, guided by environmental, economic, and social considerations.

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Further disclosure

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ORIGINAL RESEARCH ARTICLE

Diversifying cropping systems to enhance productivity using agroforestry trees: A case study of maize–pigeon pea intercropping in Ghana

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Abstract

Amid growing global challenges such as population growth, climate change, and limited natural resources, the need for sustainable farming systems to ensure food security and environmental conservation has become increasingly critical. This study – conducted in the forest zones of Ghana during the major and minor cropping seasons of 2023 – evaluates the effects of integrating *Cajanus cajan* (also known as pigeon pea), a leguminous shrub, into a maize cropping system. This maize–pigeon pea (MPP) intercropping approach is part of an innovative integrated soil fertility management strategy aimed at improving maize yield, farm profitability, and climate resilience of smallholder farmers. A split-plot experimental design was employed, with the cropping systems – MPP intercrop and sole maize – as main plots, and varying recommended inorganic fertilizer (full rate [FR], half rate [HR], and a no-fertilizer control) as subplots. The findings revealed a significant association between the MPP intercropping system and the rate of inorganic fertilizer application on maize growth and yield, with improved and comparable maize productivity observed when either the HR or FR fertilizer was applied. This suggests that integrating pigeon peas and their biomass could reduce the recommended fertilizer rate by half, thereby enhancing farmers' income and profitability while promoting sustainable maize production amid climate change. Future research should explore long-term soil fertility dynamics and broader agroecological applications.

Keywords: Agroforestry; Climate change; Integrated soil fertility management; Maize; Pigeon pea; Resource utilization

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1. Background and rationale

The escalating global demand for food production requires urgent attention to the challenges associated with agricultural intensification, particularly in resource-limited

regions such as Ghana and other parts of Africa, where smallholder farming systems predominate.^{1,2} Sustainable agriculture is a crucial strategy for reducing environmental damage and ensuring the long-term sustainability of these farming systems.³ Understanding the factors that influence farmers' adoption of sustainable practices is essential to promote their widespread implementation.³ In Ghana, maize (*Zea mays*) – a major staple crop – continues to face significant productivity challenges due to declining soil fertility and unpredictable climate changes.^{4,5} These challenges are further intensified by continuous monocropping and inadequate application of soil amendments.⁶ Despite the increase in maize production over the past decade, this growth is largely driven by the expansion of cultivated areas rather than improvements in yield per unit area.⁷ This trend highlights the urgent need for integrated soil fertility management (ISFM) strategies to enhance and maintain maize productivity.^{8–11}

One promising approach to improving maize productivity and sustainability is the integration of pigeon pea (*Cajanus cajan*), a nutrient-rich legume, into maize-based cropping systems. Pigeon pea has the capacity to fix atmospheric nitrogen through biological nitrogen fixation, thereby enhancing soil fertility and reducing the need for synthetic nitrogen fertilizers. This can lower production costs for farmers while mitigating the environmental risks associated with excessive fertilizer use. Previous studies have demonstrated that intercropping pigeon pea can improve soil structure and nutrient availability, benefiting maize and other associated crops.^{12–14} The combined use of organic and inorganic fertilizers has the potential to improve soil health, mitigate climate-related risks, and offer a cost-effective strategy for smallholder farmers. In addition, pigeon pea's protein-rich grains can enhance household nutrition and food security.

Pigeon pea is increasingly recognized as a valuable agroforestry crop – particularly in tropical and subtropical regions – due to its resilience and ability to improve soil fertility.^{12,15,16} When intercropped with maize, pigeon pea offers numerous agronomic benefits, including biological nitrogen fixation, enhanced soil structure, and reduced reliance on synthetic fertilizers.⁸ Furthermore, pigeon pea contributes to ecosystem sustainability by supporting soil erosion control, biodiversity conservation, and increased reliance to climate variability.^{8,15}

Despite these benefits, the success of maize–pigeon pea (MPP) intercropping largely depends on various factors, including agronomic practices, environmental conditions, and socioeconomic factors.^{8,13} Unlike previous studies, this research employs a comprehensive approach

to assess MPP intercropping. It examines agronomic performance, economic viability, and long-term soil fertility effects – areas that remain unexplored in Ghana. Furthermore, the research is grounded in ethnobotanical principles, highlighting the traditional knowledge and cultural importance of pigeon pea cultivation among local farmers. The integration of traditional cropping systems and local adaptation strategies distinguishes this study from conventional agronomic studies.^{5,17}

The primary objective of this study is to evaluate the agronomic and economic benefits of MPP intercropping, focusing on increased crop yields, reduced reliance on inorganic fertilizers, and improved soil health. By assessing the performance of this system in Ghana's forest zones, the research aims to provide valuable insights into its impact on maize productivity, soil fertility, and the climate resilience of smallholder farmers. Ultimately, the study aims to optimize resource use and advance sustainable maize production amid ongoing environmental challenges. The findings are anticipated to advance the current understanding of agroforestry, ISFM, and sustainable cropping systems, thereby supporting policy development, improving agricultural practices, and guiding future research efforts.

2. Materials and methods

2.1. Study location

This study was conducted between 2022 and 2024 at the Council of Scientific and Industrial Research (CSIR)–Crops Research Institute in Fumesua, Ghana (latitude: 6.7155729; longitude: –1.5316034; [Figure 1](#)). The site is located in the humid forest agroecological zone, characterized by Ferric Acrisol soils with a sandy clay loam topsoil. This region experiences a bimodal rainfall distribution, with the major rainy season occurring from March to mid-August and the minor season from September to November. Annual rainfall averages between 1,027 mm and 1,322 mm ([Table 1](#) and [Figure 2](#)).

2.2. Experimental design and intercropping arrangement

A split-plot design with four replications was employed. The main plot treatments comprised two cropping systems ([Figure 3](#)):

- (i) MPP intercropping.
- (ii) Maize monoculture (no pigeon pea [NPP]).

The subplots included three fertilizer treatments:

- (i) Full rate (FR): 250 kg/ha of 15-15-15 nitrogen-phosphorus pentoxide-potassium oxide (N-P₂O₅-K₂O) + 250 kg/ha of sulfate of ammonia (SoA).

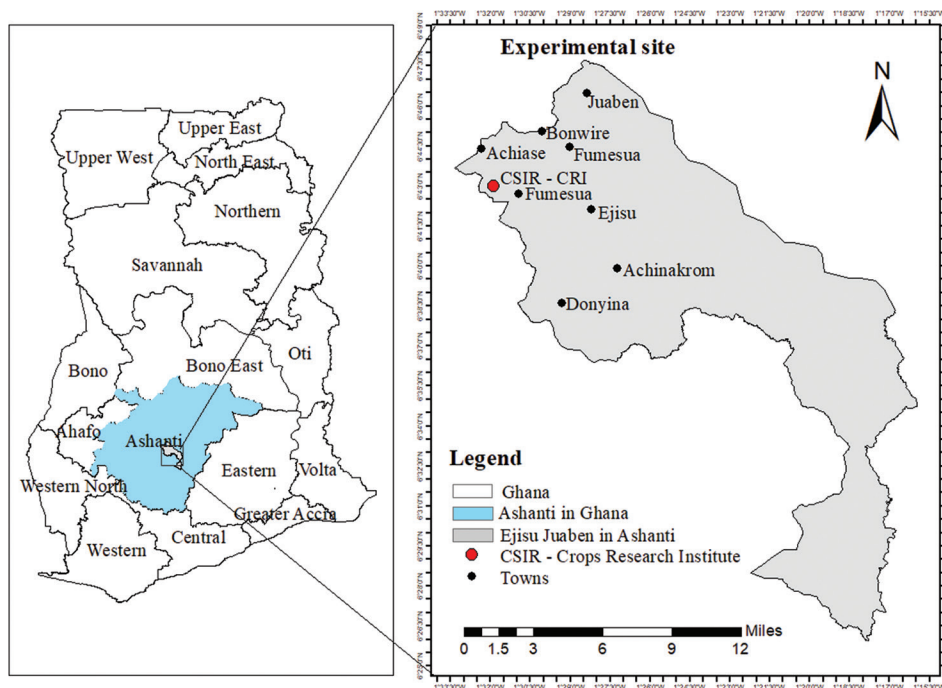


Figure 1. Location map of Ghana showing the CSIR–Crops Research Institute site in Fumesua (indicated by a red circle), where the research was conducted between 2022 and 2024

Abbreviation: CSIR: Council of Scientific and Industrial Research.

Table 1. Study location characteristics

Characteristics	Fumesua (6° 41' N, 1° 28' W)
Agroecological zone	Humid forest
Soil type	Ferric Acrisol, specifically the Asuasi series. The upper topsoil consisted of approximately 5 cm of grayish–brown sandy loam and dark brown, gritty clay loam
Temperature (min–max, °C) from 2020 to 2023	21 – 37°C
Rainfall pattern	Bimodal rainfall distribution
Major raining season	March–mid-August
Minor raining season	September–November, peak in October
Total annual rainfall (mm), from 2020 to 2023	1,027 – 1,322 mm, averaging at 1,184 mm/year

Source: Adopted from Adu and Asiamah.¹⁸

- (ii) Half rate (HR): 125 kg/ha of 15-15-15 N-P₂O₅-K₂O + 125 kg/ha of SoA.
- (iii) No fertilizer (NF): Control treatment without inorganic fertilizer application.

Pigeon pea was planted during the minor season of 2022 to allow sufficient biomass accumulation for incorporation into the soil during the 2023 cropping seasons. A late-maturing pigeon pea variety (8 months to maturity) was selected and used to maximize biomass production. The maize variety used was *Abontem*, an improved open-pollinated variety developed by the CSIR–Crops Research Institute.

Planting and crop management:

- (i) NPP: Maize was planted at a spacing of 0.8 m × 0.4 m with two plants per hill, following CSIR–Crops Research Institute guidelines,⁴ resulting in a population density of 62,500 plants/ha. Two central maize plots were designated for data collection, with adjacent rows used for destructive sampling.
- (ii) MPP: A substitution model allocated approximately 30% of the maize area to pigeon pea by alternating six rows of maize with two rows of pigeon peas. Pigeon peas were planted at a spacing of 1 m × 5.6 m (intra-row and inter-row spacing respectively), resulting in a population density of 3,571 plants/ha, while maize

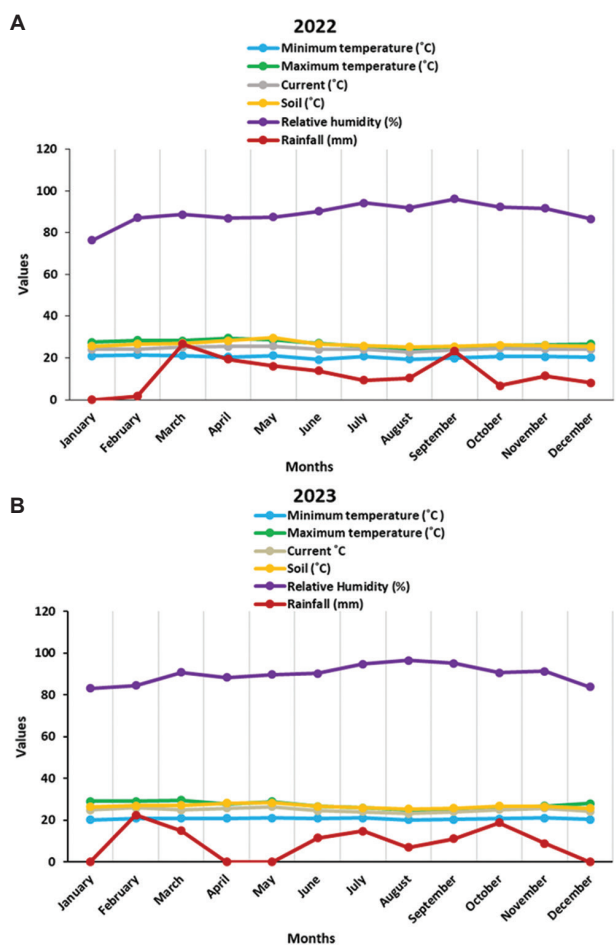


Figure 2. Monthly weather parameters recorded in Fumesua in 2022 (A) and 2023 (B), including rainfall distribution, temperature trends, and relative humidity levels

density was 4,875 plants/ha. Similar to NPP, the two central maize rows were used for data collection and adjacent rows for destructive sampling.

- (iii) Pigeon pea monoculture: Adjacent sole pigeon pea plots were established to calculate land equivalent ratios [LERs]. Pigeon pea was planted at 1 m × 0.5 m spacing, resulting in a population of 40,000 plants/ha. Planted in 2022, pigeon pea was managed as a perennial crop, while maize was grown during the major and minor seasons of 2023. Fresh pigeon pea biomass of 2,210 and 1,620 kg/ha was evenly incorporated into the soil in intercrop plots during the major and minor seasons of 2023, respectively.
- (iv) Fertilizer application: 15-15-15 N-P₂O₅-K₂O fertilizer was applied 2 weeks after planting, followed by SoA at 6 – 8 weeks.⁴

2.2.1. Measurements and determination of LER

Maize was harvested at physiological maturity, and all cobs from the designated harvest area were weighed to

determine plot yield (kg). A total of 20 cobs from each plot were shelled to measure fresh grain weight, and shelling recovery was calculated as the ratio of fresh grain weight to the total weight of the 20 cobs. Similarly, pigeon pea grain yield was determined at physiological maturity by shelling all pods from the harvest and recording the fresh grain weight (kg). Grain moisture content for both maize and pigeon peas was measured using a universal grain moisture meter (INDOSAN S6010, Indosaw, India), and grain yields were adjusted to a standardized moisture content of 15%, with final yields expressed in tons/ha, as indicated in the equations.

$$\text{Adjusted moisture content (MC}_{\text{adj}}) = \frac{100 - \text{Actual moisture content}}{100 - \text{Desired moisture content}} \tag{I}$$

$$\text{Grain yield (tons/ha at 15\% MC}_{\text{adj}}) = \frac{\text{Plot yield (kg)} \times 10,000 \text{ m}^{-2} \times \text{MC}_{\text{adj}} \times \text{SR\%}}{12 \text{ m}^{-2} \times 1,000} \tag{II}$$

To compare the productivity of monoculture and MPP intercropping, the LER was employed, calculated as follows:

$$\text{LER} = \frac{Y_m I}{Y_m S} + \frac{Y_p I}{Y_p S} \tag{III}$$

Where:

- Y_mI is maize yield under intercropping (tons/ha),
- Y_mS is maize yield under sole cropping (tons/ha),
- Y_pI is pigeon pea yield under intercropping (tons/ha),
- Y_pS is pigeon pea yield under sole cropping (tons/ha).

An LER value greater than 1 indicates a yield advantage of intercropping over sole cropping, while a value <1 indicates a disadvantage.^{19,20}

2.3. Data collection and statistical analysis

Data on the growth, biomass, and grain yields of maize and pigeon peas were analyzed using a three-way analysis of variance (cropping system × fertilizer × experimental season) with type III error at a 5% significance level (*p*<0.05). Analyses were performed using Jeffreys’s Amazing Statistics Program (version 0.19.1.0, University of Amsterdam, Netherlands), available at <https://jasp-stats.org>.²¹ Before analysis, the homogeneity of variances was verified using the Shapiro–Wilk and Levene’s tests. When significant differences were observed among treatment means, Tukey’s Honestly Significant Difference test was employed for mean separation, with groupings indicated using letter annotations.

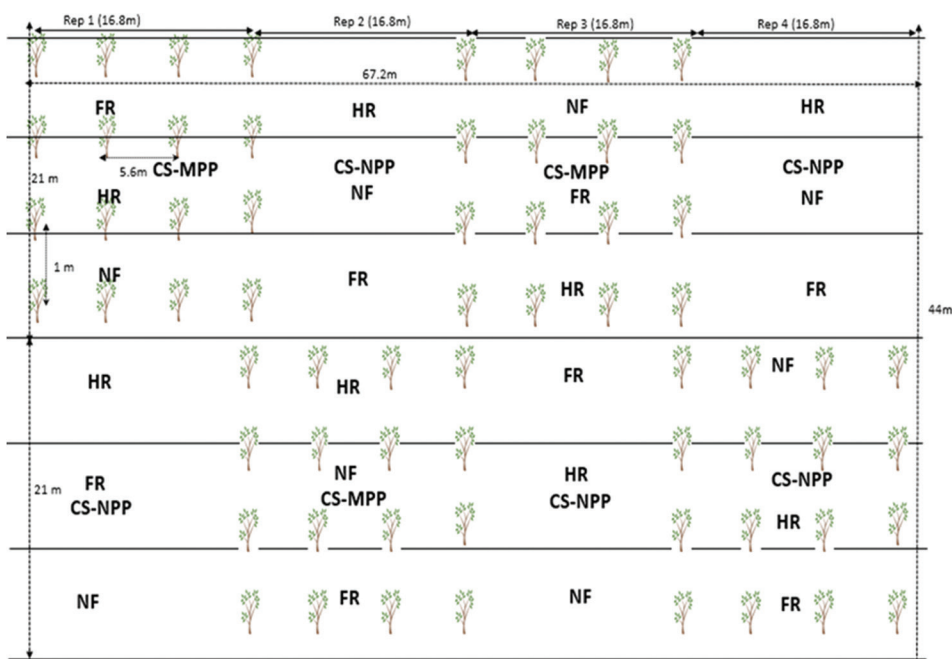


Figure 3. Plot design for maize–pigeon pea intercropping and sole maize plots at the CSIR–Crops Research Institute site in Fumesua, Ghana
Abbreviations: CS: Cropping system; FR: Full rate; HR: Half rate; MPP: Maize–pigeon pea intercropping; NF: No fertilizer; NPP: No pigeon pea/sole maize; Rep: Replicate; CSIR: Council of Scientific and Industrial Research.

3. Results

Analysis of variance across the two experimental seasons (major and minor cropping seasons) in 2023 at the CSIR–Crops Research Institute site in Fumesua shows significant factor interactions ($p < 0.05$). Consequently, growth and yield results across seasons, cropping systems, and fertilizer treatments are presented in Tables 2 & 3, and Figure 4.

3.1. Growth of maize in the MPP cropping system and fertilizer treatment

The growth performance of maize in the MPP cropping system provides valuable insights into the interaction of cropping systems, fertilizer application, and seasonal variation on growth parameters. This analysis focused on plant height, estimated leaf area, fresh leaf biomass, and dry leaf biomass, providing a comprehensive understanding of the trade-offs and synergies between intercropping and monoculture systems.

3.1.1. Plant height

Maize height growth was consistently higher with FR fertilizer across both cropping systems and seasons, peaking in the NPP system during the minor season (201.7 cm, Table 2). This highlights the critical role of nutrient availability in promoting vertical growth. The superior height observed in fertilized treatments during the minor

season suggests favorable environmental conditions, such as optimal rainfall, which enhance fertilizer efficiency. In contrast, maize without fertilizer (NF) recorded the lowest heights, particularly in the intercrop system during the major season (Table 2). This suggests that competition for resources in intercropping systems may further limit growth under nutrient-poor conditions.

3.1.2. Estimated leaf area

Leaf area – an indicator of photosynthetic capacity – followed a similar trend, with FR treatments significantly outperforming others (Table 2). The NPP system with FR treatment in the minor season recorded the largest leaf area (9,751.3 cm²), indicating reduced competition for light and nutrients (Table 2). While leaf area was lower under NF treatment, the MPP intercrop system demonstrated stability with the HR treatment, particularly in the minor season. This suggests that intercropping with pigeon peas may buffer maize against environmental stress by providing benefits such as nitrogen fixation and improved soil nutrition. However, the reduced leaf area in intercrops under low fertilizer conditions indicates a trade-off, where intercropping benefits are insufficient to fully offset resource competition (Table 2).

3.1.3. Fresh and dry leaf biomass

Biomass production – an integrative measure of growth performance – was the highest in the NPP with FR

Table 2. Maize growth parameters – height (cm), leaf area (cm²), fresh leaf biomass (g), and dry leaf biomass (g) – in pigeon pea-maize intercrop and sole maize systems during the major and minor 2023 seasons in Fumesua, Ghana

Trait	Cropping system	Fertilizer	Season	Mean	SD	SE	Rank	CV		
Plant height (cm)	MPP	FR	Major	183.333	27.429	15.836	a, b, and c	0.150		
		FR	Minor	188.600	10.800	6.235	a, b, and c	0.057		
		HR	Major	171.667	4.041	2.333	a, b, and c	0.024		
		HR	Minor	183.733	12.232	7.062	a, b, and c	0.067		
		NF	Major	165.667	6.028	3.480	a and b	0.036		
		NF	Minor	183.200	11.459	6.616	a, b, and c	0.063		
		NPP	FR	Major	186.333	12.897	7.446	a, b, and c	0.069	
	NPP	FR	Minor	201.733	5.991	3.459	c	0.030		
		HR	Major	183.000	1.732	1.000	a, b, and c	0.009		
		HR	Minor	199.800	6.264	3.617	b and c	0.031		
		NF	Major	155.000	8.660	5.000	a	0.056		
		NF	Minor	190.667	10.576	6.106	b and c	0.055		
		Estimated leaf area (cm ²)	MPP	FR	Major	3,344.000	1,111.367	641.648	a and b	0.332
				FR	Minor	5,971.227	1,262.122	728.687	b and c	0.211
HR	Major			2,444.833	722.885	417.358	a	0.296		
HR	Minor			6,222.638	854.590	493.398	b and c	0.137		
NF	Major			2,531.600	656.660	379.123	a	0.259		
NF	Minor			5,248.935	1,299.948	750.525	a, b, and c	0.248		
NPP	FR			Major	3,324.267	1,606.432	927.474	a and b	0.483	
NPP	FR		Minor	9,751.329	2,250.264	1,299.190	d	0.231		
	HR		Major	2,832.987	1,044.594	603.096	a and b	0.369		
	HR		Minor	7,609.492	451.322	260.571	c and d	0.059		
	NF		Major	2,377.856	488.550	282.064	a	0.205		
	NF		Minor	5,462.927	840.269	485.129	a, b, and c	0.154		
	Fresh leaf biomass (g)		MPP	FR	Major	15,614.993	1,767.147	1,020.263	a	0.113
				FR	Minor	25,158.700	6,642.259	3,834.910	b	0.264
HR		Major		13,638.263	2,818.075	1,627.017	a	0.207		
HR		Minor		19,418.467	1,210.187	698.702	a and b	0.062		
NF		Major		13,558.767	1,453.365	839.101	a	0.107		
NF		Minor		11,699.450	3,185.983	1,839.428	a	0.272		
NPP		FR		Major	16,528.237	2,614.294	1,509.363	a	0.158	
NPP		FR	Minor	25,605.358	11,597.683	6,695.926	b	0.453		
		HR	Major	14,281.808	2,982.279	1,721.820	a	0.209		
		HR	Minor	22,687.292	10,530.918	6,080.028	b	0.464		
		NF	Major	14,851.900	4,626.948	2,671.370	a	0.312		
		NF	Minor	11,164.533	2,197.746	1,268.869	a	0.197		
		Dry leaf biomass (g)	MPP	FR	Major	6,692.140	757.349	437.256	a	0.113
				FR	Minor	10,782.300	2,846.682	1,643.533	b	0.264
HR	Major			5,844.970	1,207.747	697.293	a	0.207		
HR	Minor			8,322.200	518.652	299.444	a and b	0.062		
NF	Major			5,810.900	622.871	359.615	a	0.107		
NF	Minor			5,014.050	1,365.421	788.326	a	0.272		
NPP	FR			Major	7,083.530	1,120.412	646.870	a	0.158	
NPP	FR		Minor	10,973.725	4,970.436	2,869.682	b	0.453		
	HR		Major	6,120.775	1,278.120	737.923	a	0.209		
	HR		Minor	9,723.125	4,513.250	2,605.726	a and b	0.464		
	NF		Major	6,365.100	1,982.978	1,144.873	a	0.312		
	NF		Minor	4,784.800	941.891	543.801	a	0.197		

Note: Means with the same alphabet ranking are not significantly different from each other.

Abbreviations: CV: Coefficient of variation; FR: Full rate of recommended fertilizer; HR: Half rate of recommended fertilizer; MPP: Maize–pigeon pea; NF: No fertilizer; NPP: No pigeon pea/sole maize; SD: Standard deviation; SE: Standard error.

Table 3. Maize yield components (cob number, cob weight per plant, hundred-seed weight, and total grain yield) in pigeon pea-maize intercrop and sole maize systems during the major and minor 2023 seasons in Fumesua, Ghana

Trait	Cropping system	Fertilizer	Season	Mean	SD	SE	Rank	CV		
Cob number	MPP	FR	Major	53.667	3.055	1.764	a	0.057		
		FR	Minor	125.667	12.097	6.984	b	0.096		
		HR	Major	45.667	7.767	4.485	a	0.170		
		HR	Minor	122.667	2.082	1.202	b	0.017		
		NF	Major	54.667	9.074	5.239	a	0.166		
		NF	Minor	56.000	24.759	14.295	a	0.442		
	NPP	FR	Major	59.000	1.732	1.000	a	0.029		
		FR	Minor	205.667	125.437	72.421	b and c	0.610		
		HR	Major	48.667	10.693	6.173	a	0.220		
		HR	Minor	104.667	21.572	12.454	b	0.206		
		NF	Major	57.333	8.083	4.667	a	0.141		
		NF	Minor	31.667	16.073	9.280	a	0.508		
		Total cob weight (g)	MPP	FR	Major	836.333	135.664	78.326	a	0.162
				FR	Minor	14,698.767	3,935.081	2,271.920	d and e	0.268
HR	Major			858.600	144.849	83.628	a	0.169		
HR	Minor			11,344.533	725.511	418.874	b, c, and d	0.064		
NF	Major			714.733	65.655	37.906	a	0.092		
NF	Minor			4,327.733	2,129.132	1,229.255	a, b, and c	0.492		
NPP	FR		Major	803.133	146.879	84.801	a	0.183		
	FR		Minor	22,279.567	8,443.772	4,875.014	e	0.379		
	HR		Major	844.933	110.630	63.873	a	0.131		
	HR		Minor	12,909.800	5,939.399	3,429.113	c, d, and e	0.460		
	NF		Major	733.633	153.568	88.662	a	0.209		
	NF		Minor	2,488.833	1,686.059	973.447	a and b	0.677		
	Hundred-seed weight (g)		MPP	FR	Major	33.500	6.384	3.686	b	0.191
				FR	Minor	27.167	0.666	0.384	b	0.025
HR		Major		32.833	7.943	4.586	b	0.242		
HR		Minor		32.467	6.401	3.696	a and b	0.197		
NF		Major		28.833	1.041	0.601	b	0.036		
NF		Minor		21.733	8.601	4.966	a	0.396		
NPP		FR	Major	37.333	5.008	2.892	b and c	0.134		
		FR	Minor	31.333	3.828	2.210	a and b	0.122		
		HR	Major	37.000	4.770	2.754	b and c	0.129		
		HR	Minor	34.033	6.809	3.931	b	0.200		
		NF	Major	33.167	2.930	1.691	b	0.088		
		NF	Minor	28.533	1.007	0.581	b	0.035		
		Total grain yield (tons/ha)	MPP	FR	Major	6.468	1.808	1.044	b	0.280
				FR	Minor	3.892	0.694	0.401	a and b	0.178
HR	Major			6.096	0.628	0.362	b	0.103		
HR	Minor			3.755	0.673	0.388	a and b	0.179		
NF	Major			3.848	0.470	0.271	a and b	0.122		
NF	Minor			2.481	0.394	0.227	a	0.159		
NPP	FR		Major	5.819	1.590	0.918	b	0.273		
	FR		Minor	3.836	1.057	0.610	a and b	0.275		
	HR		Major	6.037	1.234	0.712	b	0.204		
	HR		Minor	3.745	0.880	0.508	a and b	0.235		
	NF		Major	4.349	0.936	0.540	a and b	0.215		
	NF		Minor	1.999	0.809	0.467	a	0.405		

Abbreviations: CV: Coefficient of variation; FR: Full rate of recommended fertilizer; HR: Half rate of recommended fertilizer; MPP: Maize–pigeon pea; NF: No fertilizer; NPP: No pigeon pea/sole maize; SD: Standard deviation; SE: Standard error.

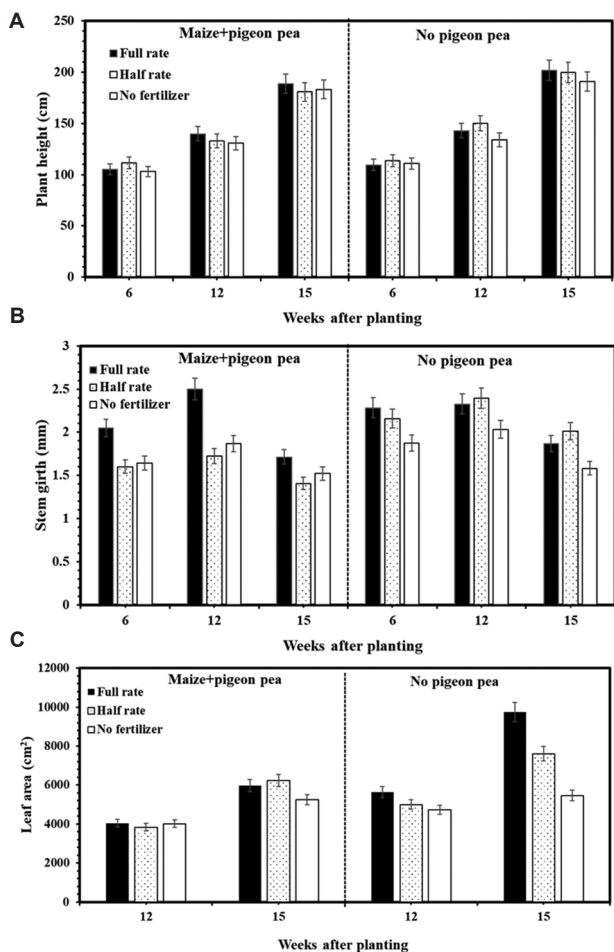


Figure 4. Growth measurements of maize height (A), stem girth (B), and leaf area (C) in maize–pigeon pea intercropping and sole maize plots, recorded at 6–15 weeks after planting during the minor season of 2023

treatment during the minor season (fresh = 25,605.4 g; dry = 10,973.7 g; Table 2). This highlights the system’s ability to effectively utilize high nutrient inputs when resource limitations – such as light and space – are minimal. Conversely, the MPP intercrop system exhibited lower biomass under NF but maintained competitive performance under HR, particularly in the minor season (Table 2). This suggests that intercropping can sustain reasonable productivity with moderate inputs, supporting principles of sustainable agriculture (Table 2).

3.1.4. Seasonal variation and system dynamics

Seasonal effects were pronounced, with growth improving in the minor season across all treatments, likely due to the accumulation of soil organic matter and nitrogen fixation from pigeon pea biomass incorporation (Table 2). In the intercrop system, HR treatments balanced growth and resource use, showing adaptive potential under moderate nutrient levels (Table 2). The NPP system performed well

under FR but showed greater variability under low-input conditions, indicating lower resilience than intercropping (Table 2).

These findings highlight a key trade-off: NPP systems excel under high input conditions but are vulnerable to nutrient and environmental constraints. In contrast, the MPP system prioritized stability and sustainability over peak productivity (Table 2). The intercrop system’s consistent growth under HR and its resilience to seasonal changes demonstrate its suitability for resource-limited environments. In addition, the ecological benefits of pigeon peas – such as nitrogen fixation, organic matter addition, and soil protection – provide long-term advantages beyond immediate growth measurements.

3.2. Maize growth as influenced by cropping system and fertilization

In the minor season experiment, the morphological growth patterns of maize in the MPP intercrop and NPP sole cropping systems were monitored from 6 to 15 weeks after planting. Plant height (cm), stem girth (mm), and leaf area (cm²) were recorded at each time point. Maize height showed no statistically significant differences between cropping systems and fertilizer treatments throughout the growth period (Figure 4A). However, the tallest plants were recorded at 15 weeks in the NPP system under FR treatment (Figure 4A). In contrast, stem girth exhibited significant differences between cropping systems and fertilizer treatments (Figure 4B), with the thickest stems observed in the NPP system under FR. The MPP system under NF treatment showed reduced stem girth development (Figure 4B).

From 12 to 15 weeks, maize leaf area (cm²) showed significant differences among fertilizer treatments and cropping systems (Figure 4C). The highest mean leaf area was recorded in the NPP system under FR, followed by HR and NF, all of which are significantly higher than the intercrop plants (Figure 4C).

3.3. Yield component of maize

Maize yield components were analyzed across the MPP intercrop and NPP systems under different fertilizer levels and seasons (Table 3). Key traits – including number of cobs per plant, cob weight, hundred-seed weight, and total grain yield – were evaluated to determine the effects of cropping system, fertilizer application, and seasonal variation on crop productivity (Table 3).

3.3.1. Cob number and weight

Cob numbers differed significantly across cropping systems and seasons. The MPP system recorded the highest cob

number under FR fertilizer treatment in the minor season (126 cobs), while NF treatment yielded the lowest counts (Table 3). In comparison, the NPP system produced the highest cob number (206 cobs) under FR treatment during the minor season, indicating that reduced competition in sole cropping enhances reproductive development under optimal nutrient conditions. Cob weight followed this pattern, with the NPP system under FR treatment in the minor season achieving the highest cob weight (22,279.6 g), underscoring the NPP system’s ability to maximize biomass production under high nutrient input (Table 3).

3.3.2. Hundred-seed weight

Hundred-seed weight was generally higher in the NPP system under FR treatment, with the highest value recorded during the major season (37.3 g, Table 3). FR treatment also resulted in competitive seed weights in the MPP system, although these were slightly lower than those observed in NPP. Under NF treatment, seed weights were notably reduced, particularly in the MPP system, suggesting that nutrient competition between maize and pigeon pea limits grain filling and reduces seed size.

3.3.3. Total grain yield

Grain yield reflects the combined effects of cob development and seed weight. In the MPP system, the highest grain yield was recorded during the major season under FR treatment (6.47 tons/ha), slightly exceeding that of the NPP system under the same conditions (5.82 tons/ha, Table 3). This suggests that intercropping under high nutrient availability can match or even surpass sole cropping in productivity due to complementary interactions between crops. However, under NF treatment, grain yield in the MPP system (3.85 tons/ha in the major season) was lower than in NPP (4.35 tons/ha), highlighting the greater impact of resource competition in the absence of fertilizer (Table 3).

3.4. LER

The LER was calculated using Equation III to evaluate the productivity benefits of intercropping maize and pigeon pea compared to their sole cropping systems:

- $Y_m I$: maize yield under intercropping (tons/ha) = 3.93
- $Y_m S$: maize yield under sole cropping (tons/ha) = 4.30
- $Y_p I$: pigeon pea yield under intercropping (tons/ha) = 0.25
- $Y_p S$: pigeon pea yield under sole cropping (tons/ha) = 0.79

$$LER = \frac{Y_m I}{Y_m S} + \frac{Y_p I}{Y_p S} = \frac{3.93}{4.30} + \frac{0.25}{0.79} = 1.23$$

An LER value of 1.23 indicates a productivity advantage for the intercropping system. Since LER values greater

than one indicate higher combined yields in intercropping compared to sole cropping, this finding highlights a more efficient use of land resources. The increased combined yield suggests enhanced resource utilization, where maize and pigeon peas benefit from shared resources, such as light, water, and nutrients. This synergy contributes to increased overall productivity in the intercropping system.

In addition, the complementary growth patterns of maize and pigeon peas in the intercropping system may contribute to the observed yield advantage. Pigeon pea, being taller, can provide partial shade during the early stages of maize growth, which helps suppress weed growth and supports soil moisture conservation. In addition, as a leguminous plant, pigeon pea also enhances soil fertility by fixing atmospheric nitrogen, thereby benefiting maize development. The higher LER value suggests that intercropping can offer improved economic returns for farmers by increasing yield per unit area, thereby enhancing overall profitability. This system also supports environmental sustainability through increased biodiversity, reduced dependency on chemical inputs, and improved soil health. Overall, an LER of 1.23 indicates a 23% advantage of intercropping maize and pigeon peas over sole cropping in terms of land-use efficiency, complementary resource utilization, economic benefits, and environmental sustainability.

3.5. Soil physicochemical properties at the Fumesua study site

Table 4 shows the physicochemical properties of soil at the Fumesua study site analyzed at the initial stage in 2022 and after 2 years of cropping under different treatments: pigeon pea alley cropping and NPP cropping. The results showed distinct variations in soil properties across depths and treatments. At the initial stage, the topsoil (0 – 20 cm) had a pH of 6.50, indicating slightly acidic conditions, with 0.26% nitrogen (N) and 49.15 mg/kg phosphorus (P). Potassium (K) measured 0.21 cmol (+)/kg, while magnesium (Mg) and calcium (Ca) measured 0.69 cmol (+)/kg and 1.35 cmol (+)/kg, respectively. Organic carbon (OC) accounted for 1.11%, and organic matter (OM) comprised 1.98%. The soil texture was loamy sand, consisting of 82.10% sand, 8.89% clay, and 9.01% silt. At a depth of 20 – 40 cm, the soil pH decreased to 6.02, accompanied by a decline in N (0.13%) and P (33.04 mg/kg). The texture at this depth was sandy loam, with a slightly lower sand content (73.43 %) and higher clay (10.88 %) and silt (15.69%) contents.

In addition, soil properties in the pigeon pea alley cropping after 2 years showed that the 0 – 20 cm layer exhibits increased N (0.39%) and P (48.42 mg/kg) levels compared to the initial stage. Both Ca and Mg levels

Table 4. Physicochemical properties of soil at the study site in Fumesua during the initial stage in 2022 and after 2 years of cropping

Soil depth (cm)	Chemical properties						Physical properties					
	pH	N (%)	P (mg/kg)	K (cmol (+)/kg)	Mg (cmol (+)/kg)	Ca (cmol (+)/kg)	OC (%)	OM (%)	Sand (%)	Clay (%)	Silt (%)	Texture class
Initial soil parameters												
0 – 20	6.50	0.26	49.15	0.21	0.69	1.35	1.11	1.98	82.10	8.89	9.01	Loamy sand
20 – 40	6.02	0.13	33.04	0.15	0.67	0.82	0.75	1.21	73.43	10.88	15.69	Sandy loam
Soil parameters in the pigeon pea alley after 2 years												
0 – 20	6.37	0.39	48.42	0.20	0.80	2.25	2.11	3.11	81.99	8.99	9.02	Loamy sand
20 – 40	6.22	0.45	30.94	0.21	0.80	1.12	1.75	2.25	73.00	11.00	16.00	Sandy loam
Soil parameters in the sole maize after 2 years												
0 – 20	6.48	0.26	48.05	0.23	0.59	1.25	0.81	0.98	81.90	8.90	9.20	Loamy sand
20 – 40	6.12	0.13	33.34	0.15	0.55	0.83	0.80	0.21	74.03	10.80	15.17	Sandy loam

Abbreviations: Ca: Calcium; K: Potassium; Mg: Magnesium; N: Nitrogen; OC: Organic carbon; OM: Organic matter; P: Phosphorus.

increased significantly to 2.25 cmol (+)/kg and 0.80 cmol (+)/kg, respectively. Moreover, OC and OM improved to 2.11% and 3.11%, respectively, suggesting enhanced soil fertility under pigeon pea cropping. At a depth of 20 – 40 cm, the concentrations of N and P were 0.45% and 30.94 mg/kg, respectively. Ca slightly decreased to 1.12 cmol (+)/kg, while Mg remained stable. Soil texture remained sandy loam, with 73% sand, 11% clay, and 16% silt.

The soil properties in the NPP system after 2 years at the 0 – 20 cm depth showed that N remains constant at 0.26%, matching the initial soil values, while P slightly decreased to 48.05 mg/kg. Ca measured 1.25 cmol (+)/kg and OM declined to 0.98%, both lower than in the pigeon pea alley cropping, suggesting reduced organic input from maize. At a depth of 20 – 40 cm, N and P levels were 0.13% and 33.34 mg/kg, respectively, comparable to the initial soil values. Ca and Mg levels were slightly lower than those in the pigeon pea alley cropping, while OM content remained low at 0.21%.

3.6. Economic analysis

The benefit–cost ratio (BCR) was employed for the economic analysis. The MPP cropping systems were compared to NPP system under varying fertilizer levels to assess resource optimization and profitability. BCR, a key indicator of economic advantage, varied across cropping systems and fertilizer applications, reflecting the relationship between input costs and yield benefits

(Table 5). In the MPP cropping system, the BCR under NF treatment was 2.16, demonstrating economic viability even under minimal input conditions. This suggests that incorporating pigeon pea, a nitrogen-fixing legume, can reduce the need for chemical fertilizers by naturally enhancing soil fertility. Under the HR treatment, the BCR slightly decreased to 1.91, indicating that the additional fertilizer cost does not proportionally increase economic returns. However, with FR fertilizer application, the BCR improved significantly to 2.81, highlighting the potential for maximized profitability when input levels are optimized (Table 5).

In contrast, the NPP system presented a slightly different trends. Under the NF treatment, the BCR was 2.04, demonstrating moderate economic returns with low input (Table 5). Interestingly, the BCR increased to 2.81 under the HR treatment, similar to the highest return observed in the MPP system. This suggests that maize responds well to moderate fertilizer application, possibly due to the alleviation of nutrient constraints that limit growth and yield. However, under FR treatment application, the BCR was reduced to 2.37, reflecting diminishing returns at higher input levels (Table 5). This indicates that the NPP system is less efficient in translating additional fertilizer into economic benefits than the MPP system (Table 5).

4. Discussion

The study highlights the crucial role of MPP intercropping systems in addressing the productivity, sustainability,

Table 5. Partial budgeting between maize–pigeon pea intercrop and sole maize systems under four different fertilization application rates averaged for the cropping seasons

Cropping system	Maize–pigeon pea			Sole maize		
	NF	HR	FR	NF	HR	FR
Maize average yields (kg/ha)	3,165	3,426	5,198	3,174	4,891	4,828
Adjusted maize yield*	2,849	3,083	4,678	2,857	4,402	4,345
Gross benefit of maize (GHC/ha)	28,485	30,834	46,782	28,566	44,019	43,452
Pigeon pea average yields (kg/ha)	250	250	250	-	-	-
Adjusted pigeon pea yield*	225	225	225	-	-	-
Gross benefit of pigeon pea (GHC/ha)	1,575	1,575	1,575	-	-	-
Gross benefit of the cropping system	30,060	32,409	48,357	28,566	44,019	43,452
Cost of pigeon pea establishment (GHC/ha)	800	800	800	-	-	-
Cost of harvesting pigeon pea (GHC/ha)	400	400	400	-	-	-
Cost of pruning and spreading pigeon pea biomass (GHC/ha)	400	400	400	-	-	-
Cost of chemical fertilizer (GHC/ha)	-	1,250	2,500	-	1,250	2,500
Labor cost for the application of fertilizer (GHC/ha)	-	400	700	-	900	1,000
Land clearing (GHC/ha)	3,000	3,000	3,000	3,000	3,000	3,000
Cost of maize seed (GHC)	200	200	200	300	300	300
Labor cost of planting (C/ha)	1,200	1,200	1,200	1,400	1,400	1,400
Cost of weeding (GHC/ha)	1,500	1,500	1,500	2,200	2,200	2,200
Harvesting cost (GHC/ha)	2,000	2,000	2,000	2,500	2,500	2,500
Total costs that vary	8,700	10,350	11,900	9,400	11,550	12,900
Total cost of the system	9,500	11,150	12,700	9,400	11,550	12,900
Net benefit	20,560	21,259	35,657	19,166	32,469	30,552
Benefit–cost/ratio	2.16	1.91	2.81	2.04	2.81	2.37

Note: Asterisk (*) represents 10% of maize average yield against inflation and price volatilities.

