

Overview of Pesticide Toxicity in Fish

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ABSTRACT

Modern agricultural practices result in indiscriminate use of various pesticides, which usually enter into the aquatic environment. The use of pesticides in the field has the potential to change the aquatic medium, affecting the tolerance limit of aquatic fauna and flora, as well as creating danger to the ecosystem. These pesticides adversely affect the non-target organisms, especially fish. The present study discusses among other issues, the toxic effects of pesticides on aquatic life with emphasis on fish and the public health implication.

Key words:

Introduction

The use of pesticides has been recognized as part of agricultural practices throughout the world. Unfortunately the indiscriminate use of these pesticides to improve agricultural production and yield may have impacts on non-target organism, especially aquatic lives and environment. The world health organization [56] reported that roughly 3 million cases of pesticides poisoning occur annually, resulting in 220,000 deaths worldwide. Many of these chemicals are mutagenic [13,27,40], linked to the development of cancers [30] or may lead to the developmental deficits [2]. Worldwide pesticide usage has increased dramatically during the past two decades, coinciding with changes in farming practices and increasingly intensive agriculture. Environmental pollution caused by pesticides, especially in aquatic ecosystems, has become a serious problem. Contamination of water by pesticides, either directly or indirectly, can lead to fish kills, reduced fish productivity, or elevated concentrations of undesirable chemicals in edible fish tissue which can affect the health of humans consuming these fish.

Residual amounts of pesticides and their metabolites have been found in drinking water and foods, increasing concern for the possible threats to human health posed by exposure to these chemicals. Contamination of surface waters has been well documented worldwide and constitutes a major issue at local, regional, national, and global levels [7,48]. Chemicals originating from agricultural activity enter the aquatic environment through atmospheric deposition, surface run-off or leaching [26] and frequently accumulate in soft-bottom sediments and aquatic organisms [33,29,25]. In all parts of the

world pesticides have been found in the aquatic ecosystem and often information of how these pesticides affect inhabiting organisms is missing. In canals in south Florida more than 700 pesticide detections were made between 1991 and 1995 [33]. Atrazine, ametryn, and bromacil were most often detected in the water samples, whereas pesticides which bind strongly to soil, are highly persistent and/or used in large amounts, e.g. DDE, DDD and ametryn, were some of the more frequently found in sediments [33]. In Chesapeake Bay, also USA, herbicides such as atrazine, simazine, cyanazine, and metolachlor were found in water samples, but not in oysters [29]. Another herbicide, trifluralin, was however detected in both water and oysters. In an oligotrophic coastal lagoon, the Mar Menor, located in the southeast of Spain, Pérez-Ruzafa *et al.* [42] found mainly endosulfan, HCH, and endrin when analyzing water, sediment and organisms. The highest concentrations, up to 1.5 mg/kg (endrin), were recorded in organisms due to bioaccumulation of the hydrophobic pesticides. High concentrations were also found in the sediments, but in the water the levels were lower. In Sweden, a recent screening monitoring program of surface waters in nine small agricultural catchments revealed that the most frequently detected pesticides were those sold in largest quantities [54]. Bentazone and MCPA were detected in all streams and in most samples from the two rivers included in the study. Other herbicides commonly detected were glyphosate and mecoprop. Occasionally, also residues of herbicides that had been withdrawn from the Swedish market were detected, e.g. atrazine, 2,4-D, and simazine. In a few cases substances were found in concentrations that may cause adverse effects to aquatic life, with the herbicide cyanazine being the most frequently

