14

Toxicology and Adverse Effects of Chemical Fertilizer and Nanobiofertilizer Pollution of the Environment; Bioaccumulation, Greenhouse Effects, and Global Warming

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Abstract
Chemical and nanobiofertilizer use in agriculture has increased recently as a result of the need to boost crop output and the rise in global food demand. However, these substances can also result in environmental contamination and have a detrimental influence on both human health and biodiversity through several pathways, including bioaccumulation, greenhouse effects, and global warming. The impacts of chemical fertilizers on crop yield are discussed in recent studies, as well as the roles that nanofertilizers play in reducing the harmful effects of chemical compounds used in fertilizer production. The different kinds of chemical fertilizers

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and nanobiofertilizers are also included in this overview, along with their effects on the environment (atmosphere, water, and soil). The impact of these fertilizers, both chemical and nano, on biotic and abiotic aspects of the environment, such as soil quality, water quality, air quality, biodiversity, ecosystem services, climate change, and human health, is also covered. It also details how heavy metals from fertilizers are biomagnified up the food chain in the environment, harming individuals in the end, as well as the method of bioaccumulation. In addition to the direct effects fertilizers have on the soil, water, and biotic elements that make up the ecosystem, it has been demonstrated that the manufacturing and use of fertilizers, both chemical and nanotechnology, greatly contribute to global warming. The analysis is concluded with some recommendations for further research and initiatives on how to boost agricultural yields and thereby support global food security through precision farming and the use of organic fertilizers, which can enable people to lessen the environmental impact that nano- and chemical fertilizers have while preserving food security for future generations.

Keywords: Toxicology, chemical fertilizer, nanobiofertilizer, pollution, environment, bioaccumulation, global warming

14.1 Introduction

Agriculture has advanced alongside humankind's development. In a bid to feed the world's ever-increasing population, there will be greater pressure on the cultivable land available by 2050 when there are around 9.6 billion people on the earth [1]. In emerging countries with agricultural land, agriculture is important [2]. Crop yield per unit area grew as a result of the industrial and green revolutions, which fulfilled the growing population's desire for food [3]. However, they also boosted artificial fertilizers used in agriculture. Conventional agricultural methods and fertilizer use are required in conventional agriculture, which can significantly increase crop growth, yield, productivity, and nutritional value. As a result, from the time of the green revolution, chemical/inorganic fertilizers have been crucial to the development of current agricultural techniques [1]. Fertilization improves product recovery quality and efficiency in agricultural activities [4]. The biggest challenge that agriculture is currently facing is how to increase the production of crops without having any adverse impact on the environment in light of the expanding human population worldwide. As they build up in water bodies and the soil via leaching and mineralization, it has been predicted that 50% or more of the total amount of pesticides and chemical fertilizers used will go wasted [1].

Additionally, it is thought that the business of fertilizer could be a source of heavy metals and natural radionuclides. According to Nadarajan and Sukumaran [5], it primarily consists of heavy metals including Cu, Ni, Pb, As, Cd, and Hg as well as naturally occurring radionuclides such ^{238}U, ^{232}Th, and ^{210}Po. The accumulation of heavy metals in plant systems and the soil may be affected by fertilization. Plants take up nutrients from the soil, which can potentially move up the food chain. As a result, fertilizer causes pollution of the land, water, and air [5]. Chemical fertilizers are starting to pose a concern in the current environment. Different variables contribute to the same thing, but rising demand has led to an overuse of artificial fertilizers. These include an increasing population, a lack of available cultivable land, and water scarcity [5]. These characteristics previously encouraged us to use chemical fertilizers. Despite the fact that conventional supplements started to improve crop growth and productivity, their extensive use for a very long time had devastating environmental effects on the entire world, including pollution of the air, degradation of soil's quality, eutrophication of water and contamination of ground water [6]. One strategy being investigated in the area of nanotechnology known as nanofertilizers is one of many that have been utilized to increase fertilizer effectiveness [6].

In order to develop nanofertilizers, nutrients are coated or encapsulated with nanomaterial to allow controlled release and delayed diffusion into the soil [1]. The application of nanoscale fertilizers may aid in limiting nitrogen loss through run-off/leaching and lessen its rapid volatility and degradation, improving the soil's fertility over time, and increasing crop output [1]. Due to their high surface area-to-volume ratio and potent penetration abilities, nanofertilizers may also be a promising alternative to chemical fertilizers [7]. By promoting stress tolerance, carbohydrate and protein synthesis, photosynthesis, and metabolism of nitrogen as well as seed germination, nanofertilizers may increase agricultural output, according to a number of studies. In addition to the other benefits, they need to be applied to the soil in comparatively less amounts, which makes them easier to apply and costs less to carry [1].

However, new uses of nanotechnology in agriculture and numerous other sectors of the global economy continue to arouse concerns and questions about potential negative impacts on environmental and human health. In fact, the intentional introduction of nanoscale elements into agricultural processes may have unforeseen health effects [1]. In this case, it is anticipated that residues of nanomaterials in soil and crops will expose more people to the environment and increase human exposure, with exposure pathways including potential bioaccumulation in the food chain and the environment in general. As a result, the predicted novel and increased application of nano-enhanced particles may bring about both new advantages and new risks to the health of people and the environment [1]. According to this perspective, the development of "green nanotechnology," a conceptual strategy to balance the benefits of nanoproducts in addressing environmental challenges with the evaluation and management of the environmental and health risk associated with nanomaterials in other to achieve the goal of sustainable agriculture [6].

Despite the fact that chemical and nanofertilizers are a significant contributor to the ability of the world to produce enough food for everyone, their excessive use is creating serious issues for both the present and the next generation in the form of polluted soil, water and air as well as the emission of greenhouse gases. According to Chandini *et al.* [3], these fertilizers not only put our environment in danger but also endanger microbial life, animals, and humans. Some of these fertilizers have been linked to health problems due to chemical and nanoparticle exposure, phytotoxicity from nanoparticle bioaccumulation in plants, and water and soil pollution from nitrate and other toxic chemical leaching, among other things [6]. Furthermore, the usage and production of chemical fertilizers causes the release of greenhouse gases, which aid in the process of global warming [6].

Thus, this chapter explains how chemical and nanofertilizers affect the well-being and maintenance of biotic and abiotic ecosystem components.