Abbreviations: FR: Full rate of recommended fertilizer; GHC/: Ghana Cedi; HR: Half rate of recommended fertilizer; NF: No fertilizer.

and resilience challenges faced by smallholder farmers in Ghana. The findings indicate that intercropping systems are more productive and sustainable than monocultures, as they efficiently utilize resources and provide ecological benefits.^{22,23} The inclusion of pigeon pea biomass significantly enhanced soil nutrient availability and improved maize growth, yield components, and total grain yield. These results support previous studies demonstrating that pigeon pea contributes to soil fertility through nitrogen fixation and the incorporation of OM.^{24,25}

The study demonstrates that maize yields in intercropping systems are comparable to those in sole cropping under FR treatment and exceed them under moderate (HR) and low fertilizer input (NF) conditions. These findings support the idea that pigeon pea biomass can supplement and partially replace inorganic fertilizers without compromising yields.^{4,12,23} This finding is particularly relevant for smallholder farmers, who often face challenges due to the high cost and limited availability of chemical fertilizers.^{13,26} Furthermore, the strong

performance of intercropping systems under varying environmental conditions highlights their resilience, making them well-suited for areas with erratic rainfall and poor soil fertility.¹⁵

The high maize yields recorded during the major season, likely due to increased rainfall, highlight the critical influence of environmental conditions on cropping system performance. While monoculture systems such as NPP demonstrated high productivity under optimal fertilizer input, they exhibited limited resilience under nutrient constraints and seasonal variability. In contrast, the intercropping system maintained yield stability, suggesting that the ecological and functional complementarities between maize and pigeon peas contribute to enhanced system resilience.²⁷ In addition, intercropping systems offer significant economic advantages. The reduced reliance on chemical fertilizers lowered production costs, thereby enhancing profitability and accessibility for resource-constrained farmers.²⁸ Pigeon pea grains also serve as a valuable dietary supplement for farm households,

contributing to improved food security and nutritional diversity.²⁹ These findings align with previous studies that highlight the role of legumes in enhancing soil fertility, reducing chemical input dependency, and improving crop profitability.^{14,30}

Beyond economic benefits, intercropping systems also contribute significantly to ecological sustainability. Pigeon pea enhances nitrogen fixation, facilitates biomass recycling, and promotes soil carbon sequestration, all of which support improved soil health and long-term productivity.^{11,16,31,32} These ecological benefits align with the principles of sustainable agriculture, positioning MPP intercropping as a promising strategy for climate-resilient farming systems.³³ However, the scope of this study is limited to a single agroecological zone, which may limit the applicability of the findings. Further research is needed to evaluate the system's performance across diverse regions. In addition, although economic benefits were inferred, detailed economic analyses incorporating BCRs and profitability metrics would provide a more comprehensive understanding.¹⁰ The observed trade-offs between productivity and sustainability highlight the need for careful optimization of planting densities, row spacing, and fertilizer application rates to maximize the system's overall benefits.³⁴

Farmers should consider integrating pigeon peas into maize cropping systems to reduce fertilizer costs, enhance soil fertility, and increase resilience to environmental stresses.³⁵ Future studies should focus on identifying optimal planting densities, row spacing, and variety selection for MPP intercropping across diverse agroecological zones. In addition, policymakers are encouraged to support the adoption of intercropping systems through targeted subsidies, extension services, and farmer training programs. The findings highlight a strategic trade-off: while monocultures may maximize yields under optimal conditions, they lack resilience, whereas intercropping systems offer a balanced approach – combining stable productivity, ecological benefits, and resilience under variable conditions.²⁷ Integrating pigeon peas into maize cropping systems can therefore support sustainable intensification, reduce environmental impacts, and strengthen food security. This study illustrates that pigeon peas can serve as a vital resource for farming communities, thriving in challenging environments while providing multiple benefits.^{36,37}

In summary, pigeon pea alley cropping enhanced soil fertility by increasing levels of N, P, OC, and Ca. NPP cropping system did not significantly enhance soil nutrients, showing values similar to those of the initial soil properties. These findings highlight the potential of pigeon

pea alley cropping in improving soil health and maintaining fertility over time. MPP intercropping systems represent a promising approach for the sustainable intensification of agriculture, effectively integrating productivity, resilience, and ecological sustainability. They offer a practical solution for smallholder farmers in Ghana and comparable settings, helping to address critical challenges such as declining soil fertility, climate variability, and limited access to inputs. Future research and policy support will be essential to achieving the full potential of these systems in ensuring food security and environmental sustainability.

5. Conclusion

An ISFM approach incorporating legume agroforestry trees, such as pigeon peas, offers a promising solution for sustainable maize production. This approach addresses the challenge of maintaining soil fertility, which has contributed to declining maize yields. Pigeon pea not only provides reliable biomass and shade that conserve soil moisture but also helps suppress weeds. These advantages of the MPP cropping systems enhance resource use efficiency and maize productivity. Therefore, ISFM – planting maize with pigeon pea combined with half the recommended fertilizer rate (125 kg/ha of 15-15-15 N-P₂O₅-K₂O + 125 kg/ha of SoA) – could be a viable strategy for sustainable maize production on continuously cropped fields. However, further research is needed to evaluate whether fertilizer rates can be reduced even further without compromising maize productivity and economic returns. This is crucial for sustaining maize production among smallholder farmers amid climate change, thereby contributing to improved food security.

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Conflict of interest

The authors declare no conflicts of interest.

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ORIGINAL RESEARCH ARTICLE

Nickel foam-supported nickel–cobalt layered double hydroxide/platinum composite electrocatalyst for ammonia oxidation reaction

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Abstract

With increasing interest in direct ammonia fuel cells, designing and developing high-activity electrocatalysts for the electrochemical ammonia oxidation reaction has become a critical research focus. In this work, a nickel foam-supported nickel–cobalt layered double hydroxide/platinum composite (Pt–NiCo-LDH) was synthesized through electrochemical deposition and displacement reactions for enhanced electrocatalytic activity. Key synthesis parameters, including reaction temperature and chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) concentration, were systematically optimized. Electrochemical characterization using cyclic voltammetry revealed that the optimal catalyst – synthesized in a solution containing 450 μL deionized water and 1,050 μL 0.1 mol/L $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ at 20°C for 8 h – showed an oxidation peak current of 154.60 mA and a low onset potential of -0.38 V (versus mercury/mercury oxide), indicating exceptional catalytic activity. The support of nickel foam provided favorable conditions to deposit NiCo-LDH nanowires, providing sites for the growth of platinum nanoparticles, thus promoting the catalytic activity of the Pt-(NiCo-LDH) electrocatalyst.

Keywords: Electrocatalyst; Ammonia oxidation reaction; Nanocomposite; Platinum; Nickel–cobalt layered double hydroxide

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1. Introduction

With the continuous consumption of fossil fuels, the development and application of clean energy sources have received increasing attention.^{1–3} Among these, hydrogen is considered one of the ideal energy carriers.⁴ However, currently, hydrogen is primarily produced from fossil fuels, which is accompanied by the generation and emission of carbon dioxide. In addition, the application of hydrogen is also limited by challenges related to storage and transportation.⁵ In contrast, ammonia, owing to its high energy density, rich hydrogen content, and low safety risks, has garnered significant attention.⁶ On one hand, decomposing ammonia into nitrogen (N_2) and hydrogen can address the problems associated with hydrogen storage and transportation. On the other hand, the electrochemical oxidation reaction of ammonia can be applied to remove ammonia nitrogen in water bodies – thereby addressing environmental issues – and for the design and development of direct ammonia fuel cells.^{7,8} The combustion of direct ammonia

fuel cells produces only water as a byproduct, making it an extremely clean fuel.

Considerable research efforts have focused on electrocatalysts for the ammonia oxidation reaction (AOR). Among noble metals, platinum (Pt) showed the best electrocatalytic activity compared to others. Various morphologies of pure Pt, including cubic Pt,⁹ sheet-like Pt,¹⁰ and flower-like Pt,¹¹ have been reported as catalysts for the electrochemical AOR. These different morphologies can be achieved by controlling the electrodeposition potentials and using surfactants. In addition, to further improve AOR activity, research has extended to certain Pt-based binary and ternary electrocatalysts. Vooyo *et al.*¹² established the nitrogen adsorption strength trend as follows: Ruthenium > rhodium > palladium > iridium > Pt >> gold, silver, and copper.¹² Therefore, Pt-based alloys, including Pt-nickel (Ni), Pt-iridium, and Pt-gold, have been synthesized, showing superior electrocatalyst performance compared to pure Pt. In addition, certain oxides, such as yttrium oxide,¹³ stannic oxide,¹⁴ and cerium oxide,¹⁵ have also been used to modify Pt. For example, cerium oxide-modified Pt showed better AOR performance, including lower onset potential and higher oxidation peak current, compared to pure Pt.

In regard to transition metals and their oxides/oxyhydroxides, Ni has been regarded as a promising candidate for AOR electrocatalysts. However, challenges remain, such as the compromised long-term stability of Ni due to corrosion during ammonia electrolysis. To overcome these issues, various Ni-based materials have been developed, including Ni-copper alloys,¹⁶ copper oxide/Ni hydroxide,¹⁷ Ni-copper oxyhydroxide,¹⁸ Ni-copper-iron oxyhydroxide,¹⁹ and Ni-cobalt (Co) layered double hydroxides. These materials aim to control the electron structure and the adsorption of ammonia. For example, Ren *et al.*²⁰ synthesized copper oxide/Ni through a one-step replacement reaction and used charge density difference and Mulliken charge analyses to explain the enhanced electrocatalytic performance.²⁰ Wang *et al.*²¹ developed a boron-modified Ni-iron layered double hydroxide (NiFe-LDH) supported on Ni foam (NF), where boron nanoclusters served as charge bridges to regulate electron redistribution in NiFe-LDH and expose more active metal sites.²¹

In this work, to fabricate a high-performance electrocatalyst for AOR, NiCo-LDH nanowires were first electrodeposited onto NF, followed by the growth of Pt nanoparticles through a galvanic replacement reaction. The ratio of chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), reaction time, and reaction temperature were systematically controlled, and the resulting samples were characterized. In addition, the samples were analyzed

using scanning electron microscopy (SEM; ZEISS 300, HITACHI, Japan) and X-ray photoelectron spectroscopy (XPS; ESCALAB 250XI, ThermoFisher, USA).

2. Methodology

2.1. The synthesis of nickel-cobalt layered double hydroxide/platinum composite

2.1.1. Pre-treatment of nickel foam

The NF was first cut into thin sheets measuring 10 mm × 25 mm × 1 mm. The sheets were then placed into a 50 mL beaker and immersed in 3 mol/L hydrochloric acid for 10 min. Next, the NF was transferred to ethanol (analytical reagent grade; Tianli Chemical Reagent Company, China) and sonicated for 10 min. Finally, the NF was washed with deionized water and dried in an oven (Shangcheng Instrument Manufacturing Company, China) at 50°C for later use. The resulting sample is referred to as NF.

2.1.2. Preparation of nickel-cobalt layered double hydroxide

First, 0.571 g of Ni(II) chloride hexahydrate (analytical reagent grade; Shanghai Macklin Biochemical Co., Ltd. China) and 0.195 g of Co(II)chloride hexahydrate (analytical reagent grade; Shanghai Macklin Biochemical Co., Ltd. China) were added into 50 mL of deionized water and stirred to form a homogeneous solution. Subsequently, 0.30 g of urea (analytical reagent grade; Shanghai Macklin Biochemical Co., Ltd. China) was added to the aforementioned mixed solution, followed by magnetic stirring for an hour to ensure complete homogenization. The resultant mixture and a cleaned NF substrate were transferred into a 100 mL teflon-lined stainless-steel autoclave (Wanruigude Company, China), which was then sealed and maintained at 120°C for 12 h in an electric oven (Shangcheng Instrument Manufacturing Company, China). After naturally cooling to room temperature, the obtained sample was collected, rinsed, and denoted as NiCo-LDH.

2.1.3. Preparation of platinum-(nickel-cobalt layered double hydroxide)

Nickel-cobalt layered double hydroxide was placed into 4 mL centrifuge tubes. Then, 150 μL, 300 μL, 450 μL, and 600 μL of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.1 mol/L) (analytical reagent grade; Shanghai Macklin Biochemical Co., Ltd. China) were added into the centrifuge tubes along with 1,350 μL, 1,200 μL, 1,050 μL, and 900 μL of deionized water, respectively, to obtain a solution with a volume of 1,500 μL. The mixtures were placed in a water bath at 20°C for 8 h. The obtained Pt-(NiCo-LDH) samples were labeled as Pt-(NiCo-LDH)-X (X = 1, 2, 3, 4). Under the optimal

concentration of 450 μL of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.1 mol/L) and 1,050 μL of deionized water, the temperature of the water bath was controlled at 30°C, 40°C, and 50°C, with heating maintained for 8 h. The obtained samples were named as Pt-(NiCo-LDH)-X (X = 5, 6, 7). In addition, the sample prepared without $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.1 mol/L) was named NiCo-LDH-8, the sample prepared without NiCo-LDH was named Pt-NF-9, and the NF was designated NF-10. Figure 1 shows the synthesis process of NiCo-LDH and Pt-(NiCo-LDH)-X.

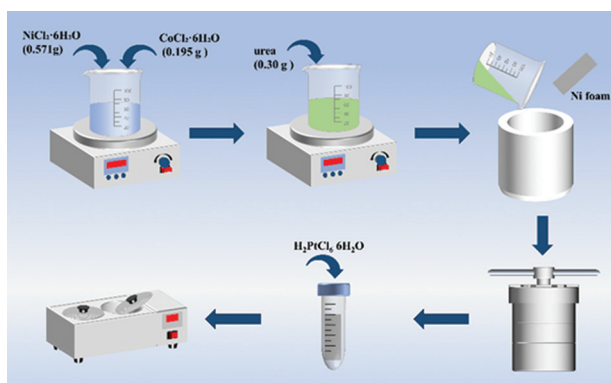


Figure 1. The synthesis process of nickel (Ni)-cobalt layered double hydroxide and platinum-(Ni-cobalt layered double hydroxide)-X

3. Results and discussion

In this work, ammonium chloride (NH_4Cl) was used as the ammonia source. The cyclic voltammetry (CV) technique was employed to analyze the electrochemical reactions based on the peak current, peak potential, and related parameters.²² The oxidation peak current is one of the important parameters to evaluate the activity of catalysts. Higher peak currents indicate better catalytic activity, characterized by faster electron transfer, accelerated electrode reaction rates, and lower reaction resistance. To select the best synthesis condition of the catalyst, the CV technique was conducted on all catalysts for the AOR. The oxidation reaction peak currents were collected and used as a key parameter to evaluate the catalyst activity. In addition, to obtain an electrocatalyst with excellent catalytic performance, the volume of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and the reaction temperatures of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and NiCo-LDH were regulated.

First, the concentrations of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ were studied. Figure 2A-D shows the CV curves of the Pt-(NiCo-LDH)-X (X = 1, 2, 3, 4) catalysts synthesized with $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ volumes ranging from 0.15 mL to 0.60 mL. In the 1 M potassium hydroxide (KOH) and 1 M KOH + 0.1 M NH_4Cl solutions, a distinct oxidation peak emerged at

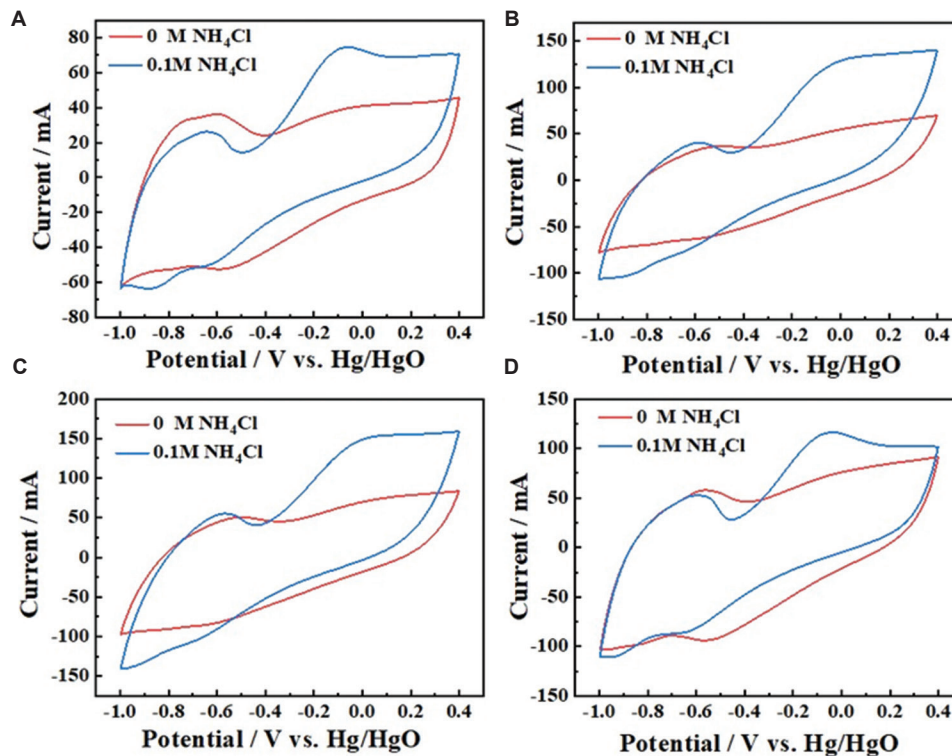


Figure 2. The cyclic voltammetry curves of platinum-(nickel-cobalt layered double hydroxide)-X (Pt-[NiCo-LDH]-X). (A) Pt-(NiCo-LDH)-1, (B) Pt-(NiCo-LDH)-2, (C) Pt-(NiCo-LDH)-3, and (D) Pt-(NiCo-LDH)-4 catalysts in 1 M potassium hydroxide (KOH) and 1 M KOH + 0.1 M ammonium chloride (NH_4Cl) solutions. Hg/HgO refers to mercury/mercury oxide used as the reference.

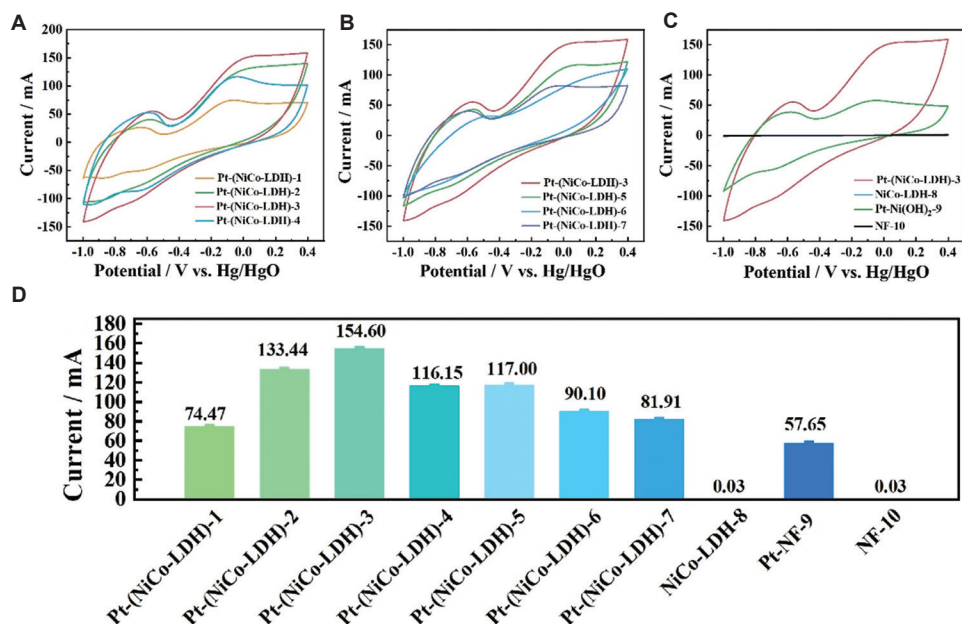


Figure 3. The cyclic voltammograms of (A) platinum-(nickel-cobalt layered double hydroxide) (Pt-[NiCo-LDH]-X) (X = 1, 2, 3, 4), (B) Pt-(NiCo-LDH)-X (X = 3, 5, 6, 7), (C) Pt-(NiCo-LDH)-3, NiCo-LDH-8, Pt-Ni foam (NF)-9, and NF-10 catalysts in the mixed solution of 1 M potassium hydroxide and 0.1 M ammonium chloride, and (D) the oxidation peak currents of all catalysts. Hg/HgO refers to mercury/mercury oxide used as the reference.

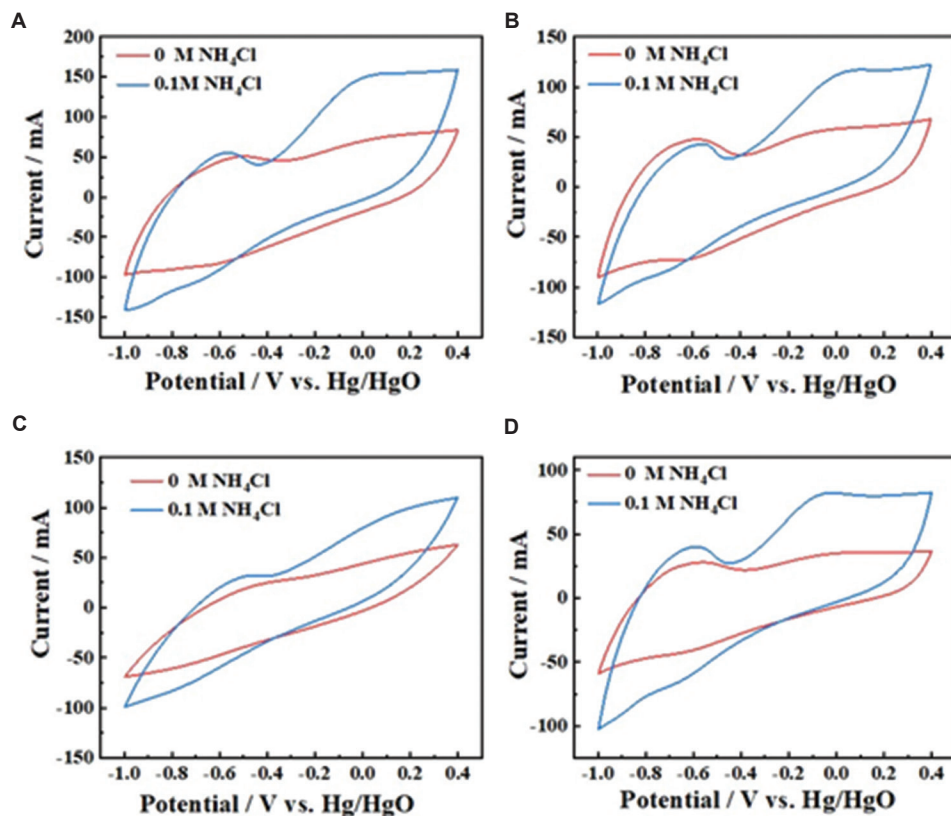


Figure 4. The cyclic voltammograms of platinum-(nickel-cobalt layered double hydroxide)-X (Pt-[NiCo-LDH]-X). (A) Pt-(NiCo-LDH)-3, (B) Pt-(NiCo-LDH)-5, (C) Pt-(NiCo-LDH)-6, and (D) Pt-(NiCo-LDH)-7 catalysts in 1 M potassium hydroxide (KOH) and 1 M KOH + 0.1 M ammonium chloride (NH₄Cl) solutions. Hg/HgO refers to mercury/mercury oxide used as the reference.

approximately -0.05 V. Figure 3A shows the CV curves of Pt-(NiCo-LDH)-1, Pt-(NiCo-LDH)-2, Pt-(NiCo-LDH)-3, and Pt-(NiCo-LDH)-4 catalysts in the mixed solution of 1 M KOH and 0.1 M NH_4Cl , with oxidation peak currents shown in Figure 3D. Notably, with an increasing volume of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, the oxidation peak current exhibited a notable upward trend, escalating from 74.47 mA to 154.60 mA, indicating an enhanced catalytic activity. However, at 0.6 mL, the catalytic activity of Pt-(NiCo-LDH)-4 decreased significantly to an oxidation peak current of 116.15 mA. This indicated that during the displacement process between PtCl_6^{2-} and Co^{2+} , a large quantity of Co^{2+} was consumed, and excessive $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ may have destabilized the NiCo-LDH structure, thereby resulting in the loss of catalytic activity.

Based on the addition of 0.45 mL of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, the reaction temperature (20°C , 30°C , 40°C and 50°C) between $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and NiCo-LDH was further controlled. Figure 4 shows the CV curves of the Pt-(NiCo-LDH)-X (X = 3, 5, 6, 7) catalysts in 1 M KOH and 1 M KOH + 0.1 M NH_4Cl solutions. Figure 3B shows the CV curves of Pt-(NiCo-LDH)-X (X = 3, 5, 6, 7) catalysts in the mixed solution of 1 M KOH and 0.1 M NH_4Cl . As shown in Figure 3B, as the reaction temperature increased, the

oxidation peak current gradually decreased. The oxidation peak currents decreased from 154.60 mA to 81.91 mA (Figure 3D), indicating that the catalytic activity gradually weakened. Increasing reaction temperatures accelerated the rate of the displacement reaction between PtCl_6^{2-} and Co^{2+} . Simultaneously, the nucleation rate of Pt was also accelerated, which hindered the formation of highly dispersed Pt and reduced the number of catalytically active sites.

To demonstrate that Pt-(NiCo-LDH)-3 exhibited better catalytic activity than NF, NiCo-LDH, and Pt-NF, the catalytic activities of NiCo-LDH-8, Pt-NF-9, and NF-10 were also tested in 1 M KOH and 1 M KOH + 0.1 M NH_4Cl solutions, as shown in Figure 5. No discernible variation in current was observed in the CV curves of NiCo-LDH-8 and NF-10, indicating that pure NiCo-LDH and NF did not show obvious catalytic activity in this measurement system. In contrast, the Pt-NF-9 catalyst exhibited a clear oxidation peak with an oxidation peak current of 57.65 mA, indicating that the Pt showed electrocatalytic activity. In addition, the oxidation peak current of Pt-(NiCo-LDH)-3 was 2.7 times that of Pt-NF-9, indicating that there is a good synergistic effect between NiCo-LDH and Pt. Table 1 shows the electrocatalytic activities of some reported

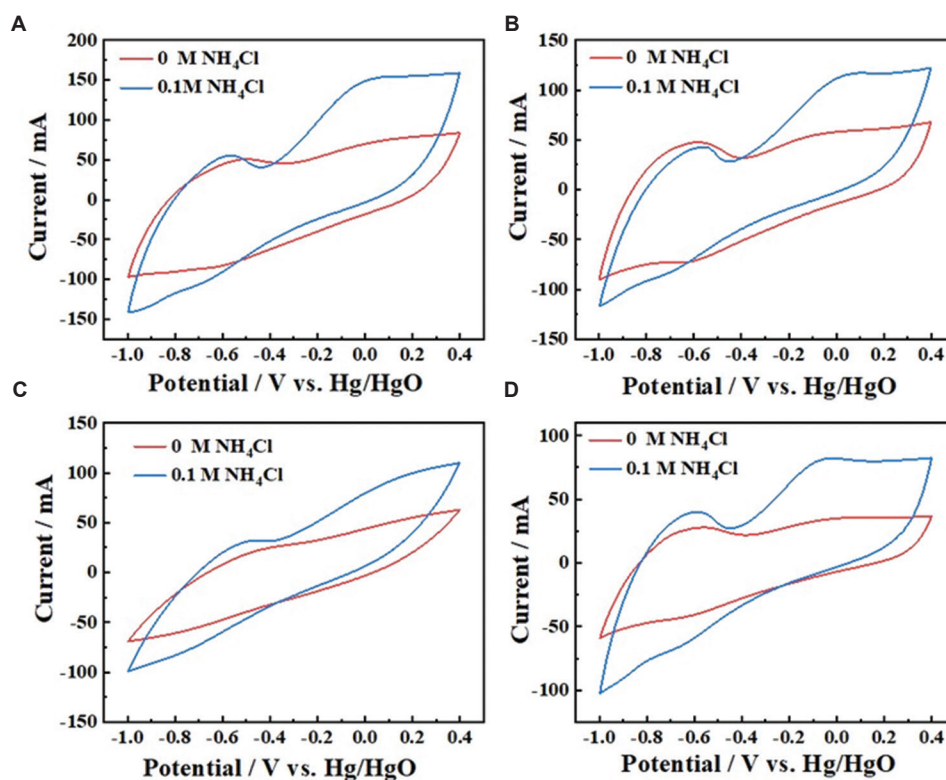


Figure 5. The cyclic voltammetry curves of (A) platinum-(nickel-cobalt layered double hydroxide)-3 (Pt-[NiCo-LDH]-X), (B) NiCo-LDH-8, (C) Pt-Ni foam (NF)-9, and (D) NF-10 catalysts in 1 M potassium hydroxide (KOH) and 1 M KOH + 0.1 M ammonium chloride (NH_4Cl) solutions. Hg/HgO refers to mercury/mercury oxide used as the reference.

catalysts. Compared to these catalysts, the onset potential and current density of Pt-(NiCo-LDH)-3 were accepted.

To find the optimal potential ranges of Pt-(NiCo-LDH)-3 for AOR, different potential ranges, including $-1 - 0.4$ V, $-0.8 - 0.6$ V, $-0.6 - 0.8$ V, $-0.4 - 1.0$ V, and $-0.2 - 1.2$ V, have been selected and measured for the electrocatalytic test. As shown in Figure 6A-D, with the rightward shift of the potential window, the oxidation peak around -0.05 V gradually decreased and eventually disappeared, whereas the oxidation peak at around 0.7 V gradually became increasingly prominent. This shift occurred because moving the potential window to the right gradually deviated from the suitable operating potential of

the Pt catalyst, revealing the potential range more suitable for NiCo-LDH. However, as shown in Figure 4C and D, the catalytic activity of NiCo-LDH alone was not significant, and the current change before and after the addition of NH_4Cl was minimal. These results indicate that the catalytic activity of Pt-(NiCo-LDH)-3 mainly originated from Pt, with the most suitable operating window range being $-1 - 0.4$ V.

To investigate the kinetics of AOR on the Pt-(NiCo-LDH)-3 surface, CV curves were recorded at scan rates ranging from 20 to 200 mV/s, as shown in Figure 7A. With increasing scan rates, the oxidation peak currents increased accordingly. Figure 7B shows the relationship between

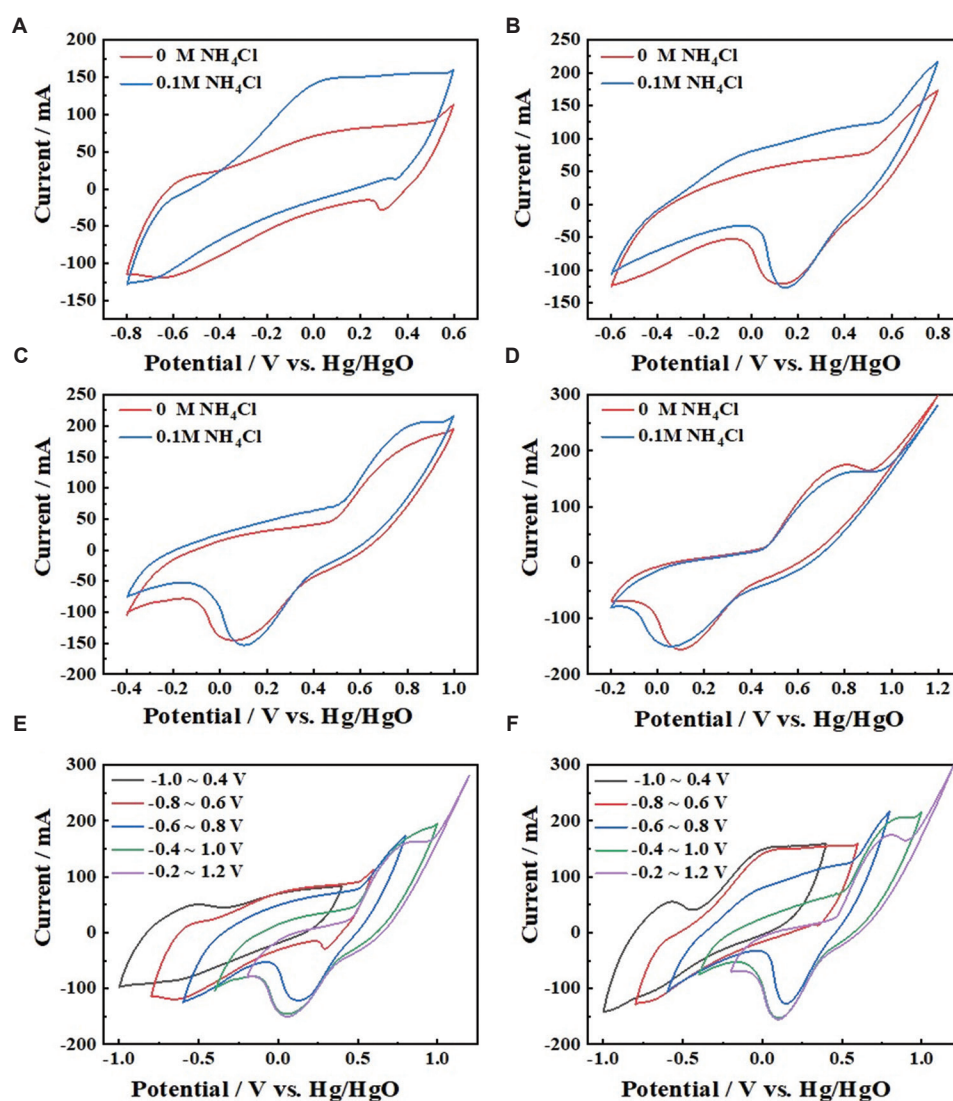


Figure 6. The potential ranges for ammonia oxidation reaction in (A, B, C and D) 1 M potassium hydroxide (KOH) and 1 M KOH + 0.1 M ammonium chloride (NH_4Cl) solutions. The cyclic voltammetry curves of different potentials (E) in 1 M KOH and (F) in 1 M KOH + 0.1 M NH_4Cl solution. Hg/HgO refers to mercury/mercury oxide used as the reference.

Table 1. The ammonia oxidation reaction test conditions and activity of reported catalysts

Electrode	Onset potential (V)	Current density (mA/cm ²)	Electrolyte	Stability	References
Platinum/cobalt–iron/nickel foam	−0.019 V _{RHE}	50.00 at 0.029 V _{RHE}	0.2 M N ₂ H ₄ ⁺ 1.0 M KOH	At −0.017 V _{RHE} for 100 h	23
Platinum–iridium–copper	0.350 V _{RHE}	40.60 at 0.500 V _{RHE}	0.1 M NH ₃ ⁺ 1.0 M KOH	At 0.650 V _{RHE} for 500 s	24
Silver/iron (II) oxide/titanate nanotubes	−0.500 V _{Ag/AgCl}	-	0.1 M NH ₄ Cl ⁺ 1.0 M phosphate-buffered saline	At −0.250 V _{Ag/AgCl} for five cycles	25
Platinum–cobalt hydroxide–nickel foam-3	0.250 V _{RHE}	10.17 at −0.200 V _{RHE}	0.1 M NH ₄ Cl ⁺ 1.0 M KOH	-	31
Nickel–copper–sulfur treated/carbon paper	1.374 V _{RHE}	110.00 at 1.690 V _{RHE}	0.2 M NH ₄ Cl ⁺ 1.0 M NaOH	At 1.640 V _{RHE} for 24 h	27
Platinum–iridium (5:5 atomic ratio)/XC-72	0.350 V _{RHE}	32.20 at 0.500 V _{RHE}	1.0 M ammonia ⁺ 1.0 M KOH	At 0.500–1.000 V _{RHE} for 4,000 cycles	28
Platinum–(nickel–cobalt layered double hydroxide)-3	−0.03 V _{Hg/HgO}	154.60 at 0.24 V _{Hg/HgO}	0.1 M NH ₄ Cl ⁺ 1.0 M KOH	At 0.24 V _{Hg/HgO} for 5,000 s	This work

Abbreviations: Ag: Silver; AgCl: Silver chloride; Hg: Mercury; HgO: Mercury oxide; KOH: Potassium chloride; NH₄Cl: Ammonium chloride; RHE: Reversible hydrogen electrode.

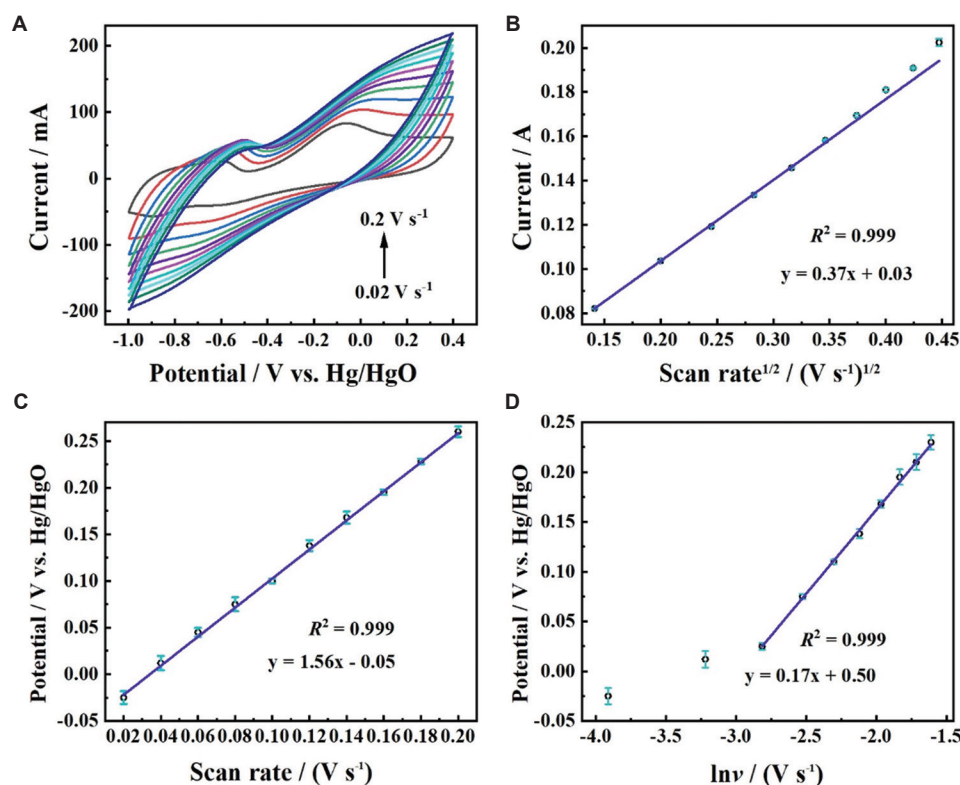


Figure 7. Cyclic voltammetry curves of platinum–(nickel–cobalt layered double hydroxide)-3 electrode in 1 M potassium hydroxide + 1 mM ammonium chloride at different scan rates. (B) Oxidation peak current densities versus (vs.) the square root of the scan rates. (C) Oxidation peak potentials vs. scan rate. (D) The effect of scan rate on peak potentials. Hg/HgO refers to mercury/mercury oxide used as the reference.

oxidation peak currents and scan rates. Based on the fitted curve, a favorable linear correlation was observed between the oxidation peak currents and the square root of the scan rate, described by the linear equation: $y = 0.37x + 0.03$

($R^2 = 0.999$), indicating a diffusion-controlled process. Moreover, with the increase in scan rates, the oxidation peak potential (E_{pa}) demonstrated a subtle positive shift. In addition, a strong linear correlation was established

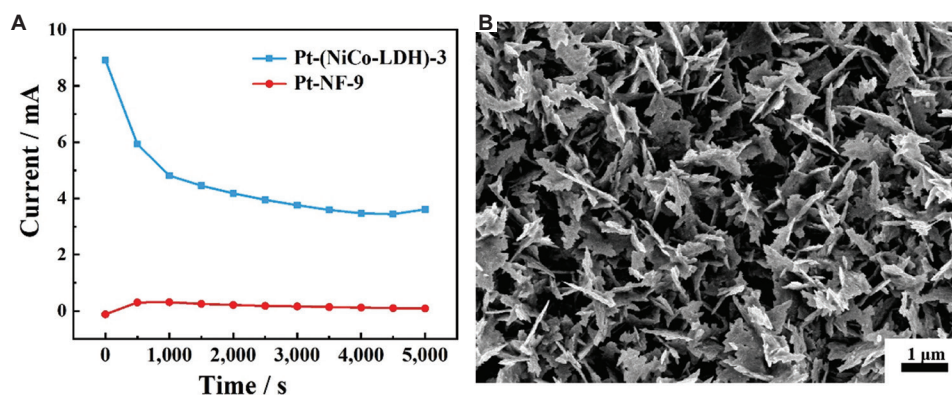


Figure 8. The stability measurement and SEM image after stability measurement of Pt-(NiCo-LDH)-3. (A) The stability measurements of platinum-(nickel-cobalt layered double hydroxide) (Pt-[NiCo-LDH]-3) and Pt-nickel foam (NF)-9. (B) The scanning electron microscopic image of Pt-(NiCo-LDH)-3 after use. Scale bar: 1 μm, magnification: 10.00 KX.

