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Review article

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Widespread use of toxic agrochemicals and pesticides for agricultural products storage in Africa and developing countries: Possible panacea for ecotoxicology and health implications

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ABSTRACT

Chemicals used for storage majorly possess insecticidal activities – deterring destructive insect pests and microorganisms from stored agricultural produce. Despite the controversy about their safety, local farmers and agro-wholesalers still predominantly use these chemicals in developing countries, especially Africa, to ensure an all-year supply of agriproducts. These chemicals could have short- or long-term effects. Despite the state-of-the-art knowledge, factors such as poor education and awareness, limited agricultural subventions, quests for cheap chemicals, over-dosage, and many more are the possible reasons for these toxic chemicals' setback and persistent use in developing countries. This paper provides an up-to-date review of the environmental and ecological effects, as well as the health impacts arising from the indiscriminate use of toxic chemicals in agriproducts. Existing data link pesticides to endocrine disruption, genetic mutations, neurological dysfunction, and other metabolic disorders, apart from the myriad of acute effects. Finally, this study recommended several naturally sourced preservatives as viable alternatives to chemical counterparts and emphasized the invaluable role of education and awareness programs in mitigating the use in developing nations for a sustainable society.

1. Introduction

Grains are integral to daily food requirements and are consumed in large quantities across Africa. Any nation's economic and social development depends on its food security. Africa is not left behind, as their livelihood and sustainability sources are agriculture [1]. Storage of cereal grains and legumes (such as cowpea, millet, wheat, rice, barley, oats, sorghum, and corn) with chemicals is a common practice amongst African farmers and sellers of agro-produce [2]. The food problem in Africa is the lack of preservative mechanisms in handling bountiful harvests after short farming seasons. Global annual storage produces losses are estimated to give 10% of all stored grain, while in sub-Saharan Africa, it ranges from 25 to 40% of grain losses [3]. Africa has become more dependent on pesticides to preserve and store its farm products. The demand for these pesticides keeps increasing due to crop production, which yields bountiful

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agricultural yields [4,5]. Many farmers have embraced the use of pesticides as the best means of insurance in protecting and preserving their crops against wanton destructions by pests, notwithstanding that many farmers are not adequately equipped with personal protective gadgets and their inability to read labels on pesticide products [6].

Growing evidence shows farmers and their families may be predisposed to severe and immediate health risks linked with pesticides, although the impacts are undetected in many cases. These chemicals inevitably get to the soil due to dispersal through washing water, excessive application, and failure on the part of farmers to adhere to their usage guidelines, inevitably distorting the soil ecosystems and microflora. Also, persistent pesticides leach into the water bodies and intermittently cause nuisance and mortality to the aquatic ecological diversities and promote climate change [5,7]. In the terrestrial biosphere, toxic chemicals can affect the skin when dermally absorbed due to splashes and spills during handling [7,8]. Health implications from consuming food with pesticide residues beyond the permissible limit are not left out. In addition to the acute effects caused by these chemicals, they also cause chronic effects even if exposed in minute amounts. Although these chemicals are used for storage, some residues have been discovered in cooked foods as well as directly in animal feeds [9]. Sadly, people have resorted to using pesticides in suicidal attempts due to stress and psychological factors [10]. About 50% of the pesticides involved in these cases have been classified as highly hazardous by WHO [11]. The risk factors associated with the usage of pesticides include but are not limited to respiratory, cardiovascular, and endocrine disruptions, metabolic disorders, and gastrointestinal, reproductive, and neurological dysfunctions [12].

Unfortunately, Africa has become the dumping site for importing banned synthetic pesticides rejected by the European Union. And this calls for questions, given the growing evidence that these toxic chemicals pose a serious threat to humans and the ecological systems and contravene the United Nations' Sustainable Development Goals on food security [13]. Moreover, pesticide manufacturers are interested in making a profit and argue about the environmental health issues concerning their products rather than the health of the end-users and the ecosystem [9,14]. As of present, globally, about three million tonnes are used annually in the forms of herbicides (50%), insecticides (30%), fungicides (18%), and other categories used for rodents and nematode prevention [1,4,11]. To worsen the situation, many farmers indiscriminately use these hazardous toxic chemicals on the farm and grain storage to avoid postharvest losses without being mindful of their dangers to human health and the ecosystems. Therefore, this review paper is geared toward re-examining the various methods of agricultural products storages using chemical pesticides, emphasizing the adverse postharvest effects on the nutritional compositions of grains, ecological effects on the soil, and aquatic organisms on the acute and chronic effects when of contact with humans. Finally, this review offered solutions and recommendations for proper and effective procedures for a green, eco-friendly and safer usage of storage chemicals in agricultural practices in Africa.

1.1. An overview of agro-produce storage in Africa: traditional and contemporary approach

Cereals and legumes (grains) are vital diet constituents globally and are rich in carbohydrates and proteins [11]. It is a significant food source and provides sustainable income and stable employment for African farmers. Food grains are usually stored in the tropic and subtropics to provide food reserves and seeds for planting. The significant grains cultivated in these regions include maize, wheat, sorghum, rice, soybean, cowpea, beans, pigeon pea, millet, and lentil [15]. Postharvest losses cause farmers an enormous economic deficit, a worrisome concern worldwide. Many food grains are destroyed after harvest due to poor storage mechanisms. Agricultural produce also suffers adversely due to periodic climate variations leading to floods, drought, and changes in rainfall patterns [4].

Table 1

Tuble I	
Classification	of agro-produce storage structures in Africa.

Types of storage structures	Stored food	Method of preservation	Disadvantages	Duration of storage	References
1. Traditional a. Aerial storage	Unshelled maize cob and cereals	Air drying and sun drying	Exposure to pests	Short	[6]
b. Storage on the ground	Cereals, grains, and any other farm products	Air drying	Not efficient in tropical areas due to damp	Short	[2]
c. Domestic structures	All grains	Tin, box, jute bag, polythene bag, earthen pot, plastic or metal containers	It does not encourage large-scale storage	Short	[16]
d. Rhombus and traditional crib	Grains and legumes	Air drying	High moisture builds up due to rain, microbial infestation	short	[16]
e. Barn, shelf, pit	Root and tuber crops	Air drying	Affected by environmental conditions	short	[2]
2. Modern a. Improved crib	Grains	Air drying	Not optimal in the rainy season	Longer storage	[17]
b. Warehouse	Bulk grains and flour	Air drying in a properly ventilated environment	Cost-effective	Longer storage	[2]
c. Silo/bin	Bulk grain storage	Air drying	Moisture migration and condensation very costly to build	Longer storage	[18]
d. Controlled atmosphere	Highly perishable crops and food materials	Freeze drying	Expensive and requires a steady power supply	Longer storage	[16]
e. Hermetic and nitrogen storage system	Highly perishable crops and food materials	Prevents air absorption into stored products	Easily contaminated if not properly handled	Longer storage	[11]

The food problem in Africa is the lack of a preservative mechanism for handling bountiful harvests after short farming seasons. And has nothing to do with the low productivity of farm produce. It has been estimated that global annual storage produces losses to give 10% of all stored grain, while in sub-Saharan Africa, it ranges from 25 to 40% of grain losses [3].