14.2 Chemical Fertilizers

Farmers employ chemical fertilizers, also known as CFs, in greater quantities to boost crop yields because they are synthetic and made of non-organic-grown materials [6]. They include any substances applied directly to the soil with the intention of promoting plant development, increasing crop yields, or enhancing crop quality [8, 9]. They can also include a single or many nutritional components. Due to their fast solubility in water, CFs can be found in both liquid and granular forms having the same composition, but are less expensive, and function more quickly than the organic fertilizers. However, P fertilizers contain some insoluble compounds, which are not readily soluble in water [6]. Examples of these fertilizers include triple superphosphate (TSP), diammonium phosphate (DAP), and monoammonium phosphate (MAP) [10].

14.2.1 Types of Chemical Fertilizers

Chemical fertilizers give plants the nutrients they need for optimum growth. Chemical fertilizers come in a variety of forms. Examples of nitrogen fertilizers include ammonium sulfate, calcium ammonium nitrate, and ammonium nitrate among others [11]. While triple superphosphate, diammonium phosphate, monoammonium phosphate, and single superphosphate are all examples of phosphate fertilizers [10]. Whereas potassium nitrate, potassium sulfate, and potassium chloride are all examples of potassium fertilizers. Various more crucial secondary plant nutrients are sulfur, magnesium, and calcium [12]. In addition to essential nutrients (NPK), these are utilized such as sulfur being added to solitary superphosphate, urea, or ammonium nitrate rather than being used directly. Iron, manganese, boron, zinc, copper, and other micronutrient fertilizers are available [12].

14.2.2 Economic Importance of Chemical Fertilizers

Chemical or inorganic fertilizers are manufactured soil improvers that are used to increase the amount of nutrients in soil. Chemical fertilizers are synthesized from inorganic material and applied to soil as fertilizers to provide the natural nutrients contained in soil that are necessary for plant growth, such as phosphorus, nitrogen, and potassium [4]. The use of chemical fertilizers has some benefits, such as an increment in the soil organic matter that increases plant root mass, an increase in crop yield and soil fertility, high efficiency, and the provision of macronutrients to plants in forms that are easily absorbed by them [2].

There are several drawbacks to utilizing chemical fertilizers as opposed to organic fertilizers made from natural sources, even while they promote plant development and boost fruit and vegetable harvests in a very short amount of time [5]. The most frequent difficulty with these fertilizers is overfertilization, which causes environmental problems since these substances pollute water sources, accumulate in crop plants, slow down plant growth, foliage burn, which ultimately promotes the susceptibility of plants to diseases and pest [13]. They also reduce soil enrichment, which prevents plants from receiving the nutrients they need as well as moisture to be extracted from the soil; it also increases soil acidity and loss of organic material and significant living organisms that enhance the soil quality [11].

14.2.3 Nanofertilizers

In order to achieve a controlled and gradual nutrient release for the improvement of soil productivity and fertility as well as the quality of agricultural products, nanofertilizers are made from bulk fertilizer materials, conventional fertilizers, or extracted from varying plants or their parts [14]. The nanosized form of the encapsulated nutrients can be released in a regulated manner so as to increase the agricultural plant's efficiency with the least amount of environmental damage, thanks to the special physicochemical qualities and benefits of nanomaterials. Nanomaterials' high reactivity causes them to interact with fertilizers, which improves and effectively increases the ability of the plant to absorb nutrients [15].

Three variables—intrinsic, extrinsic, and route of administration—affect the efficacy of nanofertilizers. The way a nano-formulation is prepared, the size of its particles, and its surface coating are intrinsic factors. The potential use of nanofertilizers may also be influenced by external factors including microbial activity, organic matter, temperature, soil texture, soil pH, and soil depth [1]. Additionally, the manner of application and pathways of administration through the leaves (foliar) or roots of plants have a big impact on how well nanofertilizers are absorbed, behave, and are bioavailable [16].

Biofertilizers are formulations that increase the productivity of the soil by fixing nitrogen from the atmosphere generating growth-promoting compounds, and solubilizing phosphorus. They do this by combining one or more microorganisms. So-called nanobiofertilizers are a combination of biofertilizers and nanostructures. The three most crucial elements of nanobiofertilizers are their interaction with microorganisms, their lifespan, and their transport (Figure 14.1).

To protect the biosafety of agriculture, bio- and nanofertilizers have replaced chemical fertilizers in recent years. Live formulations of beneficial microorganisms, such as rhizobacteria (*e.g.*, *Rhizobium*) that promote the growth of plants and other microorganisms such as *Azotobacter* and *Azospirillum* including fungal mycorrhizae, blue-green algae (BGA) and phosphate-solubilizing such as *Bacillus* sp. and *Pseudomonas* sp., which contributes greatly to the solubilization of complex insoluble organic matter as well as fixation of biological nitrogen [17]. These biofertilizers also help with soil aeration and natural fertilization. They also increase the soil's ability to retain moisture, increase the availability of nutrients (nitrogen and phosphorus) to plants, preserve the relative health of the soil by enhancing the soil's microbial state, and maintain relative soil health. As a result, they are a great alternative to synthetic fertilizers since they raise