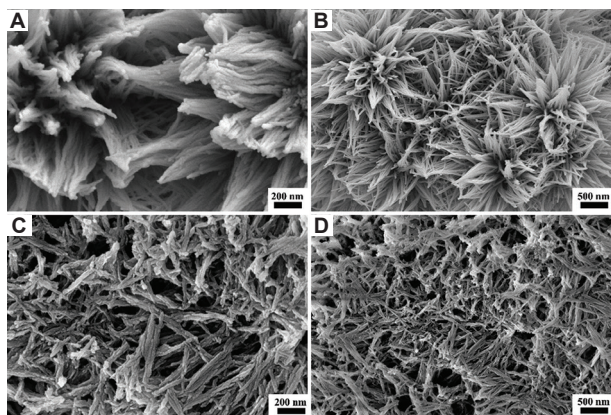


Figure 9. Scanning electron microscopy images. (A and B) Nickel-cobalt layered double hydroxide (NiCo-LDH) and (C and D) platinum-(NiCo-LDH)-3. Scale bars: 200 nm and 500 nm, magnifications: 200 nm (50.00 K), and 500 nm (20.00 K).

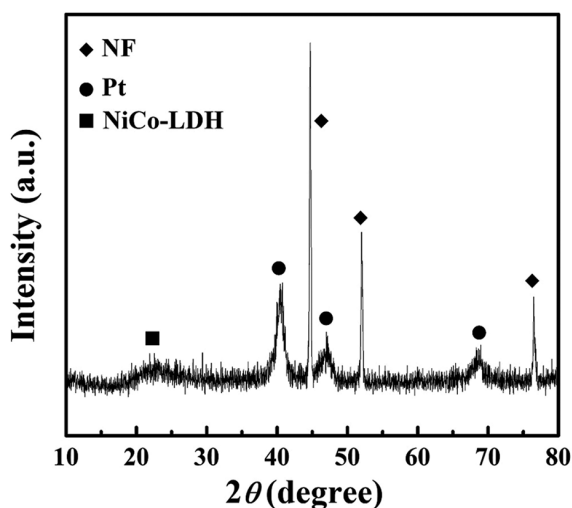


Figure 10. The X-ray diffraction pattern of platinum Pt-(NiCo-LDH)-3. Abbreviations: NF: Nickel foam; NiCo-LDH: Nickel-cobalt layered double hydroxide; Pt: Platinum.

between the E_{pa} and the scan rates ($R^2 = 0.999$) (Figure 7C). This finding suggested the presence of an irreversible process for AOR on the Pt-(NiCo-LDH)-3 electrode. A good linear relationship was observed between the E_{pa} and the logarithm of the scan rate ($\ln v$) ($v \geq 0.06$ V/s), as shown in Figure 7D. Laviron's theoretical model²⁹ was employed to fit the data, resulting in Equation I. Based on this fitting, the number of electrons (n) participating in the rate-determining step of the AOR on the Pt-(NiCo-LDH)-3 electrode can be calculated.

$$E_{pa} = E^\theta + \left(\frac{RT}{\alpha n F} \right) \ln \left(\frac{RTk^\theta}{\alpha n F} \right) + \left(\frac{RT}{\alpha n F} \right) \ln v \quad (I)$$

The parameters in Equation I were Faraday's constant ($F = 96,485$ C/mol), temperature ($T = 298.15$ K), gas constant ($R = 8.314$ J/[K·mol]), standard electrode potential (E^θ), and electron transfer coefficient (α). The standard rate constant is denoted as k^θ . The αn value was determined by the slope of the E_{pa} versus $\ln v$ as 0.15. Meanwhile, the value of α can be computed by Equation II:

$$E_{pa} - E_{p/2} = 1.857 \left(\frac{RT}{\alpha F} \right) \quad (II)$$

In Equation II, $E_{p/2}$ is the potential of the half peak. The α was calculated as 0.25, and the number of transfer electrons in the rate-determining step of AOR was determined as 0.6.

To evaluate the stability of the catalyst, stability tests were conducted on Pt-(NiCo-LDH)-3 and Pt-NF-9. The results, shown in Figure 8, indicate that Pt-(NiCo-LDH)-3 has a higher current and exhibits better catalytic stability than Pt-NF. After the stability test, Pt-(NiCo-LDH)-3 maintained its sheet-like morphology.

Three analyses, SEM, X-ray diffraction (XRD, D8 advance, Bruker, Germany), and XPS, were employed to study the morphology and composition of Pt-(NiCo-LDH)-3. Figure 9A and B show the SEM images of NiCo-LDH. It was observed that NiCo-LDH existed in the form of nanowires, with a certain degree of agglomeration. At a lower magnification (Figure 9B), it was easy to observe that these nanowires combined to form a flower-like morphology. However, after the growth of Pt after incubation in the water bath, the flower-like structure formed by the agglomeration of these NiCo-LDH nanowires degraded, as shown in Figure 9C and D. This could be attributed to two aspects: first, the addition of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ introduces a large number of H^+ , which provides a certain corrosive effect on NiCo-LDH, and second, the Co^{3+} ions within NiCo-LDH dissolve out and act as reducing agents to convert PtCl_6^{2-} to Pt. Unfortunately, the presence of Pt could not be clearly identified from the SEM images of Pt-(NiCo-LDH)-3. In addition, compared to the SEM image of Pt-(NiCo-LDH)-3 after use, the nanowire of Pt-(NiCo-

LDH)-3 showed more apparent changes, indicating that the NiCo-LDH underwent phase transitions and lattice rearrangements during the electrochemical measurement process.

Figure 10 exhibits the XRD pattern of Pt-(NiCo-LDH)-3. As shown in Figure 7, the three strong diffraction peaks at 44.7° , 52.0° , and 76.5° could be attributed to NF. In addition, three diffraction peaks could be detected at 40.5° , 47.1° , and 68.7° , attributable to the 111, 200, and 220 crystal planes of Pt.³⁰ In addition, a weaker diffraction peak of NiCo-LDH was observed at 22.8° .²⁴ The XRD diffraction peaks of NiCo-LDH and Pt confirm the successful growth of NiCo-LDH and Pt on the surface of NF.

To further characterize the chemical composition of Pt-(NiCo-LDH)-3, XPS was performed, and the corresponding results are presented in Figure 11. Figure 11A revealed four deconvoluted peaks in the Ni 2p. The peaks at 856.14 eV and 873.81 eV correspond to $\text{Ni}^{2+} 2p_{3/2}$ and $\text{Ni}^{2+} 2p_{1/2}$, respectively,³⁰ whereas the satellite peaks at 861.73 eV and 880.43 eV are attributed

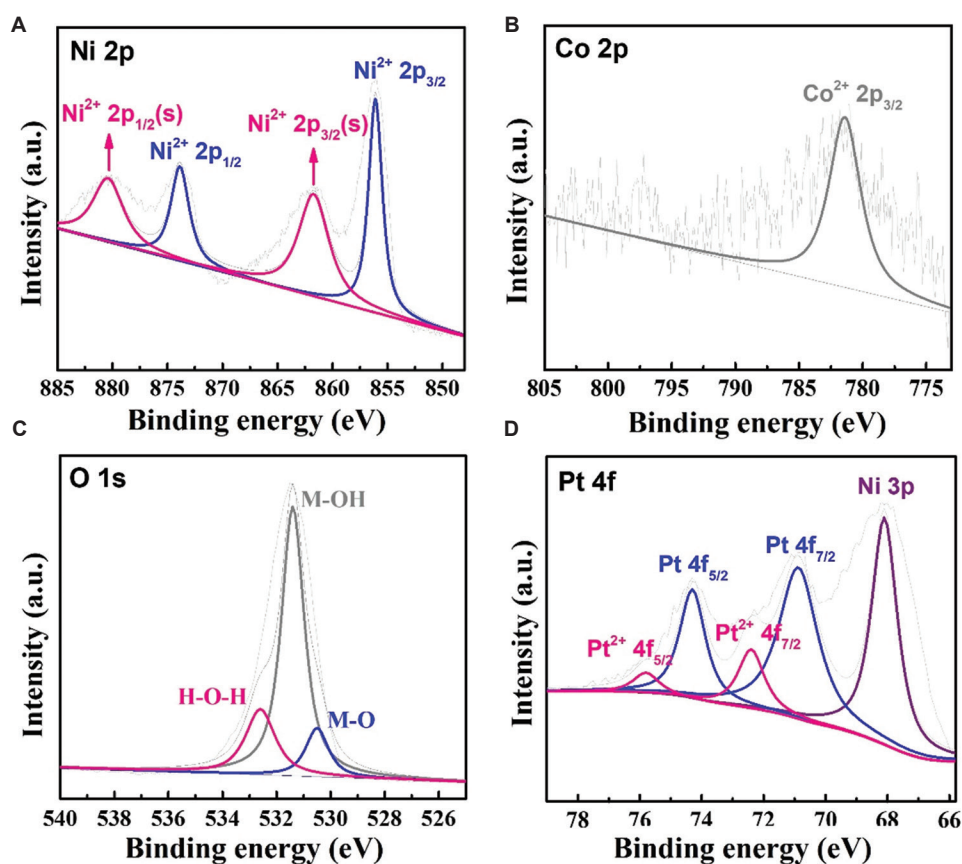


Figure 11. The X-ray photoelectron spectroscopy spectra of (A) nickel (Ni) 2p, (B) cobalt (Co) 2p, (C) oxygen (O) 1s, and (D) platinum (Pt) 4f in Pt-(NiCo-layered double hydroxide)-3

to shake-up processes. In Figure 11B, the Co 2p spectrum exhibits a prominent peak at 781.42 eV, assigned to Co²⁺ 2p_{3/2}.³¹ For the oxygen 1s spectrum (Figure 11C), three peaks at 530.52 eV, 531.44 eV, and 532.5 eV were resolved, corresponding to lattice oxygen (M-O), hydroxyl groups (M-OH), and adsorbed water (H-O-H), respectively.³¹ Collectively, these XPS results confirm the successful formation of NiCo-LDH. Finally, the XPS spectrum of the Pt is shown in Figure 11D. Two peaks at 70.87 eV and 73.31 eV could be attributed to Pt 4f_{7/2} and Pt 4f_{5/2}, indicating that Pt was zero-valent. In addition, the fitted peak at 68.10 eV could be ascribed to Ni 3p.³⁰ These results indicated that Pt nanoparticles have been deposited onto NiCo-LDH.

4. Conclusion

This study successfully developed a high-performing Pt-(NiCo-LDH) supported by NF through a solvothermal reaction and displacement reaction. All samples' catalytic activities for AOR were measured. Among the prepared samples, Pt-(NiCo-LDH)-3 exhibited superior electrocatalytic activity, with an oxidation peak current of 154.60 mA and a low onset potential of -0.38 V (versus mercury/mercury oxide). The excellent electrocatalytic activity was mainly attributed to good synergistic effects; NiCo-LDH nanowires provided a large specific surface area, offering favorable conditions for the growth of Pt, while Pt showed good catalytic activity in the electrochemical oxidation of ammonia. This work presents a potential catalyst for the AOR in direct ammonia fuel cells.

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Conflict of interest

The authors declare that they have no competing interests.

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Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data

Data will be made available upon request to the corresponding author.

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ORIGINAL RESEARCH ARTICLE

Impact of zinc oxide and titanium dioxide nanoparticles on growth parameters of chickpeas (*Cicer arietinum* L.)Anuradha Navnath Karale¹, Bhavna Nigam², and Indra Jeet Chaudhary^{1*}¹Department of Environmental Science, Savitribai Phule Pune University, Pune, Maharashtra, India²School of Environment and Sustainable Development, Central University of Gujarat, Gandhinagar, Gujarat, India**Abstract**

Agricultural productivity remains a fundamental concern for farmers and agricultural scientists. Today, global food security is increasingly threatened by environmental challenges and a rapidly growing population. Environmental stressors, such as salinity, drought, heavy metals, ozone, sulfur oxides, and nitrogen oxides have increased crop yield losses. Various agricultural management practices and techniques are being employed to reduce yield loss and minimize environmental impact on plants. Among these, the application of nanoparticles, such as nanofertilizers, nanoinsecticides, nanofungicides, and nanosensors, has emerged as a promising approach for achieving agricultural sustainability, particularly in pest and soil nutrient management. Therefore, the present study was conducted to assess the effectiveness of zinc oxide (ZnO) and titanium dioxide (TiO₂) nanoparticles on the chickpeas cultivar. Two sets of experiments were conducted: seed germination (Petri dishes) and a field experiment analyzing various physiological, morphological, and biomass parameters. In the seed germination experiment, TiO₂ nanoparticles were more effective than ZnO nanoparticles, achieving a 100% germination rate at 48 h. Furthermore, in the field experiment, the biomass of the selected cultivar was higher at a 50 parts/million (ppm) nanoparticle concentration compared to 25 ppm. Conclusively, the application of both nanoparticles showed a positive impact on seed germination and plant growth. The nanoparticles hold significant potential for future agricultural applications, offering innovative solutions for agricultural yield and environmental sustainability by enhancing nutrient delivery, soil health, and pest control. Therefore, this study will be helpful for farmers and scientists seeking to harness the potential of nanomaterials for sustainable agricultural production.

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Keywords: Zinc oxide; Titanium dioxide; Nanoparticles; *Cicer arietinum*; Seed germination; Plant growth; Biomass of plants

1. Introduction

Agricultural productivity is one of India's most complex topics, with both positive and negative aspects. The rising global population growth and simultaneous environmental challenges highlight the urgent need for innovative and sustainable solutions in agriculture to meet the growing demand for food worldwide.¹ Agricultural seeds

face susceptibility to environmental stressors, leading to compromised seed vigor, hindered crop growth, and reduced yield. While conventional seed treatments by agrochemical-based products improve seed germination, they also pose significant environmental risks.² Consequently, there is a pressing need for sustainable technologies, such as nano-based agrochemicals to address these challenges. Nano-agrochemicals offer the potential to mitigate the dose-dependent toxicity associated with seed treatments, thereby enhancing seed viability and ensuring the controlled release of active constituents. However, the excessive use of nano-agrochemicals raises authentic concerns regarding their safety, exposure levels, and impacts on the environment and human health.^{3,4} Consequently, there is a critical need for comprehensive assessments and policy regulations to evaluate and manage these risks.

Agricultural production plays a key role in the economies of developing nations, serving as the primary provider of food for a rapidly expanding population globally, which currently exceeds 7.5 billion people.^{5,6} Seeds constitute a fundamental input for sustainable agricultural productivity, and approximately 90% of crops are grown from seeds. High-quality seeds are essential for generating vigorous seedlings, thereby contributing to effective agricultural practices.⁷ However, agriculture faces multifaceted environmental challenges, such as salinity, drought, and heavy metals in soil, along with the impacts of climate change. These factors can detrimentally affect seed germination, sprout growth, and, ultimately, crop yield. Moreover, seeds are susceptible to damage from seed-borne diseases and pests, leading to irregular seed latency, reduced viability, and impaired water absorption, all of which negatively impact crop and final yield.⁸

In terms of agricultural innovation, nanotechnology is a promising new area that offers long-term solutions to the urgent problems affecting global food security. Through the utilization of nanoparticles' unique features, such as their heightened reactivity and surface area, nano-based agrochemicals and seed priming methods hold the potential to transform seed treatments, augment crop yields, and guarantee the enduring viability of farming methods. However, it is essential to proceed with caution and conduct comprehensive assessments to mitigate potential risks to the environment and human health, ensuring that nanotechnology is harnessed responsibly for the benefit of society as a whole. Nanotechnology emerged as a promising field in agriculture, offering innovative solutions to enhance crop productivity and stress tolerance.^{4,9} To guarantee sufficient crop establishment and the effective use of production resources in profitable

agriculture, fast and identical seed germination is crucial. Nano-enabled seed treatment has gained considerable attention due to its potential to increase germination and overall plant growth.

The integration of nanotechnology in agriculture has led to a new period of revolution, contributing promising solutions to increase crop yield and sustainability. Among the myriad applications of nanotechnology in agriculture, nano-enabled seed treatments have garnered significant consideration for their potential to revolutionize conventional seed germination practices and seedling vigor indices. This research delves into recent advancements in nano-enabled seed treatments and their profound impact on the germination, seedling vigor, and growth physiology of chickpeas (*Cicer arietinum* L.) cultivars. As a staple crop rich in protein and essential nutrients, chickpeas play an important role in food security worldwide. Therefore, understanding the effects of nanoparticles, specifically titanium dioxide (TiO₂) and zinc oxide (ZnO), on seed germination and seedling growth is key for improving chickpea cultivation practices. This study examines the comparative effectiveness of TiO₂ and ZnO nanoparticles on seed germination rates and vigorous indices, elucidating their respective roles in promoting robust seedling growth and overall plant biomass. By elucidating the biochemical mechanisms underlying the observed effects, including antioxidant enzyme activity, chlorophyll content, and nutrient uptake, this research contributes valuable insights to the burgeoning field of nanotechnology-enabled agriculture. Through comprehensive investigation and analyses, this study aims to inform sustainable agricultural practices and pave the way for informed decision-making in crop management strategies.

To ensure sufficient crop establishment and the effective use of production resources in profitable agriculture, fast and uniform seed germination is crucial. Many crop species have semi-permeable coatings in their seed coats that limit solute leakage while facilitating gas exchange and water absorption. The dense layer of aniline blue staining on the seed coats may have an impact on water permeability and, in turn, seed germination. With varied degrees of effectiveness, treatments, such as scarification, nicking, and removal of the seed coat have been studied to improve the permeability of the seed coat to water and oxygen, hence improving seed germination and vigor of the seedlings. However, triploid seeds still have less seedling vigor than diploid seeds. Thus, new seed priming methods are required to increase seed germination and seedling vigor.

Therefore, the present study was conducted to understand the mechanisms of ZnO and TiO₂ nanoparticles

on seed germination and plant growth development. Factors such as nanoparticle concentration, size, and shape play vital roles in determining their bio-effectiveness on plants. Therefore, this study offers a low-cost treatment approach that may enhance seed germination and support sustainable agriculture.

2. Materials and methods

2.1. Experimental design

Two experiments were conducted: (i) seed germination and (ii) a field experiment analyzing plant growth and physiology. Both experiments were conducted in triplicates. The germination experiment was conducted using 150 mm glass Petri dishes (Sidhi Trading Co., India) with a completely randomized design. Each Petri dish contains 30 uniform seeds of chickpeas (*C. arietinum* L.) treated with tap water (T1), 25 parts per million (ppm) TiO₂ (T2), 50 ppm TiO₂ (T3), 25 ppm ZnO (T4), and 50 ppm ZnO (T5), in room temperature. A total of 30 seeds were placed in dishes that were lined with cotton and watered. For the field experiment, the same treatments were applied in 1 m² plots.

2.2. Seed and nanoparticle selection

The local variety (Swetha [ICCV2]) of chickpeas (*C. arietinum* L.) was selected for seed treatment using ZnO and TiO₂ nanoparticles.

2.3. Seed germination

The germination experiment was conducted at room temperature. It was continuously monitored until the radicle length touched half of the seed length. Seed germination was assessed. The germination characteristics were measured in triplicate using the following formula in Equation I.¹⁰

$$GP = (NS \div TNS) \times 100 \quad (I)$$

Where GP refers to germination percentage, NS is the number of germinated seeds, and TNS is the total number of seeds sown.

2.4. Plant analysis

Plants were harvested 10 and 20 days after germination (DAG) and transferred to the lab for growth measurement and physiological analysis.¹¹

2.5. Growth and biomass analysis

Plant lengths (cm/plant) were measured using a meter scale (Jlab, India). The graphical method was used for measuring the leaf area of plants (cm²). The dry masses of plants were weighed after hot air oven drying at 80°C.^{11,12}

2.6. Biochemical analysis

2.6.1. Total chlorophyll and carotenoid content

Photosynthetic pigments were measured using a 100 mg leaf sample mixed with 10 mL of 80% acetone (v/v) solution. The solution's optical density was measured at 663 nm and 645 nm using the formulas described by Maclachlan and Zalik¹³ and Yentsh and Duxbury.¹⁴

2.6.2. Ascorbic acid estimation

The concentration of ascorbic acid was determined based on its ability to reduce 2, 6-dichlorophenolindophenol. A 500 mg fresh leaf sample was homogenized in 20 mL of extraction solution (containing 5 g of oxalic acid and 0.075 g of EDTA in 100 mL of distilled water) and centrifuged for 15 min at 12,000× g. From the resulting supernatant, 1 mL was mixed with 5 mL of 2, 6-dichlorophenolindophenol solution. The absorbance of the resulting pink solution (Es) was measured at 520 nm. Subsequently, in the same solution, one drop of ascorbic acid solution was added, and the absorbance (Et) was measured at the same wavelength. For the blank (Eo), 1 mL of ascorbic acid solution was used in place of the sample.¹⁵ Ascorbic acid concentration was calculated using the following formula in Equation II:

$$\text{Ascorbic acid (mg/g fresh leaf)} = \frac{\{E_o - (E_s - E_t)\} \times V}{(v \times W \times 1,000)} \quad (II)$$

2.7. Statistical analysis

The experiment was conducted with fully randomized block designs. The statistical package for the social sciences (SPSS) (SPSS Inc., version 17.0) software was used for Duncan's Multiple Range Test analysis. The least significant differences were estimated at the $p > 0.05$ level among treatments. The mean values of each parameter were given in triplicate of samples and the mean and standard deviation were calculated using Microsoft Excel (2013).

3. Results and discussion

3.1. Nanoparticle effectiveness on seed germination and vigor indices

Germination and quality of seed have a direct impact on agricultural production, with high-quality seeds making a substantial contribution to total crop yields. The Indian seed industry is essential for giving farmers access to high-quality seeds, fostering research and development, and providing a wide range of product options. Therefore, the experiment for seed germination improvements will be beneficial for crop production. In the present study, two types of nanoparticles were used to enhance seed germination. It was found that both TiO₂ and ZnO nanoparticles improved seed germination. The

vigorous index is as follows: 50 ppm TiO₂ >50 ppm ZnO >25 ppm TiO₂ >25 ppm ZnO > control (Figure 1). ZnO nanoparticles showed improved germination rates and increased seedling vigor. TiO₂ nanoparticles stimulated seed germination and promoted healthy seedling growth. TiO₂ particularly enhanced root and shoot growth, contributing to overall plant biomass. TiO₂ demonstrated a higher effectiveness in seed germination compared to ZnO nanoparticles, reaching a 100% germination rate at 48 h. Nanoparticle treatment, specifically with ZnO and TiO₂, positively impacted seed germination in chickpeas cultivars compared to untreated seeds. The germination rate – defined as the percentage of seeds that successfully sprouted – increased in nanoparticle-treated seeds.^{4,16} Nanoparticle-treated seeds exhibited faster and more uniform germination compared to untreated seeds. The improvement in seed germination indicates that nanoparticle treatment enhanced the physiological processes necessary for seedling emergence and establishment.¹⁷ According to a study, nanoparticles can improve water absorption, nutritional uptake, and stress

tolerance, which in turn can improve seed germination and seedling growth. This method is known as “nanoprimering.” It is a method that involves applying nanoparticles to induce various physiological and biochemical changes that promote faster and more reliable germination.

3.2. Nanoparticle effectiveness on plant growth and development

3.2.1. Root length

Nanoparticles can have both positive and negative effects on plant morphological characteristics depending on the type of nanoparticle, concentration, and plant species. In certain instances, higher concentrations of nanoparticles can cause inhibition and even toxicity, but lower quantities can promote plant growth. Variations in root and shoot length, seed germination, and total biomass are examples of morphological changes that can be induced by nanoparticles.¹⁸ In the present study, nanoparticle-treated plants showed an increase in root length compared to control plants. Both ZnO and TiO₂ nanoparticles likely stimulated root growth, resulting in longer and more

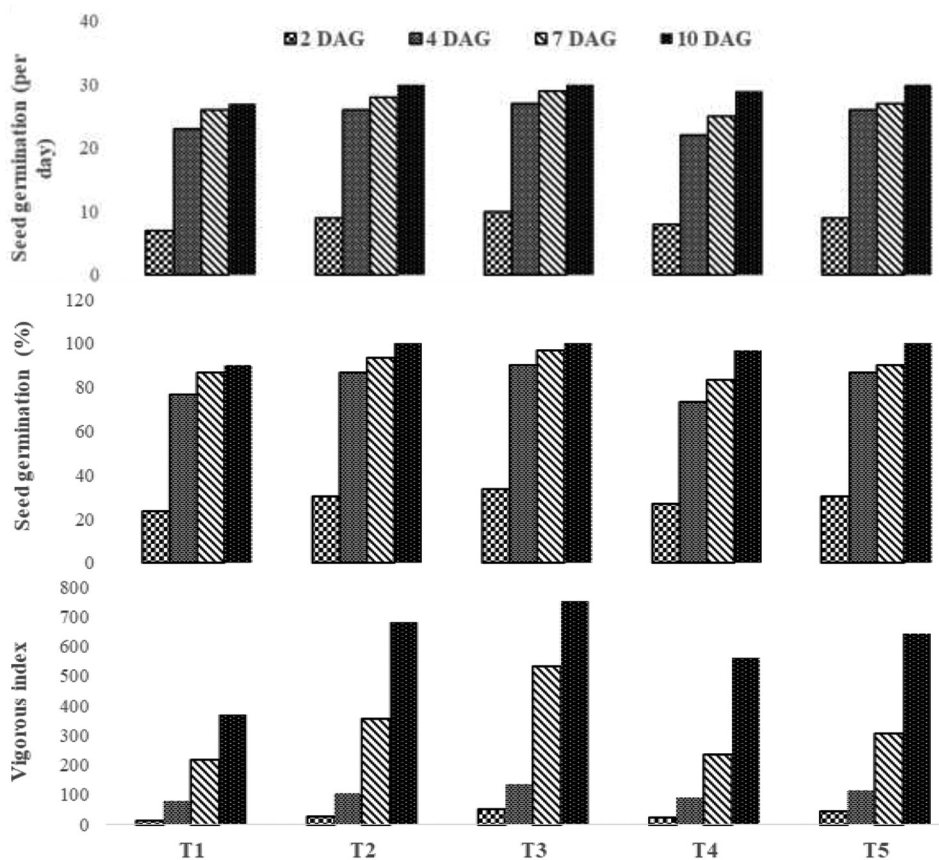


Figure 1. Effectiveness of zinc oxide (ZnO) and titanium dioxide (TiO₂) nanoparticles on seed germination and vigor index of selected *Cicer arietinum* seeds. T1 is the control, T2 is 25 parts/million (ppm) TiO₂, T3 is 50 ppm TiO₂, T4 is 25 ppm ZnO, and T5 is 50 ppm ZnO. Abbreviation: DAG: Days after germination.

extensive root systems. Longer root length is beneficial for nutrient uptake and water absorption, ultimately contributing to improved plant health and productivity. The 50 ppm TiO₂ showed the highest growth, followed by 50 ppm ZnO, 25 ppm TiO₂, 25 ppm ZnO, and control (Figure 2).

Shoot length, which refers to the length of the above-ground parts of the plant, also increased in the nanoparticle-treated cultivar. Enhanced shoot length indicates increased vegetative growth and biomass accumulation. The promotion of shoot growth by nanoparticle treatment suggests improved photosynthetic capacity and overall plant health. In this study, the shoot length followed the same trends as the root length of the cultivar. The 50 ppm

TiO₂ showed the highest shoot growth, followed by 50 ppm ZnO, 25 ppm TiO₂, 25 ppm ZnO, and control (Figure 2).

Total plant height was determined by summing root and shoot lengths. A significant increase in total height was observed with the exogenous application of ZnO and TiO₂. The increase in total height suggests that nanoparticle treatment promoted overall plant growth and development.⁹ Among the treatments, 50 ppm TiO₂ resulted in the greatest plant height, followed by 50 ppm ZnO, 25 ppm TiO₂, 25 ppm ZnO, and control (Figure 2). This result indicates a dose-dependent effect on selected cultivars. Nanotechnology represents a promising green approach for improving agricultural yield and soil fertility by activating nutrient availability and energy metabolism

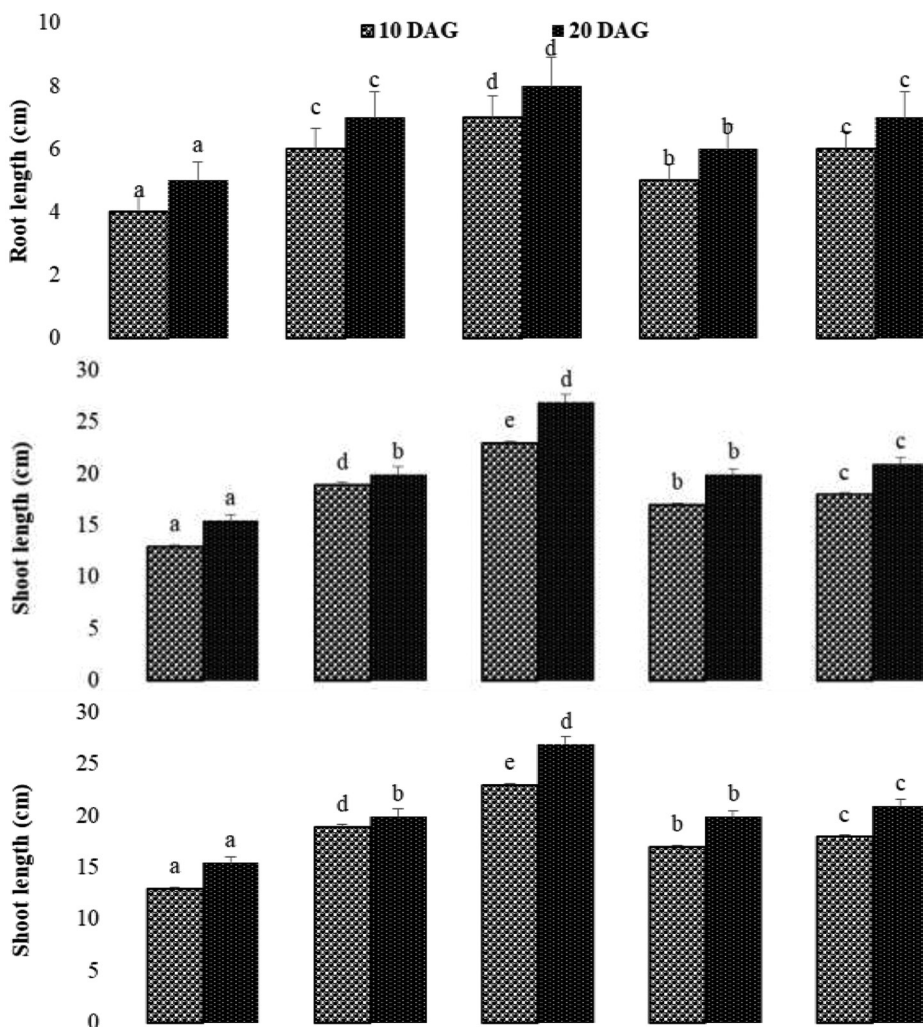


Figure 2. Effectiveness of zinc oxide (ZnO) and titanium dioxide (TiO₂) nanoparticles on root length, shoot length, and total plant height (cm) of *Cicer arietinum* cultivar. Mean ± standard deviation of three replicates is shown by thin vertical bars. T1 is the control, T2 is 25 parts/million (ppm) TiO₂, T3 is 50 ppm TiO₂, T4 is 25 ppm ZnO, and T5 is 50 ppm ZnO.

Note: Values within same letter are not significantly different $p < 0.05$, according to Duncan's multiple range test.

Abbreviation: DAG: Days after germination.

in plant cells. To increase crop yields, nanoparticles are often used as nanofertilizers, nanoinsecticides, and nanofungicides. Various nanoparticles, such as TiO₂, ZnO, silicon oxide, magnesium oxide, gold, and silver, are being used to improve soil fertility, manage nutrients, and boost crop yields.⁴

3.3. Nanoparticle effectiveness on biomass

Nanoparticles can improve plant growth through various processes, such as nutrient delivery, stress tolerance, and hormone regulation promotion. They can improve fruit quality and productivity by scavenging free radicals, enhancing nutrient uptake, and inducing stress response pathways.^{4,9} In the present study, biomass accumulation was higher in treatments with nanoparticle application, indicating their effectiveness as enhancers of plant growth pathways. TiO₂ nanoparticles showed significant efficacy in promoting biomass accumulation in chickpeas cultivars. The promotion of root and shoot heights by TiO₂ likely led to increased biomass production. ZnO nanoparticles also had a positive effect on biomass, although lower compared to TiO₂. T3-treated cultivars showed the highest biomass, followed by T2, T5, T4, and T1 (Figure 3). Nanoparticle-

treated *C. arietinum* L. cultivars exhibited higher fresh weight compared to untreated plants. The increase in fresh weight indicates greater water content and overall biomass accumulation in nanoparticle-treated plants. Enhanced fresh weight suggests improved growth and physiological activity in response to nanoparticle treatments.

Nanoparticle-treated chickpeas cultivars also showed an increase in dry weight compared to control plants. Dry weight represents the mass of the plant's tissues after removing water content, providing a measure of the plant's physical biomass. The increase in dry weight indicates enhanced accumulation of essential components such as cellulose, lignin, and proteins in nanoparticle-treated plants.¹⁹ The higher dry weight reflects improved biomass production and the potential for increased yield in nanoparticle-treated chickpeas cultivars. These changes indicate enhanced biomass accumulation, growth, and physiological activity in plants. Enhanced root and shoot growth contributed to increased biomass, suggesting the potential for improved plant yield. While both TiO₂ and ZnO nanoparticles showed positive effects on growth, TiO₂ appeared to be more effective in promoting

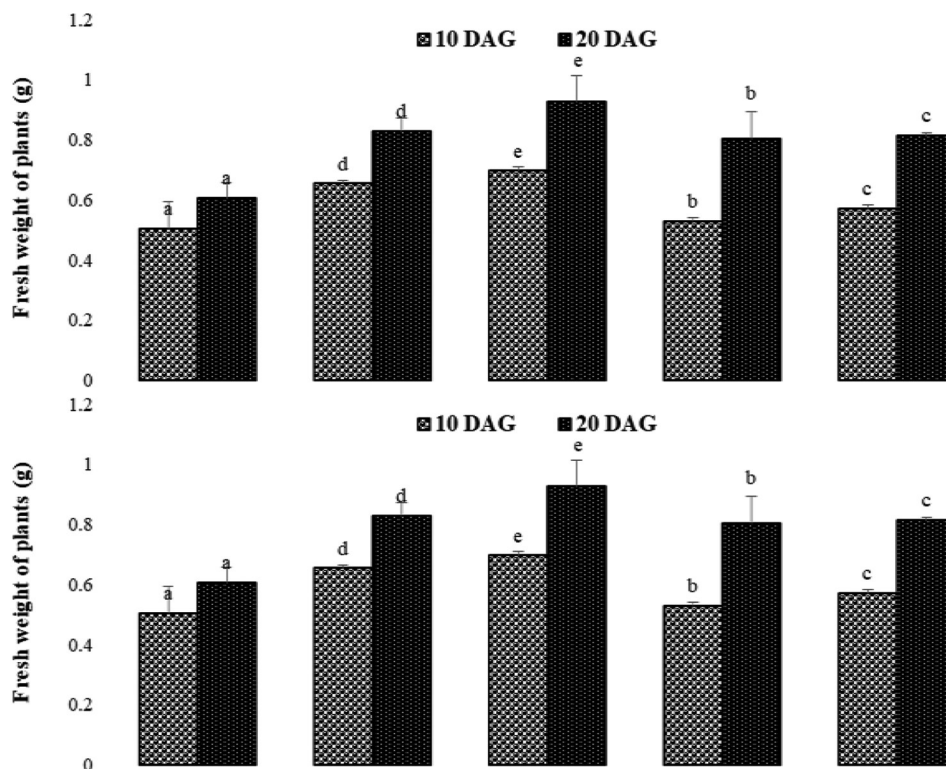


Figure 3. Effectiveness of zinc oxide (ZnO) and titanium dioxide (TiO₂) nanoparticles on fresh and dry biomass (g) of *Cicer arietinum* cultivar. Mean ± standard deviation of three replicates is shown by thin vertical bars. T1 is the control, T2 is 25 parts/million (ppm) TiO₂, T3 is 50 ppm TiO₂, T4 is 25 ppm ZnO, and T5 is 50 ppm ZnO.

Note: Values within same letter are not significantly different $p < 0.05$, according to Duncan's multiple range test.

Abbreviation: DAG: Days after germination.

biomass accumulation, suggesting its potential as a seed treatment to enhance crop productivity. The application of nanoparticles, especially TiO₂, holds promise for improving the growth and biomass production of chickpeas cultivars, which could have significant implications for agricultural productivity and sustainability.

3.4. Biochemical changes

3.4.1. Chlorophyll a, b, and total chlorophyll

Chlorophyll pigments play an important role in photosynthesis in plants, algae, and cyanobacteria. It is essential for turning light energy into chemical energy, which enables plants to make oxygen and glucose. Photosynthesis and life on Earth would not be possible without chlorophyll. Therefore, analyzing chlorophyll pigments in plants can provide valuable insights into the plant's physiology. In this study, the applied nanoparticles, ZnO and TiO₂, increased the chlorophyll content in chickpeas cultivars (Figure 4). ZnO nanoparticles enhanced chlorophyll synthesis, leading to increased chlorophyll a and b content.²⁰ Similarly, TiO₂ nanoparticles stimulated chlorophyll biosynthesis pathways, resulting in higher levels of chlorophyll a and b. The total chlorophyll content, representing the sum of chlorophyll a and b, showed a significant increase when plants were treated with nanoparticles. Higher chlorophyll content suggests improved photosynthetic capacity and light absorption, which can positively influence plant growth and biomass accumulation.^{4,11}

In the present study, higher chlorophyll contents were seen in the 50 ppm TiO₂-treated cultivars, while ZnO-treated cultivars showed the least increment of chlorophyll content compared to the control. Chlorophyll a, b, and total chlorophyll content increased with plant age, with higher levels observed at 20 DAG than at 10 DAG across all treatments (Figure 4). The application of selected nanoparticles positively impacted chlorophyll pigment levels. The findings suggest that the enhanced chlorophyll pigment in plants, resulting from nanoparticle treatment, improved overall plant growth. Plant chlorophyll may be complexly affected by nanoparticles, increasing or decreasing its content and affecting photosynthesis. By boosting ribulose-1,5-bisphosphate carboxylase/oxygenase activity and photosystem II efficiency, certain nanoparticles, such as TiO₂ and mesoporous silica, can promote photosynthesis and raise chlorophyll content. Other nanoparticles, including superparamagnetic iron nanoparticles, can have a detrimental effect on the amount of chlorophyll and the effectiveness of photosystem II, which could result in less photosynthesis. The type of nanoparticle, its size, concentration, and the type of plant

influence the effects of nanoparticles on chlorophyll content.²¹

3.4.2. Carotenoids

Carotenoids play a crucial role in photoprotection and light harvesting during photosynthesis.^{12,22} Increased carotenoid content indicates enhanced photoprotection against excess light and oxidative stress, which can contribute to improved plant resilience and productivity. Carotenoids facilitate chlorophyll in absorbing light energy and offer photoprotection by releasing excess energy as heat. In addition, they aid in the scavenging of reactive oxygen species (ROS), protecting the plant from oxidative damage caused by stressors, such as temperature. In the present study, the highest carotenoid content was noted in T3, followed by T5, compared to the control. Carotenoid content increased with plant age, with higher levels observed at 20 DAG compared to 10 DAG across all treatments (Figure 4). Generally, the application of nanoparticles enhances carotenoid production in plant cells and helps improve plant health. However, understanding the role of different nanoparticles and their mechanisms in plant cell environments will be a helpful tool for future research.

3.4.3. Ascorbic acid

Ascorbic acid is a water-soluble antioxidant that scavenges ROS and protects cells from oxidative damage.¹¹ The present study demonstrates elevated levels of ascorbic acid in nanoparticle-treated chickpeas cultivar, indicating enhanced antioxidant defense mechanisms. Ascorbic acid helps to neutralize ROS generated during stress conditions, such as high light intensity or drought, thereby protecting cellular structures and maintaining physiological functions.²³ The presence of increased levels of ascorbic acid contributes to improved stress tolerance and overall plant health in nanoparticle-treated chickpeas cultivars. It scavenges ROS and protects cellular components from damage, thereby maintaining cell integrity and function. Elevated levels of ascorbic acid indicate improved antioxidant defense mechanisms in the plant, which can enhance stress tolerance and overall plant health. In the present study, ZnO and TiO₂ nanoparticle treatments enhance photosynthetic pigments (chlorophyll a, b, and carotenoids) and antioxidant compounds (ascorbic acid). These changes collectively contribute to improved photosynthetic efficiency, photoprotection, and stress tolerance, ultimately leading to enhanced growth and biomass production in selected cultivars. Consistently, the highest ascorbic acid was noted in 50 ppm TiO₂ (3.95 mg/g fresh leaf) treatment, while 25 ppm ZnO (2.45 mg/g fresh leaf)

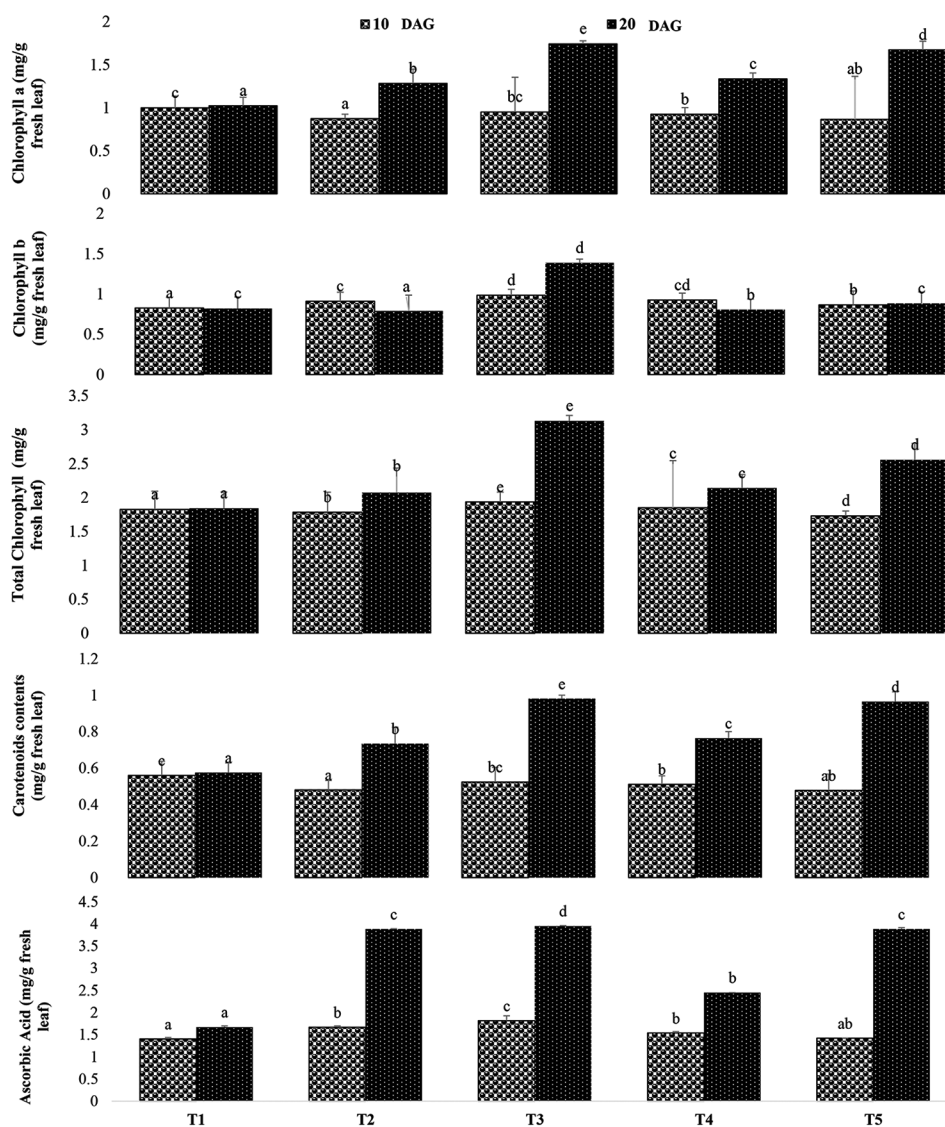


Figure 4. Effectiveness of zinc oxide (ZnO) and titanium dioxide (TiO₂) nanoparticles on chlorophyll a, b, and total chlorophyll, carotenoids, and ascorbic acid contents (mg/g fresh leaf) of *Cicer arietinum L.* cultivars. Mean± standard deviation of three replicates is shown by thin vertical bars. T1 is the control, T2 is 25 parts per million (ppm) TiO₂, T3 is 50 ppm TiO₂, T4 is 25 ppm ZnO, and T5 is 50 ppm ZnO.