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detected at concentrations exceeding the Dutch water quality guidelines [8]. In two earlier studies, Kreuger *et al.* [25] and Kreuger [24] determined commonly used pesticides in both water and sediment from a small catchment in southern Sweden. Fenpropimorph was the most dominant pesticide in sediments, but also fenvalerate, propiconazole, and Σ DDT were detected on several occasions. There was a more than 50% detection frequency for the herbicides atrazine, bentazone, dichlorprop, ethofumesate, MCPA, mecoprop, metazachlor, and terbuthiazine in the water samples. Agricultural pesticides are also found in areas not adjacent to agricultural land [19]. Eight urban streams from across the United States were monitored for high-use pesticides and pesticide transformation products. Among the 75 target pesticides and the 7 target transformation products, 13 insecticides, 28 herbicides, and one transformation product were found. The herbicides detected most frequently were prometon, simazine, atrazine, tebuthiuron, and metolachlor, and the insecticides detected most frequently were diazinon, carbaryl, chlorpyrifos, and malathion. In contrast to similar-sized agricultural streams, total insecticide concentrations commonly exceeded total herbicide concentrations in these urban streams. Consequently, the contributions of insecticides from urban and agricultural land to streams may be similar [19]. It is from all these studies clear that both commonly used pesticides and pesticides withdrawn from the market years ago do reach and/or accumulate in aquatic ecosystems and thereby constitute a threat to all aquatic organisms.

What are Pesticides?:

In nature, there are no pests. Humans label as "pests" any plants or animals that endanger our food supply, health, or comfort. To manage these pests we have "pesticides". These are products "intended for preventing, destroying, repelling, or mitigating any pest." Though pesticides are often misunderstood to refer only to insecticides, the term pesticide also applies to herbicides, fungicides, acaricides and other substances used to control pest. Under the US law, a pesticide may also refer to any substance or mixture of substances intended for use as a plant regulator, defoliant or desiccant [20]. Food and Agriculture Organization (FAO) has defined the term of *pesticide* as:

any substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm during or otherwise interfering with the production, processing, storage, transport or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or substances which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies. The

term includes substances intended for use as a plant growth regulator, defoliant, desiccant or agent for thinning fruit or preventing the premature fall of fruit. Also used as substances applied to crops either before or after harvest to protect the commodity from deterioration during storage and transport (FAO, 2002).

Under the NSW Pesticides Act 1999, a pesticide is an 'agricultural chemical product' as defined in the Agricultural and Veterinary Chemicals Code Act 1994 (Cwlth), namely:

'a substance or mixture of substances that is represented, imported, manufactured, supplied or used as a means of directly or indirectly:

1. destroying, stupefying, repelling, inhibiting the feeding of, or preventing infestation by or attacks of, any pest in relation to a plant, a place or a thing; or
2. destroying a plant; or
3. modifying the physiology of a plant or pest so as to alter its natural development, productivity, quality or reproductive capacity; or
4. modifying an effect of another agricultural chemical product; or
5. attracting a pest for the purpose of destroying it.'

Another common misconception is that pesticides made from natural substances or 'home brews' are intrinsically safer in all respects than synthetically produced or commercial pesticides. Sodium fluoroacetate (1080) occurs naturally in a number of Australian plants, however, it is a highly toxic substance that is used to kill pest animals such as rabbits, feral pigs, wild dogs and foxes. All substances whether they are synthetic or naturally derived involve some degree of risk when they are used to control pests.

Types of Pesticides:

Pesticides are categorized according to their target use. Pesticides come in many forms:

- **Piscicides** for the control of fish
- **Bactericides** for the control of bacteria
- **Fungicides** for the control of fungi & oomycetes
- **Herbicides** for the control of weeds
- **Insecticides** for the control of insects - these can be Ovicides (for eggs), Larvicides (for larva or baby insects) or Adulticides (for mature insects)
- **Miticides** for the control of mites
- **Molluscicides** for the control of slugs and snails
- **Nematicides** for the control of nematodes
- **Rodenticides** for the control of rodents
- **Virucides** for the control of viruses
- **Attractant** attracts pests for monitoring or killing
- **Predacide** for the control of vertebrate predators
- **Repellent** for repelling pests
- **Synergist** Improves performance of another pesticide

Some pesticides are absorbed by the plants and thus become part of the plants themselves. Such pesticides are called **systemic** pesticides. The poison then appear in all parts of the plants such as leaves and flowers causing many organism that consume parts of the plant to be affected, including humans. Often useful insects such as bees which pollinate plants die from this.