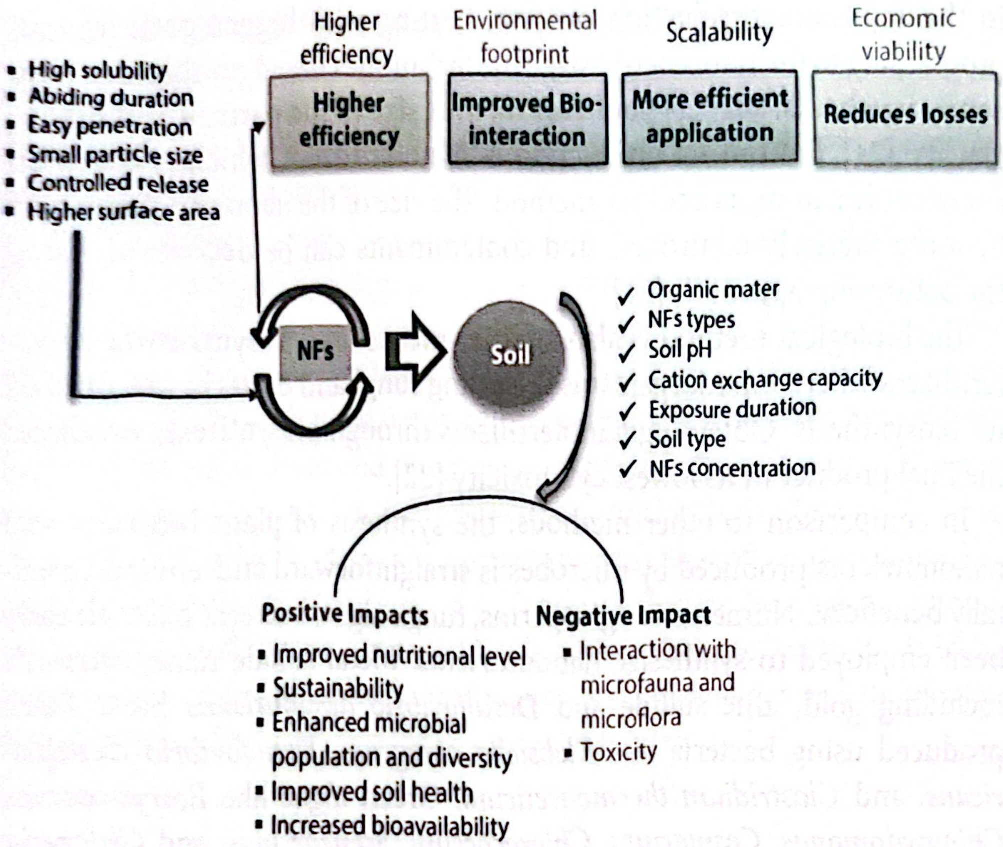

Figure 14.1 Overview of nanofertilizers' function in soil [17].

the quality of the soil and increase its potential to supply the vital nutrients required for plant growth [17].

This innovative approach does, however, have some major setbacks, such as on-field poor stability, short life-span, performance well under changing environmental factors such as radiation, temperature, pH, long-term use sustainability, vulnerability to desiccation, lack of suitable microbial strains, and importantly, the required dosage to efficiently function well in a large land mass [18].

14.2.4 Synthesis of Nanofertilizers

An effective tool for achieving sustainable agriculture and the environment is nanofertilizer. Because of their capacity to quickly assimilate and release nutrients into the plants in the correct quantity, nanofertilizers have displaced conventional fertilizers [19]. To employ nanoparticles to improve soil quality and restore disturbed fields, further work needs to be done [19].

The top-down, bottom-up, and biological methods are just a few of the many strategies to create nanofertilizers [20]. Physical techniques are used in the top-down production process, starting with bigger particles and progressing to the nanometric size. The techniques based on this idea have some drawbacks, such as poor control over size of the particle and homogeneity [21]. Bottom-up production of nanofertilizers, which is based on chemical reactions, is another method. The size of the nanostructures may be more precisely controlled, and contaminants can be decreased, using the bottom-up approach [21].

The biological method is also another means used to synthesize nanofertilizers where microorganisms including fungi and bacteria are utilized for biosynthesis. Obtaining nanofertilizers through biosynthesis produces the final product in its lowest cytotoxicity [22].

In comparison to other methods, the synthesis of plant biomass and nanonutrients produced by microbes is straightforward and environmentally beneficial. Numerous angiosperms, fungi, algae, bacteria have already been employed to synthesize nanonutrients. Metal sulfide nanonutrients including gold, zinc sulfide and *Desulfovibrio desulfuricans* have been produced using bacteria like *Klebsiella aerogenes, Desulfovibrio desulfuricans*, and *Clostridium thermoaceticum*. Green algae like *Botryococcus, Chlamydomonas, Cosmarium, Chlorococcum, Scenedesmus*, and *Chlorella* and other cyanobacteria like *Lyngbya, Phormidium, Synechocystis, Anabaena, Nostoc, Spirulina*, and others have been used to create a variety of metallic nanoparticles [23–26].

Additionally, organic or inorganic substances can be used to make nanofertilizers [27]. Metal oxides, such as silver oxide (AgO), zinc oxide (ZnO), and magnesium oxide (MgO), are primarily used in the formation of inorganic nanostructures. Polymers, carbon, and other organic compound-derived nanomaterials are employed [26, 27]. Because there are so many ways to make nanofertilizers, there are also a wide range of dangers and difficulties that can arise, including cost in greater yields with lower energy, and the synthesis of highly efficient materials. It is feasible to create agrochemicals with high performance and sustainable applications by combining these traits [20]. Consequently, it is vital to select the most appropriate procedure for each situation and intended use given the variety of options available for the production of nanofertilizers. According to Yadav *et al.* [20], the decision must be based on the economic sustainability of the production, use, preparation, and final application. The performance of the end products is another crucial aspect that needs to be assessed, and in order to do so, it's needed to understand how nutrients are absorbed in the culture being studied [20].

14.2.5 Pros and Cons of Nanofertilizers Over Chemical Fertilizers

The worldwide expansion in human population poses a serious danger to food security because agricultural land is becoming increasingly scarce and even disappearing over time. To fulfill the enormous demand for food from the growing population, it is crucial that agricultural output be greatly increased during the coming decades [28]. However, an over reliance on chemical fertilizers for crop production ultimately has very negative effects on both environmental ecology and human health [28]. Sustainable agriculture and environments can be attained with the use of nanofertilizer. Because of their capacity to quickly assimilate and release nutrients into the plants in the correct quantity, nanofertilizers have displaced conventional fertilizers [29]. Nanoparticles can be used to improve soil quality and restore disturbed lands, although more work needs to be done in this area [28]. The following are some advantages and drawbacks of using nanofertilizers instead of chemical fertilizers.

14.2.5.1 Size

Nanofertilizers are more effective in supplying nutrients to plants because they contain particles that are considerably smaller than those in chemical fertilizers [30]. Nanoparticles can interact with plant tissues and cells more than bulk particles because they have a higher surface area to volume ratio [31].

14.2.5.2 Nutrient Delivery

Chemical fertilizers dissolve in the soil and release nutrients over time, whereas nanofertilizers are made to penetrate plant tissues and give nutrients immediately to cells [1]. Through slow/controlled release techniques, such as coating or encapsulating nutrients with nanomaterials, nanofertilizers can manage the amount of nutrients that are available to crops. According to Mejias [32], nutrient losses from leaching, volatilization, fixation, or immobilization are reduced when nutrients are delivered slowly.

