Water Pollution and Agriculture Pesticide

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The agricultural industry uses substantial amounts of water (the highest in the world) mostly for irrigation purposes. Rapid population growth and, consequently, growing demand for food have increased the use of pesticide to have higher yield for crops and other agricultural products. Wastewater generated as a result of excessive use of pesticides/herbicides in agricultural industry is becoming a global issue specifically in developing countries. Over 4,000,000 tons of pesticides are currently used in the world annually and high concentrations above their threshold limits have been detected in water bodies worldwide. The generated wastewater (contaminated with pesticides) has negative impacts on human health, the ecosystem, and the aquatic environment. Biodegradable and biocompatible (including plant-based) pesticides have been introduced as green and safe products to reduce/eliminate the negative impacts of synthetic pesticides.

Keywords: wastewater ; agriculture ; pesticides ; treatment ; modeling

1. Introduction

Pesticides/herbicides use in agriculture is very common to increase production and ensure sufficient high quality affordable food for the growing population. These pesticides are mostly produced synthetically and like almost all chemicals pose a potential risk to human health and the environment. Pesticide use is inevitable in agricultural systems. New pesticides are being introduced continuously with enhanced properties for selective use and less negative impacts. Spraying is a common way of introducing pesticides over large areas of land, most of which can be carried away by wind, water runoff, and atmospheric weathering processes, and thus up to 95% of herbicides and over 98% of insecticides may not reach the targeted pests ^[1]. Physical and chemical interactions in the atmosphere can lead to formation of intermediates with negative impacts. Nevertheless, these pesticides eventually find their way to surface and ground water as well as lakes and oceans through different mechanisms. Uncontrolled application of pesticides in agriculture may result in alteration of products' quality and changes in the level of different enzymes in human body, leading to various health problems ^[2]. Traditional pesticide formulations generally have a high concentration of organic solvents with low dispersion, remaining in soil for a long time, and moving through the environment and putting biological systems at risk. Those who work in agricultural open fields and greenhouses and the pesticide industry are usually exposed to higher concentration of pesticides.

The world population is estimated to be 9–10 billion by the year 2050 ^[3], increasing the need for more food. The agriculture industry is the highest user of clean water, mainly used for irrigation purposes, which can be easily contaminated by pesticides. More than 1200 pesticides and herbicides, some of which are banned in Europe, are currently in use in the world ^[4].

Although some of these herbicides can be degraded naturally in the soil, many of them are not easily degraded and remain in the environment for extended periods of time ^[5]. Municipal, industry, and agricultural wastes are discharged directly to various water bodies in many countries. Drugs, dyes, herbicides, pesticides, and other products of daily use have been detected in ground/underground water. Irrigation and rain also facilitate transportation of pesticides into ground/underground water especially those which are soluble in water ^[6]. Health issues such as hematologic and hormonal abnormalities, infertility, fetal malformation, neurological diseases, and cancer are commonly observed among those exposed to these pesticides. The underlying mechanisms of these effects are genotoxic, neurotoxic, and endocrine-disrupting actions ^{[Z][8][9]}.

The maximum consumption per hectare of pesticides is about 25 kg and Asia is the highest in the world. Global use of pesticides is comprised of 47.5% herbicides, 29.5% insecticides, 17.5% fungicides, and others account for only 5.5% ^[10]. Pesticide use is crucial in modern agriculture. Without proper use and management of pesticides, there would be a substantial loss of agricultural products to pests (for example, about 40% in crops). Exposure to pesticides used in agriculture has been related to autoimmune diseases such as systemic lupus erythematosus ^[11]. It has also been linked to neurodegenerative and respiratory diseases and various forms of cancer ^[12].

Skin and respiratory irritations as well as diseases such as Parkinson's, leukemia, and autism were found to be higher in residential areas close to agricultural lands where pesticides were used continuously ^[13]. Excessive use of synthetic pesticides may also result in high concentrations of heavy metals (used in production of pesticides) in soil, which alters the biochemistry and microbial activities in soil with a negative impact on plants ^{[14][15]}.

Agricultural water pollution may be due to fertilizers as they have a high concentration of nutrients (containing specifically nitrogen and phosphorus). When fertilizers are utilized in crop production more than the required amount, the excess amounts will remain in soil particles and finally be washed off the soil during irrigation or by rain, finding their way to water resources. Phosphates, which are not as soluble as nitrates, may get adsorbed onto soil particles and pollute the water thorough soil erosion.