History of Pesticides:

The concept of pesticides is not new. Around 1000 B.C.E. Homer referred to the use of sulfur to fumigate homes and by 900 C.E. the Chinese were using arsenic to control garden pests. Although major pest outbreaks have occurred, such as potato blight (*Phytophthora infestans*), which destroyed most potato crops in Ireland during the mid-nineteenth century, not until later that century were pesticides such as arsenic, pyrethrum, lime sulfur, and mercuric chloride used. Between this period and World War II, inorganic and biological substances, such as Paris green, lead arsenate, calcium arsenate, selenium compounds, lime-sulfur, pyrethrum, thiram, mercury, copper sulfate, derris, and nicotine were used, but the amounts and frequency of use were limited, and most pest control employed cultural methods such as rotations, tillage, and manipulation of sowing dates. After World War II the use of

pesticides mushroomed, and there are currently more than 1,600 pesticides available and about 4.4 million tons used annually, at a cost of more than \$20 billion. The United States accounts for more than 25 percent of this market.

How Fish are Exposed:

Fish and aquatic animals are exposed to pesticides in three primary ways (1) dermally, direct absorption through the skin by swimming in pesticide-contaminated waters, (2) breathing, by direct uptake of pesticides through the gills during respiration, and (3) orally, by drinking pesticide-contaminated water or feeding on pesticide-contaminated prey. Poisoning by consuming another animal that has been poisoned by a pesticide is termed "secondary poisoning." For example, fish feeding on dying insects poisoned by insecticides may themselves be killed if the insects they consume contain large quantities of pesticides or their toxic byproducts.

Factors affecting pesticide toxicity in aquatic systems:

The ecological impacts of pesticides in water are determined by the following criteria:

<p>· Toxicity:</p>	<p>Mammalian and non-mammalian toxicity usually expressed as LD₅₀ ("Lethal Dose": concentration of the pesticide which will kill half the test organisms over a specified test period). The lower the LD₅₀, the greater the toxicity; values of 0-10 are extremely toxic [41]. Drinking water and food guidelines are determined using a risk-based assessment. Generally, Risk = Exposure (amount and/or duration) × Toxicity. Toxic response (effect) can be acute (death) or chronic (an effect that does not cause death over the test period but which causes observable effects in the test organism such as cancers and tumours, reproductive failure, growth inhibition, teratogenic effects, etc.).</p>
<p>· Persistence:</p>	<p>Measured as half-life (time required for the ambient concentration to decrease by 50%). Persistence is determined by biotic and abiotic degradational processes. Biotic processes are biodegradation and metabolism; abiotic processes are mainly hydrolysis, photolysis, and oxidation [6]. Modern pesticides tend to have short half lives that reflect the period over which the pest needs to be controlled.</p>
<p>· Degradates:</p>	<p>The degradational process may lead to formation of "degradates" which may have greater, equal or lesser toxicity than the parent compound. As an example, DDT degrades to DDD and DDE.</p>
<p>· Fate (Environmental):</p>	<p>The environmental fate (behaviour) of a pesticide is affected by the natural affinity of the chemical for one of four environmental compartments [6]: solid matter (mineral matter and particulate organic carbon), liquid (solubility in surface and soil water), gaseous form (volatilization), and biota. This behaviour is often referred to as "partitioning" and involves, respectively, the determination of: the soil sorption coefficient (K_{OC}); solubility; Henry's Constant (H); and the n-octanol/water partition coefficient (K_{OW}). These parameters are well known for pesticides and are used to predict the environmental fate of the pesticide.</p>

An additional factor can be the presence of impurities in the pesticide formulation but that are not part of the active ingredient. A recent example is the case of TFM, a lampricide used in tributaries of the Great Lakes for many years for the control of the sea lamprey. Although the environmental fate of TFM has been well known for many years, recent research by Munkittrick *et al.* [38] has found that TFM formulation includes one or more highly potent impurities that impact on the hormonal system of fish and cause liver disease.

Effects on Fish:

Pesticide toxicity to fish has been investigated in several studies [28,37,5,49,36,55,34]. However, fish are not usually target organisms for pesticides, and knowledge about effects of pesticides in the field is still sparse. Surprisingly, only a few studies have shown that fish, inhabiting natural freshwater ecosystems, may be affected by unintentional spreading of pesticides [4,9].