Grains produced are vital in the economic development of developing nations due to their seasonal nature and are preserved for a wide range of users throughout the year. For the stability of any nation's economy, quality food grain must be supplied to end-users to produce different products, marketing, and likewise available to the farmers for the next farming season [1]. To achieve this, food grains must be stored adequately throughout the year. Since time immemorial, postharvest storage facilities have been a major issue in Africa, affecting African nations' agricultural output and economic loss [4]. African nations have different storage methods that are best known and practiced. Farmers' success with different storage techniques depends on applying the storage principles of food grains. The fundamental aim of grain storage techniques is to properly preserve and secure grains from insects, rodents, and microbial degradations [15].

1.2. Common storage structures in Africa

Storage structures house stored food grains to preserve and retain their qualities. The criteria for selecting these structures depend on the culture of the farmers, harvest productivity, and climate factors [6]. There are two classes of storage structures, as presented in Table 1. The classes are.

- a. Traditional structures house the small size of farm products over a short period. It exposes farm products to infestation and contamination, usually from unrefined local materials.
- b. Modern structures usually house a large capacity of farm products with improved and refined storage materials and conditions over a long time.

The traditional storage method is the technique in storage in communities and has existed since time immemorial and has been practiced from generation to generation. Different storage methods are indigent to different nations, communities, localities, and countries [6]. It is estimated that a higher percentage of food grains produced in developing nations, especially in Africa, are stored at home using traditional methods. This entails sufficient drying of food grains and using storage facilities that are moisture free and well-ventilated. In some African countries, the prominent storage facilities are pots or baskets, indoor storage such as plastic and metal containers, granaries, platforms, pots, thatched rhombus, bags made of jute, polythene, or plant fiber and other coping strategies developed by different farmers which are aimed towards reducing postharvest losses and wastages. These include using pepper in storage, immediately selling grains after harvest, and unethical application of pesticides indiscriminately [2]. High postharvest waste of food grains has severe economic implications on the farmers and the consumers, and in all, food availability is affected. The poor farmers are adversely affected as they spend much of their income on food grains. Therefore, it is of utmost importance that postharvest strategies are given much attention as preharvest practices [16]. Better strategies for reducing food grain storage losses caused by insects, rodents, birds, and microbial pests will be vital in protecting global food security.

2. Chemical-based agro-storage systems in Africa

Using insecticides that come in contact with food grains requires a proper understanding and evaluation of their hazards and benefits [19]. The major causes of the abuse of synthetic pesticides in Sub-Sahara Africa lie that most of the farm products are predominantly produced by poor-enlighten farmers who may not be able to afford the cost of safe pesticides [18]. In many African countries, using hazardous chemicals in grain storage is part of the game because no farmers want to experience any damage to their

Table 2

Tuble 2					
Contact pesticides,	classification,	usage,	and health	implication to	humans.

Pesticides	Classes	Usage	Disadvantages	References
Organochlorine	Dichlorodiphenyltrichloroethane (DDT) ^a , dieldrin, heptachlor, dicofol, methoxychlor	Cereals and legumes	Endocrine disruption, carcinogenic action, neurological effect, embryonic development, lipid metabolism, hematology alterations	[5]
Organophosphorus	Malathion, parathion, Dimethoate	Soybean, maize	Endocrine disruption, reduced insulin secretion, carbohydrates, proteins, and fats metabolism disruptions, mitochondrial dysfunctions, oxidative stress, reproductive organ damage, cardiovascular diseases, kidney failure, DNA damage, nerves dysfunctions	[5]
Carbamate	Aldicarb, carbofuran, carbaryl ^a	cereals	Reproductive organ damage, Endocrine disruption, metabolism, and mitochondrial dysfunctions, dementia affect neurological functions.	[2]
Pyrethroids	Fenvalerate, sumithrin, permethrin ^a	Cereals and legumes	Endocrine disruption, reproductive organ damage, neurotoxicity in children	[3]
Neonicotinoid	Imidacloprid ^a , thiacloprid, gaudily	legumes	Endocrine disruption, reproductive organ damage	[3,5,13]

^a Most active.

grains by pests while ignoring the consumers' and environmental safety. Africa's high prevalence of pests is much higher, possibly due to its tropical climates. There are tendencies of infrastructural deficiencies leading to poor pest control systems [16]. The abuse of pesticides in food grain storage has caused dangerous health implications, insect pesticide resistance, and other severe environmental complications [9]. Table 2 presents the harmful health implications of these contact insecticides on farmers, end-users, and the environment.

Since the introduction of numerous agrochemicals in pest control by multinational agrochemical companies daily, current pest control practice uses synthetic chemicals with hazardous implications [5], and traditional methods of food grains storage have eroded in African storage practice.

3. Effect of storage chemicals on the qualities of agro-produce

Due to the physicochemical characteristics and chemical composition, most agro-produce are perishable and can be easily altered by biological, physical, and chemical agents [20]. Farmers use different storage chemicals to store cereal grains, which are costly and toxic. Some of these chemicals are not affordable to some farmers, and those that could afford them misuse them, resulting in environmental and health concerns. Low-income farmers may use cheap but noxious synthetic chemicals to store cereal grains.

Storage of cereal grains and legumes (such as cowpea, millet, wheat, rice, barley, oats, sorghum, and corn) with chemicals is a common practice amongst African farmers and sellers of agro-produce. Generally, chemicals usually used to protect agro-produce from pest infestation and destruction during storage are grouped into several classes, including organochlorine (e.g., dichlorodiphenyl-trichloroethane, heptachlor, and hexachlorobenzene), Organophosphate (e.g., Dimethoate, quinalphos, 2, 3-dichorovinyl dimethyl phosphate (sniper), methyl parathion, malathion, diazinon, chlorpyrifos, profenofos, monocrotophos, and), carbamate (e.g., carbendazim, carbofuran, and carbosulfan) and Pyrethroid (e.g., cyphenothrin and cypermethrin) [21,22]. The impact of these chemicals on the nutritional composition of cereal grains is of great concern. Studies have shown the prevalence of these chemical residues in stored products, affecting the health and nutritional value derived from their consumption [23–25]. The quality of these chemically stored grains is mainly influenced by the duration and method of storage [26].

A high concentration of these chemicals may interfere with the nutritional constituents of food and non-food crops (Ogelekaa and Omoregie, 2020; Mulla et al., 2020). The maximum residue limits of organophosphate and organochlorine are (0.05–1.00 mg/kg) and (0.01–1.00 mg/kg), respectively [27]. Organochlorine pesticides, also known as lipophilic chemicals, vary in their mechanisms of toxicity because of their differences in chemical structures and their buildup at the higher trophic levels, which leads to bio-magnifications within the food chain [28,27]. Pesticides and other storage chemicals potentially foster the rise of ROS in stored produce, which some studies have highlighted to promote degradation of the protein composition of crops, as well as distortion of the activities of postharvest enzymes [29].

Chemical treatment of crops for storage may have undesirable effects that lead to decreased nutritional value or altered sensory properties. Little is known about the effect of storage chemicals on the physicochemical properties (such as gel consistency, water absorption, solubility, gelatinization, and bulk density), nutritional content involving proximate profile (crude fat, ash content, moisture content, nitrogen-free extract, and crude protein), carbohydrate (amylase, starch, and amylopectin), total dietary fiber and ash content [30] of agro-produce in Africa. Based on the chemical groups present in these chemicals, there is a possibility of the adduct (or metabolites) formation resulting from chemical interactions between the nutrients and phytochemicals present in the crops, thereby reducing or limiting the availability of these nutritional components of crops and inhibiting food enzymes [31]. Studies on the nutritional composition and pesticide residue levels in some chemically stored cereals grains (wheat, sorghum, maize, and millet) sold in Africa showed the ash content and crude protein, organochlorine, and organophosphate levels were highest in wheat and lowest in maize. In contrast, the fat content was highest in millet and lowest in wheat, with all the organochlorine and organophosphate levels within the Maximum Residue Limits (MRLs) [27].