Note: Values within same letter are not significantly different $p < 0.05$, according to Duncan's multiple range test.

Abbreviation: DAG: Days after germination.

showed the least value of ascorbic acid content compared to the control (Figure 4). As plants matured, their physiological processes progressed, resulting in higher ascorbic acid content at 20 DAG compared to 10 DAG.

4. Conclusion

The global rising population and environmental stresses are contributing to agricultural losses and food crises. At present, environmental stresses and their mitigations are the main research objectives in the agriculture sector. Nanotechnology emerges as one of the best tools for

agricultural sustainability. It improves crop protection, nutrient transport, and soil management, forming the basis of plant growth and yield production strategies. Therefore, the present study was conducted to assess the effectiveness of ZnO and TiO₂ nanoparticles on the germination and growth of chickpeas. The result of the study showed that TiO₂ is more effective in promoting seed germination than ZnO nanoparticles. Both nanoparticles showed positive effects on the growth and biomass of the plants, with 50 ppm treatments stimulating greater root elongation, shoot growth, and biomass than 25 ppm.

In conclusion, TiO₂ proved more effective than ZnO nanoparticles for seed germination, while both nanoparticles showed dose-dependent results for the growth and biomass of plants. This study aimed to evaluate the mechanisms and efficacy of nanoparticles in promoting seed germination. The findings suggest that nanotechnology could be a useful tool for sustainable agriculture, ultimately helping to reduce the global food crisis. In addition, the study concluded that field research is necessary to have a more comprehensive understanding of the impacts of nanoparticles on the growth, development, and health of agricultural plants.

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Conflict of interest

The authors declare that they have no competing interests.

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Methodology: Anuradha Navnath Karale, Indra Jeet Chaudhary

Writing – original draft: All authors

Writing – review & editing: All authors

Ethics approval and consent to participate

Not applicable.

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Availability of data

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ORIGINAL RESEARCH ARTICLE

The development of the river chief in Nantong and Huzhou: Policy transfer in an authoritarian system

David P. Dolowitz^{1*}  and Ye Xiong² ¹Department of Politics, Faculty of Humanities and Social Sciences, University of Liverpool, Liverpool, United Kingdom²Department of Public Administration, Institute of Environment and Health, Nanjing University of Information Science and Technology, Nanjing, Jiangsu, China**Abstract**

The river chief system is an institutional innovation designed to mitigate the fragmentation of watershed governance in China. The idea was to develop offices of river chiefs and designate named individuals as responsible for water quality across all regions and levels of government. This article examines the mechanisms that led to the transfer of the river chief model from Wuxi to the Jiangsu Provincial government, Nantong, and Huzhou. The objective is to examine how and why Nantong officials created a virtual replica of the Jiangsu provincial policy, while Huzhou officials transformed the original Wuxi model to form their unique river chief. To do this, we undertook an extensive review of the core documents related to the river chief systems in Nantong and Huzhou, which led to a series of interviews, confirming our understanding of the procedures and outcomes of the transfer process. The result demonstrated the importance of motivation, structural context, and the ability to engage in re-engineering in policy transfer to understand the outcomes of the transfer process. As such, this study demonstrates, unlike much of the existing literature, that these aspects are worth further study when investigating the policy transfer process.

Keywords: River chief; Policy transfer; Learning; China***Corresponding author:**David P. Dolowitz
(dolowitz@liv.ac.uk)**Citation:** Dolowitz DP, Xiong Y. The development of the river chief in Nantong and Huzhou: Policy transfer in an authoritarian system. *Explora Environ Resour.* 2025;2(3):025110018.
doi: 10.36922/EER025110018**Received:** March 11, 2025**1st revised:** April 25, 2025**2nd revised:** May 5, 2025**Accepted:** May 15, 2025**Published online:** July 21, 2025**Copyright:** © 2025 Author(s). This is an Open-Access article distributed under the terms of the Creative Commons Attribution License, permitting distribution, and reproduction in any medium, provided the original work is properly cited.**Publisher's Note:** AccScience Publishing remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.**1. Introduction**

After the open door policy was launched in the late 1970s and 1980s, the Chinese central government and Chinese Communist Party (CCP) began shifting decision-making powers to lower-level governing divisions. Initially, this focused on reducing restrictions on lower-level governments' ability to engage in (or encourage) private market activities (including the launch of special enterprise zones). Based on the success and progress of these initial reforms, the party and government began to introduce policies designed to decentralize elements of environmental policymaking and implementation (particularly after the 18th and 19th national congresses of the CCP). As a result, when a cyanobacteria outbreak occurred in Lake Taihu, the Jiangsu Provincial authority authorized a pilot project that led to the first river chief system designed to address the outbreak without turning to central authorities.¹

By loosening policymaking restrictions at lower levels of government, the Chinese central government and party created “policy laborites”² that helped launch the internal policy transfer processes – phenomena that have occurred in the United States since its founding.³ As local governments engaged in policy experimentation (under an environment of intense competition to be seen as leading or advanced), the same issues that have been discussed in the policy transfer literature emerged across China, including problems associated with the transfer of what is often discussed as “best practice” models.⁴⁻¹⁶ To illustrate this, we will draw on the movement of the river chief from Wuxi to the Jiangsu Provincial government, Nantong, and Huzhou, focusing on the role of structural and individual motivations in shaping the outcomes of the transfer process.

In 2007, a cyanobacteria outbreak on Taihu Lake threatened Wuxi’s drinking water. In response, Jiangsu province issued the Wuxi City river section water quality control objectives and assessment methods policy (on a trial basis). The core idea was to allow Wuxi to establish a river chief system that held the named party and government officials accountable for water quality management and restoration. In addition to holding named individuals accountable for water quality (based on the level of core pollutants in the water), the trial instituted the office of the river chief to better coordinate the range of departments and subunits involved in water management. The problem created by having over 10 different departments and subunits involved in water management was the confusion of responsibility for overall water quality and the development of numerous approaches and policies governing the same body of water. Furthermore, having multiple agencies responsible for water led to a lack of bureaucratic and individual accountability in water management. To give a flavor of this issue, we note that the core departments involved in water management include (but are not limited to) the Water Conservancy Department, the Environmental Protection Bureau, the Bureau of Housing and Urban–Rural Development, the Development and Reform Bureau, the Department of Natural Resources, the Health Bureau, the Bureau of Agriculture and Rural Affairs, and even the Economy and Trade Bureau. This complex arrangement led to a situation where:

[T]he local water pollution control is not effective, though the local governors are accountable for this, they would shirk part of their responsibility toward the departments in the vertical line. Therefore, local governors are not motivated to take responsibility for water pollution control.^{17(p1)}

The issue becomes even more significant when it is realized that most rivers in China flow across different administrative areas. This created a situation where local governments and agencies found themselves in conflict when pollution events occurred, particularly when upstream pollution impacted downstream jurisdictions and when left and right banks fell under different administrative jurisdictions.¹⁷

To address these (and other) issues, Wuxi established river chiefs at the municipal and county levels to monitor and take direct responsibility for 79 river sections in the area. Based on Wuxi’s success in cleaning river pollution and bringing accountability to the water management system, other municipalities began their experiments with river chiefs.¹⁸ As information on the river chief system filtered up to provincial governments and eventually the central government (and the party apparatus), a decision was taken to implement the river chief nationwide between 2016 and 2018.

The problem we will examine in the remainder of this article is that the best practice developed in Wuxi turned out to be the best for only a few places outside of Wuxi.¹⁹⁻²² Part of the reason for the disjuncture is due to the need for learning in the transfer process and the complexity of the processes needed to engage in hard learning versus soft learning.^{15,23,24} This comes to the forefront when it is realized that transferred information tends to move through a range of networks, agents, and institutions during the transfer and adaptation processes.²⁵⁻³⁴

While discussions of how policies are translated (transformed) during the transfer process have added to the transfer literature, in general, these discussions fit into the original continuum offered by Dolowitz and Marsh⁵ relating to what happens to a policy as it transfers and enters its new setting. Specifically, Dolowitz and Marsh⁷ argue that transfer can fall along a continuum running from a perfect copy of the original model to being translated to such an extent that a new policy is little more than a hybrid of many different policies drawn from a range of actors and settings. As such, we will be utilizing a slightly modified version of the continuum originally offered by Dolowitz and Marsh⁵ (Figure 1) to analyze the transfer of the Wuxi river chief system.

At its base, a transfer is possible because policymakers face similar issues and challenges despite differences between systems and settings. When faced with similar issues, transfer is an attractive option because it allows for a degree of certainty and speed in developing a solution. After all, policymakers can see what has already been done to address the issue.³⁵

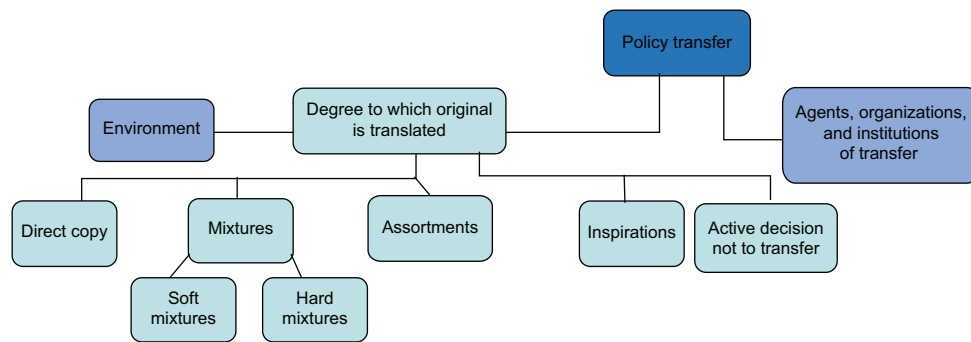


Figure 1. The transformative process of policy transfer

As shown in Figure 1, the transfer process can follow several trajectories:

- (i) Direct copy: Tends to involve little to no transformation.
- (ii) Mixtures: Tend to look much like the original but involve a greater or lesser degree of transformation during the transfer and implementation processes.
- (iii) Assortments: Tend to involve a wide network of agents and institutions that make considerable transformations of the original model (or models) during the transfer, development, and implementation processes.
- (iv) Inspiration: Involve ideational transfer but little actual policy movement, can involve a single entrepreneur or a wide number of network agents.
- (v) Non-transfer: Occurs when agents involved in the transfer process actively learn and decide that they do not want to do what others have done, regardless of the translation process involved in the decision.

In China, the attraction of turning to others for information and ideas has increased over the past 20 years, as subnational governments have engaged in a semi-encouraged competition to be seen by higher-level administrators and governing authorities as policy innovators and economic magnets for private sector investment and state-owned enterprises.¹

While transfer tends to be linked to success within the literature, we will demonstrate that despite the initial success of the Wuxi model as it entered new locations, it did not prove to be as effective even when the transfer occurred between municipalities facing similar issues were part of a single province and emerged as a virtual copy of the original model.³⁶

Part of the reason for this (despite the hierarchical nature of authoritarian systems) relates to factors that

shape actors' perceptions and motivations in the transfer process, including pre-existing structures, policies, mental maps,³⁷ values³⁸ socio-political moods, and the institutional "life spaces" agents of transfer inhabited.³⁹ As a result, transfer and learning tend to be conditioned by discursive paradigms, ideational circuits, institutional frameworks, and power structures surrounding the agents involved in the movement and implementation of transferred ideas and policies, regardless of the political system in which they operate.

Due to these internal motivational and external structural factors, transferring policy, especially when a copy is taken by a jurisdiction operating under the same authority, is not as straightforward as often presented in the transfer literature. Rather, successful transfer often involves adaptation and change, based on internal and collective needs that influence how the agents involved perceive their roles and the role of the transferred policy.

In other words, the motivations of the transfer agents and where they fit into the power relations of the policymaking system shape the outcomes of the transfer. This is true regardless of whether the transfer results in a close copy of the original model or an assortment that combines many different models (Figure 1). As a result, even when agents are predisposed to copying a model, there is no guarantee that it will work as it did in the originating system. This is particularly true when agents are inclined to see similarity where it does not exist or, as in the case of Nantong, engage in copying to gain legitimacy (particularly where promotion is based on higher-level government and agency) rather than a desire to improve the situation.

Similarly, contextual factors shape motivations and abilities, which can lead to unexpected outcomes that, despite the transfer literature's focus on success, offer little guarantee of success. This study demonstrates that contextual factors are often more important in shaping the outcomes of transfer than the policy that is ultimately developed in response to the transfer.⁴⁰

¹ While not the focus of this article, the globalization of information and spread of information technology have made accessing information related to policy ideas and little more than a mouse click away, even if it's poor, misleading, and false.

2. Methods and data

This study is designed around a traditional small-n case study,⁴¹ which takes the transfer of the river chief system from Wuxi as an example of how different motivational factors and structural constraints impact the transfer process and outcomes. Specifically, we selected two representative prefecture-level cities to observe how they transfer the river chief model. The idea was to investigate the effect of modifying a model on the outcomes in the transferring jurisdiction. We selected Nantong because it lies in Jiangsu Province, which was the home of Wuxi, thus reducing the environmental differences discussed above. Besides, the transfer occurred after the higher-level provincial government introduced a requirement that all municipalities produce river chiefs. This requirement not only provided an incentive for engaging in the transfer process, but also set a base model for the jurisdictions that had not already developed their river chief systems in the province.

Our second case, Huzhou, was selected as a comparison case as it fell under the jurisdiction of Zhejiang Province. This provided a different setting and underlying structural factors from those that embedded actors in Nantong. In addition, unlike Nantong, Huzhou transferred the river chief system without being subjected to a requirement from the Zhejiang Provincial authorities. This allowed Huzhou a degree of freedom in transferring and developing its river chief system that is unavailable to policymakers in Nantong. We argue that this structural difference (when combined with other motivational factors) led to a much more dynamic river chief policy based on a mixture of what others had done but modified to better fit their context and needs.

As Table 1 illustrates, this study utilized numerous methods to collect data from a range of sources. The core data used in this study consisted of official government documents associated with the introduction of the river

chief that were issued by all levels of the administrative hierarchy associated with Wuxi, Nantong, and Huzhou. The documents included among others: policy texts, legislative releases, manuals, and the One River and One Policy plan.^{41,42} To support this data, we also examined official government work reports associated with the implementation of the two river chief systems and performance evaluation reports of river and lake management and protection in the two regions.

In addition, we consulted a range of secondary documents extending from official press releases-relevant articles and news stories (both in Chinese and English) to organizational reports issued by international organizations (such as the World Wide Fund for Nature) and international governing organizations (such as the World Bank and the International Monetary Fund).

To gather this data, we utilized open websites found through DuckDuckGo and Google searches, internal ministerial and government search engines, institutional databases (Web of Science), and archival research within relevant ministries and departments. To prevent being overly influenced by the tendency to promote political performance in official reports, we also collected social media reports and interviews to strengthen our research findings. Finally, based on 40,000 words (in Chinese) of case material, the qualitative data analysis software NVivo 10.0 (Lumivero, USA) was used for coding and recording the text.

With the support of the National Social Science Fund of China, we also conducted a series of field investigations in Nantong and Huzhou between October and November 2019. These consisted of 26 semi-structured interviews with the staff of the river chief's office in the two municipalities. These interviews were semi-structured and based on the following questions:

- (i) Did you engage in any type of policy transfer when developing your river chief system?
- (ii) If you engaged in policy transfer, can you explain why?

Table 1. Data sources and classifications

Data sources	Data classification	Number of documents
Primary data	Transcripts of semi-structured interviews (in Chinese)	26
	On-site recordings of the debriefing sessions (in Chinese)	3
	Author's investigation diary (in Chinese)	2
Secondary data	Policy documents (in Chinese and English)	10
	Internet search data: articles, NGO/IGO documents, social media coverage, and government website coverage (in Chinese and English)	200
	Internal materials of government departments (manuals, assessment documents, and research reports [in Chinese and English])	15

Abbreviations: IGO: Intergovernmental organization; NGO: Non-governmental organization.

- (iii) Are there any major differences between your river chief system policies and those of Wuxi City?
- (iv) Was there any policy learning in the process of developing your river chief?
- (v) What achievements have you made based on the transfer of your river chief system?
- (vi) Can you discuss any problems that have been identified in the operation of your river chief system?

In addition to these interviews, we also carried out several field visits to observe the river courses and water bodies in the municipalities under investigation, all of which were underpinned by observational logs. The combination of these sources helped assure the reliability of the data.

In summary, we utilized a “most different” case study methodology. To do this, we selected two municipalities that operated under different provincial governments, addressed different types of water structure needs, implemented their river chief system at different times, and acted under different hierarchical imperatives. By doing this, we were able to gather data for a policy transfer study that expanded beyond the singular qualitative models predominant in the literature, allowing a comparative study of different jurisdictions adopting the same base policy modeled on a single data source (Wuxi). This has allowed us to look at micro-level and meso-level factors impacting decisions related to transfer that are often overlooked by single case studies and large N quantitative studies.

3. Findings

3.1. Nantong: Transfer under pressure

As illustrated in Figure 2, the transfer of the river chief in the Nantong region is a typical example of transfer within hierarchies of governance where a higher authority absorbs a policy and subsequently promotes it back down to lower-level units.^{3,43} In the case of Jiangsu, according to our interviews, administrators were heavily influenced by the Wuxi model. However, interviews and documents also indicated that the resultant policy was not a direct copy. Rather, administrators looked at many of the models that had emerged in the province after the Wuxi model and

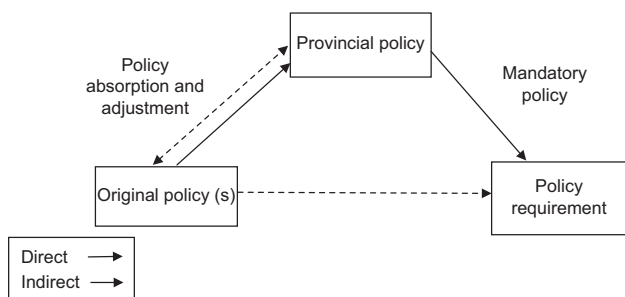


Figure 2. Policy transfer under vertical governance pressures

designed a soft mixture (Figure 1) when setting the policy that they expected lower-level governments to implement.

The Jiangsu documentation clarified the objectives, tasks, and schedule for reform. The instruction required the establishment of a river chief system in all counties, townships, village rivers, and ponds catchment areas across the province by 2015. In response, Nantong issued the Opinions on Strengthening the Work of the River Chief System of River Management in January 2014.⁴⁴ While the hierarchical pressure to comply with the directive cannot be dismissed, interviews indicated that Nantong chose to copy the Provincial model due to the local cadre’s desire “to obtain the legitimacy for the river chief system in the municipality” (X, interview, 13 September 2019).

Taking a step back, the document “Decision on Comprehensively Establishing the River Chief System and Comprehensively Strengthening the Comprehensive Improvement and Management of River Courses”⁴⁵ issued by the Wuxi Municipal Committee and the Wuxi Municipal People’s Government is the earliest official policy document related to the development of the river chief system in China. This document (and the policy contained within it) is the summary of the measures taken by Wuxi in the second half of 2007 to deal with the cyanobacteria crisis in Taihu Lake.

“Decision on Comprehensively Establishing the River Chief System” included 11 detailed policy tools covering 11 aspects of water management, including the organizational structure, appointment of river leaders, renovation planning, responsibility decomposition, work focus, law enforcement supervision, departmental division of labor, water quality monitoring, assessment and accountability, social participation, and institutional construction (“Water Quality Control Objectives and Assessment Measures for Rivers [Lakes, Reservoirs, Oscillation, and Tunnels] in Wuxi”).² The stated goal is “the complete renovation of rivers and lakes and the comprehensive improvement of the water environment.”⁴⁵

Moving back to the provincial level, Jiangsu released its river chief document in 2012.⁴⁶ This document modified the Wuxi documentation by adding a detailed explanation of the significance, guiding ideology, basic principles, and goals of the river chief system. However, the documentation also added a series of extra measures that were found in other river chief models. These were added by officials who hoped this would make Jiangsu a model province (X and Y, interviews, 14 September 2019) and, in turn, enhance the promotional prospects of Jiangsu officials. As a result,

² The annex details the list of work leadership groups and establishes an assessment indicator system.

the goal of the river chief system changed from a focus on improving water quality to a focus on the modernization of the entire river management system and river network construction across the province.

Intriguingly, while expanding the goal of the river chief beyond water quality, provincial leaders elected to simplify the choice of policy tools that had previously been used by Wuxi and other municipalities. Interviews indicated that they did this deliberately, knowing that municipal officials needed some room to maneuver once the policy was transferred back down, but “did not want to see a considerable expansion in the range of models being developed” (AAA, interview, 8 October 2019). We want to emphasize this aspect of the process because much of the literature associated with authoritarian systems overlooks how provincial leaders view their role as guides rather than dictators of the transfer process in China.

Comparing the policy texts of the river chief system in Nantong and Jiangsu Province, despite the somewhat vague nature of some elements in the Provincial documentation, Nantong chose to copy much of the language and core elements of documentation issued by Jiangsu. Specifically, we found that Nantong made only slight adjustments in the expression of the basic principles in their river chief documentation and did not change the basic spirit of provincial policies. Nantong followed the provincial policies in terms of the river chief’s guiding ideology, goals and tasks, organizational construction, and core measures. As such, from the perspective of transfer, Nantong’s river chief belongs closer to a copy than a mixture and falls well below the transformations needed to be considered an assortment of different policies when viewed from the perspective of Jiangsu Province (Figure 1).³

Significantly, this shows that when looking at transfer, it is important to consider the level of magnification being observed. When examined from the perspective of Jiangsu, Nantong appeared to have engaged in little change; however, when Nantong’s river chief is viewed from Wuxi, it appears to be more of a hard mixture because of the adjustments made by Jiangsu Provincial leadership and Nantong’s officials.

3.2. Huzhou: Assortment of policies

Huzhou issued its river chief documents, “Implementation Plan of Establishing the River Chief System in Huzhou, in 2013,”⁴⁷ and the “Implementation Opinions on Deepening

the River Chief System in 2014.”⁴⁸ Unlike Nantong, Huzhou is part of Zhejiang Province and waited until late 2017 to issue its provincial-level guidance (the “Zhejiang River Chief System Regulations”). As a result, Huzhou was able to choose how it was going to develop its river chief system without the guidance and coercive pressures of a superior governing authority.

This resulted in the development of a river chief system that involved a considerable amount of what is often discussed as hard learning, where Huzhou officials consulted a range of different river chief models. Consequently, we found that the transfer processes Huzhou undertook culminated in a system considerably more compatible with their structural and water quality needs than was the case in Nantong.

Importantly, we found that huzhou policymakers actively engaged in a hard learning process with the belief that they could discover how to embed core local party and government leaders in water management while designing a system that would be capable of holding core agents accountable for river basin governance as river chiefs (z, interview, 6 January 2020). As part of this, huzhou integrated three concepts (later transferred up to the provincial level). First, huzhou worked to develop and refine specific water control targets. To do this, huzhou put forward “three clean and three improve” goals that the river chiefs could be held accountable for achieving. These were themselves grouped into categories that specified that: the riverbank is clean, the river is smooth and clean, the water quality of the river course is significantly improved, riverbank greening is significantly improved, and the pollution intercepting capacity is significantly improved. The alterations made to these goals are important because they show that learning and adaptation occurred in the transfer process.

Second, in Huzhou, the responsibilities of river chiefs at different levels of government are explicitly established. The river chief documentation creates three core responsibilities for the municipal river chief as being: (i) the examination and approval of the work program, (ii) work promotion and coordination, and (iii) the assessment of county-level river chiefs. Implementation further defines five responsibilities for county-level river chiefs: (i) formulating and organizing the implementation of comprehensive water environment treatment plans and annual plans for river chiefs, (ii) enhancing information disclosure, (iii) organizing the supervision and assessment of township river chiefs, (iv) reporting the annual plan and summary, and (v) ensuring the delivery of key projects and works progress on time.⁴⁷⁻⁴⁹

Third, as a result of learning about its internal structural problems and how other jurisdictions dealt with the

³ This is not a surprising finding. Nantong is under the administrative control of Jiangsu. As a result of China’s hierarchical governing structure, policy outcomes tend to be closer to copies when higher-level governing authorities issue policy documents and guidelines.

divisions in the departments and other units responsible for water management, Huzhou officials wrote their documentation to specify that the municipal river chief department must take the lead in the overall coordination of the river chief system and be responsible for: (i) the development of the work program and annual plan for Huzhou, (ii) assist the river chief in performing their guidance function of lower-level river chiefs, including their coordination and supervision of the municipal and lower level activities, and (iii) to help the municipal river chief perform their routine work.

By setting out these specific responsibilities of river chiefs, not only did Huzhou move beyond the model developed in Wuxi, but it also established the expectations and conditions needed for the different levels of river chiefs to perform their duties under the coordination and guidance of the river chief office. Further showing Huzhou's efforts to learn from others was the decision to develop a more targeted and operable assessment scheme based on a scoring system that measures standards at the municipal leading department and the river chief system of the county.

In summary, in developing the river chief system, Huzhou officials examined a range of different models and then actively engaged in a learning process that led them to implement a range of policy adjustments that were based on retaining the core of the original (Wuxi) policy, but which combined this core with other municipal river chief models to better address their local needs (for specific details see: "Implementation Plan of Establishing the River Chief System in Huzhou 2013;" "Implementation Opinions on Deepening the River Chief System 2014"). As such, the transfer Huzhou undertook falls into the assortment side of the transfer continuum offered in [Figure 1](#).

4. Discussion

4.1. Situational differences, learning deficiencies, and policy failures in Nantong

Nantong has a relatively flat terrain with a water system characterized by a complex network of rivers and ditches roughly bound by the Tongyang Canal and Rutai Canal, which falls within two river basins, the Huaihe, which covers an area of more than 2,200 km² in the north and the Yangtze, that covers an area of more than 5,700 km² in the south. In this, the Yangtze River coastline in the territory is 166 km, with a surface area that extends southeast in a trumpet shape.⁴

This shows the difficulty of watershed governance in Nantong lies in the complexity of the river system within

its jurisdiction, not the lake pollution crisis that drove the design of the Wuxi river chief system.

However, rather than learning from the experience of municipalities that were facing similar water course issues, Nantong officials chose to copy much of the provincial policy, despite the implicit understanding that they could adapt the model to local needs or, as reported, "Our policy learning is mainly about the policy texts of the higher authorities. The higher authorities have also held some training meetings on the river chief system that we attended" (W, interview, 6 January 2020).

We want to highlight that the primary reason for this adherence to the provincial guidelines reflects the desire for local officials to use the river chief to gain enhanced legitimacy in the eyes of provincial leaders (allow Nantong to be seen as "good municipality") and gain performance related "points" in the belief that this would help promotional prospects. In this, Nantong officials might not be completely to blame for their adherence to systematic outlooks that led them to follow Jiangsu, given the nature of the Chinese bureaucracy and its reward and punishment mechanism.

Failing to engage in hard learning was compounded by the fact that much of Wuxi's success was not reflected in the policy texts associated with their river chief but resulted from tacit knowledge among local agents as to what was needed to address a crisis. In fact, according to the interviews with the office staff of the river chief system in Nantong, their cognition of the river chief system remained at the level of the river chief being responsible for water control (Director F, interview, 8 October 2019).

As a result of not engaging with this tacit knowledge, Nantong officials failed to incorporate critical design elements that made Wuxi's river chief system work. By focusing only on the defined policy objectives, principles, and main directions, Jiangsu and Nantong officials engaged in what is often referred to as incomplete (and, in many ways, uninformed) transfer. As a result, rather than focusing on the operational logic of the river chief, administrators in Nantong focused on daily management issues. This led them to design a management model that neglected internal and cross-departmental cooperation, which underpinned Wuxi's river chief system (Y, interview, 8 October 2019). Putting it more succinctly, an administrator in the Water Resources Bureau of Nantong noted, "Many of the contents reported today are long-term river management. there is not much about the river chief system. It is not clear what the responsibilities of the river chief are, what the current river chief has done, and what problems he has solved" (Director C, interview, 14 September 2019).

⁴ Nantong Historical Records Network. <http://www.ntszw.gov.cn/?c=index&a=show&id=2460>, (accessed 08/04/2022).⁵³

Through our document review, we also discovered that instead of focusing on methods to design the best functional river chief system, officials in Nantong saw the transfer of the river chief as an opportunity to solicit financial input from their superiors. For instance, in a working report, it was emphasized that funding for investment purposes was deemed more important than either the design of the river chief or the operation to evaluate the system completely. This was confirmed by Director C of the Nantong Water Resources Bureau:

At present, river chiefs at all levels in the city are part-time; although the city has corresponding assessment methods, its effectiveness is small, not as strict and specific as the evaluation of the Scientific Outlook on Development, unless there is a major water accident, otherwise the so-called assessment is just a formality to comply with the assessment processes (Director C, interview, 14 September 2019).

In summary, to please superiors, Nantong carried out the transfer of the river chief system to gain resources and legitimacy, which led them to neglect effective learning opportunities. This resulted in Nantong failing to effectively respond to situational differences in the model offered and their own water management needs, which ultimately resulted in lower policy performance. As found in their initial performance review, “Jiangsu Province Backbone River Management and Protection Performance Evaluation Report,” it was noted that the quality of river cleaning in Nantong was lower than the standard score received across the nation. This outcome was reconfirmed in 2019 through our field research, which found three interrelated problems. First, the function of the river chief’s office was introduced as

required, but instead of enhancing the power of the river chief, the office was found to be weak and ineffective. We believe that this was a result of the office not being an independent unit with executive power, as it was in Wuxi. Rather, the Nantong office of the river chief was set up in the municipal Water Resources Bureau, and personnel were transferred there from other departments. Unfortunately, in Nantong, the Water Resources Department has a limited role in the planning, deployment, coordination, and supervision of river management. Not only did this reduce the effectiveness of the river chief, but when the office was established, it neglected any real cross-departmental coordination and joined-up responses, which formed a core element of the more successful river chiefs and river chief offices.

Second, we found that despite the documentation relating to the implementation of the river chief, Nantong (and others) left a disjuncture between the title, powers, and activities of the river chief. As reported by the Nantong River chief’s office:

From the perspective of more than 2 years of operation, the vast majority of river chiefs are still only in name, especially some grassroots river chiefs, and they do not have a strong sense of river chiefs. They do not take the initiative to inspect, do not actively investigate, and do not timely plan and solve problems in their daily work. The river chief does not play much of an organizing and coordinating role (W, interview, 8 October 2019).

Third, we found that the assessment process used by the Nantong authorities did not link to the corresponding responsibilities of the river chief, which “led to awards with no corresponding punishments” for poor performance

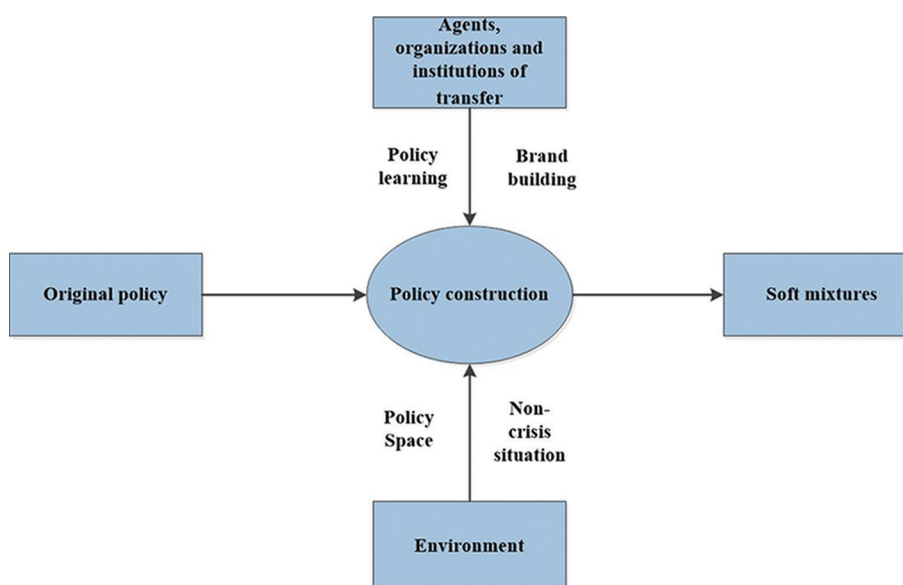


Figure 3. Huzhou’s river chief generation process

(W, interview, 8 October 2019). Overall, despite (or more accurately because) officials in Nantong following the guidance of Jiangsu Province, the performance of the river chief system has failed to reach the level found in more successful municipalities and localities.

4.2. Huzhou and the role of mixing it up

Unlike Nantong, the Huzhou river chief system reflects the constructive role that actors and the environment can play in the transfer process.⁵⁰ As illustrated in [Figure 3](#), Huzhou officials decided to develop the river chief system to be seen as a leader in the field of water management. This was itself partially motivated by the competition for acknowledgement and resources encouraged by the Chinese governing system.⁵¹

The importance of cross-governing competition was frequently mentioned in interviews with actors in Huzhou, who saw the development of the river chief as demonstrating that they were engaged in pioneering policy innovation at higher-level governing authorities. If Huzhou had merely copied Wuxi (or any of the other models that had emerged), core actors would not have been able to add “points” for high-level performance.

Not only did Huzhou administrators use the river chief to add “points” to their performance reviews, but they actively worked to make their river chief into a “brand” that could be a model for others. As reported:

In 2007, the river chief system in Wuxi formed a mature policy plan at the municipal level and was regarded as the birthplace of the river chief system. We were somewhat unconvinced about this. We want to make Huzhou River chief system a brand, even beyond the influence of Wuxi (Z, interview, 6 January 2020).

While Huzhou learned from Wuxi (D, interview, 6 January 2020), it is apparent that the two systems diverged in significant ways and that this divergence was driven, in part, by officials’ understanding of the differences in the underlying logic for setting up the river chief in Wuxi and Huzhou. Recall that the Wuxi model emerged to deal with an emergency (cyanobacteria crisis in the Taihu Lake). Huzhou’s system emerged out of the regular policy process and was seen “as a way to improve the overall watershed management” in the municipality (Z, interview, 6 January 2020).

As a result, Huzhou designed its river chief to engage in overall river management, protective work, and the development and utilization of overall water resources. This was reflected in the design of the office of the river chief, which was established “to better assist the river chief effectively perform his expanded role” (D, interview, 6 January 2020), not simply holding a person responsible

for river quality. As a result, Huzhou’s river chief office was developed not as a temporary, task-oriented organization, but as a professional organization to effectively operate and coordinate the existing bureaucratic agents involved in water management.

In addition, while Wuxi developed its system under a crisis and Nantong transferred its system under pressure from a superior level of government, Huzhou was able to transfer and construct policies autonomously. This allowed them to set their own goals by looking around for ideas and structuring them to suit their unique situation. This was supported by a constructive relationship between Huzhou and Zhejiang Province (in terms of political performance), which provided Huzhou with the resources and authority needed to construct its model of river management and protection.

Importantly, Huzhou was the first region in Zhejiang Province to design and implement a river chief system. This allowed Huzhou officials to frame their mission as making their river chief “the model for Zhejiang Province.” This led officials to include various design elements borrowed from a range of sources, packaged together to address indigenous water needs. As one interviewee noted:

The provincial government also expects us to present regional characteristics, form a demonstration effect in the region and even in the whole country, and give us a lot of support in terms of resources, including being included in the pilot innovation of river and lake management system and mechanism, and demonstration river and lake construction points (D, interview, 6 January 2020).

In summary, the transfer of the river chief system in Huzhou was based on policy learning and the assemblage of several models that were mixed with homegrown ideas. In this, policy actors were motivated by the hope of building a brand. As such, Huzhou best fits the policy transfer concept of an assembly. Because of this, when compared with Nantong, the outcome of the river chief system in Huzhou is functioning at a higher level. As reported by The Ministry of Water Resources, the Taihu Basin Administration Bureau of the Ministry of Water Resources, and the provincial Water Resources Department, the river chief in Huzhou has achieved good results in terms of improved water quality and river health (the water quality flowing into Taihu Lake remained above Class III for 13 consecutive years). In fact, in 2021, the Water Resources Bureau of Huzhou won the title of “National Advanced Collective for Comprehensively Implementing the River Chief System and Lake Chief System” issued by the Ministry of Water Resources.⁴⁹

Table 2. Movement of the river chief system

Case	Degree of transfer	Primary driving force	Degree of learning	Primary motivation	Adaptability	Outcome performance
Nantong	Copy	External	Soft	Legitimacy	Weak	Low
Huzhou	Assortment	Internal	Hard	To be seen as a leader	Strong	High

4.3. Summary discussion

This study selected Nantong and Huzhou to represent two distinctly different cases of policy transfer in developing the river chief system in China. The objective was to better understand how a core model spreads under different situations within a hierarchical governing system. We selected Nantong because its administrators were acting under the direction of a higher governing authority and chose to follow the rules and regulations developed by the offices in Jiangsu Province rather than look more widely for more appropriate models. This resulted in a near copy that failed to account for local needs or structures. Part of the reason for this was that officials were motivated to appease higher-level officials. Had Nantong officials undertaken a more informed process of policy development (including modeling their policy on what had been implemented in other “similar” municipalities within Jiangsu), based on the needs of the municipality and its water courses, we believe that the outcomes of the transfer process would have been better than those to date.

We selected Huzhou because its officials were acting under their own initiative. As a result, this study demonstrated that Huzhou represents the advantages associated with harder forms of learning in the transfer process that voluntary transfer can encourage. In the case of Huzhou, this included understanding the specific needs of the water resources in Huzhou (and the wider Zhejiang Province) and how other similar jurisdictions operated their river chief systems. This informed transfer and learning process allowed Huzhou officials to consider how different models could be assimilated into a new, more appropriate, and effective system.

Considering Chinese governing structures, once a higher-level government introduces a policy, lower-level governments must act to implement it. In the case of Nantong, while the Provincial guidelines allowed a degree of freedom in how the river chief was designed and operated, Nantong officials had to carry out the wishes of the Jiangsu Provincial government. In this, we found that this response was highly impacted by the institutional setting, structuring how actors saw the transfer and thus, what motivations they prioritized.

In contrast, Huzhou was not subjected to direct external coercive pressure, as its superior government had not issued mandatory policy requirements around river management.

As a result, Huzhou authorities had the freedom (and time) to develop and institute a river chief system based on a different set of motivational factors from those that drove officials in Nantong. One of the primary reasons that Huzhou officials voluntarily engaged in the transfer process was their desire to be seen as provincial leaders who could offer a model that was even better than the Wuxi model.

Concerning the transfer direction, Nantong reflects the vertical transfer path of “absorption radiation,” where the Jiangsu Provincial Government absorbed Wuxi’s chief river system, slightly adapted it, and then promoted it across the province. During this process, the river chief system underwent two stages of transfer translation: bottom-up and top-down. In the bottom-up process, the Jiangsu Provincial Government adjusted the original policies, adding regulatory requirements while deleting some of the specific institutional design content. In the top-down process, Nantong primarily copied the Provincial guide. This uninformed/incomplete transfer subsequently led to outcome problems (in relation to water quality measures) that are still apparent in the Nantong region.

In contrast, Huzhou’s transfer process had no time pressures, allowing transfer agents to engage in horizontal (between municipal governments) transfer at their own pace. This allowed for a considerably better learning environment that was enhanced by the motivation of officials in Huzhou to be seen as policy innovators and use the river chief to improve the conditions and operation of their river basin management.^{49,51}

We want to emphasize that despite both jurisdictions being under the direction of the central government’s authority, as shown in [Table 2](#), different motivations drove the actors in Nantong and Huzhou, and that these motivations help explain the different types of transfer that occurred. Recall that the policy transfer behavior of actors in Nantong reflects legitimacy orientation, which led them to implement the policy spirit of their superiors, complete the task goals set by their superiors, and obtain the legitimate recognition of their superiors. On the other hand, the actors in Huzhou were motivated by the desire to improve the performance of watershed governance and create a regional policy brand.

In conclusion, while the study design limits our core findings to Nantong and Huzhou, what it does suggest is that motivational factors need to be considered not only in

the transfer literature but also in the study of how lower-level governing units design and implement policies in authoritarian policy regimes. As demonstrated, with the proper motivation, learning can and does occur within authoritarian governing institutions, and this learning can be shared not only internally but also has the potential to transfer outside the Chinese governing system.

5. Conclusion

The development of the river chief system in China can provide insights into the policy learning and transfer processes occurring in authoritarian systems. For this study, two “most different” jurisdictions were selected to see how and why the transfer of a core model led to different outcomes. This study broadens the way policy transfer and learning have been studied in China by examining how two different jurisdictions engaged in the transfer process of a core model.⁵² Because we examined point-spoke transfer, one of the primary lessons to emerge from the study is that even when jurisdictions operate under the same centralized governing system, the institutional environment cannot guarantee that the transfer of policy innovations will lead to the same model emerging across jurisdictions.

This finding suggests a second major conclusion that has been emerging within the transfer literature: when examining policy transfer, policy learning (both what is learned and how the agents of transfer are engaged in the learning process) becomes an important variable in what gets transferred. In this, the better the agents of change understand their own needs and the environment they are operating in, the more likely they are (even in authoritarian systems) to engage in hard learning, and the harder the learning is, the more likely policy transfer will result in success.