Fish species are sensitive to enzymic and hormone disruptors. Chronic exposure to low levels of pesticides may have a more significant effect on fish populations than acute poisoning. Doses of

pesticides that are not high enough to kill fish are associated with subtle changes in behavior and physiology that impair both survival and reproduction [22]. Biochemical changes induced by pesticidal stress lead to metabolic disturbances, inhibition of important enzymes, retardation of growth and reduction in the fecundity and longevity of the organism [39]. Liver, kidney, brain and gills are the most vulnerable organs of a fish exposed to the medium containing any type of toxicant [21]. The fish show restlessness, rapid body movement, convulsions, difficulty in respiration, excess mucous secretion, change in color, and loss of balance when exposed to pesticides. Similar changes in behavior are also observed in several fishes exposed to different pesticides [16]. The Great Lakes fish are contaminated with chlorinated organic compounds such as PCB and dichlorodiphenyl dichloroethene, pesticides such as mirex and dieldrin, and trace amounts of metals such as lead and mercury [50]. Lake trout, which became extinct in the Great Lakes in the 1950s, has been shown to be very sensitive to dioxins and (polychlorinated biphenyls) PCBs when exposed as embryos. Several species of salmon introduced into the Great Lakes have severely enlarged thyroid glands, which is strong evidence of hormone disruption. Salmon in the Lake Erie show a variety of reproductive and developmental problems, for example, early sexual development and a loss of the typical male secondary sexual characteristics, such as heavy protruding jaws and red coloration on the flanks. Some agrochemicals can indirectly affect fish by interfering with their food supply or altering the aquatic habitat, even when the concentrations are too low to affect the fish directly. Other agricultural chemicals are capable of killing salmon and other aquatic animals directly and within a short period of time. For example, in 1996 the herbicide acrolein was responsible for the death of approximately 92,000 steel-head, 114 juvenile coho salmon, 19 resident rainbow trout, and thousands of non-game fish in the Bear Creek, a tributary of the Rogue River. Several laboratory experiments show that sublethal concentrations of agrochemicals can affect many aspects of salmon biology, including a number of behavioral effects. Under experimental conditions, rainbow trout exposed for 18-34 days to a combination of 0.05 mg/l of the organochlorine endosulfan and 0.5 mg/l of the organophosphate disulfoton showed changes in the ultrastructure of hepatic cells, with irregular nuclei, and alterations to the lysosomes and rough endoplasmic reticulum [3]. Some pesticides such as organochlorine, organophosphates and carbamates are known to cause morphological damage to the fish testis. These also affect female fish in the same way. They cause delayed oocyte development and inhibition of steroid hormone synthesis [23]. Experimental exposure of fish to them has been shown to depress protein values in brain, gills, muscle, kidney and liver. In the

kidney and the liver there is evidence of significant decrease in the protein content due to stress in elimination and also in metabolism [52]. Interference with endocrine hormones affects reproduction, immune function, development, and neurological functions in several species of wild animals. In fish, endocrine disruptors interrupt normal development and cause male fish to have female characteristics. These outward symptoms of developmental disruption are accompanied by reduced fertility and even sterility in adults, as well as lower hatching rates and viability of offspring. Many studies show a direct relationship between concentrations of pesticides and related chemicals in fish tissues and depressed hormone concentrations. Disruption of the balance of endocrine hormones during development of young fish can also cause defects of the skeletal system, resulting in deformities and stunted growth [15]. The common pesticide synergist piperonyl butoxide increases carbaryl toxicity (Carbaryl is a neurotoxic carbamate pesticide). In fish, acute toxicity of a carbaryl- piperonyl butoxide mixture was over 100 times that of carbaryl alone [46]. In addition, carbaryl increases the acute toxicity of the phenoxy herbicide 2,4-D, the insecticides rotenone and dieldrin (an organochlorine) as well as the wood preservative pentachlorophenol [47]. Sublethal effects of the organophosphate insecticide phenthoate are also synergized by carbaryl in fish, resulting in AChE inhibition [44] and both morphological and behavioral changes [44]. While the toxicity of combinations of chemicals is rarely studied, the ability of carbaryl to interact with a large number of chemical classes is striking.