Studies have shown that increasing concentrations of 2, 3-dichorovinyl dimethyl phosphate (sniper) applied on cowpea lead to the reduction of its fat, crude protein, and fiber contents, whereas the ash and carbohydrate contents were significantly increased [26]. Moreover, the decrease in protein, fat, and moisture was accompanied by an increase in microbial activities, resulting in the deterioration of protein and fat and an increase in moisture content [26,32]. The moisture content of chemically treated grains is usually maintained within the desired range since the chemicals effectively control pests' respiratory activities, increasing stored grains' moisture content [33]. The mineral nutrients were observed to increase with increased storage duration and sniper concentration. These storage chemicals add to the bulk of the grain, thus leading to increased ash content [33]. The toxicity of storage chemicals in agric-produce depends on the concentration of pesticides, rate, and duration of application, climate conditions, spraying technique, organization of flora, temperature, pH, texture, humidity, and microbial activity [29].

3.1. Ecological effects of storage chemicals

Chemicals used for storage majorly possess insecticidal activities – deterring destructive insect pests and microorganisms from stored agricultural produce [34]. Despite the controversy about their health and environmental safety, these chemicals are still predominantly used by local farmers and agro-wholesalers in developing countries to ensure an all-year supply of several agriproducts, both in and off-season [35]. The persistence in using these chemicals despite recent innovations of health and eco-friendly alternatives and government bans and regulations could majorly be due to poor or limited consequential knowledge of local farmers or wholesalers [36]. Besides the health effects of chemical pesticides used for storage, their severe implications on soil and aquatic organisms, birds, and terrestrial life cannot be over-emphasized, as severe ecological distortion may emanate from such effects [37,38]. Some of the tropics' general agricultural practices, such as unnecessary and excessive application of chemical pesticides, cheaper and more hazardous storage pesticides, and poor transportation and handling, have been implicated in fostering such negative implications [37,39]. This section presents an overview of the detrimental toxic effects of agri-storage chemicals on the ecosystem and the environment (Fig. 1).

3.2. Effects on soil organisms and agroecosystems

Agricultural produce in many developing and African countries is stored and preserved outdoors with diverse systems. Many adopt the application of chemicals to store grains, tubers, vegetables, fruits, and many more [40]. These chemicals inevitably get to the soil due to dispersal through wind, washing water, excessive application, and failure on the part of farmers to adhere to their usage guidelines. The fate and effects of these chemicals in the soils are numerous, delving from affecting the activities or death of soil microflora and invertebrate organisms to distorting nitrogen mineralization and nutrient transformation [41]. Moreover, some persistent storage chemicals with greater half-life could eventually get leached or swept away into the water bodies. They affect aquatic organisms, amphibians, fishes, and aquatic ecosystems [42,43].

Soils are an essential part of the agroecosystem. They are home to many invertebrates and microbes with significant roles in nutrient cycling, soil structure maintenance, carbon transformation, agro-pest, and disease regulation. Storage chemicals have been reported to adversely affect pests and non-target organisms such as earthworms, isopods, collembolans, mites, Termites, nematodes, and beetles [44–47]. Over 400 studies on the negative impact of about 284 chemical pesticides on over 275 soil invertebrates have been reported in a systematic study by Gunstone et al. (2021). It was reported that these chemicals, in general, generally have about 70.5% significant negative impact on the soil flora, 28.1% non-significant effects, and 1.4% positive effects. It could be deduced that although their seeming benefits of ensuring the all-year-round supply of agro produce, storage pesticides could be deduced significantly impact negatively on the soil's ecosystem [48]. At a certain concentration, soil storage chemicals cause reproductive distortion, mortality, behavioral changes, and loss of diversity, abundance, and biomass of many soil flora [49]. More significant is the indirect

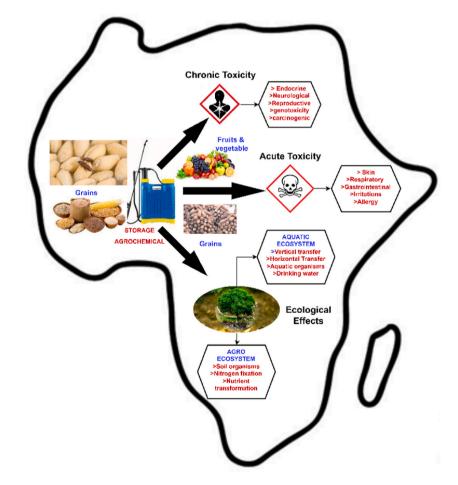


Fig. 1. Ecological and toxicity effects of chemicals used for agro-produce storage in Africa. The figure highlighted several possibilities of acute and chronic toxicity and a number of distorted ecological processes caused by the indiscriminate use of agricultural storage chemicals, especially in Africa.

negative impact of these dysfunctionalities of soil flora on plants and the rest of the agroecosystem [50]. Studies have reported the distortion of nitrogen fixation and other symbiotic activities around the root noodles of leguminous plants due to the impacts of pesticide residues escaping into agricultural soils [51].

In contrast, other studies have highlighted the indirect effects of bioremediation and carbon recycling by soil degradative microbes and enzymes. It was reported that some storage pesticides, such as organophosphorus, foster soil acidification, tremendously affecting the optimal activities of many soil organisms and microbes [52]. Contrarily, Bart et al. [53] reported that fungicides - copper oxychloride, epoxiconazole, and dimoxystrobin caused an increase in the potential nitrification activities of soils organisms well as the glucosidase, phosphatase, arylamidase, and urease activities of treated soil. A possible explanation for the contrasting increase in those enzyme activities could be as a response or defense mechanism against the toxic nature of the chemicals, especially when they are in minimal concentration (less than the lethal dose) [53].

The fate of stored chemicals and pesticides has been reported to differ across climates. According to Daam et al. (2019), only sparsely available studies have investigated the effect of these chemicals on the trophic environment. Even with other climatic regions' results, legislative efforts toward handling the mismanagement of storage chemical usage in tropical areas have been insufficient [54]. The few available studies performed in the tropic have examined the aquatic ecotoxicology of some of these chemical pesticides. Therefore, it is evident that the negative impacts of these chemicals in the agroecosystem are heightened in the tropic compared to temperate regions [55]. Several studies have reported pesticides' easy dissipation and degradation due to increased temperature

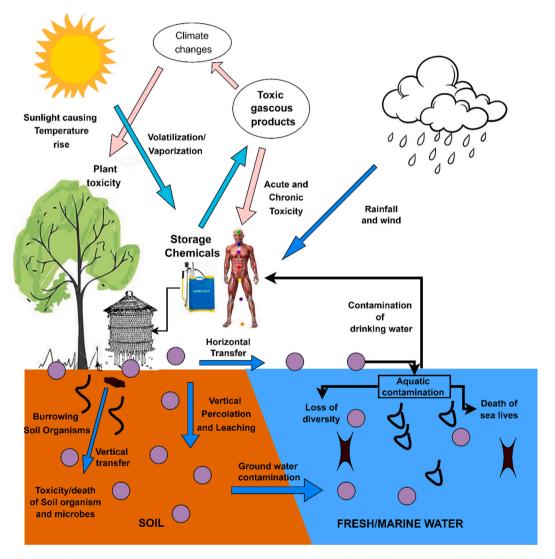


Fig. 2. Environmental effects of toxic chemicals used for agro-produce storage. These chemicals have numerous effects both on the biotic and abiotic environment. As shown in the figure, both terrestrial and aquatic organisms potentially acquire and bioaccumulate via several mechanisms of horizontal or vertical transfer. Death of organisms, as well as other biotic factors and loss of diversity, are the major potential consequences of unregulated and indiscriminate use of toxic agrochemicals.

