Pesticide Use: Properties and Environmental Fate

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Abstract

This paper reviews the benefits and risks of pesticides use with brief discussion on their properties and movement in the environment. The growing demand for food by the ever increasing world population has led to tremendous increase in the use of pesticide. However, recent developments in pesticide production has helped to reduce the volume of pesticide use due to the synthesis of more potent active ingredients and the introduction of good agricultural practices. The transportation, accumulation and degradation of pesticide residues in the environment depend on their properties. The analysis of pesticide residues on food especially fruits and vegetables which are consumed raw have been a matter of public concern, due to the health risks. Therefore, there is need to balance the expected benefits of pesticide use and their risks to human health.

Keywords: Agriculture, Degradation, Environment, Pesticide, Toxicology

1.0 Introduction

The increase in world population has led to drastic increase in demand for food supply and by implication tremendous rise in the application of chemical pesticides and fertilizers [1]. To increase agricultural production and meet the growing demand for food, pesticides are used to control pests and vectors of plant diseases [2]. Pesticides are also used for non-agricultural purposes to control and eradicate carriers of vector borne diseases such as malaria, yellow fever, typhoid fever and dengue, which are major public health concerns [3]. Pesticides are widely used to control pests of fruits and vegetables, which are important part of a healthy diet [4].

Pesticides refer to all natural and synthetic chemicals that are used to prevent, destroy, repel or fight crop pest and vectors of plant diseases [5]. Pesticides are mostly organic compound with different functional groups, forming various types of isomeric compounds [1]. They differ in their substitution groups and in their degree of ionization, octanol water coefficients, polarity, volatility and solubility in water and organic solvents. The production and applications of pesticides for agriculture and non-agriculture purposes have in no doubt led to steady increase in food production, high food quality and reduce incident of illness due to insect-borne diseases. Their continuous use has negative impacts on the environment and their presence in soil, air, water and food pose a potential health risk due to their biocide activity [6]. Therefore, pesticides must be used efficiently and effectively in order to strike a balance between their expected benefits and the possible risk to human health. This will enable their economic viability and environmental sustainability [7].

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2.0 Uses and Benefits of Pesticides

Pesticides are unavoidable input in agriculture and public health that are produced in large quality since the end of World War II [8] Their worth have been demonstrated through increase in global agricultural production, eradication of insect borne and epidemic diseases and conservation of the ecosystem [9]. The use of pesticides increase significantly in the late 1940, and thus the immediate benefit of its uses overshadowed its toxicity. The most widely used pesticides in agriculture are insecticides on insects, herbicides on weeds, rodenticides on rodents and fungicides to control fungi, mold and mildew.

In many parts of the world, especially in the developing and under-developed countries, excessive loss of farm produce to insects and other pests has led to starvation and famine [10]. Postharvest loss of crop also contributed to hunger and malnutrition which led to the death of more than 15 million children [11]. The use of pesticides seems to have allowed production of inexpensive, affordable, and low cost food especially fruits and vegetables, which are vital in the protection against cancer and heart diseases, due to the presence of some antioxidants in them [12].

The most obvious benefit of pesticides use in agriculture is in the improved yield of crops in addition to providing subtle or incremental benefits distributed over a large area. Other benefits include increase in revenue for farmers due to reduced labour cost, reduced fossil fuel use of farm machines, reduced production of highly toxic alkaloids like mycotoxins and increased shelf life of fruits and vegetables [13]. Thus higher yield of farm produce reduce pressure to cultivate un-cropped land which is beneficial for the environment, thereby conserving the natural ecosystem [13].

3.0 Risk of Pesticide Use

Pesticides are regarded as one of the most dangerous contaminants in the environments because of their persistency, biotransformation in the food chain, bioaccumulation in animals, mobility in the environment and their possible risks to human health [14]. Due to non-selectivity of pesticides for the target species, they always cause an adverse effect on non-target organisms [10]. Pesticides affect normal and basic metabolic activities in human systems. Pesticides are meant to be poisonous and a great danger is associated with their production, transport and applications, while their normal use often lead to contamination of the environment. Pesticides alter the electrophysiological properties of nerve cell membrane and its associated enzymes, disrupting the kinetics of essential mineral ions flowing in the membrane. They interfere with sodium channel in the axonal membrane and cause imbalance in the ratio of sodium and potassium surrounding the nerve fibers [10, 15]. This results in nerve motor unrest and increased frequency of continuous transmission in the nerves and abnormal susceptibility to external stimuli.