14.2.5.3 Nutrient Uptake

Chemical fertilizers rely on soil characteristics and plant physiology for nutrient uptake, whereas nanofertilizers are made to increase nutrient uptake by plants [30]. In addition to altering root architecture and physiology to enhance nutrient uptake, nanofertilizers can increase the solubility, mobility, and bioavailability of nutrients in the soil-plant system [33].

14.2.5.4 *Nutrient Utilization*

Chemical fertilizers may result in nutritional imbalances or plant toxicity, whereas nanofertilizers are made to increase the utilization of nutrients by plants [26]. Nanofertilizers can regulate gene expression and metabolic pathways that are involved in nutrient assimilation and metabolism, as well as the distribution and transport of nutrients within plant tissues and organs [31].

14.2.5.5 *Crop Yield*

Chemical fertilizers if applied inappropriately often have an adverse impact on crop health and the environment, however, nanofertilizers are intended to boost agricultural output and quality with minimal adverse effect on the plant or the environment [1, 34]. Crop growth, development, and production can all be improved by using nanofertilizers, as well as crop resilience and tolerance to abiotic and biotic challenges. Nanofertilizers can also increase the nutritional value, flavor, color, and shelf life of crops [35].

14.2.5.6 *Environmental Impact*

Chemical fertilizers can contribute to environmental pollution and global warming, whereas nanofertilizers are made to minimize the environmental effects of fertilizer use [34, 36]. Nanofertilizers can reduce the quantity of fertilizer needed per square foot and the amount of greenhouse gases (GHGs) released during fertilizer manufacturing, transportation, and use. Additionally, soil quality, biodiversity, and ecosystem services can all be improved or preserved by using nanofertilizers [33, 37].

However, compared to chemical fertilizers, nanofertilizers also have several drawbacks and difficulties, including:

14.2.5.7 *Cost*

High cost of nanomaterial synthesis, characterization, and application has made nanofertilizers more expensive than chemical fertilizers when used in agriculture [34]. The volume of production, distribution, and use affects how cost-effective nanofertilizers are [33, 38].

14.2.5.8 *Safety*

There are various safety issues surrounding the use of nanomaterials; human exposure, aggregation, and toxicity offer potential dangers to human health and the environment [34]. More study is needed to determine the fate, transport, and interactions of nanomaterials throughout the soil-plant-animal-human continuum in order to assess the safety of nanofertilizers [33, 37, 38].

14.2.5.9 *Regulation*

Clear definitions, criteria, and rules for the creation, evaluation, and approval of nanofertilizers are lacking. Researchers, farmers, consumers, policy makers, and regulators all need to work more collaboratively to regulate nanofertilizers [33].

14.3 Environmental Pollution Caused by Use of Chemical and Nanofertilizers

Chemical and nanofertilizer use has reportedly been linked to environmental contamination in the past, including effects on the water, soil, and air as detailed in these following sections.

14.3.1 Effect of Chemical and Nanofertilizers on Water Pollution

The most crucial element for human survival is water. Due to water's presence, which covers about three-fourths of the earth's surface, it is known as the "blue planet." In addition to being necessary for the life of all living things, water also generates economic riches and a beautiful environment. Phosphates and nitrates found in chemical fertilizers have the potential to be the principal contributors to water pollution [39].

Nitrate leaching is particularly related to agricultural activities like fertilizer and crop growth. Some of the irrigated agricultural land in arid and semiarid regions increases water evaporation and nitrate buildup in the soil. Depending on the situation, nitrate builds up and leaches at varying rates [34]. Nitrate, the main ingredient in fertilizer, is one of the most significant factors in water contamination. Agricultural practices raise the nitrate levels in both surface and groundwater. The most prevalent type of dissolved nitrogen in groundwater is nitrate [40]. However, it can also be found as organic nitrogen, nitrogen oxide (N_2O), nitrogen (N_2), and nitrite (NO_2^-). Nitrate is absorbed in the digestive tract 4–12 hours after consumption of water by the body and is then attacked by the kidneys [41]. Through this mechanism and the salivary gland, nitrate can be concentrated. Due to this, in an anoxic environment, the nitrate in the mouth is converted to nitrite [41].

The term "eutrophication" refers to the rise in nitrogen and phosphorous compounds in water brought on by the expansion of aquatic plants and algae. This causes the water ecosystem and water quality to decline. Fish kills, a decrease in the number of living organisms in the aquatic environment, the proliferation of undesired species, as well an odor problem, and the media's apparent unsuitability for recreation are all effects of eutrophication in the bottom layer, which results in an anoxic environment that is unfit for drinking and water supply [2].

14.3.2 Effect of Chemical and Nanofertilizers on Soil

The use of chemical synthetic fertilizers, pesticides, herbicides, and soil conditioning agents in modern agricultural techniques is to blame for soil pollution, which turns fertile soil into infertile soil. Because soils have a great buffering ability because of their components, the impacts caused on the soil by the chemical fertilizers are not immediately apparent, according to studies and research [3]. It has been proven over time that the degradation of the current elemental balance is brought on by soil degradation reactions and the pollution-related loss in soil fertility. Additionally, harmful chemicals build within food crops and have an adverse impact on both people and animals when used [4].

Overuse of chemical fertilizers causes soil pollution, which negatively affects soil productivity and the population of soil-microbial organisms by building up hazardous substances in the soil structure [3]. Furthermore, an excess of synthetic fertilizers can result in crust development and soil acidification, which reduces the amount of beneficial population of organisms, humus, and organic matter [7]. Additionally, it may result in stunted plant development, a change in the soil pH, an increase in pests, or even help to produce greenhouse gases. According to Savci [4], the development of soil acidity limits phosphate amount that crops absorb; increases the concentration of ions that are harmful in the soil, and slows crop growth.

Eutrophication is brought on by the nitrate and phosphate runoff from agricultural fields and discharged into the nearby bodies of water. Methemoglobinemia in humans is brought on by consuming water with a higher nitrate content. Consumption of vegetables cultivated in soil high in

NO_3 may result in this illness, particularly in young children. These toxins continue to be active in soil hundreds of years later. The application of large amounts of potassium fertilizer affects the ability of the plant to receive nutrients from the soil's Zn, Fe, and Ca concentrations. The negative effects on organisms, however, have proved lethal and devastating given the variety of worms and soil mites [3].

