Chapter

Toxicity Status and Risks of Common Active Ingredients in Open Markets

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Abstract

Agrochemical stores in selected geographical locations in North Central Nigeria were surveyed, a structured questionnaire administered and students of selected Universities and staff of the Ministry of Agricultural and Rural Development were sampled. Seventeen active ingredients: Paraquat dichloride, Glyphosate, Permethrin + pyriproxyfen, Dimethylamine salt, Cypermethrin, Chlorpyrifos, Dichlorvos, Lambda-cyhalothrin, 2,2-dichlorovinyl Dimethyl phosphate, Hexaconazole, Imidacloprid, Dimethoate, Nicosulfuron, Profenofos + cypermethrin, S-metolachlor, Carbendazim, and Mancozeb were recorded, and dominated by herbicides and insecticides. Toxicity analysis of active ingredients in open markets based on the recommendation of international standard organizations showed that some common active ingredients were not approved and some others were not listed for agricultural use. Many of the active ingredients negatively affect plant pollinators, aquatic animals, are highly toxic to birds, honey bees, and poses risk to wildlife. Some others are a possible carcinogen, fatal if inhaled, highly hazardous with high environmental toxicity posing a serious health risk to humans by disrupting the endocrine system, inducing heritable mutations in germ cells, impair fertility and reproductive toxicity.

Keywords: pesticides, active ingredients, residue, toxicity, standards, risks

1. Introduction

The rise in the number of chemicals being introduced into agriculture and horticulture has given rise to some concerns over the safety of the food crop and that of the operator. A working party was established in the UK which passed some regulations over the possible risks to consumers of treated crops. This led directly to the formation of the Advisory Committee on Poisonous Substances used in agriculture, which extended concern to effects on the environment. However, new toxic chemicals and their formulations need to be brought to the notice of the Government before being put on the market. The introduction of the Pesticides Safety Precautions Scheme (PSPS) strengthened the requirement in which manufacturers of the new chemical were required to provide data relating to the safety of the product; full description, proposed uses, mode of action, toxicity and persistence, relevant to the user of the product, consumer of treated produce, domestic animals and wildlife.

The outcome of such products was published with the key elements included on product labels; advice on operator safety, target crops, dose rate limitations, harvest interval, and environmental safety. The PSPS was accompanied by the voluntary scheme which evaluates the efficacy of crop protection chemicals prior to the approval of chemical and based on trials efficacy data.

The increasing regulatory requirements are seen over decades, and especially in the past 20 years, have placed much financial pressure on the research-based crop protection companies. Increasing demands for toxicology, metabolism, and environmental data to support registration applications have resulted in a cost of approximately £100 million to discover research, develop and register a new product. Earlier, horticultural and vegetable markets were targeted pesticides markets, today such are far too small to justify the investment in required regulatory studies and can only be considered as "add-on markets" to be considered once success in a major market has been achieved. Markets must also be considered at the international level no single country market would justify the investment in pesticides research and development.

2. Pesticides in agriculture

Pesticide is defined as a product that kills or controls various types of pests, plant, or animal that is harmful to man or the environment. Pesticides are used in agriculture to protect crops against insects, fungi, weeds, nematodes, and parasitic plant pests, as well as to protect public health in controlling vectors of tropical diseases. They can also be used to prevent, destroy, repel, or mitigate any pest and can either kill pests or render them ineffective. Pesticides are used on fruits, vegetables, wheat, rice, olives, tree crops, canola pressed into oil, and on non-food crops, such as cotton, grass, and flowers. Pesticides applied to food crops in the field can leave potentially harmful residues after pesticides are applied to the crops, they may interact with the plant surfaces, be exposed to environmental factors, such as wind, sun, and maybe washed off during rainfall. The pesticide may be absorbed by the plant surface (waxy cuticle and root surfaces) and enter the plant transport system (systemic) or stay on the surface of the plant (contact). The pesticides that get into the plant tissues may be transformed (metabolized) or sequestered in the tissues to form the pesticide residue.

Pesticide residues are the deposits of pesticide active ingredients, their metabolites or breakdown products are present in some components of the environment after their application, spillage, or dumping. The presence of pesticide residues is a concern for consumers because pesticides are known to have potentially harmful effects on other nontargeted organisms than pests and diseases. Infants, children, and adults are commonly exposed to pesticides by eating them on and in food and animals equally ingest such through feeds and mills. Pesticides are potentially toxic to humans and have been linked to a wide range of human health hazards, ranging from short-term impacts, such as headaches and nausea to chronic impacts, such as cancer, reproductive harm, and endocrine disruption.