[56-58].

Moreover, the possibilities of these temperature transformations of these chemical pesticides into more toxic analogs and increased pesticide runoff in the aquatic environment are evident [54,59,60]. Apart from the high temperature predominant in Africa and tropical countries, other environmental factors may predispose these regions to more significant detrimental impacts. Some of these factors are. First, higher soil humidity fosters easy volatilization of the chemicals. Second, the prevalence of more clayey content with minerals such as montmorillonite and kaolinite, which foster clays, catalyze the hydrolysis of some pesticides, such as chlorpyrifos and acephate [61,62]. Third, more prevalence of acidic pH has been reported to foster more desorption and persistence of polar pesticides [57]. Other factors could result from depleted organic carbon and a significant increase in the anion exchange capacity of tropical soil [63].

Despite the climatic predisposition of more ecotoxicity of storage chemicals in Africa, there have not been well-standardized ecotoxicological tests or assessments to examine their effect on floras of the agroecosystems properly. It is paramount that this information will foster a more informed policy on the restriction and controls of these pesticides mismanagement for storage of agro produces in tropical African nations.

3.3. Effects on the aquatic ecosystem

Although Storage chemicals are mainly used for agricultural plant produce, these chemicals seldom get into water bodies through vertical and horizontal transfer [64]. These chemical residues are leached or sipped downwards by vertical transfer until they are deposited into the water table. Burrowing activities of soil organisms, downward percolation of rain, and human activities distorting native soil compartments foster these vertical transfers. Generally, running water washing away these chemical residues from the top surface of the soil into small and large water bodies is the primary horizontal transfer route [65]. Wind and climatic changes (temperature rise and fall) may volatilize some pesticide residues, dispersal, or condensation in waterbodies (Fig. 2). Studies have reported the occurrence of pesticides such as alachlor, metolachlor, trifluralin, monocrotophos, and profenofos in rainwater, of which the route of entry gain was by vaporization of some of these pesticides [58].

A report by K'oreje et al. [66] listed a few storage pesticides as a contaminant of emerging concerns in Africa's aquatic environment. The fate of these pesticides in the aquatic environment is diverse. Like soil invertebrates, these chemicals could distort aquatic life's reproduction, behavior, and diversity [67]. Several reports show that some pesticides induce neurological and endocrine disruption in these organisms [68,69]. Moreover, the trophic transfer of storage chemical residues from lower water invertebrates to amphibians, fishes, and other aquatic mammals is evident. These residues in water bodies get adhered to or sequestered by microplastics and biofilms and are ingested. On ingestion, apart from the acute toxicity or death (for very toxic chemical) consequences, these chemicals, especially recalcitrant, persist and bioaccumulate in this organism [70,71]. Humans, appearing towards the end of the trophic level, could ingest these bioaccumulated chemicals to consume fish and other aquatic life [72]. Moreover, the presence of pesticides in drinking water has caused severe worries. Studies have reported their occurrence beyond tolerable limits for humans, posing significant acute and chronic threats, which will be discussed later.

4. Toxicity and health impacts of chemical storage

4.1. Chronic toxicity of agrochemicals and pesticides used for agro-produce storage

Most farmers and traders use storage chemicals to preserve foods such as corn, millet, beans, rice, and other staples/cereals to avoid/reduce the extent of spoilage. Individuals come into contact with pesticides through their occupations or nutritional and environmental exposure. Using storage chemicals/pesticides is linked with several environmental and health hazards. These chemicals may be metabolized, excreted, stored, or bioaccumulated in human or animal body fat. Some factors determine the extent of toxicity of individuals and include current health status, chemical type (especially chemical structure), quantity, age, sex, period, and path of exposure ([12,73]). In addition to the acute effects caused by these chemicals once exposed, they also have some chronic effects even if exposed in minute amounts. Even though these chemicals are used for storage purposes, some residues have been discovered in ready-to-eat foods such as cooked foods, fruit juice, water, as well as breast milk [12,74–76].

The toxicological effects caused by these chemicals for agro-produce storage may be acute or chronic. While acute poisoning may be accidental or exposure over a short period, chronic toxicity is usually due to occupational poisoning or ingestion over a period. Also, it takes time to manifest/manage [73]. Some of the chronic harmful effects connected with the use of chemicals for storage of agro-produce include but are not limited to the following (Fig. 2).

4.1.1. Neurological dysfunction

Neurological toxicity, distortion, and damage have been reported in the literature to be fostered by prolonged exposure to toxic agrochemicals and pesticides [12,73,77]. Organophosphorus chemicals such as azamethiphos, dichlorvos, idofenphos, malathion, and pirimiphos-methyl suppress acetyl-cholinesterase hydrolysis, the enzyme which regulates a neurotransmitter, consequently affecting the nervous system. The serine hydroxyl group of acetylcholinesterase (AChE) covalently binds with the organophosphate leading to the accumulation of acetylcholine due to inactivation, which in turn affects the receptors in the nervous system via overstimulation of nicotinic and muscarinic receptors. The resultant effect is irregular/abnormal heart rhythms, high and low blood pressures, heart rate variability, cardiac muscle contraction, and elevated serum creatinine and lactate dehydrogenase [78]. Reduced gestational periods and severe neurological dysfunction in infants have been linked to exposure to organophosphate in pregnant women. Such

neurological misbehavior is usually evident in adulthood but can be traced back to exposure during the neuronal development of the fetus [79].

Many studies have evaluated the effects of these pesticides even at allowed dosage in animal models, and their neurological disturbances are worrisome. A recent study has reported adverse neurological defects such as impaired memory loss and learning disabilities arising from the long-term exposure (90 days) of Male Wistar rats to low doses of pesticide mixture via drinking water constituting chlorpyrifos (40.8%), deltamethrin (2.5%), acetamiprid (20%), abamectin (1.8%) and kresoxim-methyl (50%) [80]. The dosage of 0.25–5 times of acceptable daily intake in mg/kg body weight/day caused worrisome effects on the animals' neurological well-being. This was evaluated through the Morris water maze, elevated plus maze, and open field tests. Other biochemical and histopathological alterations in the hippocampus were reported at such doses [80]. A similar study investigated the neurotoxicity effects of two organophosphates (chlorpyrifos and dichlorvos) on Wister rats at a dosage of 14.9 and 8.8 mg/kg, respectively, for 14 days. Anxiety-like behavior and amygdala-dependent fear learning were observed after the 10 days using the open field and elevated plus maze paradigms. Moreover, oxidative damage and neurogenic cell loss of the hippocampus and the amygdala were observed in the exposed animals [81].