14.3.3 Effect of Chemical and Nanofertilizers on Air Pollution

Chemical fertilizer is used at high rates to improve crop productivity, but this practice releases a lot of hazardous greenhouse gases, damages the ozone layer, and exposes people to harmful ultraviolet (UV) rays [3]. Agriculture is the largest source of anthropogenic N_2O emissions, accounting for around 60% of these emissions from soils. The production of nitrogen fertilizer results in the production of greenhouse gases including CO_2, CH_4, and N_2O. A similar amount of CO_2 can be produced by combining the effects [3].

Bacteria in the soil can turn nitrogen fertilizer into nitrous oxide, a greenhouse gas. Nitrogen fertilizer can cause severe air pollution, whose excessive use releases nitrogen oxides into the atmosphere [42]. The depletion of the ozone layer is being enhanced by the presence of chlorofluorohydrocarbons, hydrogen sulfide, methane, carbon dioxide, and water vapor. After carbon dioxide and methane, N_2O has emerged as the third most significant greenhouse gas. It has 310 times more potential to cause global warming than carbon dioxide. The main problem with nitrous oxide emissions is how they contribute to ozone depletion, which creates atmospheric "holes," which expose people and animals to excessive ultraviolet light and contribute to global warming [43]. Ammonia from fertilized land that has been volatilized or released, which is then deposited in the atmosphere and oxidized to form nitric acid and sulfuric acid, is the cause of acid rain. According to Mehta *et al.* [43], acid rain can harm plants, structures, and species that reside in lakes and reservoirs. Methane emissions from transplanted paddy fields are also a serious concern because methane is a potent greenhouse gas and the usage of fertilizers containing ammonium increases the gas' concentration [3].

14.4 Toxicological Effects of Fertilizers

The use of chemicals and nanofertilizers to raise agricultural production and increase the availability of plant nutrients is receiving more attention, nevertheless, there are some associated toxicity risks. Because smaller particles can penetrate biological systems more deeply and consequently pose greater potential dangers that still need to be assessed, it is yet unknown how poisonous, safe, and what effect chemical and nanofertilizers will have on the environment [4, 43]. The toxic chemicals in fertilizers are absorbed by plants and make their way into vegetables, cereals, and water, where they enter the food chain. Contaminated water may have high levels of nitrates and nitrites, which can lead to hemoglobin disorders. Heavy metals like Hg, Pb, Cd, and uranium, which have the potential to cause harm to the liver, lungs and kidneys as well as cause cancer, have been demonstrated to be present in fertilizers [43].

The size, shape, surface area, charge, solubility, crystal phases, coatings, material types, and dose concentrations of many nanoparticles (NPs) are thought to represent potential dangers to human health [45]. Additionally, NP behavior, transport, and toxicity may be affected by environmental variables such as temperature, pH, ionic strength, salinity, and organic matter taken as a whole. The various reaction settings, soil characteristics, and dosages utilized in the trials have been demonstrated by recent research that NPs have negative impacts on the dynamics of soil organic matter [45]. Although the toxicity of NPs created using biological processes is still being thoroughly investigated, NPs created using chemical and physical processes are more harmful than those created using biological processes [46].

Dangerous 22 heavy metals such as vanadium, thallium, selenium, nickel, and silver, which are all directly associated with risks to human health, were found in over 29 well-known fertilizers. Exposure to ammonium nitrate can result in a burning feeling in the eyes and skin as well as other health issues. The nose, throat, and lungs may get irritated as a result of inhalation exposure. Additionally, one may have headaches, nervousness, uncontrollable muscle movements, flushing of the neck and face, vomiting, nausea, faintness, and collapse [47].

14.4.1 Toxicological Effects of Fertilizers on Living Things

Fertilizers are compounds that give plants nutrition and promote their growth and productivity. However, if living species are exposed to fertilizers in high quantities or for an extended period of time, such as humans, animals, or aquatic organisms, fertilizers can also have toxicological effects on them. Following are a few examples of how fertilizers affect living beings toxicologically:

14.4.1.1 *Nitrate Poisoning*

Nitrogen, a component of fertilizers, can decompose into nitrates and leak into surface or ground water [47]. If consumed or inhaled in large quantities, nitrates can be detrimental to living beings [47]. Methemoglobinemia, a disorder that lowers the quantity of oxygen available to the tissues, can be brought on by nitrates interfering with the blood's ability to carry oxygen [48, 49]. Nitrate poisoning can cause cyanosis (bluish skin), headache, dizziness, nausea, vomiting, diarrhea, trouble breathing, coma, and death [49]. Below is a discussion of some of the harmful toxicological effects of fertilizer-induced nitrate toxicity.

14.4.1.1.1 Methemoglobinemia

Methemoglobinemia, a disorder that lowers the quantity of oxygen available to the tissues, can be brought on by nitrates interfering with the blood's ability to carry oxygen [50]. When nitrates are transformed into nitrites by digestive tract bacteria or by body enzymes, methemoglobin, a kind of hemoglobin that cannot bind oxygen, can build in the blood [50]. According to Thompson [50], methemoglobinemia can cause cyanosis (bluish skin), headaches, dizziness, nausea, vomiting, diarrhea, trouble breathing, coma, and even death. Both humans and animals can have methemoglobinemia, however, it is more prevalent and severe in young children, pregnant women, and those who have certain genetic diseases [50].

14.4.1.1.2 Carcinogenesis

The production of nitrosamines, which are powerful carcinogens, nitrates can also raise the risk of cancer, particularly in the digestive system [51]. When nitrites and amines, which are substances originating from proteins, interact, nitrosamines are created [46, 51]. According to Ahmed *et al.* [51], nitrosamines can alter deoxyribonucleic acid (DNA) and result in mutations that can result in the growth of tumors. High nitrate intake, poor antioxidant intake, high consumption of red and processed meat, smoking, and bacterial infections are a few variables that can contribute to the development of nitrosamines [46, 51].