Effects on Aquatic Life:

A major environmental impact has been the widespread mortality of fish and marine invertebrates due to the contamination of aquatic systems by pesticides. This has resulted from the agricultural contamination of waterways through fallout, drainage, or runoff erosion, and from the discharge of industrial effluents containing pesticides into waterways. Historically, most of the fish in Europe's Rhine River were killed by the discharge of pesticides, and at one time fish populations in the Great Lakes became very low due to pesticide contamination.

Fish and other aquatic biota may be harmed by pesticide-contaminated water. Pesticide surface runoff into rivers and streams can be highly lethal to aquatic life, sometimes killing all the fish in a particular stream [53].

Application of herbicides to bodies of water can cause fish kills when the dead plants rot and use up the water's oxygen, suffocating the fish. Some herbicides, such as copper sulfite, that are applied to water to kill plants are toxic to fish and other water animals at concentrations similar to those used to kill

the plants, Repeated exposure to sub lethal doses of some pesticides can cause physiological and behavioral changes in fish that reduce populations, such as abandonment of nests and broods, decreased immunity to disease, and increased failure to avoid predators, [17].

Application of herbicides to bodies of water can kill off plants on which fish depend for their habitat [17]. Pesticides can accumulate in bodies of water to levels that kill off zooplankton, the main source of food for young fish. [43]. Pesticides can kill off the insects on which some fish feed, causing the fish to travel farther in search of food and exposing them to greater risk from predators. The faster a given pesticide breaks down in the environment, the less threat it poses to aquatic life. Insecticides are more toxic to aquatic life than herbicides and fungicides. [17].

Public Health Implication:

Bioaccumulation is the accumulation of pollutants in the organs of fish and animals. The process of bioaccumulation starts when pesticides applied to agricultural land runoff during storms into rivers, streams and eventually the ocean. The pesticides become part of the water column and fish ingest the pesticides, usually through their gills, although sometimes through their fish scales. The pesticides go into their organs and fat tissue and are sequestered there. More and more pesticides are ingested and stored in organs and tissues as fish get oxygen from the water column for survival. These accumulated pesticides accumulate up the food chain as big fish eat little fish and eventually as humans eat the fish.

The effects of pesticides on human health are more harmful based on the toxicity of the chemical and the length and magnitude of exposure. Pesticides are known to be toxic to man [1]. Some of the symptoms of pesticides poisoning include irritation, dizziness, tremor, tonic and chronic convulsion [57]. Exposure to pesticides can range from mild skin irritation to birth defects, tumors, genetic changes, blood and nerve disorders, endocrine disruption, and even coma or death [32]. Developmental effects have been associated with pesticides. Recent increases in childhood cancers in throughout North America, such as leukemia, may be a result of genotoxic and nongenotoxic pesticides due to somatic cell mutations [11]. Insecticides targeted to disrupt insects can have harmful effects on the nervous systems of mammals, due to basic similarities in system structure. Both chronic and acute alterations have been observed in those who are exposed. Pesticides can act in the promotion and proliferation of cancer while causing hormone imbalance. DDT and its breakdown product DDE, with levels still present in the environment, despite its ban, are known to disturb estrogenic activity and possibly

lead to breast cancer. Exposure to pesticides, for example DDT, in fetal stages has been proven to alter male penis size in animals to that much smaller than average as well as develop undescended testicles. Exposure to pesticides may occur in postnatal early stages of development, in utero, and even if either parent was exposed before conception took place. Reproductive disruption has the potential to occur by chemical reactivity and through structural changes to a system [18].