Pesticide exposure can result from occupational and accidental activities as well as pesticide residues in food and can be contacted through skin, mouth, nose and eyes [16]. Acute exposure to pesticides can lead to a wide range of chronic effect including blood disorder, reproductive and birth defect, benign or malignant tumor, endocrine disruption, nerve disorder and genetic change. Symptoms such as nausea, vomiting, diarrhea, severe headache, dizziness, tonic and clonic convulsions, muscle fasciculation, joint swelling, leg and back pain, hypertension, drowsiness, increased sweating, abdominal pain, anorexia, skin dryness and nail discolouration. They also cause memory loss, hyper-susceptibility to external stimuli, tremor, flaccid paralysis, emotional liability, restlessness, loss of coordination and in some cases enlargement of the liver. Some are carcinogenic and have been used for suicidal purposes [10, 16, 17].

Pesticide use has been estimated to cause deaths of about 220,000 people, with 3 million cases of poisoning reported and 750,000 cases of chronic illness, most especially in the developing countries [18]. Exposure of people to pesticide also reduces their productivity due to declining health condition, economic loss due to payments for health services and change in social behavior due to loss of household income as a result of ill-health [19].

4.0 Pesticide Residues and Legislation

The production, sale and use of pesticides require strict rules and regulations to ensure the protection of human health and the environment [10, 17, 20]. Pesticide legislations are formulated to increase the level of protection to human health, animal welfare and the environments. In addition, the legislations are aimed at enhancing the efficacy of pesticide products for their

proposed use and to protect the financial interest of a country in internal trade [21]. Over the years, there has been a lot of public awareness about the presence of pesticide residues in food, drinking water and the environment. Therefore, there is need to pay greater attention in order to regulate the use of pesticides.

There have been international and national legal frameworks guiding the trade and use of pesticides. The Food and Agricultural Organization (FAO) of the United Nations, designed an International Code of Conduct on the Distribution and Use of Pesticides [22], to provide universal standards on the conduct of all stakeholders involved in pesticides industry. Although some of these legal frameworks are subjected to constant review and redesigning. The design of international regulatory framework involved FAO, United Nation Environmental Programme (UNEP), World Health Organization (WHO), and International Labour Organisation (ILO), some of which are legally binding and some not, but implicate pesticides management [21].

The regulatory instruments that are legally binding on member nations include:

- (i) Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Pesticides and Industrial Chemicals in International Trade, 1998, Revised 2013
- (ii) Stockholm Convention on Persistent Organic Pollutants, 2001
- (iii) Basel Convention on the Transboundary Movement of Hazardous Wastes and their Disposal, 1989
- (iv) Montreal Protocol on Substances that Deplete the Ozone Layer, 1987
- (v) ILO Convention on Safety and Health in Agriculture, 2001
- (vi) ILO Convention Concerning Safety in the Use of Chemicals at Work, 1990

The regulatory instruments that are voluntary and are not legally binding on members nations include:

- (i) FAO International Code of Conduct on the Distribution and Use of Pesticides, 2002
- (ii) FAO International Code of Conduct on Pesticide Management, 2014
- (iii) Standards of the Codex Committee on Pesticide Residue, 1999, 2009, 2010 and 2012
- (iv) UN/ECOSOC Globally Harmonized System of Classification and Labeling of Chemicals, 2011

The United State Environmental Protection Agency (USEPA), Food and Drug Administration (FDA) and United States Department of Agriculture (USDA) are saddled with the responsibility of regulating the use and sales of pesticides in the United States. The US pesticide legislations include the Federal Insecticide Act, Federal Food Drug and Protection Act and Food Quality and Protection Act [10, 20]. The legislation also involves the assignment of Maximum Residue Levels (MRLs), which can be estimated from toxicological characteristics such as Acceptable Daily Intakes (ADI) [23], and median lethal dose (LD $_{50}$). The regulatory status also indicates if the active ingredient is a General Use Pesticide (GUP) or as a Restricted Use Pesticide (RUP) according to USEPA guidelines [15]. The various legislations and directives were proposed in order to check overuse and misuse of pesticides in the environment and curb adverse effects of pesticides on human health and reduce environmental pollution.

5.0 General Properties and Environmental Fate of Pesticides

The biotic and abiotic environmental processes are influenced by the physical and chemical properties of pesticides. The environmental and biological processes determine pesticides persistency, mobility, transport, partitioning and fate [24, 26, 27]. Their chemical structures determine the stability in terms of resistance to photolysis, chemical hydrolysis and microbial degradation [28]. The knowledge of their properties (physical and chemical) is also essential in the choice of extraction technique and method development in residue analysis.