In another study, exposure of male Wistar rats to hexaflumuron and hymexazol at a concentration of $1/100 \text{ LD}_{50}$ for 14 days caused severe histopathological alteration such as neuronal necrosis and gliosis of the cerebral cortex, striatum, hippocampus, and cerebellum of the brain [82]. Moreover, the MDA levels were significantly increased while the GSH and CAT activities of the brain decreased compared to the unexposed control. In addition, the transcriptomic analysis revealed an upregulation in the mRNA level of apoptotic transcription factors such as JNK and Bax and a downregulation of Bcl-2 [82]. In the same vein, Vilena and his colleagues [83] reported decreased and distorted cholinesterase (ChE) activities and increased oxidative stress markers in Wistar rats exposed to 0.015–2.186 mg/kg bw for 28 days. Owing to the results from these studies, there is a need for a re-evaluation program of some of the acceptable pesticides and their permissible limits to prevent some of these chronic effects.

4.1.2. Reproductive effects

Exposure to pesticides and organic chemicals has been shown to adversely affect the reproductive function of both vertebrates and invertebrates. Reproduction disorders and congenital disabilities could result from exposure to several pesticides used for food storage. A recent study has reported the combo effects arising from multiple exposures to several pesticides, such as cypermethrin, mancozeb, and metalaxyl dosage more than 50% lower than their LD50 for 8 weeks. The researchers observed a significant decrease in the testis and epididymis weight and testosterone and cholesterol levels. Moreover, the sperm concentration, motility, viability, and antioxidant level significantly decreased compared to the control [84]. Although below the NOAELS (No observable Adverse Effect Levels), Hass and his colleagues [85] reported that a combined exposure of several pesticides, such as cyromazine, MCPB, pirimicarb, quinoclamine, thiram, and ziram, could cause a decrease in birth weight of Wistar rats and other abnormality in prenatal developments.

In another study, exposure of Male Wistar rats to a concentration of 3.83 mg/kg bw for 14 days caused similar effects as the abovementioned such as a decrease in weight of testis and epididymis, sperm head counts, sperm motility, and others [86]. In addition, other critical reproductive hormones such as follicle-stimulating hormone (FSH), luteinizing hormone (LH), and serum testosterone were significantly affected. Finally, an alarming increase in oxidative stress, lipid peroxidation, and a decrease in antioxidant enzymes was reported [86]. Similarly, Lovaković et al. [87] reported the toxicity effects of Imidacloprid on the reproductive organs of adult male rats as well as their detrimental activities on the antioxidant state, DNA, and level of essential elements. In their study, the experimental animals were exposed to the pesticide at doses comparable to the standard health-based reference value, between 0.06 (ADI) and 2.25 (1/200 LD50) mg/kg b. w./day for 28 days. Consequentially, exposure to such concentration of pesticides resulted in lower testis weight (1.30 \pm 0.17 g) compared to the control (1.63 \pm 0.15 g). Moreover, the glutathione level and the corresponding activities of its peroxidases in the epididymis were reduced [87]. In the same vein, Acetamiprid, in another study, was reported to show worrisome reproductive toxicity, such as a dose-dependent decrease in sperm concentration and plasma testosterone levels. Even at a low exposure concentration of 12.5 mg/kg for 90 days [88].

4.1.3. Genetic mutations and cancers

Pesticide and storage agrochemicals have been implicated in causing some genotoxic effects. Studies on some organophosphates such as chlorpyrifos (4 h LC₅₀ 0.2 mg/L), methyl parathion (4 h LC₅₀ 0.135 mg/L), and malathion (4 h LC₅₀ > 5.2 mg/L) administered at concentrations of a fraction of LC₅₀ (1/20, 1/10, 1/8, 1/6 and $\frac{1}{4}$ LC₅₀) into the peripheral blood lymphocyte of Wistar rat; after 4 h of exposure, caused an increase in oxidative stress which induced DNA damage - a dose-dependent single and double-stranded breaks in the DNA, shown by the single cell gel electrophoresis (SCGE) and comet assay [89]. In another study, carbamates, specifically pirimicarb and zineb, and their formulation (50% pesticide composition) as Aficida and Azzurro, respectively, were reported to cause genotoxicity and fostered apoptosis in Chinese hamster ovary (CHO–K1) cells. In addition, at a concentration of 10–300 µg/ml of those carbamates pesticides under 24 h exposure, there was a significant increase in the frequency of micronuclei, a worrisome reduction in the nuclear division, alternation in cells morphology, distortion of cell viability and inhibition of succinic dehydrogenase [90].

The insecticide ethylene dibromide (CH2Br·CH2Br), also known as dibromoethane, has been carcinogenic [12]. Some findings report that pesticide exposure increases the risk of non-Hodgkin lymphomas, skin cancer, blood, prostate, kidney, liver, breasts, intestines, and brain tumors [91]. Generally, these storage chemicals hinder cell division by altering the tubulin and microtubules that split chromosomes during division. They can also cause a decline in DNA repair ability by altering molecular and biochemical processes involving DNA repair enzymes [78]. Cases of cancers, especially; leukemia, non-Hodgkin's lymphoma, soft tissue sarcoma, multiple myeloma, stomach and prostate cancers, colorectal, endocrine glands, and brain cancers, have been reported among farmers who use pesticides more than just ingestion from food [78].

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4.1.4. Endocrine disruption

Chemicals that interfere with hormonal functions are generally known as endocrine-disrupting chemicals (EDCs) EDCs are external agents that affect natural hormones (from production to elimination) in the human system that ensures the maintenance of homeostasis, reproduction, and development [92]. Some health concerns have been reported in dichlorodiphenyltrichloroethane (DDT), a ubiquitous organochlorine insecticide. DDT has recorded endocrine dysfunction and its metabolite, p. p-dichlorodiphenyldichloroethylene (DDE) [12]. Most of these chemicals that disrupt the endocrine system have a strong affinity for hormone receptors such as androgen and estrogen, acting by interference. They may act both as agonists or antagonists. As agonists, they bind to the hormone receptors and activate them, acting as the natural hormone while exhibiting inhibitory actions as antagonists. Some chemicals decrease the activity and concentration of the hormones by inhibiting their production, uptake, and metabolism and may even eliminate them [93].

In a study conducted by Rini Ghosh and his colleague [94], the endocrine-disrupting activities of Lambda-cyhalothrin in female rats were evaluated. Experimental animals administered with a dosage of 6.3-11.33 mg/kg BW daily for 14 days reported a significant decrease in adrenal cholesterol, with a corresponding decrease in ovarian 3β - and 17β -hydroxysteroid dehydrogenase activity, whereas an increase in ovarian cholesterol and a corresponding increase in adrenal 3β - and 17β -HSD activity were recorded. Other hormonal imbalances, such as a worrisome reduction in estradiol and progesterone, were reported. Moreover, Gene expression data showed reduced expression of ovarian 17β -HSD and steroidogenic acute regulatory protein [94].

A single low dosage of the organophosphate chlorpyrifos (100 mg/kg while LD50 229 mg/kg) was shown to foster endocrine disruption of butyrylcholinesterase, cortisol, free triiodothyronine, thyroxine, thyroid-stimulating hormone and prolactin from their baseline value in Wistar rats administered after 4 h. Their results showed butyrylcholinesterase activities and expression significantly decreased, whereas cortisol, prolactin, triiodothyronine, and thyroxine significantly increased after exposure [95]. Similarly, in another study, exposure of *Albino/Swiss* mice to deltamethrin at a dosage of 5 mg/kg daily for 35 days caused a significant decrease in testosterone and inhibin B levels, which invariably affect reproductive performances [96].