3. Benefits and risks of pesticides

The application of any chemical to a crop or food raises the question of risks and benefits. This discussion of risk has shifted from dealing with toxicity to the user in the field and the consumer to a much wider focus that includes the whole environment and the ecosystem in which the crops are growing. As a consequence, more and more studies are required before a fungicide can be used, leading to enormous development costs. This leads the industry to concentrate on the big markets, while smaller markets are increasingly left out and in urgent need of effective fungicides. Overall, most analyses come to the conclusion that the benefits of fungicides far outweigh the risks, if they are used carefully and according to the label recommendations. Currently, more than 80% of the fruit and vegetable crops have been known to receive a fungicide every season.

4. International standard and requirements

There are standard organizations of international reputes that certify and license agricultural products for safe consumption and to fulfill the international requirement for the trade. These standard organizations are also functional at regional and national levels and requirements at these levels are often benchmarked with the provision of the international organizations. Such organizations include but are not limited to 4C Association, Bonsucro (Better Sugar Cane Initiative), Better Cotton Initiative (BCI), Fairtrade International, FSC, RSB, SAN (Sustainable Agriculture Network), and UTZ.

Growers, produce buyers and agents, warehouse owners, manufacturers, and even the general public, have perceived the use of chemicals for various purposes as part of everyday life, either for domestic or agricultural. This has led to the indiscriminate use of pesticides for varied reasons and in search of quick action and effect. The uncoordinated system in this sector of agriculture, lacking regulation and enforcement required for best practices and safety measures in the handling of agrochemicals prompted this study. This in a way undermined the associated risks of indiscriminate use of these agrochemicals, their toxicity, and residues on plants, animals, man, and the environment. Agrochemicals commonly sold in open markets were surveyed; the target crops, associated hazards/risks, and their safety statuses were evaluated based on the benchmark by international standard organizations.

5. Study geography and analysis

The survey of agrochemical stores and trading facilities was conducted in North Central Nigeria. Agrochemical dealers in three major farm-based stores in central towns were randomly selected and visited with a structured questionnaire. The questionnaire was duly completed with the co-operation and support of the respondent and the interviewee. The identity of the chemical stores in selected locations was kept anonymous. Information was sought on the trade name, type of agrochemicals (herbicide, insecticide or fungicide, etc.), active ingredient(s) present in the pesticides, and the crop(s) in which the pesticides were targeted. However, the trade names of the agrochemicals and locations were kept anonymous but the active ingredients were used as the bases of this report. The active ingredients were benchmarked with the requirements of the international standards organization.

The information obtained from the agrochemical stores on the active ingredients on sale in the open market were subjected to the benchmarks of the international standards organizations, such as 4C Association, BCI, Bonsucro, FSC, Fairtrade, RSB, Rainforest Alliance, SAN, and UTZ, as related to the toxicity, restriction status, and effect of such active ingredients on human, animal, and environment.

6. Status of agrochemicals in open market

The survey of farmers–based agrochemicals stores showed the presence of seventeen (17) active ingredients common in the open market. A total of eighteen (18) trade names; Weed Crusher, Parae Force, Weed Cut, Grass Cutter, Touch Down, Clear Weed, Force Up, Drysate, Round-Up, Sunsate, Cyperthrone, Vestamine, Relimine, Amino Force, Amino Force Granular, Guard Force, Gramaxone and Meta Force were herbicides, thirteen (13) trade names; Super Care, Cyper Force, Cyper-DiForce, Flush Out, Termifos, Termiclor, Pest Off, Rid-Off, LaraForce, Magic Force, Knock Off, DD-Force and Iron Force were insecticides and nine (9) trade names; Fungi Care, Confidor, Storm Force, ImiForce, Dime Force, Fungus Force, ForceLet, Z-Force, and Zeb-Care were fungicides. No record of nematicides or any agrochemicals against parasitic pest plants were found in the study geographies. These agrochemicals were also dominated by herbicides which were 42.67% on average, the insecticides were 35.0% of the stocks while only 25.5% of agrochemicals across study geographies were fungicides (**Tables 1–3**). This information implied that pesticides used in the geographies were mostly for weed management and insect pests' control both for agricultural and domestic purposes. The commonly used active ingredients by the indication of sales from the selected geographies showed Paraquat dichloride, Glyphosate, Permethrin + pyriproxyfen, Dimethylamine salt, Cypermethrin, Chlorpyrifos, Dichlorvos, Lambda-cyhalothrin, 2,2-dichlorovinyl Dimethyl phosphate, Hexaconazole, Imidacloprid, Dimethoate, Nicosulfuron, Profenofos + cypermethrin, S-metolachlor, Carbendazim, and Mancozeb. The common active ingredients cut across varied pesticides types across the geographies.

Table 1 showed that geography I was dominated by herbicides with 45%, 36% insecticides, and only 27% were fungicides. Targeted crops were mostly grains, legumes, vegetables, a few tubers, fruits, and tree crops.