2. Water Pollution by Pesticides

Water contamination is mostly the result of agricultural and urban runoff, where herbicides/pesticides find their way through leaching in soil or by direct discharge of contaminated wastewater ^[16].

Pesticides interact with water in different ways due to their physical and chemical properties. All pesticides have main ingredients that are mixed/dissolved in inert compounds (e.g., solvent) to adjust their concentration. Therefore, water pollution in agricultural systems may be due to the presence of active ingredients as well as fillers and impurities or intermediates during the degradation process. Diffusion, dispersion, and permeation are the main mechanisms for transfer of pesticides in soil and water. At the same time, the natural degradation of pesticides in soil or water may result in the formation of intermediates. Interaction between pesticide and soil and/or water is a complex phenomenon with little information in the literature. The stability of pesticides is generally related to their half-life. Persistent pesticides have a long half-life and pose threats for a longer time.

Although municipal and industrial wastewater discharges substantial amount of wastewater into water bodies, agriculture accounts for 70 percent of water abstractions worldwide. Large amounts of agrochemicals (mostly pesticides/herbicides) are discharged into the water, endangering human health, aquatic ecosystems, and plants ^[17]. According to FAO, the agricultural land, which requires irrigation, has more than doubled (about 320 Mha in 2014) in recent decades ^[18], which has increased the use of pesticides and eventually affected ground/underground water quality.

About 85–90% of all fresh water is used for irrigation of agricultural land in Africa and Asia. Agriculture withdrew 67% of the world's total freshwater in 2000 ^[17].

Based on the U.S. Geological Survey (USGS) carried out in mid 1990s, 90% of major rivers' water and fish samples close to agricultural and urban land contained pesticides ^[19]. The herbicides 2,4-D, diuron, and prometon were among the 21 pesticides detected most often in surface and ground water across the nation with concentrations above the guidelines. High concentrations of pesticides above their threshold limits were detected at 13–30% of all surface and ground waters in Europe between 2013 and 2019, as shown in **Figure 1** ^[20].



Figure 1. Pesticide concentrations in surface and ground water [21].

Figure 1 shows one or more pesticides with concentrations above their threshold for all surface water monitoring sites each year between 2013 and 2019. The number of pesticides in surface water ranged from about 10 to over 100 with the

lowest being in Austria [6] and the highest in France [22].

Pesticide concentrations higher than the acceptable limit were also reported in surface waters in Mexico (Cienega area of Jalisco). In a comprehensive study on the concentration of pesticide in India, high concentrations were also observed in river water, surface water, ground water and, interestingly, rainwater ^[23].

An analysis of samples from 1204 wells across the United States showed the presence of 109 pesticides and 116 pesticide degradates. Among those, about two-thirds contained pesticides and three-quarters contained degradiant. The most common detected pesticides were Atrazine, Hexazinone, Prometon, Tebuthiuron, four Atrazine degradates, and one metolachlor degradates, detected in >5% of the wells with 1.6% of the wells having concentrations approaching levels of potential concern ^[6].

The annual use of conventional pesticides in the United States between 2005–2012 was about 400–450 million kg, excluding biological and antimicrobial pesticides. Glyphosate, atrazine, metolachlor-(S), 2,4-D, and acetochlor were the most commonly used herbicides in United States between 1992–2017 [24].

Pesticides are being transported from land to ground water by rain fall and irrigation, where permeable soil is more susceptible to the process. Pesticides with high persistence and a low tendency to adsorb to soils and sediments are detected easily ^[25]. A higher concentration of pesticides is generally observed in shallower groundwater than deeper, and older groundwater, as drainage systems in agricultural areas can divert shallow groundwater to surface water ^[26].

In five studies, when evaluating up to 80 pesticide compounds and 9 degradates, Atrazine and its degradant deethylatrazine (DEA) were the most detected $^{[20]}$. The eighth most detected compound was Dieldrin, an insecticide (3.1%) while Propoxur concentration was reported as 1.8%. The most detected fungicide was Metalaxyl (0.7%) $^{[27][28]}$.

The formulation of green, safe, and efficient pesticides is one of the ongoing challenges in the pesticide industry. Design and production of targeted environmentally friendly pesticides with controlled release through chemical modification offers great potential for new formulations. One of the emerging technologies is production of pesticides using genetically modified plants.

