

A REVIEW ON THE EFFECTS OF SOME SELECTED PYRETHROIDS AND RELATED AGROCHEMICALS ON AQUATIC VERTEBRATE BIODIVERSITY

* Farhana Ali, Ben HH Shieh, Zeyad Alehaideb, MZ Khan, Alvin Louie, Noor Fageh and Francis CP Law

Department of Biological Sciences, Simon Fraser University
8888 University Drive, Burnaby, BC V5A 1S6 Canada

ABSTRACT

Pollution in the aquatic ecosystem by pesticides, their metabolites and by-products is considered critical in the conservation of biodiversity and natural resources. Several studies have reported the toxicological issues and adverse effects of pesticides in aquatic biodiversity. After the development of the field ecotoxicology, researchers have expanded their studies towards the effects of pesticides in aquatic ecosystems. Pesticides containing chemicals such as Pyrethroids, cypermethrin, deltamethrin, cyphenothrin and other related compounds have been shown to cause adverse effects on the development, behaviour and mortality of different species of fish, birds, amphibians and aquatic mammals. This review article summarizes the adverse impact of the use of pesticides and related agrochemicals in populations of aquatic, amphibian and avian species.

Keywords: Aquatic biodiversity, pesticides, pyrethroid, cypermethrin, deltamethrin.

INTRODUCTION

The term "biodiversity" is a contracted version of "biological diversity". The conventional view on Biological Diversity defines biodiversity as "the variability among living organisms from all sources including, *inter alia*, terrestrial, marine and other aquatic ecosystems and the ecological complexes of which they are a part; this includes diversity within species, between species, and of ecosystems" (Lloyd, 2010). Aquatic ecosystems provide a habitat for phytoplankton, zooplankton, aquatic plants, insects as well as many vertebrates such as fish, water birds, amphibians and aquatic mammals. In addition, aquatic ecosystems are also an important source of food and medicines while also providing an area for recreational and commercial purposes.

There are many factors that can affect and change biodiversity within aquatic ecosystems. Aquatic biodiversity may decrease due to habitat destruction, fragmentation, pollution or the introduction of an invasive species. In many countries, anthropogenic activities have lead to aquatic organisms being at a higher risk for extinction compared to terrestrial mammals and birds.

Aquatic organisms may be exposed to pesticides through the consumption of contaminated food and water, breathing in pesticide residues or through the absorption of pesticides through their skin. This is a cause for concern as predators (i.e. birds) may be acutely poisoned by eating animals that have been exposed to pesticides. Pesticides are a major factor affecting aquatic biodiversity along with habitat loss and climate change. They can have adverse effects in the short term by directly affecting the

organisms, or long-term effects by causing changes in habitat and the food chain. In Canada, losses among 62 imperilled species were significantly more related to rates of pesticide use and species loss was highest in areas with intensive agriculture (Gibbs *et al.*, 2009).

Many pesticides affect the nervous system of animals, which can interfere with their ability to survive. The contamination of the environment by toxic substances is linked with both agriculture and industrialization. Toxic substances are introduced into aquatic ecosystems from discharges and leaks of industrial products, as well as agricultural runoff. Aquatic ecosystems are important in that there is a continuous exchange of pesticides between land, sediment water interface, air-water interface, and aquatic organisms.

The indiscriminate use of pesticides is considered one of the important factors that change the environment by causing imbalances in the ecosystem, especially in biota of the aquatic system (Sancho *et al.*, 1998).

Many agro and related chemicals are found in aquatic ecosystems and have the potential to affect the natural communities within. Among the agrochemicals, pesticides may cause major problems because they are specifically formulated to kill living organisms and are intentionally released into the environment. Impacts of agriculture on aquatic biodiversity may result from many sources, including channelization, removal or alteration of riparian vegetation, dredging, and inputs of contaminants, including sediment, nitrate, phosphate, and pesticides (Brown *et al.*, 2007).