Thyroid hormone synthesis can be inhibited by some chemicals: pentachloronitro-benzene, pyrimethanil, amitrole, and others. Carbofuran and aldicarb are carbamates, which may harm endocrine function [93]. Some factors such as occupation, age, and sex affect the level of impact of these endocrine-disrupting chemicals. Age is particularly interesting, as neonates and children are mostly affected compared to adults. This is because significant damage is done during the early stage after fertilization and development of the fetus due to bioaccumulation in the maternal fat stores, which can also increase during lactation. These effects remain hidden and are observed in adulthood with antecedent adverse effects such as impaired and disrupted central nervous system function [93].

4.1.5. Other metabolic disorders

Alteration of lipid metabolism in the liver and hematological dysfunction have been reported in the use of DDT and DDE. Metabolic disorders like diabetes, increased blood pressure, stroke, kidney failure, and Parkinson's and Alzheimer's diseases have been linked to the use of organophosphate [12]. The use of triazine has been associated with oxidative stress. Pentachlorophenol, a chemical fungicide used in agro-produce storage, disrupts oxidative phosphorylation, thereby increasing metabolic rate [73]. Acute toxicity caused by breathing in phosphine (PH₃) may lead to severe hypotension, pulmonary edema, seizure, and sudden loss of consciousness [73]. Storage chemicals release free radicals, which cause lipid peroxidation. Since fatty acids are components of blood lipoprotein, it could lead to atherosclerosis, thereby increasing the risk of coronary artery diseases [78].

4.2. Acute toxicity

Storage of agricultural products is essential to preserve them for future purposes – in cases of food scarcity. Pesticides are applied during food storage to deter pests and preserve agricultural products, leading to occupational exposure to pesticides. Pesticide residues are also found in stored agricultural products, exposing the general population to these pesticides. Examples of pesticides preserving stored agricultural products include dichlorvos, zinc phosphide, aluminum phosphide, benomyl, permethrin, pirimiphos-methyl, gamalin, chlorpyriphos, DDT, and carbofuran [97,98]. Food preservation is also an essential component of food storage. It helps improve agricultural products' quality, taste, and shelf life by preventing the growth of bacteria, mold, and yeast. This is achieved by adding certain additives and preservatives to pre-packaged products during processing before storage [99]. Chemicals in stored agricultural products could be due to these additives, such as antimicrobials, antioxidants, and anti-enzymatic [100], or pesticides such as insecticides and fungicides, bactericides, nematicides, rodenticides and fumigants [101]. Toxic chemicals can also migrate into agricultural products through the different packaging materials used in preserving food. Packaging involves using additives such as stabilizers, plasticizers, antioxidants, and slipping agents to improve the properties of the packaging materials [102,103]. Pesticides are also used in packaging materials to prevent the proliferation of insects, bacteria, and fungi [104]. There are possibilities that some of such chemicals, which have identified toxic doses, may directly or indirectly be incorporated into agricultural products and may pose severe human threats when consumed indiscriminately [105,106].

The effects could be acute/short-term, or long-term - due to constant exposure to or accumulation of the toxic chemicals—acute toxicity results from exposure to the toxic chemical once and the immediate manifestation of the toxic symptoms. Toxic symptoms could also emerge within a few hours or 24 h of exposure to the chemical [7]. This effect could be local, occurring at the point of contact of toxicant with the body, majorly the skin. Local effects could also occur in the lungs if the toxic chemical were inhaled or if the toxic chemical was ingested in the gastrointestinal tract. Systemic effects occur if the toxic chemical has been absorbed, transported to other body parts, and causing adverse effects in susceptible organs.

Acute toxicity is documented using oral LD_{50} (lethal dose 50) or LC_{50} (lethal concentration 50) values, which is the amount of

chemical in milligrams (mg) per kilogram (kg) body weight (b.wt.) needed to kill 50% of test animals [107,108]. A lower LD_{50} or LC_{50} value represents higher toxicity to humans and animals. Based on acute oral toxicity, pesticides with LD_{50} less than 50 mg/kg b. wt. are incredibly hazardous; those with LD_{50} between 5 and 50 are highly hazardous, while those with LD_{50} between 50 and 2000 are moderately hazardous. LD_{50} values of over 2000 mg/kg b. wt. are slightly hazardous, while LD_{50} is more significant than 5000 mg/kg b. wt. It may not produce acute hazard [108,109]. Acute toxicity values based on inhalation and dermal LD_{50} have also been documented [110]. The following are some acute effects of introducing chemicals to agricultural products during storage (Fig. 3).

4.2.1. Effects on the skin

When dermally absorbed, toxic chemicals affect the skin due to splashes and spills during handling [7]. This is primarily true when applying pesticides during the storage of agricultural products. The rate of dermal exposure to chemicals differs for different skin parts, with the genitals and ear canal being the most susceptible [104]. There are three types of chemical-skin interaction: direct skin effects, which include irritation, corrosion, and necrosis; immune-mediated skin effects resulting in allergic reactions on the skin or other sites, such as the respiratory tract; and systemic effects, which lead to organ toxicity [111]. Dermal exposure to storage chemicals results in contact dermatitis – irritant contact dermatitis (ICD) or allergic contact dermatitis (ACD), allergic urticaria, and asthma. Acute contact dermatitis results in local inflammatory signs such as redness, itching, swelling, pain, and rash. This is manifested in dermal exposure to the pyrethroid insecticide deltamethrin. Dermal exposure to deltamethrin also results in numbness and tingling of the legs, mouth, and tongue [112]. It was reported that exposure to about 5 g/L of deltamethrin fostered the development of paraesthesia of the legs, mouth, and tongue and diarrhea in an agricultural worker [112]. Other non-common effects of toxic chemicals on the skin include eczema, non-allergic urticaria, folliculitis, and skin cancer, as summarized in the well-written review study [111]. Food additives like tartrazine have also been linked with urticaria, asthma, and dermatitis [113]. The antimicrobial - benzoates cause skin rashes and asthma [114]. Antioxidants such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), sulphites, and sorbates are also implicated in urticaria. Other skin effects of sulphites include dermatitis and flushing [115].