Either one or two of the selected geographies had Paraquat dichloride, Glyphosate, Cypermethrin, Dichlorvos, Lambda-cyhalothrin, Imidacloprid, and Dimethoate common to them while Glyphosate and Cypermethrin are most frequent on sale across all the geographies surveyed. These active ingredients were variedly targeted

S/N	Status	Active ingredient(s)	Targeted crop(s)
1	Herbicide	Paraquat dichloride	Maize, weeds, cowpea, rubber, oil palm
2	Herbicide	Glyphosate	Grasses, weeds, woody shrubs
3	Herbicide	Permethrin + pyriproxyfen	Maize, weed
4	Herbicide	Dimethylamine salt	Maize, tomato, cotton, fruit trees
5	Insecticide	Cypermethrin	Smaller insects
6	Insecticide	Chlorpyrifos	Vegetables, rice, soya beans, cocoa
7	Insecticide	Dichlorvos	Insect of vegetable, rice, yam, cowpea
8	Insecticide	Lambda-cyhalothrin	Insect pest in maize, vegetables, rice
9	Fungicide	Hexaconazole	Pepper, vegetable
10	Fungicide	Imidacloprid	Pepper, watermelon, groundnut, cocoa
11	Fungicide	Dimethoate	Carrot, beans, groundnut

Table 1.
Active ingredients in Geography I and Targeted crop(s).

S/N	Status	Active ingredient(s)	Targeted crop(s)
1	Herbicide	2,4-dimethylamine salt	Rice, rubber, wheat, sugar cane
2	Herbicide	Nicosulfuron	Maize
3	Herbicide	Glyphosate	Sugar cane, weeds
4	Insecticide	2,2-dichlorovinyl Dimethyl phosphate	
5	Insecticide	Lambda-cyhalothrin	Pineapple, carrot, orange, rice, beans
6	Insecticide	Profenofos + cypermethrin	Maize, cotton, orange
7	Insecticide	Cypermethrin	Carrot, cocoa, groundnut, onion
8	Fungicide	Imidacloprid	Pepper, groundnut, cocoa
9	Fungicide	Carbendazim	Fruit and vegetables

Table 2.
Active ingredients in Geography II and Targeted crop(s).

S/N	Status	Active ingredient(s)	Targeted crop(s)
1	Herbicide	Glyphosate	Annual grass, sugar cane,
2	Herbicide	Paraquat dichloride	Non-selective, grasses, broad-leaved weeds
3	Herbicide	S-metolachlor	Potato, yam, groundnut
4	Herbicide	Di-methylamine	Corn, weeds, sugarcane
5	Insecticide	Cypermethrin	Corn, tomato, cocoa, watermelon
6	Fungicide	Dimethoate	Beans, groundnut
8	Fungicide	Mancozeb	Fruits, vegetable

Table 3.
Active ingredients in Geography III and Targeted crop(s).

to manage weeds, insects, and pathogens in grains, legumes, nuts, tubers (root and stem), fruits and vegetables, and tree crops (**Tables 1–3**).

The presence of insecticides was higher in geography II showing 44% occurrence, the fungicides were only 22% while herbicides showed 33% of the agrochemicals in the open market and these were targeted against varied crop types, for example, corms, vegetables, fruits, grains, and some tree crops (**Table 2**).

However, the report of geography III as shown in **Table 3** indicated that only 12.5% of agrochemicals were fungicide which was the least across the selected geographies and likewise was the 25% insecticides but herbicide occurrence was highest (50%) of the agrochemical in all the geographies (**Table 3**).

7. Toxicity of active ingredients in open market

The toxicity analysis of the active ingredients commonly on sale in the open market was based on recorded cases of pesticide active ingredients and formulations that have shown a high incidence of severe or irreversible adverse effects on human health or the environment, in accordance with the recommendation of the standard organizations and Pesticide Action Network International list of highly hazardous pesticide (PAN-HHP).

S/N	Active ingredient(s)	Status in EU database	Status in Standard Organizations (BCI/RA/FSC/4C/SAN/UTZ)	Status in PAN-HHP
1	Paraquat dichloride	Not approved	Prohibited, to be faced out by 2024 Fatal if inhaled/may cause severe effects Highly toxic to birds/ may cause severe effect	Added to PAN-HHP list in 2011, 2019. Acute toxicity: Fatal if inhaled. Not yet formally listed but agreed by PIC
2	Glyphosate	Approved	May only be used under specific, defined conditions Probable carcinogenic	Added to PAN-HHP list in 2011,2014, 2019. Long-term health effects: possible carcinogens. Environmental toxicity: very persistent in water/sediment.
3	Permethrin + pyriproxyfen	Approved	Prohibited, highly restricted/ restricted use/risk-specific mitigation measures are mandatory Identified as hazardous, use with extreme caution Minimization of use Probable carcinogen Highly toxic to honey bees Aquatic risk, pollinator risk, wildlife risk	Added to PAN-HHP list in 2011, 2019. Long-term health effects: probable/ likely carcinogen. Environmental toxicity: highly toxic to bees
4	Dimethylamine salt	Not listed	Not listed	Not listed
5	Cypermethrin	Approved	Highly restricted/ restricted use, Risk specific mitigation measures are mandatory Highly aquatic toxicity Highly toxic to honey bees, aquatic risk, pollinator risk	Added to PAN-HHP list in 2011, 2019. Environmental toxicity: highly toxic to bees
6	Chlorpyrifos	Not indicated	Potentially to be prohibited Highly restricted/ restricted use/risk-specific mitigation measures are mandatory May only be used under specific conditions/ minimization of the use Inhalation risk, high aquatic toxicity/ highly toxic to bees, birds, aquatic risk. Pollinator risk, wildlife risk	Added to PAN-HHP list in 2011, 2019 Environmental toxicity: highly toxic to bees