14.4.1.1.3 Endocrine Disruption

The endocrine system, which controls the body's hormones and metabolism, can also be impacted by nitrates [40]. In the prevention of the uptake of iodine, which is necessary for the manufacture of thyroid hormones, nitrates can interfere with the thyroid's ability to function [40]. The body's energy balance, reproduction, development, and growth are all regulated by thyroid hormones. Hypothyroidism, a disorder marked by weariness, weight gain, depression, cold sensitivity, and goiter (enlarged thyroid gland), can be brought on by low thyroid hormone levels [40].

14.4.1.1.4 Neurotoxicity

Change in the amounts of neurotransmitters and inducing oxidative stress, nitrates can also have neurotoxic effects on the brain and nervous system [49]. According to Chavoustie and Gabbey [49], neurotransmitters are chemical messengers that aid in communication between neurons (nerve cells) and other cells in the body. Reactive oxygen species (ROS), chemicals that can harm cells and tissues, are produced and eliminated in an inefficient manner during oxidative stress [49]. Tremors, convulsions, memory loss, cognitive decline, and behavioral changes are a some of the neurological signs of nitrate overdose [49].

14.4.2 Heavy Metal Toxicity

Providing plants with nutrients and enhancing their growth and output are the functions of fertilizers and nanofertilizers [52]. Heavy metal poisoning, a condition that happens when living organisms are exposed to too much heavy metal from soil, water, or food sources, can also be brought on by fertilizers and nanofertilizers [52]. Mercury, lead, cadmium, arsenic, and chromium are examples of heavy metals, which are elements with high atomic weights and densities [52]. The brain system, immunological system, reproductive system, kidneys, liver, lungs, and other organs and systems of living beings can all be negatively impacted by heavy metals [52]. The toxicological consequences of heavy metal toxicity brought on by fertilizers and nanofertilizers include, among others:

14.4.2.1 Kidney Damage

Nephrotoxicity, or damage or failure of the kidney cells, is a result of heavy metal accumulation in the kidneys [45]. Nephrotoxicity can make it harder for the kidneys to filter waste materials and control the body's fluid and electrolyte balance. Proteinuria (protein in the urine), hematuria (presence of blood in the urine), oliguria (low output of urine), anuria (no output of urine), edema (swelling), hypertension (high blood pressure), and renal failure (loss of kidney function) are all signs of kidney injury [45].

14.4.2.2 *Liver Damage*

Hepatotoxicity, or the harm or dysfunction of the liver cells, is another effect of heavy metal accumulation in the liver [45]. According to Wang *et al.* [45], hepatotoxicity can affect the liver's capacity to release bile, manufacture proteins and hormones, store glycogen and vitamins, and metabolize medications and poisons. Jaundice, which causes the skin and eyes to turn yellow, ascites, hepatic encephalopathy (brain dysfunction brought on by liver failure), coagulopathy (bleeding condition), and liver cirrhosis (scarring of the liver tissue) are all signs of liver disease [45].

14.4.2.3 *Lung Damage*

Intake of heavy metal particles via inhalation can also result in pneumotoxicity, which is the destruction or malfunction of lung cells [45]. According to Wang *et al.* [45], pneumotoxicity can make it harder for the lungs to fight off infections, control pH and blood pressure, and exchange oxygen and carbon dioxide. Dyspnea (difficulty breathing), coughing up blood, wheezing, chest pain, pulmonary edema (fluid accumulation in the lungs), pulmonary fibrosis (scarring of the lung tissue), and respiratory failure (insufficient gas exchange) are all signs of lung injury [45].

14.4.2.4 *Neurological Damage*

In addition to damaging or impairing brain and nervous system cells, heavy metals can also pass the blood-brain barrier and produce neurotoxicity. Neurotoxicity can impede the brain's capacity for information processing, motor control, emotional regulation, and homeostasis maintenance. A headache, dizziness, nausea, vomiting, tremors, seizures, memory loss, cognitive impairment, behavioral abnormalities, mood disorders, psychosis, and coma are examples of neurological injury symptoms [53].

14.4.2.5 *Immunological Damage*

The change in the development and operation of immune cells including lymphocytes, macrophages, and natural killer cells, heavy metals can also have an impact on the immune system [53]. Immunotoxicity can make it more difficult for the immune system to maintain tolerance to self-antigens, destroy aberrant cells, and fight infections. Increased vulnerability to infections, autoimmune conditions, allergies, inflammation, and cancer are signs of immunological impairment [53].

14.4.2.6 *Reproductive Damage*

Interfering with the production and function of sex hormones including estrogen, progesterone, and testosterone, heavy metals have been reported to have adverse effect on the reproductive system [53]. According to Balali-Mood *et al.* [53], reproductive toxicity can affect the reproductive system's capacity to create gametes (sperm and eggs), support pregnancy, promote fetal development, and control sexual behavior. Infertility, miscarriage, stillbirth, birth abnormalities, low birth weight, early delivery, and developmental issues are all signs of reproductive harm [53].

14.4.3 Eutrophication

In excess nutrients like nitrogen and phosphorus, fertilizers can also lead to eutrophication, a process that encourages the growth of algae and other aquatic plants in water bodies [54]. According to Semenov *et al.* [54], eutrophication can lower the amount of dissolved oxygen in the water, resulting in hypoxic or anoxic conditions that can smother or kill fish and other aquatic species. Aquatic environments' biodiversity and ecosystem balance can be impacted by eutrophication as well [54].

14.4.4 Bioaccumulation of Heavy Metals Caused by Nanofertilizers in the Food Chain

Nanoparticles, or particles with at least one dimension between 1 and 100 nm, are present in nanofertilizers, which are fertilizers. According to Ali *et al.* [52], nanoparticles can have particular qualities that promote the solubility, mobility, reactivity, and bioavailability of fertilizers. But there are other negative effects of nanofertilizers on the ecosystem, like the bioaccumulation of heavy metals in the food chain.

Cadmium, lead, and zinc are examples of heavy metals, which are elements with high atomic weights and densities. Owing to their toxicity, environmental persistence, and bio-accumulative properties, they are well-known environmental contaminants [55]. While their natural causes include weathering of metal-bearing rocks and volcanic eruptions, their manmade origins include mining and various industrial and agricultural operations [55].