Third, when engaging in and studying instances of policy transfer, it is important to understand one’s environment; it is just as important to understand what is being transferred. While it is possible to copy a model successfully, it is unlikely that the model will bring the same success that drew policymakers to it when implemented into a new environment. As such, when engaged in policy transfer, the more models that are examined, the better they are understood technically and tacitly, hence the better the policy will be developed once it is introduced by those engaged in the transfer.

Fourth, while seldom discussed in the transfer literature, the motivations and structural boundaries that restrict and shape decisions of those involved in the transfer are vital. Not only can motivations derail or encourage more advanced forms of learning and policy development, but when viewed through system constraints and facilitators, these motivations can help to explain the type of transfer that

occurs. In short, policy transfer always involves changing the policy operating context. This means that a policy innovation that produces improved performance in the original models cannot be guaranteed to produce the same outcome in the new setting, particularly if the motivations for the transfer are not aligned with harder forms of learning.

While these findings are robust, we offer three suggestions for future research based on our findings. First, those interested in policy transfer and how it relates to policy leaning and modification should start to engage in point-spoke studies. More specifically, transfer studies in China should start to look at how a single model is transferred and transformed (or not) across multiple jurisdictions (e.g., municipalities, provinces, villages). This will better enable researchers to understand the hidden factors in the policymaking processes that influence decision-making and policymaking at lower levels of government as they function in the hierarchical structures of the state and party in China. Second, while we have focused on an area with a degree of freedom to alter and develop a policy model, similar studies should be conducted in areas where freedom is less apparent. This could help better explain the role of system-level factors in the transfer process. Third, while a range of studies investigate different levels of governance in the transfer process, more work needs to be done in China. This research should involve not only how policies move across governing levels (and bodies), but also how different provinces engage in the transfer process. This should help researchers and policymakers understand how governance operates in the Chinese setting.

Overall, through the two representative cases of replication and hybridization, our study of the river chief system attempts to break the stereotypical perception of policy transfer in authoritative countries as an undifferentiated replication. This study also reveals the experience of policy learning under Chinese hierarchical interactions that endowed policy innovations with situational adaptability, which is undoubtedly of theoretical value to the study of policy transfer. This suggests future studies should focus not only on what was transferred, but also on how it occurred and the motivations driving the process. These motivations are often embedded in institutional structures that shape not only what is possible but also what is perceived to be appropriate during policy transfer and development.

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Conflict of interest

The authors declare that they have no competing interests.

Author contributions

Conceptualization: All authors

Investigation: All authors

Methodology: All authors

Writing – original draft: All authors

Writing – review & editing: All authors

Ethics approval and consent to participate

This study was reviewed and approved as part of the grant application process (Approval ID.: 24CZZ006). Informed consent was obtained from all individual participants included in the study, and autonomy was guaranteed.

Consent for publication

All participants agreed to the quoted material on condition of autonomy unless otherwise indicated.

Availability of data

Data used in this work are available from one of the authors (825654699@qq.com) upon reasonable request.

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ORIGINAL RESEARCH ARTICLE

Comparative analysis of chlorination byproduct formation in galvanized iron and high-density polyethylene pipes using low-cost filtration techniques

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Two prominent chlorination disinfection byproducts (DBPs)—trihalomethanes and trihaloacetic acids—are formed in drinking water when chlorine reacts with other constituents. The production of these DBPs has emerged as a significant public health concern. At the same time, disinfection of potable water remains essential as a safety measure to effectively combat waterborne diseases by eliminating pathogenic microorganisms. To regulate the formation of these two major DBPs in the water distribution network, one of the key factors is the nature of the pipe material used, along with the implementation of cost-effective abatement techniques. This study compared two types of potable water supply pipe materials—galvanized iron and high-density polythene pipes—for their role in the production of chlorine DBPs. Both materials showed different weightage ratios of DBP formation when chlorinated water came into contact with the inner surface of distribution pipes. Two filtration setups, i.e., granular activated carbon (GAC) and sand filtration media, were evaluated as abatement techniques for removing DBPs, depending on the water source and pipe material used. The findings contribute to understanding the differences in the generation of major DBP species under known supply media, as well as the removal efficiency of DBP precursors by GAC and sand filtration. Overall, the results reveal that GAC and sand filtration media can serve as low-cost and sustainable alternatives to costly, complex filtration membranes for DBP removal.

Keywords: Controlled chlorination; Chromatograms; Mass spectrometry; Granular activated carbon; Silica medium; Dissolved organic matter

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1. Introduction

In recent years, drinking water disinfection has emerged as an important public health measure, effectively preventing waterborne diseases by removing pathogenic microorganisms. With the advancement of technology, concerns over water pollution have increased significantly.¹ Chlorination is one of the most effective and low-cost methods to eliminate microorganisms and is a viable approach for suppressing microbial

activity in the water supply network.² A free chlorine residual of up to 0.2 mg/L is typically maintained in the distribution system, as it helps minimize the risk of further contamination. However, chlorine concentration tends to decline over time due to its dissolution behavior. These findings by Al-Jasser³ are fully supported by the findings of Clark and Wymer;⁴ however, Jahin *et al.*⁵ noted that higher chlorine dosages are commonly applied worldwide to ensure effective disinfection.³⁻⁵

Dissolved organic matter is a complex natural component found in water, often introduced through anthropogenic activities, and is recognized as a primary contributor to the formation of chlorination disinfection byproducts (DBPs).⁶ Substances such as organic impurities, ammonia compounds, and residual metallic ions (e.g., ferrous ions, magnesium) are prominent components that interact with chlorine and are consumed during the reaction.³

Kali *et al.*⁷ found that the most prevalent DBP groups are trihalomethanes (THMs) and trihaloacetic acids (THAAs), which are formed when chloramine and chlorine react with organic and inorganic matter. In addition, Maul *et al.*⁸ and Rossman *et al.*⁹ observed a rapid decrease in both free and total chlorine residuals in the water distribution system (WDS) as hydraulic residence time increased. Due to limitations in chlorine persistence within the WDS, secondary chlorination is often required to maintain effective sterilization and disinfection of drinking water. However, this secondary chlorination can further react with natural organic matter (NOM) and microbial contaminants, leading to the formation of additional DBPs during water delivery.¹⁰

WDSs play a crucial role in the secondary formation of DBPs, potentially increasing the risk of excessive DBP accumulation during water transport.¹¹ The complex environment within WDS, including residual chlorine and organic matter, influences further DBP formation. A study by Charisiadis *et al.*¹² found a significant positive correlation between hydraulic residence time and THM levels in the WDS.

Different regions use varying pipe materials based on supply conditions and regulatory standards. Cast iron, the most widely used material, is prone to corrosion, releasing iron ions that accelerate DBP formation.¹³ In comparison, galvanized steel pipes exhibit a higher rate of chlorine decay.¹³ Hydraulic shocks in plastic pipes can lead to microplastic release, which may contribute to DBP formation, further deteriorating water quality.¹⁴

He *et al.*¹³ reported that the rate of haloacetic acid formation among four plastic pipe materials followed the order: high-density polyethylene (HDPE) > polypropylene

(PP) > polyvinyl chloride. In another study, Chen *et al.*¹⁵ found that biofilm accumulation in pipes used for 2 years increased THM and THAA concentrations to 59.5–123 µg/L and 35.1–51.6 µg/L, respectively—significantly higher than levels in new pipes.

Volatile chlorinated hydrocarbons, which are known carcinogens, have been regulated by the United States (US) Environmental Protection Agency (EPA) at a maximum contaminant level of 0.005 mg/L.¹⁶ Even though chlorination is the most widely used technique for disinfecting water, it has some disadvantages. Long-term exposure can lead to cancer due to the formation of DBPs, which can also negatively affect the kidney, liver, and contribute to other health issues.¹⁷ Moreover, the factors influencing DBPs formation in WDS (e.g., pipe materials, deposits, and biofilms) are not isolated but act synergistically to promote DBP formation.¹¹

Different countries report varying average concentrations of THMs, ranging from 0 to 1000 mg/L. For instance, the average THM concentrations in treated water samples in Nigeria range from 0 to 95 mg/L.¹⁸ Similarly, up to 18 mg/L of DBPs were detected in finished water and up to 22 mg/L of DBPs in distribution systems in the US.¹⁹ In China, the average concentrations of THMs and HAAs throughout the treatment process were 19.9 mg/L and 3.4 mg/L, respectively.²⁰ These data indicate that DBP concentrations in WDS are spatially variable.²¹

In the Chinese WDS, the concentration of THMs ranged from 3.67 µg/L to 30.30 µg/L, while tribromomethane concentrations were below 3.15 µg/L.²² The average total THM concentration in China was approximately 16.6 µg/L, which is lower than that reported in the US and Saudi Arabia (33.6 µg/L).²³ HAAs in China ranged from 0.83 to 18.8 µg/L in WDS water, with dichloroacetic acid and trichloroacetic acid showing similar concentration ranges in WDS samples.²⁴

In addition, Amjad *et al.*²⁵ found that higher levels of total THMs were reported in Islamabad compared to Rawalpindi, possibly due to Islamabad's reliance on surface water, whereas Rawalpindi residents primarily access groundwater through tube wells, open wells, or pressure pumps. This suggests that groundwater, which contains lower concentrations of NOM, may lead to reduced DBP formation. In densely populated Pakistan, with an average life expectancy of 70 years, cancer cases related to THM exposure are reportedly increasing. Karachi, the largest metropolitan city with approximately 18 million residents, is projected to have a high burden of cancer cases linked to DBP exposure.²⁶ However, according to Pejman *et al.*,²⁷ both Rawalpindi and Islamabad have still reported fewer cases than Tehran.

According to Clark *et al.*,²⁸ there are four main strategies for controlling DBPs and microbial contaminants in drinking water: biological filtration, conventional filtration, membrane technology, and coagulation. Chaukura *et al.*²⁹ further identified effective methods for DBP removal, including adsorption, air stripping, ozonation, chlorination, enhanced coagulation, membrane filtration, and advanced oxidation processes. In general, Jiang *et al.*¹⁰ categorized DBP control into three major strategies: source control, the use of alternative disinfectants, and precursor removal. Source control includes implementing environmental management policies or replacing chlorine with alternative disinfectants such as chloramines or chlorine dioxide, although these alternatives can still pose health risks. Due to its low cost, simplicity, and minimal energy requirements, sand filtration is widely used in drinking water treatment. Similarly, ultrafiltration has been recognized as a promising technique. However, the removal efficiency of ultrafiltration depends on the membrane pore size and the characteristics of NOM.³⁰

For the quantification of THMs and HAAs, Kennedy *et al.*³¹ conducted a pipe setup experiment similar to that of Liao *et al.*,³² in which a 56-day testing period was selected to investigate DBP formation under maintained booster chlorination dosages throughout the experiment. In addition, EPA³³ examined the effects of initial chlorine dosages across various pipe materials and analyzed the formation and transformation of DBPs in WDS following booster chlorination.

DBP concentrations in each sample were measured using gas chromatography-mass spectrometry equipped with an electron capture detector (GC-MS [ECD]). In this study, chlorine dosage levels were separately assessed—ranging from initial chlorination (0.43 mg/L) to booster chlorination (1.03 mg/L)—to evaluate their impact on DBP formation. GC-MS(ECD) is employed in DBP research due to its high halogen sensitivity and has been recommended by Chakraborty *et al.*³⁴ In comparison, Seyed Khademi *et al.*³⁵ utilized Raman spectroscopy to trace impurities in water, while González García *et al.*³⁷ used ion spectroscopy to identify dissolved ions and contaminants. Similarly, González García *et al.*³⁷ explored the variation of HAAs in a laboratory-scale distribution system consisting of four independent pipe loops made of HDPE, polyvinyl chloride, PP, and galvanized steel.

Although the generation of these prominent harmful chlorine DBPs in the water supply has been characterized and quantified based on the nature of the pipe material, there remains a need for cost-effective techniques suited to the specific pipe medium used. Some techniques discussed in Chaukura *et al.*²⁹ such as adsorption, air stripping, ozonation followed by enhanced coagulation,

and membrane technology, are well-known but cannot be considered as cost-effective or sustainable when compared to sand filtration media, granular activated carbon (GAC), or even the adsorbing filter made from banana peels studied in Jahin *et al.*⁵ Moreover, multiple studies have shown that sand filtration and GAC play a significant role in the removal of NOM, a known precursor of DBPs.⁶ Specifically, carbon-based adsorbents have been shown to significantly reduce emerging contaminants in water.³⁸ To the best of our knowledge, no comparative study has examined the formation and removal of major DBPs in relation to the cost-effective treatment of water distributed through galvanized iron (GI) and HDPE pipes.

This study was conducted in District Mardan (geographic coordinates: 34°05'N–34°32'N and 71°48'E–72°25'E), one of the central districts of Khyber Pakhtunkhwa (KP) Province, Pakistan. The study area was divided into three zones based on groundwater hydrology: an urbanized/industrial zone (Shergarh and Takhtbhai) and a non-industrial (control) zone (Surkhahi), referred to as Zone 1, Zone 2, and Zone 3, respectively, as shown in Figure 1. The industrial zones are characterized by activities such as manufacturing, car washes, markets, and other commercial processes, while the non-industrial zone involves anthropogenic activities unrelated to industrial production.

A total of 10 water samples were collected across the three zones for the identification and quantification of DBPs. Of these, six samples (three for each pipe type under non-filtration conditions) and four samples (two for each pipe type under filtration conditions) were analyzed. Each sample was tested under controlled chlorine dosages.

A prototype laboratory-scale experimental setup was constructed to replicate a municipal WDS, simulating water flow through GI and HDPE pipes under controlled conditions. Water samples were analyzed both without filtration and with filtration, using abatement techniques such as sand filtration media and a combined sand-GAC

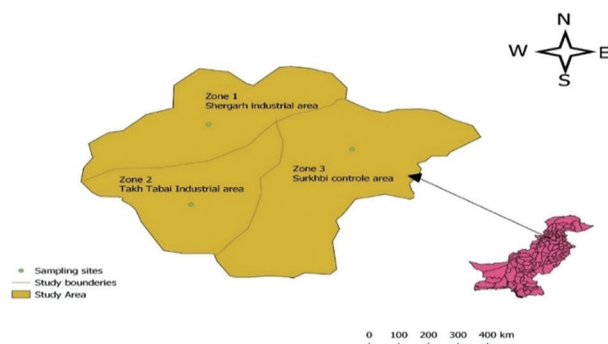


Figure 1. Study area division

filtration system in a rapid, small-scale column test. The two main chlorination DBPs—THMs and THAAs—were quantified using GC-MS (ECD), both with and without the application of filtration media.

2. Materials and methods

2.1. Chemicals and reagents

Granular chlorine powder (calcium hypochlorite) was obtained from the Water Quality Laboratory, Public Health Engineering Department, KP, Pakistan. Two DBP standard compounds—chloroform and THAAs—were purchased from certified chemical suppliers in Pakistan. The solvent for liquid-liquid extraction (LLE), ethyl acetate, was also obtained from the Public Health Engineering Department, KP, Pakistan, and was used to separate solutes from water samples. Distilled water used throughout the study was obtained from the Water Quality Laboratory, Public Health Engineering Department, KP, Pakistan. Fluorescence spectrometry was performed at the Central Resource Laboratory, University of Peshawar, KP, Pakistan.

2.2. Sampling site

In this study, multi-stage random sampling was employed to ensure systematic and representative sampling across all three zones of District Mardan. Primary sampling units were selected in each zone—two in industrial zones and one in the controlled (non-industrial) zone—to identify and quantify the formation of chlorination DBPs. In contrast, secondary sampling units consisted of two samples—one from the industrial zone and one from the controlled or non-industrial zone—which were used for the assessment of DBP abatement techniques through both quantitative and qualitative analysis.

In all three zones, groundwater was the selected source, and elevated head tanks or overhead reservoirs were utilized to provide head elevation and facilitate water distribution to consumers. Tubewells served as the intake source at each site. The groundwater potential for most sources was between 90 m and 120 m, with a static water level ranging from 18 to 30 m. The average yield per tubewell was 6–8 m, and the discharge rate varied between 0.00315 m³/s and 0.00526 m³/s. For consistency in sample analysis, only water from tubewells older than 10 years, connected to a minimum 5 km distribution network, was selected. All samples were collected at terminal (end-user) points of the distribution system.

Before analysis with GC-MS (ECD), key water quality parameters influencing DBP formation were measured. These included pH (using a pH meter), dissolved oxygen (DO) (using a DO meter), turbidity (using a nephelometer), taste (evaluated by taste test), dissolved

organic matter (DOM) (using fluorescence spectrometry), temperature (measured with a thermometer), and water hardness (determined using the titration method), as shown in Table 1.

2.3. Setup

For all sampling procedures, appropriate glassware was used throughout the entire analysis. Sampling containers were thoroughly washed with detergent, rinsed with tap water, followed by ultrapure water, and then dried in an oven at 150°C for 1–2 h. Samples were collected in 100 mL amber glass bottles with PP screw caps and tetrafluoroethylene-lined septa. Bottles were carefully filled to avoid the presence of air bubbles.

In addition, a laboratory-scale pilot WDS was constructed to evaluate the effects of different chlorine dosages. It consisted of pipe loops made of GI and HDPE, as shown in Figure 2. Each loop measured approximately 1.5–3 m in length, with a pipe diameter of 25 mm. The loops were equipped with ball valves, elbows, unions, and sockets to monitor water flow behavior, as well as control pressure and velocity. They were also used to direct water flow in the desired direction. Flow velocity was maintained between 0.2 m/s and 1.8 m/s. A 0.3 HP centrifugal pump (Model QB60, Taifu, Pakistan) was installed to ensure continuous water circulation.

In the distribution network, a 0.189 m³ (50-gallon) water reservoir was used to receive water samples directly from the field site. Special attention was given to collecting grab samples from different zones while monitoring temperature and sunlight exposure using the mobile water quality testing laboratory of the Public Health Engineering Department, KP. Before introducing water samples into the pilot-scale laboratory distribution system, the system was rinsed with ultrapure water for 30 min to remove any residual contaminants.

The methodology for operating the laboratory distribution system consisted of four main steps: flushing,

Table 1. Summary of water sample characteristics and their observed ranges

Parameters	Range
pH	7.2–7.8
Dissolved oxygen	5–5.7 mg/L
Turbidity	1–3 NTU
Taste	Fair
Temperature	30–38°C
Hardness	Soft water
Dissolved organic matter	1.8–2.2 mg/L

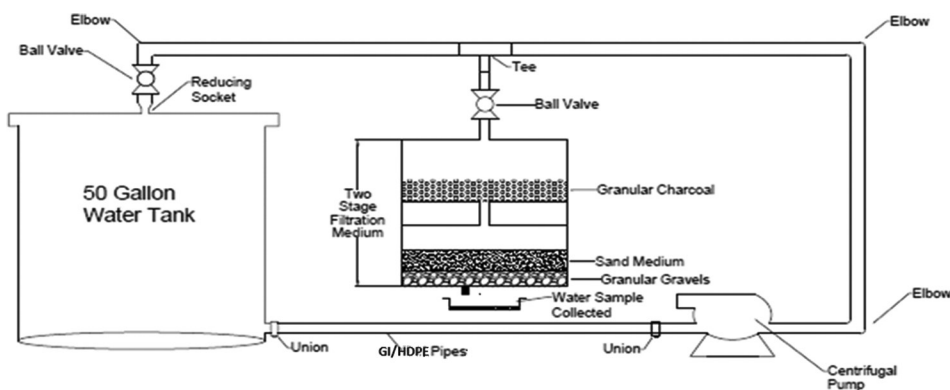


Figure 2. Schematic diagram of the laboratory-scale experimental water distribution setup
Abbreviations: GI: Galvanized iron; HDPE: High-density polyethylene.

parameter adjustment, chlorine dosage application, and sampling. After flushing with ultrapure water, samples were added to the 0.189 m³ (50-gallon) reservoir and suctioned into the system using a centrifugal pump. The flow and velocity within each loop were maintained uniform and uninterrupted, ensuring homogenous mixing of particles upon chlorine addition. Chlorine dosages of 0.2 mg/L, 1.8 mg/L, and 2.4 mg/L were then introduced sequentially into the system—0.2 mg/L for Zone 1, 1.8 mg/L for Zone 2, and 2.4 mg/L for Zone 3. THMs and THAAs were subsequently identified and quantified at each dosage level.

2.4. Abatement techniques

For the abatement technique, two filtration media—GAC and sand filtration—were introduced as rapid, small-scale column tests, controlled by a ball valve installed between the distribution network sections under a fixed chlorine dosage of 2.4 mg/L. This ball valve diverted water flow toward the filtration media while isolating the reservoir line. The small-scale column test setup was designed to simulate pilot- or full-scale fixed-bed GAC and sand filters.

The rapid column test was conducted to evaluate the adsorption efficiency of GAC and the filtration capacity of sand media. The carbon fraction used had a particle size of 170–230 mesh (mean diameter: 76 μm), and it was washed with ultrapure water and dried overnight. The dried carbon was then stored in a desiccator before use. The GAC column was packed with the prepared GAC particles. The minimum velocity was calculated using the Reynolds number (Re_{min}), and according to the US EPA/Chromium Manual, the recommended range to maintain laminar flow is $Re = 0.5\text{--}1.0$.³⁹

The physical characteristics of GAC were determined according to the American Society for Testing and Materials (ASTM) standard test methods, including: moisture

content (ASTM D2867), ash content (ASTM D2866), iodine number (ASTM D4607), bulk density (ASTM D2854), hardness number (ASTM D3802), and uniformity coefficient (ASTM D2862).

For the sand filtration media, a column-shaped setup was used, comprising a 1000 mm quartz sand layer, operated in downflow mode at a specified filtration rate. The bed depth of the sand filter column was 700 mm, filled with silica sand of 0.7 mm particle size and a uniformity coefficient of 1.4. The granular filter column operated at a filtration rate of 4.6 m/h under a rising head.

Before determining the formed DBPs, EPA Method 551.1³⁴ was slightly modified by replacing the original LLE solvent—methyl tert-butyl ether—with ethyl acetate, due to environmental concerns outlined in.³⁴ The negative environmental impact of methyl tert-butyl ether, particularly in drinking water contamination, has been well documented.⁴⁰ The LLE separation process was conducted after the samples had completed the distribution phase in the laboratory-scale water distribution model. A separatory funnel was used, and a 1:2 solute-to-solvent ratio was maintained. In this case, the solutes were THMs and THAAs, and the solvent was ethyl acetate. The extraction began by partially combining the solute and solvent, followed by vigorous shaking for 5 min. Then, an additional 10 mL of solvent was added, and the mixture was again shaken for 5 min. This process was repeated 5 times, resulting in the extraction of a 100 mL sample using 50 mL of solvent, with 5-min shaking intervals after each addition. After extraction, the separatory funnel formed two distinct layers. The water layer was removed using a funnel dropper, leaving behind the solvent layer containing the extracted compounds.

To determine THMs and THAAs, as recommended by EPA Method 555.1,³⁴ GC-MS (ECD) analysis was conducted using a GCMS-5977B system (Agilent

Technologies, United States of America). A fused silica capillary DB-1 column (30 m × 0.32 mm inner diameter × 0.25 μm film thickness) was used. Helium (99.99% purity) served as the carrier gas, and nitrogen (99.99%) was used as the makeup gas. The analytical operating conditions are summarized in Table S1.

Standard internal peak areas were used to prepare the calibration standards. A linear regression equation was applied to generate the calibration curve and calculate the concentration in the extract (C_{extract}), as shown in Equation II. After obtaining C_{extract} , the concentration in the water sample (C_{water}) was determined using Equation III, based on the sample and extract volumes. Finally, both values were inserted into Equation I to calculate the total concentration of chlorine DBPs, with full equation details provided in the Supplementary File.

$$\text{TTHMs} + \text{THAAs} = \text{Prominent chlorine DBPs} \quad (\text{I})$$

$$C_{\text{extract}} = \frac{\text{Measured peak area}}{\text{Peak area of internal standard}} \times (m + b) \quad (\text{II})$$

$$C_{\text{water}} = \frac{C_{\text{extract}} \times V_{\text{extract}}}{V_{\text{water}}} \quad (\text{III})$$

3. Results and discussion

3.1. Fraction of DBPs in selected zones under controlled dosages

To assess the occurrence of chlorine DBPs, EPA³³ conducted a sequence-wise batch chlorination of the

water distribution network model and observed the corresponding variations in DBP formation at different controlled chlorine dosages.

In this study, the fractions of DBPs detected in water samples from Zone 1, Zone 2, and Zone 3 varied. Key psychochemical characteristics contributing to DBP formation were identified for each sample. The analysis was carried out in phases, beginning with a dosage of 0.2 mg/L, followed by 1.8 mg/L, and finally 2.4 mg/L, applied to both pipe materials.

At the initial chlorine dosage of 0.2 mg/L, the results (Figure S1) show no detectable levels of THMs and THAAs in the chromatograms for both pipe types (Figure S2). Other chlorine-related compounds with chromatographic retention are identified and listed in Table S2. The absence of THMs and THAAs may be attributed to the very low residual chlorine concentration, which is likely insufficient to initiate significant DBP formation.

A chlorine dosage of 1.8 mg/L was applied to the Zone 2 water sample to evaluate the formation of THMs and THAAs in water samples passed through GI and HDPE pipes. Key water quality parameters—including pH, DO, turbidity, taste, temperature, hardness, and DOM—were measured before GC-MS (ECD) analysis, as shown in Figure S3. GC-MS analysis of the GI pipe water sample initially detected 11 compounds, as summarized in Table S3. Among the target DBPs, trichloromethane was identified at a retention time of 1.532 min, corresponding to peak number 4, with a molecular weight of 119 g/mol and a mass spectrometry signal area of 3,029,057, as shown in Figures 3 and S4.

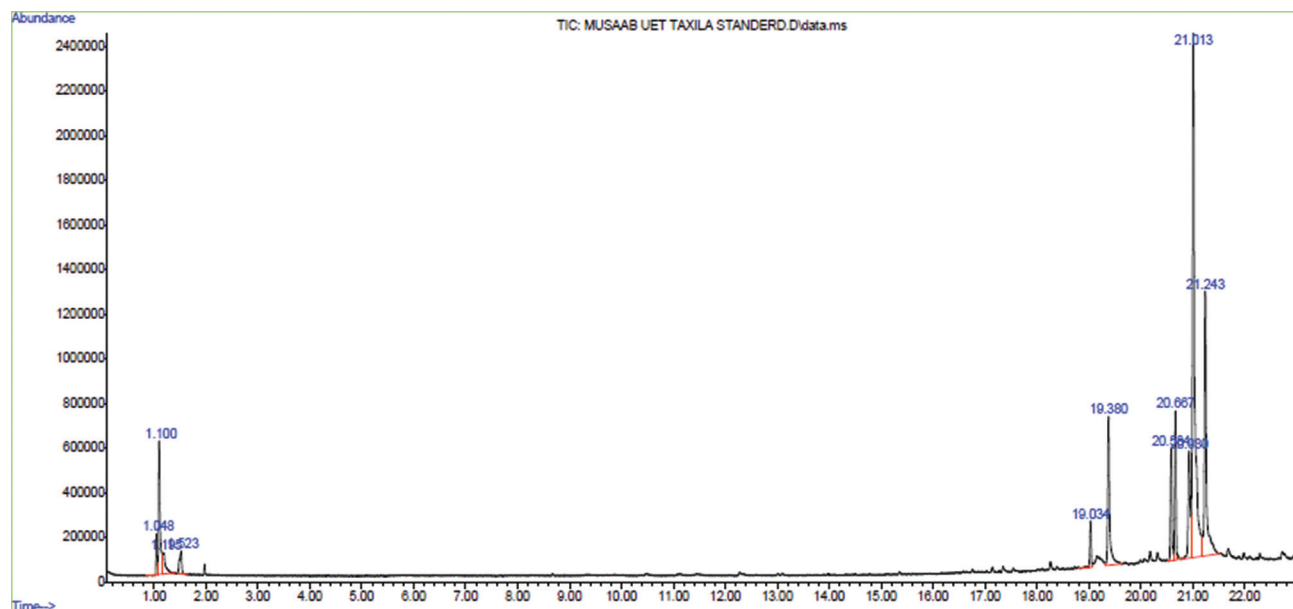


Figure 3. Chromatogram of the galvanized iron pipe water sample treated with a 1.8 mg/L chlorine dosage

Since gas chromatography separates compounds based on their volatility, trichloromethane—a small and volatile molecule—was eluted earlier than larger, less volatile compounds such as fatty acids (e.g., hexadecenoic acid and oleic acid), which exhibited longer retention times due to stronger interaction with the stationary phase. In addition, due to the use of an ECD, the system displayed higher sensitivity to halogenated compounds, while non-halogenated compounds generated weaker signals.

After analyzing the GI pipe water sample, the HDPE pipe water sample was examined using GC-MS (ECD) over an 8–9-h run time. However, no halogenated chlorine DBPs or related compounds were detected. The absence of THMs and THAAs in the HDPE water sample from Zone 2 suggests a lower production rate of chlorine DBPs, likely due to reduced interactions between the HDPE pipe surface and the water, even in the presence of organic matter. Furthermore, the non-identification of DBPs in HDPE water samples may be attributed to the shorter contact time and the inert, smooth surface of HDPE, which minimizes chlorine reactions with pipe material and precursors. This observation supports the hypothesis that HDPE pipe material results in lower DBP formation compared to GI pipes.

Secondary chlorination can further react with NOM and residual microorganisms to form additional DBPs during water distribution.¹⁰ Therefore, for this phase of secondary chlorination, the chlorine dosage was increased to 2.4 mg/L. Water samples from both GI and HDPE pipes in Zone 3 were analyzed under this dosage, with

the corresponding water quality parameters presented in Figure S5.

The GI pipe water sample was evaluated using GC-MS (ECD). Both targeted halogenated DBP families—THAAs and THMs—were detected, with peak number 2 appearing at a retention time of 4.452 min, as shown in Figure 4, and corresponding mass spectra provided in Figure S6. In addition to these target DBPs, other compounds with their respective retention times are listed in Table S4.

For the HDPE pipe water sample, both DBPs—THAAs and THMs—were detected at peak number 2, with a retention time of 4.340 min, as illustrated in Figure 5, and the corresponding mass spectrum is shown in Figure S7. The detection of these DBPs in the HDPE water sample underscores the material's potential role as a source or mediator in DBP formation within the WDS. Additional detected compounds and their retention times are summarized in Table S5.

However, for the GI pipe water sample, it was found that under a chlorine dosage of 2.4 mg/L, approximately 0.212 mg/L of THAAs and 0.199 mg/L of THMs were detected after running under controlled conditions. Moreover, under a chlorine dosage of 1.8 mg/L chlorine in the same GI pipe, approximately 0.193 mg/L of THMs were detected. Similarly, for the HDPE pipe under a chlorine dosage of 2.4 mg/L, approximately 0.2 mg/L of THAAs and 0.167 mg/L of THMs were detected, as shown in Figure 6.

According to a previous study by Chen *et al.*,¹⁵ biofilms in 2-year-old pipes increased the concentration of THMs

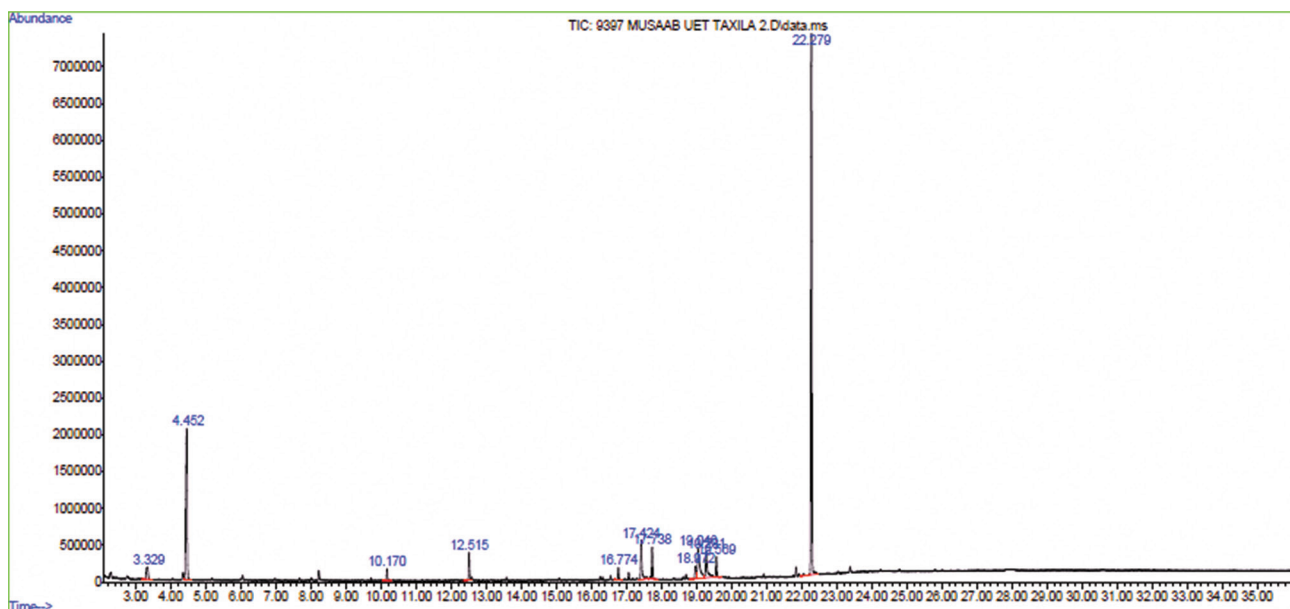


Figure 4. Chromatogram of the galvanized iron pipe water sample treated with a 2.4 mg/L chlorine dosage

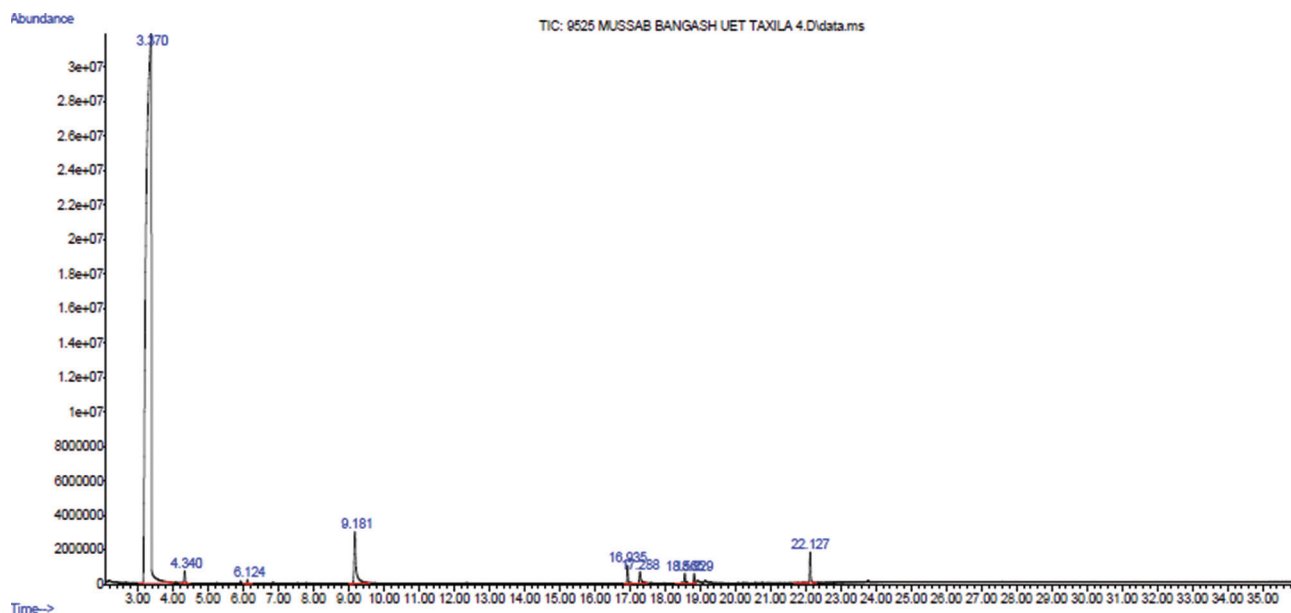


Figure 5. Chromatogram of the high-density polyethylene pipe water sample treated with a 2.4 mg/L chlorine dosage

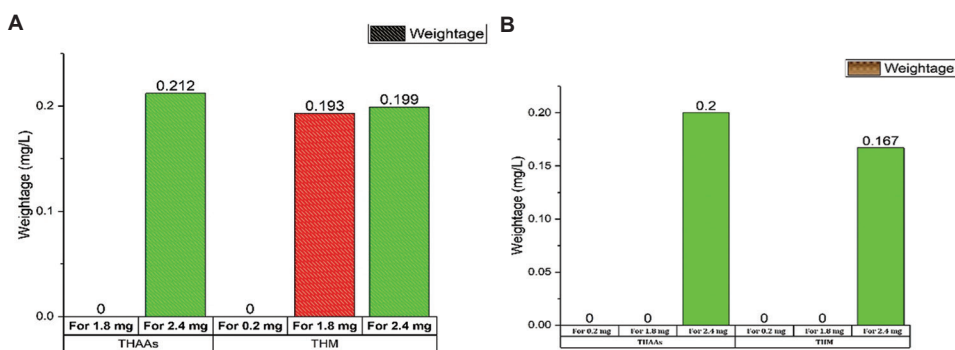


Figure 6. Concentration of chlorination byproducts in water samples passed through two pipe materials under varying chlorine dosages: (A) Galvanized iron; (B) High-density polyethylene
Abbreviations: THAA: Trihaloacetic acid; THM: Trihalomethane.

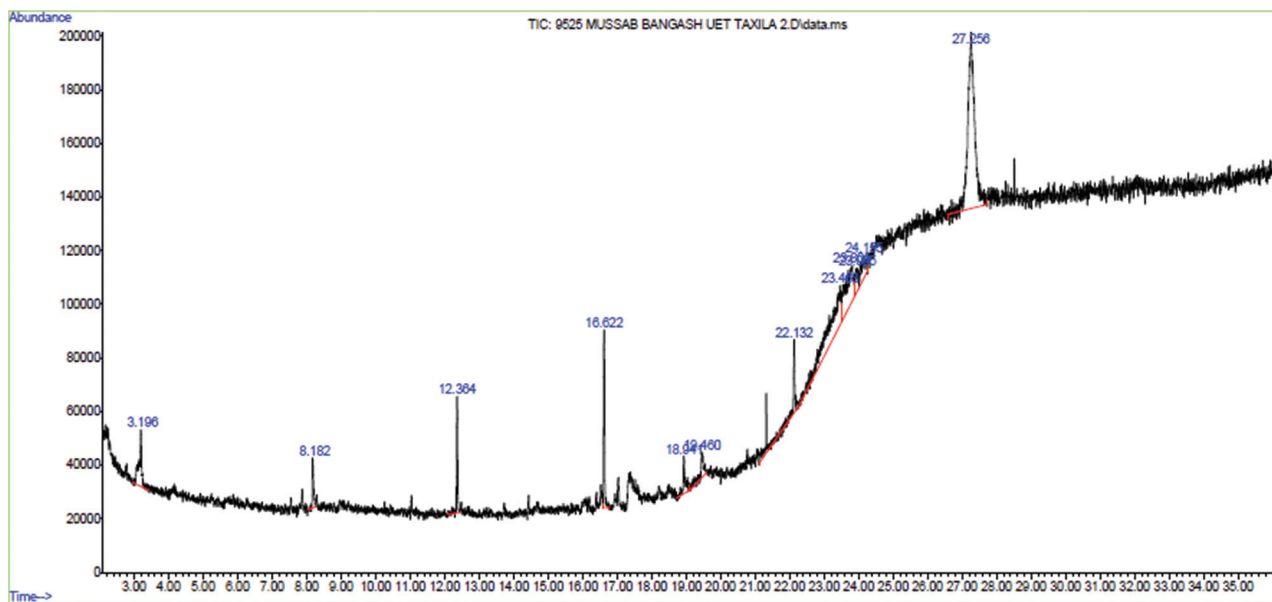
and THAAs to 59.5–123 $\mu\text{g/L}$ and 35.1–51.6 $\mu\text{g/L}$, respectively. These values are significantly lower than the concentrations found in this study, where 0.212 mg/L of THAAs and 0.199 mg/L of THMs were detected in GI pipes and 0.2 mg/L of THAAs and 0.167 mg/L of THMs in HDPE pipes.

In addition, mean concentrations of THMs vary significantly across countries. For instance, in Nigeria, the mean concentrations of THMs range from 0 to 1000 mg/L, with treated water samples containing 0 to 95 mg/L.¹⁸ In the US, up to 18 mg/L of DBPs have been detected in finished water and up to 22 mg/L of DBPs in distribution systems.¹⁹ In China, the average concentrations of THMs and HAAs throughout the treatment period were 19.9 mg/L and 3.4 mg/L, respectively.²⁰

3.2. Filtration media

In a study by Yu *et al.*,⁴⁰ prominent DBPs were partially removed through the use of cost-effective sand filtration media and a GAC filter. A composite filtration setup was developed, consisting of a top sand layer, a GAC layer beneath it, and a bottom layer of fine sand mixed with angular gravel. The gravel size ranged from 2 to 4 mm, designed to assess water quality as it passed through the medium.

To evaluate the effectiveness of the filtration media in removing chlorine DBPs, two separate filtration setups were investigated: the first setup consisting of sand media, and the second setup using GAC—recognized as one of the most versatile and widely used adsorbents for water purification.⁴¹



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Page: 1

Figure 7. Chromatogram of the galvanized iron pipe water sample after treatment with the first filtration media setup

Sand filtration media have been shown to be effective in removing turbidity and suspended particles when properly applied. In this study, the GI pipe-passed water sample, treated with sand filtration and subsequently analyzed using GC-MS after the application of a 2.4 mg/L chlorine dosage, shows a notable reduction in THMs in the resulting chromatogram. However, THAAs are still detected at a retention time of 3.196 min, identified at peak number 1 with an area of 1,115,036. The corresponding mass spectrum indicates a molecular mass of 165 g/mol, as shown in Figure 7, with the three best-hit mass spectra illustrated in Figure S8. Other non-DBP elements and their retention times are summarized in Table S6.

The absence of THMs and the presence of THAAs demonstrate the partial effectiveness of the sand filtration media setup in removing chlorine DBPs, as shown in Figure 8. This indicates that THM removal can be achieved by controlling the sources of DBP formation—particularly by reducing suspended and dissolved particles and retaining organic matter in water, which is considered a key precursor to chlorine DBPs. However, the presence of THAAs in the mass spectra challenges the full effectiveness of the first filtration media setup.