4.2.2. Effects on the respiratory tract

Inhalation is the primary route of occupational exposure to storage pesticides. Inhalation exposure to pesticides is exacerbated if the pesticides are applied in confined places and at high temperatures [104]. Inhalation affects the nose, throat, and lung tissues as the pesticides reach the body in vapors, aerosols, dust, or mist [116]. Spray mists are often esters, strong acids, phenols, and amines, and inhaling the mist results in dizziness, coughing, a burning sensation in the nasal passages, and chest tightness [110]. Due to pesticides, other acute respiratory symptoms include dyspnoea, wheezing, dry/sore throat, airway irritation, nose secretion, and dryness. Other local or systematic manifestations include fatigue, headache, vomiting, dizziness, abdominal pain, seizures, ataxia paraesthesia, tremor, and dysfunction of other organs [101]. Pesticide exposure due to inhalation also results in asthma (OR 1.8, 95% CI 1.01–3.01), chronic bronchitis (OR 1.38, 95% CI 1.09–1.78), and chronic obstructive pulmonary disease (COPD) (OR 1.58, 95% CI 0.59–4.25), as well as impairments in lung function, and lung cancer [98,110,111]. Specifically, organophosphorus pesticides are associated with asthma as they can directly alter the bronchial lining via irritation, inflammation, and immunosuppression [116]. They also lead to respiratory failure due to bronchoconstriction, bronchorrhea, and alveolar edema [117]. Nitrophenol derivative pesticides also affect respiration through their effect on oxidative phosphorylation [108]. Synthetic preservatives are linked to respiratory problems,

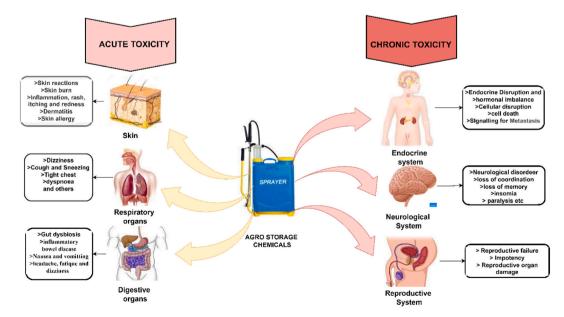


Fig. 3. Acute and chronic health effects of toxic chemicals used for agro-produce storage. The potential specific effects of toxic agrochemicals on significant organs and systems of humans are detailed in the figure'.

allergic reactions, and anaphylactic shock [118]. Sulphur dioxide often used to preserve wines, has been found irritating asthmatic individuals' bronchial tubes [113].

4.2.3. Effects on the gastrointestinal tract

The first physical and biological barrier to ingested food exposure to chemicals used in food storage predisposes the gastrointestinal tract (GIT) and gut microorganisms, referred to as the gut microbiota, to these chemicals [119]. These microorganisms, such as bacteria, fungi, and viruses, mutually link with the host gastrointestinal tract. The most abundant phyla of the human intestinal microbiota include Firmicutes, Bacteroidetes, Verrucomicrobia, Fusobacteria, Proteobacteria, Actinomycetes, and Cyanobacteria [120]. They are involved in developing the GIT, play a role in the digestion of fiber, assimilation of nutrients, absorption of minerals and fatty acids, synthesis of amino acids and vitamins, and act as a protective barrier against pathogenic organisms and toxins [121]. Gut microbiota composition could be influenced by diet, antibiotics, and toxins [122]. The transition from eubiosis to dysbiosis (microbial imbalance) could be due to exposure to contaminated food, which could be chemicals such as pesticides, preservatives, fertilizers, and sweeteners found in ingested food [123]. Gut dysbiosis is, therefore, highly implicated in a variety of disorders, such as inflammatory bowel disease (IBD), obesity, colorectal cancer, and diabetes [124]. Common manifestations of the acute effects of pesticides on the gastrointestinal tract include nausea and vomiting, as documented by the storage pesticides – DDT [107]. Pyrethroid poisoning is accompanied by epigastric pain, dizziness, headache, nausea, vomiting, fatigue, and increased stromal secretion within 10 min to 1 h after ingestion [112]. Food additives such as bromates and saccharin also affect the gastrointestinal tract [114].

4.2.4. Other acute toxicity effects

Toxic chemicals also affect the eyes due to highly toxic pesticides, granular pesticides, and pesticide application using power equipment [104]. Eye exposures due to pyrethroid toxicity may result in mild to severe corneal damage [112]. Organophosphate insecticides result in an increased incidence of myopia and the more advanced Saku disease. On the other hand, Carbamates cause constriction of pupils [107]. Pesticides such as pyrethrin also affect body weight, as revealed in pups [109]. Storage pesticides have also been linked with hepatotoxicity, renotoxicity, and haematotoxicity. Haematotoxic properties of pesticides include neutropenia, agranulocytosis, and aplastic anemia. Acute pesticide toxicity can also result in death.

5. The use of natural products as alternative preservatives: how sustainable?

Chemical additives have been widely utilized to inhibit postharvest pest survival and proliferation, although their safety and human health impact are still being debated. Several emerging alternatives are being developed to preserve agro products better and reduce the hazardous impacts of chemicals on health and the environment. Some of these solutions include using natural products of plant, animal, and microbial origins, as well as their nanoparticle derivative [125]. The use of natural products has drawn the attention of many contemporary studies primarily due to their application in post-field activities as well as their relative health and environmental safety profile [126]. However, their practical application and sustainability for mass-produced agro-products such as grains, cereals, and legumes are still questionable. This section summarizes the current understanding of the use of natural derived products from animals, plants, fungi, bacteria, and algae. It hopes to examine advances that may foster their sustainability to become workable alternatives to chemical preservatives.

5.1. Natural preservatives of plant origin

Natural herbs and spices have preservative potentials depending on the spoilage organisms' nature, type, and concentration. These herbs and spices contain volatile chemicals that produce preservatives after extraction using different methods [127]. Essential oils from plant and plant extracts have been used as a preservative and therapeutic agent in folkloric medicine [123]. Plant extracts contain some antimicrobial and antioxidant agents, and essential oils are reported to possess good preservative quality. Some chemical compounds such as thiosulfinates, organic acid, flavonoids, phenolics saponin, and glucosinolates can potentially replace synthetic chemical preservatives [128]. It is well known that the phenolic compounds in plants, such as aliphatic alcohols, isoflavonoids, ketones, acids, aldehydes, and terpenes, are the main component with antimicrobial properties [129]. The phenolic compounds act as reducing agents, donating hydrogen and suppressing oxygen, producing an antioxidant effect on the product.

Similarly, some phenolic compounds such as flavonoids which are widely distributed in herbs, spices, fruits, and vegetables, are metal ion chelators acting as catalysts in oxidation chemical reactions as well as inhibit cyclooxygenase and lipoxygenases, two key enzymes implicated in the progression of oxidative rancidity in food products [130]. The antimicrobial effects of lemon and grapefruit extract against fish spoilage microorganisms *Shewanella putrefaciens, Photobacterium phosphorus, and Pseudomonas fluorescens* have been studied in hamburgers resulting in increased microbial stability [131]. Previous studies showed that lemon essential oil used as a microemulsion in salty sardine significantly reduced the microbial count of lactic acid bacteria (LAB), *Staphylococcus* spp., *Enterobacteria*, and low yield histamine relative to the control [132]. Furthermore, the antimicrobial and antioxidant potentials of Matricaria recutita L. (chamomile) have been reported for their efficiency in preserving dairy products [133]. Foeniculum vulgare Mill (Funcho) showed high preservative activity of cottage cheese due to its high phenolic content showing significant antioxidant activity [134]. The available evidence shows that phenolic extract from blackcurrant leaves and cherry trees showed good preservative antimicrobial and antioxidant properties in meat products, significantly increasing the shelf life of vacuum-packed sausages with a significant decrease in the level of malondialdehyde produced in this product [135]. The antimicrobial and antioxidant properties of essential oils from onion (Allium cepa L.) against spoilage microorganisms such as *Staphylococcus aureus*, Bacillus subtilis, and

Escherichia coli demonstrate huge preservative potentials in this food [136].