5.1 Water Solubility

The solubility of pesticide in water describes amount of pesticides in milligram that will dissolve in a liter of water and is usually given in milligram/liter (mg/L or ppm) measured at room temperature [29]. The knowledge of pesticide solubility in water can be used to trace its environmental distribution in water, soil, air, organisms and degradation pathways [20, 28, 30], as well as partitioning ability between solid and liquid phases in the environment and its persistence on the plant surface [31]. The solubility of pesticides is determined by factors such as polarity, presence of hydrogen bonding, pH, molecular weight and temperature [30, 32].

Pesticide mobility from soil to groundwater depends on its solubility [33], and is an indication of its ability to be leached into ground and surface water or precipitated on soil surface [34]. Thus, the higher the solubility of pesticide in water, the more their run off by leaching, the less their accumulation in the environment and they can easily be degraded by hydrolysis [29, 32, 35].

5.2 Vapour Pressure and Henry's Law Constant

Vapour pressure is a measure of the volatility of a pesticide in its pure state from water or moist soil [29, 32, 33, 35], which is described by Henry's law constant. Henry's law constant, measures the pesticide volatility as a function of its vapour pressure and its solubility in water. It is defined as the ratio of concentration of pesticide in air and its concentration in solvents, estimates by the vapour pressure, temperature, molecular weight and water solubility [30, 32, 33]. The higher the vapour pressure and the Henry's law constant of a pesticide, the higher its volatilization and therefore it will more distributed and disperse over a wide area in the environment, while pesticides with low vapour pressure and Henry's law constant tend to be more accumulated in the environment and have high leaching potential [28, 30].

5.3 Octanol/Water Partition Coefficient

Octanol/water partition coefficient is the indication of distribution and solubility of substance at equilibrium between organic solvent (octanol; relatively non-polar) and aqueous solvent (water; polar) [33]. It is a measure of dissolved mass substances at equilibrium between equal volumes of n-octanol and water. It is the ratio of the concentration of pesticide in n-octanol and its concentration in water [36]. It is used to predict the environmental fate and transport of pesticide and their partitioning between organic and aqueous phases [25, 37]. Partition coefficient is dependent on polarity, solubility, molecular weight and density of the pesticide [28, 30].

The octanol/water partition coefficient is used to estimate and predict pesticide characteristics, such as lipophicity, structure-activity relationship, distribution between the environmental compartment, bioaccumulation and bioconcentration factor [25, 27, 28, 36]. Pesticides with higher coefficient are partitioned in organic phase, while those with lower partition coefficient can easily leached due to their high solubility in water. It is the difference in the free energy of solvation of solute in organic phase and the free energy of solvation in aqueous phase [38] and is given by the equation:

 $K_{ow} = \frac{Pesticide\ concentration\ in\ octanol}{Pesticide\ concentration\ in\ water}$

$$pK_{ow} = -\log_{10} K_{ow}$$

5.4 Sorption and Desorption of Pesticides

Sorption and desorption of pesticides refer to the attraction and retention of pesticides on the surface of a solid or liquid substrate and describes the attractive force between pesticide and soil particle [32, 39, 40]. Chemisorption (chemical sorption) occurs, when the pesticide molecules is retained on the surface through formation of chemical bond, while physisorption (physical sorption) is the retention of the pesticide molecules on the soil surface through the formation of weak intermolecular attraction (van der Waal forces). The interactions of pesticides with soil and other environmental substrates are greatly affected by sorption and desorption processes [41], and also on the rate of other physicochemical properties such as biodegradation, hydrolysis, volatilization and photochemical oxidation [24].

Sorption can either be adsorption on the surface of substrate or absorption into interior of the sorbent matrix such as organic matter [40]. Adsorption of pesticides to soil or other solid substrate is due to the attraction between the positively charged pesticide molecules and negatively charged soil or solid particles [39]. Pesticides molecules that are strongly sorbed into the soil particle are not likely to leach, are less available for plant uptake and degradation and are more persistence in the environment [29, 32]. Pesticides molecules that are weakly sorbed will leach depending on their solubility in water. Sorption of pesticides on soil particles are influence by factors such organic carbon content, polarity, solubility, soil surface area and size, chemical function, octanol/water partition coefficient, organic matter in solution, salinity, pH (for weakly acidic and basic pesticides), and soil moisture and texture [24, 30, 32, 39, 40].

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Adsorption of pesticides to soil particles is quantified using distribution coefficient (or adsorption partition coefficient), K_d , which is the ratio of concentration of pesticide sorbed onto soil particles to the concentration of pesticide in solution, i. e. the ratio of sorbed-phase concentration ($\mu g/g$) to the solution phase concentration (($\mu g/mL$) at equilibrium. The distribution coefficient depends on the soil characteristic and therefore the need to adjust its value by the percentage of organic carbon content of the soil. This gives sorption coefficients (K_{oc}) which describes the affinity of pesticides to soil organic carbon content and is independent on soil type [29, 30, 32, 33, 39, 40].