S/N	Active ingredient(s)	Status in EU database	Status in Standard Organizations (BCI/RA/FSC/4C/SAN/UTZ)	Status in PAN-HHP
7	Hexaconazole	Not approved	Not listed	Added to PAN-HHP list in 2011. Long-term health effects: possible carcinogens. Environmental toxicity: very persistent in water, highly toxic to bees.
8	Dichlorvos	Not approved	Highly restricted/prohibited, to be phased out by 2024 May only be used under a specific, defined condition Highly hazardous, fatal if inhaled. Highly aquatic toxicity/highly toxic to honey bees, birds	Added to PAN-HHP list in 2011, 2019. Acute toxicity: highly hazardous, fatal if inhaled. Long term health effect: possible carcinogen Environmental toxicity: highly toxic to bees
9	Lambda-cyhalothrin	Approved	Highly restricted/minimization of use/may only be used under a specific condition, to be phased out by 2024 Fatal if inhaled Endocrine disruptor, highly aquatic toxicity/highly toxic to honey bees/aquatic risk, pollinator risk	Added to PAN-HHP list in 2011, 2019. Acute toxicity: Fatal if inhaled. Long-term health effects: Endocrine disruptor, reproductive toxicity. Environmental toxicity: highly toxic to bees
10	Imidacloprid	Approved	Restricted, prohibited with an exception for certain pests in certain crops and regions/minimization of use. Prohibited without exception/potentially prohibited May cause severe effects Highly toxic to honey bees, birds/Neonicotinoid/may cause severe effects	Added to PAN-HHP list in 2011, 2019. Environmental toxicity: highly toxic to bees
11	Dimethoate	Not approved	Restricted, minimization of use/potentially to be prohibited Inhalation risk Highly toxic to honey bees/highly toxic to birds/aquatic risk, pollinator risk, wildlife risk	Added to PAN-HHP list in 2011, 2019. Long-term health effects: probable carcinogen, Endocrine disruptor, reproductive toxicity. Environmental toxicity: highly toxic to bees

S/N	Active ingredient(s)	Status in EU database	Status in Standard Organizations (BCI/RA/FSC/4C/SAN/UTZ)	Status in PAN-HHP
12	Nicosulfuron	Approved	Not listed	Added to PAN-HHP list in 2019. Very persistent in water /sediments
13	2,2-dichlorovinyl Dimethyl phosphate	Not listed	Not listed	Not listed
14	Profenofos + cypermethrin	Not approved + Approved	Restricted, identified as hazardous. Use with extreme caution High aquatic toxicity/ high toxic to honey bees	Added to PAN-HHP list in 2009, 2011,2019. Environmental toxicity: highly toxic to bees
15	Carbendazim	Not approved	Prohibited/potential to be prohibited, exceptions may apply for certain pests, in certain crops and regions. May only be used under specific, defined conditions Minimization of the use Mutagenic, Reproductive toxin	Added to PAN-HHP list in 2011, 2019. Long term health effect: induce heritable mutations in germ cells of humans, impair fertility in humans, cause developmental toxicity to humans, probable likely carcinogen, Endocrine disruptor, reproductive toxicity
16	S-metolachlor	Approved	Restricted use, Risk specific mitigation measures are mandatory Aquatic risk	Not listed
17	Mancozeb	Approved	Restricted use of pesticides, risk-specific mitigation measures are mandatory. May only be used under specific, defined conditions. Minimization of use, prohibited/potentially to be prohibited Probable carcinogen. Endocrine disruptor, wildlife Risk	Added to PAN-HHP list in 2011, 2019. Long-term health effects: Probable likely carcinogen, Endocrine disruptors, reproductive toxicity.

Table 4.
Pesticides hazardous nature and toxicity status.

The hazard criteria of the active ingredients were grouped into—acute toxicity, long-term health effects, environmental toxicity, and international regulations (global pesticide-related conventions). The pesticides grouping, hazard, and toxicity status (**Table 4**) were the recommendations of globally harmonized system of classification and labeling of chemicals (GHS), World Health Organization (WHO) recommended classification of pesticides by hazard, the international agency for research on cancer (IARC), U.S. environmental protection agency (U.S. EPA), and European Union categorization of endocrine disruptors. The recommendation of these organizations was benchmarked by the 4C Association, Bonsucro (Better Sugar Cane Initiative), Better Cotton Initiative (BCI), Fairtrade International, FSC, RSB, SAN (Sustainable Agriculture Network), and UTZ.