The second filtration media setup (GAC) was analyzed using GC-MS (ECD) under controlled conditions. For the GI pipe water sample treated with the GAC setup and exposed to the controlled chlorine dosage, the performance was evaluated using chromatograms and

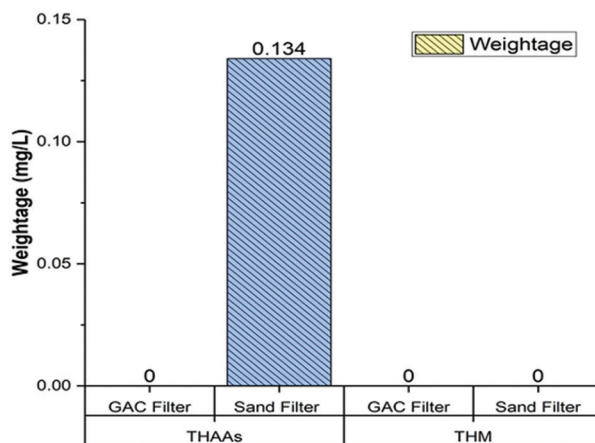


Figure 8. Concentration of chlorination disinfection byproducts in the galvanized iron pipe water samples after treatment with the first and second filtration media setups
Abbreviations: GAC: Granular activated carbon; THAA: Trihaloacetic acid; THM: Trihalomethane.

mass spectra. The resulting chromatograms did not show any detectable presence of the target DBPs (THMs or THAAs), nor any related halogenated compounds, as shown in Table S7. This demonstrates the strong removal capacity of the second filtration setup.

Based on the results, the first filtration setup (sand media) reduced THAAs in the GI pipe water sample from 0.212 mg/L to 0.134 mg/L, indicating a removal efficiency of 36.8%. It also reduced THMs from 0.193 mg/L and

0.199 mg/L to negligible levels, indicating an approximate removal efficiency of 99%. The second filtration setup (GAC media) achieved an estimated 99% removal of both THMs and THAAs, thereby demonstrating its superior performance.

In the HDPE pipe, water samples from Zone 3 were analyzed after passing through both the first (sand media) and second (GAC media) filtration setups. Based on the obtained chromatograms, no prominent chlorine DBPs—or related halogenated compounds—were detected. The absence of THMs and THAAs after filtration demonstrates the combined effectiveness of the pipe material and the filtration media in reducing precursors, including dissolved and suspended organic particles. This highlights adsorption-based filtration as a cost-effective abatement strategy. Both filtration setups successfully reduced the initially identified 0.2 mg/L of THAAs to negligible levels, indicating a high removal capacity for the HDPE pipe system. The reduction in dissolved organic carbon content following filtration is illustrated by the fluorescence spectra in Figure 9.

3.3. Comparison

From a comparative perspective on the formation of DBPs in water samples passed through GI and HDPE pipes, it was observed that in the GI pipe water samples, approximately 0.212 mg/L of THAAs and 0.199 mg/L of THMs were detected under a chlorine dosage of 2.4 mg/L, while approximately 0.193 mg/L of THMs were detected under a chlorine dosage of 1.8 mg/L in a controlled environment.

Similarly, in the HDPE pipe water sample, under a chlorine dosage of 2.4 mg/L, approximately 0.2 mg/L of THAAs and 0.167 mg/L of THMs were detected. These results indicate that lower chlorine dosages resulted in lower concentrations of chlorine DBPs. With a 33% increase in chlorine dosage, THAAs in the GI pipe water sample increased to 0.212 mg/L, and THMs increased by 3.11%, while a comparable trend was observed in the HDPE pipe water samples. This pattern supports the hypothesis that an increased chlorine dosage enhances reactions with NOM in the water and that longer contact time promotes the formation of DBPs.

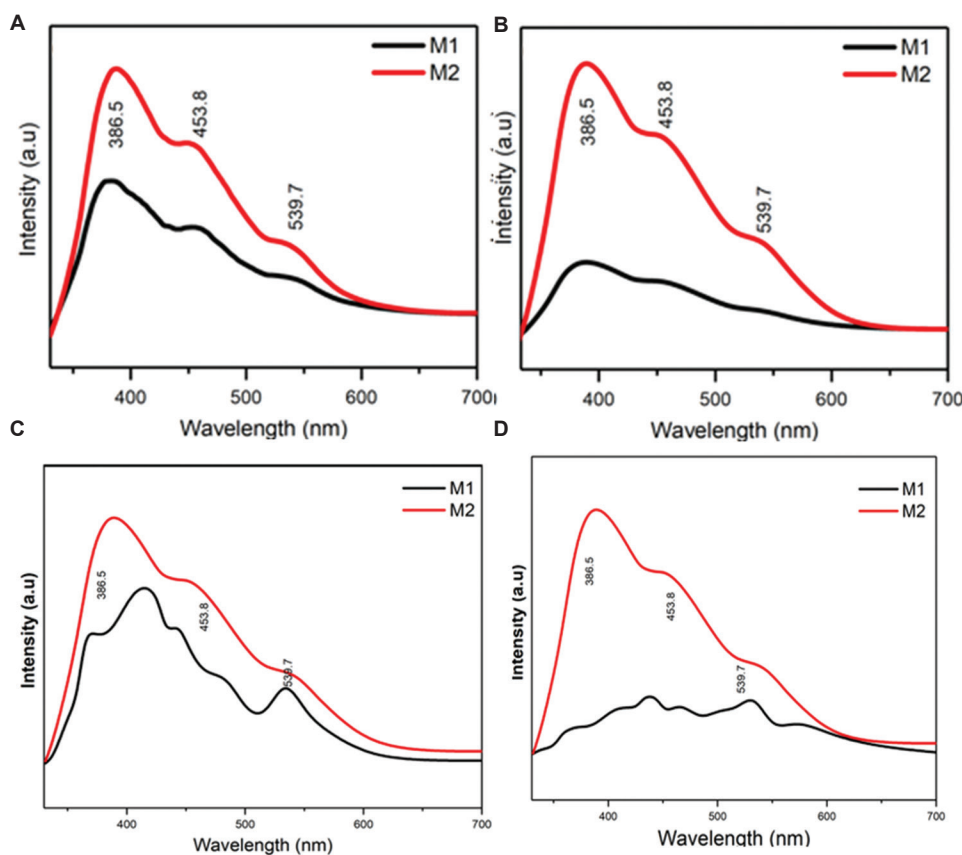


Figure 9. Fluorescence spectra of dissolved organic matter in water samples before (M2) and after (M1) filtration: (A) High-density polyethylene pipe—first filtration medium; (B) High-density polyethylene pipe—second filtration medium; (C) Galvanized iron pipe—first filtration medium; (D) Galvanized iron pipe—second filtration medium

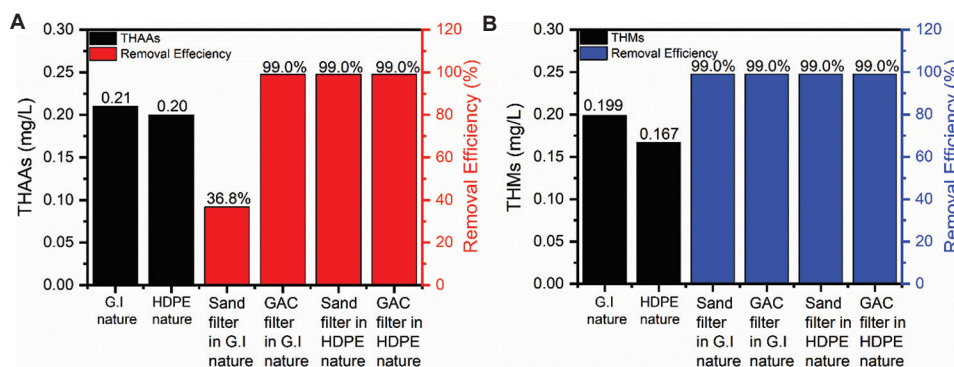


Figure 10. Comparison of detected chlorination disinfection byproducts in water samples and their removal efficiency by filtration setups
Abbreviations: GAC: Granular activated carbon; GI: Galvanized iron; HDPE: High-density polyethylene; THAA: Trihaloacetic acids; THM: Trihalomethane.

Moreover, it was observed that the second filtration media setup was more efficient than the first filtration media setup, particularly in the case of the GI pipe. In the GI pipe water sample, the first filtration media setup removed approximately 36.8% of THAAs and 99% of THMs. In contrast, for the HDPE pipe, both filtration setups were effective in removing approximately 99% of chlorine DBPs, due to the lower formation rate of chlorine DBPs. This shows that both filtration setups are effective in reducing DBPs, although their efficiency may vary depending on pipe material.

However, due to its non-absorptive nature, the second filtration media setup may not retain chemical contaminants through absorption, including DBPs. Instead, it is specifically designed for the adsorption of organic compounds, featuring a GAC layer positioned beneath a sand layer and above a gravel pack, and operates through a multi-stage process. Initially, suspended particles, particularly organic matter, are removed by the sand layer. The water then penetrates the fine GAC medium, where adsorption of DBPs occurs. Finally, the gravel layer provides additional filtration and helps stabilize the water's physical properties. This setup effectively removes THMs and THAAs under controlled conditions, as shown in Figure 10.

4. Conclusion

The following conclusions were drawn from the investigation of the water samples:

- (i) The formation of chlorine DBPs—particularly THMs and THAAs—increased with higher chlorine dosages under controlled conditions for both pipe materials
- (ii) The material properties of GI pipes—such as their tendency to corrode, release metal ions, and trap organic matter—contribute more significantly to the formation of chlorine DBPs compared to HDPE pipes
- (iii) Sand filtration is a cost-effective method for reducing chlorine DBPs; however, it is insufficient

on its own to achieve the desired DBP removal due to its limited effect on DOM. In contrast, the GAC filter—due to its high adsorptive capacity—can be considered a more effective and feasible option for removing chlorine DBPs under controlled chlorination. This highlights the superior performance of adsorption-based over absorption-based filtration techniques

- (iv) Optimizing chlorine dosage in the water supply can help balance effective disinfection while minimizing DBP formation.

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Conflict of interest

The authors declare that they have no competing interests.

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Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data

The data supporting the study's findings are available from the corresponding author upon request.

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ORIGINAL RESEARCH ARTICLE

Tuning enzyme concentration and particle size for LDPE biodegradation using lipase and laccase systems

Muhammad Jimada Aliyu¹, Benjamin Obinna Uloh¹, Moses Aderemi Olutoye¹, and Abdulhalim Musa Abubakar^{2*}¹Department of Chemical Engineering, School of Infrastructure, Process Engineering, and Technology, Federal University of Technology Minna, Minna, Niger State, Nigeria²Department of Chemical Engineering, Faculty of Engineering, Modibbo Adama University, Girei, Adamawa State, Nigeria**Abstract**

The persistent accumulation of low-density polyethylene (LDPE) waste in the environment has necessitated the exploration of eco-friendly degradation methods. This study aimed to degrade LDPE films using lipase (Lip) and laccase (Lac) enzymes obtained from *Aspergillus flavus*. The effects of enzyme concentration and LDPE particle size on the degradation rate were examined. LDPE samples were prepared in three particle sizes: 0.5, 1, and 2 cm. These samples were incubated with Lip, Lac, and a combination of both enzymes (Lip-Lac) at two concentration levels: 50% and 100% (v/v). The degradation process or extent of degradation was monitored over 10 and 30 days by analyzing percentage weight loss and observing surface morphology using scanning electron microscopy (SEM). Results indicated that the highest degradation occurred in the Lip-Lac system with 0.5 cm particles at 100% enzyme concentration, yielding a weight loss of 23.81% after 30 days, thereby suggesting that the blend performed better than the single enzyme system. SEM analysis confirmed extensive surface erosion and cracking in smaller particles treated at higher enzyme concentrations. This study also demonstrated that both enzyme concentration and LDPE particle size significantly influence biodegradation efficiency. Taken together, the bifunctional enzyme system is an efficient treatment method for enhancing the degradation process of plastics such as LDPE.

Keywords: LDPE plastic; Enzymatic degradation; *Aspergillus flavus*; Lipase; Laccase

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Abdulhalim Musa Abubakar
(abdulhalim@mau.edu.ng)**Citation:** Aliyu MJ, Uloh BO, Olutoye MA, Abubakar AM. Tuning enzyme concentration and particle size for LDPE biodegradation using lipase and laccase systems. *Explora Environ Resour.* 2025;2(3):025220042.
doi: 10.36922/EER025220042**Received:** May 28, 2025**1st revised:** June 2, 2025**2nd revised:** July 17, 2025**3rd revised:** July 29, 2025**Accepted:** July 30, 2025**Published online:** August 18, 2025**Copyright:** © 2025 Author(s). This is an Open-Access article distributed under the terms of the Creative Commons Attribution License, permitting distribution, and reproduction in any medium, provided the original work is properly cited.**Publisher's Note:** AccScience Publishing remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.**1. Introduction**

Plastics are primarily made of synthetic polymers consisting of chains of carbon atoms with other elements—such as hydrogen, oxygen, nitrogen, and sulfur—attached to them.¹ Polymers are widely used due to their durability and stability. Common examples include polystyrene,² polyethylene (PE),³ polyurethane,⁴ nylon,⁵ PE terephthalate (PET),⁶ polypropylene,⁷ and polyvinyl chloride, all of which are present in almost every aspect of our lives.⁸ Since the discovery of plastics in the 1950s, there has been a significant increase in their production to meet the global demand.⁹ It is estimated that more than 6.3 billion metric tons of plastic waste have been generated over the past 75 years,¹⁰

from a total of over 450 million tons produced annually worldwide.^{11,12} This increase in production is mainly due to the manufacturing of single-use disposable plastics, which make up around 50% of all plastic products. The significant increase in plastic waste disposal, which consists of materials that do not easily break down and thus remain in the environment, has resulted in land¹³ and ocean pollution.^{14,15} Due to their practical physicochemical qualities (e.g., crystallinity, molecular weight, hydrophobicity, and additive composition), some polymers, such as low-density PE (LDPE), are utilized in a variety of applications.¹⁶ At present, PE is derived from thin polyolefin plastic sheets and films utilized in the packaging of products. Furthermore, plastic bags constitute 60% of the total plastic production, which includes LDPE, and are considered the most common form of solid waste.¹⁷ LDPE is characterized by good strength, chemical resistance, flexibility, and transparency. Its hydrophobic nature prevents microorganisms from accessing it.¹⁸ The resistance of LDPE to microbial degradation is largely due to its high molecular weight, which limits enzyme accessibility, and the absence of functional groups, which prevents effective microbial attachment or breakdown.¹⁹ In addition, its low surface energy further hinders microbial colonization by reducing surface wettability and interaction with enzymes.²⁰ LDPE is characteristically inert, and its rate of degradation is extremely slow, taking several decades, which causes it to remain in nature for an extended period. Due to its complicated 3D structure and large molecular weight, it is recalcitrant to degradation.²¹ Despite being widely used for managing LDPE waste, incineration and landfilling methods are linked to several environmental drawbacks. Thus, biodegradation has been demonstrated to be the optimal choice for managing plastic waste.²²

Since it is virtually impossible to eliminate their manufacture, there is growing interest in developing more effective and rapid methods for reducing the accumulation of these widely used yet environmentally harmful plastic items.^{23,24} It is highly likely that scientists, who are constantly engaged in researching and developing biologically safe methods, will identify a solution to address the rapid accumulation of plastic waste. Researchers have identified particular microorganisms that can generate enzymes capable of decomposing these polymers.²⁵⁻²⁸ Enzymes that degrade the carbon backbone of polymers are classified under the hydrolase family, including esterases,²⁹ lipases (Lips),³⁰ depolymerases,³¹ and PETases.³² Buchholz *et al.*³³ enumerated and discussed enzymes that require water to function. These enzymes can break down the plastic polymer into simpler monomeric units that are easily decomposable within the environment and can serve as a carbon source for microorganisms.³⁴ The microorganisms

then further metabolize these units into end products, such as CO₂, H₂O, CH₄, and N₂. Ehrhardt and Rothenberg³⁵ noted that green hydrogen is also a realizable outcome. The by-products of microbial plastic degradation offer significant potential for addressing plastic pollution by repurposing these products in other applications, thereby creating a recycling loop for these harmful materials that are otherwise difficult to eliminate and contribute to environmental pollution. Municipal and public waste management is currently the biggest environmental issue affecting emerging countries, especially Nigeria,³⁶⁻³⁹ where some cities are stench-filled with tons of uncontrollable solid and plastic waste.⁴⁰⁻⁴⁴ As a result of Nigeria's current economic state, LDPE sachets are commonly used for packaging water, popularly known as "pure water."⁴⁵ These pure water sachets (PWS) represent the most affordable packaging option.⁴⁶ While the use of LDPE has gained widespread acceptance across various communities, it has unfortunately resulted in the rise of a solid waste stream, as LDPE degrades at an extremely slow rate.

This study was initiated to investigate how Lip and laccase (Lac) enzymes impact the degradation rate of LDPE wastes (specifically PWS). While several studies have explored LDPE degradation using microbial enzymes, most have focused on either enzyme concentration or polymer structure in isolation. For instance, Liu *et al.*⁴⁷ examined LDPE degradation using *Yarrowia lipolytica*, but without optimizing for both enzyme load and particle size simultaneously. Mazaheri and Nazeri⁴⁸ reported the effectiveness of *Stenotrophomonas* spp. and *Alcaligenaceae* in degrading LDPE, demonstrating microbial potential, though their work did not incorporate enzymatic concentration gradients or particle size variations as interactive variables. Khandare *et al.*⁴⁹ used marine bacteria for LDPE biodegradation and highlighted particle preparation and treatment time, but lacked an integrative assessment of enzyme-specific parameters, such as those studied with *Aspergillus flavus* enzymes in this research. DSouza *et al.*⁵⁰ worked with an *Aspergillus* consortium to degrade LDPE under controlled conditions, yet did not combine enzyme concentration and plastic size optimization, a gap this study aims to bridge using a bifunctional Lip-Lac system. The novelty of the study is that it is the first to simultaneously optimize both enzyme concentration and plastic particle size to maximize LDPE degradation using enzymes from *A. flavus*. The study supports Sustainable Development Goal (SDG) 12 (Responsible Consumption and Production) and SDG 13 (Climate Action). By utilizing microbial enzymes from *A. flavus* (a naturally occurring fungus) for the degradation of LDPE plastic waste, our study promotes the development of green technologies aligned with the

United Nations Agenda 2030. Our proposed enzymatic approach holds promise for application in decentralized waste treatment facilities, bioreactors for plastic waste remediation, and as a pre-treatment step to accelerate subsequent biodegradation. More importantly, such eco-friendly strategies can reduce the environmental footprint of incineration and landfilling, which aligns with circular economy principles and global sustainability targets.

2. Materials and methods

2.1. Materials

Low-density PE (LDPE) samples (PWS) were collected from dumpsites within Gidan Kwano village (Nigeria). Enzymes used were produced at the Step B Laboratory, Centre for Genetic Engineering and Biotechnology, Federal University of Technology, Minna (FUTMinna), Bosso Campus, Nigeria. The incubation media used for the LDPE samples and all analytical chemicals were procured from the Department of Chemical Engineering, FUTMinna (Nigeria).

2.2. Preparation of PE films

The LDPE samples were cut into 0.5×0.5 , 1×1 , and 2×2 cm strips and weighed using a digital weighing balance (MAB220, Wensar, India), as previously reported.^{49,51} The samples underwent a rigorous cleaning process, which involved immersion in a solution of 70% ethanol for 30 min, followed by washing with distilled water, and drying in an oven at 50°C for 20 min.

2.3. Production of degrading enzymes

Ab initio, the medium was prepared through the following steps. First, the Sabouraud Dextrose Agar was prepared by dissolving 20 g of the powdered non-synthetic medium in two separate 2000 mL conical flasks labeled “Lipase” and “Laccase,” respectively, each containing distilled water.⁵² For the Lip medium, 2 mL of olive oil (0.1% substrate concentration) was added. For the Lac medium, 2 mL of guaiacol (0.1% substrate concentration) was added.⁵³ Both media were sterilized in an autoclave at 121°C for 3 h under a pressure of 1.5 N/m. After autoclaving, the medium was removed from the autoclave and allowed to cool before inoculation. The 72-h-old broth culture of *A. flavus* (5 mL) was inoculated into 1 L of each medium and incubated for 5 days on a shaker incubator at ambient or room temperature ($25\text{--}28^\circ\text{C} \pm 2^\circ\text{C}$). After 5 days, crude enzymes were readily produced. The crude enzyme solutions were centrifuged at 4000 rpm using a high-speed refrigerated centrifuge. The supernatants contained the crude enzymes, while the sediments consisted of fungal spores. The Bradford protein assay was used to quantify the total protein content in the crude extract, using bovine

serum albumin as the standard.⁵⁴ The crude enzyme concentration was measured at 10 mg/mL (20% purity). To reduce the concentration for further assays, 10 mL of the extract was diluted with an equal volume of distilled water, resulting in a final protein concentration of 5 mg/mL, while maintaining the purity at 20%.

2.4. Incubation of PE samples

2.4.1. Isolation of LDPE film in the single-enzyme system

The pre-weighed LDPE films (0.5×0.5 , 1×1 , and 2×2 cm) were aseptically transferred into three pre-labeled 100 mL conical flasks, respectively. About 20 mL of the prepared degrading enzyme was added to each conical flask and thoroughly mixed with the LDPE samples. For assessing the effect of different enzyme concentrations, the prepared LDPE strips (1×1 cm each) were transferred into two pre-labeled 100 mL conical flasks, respectively.⁵⁵ Then, 100% pure Lip and a 50% diluted Lip solution were added separately to each flask and thoroughly mixed with the LDPE samples. To minimize heat dissipation and preserve a sanitized environment, a foil stopper was used to seal the conical flasks.¹² The procedure was repeated for Lac. After 10 days of incubation, samples were collected, and the LDPE films were cleaned with ethanol and distilled water, then allowed to air-dry naturally. Following that, the LDPE samples were evaluated to determine their level of biodegradability. After 30 days, the process was terminated. The 30-day incubation period was selected to allow sufficient time for measurable enzymatic degradation of LDPE by Lac and Lip.

2.4.2. Isolation of LDPE film in the two-enzyme system

The pre-weighed LDPE films (0.5×0.5 and 2×2 cm) were transferred into two pre-labeled 100 mL conical flasks, respectively. Lip and Lac enzymes (20 mL) were added to each conical flask and thoroughly mixed with the LDPE samples. For assessing the effect of different enzyme concentrations, the prepared LDPE strips (1×1 cm) were transferred into two pre-labeled 100 mL conical flasks, respectively.⁵⁵ The Lip-Lac enzyme mixture at 100% and 50% concentrations was added to the two conical flasks, respectively. To minimize heat dissipation and preserve a sanitized environment, a foil stopper was used to seal the conical flasks.¹² The solution was gently stirred to obtain a homogeneous mixture. The LDPE films were cleaned using ethanol and distilled water, then allowed to air-dry naturally. Biodegradation of the LDPE samples was analyzed after 10 days of incubation. Following that, the LDPE samples were evaluated to determine their level of biodegradability. The process was terminated after 30 days, in accordance with Yang *et al.*⁵⁶

2.5. Physicochemical analysis of LDPE degradation

2.5.1. Determination of dry weight of residual LDPE

To obtain the dry weight of residual LDPE, the LDPE films were extracted from the degradation medium and cleaned using a 70% ethanol solution, followed by rinsing with distilled water. The purified LDPE films were allowed to air-dry to a constant weight. The percentage of weight reduction was calculated using Equation I.⁵¹

$$\text{Percent weight loss (\%)} = \frac{\text{Initial sample weight} - \text{Final sample weight}}{\text{Initial weight}} \times 100 \quad (I)$$

2.5.2. Scanning electron microscopy (SEM)

Following weight analysis, the LDPE samples were cut into 5 mm fragments. To observe the surface morphology of the LDPE, SEM (SU3800/SU3900, Hitachi High-Tech, Japan) was employed.⁵⁷ Each sample was carefully mounted onto a specimen holder (stub) to ensure proper placement and fit within the SEM chamber, with all fragments trimmed to suitable dimensions for imaging.

3. Results and discussion

3.1. Effect of enzyme concentration on LDPE degradation

After incubation of LDPE in 50% and 100% enzyme concentrations for 10 and 30 days, the weight of the residual samples was measured (Table 1). The initial weight and size of the material influence degradation. Smaller particles have a higher surface area-to-volume ratio, facilitating better enzyme interaction and, consequently, higher degradation rates. Therefore, reducing the initial size of the material can enhance the degradation process. As displayed in Table 1, Lip and Lac enzymes were incubated

Table 1. Percentage weight loss of LDPE samples at different enzyme concentrations

Enzyme	Concentration (%)	Initial weight (g)	Final weight (g)		Weight loss (%)	
			Day 10	Day 30	Day 10	Day 30
Lip	50	0.0036	0.0035	0.0034	2.78	5.56
	100	0.0036	0.0034	0.0032	5.56	11.11
Lip-Lac	50	0.0043	0.0041	0.0039	4.65	9.30
	100	0.0046	0.0043	0.0039	6.52	15.21
Lac	50	0.0039	0.0039	0.0037	0.00	5.13
	100	0.012	0.012	0.011	0.00	8.33

Abbreviations: Lac: Laccase; LDPE: Low-density polyethylene; Lip: Lipase.

with the LDPE samples at 50% and 100% concentrations. At 50% Lip concentration, the weight reduced from 0.0036 to 0.0035 g (day 10) and 0.0034 g (day 30), corresponding to 2.78% and 5.56% LDPE weight loss, respectively, thereby indicating greater degradation over time. The 100% enzyme concentration observed a higher percentage weight loss compared to the 50% enzyme concentration; for instance, the Lac enzyme system reported 5.13% and 8.33% weight loss at 50% and 100% Lac concentration, respectively, after 30 days. Likewise, Liu *et al.*⁴⁷ recorded a weight loss of 8.9% and 11.8% for LDPE films at day 7.

In terms of degradation efficiency, LDPE incubation in 100% Lip, 100% Lip-Lac, and 100% Lac recorded 11.11%, 15.21%, and 8.33% weight loss, respectively. This observation is relatively consistent with the 10.15% loss reported by Mazaheri and Nazeri⁴⁸ with *Stenotrophomonas* spp. enzymes. This implies that LDPE was more effectively degraded by the Lip-Lac enzyme system, suggesting that while Lip alone exhibits notable degradation efficiency, the Lip-Lac enzyme system has much higher degradation efficiency. In addition, higher enzyme concentrations enhance the degradation efficiency, as observed from Table 1. Our findings corroborated that of Kunlere *et al.*,⁵⁸ who used *A. flavus* to degrade LDPE. Concentrations below 50% are likely to result in even lower degradation rates. Given that 50% concentration already yields modest weight loss (*e.g.*, 5.56% in the Lip system), reducing the concentration further would likely diminish the degradation efficiency, making it less effective for practical purposes. Increasing the incubation period beyond 30 days may further enhance degradation, as the enzymes have more time to act on the material. Conversely, reducing the incubation time might not allow for sufficient degradation, leading to lower weight loss percentages. Therefore, longer incubation periods are generally favorable for improved degradation. Yao *et al.*⁵⁹ reported a high weight loss on day 30 for their LDPE film samples. Similarly, in this study, optimal degradation was observed on day 30 across all systems. For instance, the Lip-Lac system at 100% concentration reported weight loss of 15.21% on day 30 compared to 6.52% on day 10. This indicates that prolonged exposure of LDPE to the enzyme system enhances the degradation process. In a previous study, untreated LDPE reported a weight loss of 38.82% using a combined system of Lip, Lac, esterase, and manganese peroxidase.⁵³ Figures 1-4 illustrate the relationship between enzyme concentration and LDPE weight loss, as derived from the data in Table 1.

A high weight loss denotes effective biodegradation, indicating that the material is efficiently broken down by the enzymes. Conversely, a low weight loss suggests limited degradation, which may be inadequate for practical

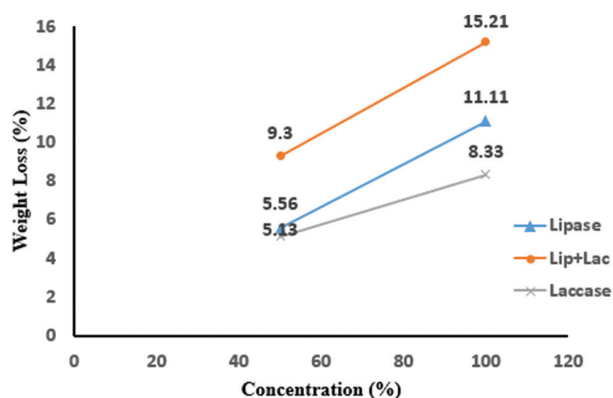


Figure 1. Weight loss (%) of low-density polyethylene as a function of enzyme concentration for all systems (lipase [Lip], laccase [Lac], and Lip-Lac)

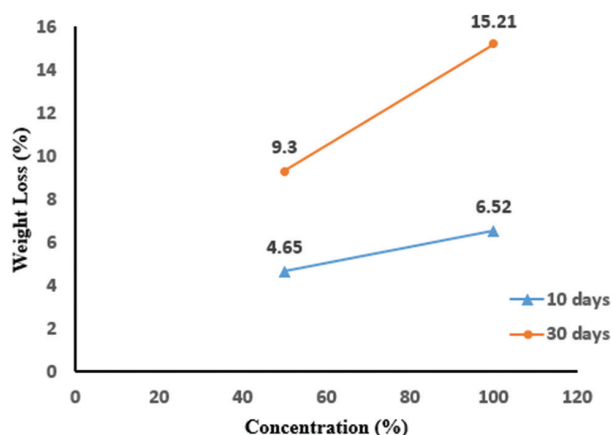


Figure 3. Weight loss (%) of low-density polyethylene as a function of enzyme concentration for the lipase-laccase enzyme system

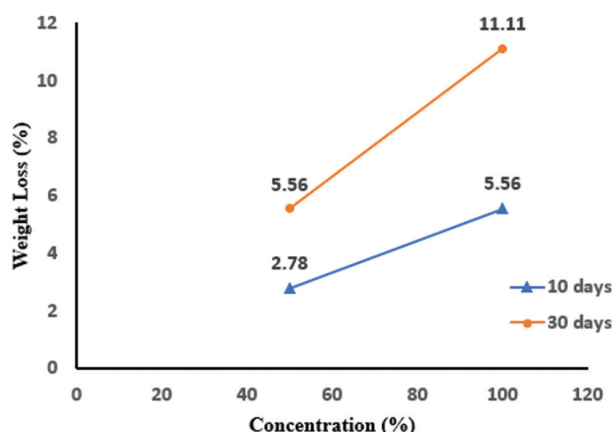


Figure 2. Weight loss (%) of low-density polyethylene as a function of enzyme concentration for the lipase enzyme system

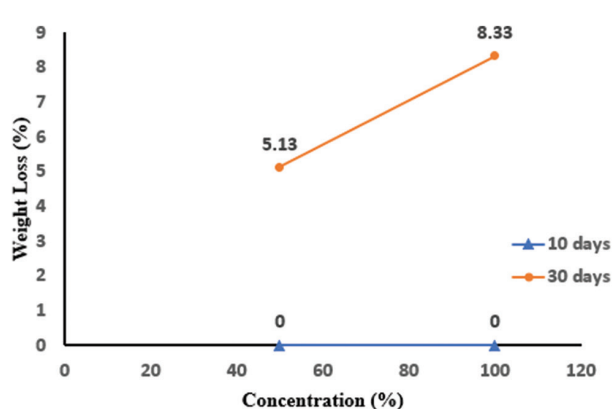


Figure 4. Weight loss (%) of low-density polyethylene as a function of enzyme concentration for the laccase enzyme system

applications. Therefore, achieving higher weight loss is desirable for effective waste management. The Lip-Lac system exhibited the most significant weight loss (Figure 3). At 100% concentration, the weight loss reaches 15.21%, indicating a high degradation rate. This suggests that the combined action of Lip and Lac enzymes synergistically enhanced LDPE degradation.

3.2. Effect of LDPE particle size on LDPE degradation

Harrat *et al.*⁶⁰ previously reported weight loss of 7.6% and 5.53% using *Candida tropicalis* SLNEA04 and *Rhodotorula mucilaginosa* SLNEA05, respectively. Their findings are consistent with our results for the Lip system on day 10 for 0.5–1 cm LDPE samples. Table 2 presents the initial and final weights of LDPE samples with varying particle sizes after enzymatic treatment. The data indicate that smaller particles (0.5 cm) experienced greater weight loss compared to larger ones (1.5 and 2.0 cm). This suggests that reducing particle size enhances the surface area

available for enzymatic action, leading to more efficient degradation. The influence of incubation time is most pronounced in the 0.5 cm particle size across all enzyme systems, particularly in the Lip-Lac system. Weight loss percentages increased significantly from day 10 to day 30, indicating that longer exposure enhances degradation. If the incubation period were extended to 60 days, it would be reasonable to anticipate further degradation, potentially leading to higher weight loss percentages, assuming enzyme activity remains stable over time. Notably, no formal enzyme activity assay was conducted before the degradation experiments. This assumption is supported by DSouza *et al.*,⁵⁰ who reported a peak weight loss of 26.15% after 55 days of incubation. Similarly, Awasthi *et al.*⁶¹ conducted experiments over a comparable timeframe (10–30 days) using *Rhizopus oryzae*, a fungus known to secrete Lip.

According to Table 2 and Figures 5-8, the smallest particle size of 0.5 cm consistently resulted in the highest

Table 2. Percentage weight loss of enzyme-treated LDPE samples with varying particle sizes

Enzyme	Sample size (cm)	Initial weight (g)	Final weight (g)		Weight loss (%)	
			Day 10	Day 30	Day 10	Day 30
Lipase	0.5	0.0015	0.0014	0.0012	6.67	20.00
	1.0	0.0036	0.0034	0.0032	5.56	11.11
	2.0	0.0117	0.0116	0.0114	0.85	2.56
Lip-Lac	0.5	0.0021	0.0019	0.0016	9.52	23.81
	1.0	0.0046	0.0043	0.0039	6.52	15.21
	2.0	0.0111	0.0108	0.0104	2.70	6.31
Laccase	0.5	0.0016	0.0016	0.0014	0.00	12.5
	1.0	0.0038	0.0037	0.0035	2.63	7.89
	2.0	0.0105	0.0105	0.0103	0.00	1.90

Abbreviations: Lac: Laccase; LDPE: Low-density polyethylene; Lip: Lipase.

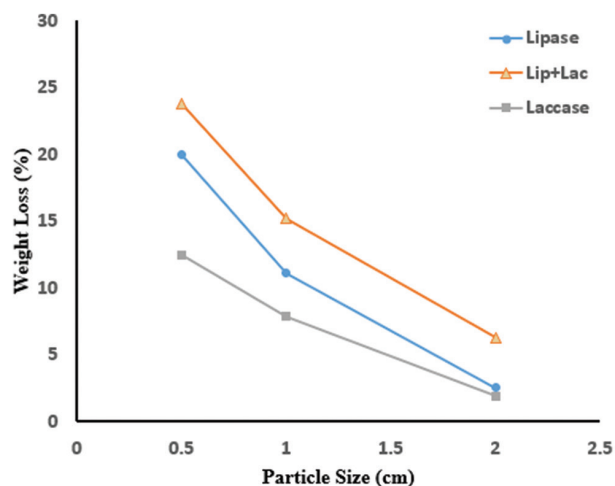


Figure 5. Relationship between low-density polyethylene weight loss (%) and particle size for all enzyme systems (lipase [Lip], laccase [Lac], and Lip-Lac).

percentage weight loss across all enzyme systems. However, on day 10, 0% weight loss was recorded for particle sizes of 0.5 and 2 cm in the Lac system, despite Lac being among the main fungal enzymes involved in PE biodegradation.⁶² Smaller particle sizes provide a larger surface area-to-volume ratio, facilitating better enzyme-substrate interactions. This principle is well-established in biodegradation studies, where increased surface area enhances microbial and enzymatic activity, thereby resulting in higher degradation rates. During LDPE degradation, several physical and mechanical properties have been reported to decline, including tensile strength, tear strength, elongation at break, Young's Modulus, stiffness, hardness, and weight by 10.15%.⁶³

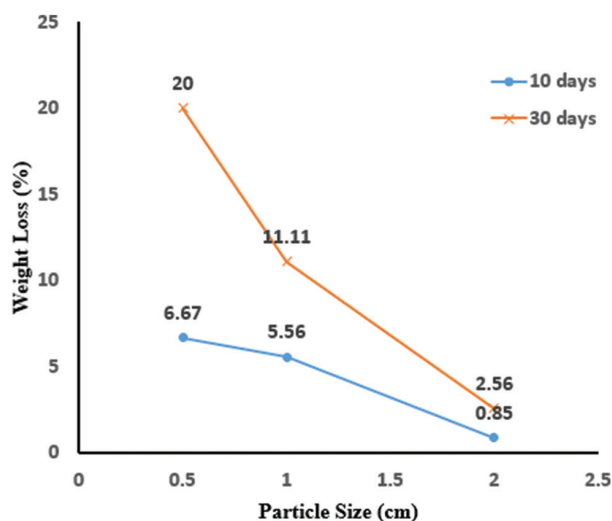


Figure 6. Relationship between low-density polyethylene weight loss (%) and particle size for the lipase enzyme system

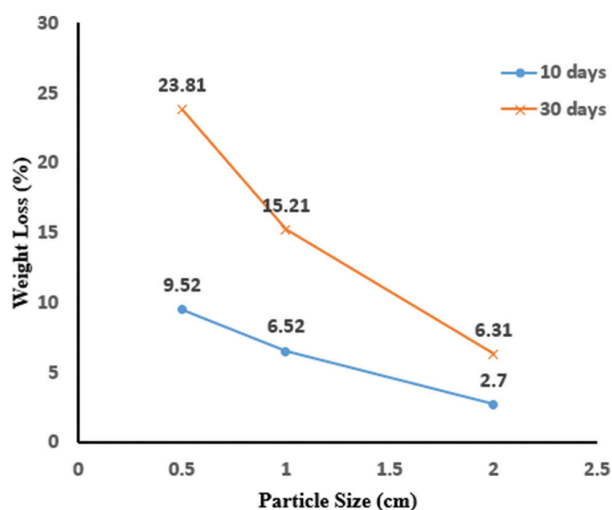


Figure 7. Relationship between low-density polyethylene weight loss (%) and particle size for the lipase-laccase enzyme system

Reducing the particle size below 0.5 cm could potentially increase degradation rates due to a greater surface area. However, practical limitations, such as handling difficulties and potential agglomeration, may arise. Conversely, increasing the particle size beyond 2 cm would likely decrease degradation efficiency, as the reduced surface area would limit enzyme access to the polymer chains. Optimal LDPE biodegradation is achieved by combining smaller particle sizes (0.5 cm) with higher enzyme concentrations (100%). Such a combination maximizes the surface area for enzyme interaction and ensures sufficient enzymatic activity to effectively break down the polymer chains. The Lip-Lac system demonstrates the most favorable results,

consistently achieving higher weight loss percentages across all particle sizes. This synergistic effect enhances LDPE breakdown, making it the preferred enzymatic treatment for effective biodegradation.

3.3. Microscopy imaging of enzyme-treated LDPE samples

3.3.1. Effect of different enzyme concentrations

Rough surfaces and pore structures are observed in all LDPE samples incubated with enzymes, and the features are more significant in samples incubated in 100% enzyme concentration, likely due to enzymatic activity on the LDPE samples.⁶⁴ Figures 9-12 display the SEM images of LDPE films (1 × 1 cm). Each image illustrates the surface morphology of LDPE under different treatment conditions: untreated/control (Figure 9), Lip-treated (Figure 10), Lip-Lac-treated (Figure 11), and Lac-treated (Figure 12). The consistent sample size and imaging technique across these figures facilitate a comparative analysis of the effects of enzymatic treatments on LDPE surface degradation. The SEM images in Figure 9 serve as a baseline, showcasing the pristine condition of the LDPE film without any enzymatic treatment. The smooth and defect-free surface

confirms the material's resistance to degradation in the absence of enzymatic activity. These control images are crucial for comparing the extent of degradation observed in the enzyme-treated LDPE samples. It was previously established that the PE surface changes after 30 days of incubation with enzymes.⁶⁵

Figure 9, representing the control LDPE film, exhibits a smooth and uniform surface, indicating no degradation. In contrast, Figure 10, depicting the LDPE film treated with Lip, displays noticeable surface alterations, such as pits, grooves, and rough textures, similar to a previous observation using *Bacillus* spp. YP1.⁶⁶ Das and Kumar⁶⁷ inferred that Lip treatment initiates the LDPE degradation process, leading to polymer surface breakdown. Figure 10 presents the SEM images of LDPE films treated with Lip at different magnifications. The images reveal the formation of surface irregularities, including pits and cracks, indicating the onset of enzymatic degradation.^{68,69} Higher magnifications highlight more detailed degradation features, such as micro-cracks and increased surface roughness. The presence of white and dark areas in the images corresponds to differences in electron density, with white regions typically representing denser or elevated areas and dark regions indicating depressions or voids.⁷⁰ Figure 11 comprises six SEM images (at different magnifications) of LDPE films treated with a combination of Lip and Lac at various concentrations. The images demonstrate that higher enzyme concentrations lead to more pronounced surface degradation, evident through extensive cracking, pitting, and roughness.⁷¹ At higher magnifications, the images reveal finer degradation details, such as micro-fissures and increased porosity. The similarities across the images include the presence of degradation features, while differences arise from the varying degrees of surface damage corresponding to enzyme concentration.