5.2. Natural preservatives of animal origin

Bioactive chemicals from animal fluids or defense mechanisms can also be preservatives. Bioactive substances are abundant in animals. These bioactive substances demonstrate that eating animal-based foods has biological impacts on human health. Antimicrobial enzymes, antioxidant peptides, and antimicrobial peptides are extensively used in food preservation. The ability of an alginate coating with a Lactoperoxidase system (LPOS) to inhibit Listeria monocytogenes and E. coli in rainbow trout fillets was studied. The combination of alginate and LPOS was found to have a considerable inhibitory impact on these bacteria [137]. The activities of cathledicin against viruses, fungi, and bacteria in mammals have been reported [138]. Chitosan is extensively found in the exoskeletons of arthropods and crustaceans [139]. Antimicrobial peptides (AMPs) have been shown to exhibit antimicrobial activities against various food-borne pathogens implicating their preservative potentials [140]. Cationic AMP saline derived from salmon milt delayed the growth of Listeria monocytogene on smoked salmon [141]. Previous studies show that proteins, peptides, hydrolysates, and amino acids have significant antioxidant activity [142,143]. Protein's antioxidant activities result from the presence of amino acids in their structure and bioactive peptides from enzymatic hydrolysis. The antioxidant activities of peptides depend on the free radical binding properties and metal ions [143,144]. Hydrolysates from meat and fish have been reported to possess antioxidant activity, and adding hydrolysates to minced meat significantly inhibited lipid peroxidation [142]. The DPPH (2,2-diphenyl-1-picrylhydrazyl) radical scavenging activity in the hydrolysates collected from mechanically separated chickens was high [145]. By-products from fish are good sources of antioxidant peptides; protein hydrolysate showed DPPH radical scavenging activities comparable to synthetic antioxidant [146]. The gelatin hydrolysate from the skin of Carcharhinus limbatus (black shark) showed a cryoprotective effect preventing surimi protein denaturation [147]. The peptide (Pro-Ala-Gly-Tyr) isolated from skin gelatin of Amur sturdeon showed significant cryoprotective and antioxidant properties on Japanese sea bass (Lateolabrax japonicus) and muscle proteins [148]. Similarly, gelatin hydrolysate isolated from farmed Amur sturgeon showed a cryoprotective effect on protein by preventing the displacement of water molecules between various compartments and stabilizing water molecules in minced seabass [149].

5.3. Preservative from microorganisms and their metabolites

Bacteria produce many substances that can prevent or inhibit spoilage and the growth of pathogenic organisms. Food-grade mos can produce a variety of chemicals that prevent the growth of other microbes. This is due to the microbial ecosystem's natural balance. The bio-preservative properties of these food-grade mos vary depending on the antimicrobial compounds (enzymes, bacteriophages, bacteriocins, and metabolites) and the form of compounds, whether fermentative, protective culture, or purified compound.

6. Recommendation - possible panacea to widespread toxic chemical usage for agro-produce preservation, especially in Africa

Despite the tremendous efforts by contemporary studies in developing competitive and workable alternatives to chemical pesticides and preservatives, especially from nature-derived products and nanosystems, their success is still far from becoming for crops produced in large quantities and for commercialization. Evidence has shown that the heat of this widespread of these toxic chemicals usage is more in Africa and many developing nations, notwithstanding their established health and ecotoxicological effects. Therefore, the need for prompt proactive and reactive measures to curb the menace of this *timing bomb*. Highlighted in this section are some of our recommendations.

i) Reassessment of toxic effects of widespread pesticides in developing nations

As early mention, Africa and many developing countries are still the dumping ground for many toxic pesticides, as evidenced in the PAN international consolidated lists of banned pesticides (https://files.panap.net/resources/PAN-Consolidated-List-of-Bans.xlsx). Out of about 530 documented chemicals with worrisome toxicities, many African and developing countries have a non-strict ban on less than 5% of the abovementioned number. In contrast, developed nations such as the United kingdom maintain a strict ban on about 195 pesticides from the PAN international consolidated list (https://files.panap.net/resources/PAN-Consolidated-List-of-Bans.xlsx).

It is crucial and recommended that Africa and other developing nations reassess prevalent pesticides among their farmers and update their list of banned chemicals.

ii) Prohibiting the distribution of banned pesticides

To ensure that the distribution of banned pesticides is prohibited, governments of nations are to set up new compliance enforcement agencies or re-train existing ones to ensure that they strictly intercept and prevent the easy distribution of banned pesticides. Moreover, the illegal distribution/usage of such chemicals should be passed into law to be a criminal offense, in which both distributor and end-users of such chemicals could be prosecuted if found guilty.

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iii) Collection of obsolete stocks
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After the ban, the obsolete stock of toxic chemicals will be collected from distributors and farmers and replaced with less toxic alternatives. Compensation could be paid to investors of these chemicals who willingly submit their old stocks immediately after the formalized ban on such chemicals. These old stocks could be treated using ecofriendly alternatives before disposal or reused as feedstock for non-toxic products.

iv) Focused group and Public awareness campaign

Focused group and public campaigns on social media platforms, television and radio media, publications, and magazines should be embarked on to create awareness of the updated list of banned toxic agrochemicals. Moreover, these platforms can inform subsistence and commercial farmers about some agrochemicals' proper usage and safety precautions. Other new findings on ecotoxicology information and health effects can be quickly disseminated. Feedback from farmers can also be received to generate statistics that will better inform the government on alternatives to target their subventions and subsidies to promote a green and robust agricultural yield better.

v) Education of farmers by maintaining a wide-scale advisory system.

Ensuring proper education of farmers through grassroots extension services, as well as a wide-scale advisory system, can be very helpful in managing the usage/application of toxic agrochemicals for their farming operations. Alternative sustainable and eco-friendly systems could be thought to farmers and the adverse impact of the banned toxic agrochemicals on human health.

7. Conclusion

Customer demand for increasingly nutritious and shelf-stable goods has spurred the quest for food preservatives with common potential health concerns. Conventional food storage chemical has been shown to impact numerous health challenges through various mechanisms and alter agro-products' physicochemical and other sensory properties. Food safety has become a top concern and a top priority for many countries and governments. The globalization of food supply, the better ability to detect food safety issues, and the increased global demand for food all lead to a necessity to process more and more food. Today, in the century of speed, consumers expect food to be immediately available, tasty and nutritious, safe for consumption, not endanger their health and have a good shelf life. Plants and other phyto-derivatives are viable alternatives in food preservation, ensuring the stability of these items' nutritional and organoleptic qualities and their safety and quality. Recently, the demand for natural preservatives (antioxidants, inhibitory factors, antimicrobials, plants, and their derivatives, as well as animal sources) with biocompatibility, biodegradability, antimicrobials, low toxicity, and low-cost efficiency has increased exponentially. Phenolic derivatives, essential oils, spices, organosulfur compounds, lysozyme, bacteriocins, lactoperoxidase system, chitosan, lactoferrin, and agarose are natural products and metabolites extensively employed as bio-based preservatives in the food industry. Moreover, more proactive measures such as prohibiting the distribution of obsolete stock of banned pesticides, concerted efforts towards engaging in focused group and public awareness campaigns, education of farmers and maintenance wide-scale advisory system are more practicable. Future research efforts could be directed towards developing nanobiotechnology alongside natural products for more effective preservative outcomes and less health and ecotoxicological effects.

Author contribution statement

All authors listed have significantly contributed to the development and the writing of this article.

Data availability statement

Data included in article/supp. Material/referenced in article.

Additional information

No additional information is available for this paper.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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