Glyphosate, herbicide, and very common active ingredient are used for the management of weeds both in agriculture and domestically. The active ingredient is classified as highly restricted for use, with mandatory risk-specific mitigation measures. The active ingredient is prohibited, identified as hazardous and its use should be extremely cautious and minimized. Di-methylamine (2,4 dimethylamine salt) was found to be commonly used by growers and the public in weed management but no record of this active ingredient was found in the databases of EU, Pesticide Action Network International, and other international standard organizations.

Nicosulfuron is an approved active ingredient for the management of weeds but with the environmental hazard of being very persistent in water/sediment. Profenofos + cypermethrin, an insecticide combination is restricted, to be used with extreme caution, shows high toxicity to honey bees and high aquatic toxicity according to FSC and Fairtrade. Another approved herbicide is S-metolachlor although recommended for restricted use and mandatory risk-specific mitigation measures to be taken and has aquatic risk according to RA, SAN.

8. Safety statuses of active ingredients in the open market

The three geographies surveyed were major agrochemical markets in the state, which were purposefully selected for the study. Pesticides poisoning most often comes from swallowing chemicals, after consuming contaminated foods or beverages. Frequently exposed persons are also susceptible to poisoning that can cause organs or systems damage.

Paraquat is a leading cause of fatal poisoning in parts of Asia, the Pacific Islands, and the South and Central Americas. It is rapidly but incompletely absorbed and then largely eliminated unchanged in urine within 12–24 hours, the very high case fatality of paraquat is due to inherent toxicity and lack of effective treatments [1]. Paraquat dichloride was shown to be very immobile in the soil, does not hydrolyze nor photodegrade in aqueous solutions, and is resistant to microbial degradation under aerobic and anaerobic conditions. The primary route of environmental dissipation of paraquat is adsorption to biological materials and soil clay particles [2], Paraquat dichloride is highly toxic to birds/may cause severe effects [3]. It is reported that more than 70% of trusted sources of paraquat poisonings result in death. Ingesting small to medium amounts of it can lead to fatal poisoning, lung scarring, and the failure of multiple organs, heart, respiratory, kidney, and liver failure. Ingesting large amounts of paraquat causes confusion, muscle weakness, seizures, difficulty breathing, fast heart rate, and coma [4]. Paraquat dichloride is not an approved active ingredient by the EU standards on safe pesticides. It has been recently listed in PAN as a highly hazardous pesticide in 2019 [5], with restricted use, it is prohibited from use and to be faced out by the year 2024. The effect on humans includes fatality if inhaled and may cause severe effects (SAN, PIC).

Glyphosate and its formulations may not only be considered as having genotoxic, cytotoxic, or endocrine-disrupting properties but a causative agent of reproduction abnormalities in both wildlife and humans. Furthermore, the extensive use of glyphosate-based herbicides in genetically modified glyphosate-resistant plants grown for food and feed should be of grave concern since they can be sources of genotoxicity, cytotoxicity, and reproductive toxicity in wildlife and humans [6]. Although glyphosate is approved for use by the EU, other standards organizations have listed it as a highly hazardous pesticide in 2011, 2014, and 2019 [5]. This active ingredient has been restricted, only be used under specific and defined conditions. It is also a probable carcinogenic substance to humans and has environmental toxicity by being very persistent in water and sediments [7]. Glyphosate provokes oxidative damage in the liver and kidneys of mammals by disrupting mitochondrial metabolism, disrupting endocrine-signaling systems and residues from glyphosate may pose higher risks to the kidneys and liver, reproductive development impairment [8]. Increases in the frequency of serious, chronic kidney disease were observed among male agricultural workers in some regions with heavy glyphosate use and "hard" water. And that the possible adverse effects of glyphosate exposure on kidney and liver warrant a focused, international research effort [9, 10]. Glyphosate can alter the functioning of hormonal systems and gene expression patterns at various dosage levels. Such effects will sometimes occur at low and likely environmentally-relevant exposures. Contemporary endocrine science has demonstrated that dose-response relationships will sometimes deviate from a linear increase in the frequency and severity of impacts expected as dose levels rise [11]. The timing, nature, and severity of endocrine system impacts will vary depending on the levels and timing of glyphosate exposures, this is pertinent as agrochemical users in Nigeria are indoctrinated in terms of dosage, rate, and timing of application.

Permethrin + Pyriproxyfen is used to kill a large range of pests; fleas, ticks, cockroaches, flies, and mosquitoes. The environmental protection agency (EPA) reviewed the pesticides register showed that permethrin stays a long time in the soil, very low amount stays in the water. Permethrin has some health risks; headaches, dizziness, nausea, shortness of breath, skin irritation, and redness of eyes when used at higher levels [12]. However, it is highly hazardous, with probable carcinogen in humans [13], and highly toxic to honey bees [14], aquatic, pollinator, and wildlife risk [5].