Figure 12 displays six SEM images of LDPE films treated with Lac at different concentrations. Sowmya *et al.*⁷² assessed the degradation potential of crude Lac on PE using weight loss, SEM, and Fourier transform infrared (FTIR) analysis. Consistent with the present study, the

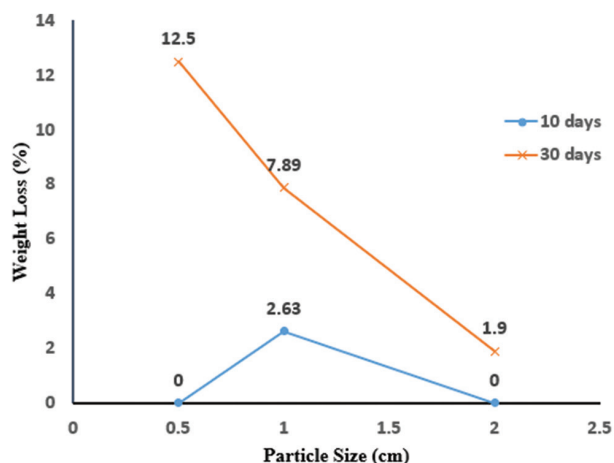


Figure 8. Relationship between low-density polyethylene weight loss (%) and particle size for the laccase enzyme system

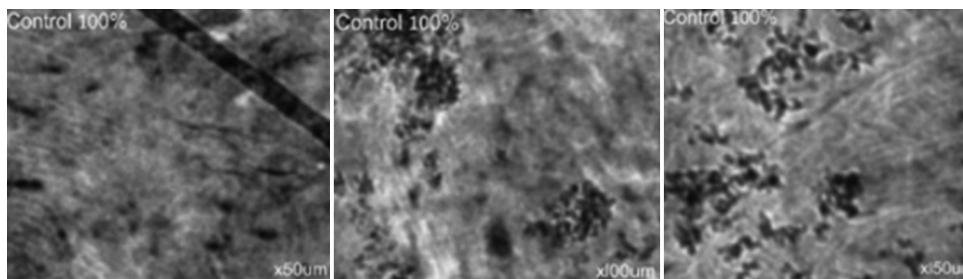


Figure 9. Microscopic images of untreated/control low-density polyethylene films (1 × 1 cm). Magnifications: ×50 (left); ×100 (middle); ×150 (right).

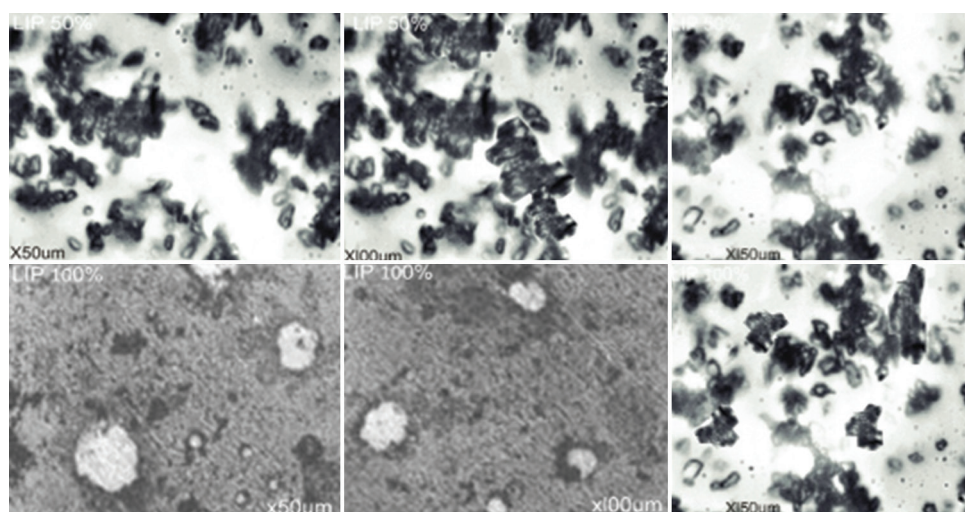


Figure 10. Microscopic images of low-density polyethylene films (1 × 1 cm) treated with lipase. Magnifications: ×50 (left); ×100 (middle); ×150 (right).

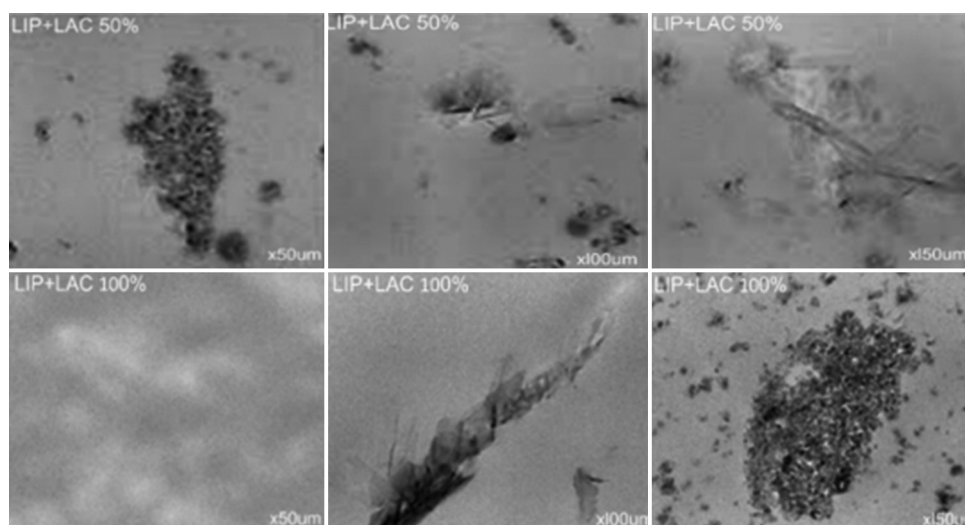


Figure 11. Microscopic images of low-density polyethylene films (1 × 1 cm) treated with lipase-laccase enzymes. Magnifications: ×50 (left); ×100 (middle); ×150 (right).

SEM images reveal that higher Lac concentrations induce more significant surface degradation, characterized by increased roughness, cracking, and pit formation. These degradation features align with observations reported by Mumtaz *et al.*⁶⁸ However, the severity and extent of surface damage differ across the images and correlate directly with the enzyme concentration used.

3.3.2. Effect of different LDPE particle sizes

Figure 13 presents SEM images of untreated LDPE films at three different particle sizes: 0.5, 1, and 2 cm. The first image (left; 0.5 cm) appears darker, indicating a smoother and more uniform surface with minimal electron scattering. The second image (middle; 1 cm) exhibits a gray tone, suggesting slight surface irregularities. The third

image (right; 2 cm) is lighter, implying increased surface roughness or contamination. Variations in shading reflect differences in surface topography and electron density, with darker areas representing smoother surfaces and lighter areas indicating rougher textures.⁷³ The images displayed irregular/rough surfaces observed for LDPE samples with a particle size of 0.5 cm in all enzyme systems and less rough surfaces as the sizes increase. The surface erosion observed suggests high enzymatic activity on the films compared to the smooth surface observed in the control samples.⁷⁴

The control SEM images in Figure 13 serve as a baseline, showcasing the pristine condition of LDPE films without enzymatic treatment. The smooth and uniform surfaces confirm the material's resistance to degradation in

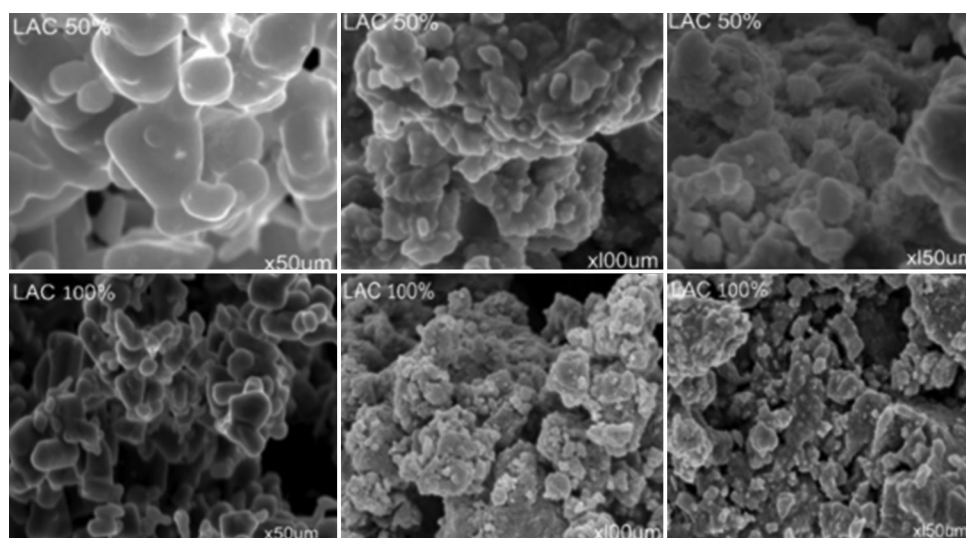


Figure 12. Microscopic images of low-density polyethylene films (1 × 1 cm) treated with laccase. Magnifications: ×50 (left); ×100 (middle); ×150 (right).

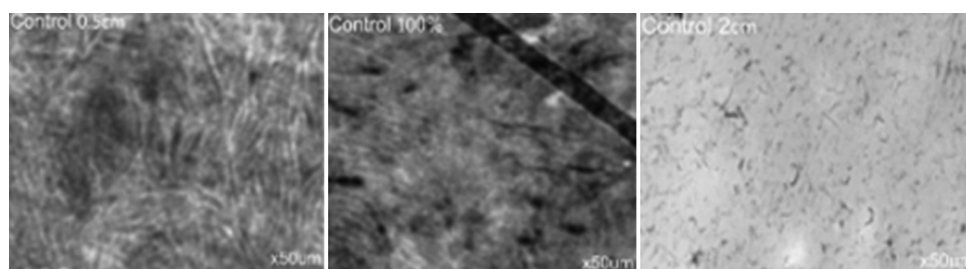


Figure 13. Microscopic images of untreated/control low-density polyethylene films with particle sizes of 0.5 (left), 1 (middle), and 2 cm (right). Magnifications: ×50.

the absence of enzymatic activity. These images are crucial for comparing the extent of degradation observed in the enzyme-treated samples. Figure 14 comprises nine SEM images arranged into three columns, with each column corresponding to a specific particle size (0.5 [left], 1 [middle], and 2 cm [right]) and each row corresponding to a specific magnification (50× [top], 100× [middle], and 150× [bottom]). When the particle size is 0.5 cm, the images (magnification: 50×) revealed significant surface degradation characterized by pits, cracks, and rough textures. Similar characteristics were observed by Khandare *et al.*⁴⁹ after 30 and 90 days of incubation for control and bacterial-degraded LDPE. These features indicate effective enzymatic action by Lip on smaller particles. The images for the 1 cm samples displayed moderate degradation with visible surface irregularities, though less pronounced than in the 0.5 cm samples. However, a minimal surface change was observed when the particle size is 2 cm, suggesting that larger particles are less susceptible to Lip-mediated degradation. Similarities across the images include the presence of degradation features, while the differences lie in the severity and extent of surface damage, which

correlate with particle size and magnification levels, as also observed by Azeko *et al.*⁷⁵

The SEM images in Figures 14-16 reveal degradation patterns consistent with established literature, such as surface roughness, cracks, and pits resulting from enzymatic action. However, unexpected features, such as excessive degradation in larger particles or minimal changes in smaller ones, could indicate anomalies in the experimental setup or enzyme activity. Such deviations warrant further investigation to ensure consistency with known biodegradation mechanisms. Figure 15 mirrors the LDPE structure observed in Figure 14, displaying SEM images for the same particle sizes and magnifications but treated with a combination of Lip and Lac enzymes. At 0.5 cm particle size, the structure exhibited extensive surface degradation, including deep cracks, pits, and erosion; according to Yang *et al.*,⁵⁶ it indicates a synergistic effect of the enzyme combination. Moderate degradation was observed when the particle size was 1 cm, with more pronounced features than in the Lip-only treatment. Surface changes are minimal at 2 cm particle size, similar to the Lip-only treatment. Compared to the structure in Figure 14, the structure presented in Figure 15 demonstrates enhanced

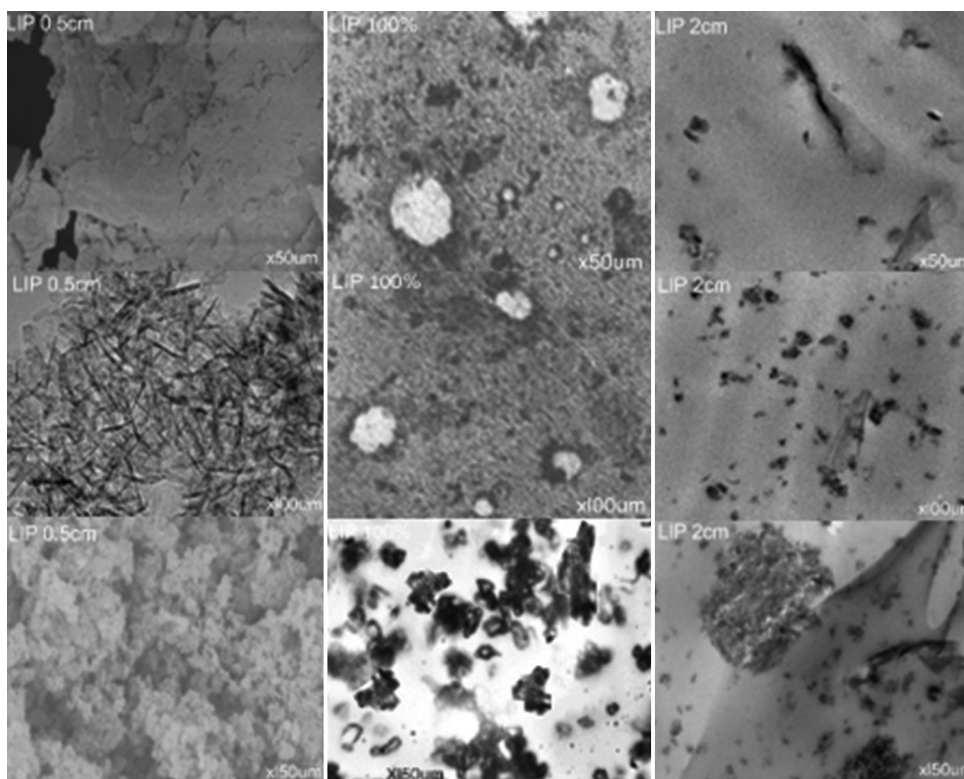


Figure 14. Microscopic images of lipase-treated low-density polyethylene films with particle sizes of 0.5 (left), 1 (middle), and 2 cm (right). Magnifications: $\times 50$ (top); $\times 100$ (middle); $\times 150$ (bottom).

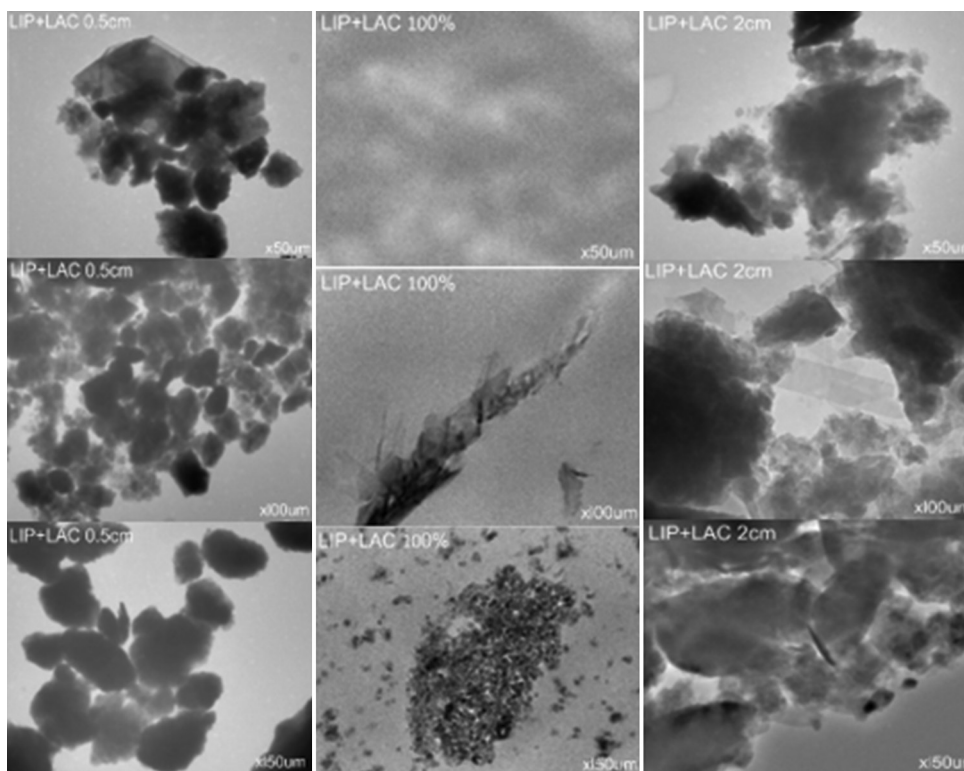


Figure 15. Microscopic images of lipase-laccase-treated low-density polyethylene films with particle sizes of 0.5 (left), 1 (middle), and 2 cm (right). Magnifications: $\times 50$ (top); $\times 100$ (middle); $\times 150$ (bottom).

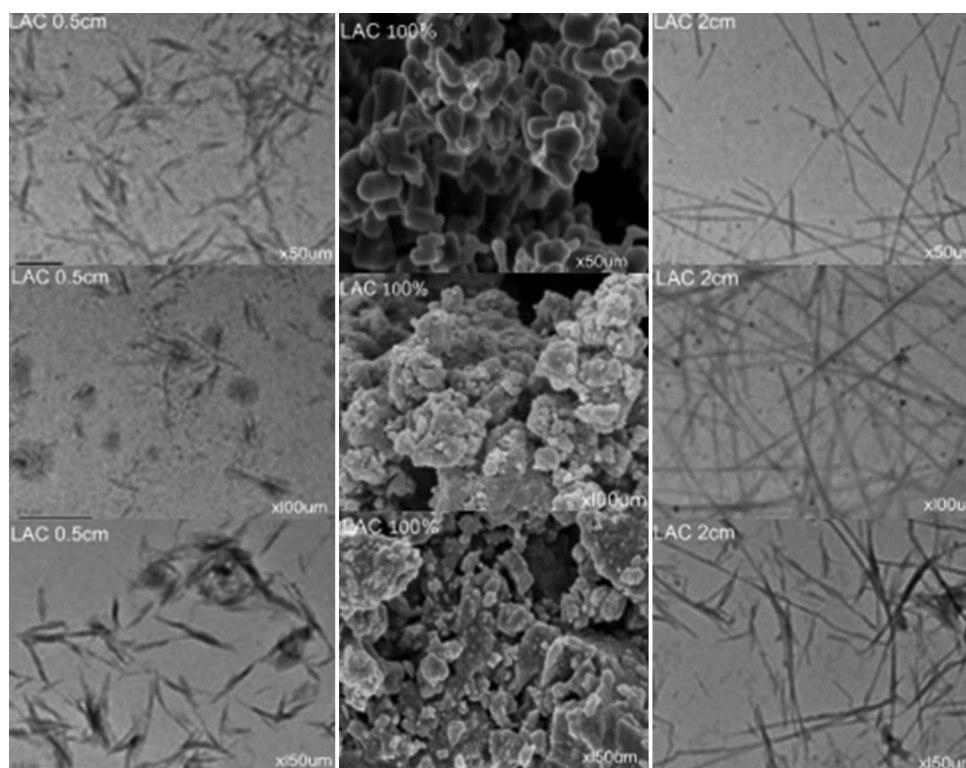


Figure 16. Microscopic images of laccase-treated low-density polyethylene films with particle sizes of 0.5 (left), 1 (middle), and 2 cm (right). Magnifications: $\times 50$ (top); $\times 100$ (middle); $\times 150$ (bottom).

degradation, particularly in smaller particles, due to the effectiveness of the combined enzymatic treatment.

Figure 16 presents nine SEM images of LDPE films (with different particle sizes) treated with Lac. The images demonstrate significant surface degradation at 0.5 cm particle size, including cracks and pits, indicating effective enzymatic action. When the particle size is 1 cm, moderate degradation is observed, with visible surface irregularities. Finally, 2 cm particle size exhibited a minimal surface change due to the limited enzymatic impact on larger particles. The similarities across the images include the presence of degradation features, while the differences relate to the severity of surface damage, which correlates with particle size and enzyme concentration.

In the present study, the magnifications ranged from 50 to 150 μm , whereas Yao *et al.*⁵⁹ only analyzed their samples at 20 μm . Figures 9-12 emphasize the effect of enzymatic treatments on LDPE films without considering particle size variations, while Figures 13-16 examine the combined impact of enzyme treatments and particle sizes. The latter set provides a more comprehensive understanding of how particle size influences enzymatic degradation, highlighting the importance of optimizing both parameters for effective biodegradation. The proposed enzymatic treatment offers a low-cost, eco-friendly, and scalable method for the

management of PE-based plastic waste, particularly sachet water LDPE films, which are a major contributor to solid waste in many developing countries, including Nigeria. The findings support potential integration of the enzyme system into municipal solid waste (MSW) management systems or decentralized waste treatment facilities, whereby enzymatic formulations may be used to accelerate LDPE degradation under controlled conditions.

4. Conclusion

Enzymes possess the ability to degrade PE materials, which constitute a significant portion of environmental pollutants that pose serious threats to humans, animals, and plants. After incubation periods of 10 and 30 days, both Lip and Lac enzymes demonstrated the ability to degrade LDPE material, with the 30-day incubation resulting in significantly higher LDPE degradation. The effects of enzyme concentration and LDPE particle size on degradation rate were investigated. Weight loss analysis revealed a higher degradation rate of 15.21% after the 30-day incubation period in 100% Lip-Lac. Surface imaging of the LDPE films treated with different enzyme concentrations indicated a higher surface change in films treated with higher enzyme concentrations due to higher enzymatic activity. The results demonstrate that higher enzyme concentrations and longer incubation

periods lead to greater LDPE degradation, establishing a proportional relationship between enzyme concentration, incubation time, and the extent of degradation. The effect of particle size on degradation rate was determined. A higher percentage degradation rate of 23.81% was observed after the 30-day incubation period for LDPE samples with a particle size of 0.5 cm. Surface imaging revealed that smaller particle sizes exhibited rougher surfaces compared to larger ones, indicating more extensive surface degradation. The degradation efficiency was significantly enhanced when a two-enzyme system (Lip-Lac) was employed, compared to single-enzyme systems. Furthermore, a decrease in particle size corresponded with an increase in the degree of degradation. This study supports previous findings that certain microbes and enzymes can be employed to degrade LDPE plastics. Future studies should explore enzyme immobilization and reusability strategies, building on the findings from this study.

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Conflict of interest

The authors declare that they have no competing interests.

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Availability of data

Data are available from the corresponding author upon reasonable request.

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ORIGINAL RESEARCH ARTICLE

Evaluation of yield performance of *Capsicum annuum* (chili) cultivated using a low-cost, sustainable hydroponic systemSomroop Chakravarti^{1†}, Arnab Sarkar^{1†}, Anirban Maity², Bishal Roy¹,
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Abstract

One of the most pressing global challenges in conventional agriculture is climate change, which adversely affects crop productivity. Global food security is increasingly threatened by shifting climate patterns, depleting groundwater levels, and rapid urbanization. In this context, soilless hydroponics cultivation offers a sustainable solution, requiring minimal inputs, minimizing pesticide and agrochemical use, and enabling resource-efficient water management. This approach allows for climate-resilient production with precisely controlled yields under indoor farming conditions. *Capsicum annuum* (chili), a widely consumed food crop with high nutraceutical value, faces serious cultivation threats due to unpredictable weather fluctuations. This study evaluates the growth performance of *C. annuum* under a low-cost, water-efficient hydroponic system designed for indoor cultivation, utilizing repurposed mineral water bottles as growing units. A comparative assessment between soilless hydroponics and conventional soil-based cultivation was conducted to determine the potential of this system under controlled indoor conditions. The findings indicate that plant growth characteristics, yield performance, and nutraceutical quality were enhanced in the low-cost, non-circulating hydroponic setup. Key physiological parameters, including reactive oxygen species generation and antioxidant activity, were systematically measured. Overall, the results demonstrate that this sustainable hydroponic approach not only contributes to water-efficient, climate-resilient, and space-saving household chili production but also addresses solid waste management by repurposing discarded plastic bottles, thereby aligning with broader environmental sustainability goals.

Keywords: Hydroponics; Yield performance; Indoor cultivation

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doi: 10.36922/EER025250050**Received:** June 16, 2025**Revised:** August 8, 2025**Accepted:** August 14, 2025**Published online:** August 28, 2025**Copyright:** © 2025 Author(s). This is an Open-Access article distributed under the terms of the Creative Commons Attribution License, permitting distribution, and reproduction in any medium, provided the original work is properly cited.**Publisher's Note:** AccScience Publishing remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

1. Introduction

With the rapidly growing global population, one of the major challenges today is producing sufficient food to meet rising demands.¹ Urbanization and industrialization

are reducing the availability of arable land and water, while climate change and soil degradation further decrease agricultural productivity.^{2,3} Open-field cultivation has become increasingly challenging due to adverse climatic conditions, such as extreme heat, delayed monsoons, groundwater scarcity, and natural disasters, especially in climate-sensitive regions.^{4,5} These factors contribute to extensive crop losses, malnutrition, and hunger, which ultimately threaten global food security.

In pursuit of maximizing yields, farmers often rely heavily on chemical fertilizers and pesticides. While such practices can increase productivity, they also contribute to severe soil and water pollution, thereby affecting entire ecosystems.⁶ The overuse of agrochemicals also leads to bioaccumulation and biomagnification, causing a range of human health complications.⁷

To combat these challenges, soilless agricultural methods are being explored as alternatives, allowing crops to be cultivated without soil, even under indoor conditions.⁸ Hydroponics, in particular, has emerged as a promising and relatively accessible solution, enabling crops to grow with their roots suspended in nutrient-rich aqueous solutions.⁹

Despite its advantages, conventional hydroponic systems pose significant challenges for small-scale or resource-constrained users. The high initial setup cost, requiring pumps, nutrient delivery systems, and other infrastructure, can be prohibitive.¹⁰ Moreover, skilled technical expertise is often required to maintain optimal nutrient balance and environmental parameters for consistent growth and yield. In many cases, urban farming is practiced on windowsills, balconies, or rooftops, where space constraints and the need for reliable electricity further hinder the adoption of conventional systems. In addition, because plants in conventional hydroponic setups share a common nutrient medium, any imbalance in solution quality or outbreak of pests and diseases can spread rapidly, whereas household-level systems using individual containers (e.g., one plant per bottle) may mitigate this risk.¹¹

Vegetables, second only to cereals, are critical for nutritional security across all cultures due to their central role in daily diets. According to the Food and Agriculture Organization statistics (FAOSTAT),¹² global per capita vegetable consumption reached approximately 150 kg in 2022. To bridge the demand–supply gap in vegetable production caused by adverse climatic conditions and shrinking cultivatable lands, a transition from soil-based to soilless cultivation systems, such as hydroponic systems, may provide a suitable solution. *Capsicum annuum* L. (chili) is one such vegetable with high global demand owing to its culinary versatility, nutritional value, and

medicinal properties. FAOSTAT estimates¹³ indicate that in 2023, chili was harvested from 2,065,408 ha worldwide, producing approximately 38,310,350 tons, with India contributing 73,914 tons from 8,616 ha. According to FAOSTAT's 2023 report,¹⁴ global chili exports reached 3,891,395 tons, value at US \$7,237,728,000, of which India alone exported 82,463 tons, valued at US \$56,561,000. Rich in ascorbic acid (vitamin C), chili is particularly valued for its bioactive compound capsaicin (IUPAC: 8-methyl-N-vanillyl-6-nonenamide), which exhibits a wide range of pharmacological effects, including antioxidant and antimicrobial,¹⁵ anti-inflammatory,¹⁶ anticancer,¹⁷ anti-obesity,¹⁸ antidiabetic,¹⁹ cardioprotective,²⁰ and gastroprotective²¹ properties.

In open-field agriculture, chili plants are highly susceptible to unpredictable weather fluctuations, soil-borne pests and diseases, weed competition, and the excessive use of agrochemicals.²² Consequently, soilless cultivation methods may represent a viable alternative.²³ However, conventional hydroponic systems remain expensive, technical demanding, and dependent on electricity, restricting their large-scale application to a limited number of commercial farms.²⁴ Although many studies have emphasized the advantages of hydroponics over soil-based systems, a substantial research gap remains concerning the high establishment costs and the need for skilled management of conventional hydroponic systems.

The current study aims to address these challenges by evaluating the yield performance of *C. annuum* using a low-cost, sustainable hydroponic system constructed from locally available and repurposed materials, such as discarded mineral water bottles. This approach requires minimal technical expertise and is especially suited for peri-urban settings and smallholder or household-level cultivation.

2. Materials and methods

2.1. Plant material

C. annuum seeds were generously provided as a research gift by the Department of Horticulture, Bidhan Chandra Krishi Vidyalaya, Mohanpur, West Bengal, India. The experiment was performed at Adamas University (22°44'21.70" N, 88°27'21.43" E) under indoor conditions, utilizing natural sunlight on an open balcony.

2.2. Seed preparation and germination

Seed viability was tested using randomly selected seeds from the stock, and germination percentage was determined following the protocol by Demir and Ellis (1992).²⁵ Healthy seeds were surface-sterilized using 10% hydrogen peroxide (H₂O₂) for 10 min, followed by 1% calcium hypochlorite for

1 h.²⁶ Sterilized seeds ($n = 100$) were placed in plantation trays containing coco peat as the growth medium and were watered periodically. A control group was maintained by planting seeds in soil obtained from a local nursery. Germination percentage was recorded through regular observations. After 10 days, healthy seedlings (4–5 cm in length) were randomly selected from both plantation trays (coco peat and soil) to assess the seedling vigor index (SVI-I), calculated using Equation I:²⁷

$$SVI - I = \text{Seedling length} \times \text{Germination percentage} \quad (I)$$

2.3. Experimental setup and plant growth monitoring

Discarded plastic bottles of various sizes were thoroughly cleaned and repurposed as nutrient reservoirs to construct a low-cost, non-circulating hydroponic system (Set I) (Figure 1A and B). A conventional hydroponic system, similar to those commonly used in commercial cultivation, was prepared using an opaque container as the nutrient reservoir, equipped with an electric air pump for aeration and plastic net cups (Set II) (Figure 1C). The nutrient solution was prepared by mixing all the required chemicals (Table A1) following the protocol by Hoagland and Arnon.²⁸

Forty randomly selected, healthy seedlings germinated in coco peat were transferred to the hydroponic systems: 20 to Set I and 20 to Set II. In Set I, seedling roots were immersed directly in the nutrient solution, while the stem was secured at the bottle opening with cotton plugs. In Set II, the roots were suspended in the nutrient reservoir, whereas the aerial parts were supported above the lid using net cups. Electrical conductivity (EC) and pH of the nutrient solution were maintained at 1.4–1.8 mS/cm and 5.8–6.5, respectively.²⁹ These parameters were monitored using commercially available pH paper and a portable EC meter (AP-IS11A058FBA, Aptechdeals, China) and adjusted as

necessary by adding water or nutrients. Both hydroponic systems were maintained indoors under natural sunlight on an open laboratory balcony at Adamas University, with a temperature of 22–27°C, relative humidity (RH) of 75–80%, and light intensity of 1,000–3,000 $\mu\text{mol}/\text{m}^2/\text{s}$ for approximately 11–13 h/day. A soil-based system ($n = 20$) served as the control (Set III) (Figure 1D).

In summary, the experiment consisted of three treatments:

- Set I: Low-cost hydroponics using plastic bottles (22–27°C, RH 75–80%, 1,000–3,000 $\mu\text{mol}/\text{m}^2/\text{s}$ for 11–13 h/day)
- Set II: Conventional hydroponics using a nutrient reservoir, net cups, and an electric air pump (same conditions as Set I)
- Set III: Soil-grown plants serving as control (same conditions as Set I).

Data were recorded for shoot height (cm), days to first flowering, days to first fruiting, days to full fruit maturation (red-ripe stage), fruit weight, and total yield per plant. Fruit development was monitored visually, and red, fully matured fruits were harvested. Measurements included individual fruit weight and total yield per plant.

2.4. Comparative analysis of stress response

A comparative study was performed using randomly selected leaves from fruit-bearing plants across all three experimental sets. The following assays were conducted:

- H_2O_2 content: Leaf tissue was extracted in 100 mM potassium phosphate buffer containing 5 mM potassium cyanide, and absorbance was measured at 560 nm³⁰
- Lipid peroxidation: Malondialdehyde (MDA) content was quantified, and absorbance was read at 532 nm³¹
- Superoxide dismutase (SOD) activity: Measured at 540 nm using p-nitro blue tetrazolium chloride

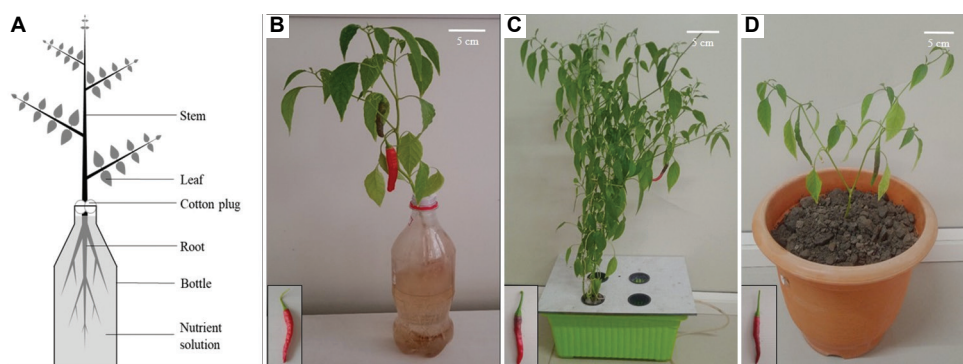


Figure 1. Indoor farming systems: (A) schematic diagram of the low-cost bottle hydroponic system; (B) Set I - plant grown in low-cost hydroponics using a plastic bottle; (C) Set II - conventional hydroponics with nutrient reservoir, net cups, and electric air pump; (D) Set III - soil-grown control plants. Harvest fruits from each system are shown in the corresponding insets.

(NBT). One unit of SOD activity was defined as the amount of enzyme required to inhibit 50% of NBT photoreduction³²

- Catalase (CAT) activity: Leaf extracts were prepared in the presence of 50 mM phosphate buffer and 20 mM H_2O_2 , and absorbance was monitored at 240 nm. One unit of CAT activity was defined as the amount of H_2O_2 decomposed (in μmol) per minute.³³

2.5. Nutritional quality analysis

Nutritional quality was assessed in randomly selected mature fruits from all three experimental sets by estimating vitamin C and capsaicin content.

- Vitamin C: Fresh fruits were homogenized in 0.4% oxalic acid, and ascorbic acid content was quantified spectrophotometrically at 520 nm following reaction with 2,6-dichlorophenolindophenol³⁴
- Capsaicin: Shade-dried fruits were extracted in ethyl acetate, and the absorbance of the extract was measured at 280 nm to determine capsaicin yield.³⁵

2.6. Correlation analysis of stress responsiveness and yield performance

Correlation analyses were performed using RStudio (version 2024.12.1+563; posit.co/products/open-source/rstudio/) to evaluate the correlations between oxidative stress generation (H_2O_2 , MDA), antioxidant enzyme activities (SOD, CAT), yield traits (fruit number, fruit weight, and total yield), and nutritional quality parameters (Vitamin C, capsaicin content). Kendall's tau (τ) correlation coefficient was employed to measure the strength and direction of associations. The statistical significance of correlations was tested using Kendall's tau rank correlation method.

2.7. Usability assessment

A detailed demonstration and hands-on training for the low-cost hydroponic system was conducted on the university campus with 20 underprivileged households, each represented by one member recommended by the local administration (Figure A1). Participants were provided with a basic setup, user manuals written in local languages, and 1 month of cultivation experience. Their feedback was collected to assess the system's accessibility, technical feasibility, and cost-effectiveness from their perspective.

2.8. Statistical analyses

Experiments were replicated 3 times, and data were analyzed using analysis of variance followed by Duncan's multiple range test at $p < 0.05$, performed in Statistical Package for the Social Sciences software (version 17.0.0; IBM, United States).³⁶

3. Results

3.1. Evaluation of seedling growth potential

Randomly selected seeds from the stock were viable and demonstrated promising germination in plantation trays with both soil and coco peat as substrates. However, seeds raised in coco peat exhibited slightly higher germination performance (80% in soil vs. 100% in coco peat). After 10 days of germination, comparative analysis revealed that the SVI-I was significantly higher—by approximately 70%—in seeds germinated in coco peat in comparison to those grown in soil (Figure 2 and Table A2).

3.2. Plant growth parameters

As shown in Figure 3, plants grown under conventional hydroponics (Set II) exhibited significantly greater shoot height compared with plants grown in low-cost hydroponics (Set I) or soil (Set III), the latter two showing similar height. In addition, plants in soil (Set III) required significantly more time to reach both first flowering and first fruiting stages than those in the two hydroponic systems (Figure 4). Likewise, the number of days required for complete fruit maturation (red-ripe stage) was significantly higher in Set III compared to Sets I and II (Figure 4).

Fruit traits also differed among systems: Both fruit weight and total yield per plant were significantly higher in Sets I and II, while Set III plants displayed a 50–60% reduction in yield (Figure 5). Overall, Set III consistently underperformed relative to the hydroponic systems across all measured parameters. Between Sets I and II, no significant differences were observed, except for plant height, which was greater in conventional hydroponics (Set II) (Figures 1 and 3; Table A3).

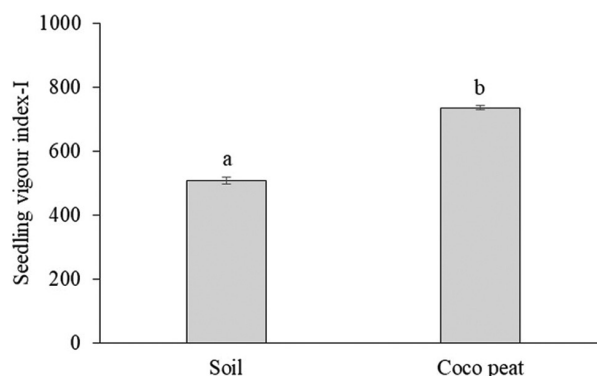


Figure 2. Seedling vigor index-I for soil- versus soilless-grown (coco peat) seedlings. Data were recorded after 10 days of germination and are presented as mean \pm standard deviation. Different letters indicate statistically significant differences according to Duncan's multiple range test ($p < 0.05$).

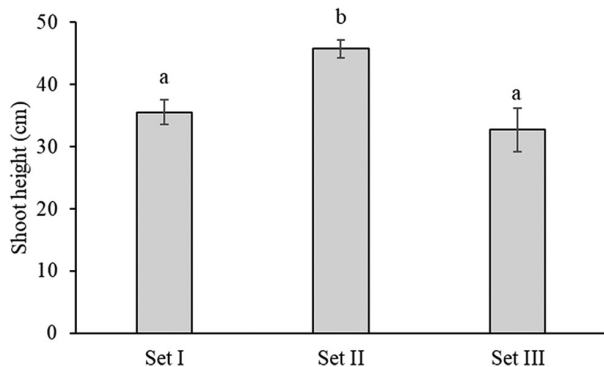


Figure 3. Plant height in the three experimental sets: Set I - low-cost hydroponics using plastic bottles; Set II - conventional hydroponics; Set III - soil control. Data were recorded after 140 days of cultivation and are presented as mean ± standard deviation. Different letters indicate statistically significant differences according to Duncan's multiple range test ($p < 0.05$).

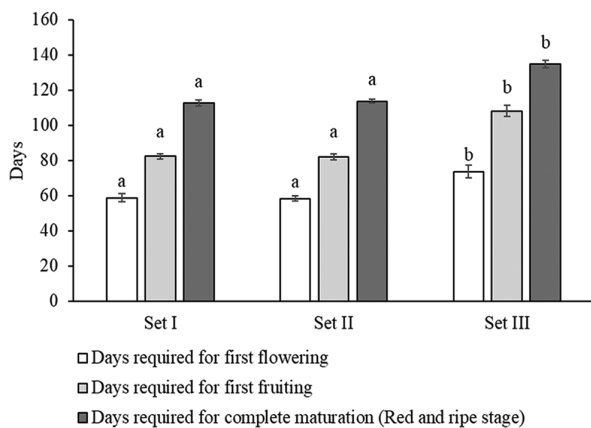


Figure 4. Days required for first flowering, first fruiting, and complete fruit maturation (red-ripe stage) in the three experimental sets: Set I - low-cost hydroponics using plastic bottles; Set II - conventional hydroponics; Set III - soil control. Data are presented as mean ± standard deviation. Different letters indicate statistically significant differences according to Duncan's multiple range test ($p < 0.05$).

3.3. Nutritional quality of fruit

Both ascorbic acid and capsaicin contents in mature harvested fruits were significantly higher in plants grown under low-cost hydroponics (Set I) and conventional hydroponics (Set II) compared to soil-grown plants (Set III). As shown in Figure 6, no significant differences were observed between Sets I and II in terms of these nutraceutical parameters (Table A3).

3.4. Physiological response of plants

Leaf peroxide content and MDA levels were two- to threefold higher in soil-grown plants (Set III) compared to either hydroponic systems (Sets I and II) (Figure 7).

Conversely, antioxidant enzymatic activities, including SOD and CAT, were nearly twofold lower in Set III plants relative to hydroponic plants (Figure 8). Plants grown under Sets I and II displayed similar physiological responses to stress (Table A4).

3.5. Association analysis of stress responses with yield and nutritional quality traits using Kendall's tau correlation

Kendall's τ correlation analysis (Figure 9 and Table A5) revealed several statistically significant associations between four stress response parameters (H_2O_2 , MDA, SOD, and CAT) and three agronomic or nutritional traits (yield, vitamin C content, and capsaicin levels). For yield, significant positive correlations were observed with both SOD ($\tau = 0.77$) and CAT ($\tau = 0.737$), indicating that increased antioxidant enzyme activity is strongly associated with increased yield. Conversely, MDA showed a significant negative correlation ($\tau = -0.604$), suggesting that lipid peroxidation is inversely related to yield. The correlation with H_2O_2 was weak and not statistically significant ($\tau = -0.208$).

For Vitamin C content, moderate positive correlations were detected with SOD ($\tau = 0.567$) and CAT ($\tau = 0.476$), indicating that antioxidant enzymes may play a role in maintaining or enhancing Vitamin C levels. H_2O_2 showed a significant negative correlation ($\tau = -0.385$), suggesting oxidative stress may reduce Vitamin C accumulation. The correlation with MDA was weak ($\tau = -0.206$) and not statistically significant. For capsaicin content, significant positive correlations were detected with SOD ($\tau = 0.648$) and CAT ($\tau = 0.553$). These findings reinforce the pattern observed with yield and Vitamin C, emphasizing the protective or enhancing role of antioxidant enzymes in capsaicin accumulation. Significant negative correlations with H_2O_2 ($\tau = -0.301$) and MDA ($\tau = -0.247$) further indicate that oxidative stress markers may be detrimental to capsaicin synthesis.

3.6. Feedback analysis from local users

More than 60% of participants provided positive feedback on the system's accessibility and cost-effectiveness, while relatively few reported technical difficulties (Figure 10 and Table A6). Overall, the feedback supports the system's practical applicability, affordability, and potential replicability in resource-limited settings.