Distribution Coefficient = <u>Sorbed-phase concentration</u>

Solution-phase concentration

Sorption Coefficient $K_{oc} = \underline{Distribution Coefficients (Kd)}$ x 100

Organic Carbon (OC)

Adsorption determines the mobility and bioavailability of pesticides in the environment. The higher the value of sorption coefficient, the more the pesticides is sorbed onto the soil particle and the less its mobility. The sorption potential of pesticides are determined using sorption isotherm (describes the relationship between the mass of sorbate per unit mass of sorbent and the concentration of the sorbate) with the assumption that the isotherms (Freundlich and Langmuir) are linear and reversible [39, 40].

5.5 Toxicity and Mode of Action of Pesticides

Toxicity is the tendency of pesticide to produce adverse or harmful effect due to chronic or acute exposures which may range from mild to severe symptoms [42]. Toxicity is directly proportional to exposure and exposure is a function of time and dose. Hazard which is the harmful effects of pesticide is a function of toxicity and exposure [43]. The scientific study of the qualitative and quantitative adverse and harmful effects of pesticides and other chemicals on human, plants and animals is called toxicology [43, 44].

Mode of action of pesticides can be defined as a series of processes starting with the exposure and interaction of pesticide with organisms to biological response which result in harmful or adverse effect giving a set of physiological and biological signs [45, 46]. Toxicity effect of pesticides are demonstrated using experimental animals exposed to various levels of pesticides active ingredient on long term study [44]. It is usually estimated using a dose-response and exposure relationship which is expressed in dose per unit weight lethal (mg/kg) to 50% of the population (LD₅₀) of the animals, or the concentration of the pesticides in an external media that will kill half of the test population (LC₅₀) under certain conditions [20, 28, 42]. The smaller the values of LD₅₀ and LC₅₀ the more toxic the pesticides, since it shows that small amount of the pesticides can kill half of the test animals.

Toxicology tests embrace all the circumstances of exposure of human to pesticides including tests for hazard identification in animals such as genetic toxicity, acute toxicity, short-term toxicity, chronic toxicity, immunetoxicity, reproductive toxicity and neurotoxicity [20, 28, 42, 47, 48]. The tools developed to evaluate and analyze the toxic effects of pesticide include pesticide risk indicator (PRI) [49], toxic unit (TU) [46] and pesticide toxicity indicator (PTI) [50].

5.6 Bioconcentration Factor of Pesticides

Bioconcentration of pesticide is the increase in the concentration that is present inside and/or on the surface of an organism in relation with the concentration present in an external medium such as soil or water [51, 52]. The bioconcentration factor describes the extent to which pesticide will accumulate in organisms [30, 53]. It is a numeric value which evaluates the bioconcentration of pesticide, and expresses the partition of pesticide between organisms and the external medium [52]. It is also described as the ratio concentration of chemical in an organism to the concentration in water at steady state [30, 51-54]. The higher the bioconcentration factor values, the higher the level of accumulation in lipid membrane [53] and thus the measurement of bioconcentration factor values is required to allow for estimation of daily pesticide intake through consumption of fruits and vegetables [51]. The bioconcentration factors depend on pesticides' solubility, polarity, metabolism, lipid content and the habitats, and has a direct proportion to the pesticide octanol water partition and adsorption coefficients [30].

5.7 Degradation of Pesticides

Degradation of pesticides refers to chemical processes through which pesticide molecules are broken down into smaller units, which may be less toxic compared to the parent molecule [20, 35]. The chemical reactions involved in pesticide degradation include abiotic reaction, such as photodegradation which occur in the presence of sunlight and biotic reaction (biodegradation), which occurs under enzymatic control in the presence of microorganisms. Both chemical and microbial degradation could lead to any of the following chemical reactions; oxidation, reduction, hydrolysis, isomerization, elimination, conjugation and dechlorination of pesticide molecules [20, 27, 54]. The rate of degradation which depend on the nature of pesticides is expressed as the half-life of the pesticide molecule in soils and the type of degradation process of pesticide largely depend of the physico-chemical properties of pesticides and the environmental conditions.

6.0 Conclusion

Pesticides are artificially synthesized compounds produced to fight the pest and diseases of plant to increase and improve agricultural products. Although their applications have tremendously increased agricultural production in many parts of the world, their uses have been of concern due to their biocide activities and effects on human health. The need for frequent monitoring of pesticide residues and other contaminants in food commodities has led to the development of various sample preparation techniques. Some of these techniques have proved to be efficient, fast, and accurate for qualitative and quantitative analyses of pesticide residues, Pesticide analysis has continued to attract the attention of various stakeholders in the agricultural and food industries.

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