Cypermethrin is a pyrethroid insecticide, first synthesized in 1974, widely used to kill insects as it works quickly by affecting the nervous system, toxicity level in animals varies,for example, in rats includes tremors, seizures, and salivation, in cockroaches when exposed to little amount as 0.02 micrograms per gram causes brain paralysis, restlessness, and prostration. Cypermethrin is approved for use to manage agricultural insect pests. It is however listed as a highly hazardous pesticide in 2011 and 2019. It is classified as highly restricted use with mandatory risk-specific mitigation measures [3, 5]. It has highly aquatic toxicity, toxic on honey bees, and also with aquatic and pollinator risk [15]. Effect of cypermethrin in humans when exposed sometimes causes itching and tingling sensations. The half-life of cypermethrin in the environment takes about 30 days, soil microbes easily break it down because of the low potential to move in the soil but poses little to no risk when used responsibly [2].

The toxicity status of Chlorpyrifos is similar to cypermethrin except that it is not indicated in the EU database but UTZ classified it as highly restricted, may only be used under the specific condition with risk-specific mitigation measures, and is potential to be prohibited. Chlorpyrifos classified as highly hazardous in 2011 and 2019, poses inhalation risk to humans, high aquatic toxicity, highly toxic to bees [14], birds with aquatic pollinator, and wildlife risk [3].

Dichlorvos an organophosphate insecticide, also used as a public health vector control for animals, is registered worldwide for varieties of uses, majorly used as a post-harvest fumigant for control of various pests in food, the acceptable daily intake (ADI) for Dichlorvos was established as 0.004mg/kg bw and the acute reference dose was 0.1mg/kg bw. It can be applied with aerosols, fogging, and sprays equipment. It also breaks down rapidly in humid air, water, and soil, it takes longer time on wood when exposed to humans through food can be acutely toxic with typical cholinergic signs that are highly hazardous, dichlorvos is not teratogenic in mice and rats' half-lives of recovery is about 15days in human and 2 hours in rats [16].

Dichlorvos is not approved for use but found in open markets, it is restricted in use and meant to be phased out by the year 2024 (BCI). It is highly prohibited, may only be used under specific, defined conditions. The active ingredient is classified as highly hazardous to humans [17], it is fatal if inhaled according to the EU and globally harmonized system (EU, GHS). It is a possible and probable carcinogen [2, 7], with high aquatic toxicity and highly toxic to honey bees and birds [15, 18–20].

Dimethoate comes in different forms; dustable powder (DP), wettable powder (WP) soluble concentrate, its toxicity was evaluated in 1992 by (WHO), it is used to control a wide range of insects and pests, in cereals, citrus, coffee, cotton, fruits, grapes, potatoes, beetroot, tea, and vegetables. It can also be used to control flies because of its systemic nature and acaricide the solubility of dimethoate in water at 90% purity has 39.8 at 25°C after 4 hours, equilibrium. In rats, the toxicity of dimethoate is mostly acute, such as oral irritation, dermal sensitization, eye irritation in humans, WHO hazard classification of dimethoate is "class moderately hazardous," UN classification is "Toxic class 6.1," US EPA Classification is; (Formulation) 11, EC Classification; Risk Xn (R21/22) Reviews by WHOEHC (1986) concluded that when used in proper level and accordingly exposure of human through the air, food, or water can be negligible.

Nicosulfuron is used as post-emergence in forage maize, found to have low dermal and inhalation toxicity, can be slightly irritating in rats, and has not been evaluated by the FAO, JMPR, and WHO/IPCS, although it is currently under review, it is registered in the U.S.A, the WHO Classification of Nicosulfuron is U; unlikely to cause an acute hazard in normal use. This active ingredient does not meet the criteria established in the UN recommendations on the transport of dangerous goods and therefore is not considered hazardous for transportation purposes. It is also not co-formulated with other active ingredients; toxicity in rats includes acute dermal irritation and eye irritation [21].

Profenofos + Cypermerthrin is a co-formulated organo-phosphorous insecticide, studies have shown its toxicity levels on animals, plants, and even the environment's fate when it comes in contact. Profenofos was evaluated by JMPR in 1990, 1992, 1994, and 1995, toxicological, reviews were also conducted in 2007 when an ADI OF 0 to 0.03mg/kg bw and ARfD of 1mg/kg bw were established, profenofos is a clear liquid with weak odor, its solubility in water at 22°C is 2.8mg/l at a pH of 6.9, profenofos is slowly absorbed in metabolized, it was major residue when crops are harvested several weeks after the last applications, its residues are not expected to occur in succeeding crops. Reviewed by JMPR health risk shows that profenofos is unlikely to present a public health concern.