4. Discussion

The results of the present study clearly demonstrate the potential of hydroponic cultivation practices to enhance plant growth and improve both quality and yield in

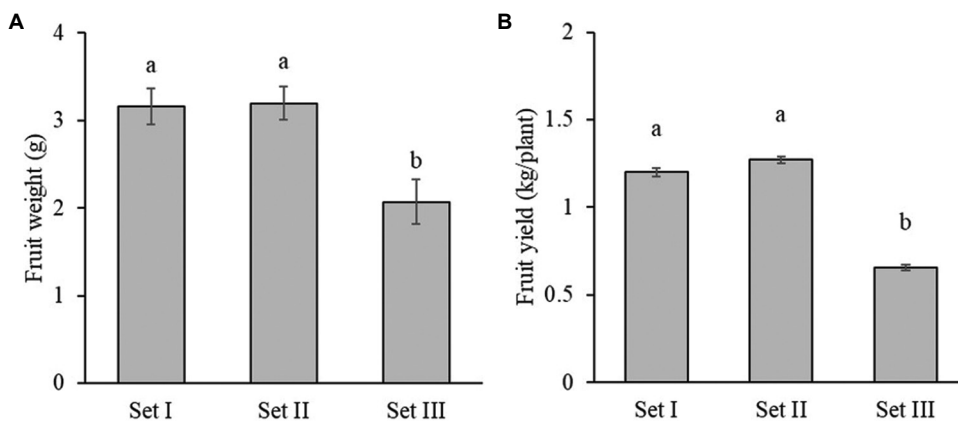


Figure 5. Fruit characteristics in the three experimental sets: (A) average fruit weight; (B) yield per plant. Set I - low-cost hydroponics using plastic bottles; Set II - conventional hydroponics; Set III - soil control. Data are presented as mean \pm standard deviation. Different letters indicate statistically significant differences according to Duncan's multiple range test ($p < 0.05$).

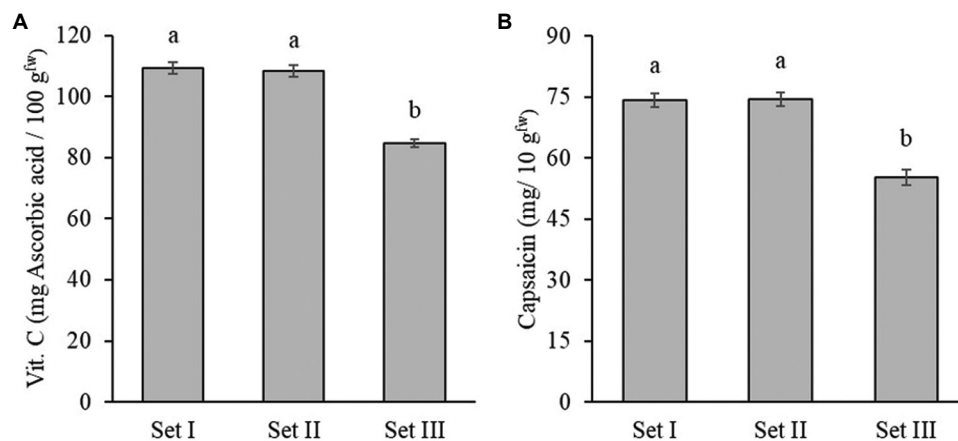


Figure 6. Nutritional quality of fruits in the three experimental sets: (A) Vitamin C (ascorbic acid) content and (B) capsaicin content. Set I - low-cost hydroponics using plastic bottles; Set II - conventional hydroponics; Set III - soil control. Data are presented as mean \pm standard deviation. Different letters indicate statistically significant differences according to Duncan's multiple range test ($p < 0.05$).

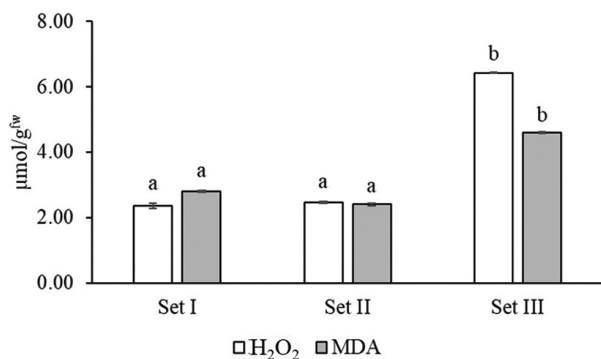


Figure 7. Leaf hydrogen peroxide (H₂O₂) and malondialdehyde contents in mature, fruit-bearing plants from the three experimental sets: Set I - low-cost hydroponics using plastic bottles; Set II - conventional hydroponics; Set III - soil control. Data were recorded after 140 days of cultivation and are presented as mean \pm standard deviation. Different letters indicate statistically significant differences according to Duncan's multiple range test ($p < 0.05$).

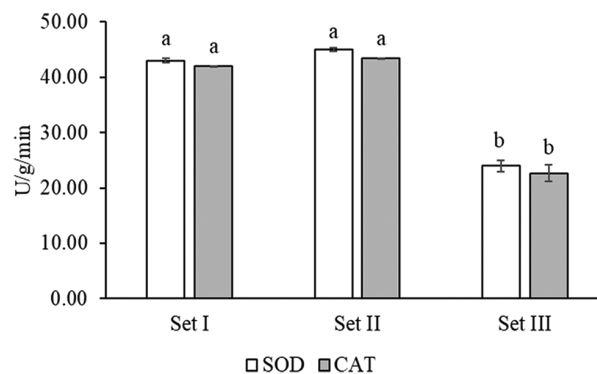


Figure 8. Superoxide dismutase and catalase activity in mature, fruit-bearing plants from the three experimental sets: Set I - low-cost hydroponics using plastic bottles; Set II - conventional hydroponics; Set III - soil control. Data were recorded after 140 days of cultivation and are presented as mean \pm standard deviation. Different letters indicate statistically significant differences according to Duncan's multiple range test ($p < 0.05$).

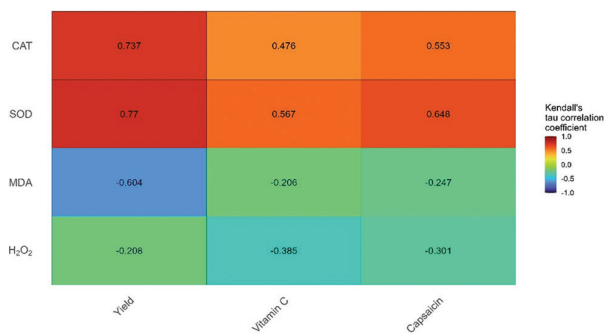


Figure 9. Heatmap of Kendall's tau correlation between oxidative stress markers (H₂O₂, MDA), antioxidant enzymes (SOD, CAT), fruit yield, and nutritional quality traits (vitamin C, capsaicin content). The scale on the right indicates correlation values, with 1 representing a perfect positive correlation, -1 a perfect negative correlation, and 0 no correlation. All values are significant at $p < 0.05$.

Abbreviations: CAT: Catalase; H₂O₂: Hydrogen peroxide; MDA: Malondialdehyde; SOD: Superoxide dismutase.

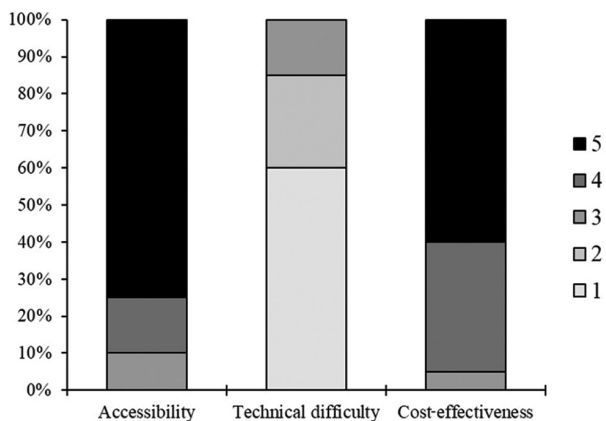


Figure 10. Participant responses (1–5 scale) regarding accessibility, technical difficulty, and cost-effectiveness of the low-cost hydroponic system using plastic bottles

C. annuum while reducing the stress typically experienced by plants grown in soil. Coco peat proved to be a superior germination medium in comparison to soil, most likely due to its higher water-holding capacity. This result is consistent with previous reports, which highlighted the advantages of coco peat—including high porosity, water retention, and moisture content—over soil-based plantation systems.³⁷

In terms of vegetative growth, plants in the conventional hydroponic system (Set II) exhibited the greatest performance. This outcome can be attributed to the aeration pump, which enhanced dissolved oxygen availability in the nutrient solution and promoted robust root activity, thereby supporting improved plant stature.^{38,39} By contrast, plants in the low-cost bottle-based hydroponic system (Set I) and soil-grown plants (Set III) exhibited shorter

stature. While this represented a limitation compared to Set II, the compact growth habit may be advantageous for indoor and vertical farming, where space is restricted. Compact plants that maintain high productivity are desirable in such contexts.⁴⁰ Therefore, the establishment of this low-cost hydroponic system using recycled plastic bottles (Set I) represents a promising alternative production strategy for space-constrained urban farming. It supports decentralized food production and urban nutritional security initiatives and can be implemented with minimal infrastructure investment.

Concerning the fruit and yield characteristics, soil-grown plants (Set III) exhibited significantly poorer performance compared to plants cultivated under soilless conditions with hydroponic nutrient solutions (Sets I and II). This may be attributed to the lower moisture content and reduced water-holding capacity of soil, which limited nutrient availability in desiccated conditions and ultimately compromised productivity.⁴¹ In contrast, the production of heavier fruits and higher yields in both hydroponic systems underscores the important role of efficient water and nutrient delivery.⁴² The balanced availability of essential nutrients also promoted increased biosynthesis of capsaicin in mature *C. annuum* fruits, consistent with earlier reports.⁴³

The compromised growth and yield in soil-grown plants may be explained by the higher levels of stress experienced under soil conditions. Elevated peroxide and MDA levels indicated severe oxidative stress, leading to cellular damage.⁴⁴ This was further reflected in the rapid depletion of antioxidant enzymes such as SOD and CAT, which play a crucial role in mitigating oxidative damage. Their significantly reduced activities in soil-grown plants further confirm this mechanism.⁴⁵ The fruits of *C. annuum* are highly demanded worldwide and widely used in daily cooking. The present study demonstrates that the use of repurposed bottles or other household containers for hydroponics does not compromise either yield (quantitative aspect) or nutritional value (qualitative aspect). Therefore, this approach can be considered a viable and sustainable option for household-level indoor cultivation, as well as for large-scale applications under net or polyhouse conditions.

The present study also underscores the pivotal role of oxidative stress and antioxidant defense in shaping both plant yield and nutritional quality. Yield showed strong positive correlations with the antioxidant enzymes SOD and CAT, indicating that enhanced enzymatic activity supports greater productivity, likely through the mitigation of oxidative damage. In contrast, the significant negative correlation with MDA highlights the detrimental effects of lipid peroxidation on yield. Although the negative

correlation with H_2O_2 was weak and not statistically significant, it may suggest limited or threshold-based oxidative signaling effects. Moreover, both vitamin C and capsaicin content were positively correlated with SOD and CAT, reinforcing the idea that antioxidant defense not only supports plant growth but also enhances the biosynthesis of nutritionally valuable metabolites. Their inverse relationships with MDA and H_2O_2 further affirm the detrimental impact of oxidative stress on metabolic quality, consistent with earlier studies.⁴⁶⁻⁴⁸

Previous reports have also demonstrated the successful use of plastic bottles, beverage containers, and discarded materials in hydroponic vegetable production, employing simple, low-cost designs without reliance on electricity or expensive resources.⁴⁹⁻⁵¹ As traditional agriculture faces mounting challenges in addressing food security under climate change, land scarcity, and water shortages, innovative approaches for climate-resilient urban agriculture and cultivation in non-productive areas have gained enormous interest. Such systems are expected to become major contributors to food supply in urban and suburban/peri-urban regions in the near future.⁵²

However, one limitation of traditional passive hydroponic systems, such as the wick method or the Kratky method, is that they are primarily suited for leafy greens.⁵³ These systems are less effective for fruiting crops, which require larger root zones to ensure adequate aeration and nutrient circulation. By contrast, the results of the present study demonstrate that hydroponics using plastic bottles and nutrient solutions achieved yield levels comparable to those obtained with conventional hydroponics. Therefore, beyond its advantages of low cost, space efficiency, and minimal energy requirements, this simple and user-friendly system is also adaptable for underprivileged or urban households. The positive feedback and strong acceptance observed among local communities further highlight its adaptability and potential scalability in the future.

5. Conclusion

The present study evaluated the potential of a low-cost, non-electric, sustainable hydroponic system designed for indoor environments for the production of *C. annuum*. This in-house-built system produced plants with compact, manageable stature and demonstrated both quantitative (fruit yield) and qualitative (vitamin C and capsaicin content) performance comparable to conventional hydroponics systems that rely on electrical inputs. These findings highlight the system's potential as an alternative production model for peri-urban areas and regions facing constraints in arable land availability.

The use of repurposed household materials, such as water and soft drink bottles, not only enhances cost-effectiveness and user accessibility but also promotes recycling of disposable items, directly contributing to Sustainable Developmental Goal (SDG) 12 (responsible consumption and production). The promising yield performance of this system, achieved with minimal resource inputs, aligns with SDG 2 (zero hunger) while also supporting SDG 5 (gender equality) and SDG 8 (decent work and economic growth) by providing opportunities for women and marginalized communities in rural and peri-urban areas. Adoption of this technique could enhance nutritional security at the household level while simultaneously strengthening local economies and promoting gender empowerment. The system can be recommended for large-scale use by women-led self-help groups as a means of advancing gender equality (SDG 5). Overall, this system not only advances sustainable agricultural practices but also contributes to sustainable livelihoods (SDG 8) and circular economies through the use of recycled materials and reliance on locally available inputs.

Ongoing work is focused on evaluating the scalability and the long-term durability of plastic bottles in terms of sustainability. Current experiments include incorporating rainwater harvesting for nutrient solution preparation and foliar spraying to address water conservation, as well as testing a large-scale model using low-cost, locally available containers such as drums. To mitigate environmental concerns regarding plastic degradation, biodegradable or recycled alternatives are also being explored, which will further enhance the ecological footprint of the system.

A forward-looking, integrated research approach will be required for large-scale implementation, focusing on cost-benefit analysis and system scalability. In addition, assessing the applicability of this model to other vegetable crops could broaden its relevance. Collectively, these initiatives could make significant contributions to universal nutritional security in the face of mounting environmental challenges and energy constraints.

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Conflict of interest

The authors declare they have no competing interests.

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Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data

Data used in this work are available from the corresponding author upon reasonable request.

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Appendix

Table A1. Hydroponic nutrient solution (Hoagland and Arnon¹)

Nutrient	Concentration	Amount
Solution 1		
KH ₂ PO ₄	1 M	1 cc/L nutrient solution
KNO ₃	1 M	5 cc/L nutrient solution
Ca (NO ₃) ₂	1 M	5 cc/L nutrient solution
MgSO ₄	1 M	2 cc/L nutrient solution
Supplementary solution a		1 cc/L nutrient solution
H ₃ BO ₃	2.86 g/L water	
MnCl ₂ .4H ₂ O	1.81 g/L water	
ZnSO ₄ .7H ₂ O	0.22 g/L water	
CuSO ₄ .5H ₂ O	0.08 g/L water	
H ₂ MoO ₄ .H ₂ O	0.02 g/L water	
Supplementary solution b		1 cc/L nutrient solution
Iron tartrate	0.5%	

Table A2. Seedling vigor index-I of plants after 10 days of germination in different growing media

Growing medium	Seedling vigor index
Soil	509.33 (11.15) ^a
Coco peat	736.67 (7.13) ^b

Notes: Data presented as the mean (SD); means followed by the same letters are not significantly different ($p < 0.05$).

Table A3. Plant growth parameters and nutritional quality of fruit

Experimental group	Set I	Set II	Set III
Shoot height (cm)	35.57 (1.94) ^a	45.73 (1.39) ^b	32.70 (3.50) ^a
Days required for first flowering	58.65 (2.37) ^a	58.35 (1.43) ^a	73.65 (3.62) ^b
Days required for first fruiting	82.35 (1.57) ^a	82.00 (1.62) ^a	108.00 (3.16) ^b
Days required for complete maturation	112.65 (1.66) ^a	113.65 (1.18) ^a	134.65 (2.06) ^b
Fruit weight (g)	3.16 (0.20) ^a	3.20 (0.19) ^a	2.07 (0.25) ^b
Fruit yield (kg/plant)	1.20 (0.025) ^a	1.27 (0.017) ^a	0.66 (0.017) ^b
Vit. C (mg Ascorbic acid/100 gfw)	109.37 (2.03) ^a	108.43 (1.79) ^a	84.86 (1.33) ^b
Capsaicin (mg/10 gfw)	74.26 (1.75) ^a	74.50 (1.75) ^a	55.37 (1.91) ^b

Notes: Data presented as the mean (SD); means followed by the same letters are not significantly different according to Duncan's multiple range test ($p < 0.05$).

Table A4. Physiological response of plants

Experimental group	H ₂ O ₂ content (μmol/g ^{fw})	MDA level (μmol/g ^{fw})	SOD (U/g/min)	CAT (U/g/min)
Set I	2.37 (0.079) ^a	2.80 (0.036) ^a	43.00 (0.382) ^a	42.00 (0.034) ^a
Set II	2.47 (0.028) ^a	2.40 (0.032) ^a	45.00 (0.279) ^a	43.33 (0.031) ^a
Set III	6.43 (0.019) ^b	4.60 (0.032) ^b	24.00 (1.009) ^b	22.67 (1.456) ^b

Notes: Data presented as the mean (SD); means followed by the same letters are not significantly different according to Duncan's multiple range test ($p < 0.05$).

Abbreviations: CAT: Catalase; H₂O₂: Hydrogen peroxide; MDA: Malondialdehyde; SOD: Superoxide dismutase.

Table A5. Correlation analysis between yield and nutritional performance (Vitamin C and capsaicin) with stress markers (H₂O₂, MDA) and antioxidant enzymes (SOD, CAT)

Parameters	Variables	Correlation coefficient (τ)	<i>p</i> -value*
Yield	H ₂ O ₂	-0.208	<0.05
	MDA	-0.604	<0.05
	SOD	0.770	<0.05
	CAT	0.737	<0.05
Vitamin C	H ₂ O ₂	-0.385	<0.05
	MDA	-0.206	<0.05
	SOD	0.567	<0.05
	CAT	0.476	<0.05
Capsaicin	H ₂ O ₂	-0.301	<0.05
	MDA	-0.247	<0.05
	SOD	0.648	<0.05
	CAT	0.553	<0.05

Note: * $p < 0.05$ indicates significant statistical correlation.

Abbreviations: CAT: Catalase; H₂O₂: Hydrogen peroxide; MDA: Malondialdehyde; SOD: Superoxide dismutase.

Table A6. Participants' responses ($n=20$) on a 1–5 scale regarding accessibility, technical difficulty, and cost-effectiveness of the low-cost hydroponic system using plastic bottles

Parameter	1	2	3	4	5	Total response
Accessibility	0	0	2	3	15	20
Technical difficulty	12	5	3	0	0	20
Cost-effectiveness	0	0	1	7	12	20

Note: Scale: 1=very low; 5=very high.

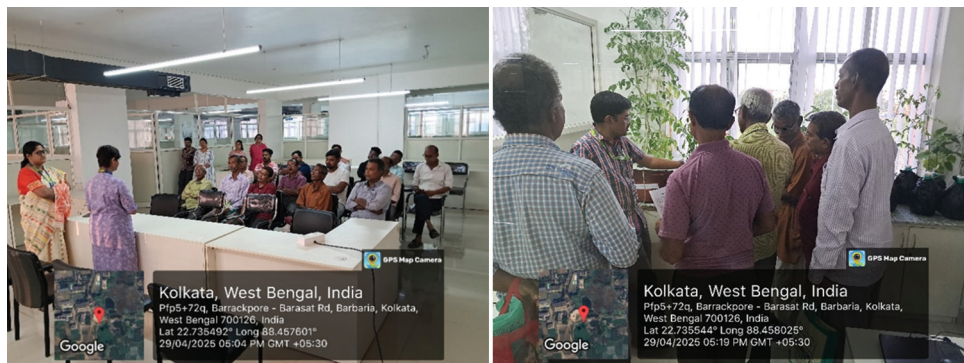


Figure A1. Farmers' training workshop on the low-cost hydroponics setup at Adamas University, Barasat, West Bengal, India

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ORIGINAL RESEARCH ARTICLE

Adoption of indigenous practices for climate change adaptation by sweet potato farmers in Ebonyi State, Nigeria

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Abstract

Existing literature recognizes the role of indigenous practices in building resilience to climate change, yet few empirical studies have examined crop- and location-specific strategies. This research assessed that gap by assessing the indigenous adaptation practices of sweet potato farmers in Ebonyi State, Nigeria. Indigenous practices are defined as traditional farming approaches, skills, and strategies passed down through generations within a specific locality or culture. Data were collected through a multistage sampling procedure and analyzed using mean scores, percentages, and probit regression analysis. Results showed that most sweet potato farmers widely adopted indigenous practices such as changing planting dates (\bar{x} score = 3.5), crop rotation (\bar{x} score = 3.2), mixed farming (\bar{x} score = 3.4), and crop diversification (\bar{x} score = 3.1). The challenges associated with the utilization of indigenous practices included a lack of real-time and accurate information (74%), limited knowledge of potentially feasible options (79%), and competing resource use (87%). Age ($\beta = 0.326$) positively influenced the extent of indigenous practice use, while distance to farm ($\beta = -0.101$), religion ($\beta = -0.213$), and membership in cooperative associations ($\beta = -0.652$) had negative effects. Overall, sweet potato farmers extensively employed indigenous practices as part of their strategies for adapting to climate change. Christian organizations and cooperative associations should be encouraged to support the adoption of these strategies among farmers. Furthermore, the study recommends that agricultural credits and loans be provided through the national agricultural bank to help farmers overcome financial constraints in implementing indigenous climate change adaptation practices.

Keywords: Adaptation practices; Challenges of indigenous practices; Determinants of use

1. Introduction

Climate change is a global phenomenon, although its impacts are not evenly distributed across the world. Its increasing threats have become a global problem, making it more difficult to achieve sustainable livelihoods. African countries, including Nigeria, are contending with the growing threats of climate change alongside a rising population. These challenges have resulted in a disturbing trend of reduced crop yields, soil degradation, decreased soil moisture, and accelerated desertification.¹ Grigorieva *et al.*² observed that the vulnerability of the agricultural sector is not assessed solely by the extent of environmental stress, like changes in climatic variables but also by the capacity to adjust and recover from the adverse outcomes of such changes. Although the ability of farmers to adapt and their degree of vulnerability are associated with environmental changes, these are also influenced by social factors such as indigenous practices and land tenure systems.

Indigenous practices are unique to specific cultural settings, developed through years of experience, ingenuity, sociocultural norms, belief systems, experimentation, and close observation of vulnerable natural systems. These practices represent strategies cultivated over generations,³ often transmitted orally, and have significantly contributed to solving agricultural challenges, including those related to climate emergencies. The retention of indigenous knowledge by rural farmers and its application in farming activities serves as a reservoir of indigenous practices.⁴ These practices offer valuable insights that extend beyond their cultural contexts, informing scientists and development planners in efforts to improve rural livelihoods. Farmers are among the households most severely affected by changes in weather patterns.⁵ Hence, indigenous practices are actively implemented by experts in their interactions with the environment.

In agricultural production, indigenous experts have developed these practices as a form of social capital to support the survival of vulnerable farmers. Juah and Nhamo⁶ emphasize that indigenous practices are essential for initiating successful climate change adaptation research and implementation in rural farming communities. They represent a reliable alternative for mitigating the adverse effects of a worsening climate. In farming, such practices include managing hazards induced by climate change through innate wisdom and approaches. However, these practices are at risk of extinction due to the incursion of development ideas that often promote unsustainable expectations of quick solutions to rural farmers' challenges.⁷⁻⁹ Before the emergence of these foreign strategies, rural farming households relied on indigenous practices as their primary means of adapting to climate change.

Nigeria's gross domestic product benefits significantly from the production of sweet potato, an underappreciated tuber crop. The cultivation of sweet potato can substantially support food security and boost the income of rural households.¹⁰ Most farmers in Ebonyi state cultivate sweet potatoes at both subsistence and commercial levels.¹¹ A report by Osuji *et al.*¹¹ shows that unexpected climate fluctuations have restricted the capacity of sweet potato farmers to scale up production, leading to decreased output, poor returns, and adverse effects on farmers' livelihoods. Rising temperatures and altered rainfall cycles have also affected the sweet potato production value chain. An increase in temperature distorts the germination of sweet potato tubers and poses a severe threat to leaf maturity in sweet potato cultivation. Researchers have observed notable changes in sweet potato farming practices in Ebonyi State. These challenges contribute to food insufficiency and insecurity in the state, as the demand for sweet potatoes exceeds the available supply.¹¹

Studies have shown that the socioeconomic characteristics of farmers affect their adoption of indigenous practices in agriculture. According to Osuji *et al.*,¹¹ understanding the impact of these characteristics on the implementation of indigenous practices will help accelerate their adoption in agricultural production. Shelembe *et al.*¹² and Oparaojiaku *et al.*¹³ reported that gender, age, level of education, and access to agricultural credit influence the use of indigenous practices among farmers. Osuji *et al.*,¹¹ Oti *et al.*,¹⁴ and Onyeneke *et al.*¹⁵ noted that farmers have developed resilience to climate change over many decades by employing agricultural risk management approaches. However, these studies have largely focused on the adoption of innovative farm practices, without giving adequate attention to the favorable disposition of farmers toward indigenous practices. This lack of attention has created a gap in the literature regarding why many farmers continue to implement traditional agricultural practices, despite efforts by governmental and non-governmental organizations to promote climate-smart agriculture aimed at strengthening farmers' adaptive and buffering capacities.

Although there are existing studies related to climate change and sweet potato cultivation,¹¹ including factors affecting the adoption of climate-smart agriculture by potato farmers¹⁶ and the sweet potato processing capabilities of households,¹⁰ none have assessed the application of indigenous practices in sweet potato farming. Ayi and Undiandeye³ noted that governmental and non-governmental initiatives to build climate change resilience are unlikely to succeed if farmers fail to incorporate indigenous practices into their adaptation and

mitigation strategies. While it may be difficult to define what constitutes a favorable climate change adaptation among farmers, this study aims to provide insights into the indigenous practices currently implemented by sweet potato farmers. Therefore, this study makes a significant contribution by empirically assessing the application of indigenous practices for climate change adaptation in sweet potato production. The findings will help document the extent to which indigenous practices are utilized as physical adaptation strategies in sweet potato cultivation. Specifically, the study:

- (i) ascertained respondents' awareness of climate change
- (ii) described sweet potato farmers' perceptions of climate change
- (iii) analyzed the extent to which farmers use indigenous practices
- (iv) identified the challenges associated with implementing indigenous practices.

This study hypothesized that a significant relationship does not exist between respondents' socioeconomic characteristics and the extent of their use of indigenous practices in climate change adaptation.

2. Methodology

Nigeria's southeastern region is home to Ebonyi State. The land area is about 5935 km² and lies between latitudes 5°40' and 6°45' north and longitudes 7°30' and 8°46' east. Sweet potato and rice cultivation are the primary agricultural activities among farmers in Ebonyi State.⁸ Sweet potato farmers in the state struggle with climate variability, as extreme temperatures, pests, diseases, and declining soil fertility directly affect their crops, which depend on natural rainfall. In addition to sweet potatoes, farmers also cultivate yams, oil palm, groundnuts, and cucumbers. The National Root Crop Research Institute, Umudike—mandated with research and development targeting root and tuber crops—has an outstation in Ebonyi state.

Data were collected through an interview schedule and analyzed using descriptive and inferential statistics. To validate the data collection instrument, its design was guided by the researcher's supervisors and other experts in agricultural extension, climate change studies, and rural sociology to ensure both face and content validity. Instrument reliability was established through the test-retest technique. The instrument was first administered to 20 sweet potato farmers in a neighboring state. A second round of questionnaires was distributed to the same farmers after four weeks. The scores obtained were correlated using Pearson's product-moment correlation coefficient. The resulting coefficient was 0.8; hence, the instrument was deemed reliable for the study.

A multistage sampling procedure was employed. The researchers purposively selected north and south of Ebonyi due to the concentration of sweet potato cultivation in these zones. Fifty percentages of agricultural extension blocks focused on sweet potato cultivation were selected from each zone—specifically, two blocks from north Ebonyi and four blocks from central Ebonyi, totaling six blocks, based on the list of extension blocks. From these, 40% of agricultural extension circles (from a total of 82 extension circles) focused on sweet potato cultivation were selected, resulting in the inclusion of 33 circles. In the final stage, 40% of sweet potato farmers (from a list of 3282 sweet potato farmers) were selected from each circle, yielding a total of 132 farmers who participated in the study.

Awareness and perception of climate change, as well as the challenges in using indigenous practices, were assessed using a binary scale ("yes" or "no") and scored accordingly (1 for "yes" and 0 for "no"). Data on respondents' extent of use of indigenous practices were measured using a Likert-type scale: very great extent = 5, great extent = 4, moderate extent = 3, low extent = 2, and very low extent = 1. Mean scores of 3.0 and above represented a high extent, while scores below 3.0 indicated a low extent. The following variables were also measured:

X_1 = Age (years)

X_2 = Gender (male = 1, female = 0)

X_3 = Distance to farm (actual kilometers between the farmer's residence and farmland)

X_4 = Access to weather information (yes = 1, no = 0)

X_5 = Access to credit (yes = 1, no = 0)

X_6 = Membership in a cooperative association (yes = 1, no = 0)

X_7 = Extension contacts (number of visits to/by an extension agent)

X_8 = Religion (Christian = 1, others = 0).

3. Results and discussion

3.1. Climate change awareness among farmers

Figure 1 indicates that 89% of sweet potato farmers are aware of climate change. This result suggests that farmers possess knowledge of the various ways climate change affects sweet potato production. Climate change awareness is a critical first step in forming perceptions and adopting resilient practices. This finding aligns with Oti *et al.*,¹⁴ who reported a high level of climate change awareness among farmers in rural communities. The percentage of sweet potato farmers aware of climate change in this study is higher than in some other locations in the country. For instance, awareness levels were reported as 52.5% in Edo state¹⁷ and 83% in Oyo state.¹⁸ Oparaojiaku *et al.*¹⁹ noted that even where climate change awareness is

relatively low, farmers in Nigeria have long implemented indigenous climate adaptation practices, even before the concept became a widely discussed topic in agricultural development. Although farmers may not fully understand all the effects of climate change on their farms, they leverage their awareness to apply indigenous practices, thereby contributing to agricultural development.

3.2. Perception of farmers toward climate change

Respondents held varying views on climate change, as shown in Table 1. Many perceived climate change as an increase in the intensity of sunshine (92%), temperature (86%), the occurrence of pests and disease (78%), rainfall intensity (74%), and the frequency of flooding (67%). In addition, 79% of the farmers perceived climate change as a decrease in soil moisture. These findings indicate that farmers have observed the consequences of climate change over the years. Reports from the Nigerian Meteorological Agency show an increase in temperature, rainfall intensity, and the frequency of flooding in the study area between 2011 and 2021.²⁰ The findings support Onyeneke *et al.*,¹⁵ who noted that Nigerian farmers perceive climate change in various forms. The respondents' perception of increased pest and disease infestation aligns with the observations of Oti *et al.*¹⁴ Similarly, the heightened perception of rising temperatures, sunshine intensity, and increased flooding frequency reflects the alarming impact of these hazards on sweet potato production. Osuji *et al.*⁸ documented that an increase in temperature alters seed germination and leads to severe damage to sweet potato leaf development. Furthermore, it impacts sweet potato storage, contributing to the rising rate of post-harvest losses. Perception is an essential prerequisite for enhancing climate change adaptive capacity. However, Shrestha *et al.*²¹ reported that indigenous farmers' perceptions of climate change

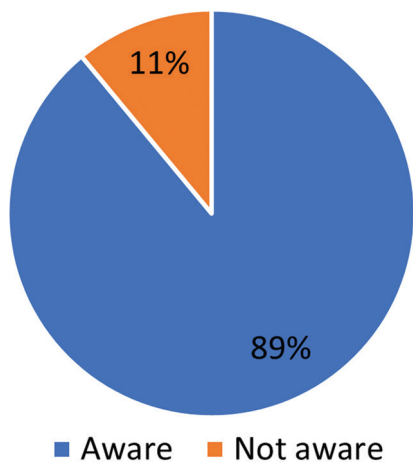


Figure 1. Awareness of climate change

may not always align with empirical meteorological data. Nonetheless, local knowledge and metrological data can complement each other in developing effective climate change resilience strategies.

3.3. Extent of indigenous practice application

Table 2 presents the extent to which farmers utilize indigenous practices as climate change adaptation strategies. The results show that respondents changed their planting dates ($\bar{x} = 3.5$), practiced crop rotation ($\bar{x} = 3.2$), engaged in mixed farming ($\bar{x} = 3.4$), and diversified their crops ($\bar{x} = 3.1$). These findings indicate that sweet potato farmers are employing indigenous practices to a great extent to ameliorate the harsh effects of climate change. The result aligns with Ayi and Undiandeye,³ who identified crop rotation, mixed farming, and crop diversification as the main indigenous adaptation practices among Nigerian farmers.

Mixed farming enables farmers to generate additional income, thereby building their buffer capacity against

Table 1. Respondents' perception of climate change

Variable	Increased (%)	Decreased (%)	No change (%)	Do not know (%)
Temperature	86	17	25	4
Rainfall intensity	74	32	6	20
Sunshine intensity	92	22	10	8
Drought	34	23	3	72
Flooding frequency	67	16	34	15
Soil moisture	23	79	14	16
Incidence of pests and diseases	78	12	32	10

Table 2. Extent of use of indigenous practice in climate change adaptation

Practices	\bar{x}	SD
Changing planting dates	3.5	1.0
Mixed farming system	3.4	1.1
Crop rotation	3.2	0.8
Crop diversification	3.1	0.9
Manuring	2.6	0.6
Planting of cover crops	2.6	0.6
Use of ashes for on-farm pest control	2.4	0.7
Multiple cropping	2.3	1.2
Raising mounds and ridges	2.1	1.1
Late planting	1.9	0.5
Mulching	1.7	0.8
Fallowing	1.5	0.9
Terracing	1.1	0.6

crop failure. It also supports the protection of rangeland and promotes its sustainable use for livestock production, rather than continuous ploughing, which can lead to soil compaction.²²

Crop diversification enhances agricultural production by increasing variety. Ihenacho *et al.*⁷ observed that diversification improves soil productivity, reduces the incidence of pests and diseases, and contributes to higher crop yields. This approach offers a more environmentally friendly and sustainable alternative to the use of agricultural chemicals.

Farmers in the study area consider adjusting planting dates crucial, as they rely on natural precipitation for agricultural production. Sweet potato farmers take advantage of early rains to ensure sufficient moisture for crop growth and reduce vulnerability to pests and diseases.

Atasié *et al.*²² documented that most farmers in the zone practiced bush fallowing as a climate change adaptation strategy. However, the low extent of fallow use observed in this study could be attributed to increasing pressure on agricultural land caused by population growth and urbanization. Izuogu *et al.*²³ noted that Nigerian farmers face challenges such as competing land use, limited knowledge, and land tenure issues that hinder the implementation of fallow systems. As an indigenous adaptation strategy, late planting helps farmers avoid extreme weather.¹³ However, climate variability has frustrated the effective use of late planting, as predicting rainfall patterns and duration has become increasingly difficult.

3.4. Challenges faced by farmers implementing indigenous adaptation strategies

The main obstacles to effective indigenous climate change adaptation, as presented in Table 3, include insufficient access to accurate information (74%), limited knowledge about viable alternative options (79%), and competing resource use (87%). These findings align with Juah and Nhamo,⁶ who reported that insufficient resources and poverty hinder the use of indigenous climate change adaptation practices among farmers. For instance, the inability to strengthen adaptation strategies has led to a lack of information among rural farmers, leaving many unaware of viable alternatives.

Sweet potato farmers, however, do not consider the reliability of indigenous practices to be a major challenge (27%). These findings contradict Juah and Nhamo,⁶ who argued that indigenous practices have lost credibility over time due to their unreliable predictions and inconsistent outcomes. However, because these practices are passed down through generations, sweet potato farmers continue to access, own, and rely on them. This response suggests

that indigenous practices and knowledge systems remain effective tools for climate change adaptation among sweet potato farmers. In addition, these systems are easily accessible to them.

3.5. Factors determining the extent of indigenous practice utilization by sweet potato farmers

Table 4 reveals that several factors influence the extent to which farmers utilize indigenous practices. The age of sweet potato farmers shows a significant positive relationship ($\beta = 0.326$) with the extent of utilization of indigenous practices. This indicates that as respondents advanced in age, they implemented more indigenous adaptation strategies. These findings agree with Juah and Nhamo,⁶ as well as Izuogu *et al.*,²³ who reported that indigenous adaptation practices become increasingly

Table 3. Challenges in implementing indigenous climate change adaptation strategies

Challenges	%
Competing resource use	87
Inadequate knowledge about potentially feasible options	79
Absence of accurate and timely information and technical advisory services	74
Poor access to adequate information about climate change	68
Shortage of land	66
Unavailability and lack of access to inputs	62
Lack of promotion of indigenous practices	38
Concerns about the reliability of indigenous practices	27
Lack of adequate education on the role of indigenous practices in climate change adaptation	23

Table 4. Determinants of the extent of indigenous practice utilization

Variables	Coef.	SE	z	Prob
Age	0.326***	0.315	3.461	0.001
Gender	0.421	0.120	2.856	0.085
Distance to the farm	-0.101**	0.166	1.459	0.060
Access to weather information	2.454	0.660	0.287	0.658
Use of weather information	1.032	0.111	4.739	0.031
Access to credit	0.112	0.121	7.633	0.006
Extension contacts	-0.532	0.928	0.125	0.907
Religion	-0.213***	0.145	0.114	0.004
Membership in a cooperative association	-0.652**	0.725	1.813	0.058
Constant	254.7	317.5	-0.614	0.685
R ²	0.567	-	-	-
Observations	132	-	-	-

Note: ** $p < 0.05$, *** $p < 0.01$.

Abbreviations: Coef.: Coefficient; SE: Standard Error.

preferred over modern approaches as farmers grow older. As farmers age, tasks such as carrying a knapsack sprayer to apply chemicals or handling inorganic fertilizers become more cumbersome compared to sprinkling ash or using poultry droppings. Furthermore, the health risks posed by chemical inputs worsen with age.⁶ Experienced farmers tend to implement agronomic practices that promote environmental conservation and sustainable food production. In contrast, younger farmers are more likely to adopt innovative practices such as using pesticides to maximize economic gains, often without fully considering environmental impacts.

The distance from the farmers' residence to the farm ($\beta = -0.101$) negatively influenced the extent of indigenous practice use. Farmers whose farms were located closer to their homes implemented indigenous practices to a greater extent than those with farms farther away. Home gardens are typically more carefully managed and tend to use fewer inorganic inputs, such as pesticides and herbicides more than long-distance farms. This is partly due to the proximity to children and other vulnerable individuals who may harvest crops directly, increasing the importance of minimizing chemical use. Rural households also often lack adequate knowledge of the safe handling and application of agrochemicals.²²

Religious affiliation of respondents ($\beta = -0.213$) also had a significant negative relationship with the implementation of indigenous adaptation strategies. The result suggests that strongly Christian respondents are more likely to adopt modern climate change adaptation practices. Traditional beliefs, which promote deeper ties with cultural norms and values, tend to support the use of indigenous practices. Consequently, farmers are more inclined to implement practices that align with their cultural traditions. Chu *et al.*²⁴ and Ankras *et al.*²⁵ documented that religious beliefs can positively or negatively moderate participation in traditional practices. They argued that religion can influence personal decisions by shaping farmers' perceptions and preferences, and that religious institutions can play a key role in promoting or discouraging the adoption of indigenous practices.

Membership in an agricultural cooperative association ($\beta = -0.652$) had an inverse relationship with the extent of indigenous practice use. This finding agrees with Izuogu *et al.*,²³ who reported that 76% of respondents in farmer associations adopted innovative adaptation strategies. Cooperative associations provide access to training and agricultural information that emphasizes improved farm practices with higher returns on investment, often overlooking indigenous methods.^{23,26} As a result, members

of these groups are more likely to discontinue the use of indigenous practices.¹⁹

4. Conclusion

This study highlights the essential roles of indigenous practices in developing climate change resilience among farmers in Ebonyi State. It also offers valuable insights into strategies that can be adopted for the efficient and sustainable management of climate change effects. Further studies are needed to assess the evolving trends in the adoption of indigenous practices for climate change adaptation and mitigation, ensuring that government interventions address the actual needs of farmers. To mitigate the effects of climate change, farmers have extensively adopted several indigenous practices. Age, distance to farm, religion, and cooperative membership were significant determinants of the extent to which sweet potato farmers adopted these practices. Competing resource use and limited knowledge of potentially feasible options were among the key challenges affecting the use of indigenous practices.

Cooperative organizations should encourage the adoption of indigenous climate change adaptation strategies by promoting the exchange of information and local resilience practices. Agricultural extension service providers should support the integration of indigenous knowledge with modern scientific adaptation strategies through training on climate-resilient farm techniques. Agricultural Development Banks should facilitate the adoption of indigenous practices by providing agricultural credits and loans. Access to credit will encourage greater investment in indigenous climate adaptation practices and enhance farmers' capacity for resilience. To support implementation, agricultural development agencies must expand channels for farmer education and training on indigenous climate strategies.

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Conflict of interest

The authors declare that they have no competing interests.

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Ethics approval and consent to participate

Informed consent was obtained from all respondents before their participation in the study. In addition, permission was secured from community leaders, including contact farmers, before the field investigation was conducted.

Consent for publication

Respondents consented on the publication of their data.

Availability of data

The data analyzed in this study are available from the corresponding author on reasonable request.

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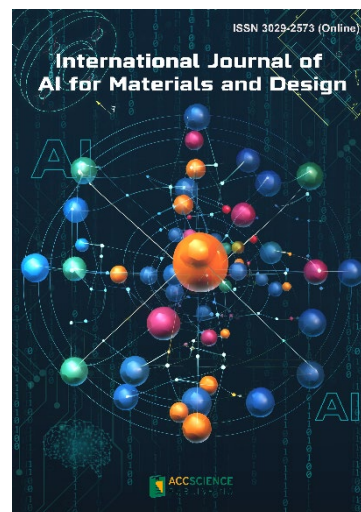
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