Reducing the Risk of Pesticides:

Prior to using a pesticide, consider the following:

1. Use a Pesticide Only When Necessary
 - Is the problem bad enough to justify the use of a toxic chemical? Are there alternative ways of treating the problem? Landowners should consider the costs and consequences of pesticide treatment relative to the problem.
2. Use Less Toxic Pesticides
 - One way to reduce the effects of pesticides on aquatic systems is to use those chemicals that are least poisonous to aquatic life. Select the least toxic material.
3. Use Safe/Sensible Application Methods
 - The first rule of responsible pesticide use is to read and then reread the pesticide label and follow the directions precisely. Label instructions sometimes can be confusing. If you don't understand the instructions, contact your Extension Agent, your supplier, or the pesticide company for more information.
 - Pay particular attention to warning statements about environmental hazards on the label. Look for: "This product is toxic to fish." If you see such a warning, consider another pesticide or an alternative control method.
 - Ensure that your application equipment is in good working condition. Check for leaks, replace worn parts, and carefully calibrate your equipment.
 - When preparing the pesticides for application, be certain that you are mixing them correctly.
 - Never wash spray equipment in lakes, ponds, or rivers. If you use water from natural ponds, lakes, or streams, use an antisiphon device to prevent backflow.
 - If you are applying pesticides near water, check the label to find the recommended buffer zone. Buffer strip widths between the water and the treatment areas vary. Leave a wide buffer zone to avoid contaminating fish and aquatic animals.
 - Store and dispose of unused chemicals and their containers according to the label instructions.
 - Avoid pesticide drift into nontarget areas, or applications during wet, windy weather that might promote runoff to non-target streams, ponds, or lakes. Spray on calm days, or early in the morning or evening when it is less windy.

Eliminating pesticides:

Many alternatives are available to reduce the effects pesticides have on the environment. There are a variety of alternative pesticides such as manually removing weeds and pests from plants, applying heat, covering weeds with plastic, and placing traps and lures to catch or move pests. Pests can be prevented by removing pest breeding sites, maintaining healthy soils which breed healthy plants that are resistant to pests, planting native species that are naturally more resistant to native pests, and use biocontrol agents such as birds and other pest eating organisms (Take Action! How to Eliminate Pesticide Use, 2003)

There is much debate over alternative methods of controlling pesticides. In many instances, biological controls such as resistant plant varieties and the use of pheromones, have been successful and at times resolving a pest problem permanently [31]. Integrated Pest Management (IPM) has also been one practice in pest management which establishes chemical use on a need basis only. IPM is a more socially accepted practice and causes less harm to the health of humans and the environment. The focus is on the pest culture, life cycle, and role in the environment [14]. Biotechnology can also be an innovative way to control pests. Technological advances, such as genetically modified (GM) plants, may have a stronger resistance to pests and could eliminate pesticides use in the future [31].

Best Management Practices for Protecting Water Quality:

- Use Integrated Pest Management (IPM) practices so chemical controls will be used only when necessary. Before using any pesticide, be sure the application is needed, and can be accomplished safely and effectively.
- Evaluate chemical control options. Select the option that is least likely to have a negative impact on water quality. Select products that minimize waste and applicator exposure.
- Read and follow all label directions. Use pesticides only as directed. Pay careful attention to application site requirements, methods, and rates. Pesticide label directions are not advice, they are legal requirements.
- Use care when mixing and loading pesticides. Be sure the equipment is working correctly and is properly calibrated. Prepare only the amount of pesticide mix needed for the immediate application.
- Apply pesticides at the proper time. Consider weather and pest life cycle when planning applications.
- Store pesticides safely in a ventilated, well lighted, and secure area free from flooding.
- Dispose of empty containers and rinse water properly.

- Keep records of all pesticide use. Records will allow evaluation of pest control efforts and help plan future treatments.

Conclusion:

Environmental pollution caused by pesticides, especially in aquatic ecosystems, is a serious problem. Contamination of fish by pesticides, either directly or indirectly, means a continuous health hazard for the population. So, human population is at high risk by consuming these toxicated fishes. This implies that one should take the necessary precaution in the application of pesticides to target organisms as this may also affect the non target organism including fish and other aquatic fauna. There is serious need for the monitoring of these pesticide residues in water, food and the environment, as this will go a long way towards preventing various environmental and public health hazards.

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