S-metolachlor is used for varieties of crops for control of grasses, for example, pigweeds (*Amaranthus* spp.); they are different commercial brands, herbicides that contain metolachlor as active ingredients although formulation and chemical composition may differ, some products metolachlor safeners are added some, no safeners added. A safener is added to metolachlor to reduce injury to crops, such as corn, but injuries to other crops solely depend on the amount of safener used or environmental concerns. Metolachlor has four different isomers but can be grouped into two, which are S-metolachlor isomers and R-metolachlor isomers, both are made from the same materials but S-metolachlor isomer is more active in herbicidal effects compared to R-metolachlor.

Lambda-cyhalothrin is a synthetic pyrethroid insecticide used in agricultural and public health to control a wide range of insects and pests at developmental stages, it is a nonsystemic chemical, does not stay long in the soil so has an only limited function when used as soil insecticide. Lambda-cyhalothrin can be applied by spree spraying and residual spraying. Additionally, the provided data on acute toxicity, skin irritation, and sensitization. The mutagenic study reviewed that Lambda-cyhalothrin is nonmutagenic, JMPR has defined an acceptable daily intake (ADI) of 0 0.02mg/kg bw, water solubility is 0.005 mg/l. The IPCS hazard classification of Lambda-cyhalothrin is moderately hazardous Class II (WHO). Lambda-cyhalothrin is approved for use in weed management but listed as highly hazardous in 2011 and 2019 [5]. It is to be phased out by the year 2024 and with highly restricted use, only be used under specific conditions, and according to the globally harmonized system (GHS), it poses a fatal risk to humans if inhaled. This active ingredient also poses a long-term health effect as an endocrine disruptor and as having reproductive toxicity [22].

The 2,2-dichlorovinyl dimethyl phosphate is another insecticide that is not listed in the active ingredients database of the EU. It is however listed as a highly hazardous substance in PAN as an endocrine disruptor, has highly aquatic toxicity, is highly toxic to honey bees, aquatic, and pollinator risk [5].

Carbendazim is a very common fungicide but was recently listed as highly hazardous in 2019 [5] and not on the approved list of EU pesticides. It is restricted, prohibited with exceptions for certain pests, in certain crops and regions, and may only be used under specific, defined conditions as recommended by Fairtrade. This active ingredient has a mutagenic effect on humans and it is a reproductive toxin according to EU and GHS [13, 23]. Carbendazim is a widely used systemic fungicide that is mainly used for protective and curative functions. It is used to control a large number of fungal diseases, such as mold, mildew, rot, and blight, in some crops, such as ginger, nuts, legumes, and even fruits. Additionally, carbendazim has been nominated for chemical program review under Australia Pesticide and Veterinary Medicines Authority (APVMA) because of its effect known to cause impaired human fertility and cause birth defects, the review made a conclusion it causes the above effects, the half-life of carbendazim is as long as 6 months, recommended warning for registered carbendazim products that it must contain the following stated warning "Contains carbendazim which causes birth death and irreversible male infertility, in laboratory animals, avoid contact with carbendazim" recommended usage level in drinking water is 0.09 mg/ls [24]. For safety operators mixing and loading carbendazim must wear gloves to avoid skin irritation, respirator face shield should be worn to prevent ingestion. Even with the use of these safety measures the risk cannot be mitigated, the use of carbendazim is no longer supported for occupational health and safety grounds [2].

Another active ingredient similar to carbendazim is mancozeb, also a fungicide with the recent addition to the highly hazardous list; also has restrictions of use, prohibited, risk-specific mitigation measures are mandatory and may only be used under specific, defined conditions according to FSC, RA, and Fairtrade standards. Mancozeb is a probable carcinogen to humans [13, 23], an endocrine disruptor, and has wildlife risk [3]. Mancozeb is used for a wide range of fungal diseases as protective fungicides for horticultural and agricultural purposes. Mancozeb is a member of the ethylenebisdithiocarbamate (EBDC) group of fungicides which maneb and metiram are some of the related active ingredients, used on crops, such as potatoes, apples, grapes, onions, tomatoes, and melons. Its effects on human health can be toxic because it is majorly harmful to thyroid organ, reviewed to cause thyroid toxicity, thyroid lesions, and thyroid tumors, the residual composition of mancozeb is not to a level of concern to the EPA and other effects, such as cancer risk, effects on terrestrial and aquatic species, are feasible by using restrictions [25].

The 2,2dichlorovinyle dimethyl phosphate is also known as (dichlorvos); it is a colorless to amber liquid, an agricultural chemical used to control insects, diseases, and eliminate storage pests and crops. Application of dichlorvos is mainly expelled into the air for household pesticides and it is usually distributed into the water for pesticide control and sprayed on land when used for agricultural purposes. Furthermore, it is eliminated by hydrolysis and biodegradation, some toxic effects on animals and humans include acute effects such as weakness, severe anemia, anticholinergic symptoms other effects on gastrointestinal tracts and nervous system in rabbits, it causes severe skin irritation. The current regulation in Japan for dichlorvos is Deleterious substance, Class I designated chemical substance.