According to Mallikarjunaiah *et al.* [55], bioaccumulation is the process by which organisms take in compounds from their environment at a rate greater than the pace at which they can eliminate those substances from their tissues or organs. According to Mallikarjunaiah *et al.* [55], bioaccumulation can take place directly from water, soil, or air as well as indirectly via food. Biomagnification, which is the process by which a substance's concentration rises along the food chain as one organism consumes another, can result from bioaccumulation [55].

Several processes exist by which nanofertilizers can contribute to the bioaccumulation of heavy metals in the food chain. They include:

14.4.4.1 Contamination

Heavy metal contamination of nanofertilizers can occur during production, storage, transport, or application [34, 52]. According to Butt *et al.* [34] and Ali *et al.* [52], these heavy metals can leak into the soil or water and be ingested by plants or aquatic species. For instance, certain nanofertilizers contain silver nanoparticles that, during their manufacture, may have been polluted with cadmium [52].

14.4.4.2 Enhancement

By enhancing the solubility, mobility, or availability of heavy metals in the soil or water, nanofertilizers can facilitate their uptake by plants or aquatic creatures [34, 52]. For instance, iron oxide nanoparticles found in some nanofertilizers can make lead more soluble in soil by lowering lead's oxidation state [52].

14.4.4.3 Interaction

According to Butt *et al.* [34] and Ali *et al.* [52], nanofertilizers can interact with heavy metals in soil or water to create complexes or aggregates that can be ingested by plants or aquatic life. Consider the carbon nanotubes found in some nanofertilizers, which can bind to zinc and make it easier for zinc to pass plant membranes [52].

14.4.5 Adverse Effects of Bioaccumulation of Heavy Metals

The health and quality of plants, animals, and people who consume them can be negatively impacted by the bioaccumulation of heavy metals brought on by nanofertilizers. A few of the results are:

14.4.5.1 *On Plants*

According to Butt *et al.* [34], heavy metals can have an impact on a plant's physiology, morphology, biochemistry, and metabolism. Reduced growth, development, yield, and quality are a few of the impacts. Others include changed nutrient absorption and translocation, impaired photosynthesis, respiration, and enzyme activity, increased oxidative stress and antioxidant defense, and changed gene expression and regulation [34].

14.4.5.2 *On Animals*

Animals that consume contaminated plants or aquatic organisms may experience health problems or change in behavior [34, 55]. Reduced growth, reproduction, and survival are a few impacts, along with decreased organ development and function, changed immunological and hormone levels, increased oxidative stress and DNA damage, and a higher chance of illnesses and disorders [34, 55].

14.4.5.3 *On Humans*

When humans ingest contaminated plants or animals, heavy metals can have an impact on their health and well-being [34, 55]. Reduced nutritional quality and value, impaired organ function and development, altered immune and hormone levels, increased oxidative stress and DNA damage, and an increased risk of diseases and disorders like anemia, renal failure, liver cirrhosis, pulmonary fibrosis, neurological disorders, cancer, and birth defects are just a few of the effects [34, 55].

14.4.6 Effects of Bioaccumulation of Chemical Substances Found in Fertilizers on the Health of Animals and Humans

To give nutrients for the growth and development of plants or soil, fertilizers are compounds that are applied. There are two types of fertilizers: inorganic (or chemical) and organic. In contrast to inorganic fertilizers, which are created from mineral or synthetic sources like ammonium nitrate, urea, or superphosphate, organic fertilizers are generated from natural sources like animal dung, compost, or green manure. Fertilizers can improve soil health and crop output by making vital nutrients like nitrogen, phosphorous, and potassium more readily available. By producing pollution, eutrophication, and the bioaccumulation of dangerous chemicals, fertilizers can also have a detrimental impact on soil health and biodiversity [56–58]. According to Bitesize [55], bioaccumulation is the process by which organisms collect substances in their tissues or organs at a rate greater than the rate at which they are eliminated by catabolism and excretion. Direct uptake from water, soil, or air can lead to bioaccumulation, as can indirect uptake from food [58]. Biomagnification, which is the process by which a substance's concentration rises along the food chain as one organism eats another, can result from bioaccumulation [58].

Animals and people who consume polluted organisms may suffer negative health effects from the bioaccumulation of chemicals contained in fertilizers. Among the results are:

14.4.6.1 On Animals

Animal physiology, behavior, reproduction, and survival may be impacted by the bioaccumulation of chemicals present in fertilizers [56, 58]. Several of the outcomes include:

14.4.6.1.1 Reduced Growth and Development

Animals' hormone levels, enzyme activity, gene expression, and organ function can all be affected by bioaccumulated chemicals, which can also interfere with normal growth and metabolic disorder [56, 58]. For instance, nitrate can lower blood's ability to carry oxygen, resulting in blue baby syndrome (also known as methemoglobinemia) in newborns and young animals [56].

14.4.6.1.2 Reduced Reproduction and Fertility

By changing hormone levels, gamete production, mating behavior, and offspring viability, bioaccumulative chemicals can have an impact on an animal's reproductive system and fertility [56, 58]. For instance, the pesticide atrazine, which is used to grow corn, can make fish and amphibians infertile and damage their endocrine systems [56].

14.4.6.1.3 Reduced Survival and Immunity

By making animals more vulnerable to illnesses, parasites, predators, and environmental stressors, bioaccumulative chemicals can have an impact on animal survival and immunity [56, 58]. For instance, cadmium, a heavy element included in phosphate fertilizers, has been linked to immunosuppression, anemia, and kidney damage in mammals [56].

14.4.6.2 On Humans

When humans ingest contaminated plants or animals, the bioaccumulation of fertilizer-related chemicals can have an impact on their health and well-being [56, 58]. Several of the outcomes include:

14.4.6.2.1 Reduced Nutritional Value and Quality

By altering food's flavor, aroma, color, texture, and shelf life, bioaccumulated chemicals can lower the nutritional value and quality of the food [56, 58]. For instance, rice's protein quantity and quality might be affected by arsenic, a metalloid that causes cancer and is present in several fertilizers [56].

14.4.6.2.2 Impaired Organ Function and Development

By influencing hormone levels, enzyme activity, gene expression, and cell growth, bioaccumulated chemicals can harm the growth and development of a variety of human organs [56, 58]. For instance, fluoride, a trace element present in several fertilizers, has been linked to both skeletal and dental fluorosis in humans [56].