3. Modeling and Simulation

Large quantities of wastewater are generated in agriculture, therefore experimentation, management, and control at such levels are time consuming and costly. Models that are simplified representations of real-world systems are used to simulate the fate of pollutants and estimate the changes in water quality at different locations to an acceptable level. Due to the complexity of real-world problems, simplifying assumptions are used and therefore models cannot be completely accurate; however, they are reliable enough to help in providing policies, strategies, and actions for mitigation purposes. Models with different strengths and limitations are used in the field of water quality. These can be applied at different scales to support planners and policymakers in designing cost-effective measures for addressing water pollution in agriculture ^{[29][30]}.

The models are mainly related to the flux of polluted water and transformation processes. Water transportation, quality, meteorology and hydrology, land characteristics and management and transformation processes are of main concern. Irrigation and type of agriculture as well as plants, soil, and the environment make such modeling activities a challenging task. Leaching and water runoff are generally the first stages in pesticide transportation.

A mathematical model based on a system of ordinary differential equations was developed to provide farming alertness for pest administration in crops production, considering plant biomass, type of pest, and control level. Using the local pest-free and coexistence equilibria and applying the control theory, the criteria to decrease pest contamination in crop fields were achieved ^[31].

To control the pest population in crop fields under different dynamic regimes, a mathematical model based on Z-type control was applied. The pest population and its fluctuation were successfully controlled, and the results were verified by actual field data ^[32].

Despite the unique advantages of biopesticides, they suffer from time requirements as well as cost. However, a combination of biopesticides with chemical/synthetic pesticides has shown to reduce time and cost. A mathematical model was developed to show the effectiveness of such an approach to pest control for Jatropha curcas plantation. The model

successfully predicted the optimum concentration profile for biopesticides and chemical pesticide using optimal control theory, minimizing negative impacts, and improving feasibility. The numerical simulations justified the results ^[33].

Bacteria, algae, fungi, protozoa, and viruses have been used as microbial pest control agents used for specific pests. Viruses such as Baculoviridae (nucleopolyhedroviruses) [NPV] and granuloviruses are among very strong biopesicides. More than 400 insect species have been reported as hosts for baculoviruses. A mathematical model was stablished to study the interaction between a virus and a pest. The interaction follows the Michaelis–Menten type and the virus attacks the pest population only with no recovery or immunization of the pest. A good agreement was reported compared to available data in the literature ^[34].

Jena and Kar proposed and analyzed an ecological system and studied the dynamics of pest control systems using the prey-predator model. They developed a mathematical model with three state variables, namely the susceptible pest, the infected pest, and the biological predator to the pest. Additional food sources were considered in the model to help the predator to survive when the prey concentration is negligible. The role of additional food is very much important in relevance to pest control because it helps to protect predator populations when the pest population is not sufficient. Considering the cost and environmental impact and using Pontryagin's maximum principle, the optimal pest control strategy was obtained ^[35].

An ecophysiological model of plant–pest interaction and multi-criteria decision analysis was developed to optimize crop management when considering two contrasting objectives: (1) maximizing crop production and (2) minimizing environmental impact related to fertilization, irrigation, and pesticide deployment. A mechanistic plant growth model and a pest population model were considered [36].

Pesticide dissipation is a complex phenomenon which depends on pesticide type, environmental factors, transfer processes, degradation phase partitioning, etc. Prediction of pesticide dissipation half-life in plants is important in estimating the fate of pesticides. Over 4500 data points on pesticides' half-lives were used with four machine learning models (i.e., gradient boosting regression tree [GBRT], random forest [RF], supporting vector classifier [SVC], and logistic regression [LR]) to predict dissipation half-life intervals using extended connectivity fingerprints (ECFP), temperature, plant type, and plant component class as model inputs. Despite successful outcomes of the model, due to the large number of variables and uncertainty involved in their prediction, more data is required to improve the models' performance [37].

Yadav and Kumar used mathematical modeling to study an ecosystem consisting of two types of preys and their predators in agriculture. The two preys had a long time and short time to grow (sugarcane and vegetable, respectively) with predators that can attack them both simultaneously. The various equilibria of the system were obtained, and the stability conditions were analyzed ^[38].

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