Imidacloprid is a new insecticide that is related to nicotine chemically, just like nicotine, imidacloprid acts on the nervous system, it is used in large quantities in crops, pests, and turf grasses, when imidacloprid is exposed to animals or humans some of the effects includes, Apathy, emaciation, convulsion, labored breathing, when exposed for a long time it causes loss of weight and thyroid lesions in human. It can be acutely toxic in some animals, bird species, and plants by causing decreasing growth levels.

Hexaconazole is a systemic triazole fungicide that is used in the control of a wide range of diseases of crops example of some diseases are black and yellow Sigatoka diseases of banana, used on banana foliar to control diseases, The Health Effects Division Hazard Identification Assessment Reviews Committee (HIARC), evaluated the toxicological level of hexaconazole on human and animals is reviewed to have enhanced sensitivity to infants and children. In animals such as rats, the study revealed a decrease in body weight gains and decreased pub survival, although the aggregate exposure risk is limited to dietary exposure only, hexaconazole has low toxicity by oral, dermal, and inhalation mode of exposure, it can be slightly irritating to the eye and skin sensitization in animals.

Hexaconazole was found in the open market but not approved by the EU, classified as a highly hazardous substance, a possible carcinogen [26] very persistent/water, and highly toxic to bees [5].

Imidacloprid, a fungicide approved by the EU for the management of fungal diseases in crops, although approved, it is however prohibited with an exception for certain pests in certain crops and without exceptions by some other standards. The active ingredient may cause severe effects on humans and be highly toxic to honey bees and birds [5, 14].

A fungicide named dimethoate is not on the approved list of the EU, it is listed as highly hazardous in 2011 and 2019 [5]. Dimethoate is classified as a probable carcinogen and with reproductive toxicity according to globally harmonized system [13, 23]. This active ingredient is recommended as restricted with minima use and potentially to be prohibited according to FSC, RA, UTZ. It also has inhalation risk to humans, highly toxic to honey bees, birds, and aquatic, pollinator, and wildlife risk according to SAN [21].

9. Handling and disposal of agrochemicals

People are exposed to pesticides through varied means of handlings for domestic and agricultural purposes. Exposure can be through spray drift, residues in the environment, contaminated food, or drinking water and these can be directly or indirectly.

This exposure can also be through absorption through the skin, ingestion through food, or inhalation during the application or perceived from the environment. Exposure has an impact on the human body as related to the amount of pesticides exposed to (dose) and length of pesticides exposure (time). The health risks associated with pesticide use are a combination of toxicity and exposure. However, responsible pesticides use involves applying the right pesticide, in the right way, dosage, interval, and at the right time.

Figure 1 shows a typical practice of some farmers on the use of pesticides on stored products in rural communities and poor urban areas. Pesticides were applied directly to the product to extend the shelf life in storage, especially against insect infestation. The pesticides were sprayed in overdose, at the wrong time as shown in **Figure 1** (around afternoon as depicted in the shadows) and the products were bagged immediately.

Apart from hazards of residue contamination in the food crops, the human and environmental hazards are also very loud. The humans were not in any way protected from spray drift on their skin and through inhalation or direct exposure. Likewise, was the volatility escape of the sprays into the environment, contaminating and polluting nearby produce and passersby. This practice showed wrongness in terms of quantity of agrochemicals applied, time of application, exposure of the crop, the farmers also unprotected and the environment been polluted.

The indiscriminate disposal of agrochemical contents into the soil, environment, and wrong handling are shown in **Figure 2**. Rural farmers use this method to prepare pesticides in containers, mixed with hands and occasionally tasted to "ascertain efficacy" of the pesticides.

Figure 1.
Over dose application of pesticides on stored product.

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Figure 2.
Indiscriminate disposal and preparation of pesticide on farm.

This practice proves the level of ignorance and literacy of potential risks agrochemicals pose to human health beyond a reasonable doubt. The pesticides residues contaminant in soils were usually washed into the streams during rains, the same water is used for domestic activities, bathing, and even drinking.

10. Conclusion

The study showed that many of the agrochemicals in open markets have some level of restriction of use or approval based on the recommendation of international standard organizations, with proved risks to humans, animals, and the environment. The general handling and indiscriminate use of these active ingredients in open markets and farmer's fields showed deficient knowledge and awareness of the potential danger they pose to crops, humans, and the environment.

11. Recommendation

Enlightenment programs on local broadcasting stations, such as radio, television, and marketplace campaign should be launched to create awareness of the risks and dangers associated with agrochemical use and misuse both for domestic and agricultural purposes. These avenues will reach the rural dwellers who are the most vulnerable to the potential risks. The relevant government/regulatory agencies should fulfill their mandate agrochemical related matters like control/enforcement, acceptable active ingredients, monitoring and safety measures as well as prosecution of offenders of national agrochemical laws.

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