14.4.6.2.3 Increased Risk of Diseases and Disorders

By producing oxidative stress, inflammation, DNA damage, and mutation in humans, bioaccumulated chemicals can raise the chance of developing a variety of diseases and disorders [56, 58]. For instance, nitrosamines, which are carcinogenic substances in humans, can be created when nitrite, a byproduct of nitrate reduction, reacts with amines, which are present in meat [56]. The bioaccumulation of fertilizer-related chemicals is a significant environmental issue that endangers both human and animal health. As a result, it is critical to monitor, control, and minimize the usage of hazardous chemicals and their release into the environment. Education regarding the dangers and effects of bioaccumulation and biomagnification is also crucial.

14.4.7 Contribution and Effects of Chemical Fertilizers and Nanofertilizers on Global Warming

The average temperature of the Earth's surface and atmosphere rising as a result of a stronger greenhouse effect is known as global warming.

The natural phenomena known as the greenhouse effect causes some solar energy to be captured by greenhouse gases in the atmosphere, keeping the Earth warm and hospitable. However, due to anthropogenic activities like fossil fuel burning, deforestation, and agriculture, the greenhouse gas concentration in the atmosphere has increased, amplifying the greenhouse effect and contributing to global warming. These gases include CO_2 (carbon dioxide), CH_4 (methane), and N_2O (nitrous oxide) [59].

The effects of global warming on the environment and human health are numerous, including the melting of glaciers and ice caps, increasing sea levels, extreme weather, loss of biodiversity, failed crops, water shortages, heat stress, infections, and armed conflicts [59]. Because of this, it is critical to cut greenhouse gas emissions and slow global warming.

About 24% of all anthropogenic emissions in 2010 came from agriculture, making it one of the biggest contributors to greenhouse gas emissions [59]. The use of fertilizers, particularly chemical fertilizers, is one of the main causes of agricultural greenhouse gas emissions. By making vital elements like nitrogen, phosphorous, and potassium more readily available, chemical fertilizers can improve crop yield and food security. However, due to pollution, eutrophication, and greenhouse gas emissions, chemical fertilizers can potentially have a negative impact on the environment and climate [17, 59].

14.4.8 Ways Through Which Chemical Fertilizers Contribute to Global Warming

The effects and contribution of chemical fertilizers to global warming have been the subject of numerous reports. Some of the following effects were observed both during and after their application.

14.4.8.1 During Their Production

Chemical fertilizer synthesis consumes a significant amount of energy, primarily from fossil fuels that release CO_2 into the environment. The Haber-Bosch process, which uses high pressure and temperature to change atmospheric nitrogen (N_2) into ammonia (NH_3), is also used in the creation of nitrogen fertilizers. According to Manthiram and Gribkoff [59] and Verma *et al.* [17], this process uses roughly 1% of the world's energy resources and emits roughly 1.4% of the world's CO_2 emissions.

14.4.8.2 *After Their Application*

After farmers employ chemical fertilizers on their farms, greenhouse gases are also produced. Only around half of the nitrogen that crops receive from fertilizers is actually absorbed by the plants [60]. A significant portion of the fertilizer sprayed washes off into streams or is decomposed by soil bacteria, releasing the strong greenhouse gas N_2O into the sky. N_2O lingers in the atmosphere for 100 years and has a 300-fold larger global warming potential than CO_2 [59, 60]. About 60% of all greenhouse gas emissions from agriculture are N_2O emissions [59].

Alternative approaches have been put forth to lessen the negative effects that chemical fertilizers have on the environment and climate, such as enhancing soil carbon sequestration, increasing fertilizer use efficiency, and switching to organic farming practices [59, 60].

14.5 Conclusion

The production of agricultural food grains is essential for human nourishment, necessitating technological advancements that are also economically feasible and environmentally sustainable. Globally, food grain production has increased as a result of the "green revolution," but at the same time, the overuse of synthetic fertilizers has seriously damaged the environment and needs to be addressed. Examining and vetting organic, environmentally friendly, and resilient nutrient sources is safe for the agroecosystem. In comparison to traditional chemical fertilizers, biologically generated fertilizers provide a wide range of advantages. They can also be tailored to optimize plant nutrient uptake efficiency, rate of release, and crop spread. Biologically produced, nutrient-rich biomass from microbial cells can supply nutrients, growth-promoting macromolecules, and other critical elements for healthy plant development and vigor. In contrast to the rapidly penetrating and nutrient-rich runoff from applied chemical fertilizers, nutrients abundantly present in wastewater can be adequately channeled to the crops through algae. To reduce losses and prevent environmental pollution, one of the most important jobs is to improve the nutrients' assimilation capacities and regulate the release rates from fertilizers. In this situation, green biomass, such as algae, can be reduced to nanoscale levels with the right shape, size, and structure together with the perfect surface qualities to create a new agro-nanofertilizer that is more effective and significantly lessens our reliance on synthetic fertilizer. Economic systems based on nanofertilizers would create the best circumstances for increased production, better resource management, and a cleaner environment, opening the way for a thriving agro-economy. It is crucial to do a proper investigation of how these nanofertilizers affect the environment.

14.6 Future Perspective

Due to their possible negative impacts on the environment, the usage of chemical fertilizers and nanobiofertilizers has been a source of worry. These fertilizers can pollute the environment, which can cause bioaccumulation, greenhouse effects, and global warming. It is critical to act to lessen the adverse effects these substances have on the environment because they are a source of growing worry. Future agricultural practices are predicted to move in favor of those that are more environmentally friendly and sustainable. Since organic fertilizers are less damaging to the environment, this change will involve their utilization. Natural materials like animal manure, compost, and bone meal can be utilized to make organic fertilizers. They are nutrient-rich and contribute to bettering the condition of the soil, which enhances agricultural yields. Precision agriculture is a different strategy that is anticipated to gain popularity in the future. This strategy involves maximizing crop yields while reducing the use of pesticides and fertilizers by using technology like sensors, drones, and global positioning system (GPS) mapping. Farmers can use precision agriculture to boost productivity while minimizing their negative environmental effects. In conclusion, it is obvious that both chemical and nanobiofertilizer use have detrimental consequences on the environment. However, as we transition to more environmentally friendly and sustainable agricultural practices, there is promise for the future. Precision farming and the use of fertilizers that are organic in nature in order to allow us to lessen our impact on the environment while preserving food security for future generations.

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