* Corresponding author email: saraa@sfu.ca

Globally, excessive loss of food crops to insects or other pests may contribute to possible starvation, and use of pesticides seems to have a favourable cost-benefit relationship (Murphy, 1986). It is commonly believed that there is a continuous increase in the use of pesticides, thus it is a major factor affecting biological diversity, along with habitat loss.

Many biochemical and physiological changes in aquatic organisms are caused by pesticides which influence the activities of several enzymes (Khan and Law, 2005). Several pesticides are toxic to amphibians, fish, birds and mammals. Normally, pesticides accumulating in the food chain, particularly those which cause endocrine disruption, pose a long-term risk to mammals, birds, amphibians, and fish. One-third of the 6,000 amphibian species found worldwide are at risk. Besides habitat loss, overexploitation and introduced species, amphibians are also affected by the pollution of surface waters with fertilisers and pesticides from agriculture (IUCN, 2011). Amphibians have shown vulnerability to agrochemicals that are cholinesterase inhibitors (Wang and Murphy, 1982; Khan *et al.*, 2006).

Agricultural activity may intensify the infection of frogs by harmful nematodes (King *et al.*, 2008). Aquatic ecosystems have deteriorated over time as anthropogenic activities encroach in water, once primarily the realm of biodiversity (Khan and Yasmeen, 2005).

Several pesticides, such as pyrethroid insecticides, are toxic to most aquatic organisms including aquatic vertebrates. It is evident that pesticides cause major loss in global fish production (Rand, 1995). Many pesticides interfere with the physiological processes of living organisms, and can be passed from one organism to another in the food chain. Therefore, many adverse environmental effects may result from the indiscriminate use of pesticides. Several agrochemicals such as organophosphates, organochlorines and carbamates may cause morphological changes to fish sex organs, which leads to the inhibition of steroid hormone synthesis and delayed oocyte development (Kim, 1998; Khan and Law, 2005).

Pyrethrins and pyrethroids are pesticides included in over 3,500 registered products used for controlling pests (US EPA, 2010). Pyrethroids are used widely as insecticides both in households and in agriculture. They are known to alter the normal function of insect nerves by interfering with the kinetics of voltage-sensitive sodium channels (Soderlund *et al.*, 2002). Pyrethrins are natural pesticides produced from *inter alia* pyrethrum, whereas pyrethroids are structurally very similar compounds rendered photostable by many substituent groups like bromine and

chlorine on the basic structure (Bryan *et al.*, 1993).

Field and lab investigations have proved that pyrethroids are highly toxic to a number of non-target organisms such as freshwater fish, amphibians and other aquatic organisms; even at very low concentrations (Oudou *et al.*, 2004). Non-target species such as aquatic animals are extremely sensitive to the neurotoxic effects of these pesticides when they enter surface water-courses (Philip *et al.*, 1995).

Bradbury and Coats (1989) reviewed the adverse effects of pyrethroids in different species of fish and stated a 96 hour cypermethrin toxicity (LC₅₀; µg/l) of 0.9–1.1 to Carp (*Cyprinus carpio*); 1.2 to Brown Trout (*Salmo trutta*); 0.5 to Rainbow Trout (*S. gairdneri*); 0.4 to *Scardinius erythrophthalmus* and 2.2 to *Tilapia nilotica*.

The aim of this review is to summarize the effects of pyrethroids and related agrochemicals on aquatic biodiversity and give the picture of their detrimental effects on the environment and biodiversity.

Effects on Fish

The balance of an aquatic ecosystem may be disturbed or altered under the effects of pesticides. Many pesticides indirectly influence fish by affecting their food supply and/or deteriorating the aquatic habitat. Thus the growth and survival of fish is greatly disturbed by use of pesticides in or near a body of water (Ewing, 1999).

There are three ways in which fish and other aquatic creatures are exposed to pesticides: oral, by drinking/feeding on pesticide-contaminated water/prey; dermal, by absorption of pesticides through skin in contaminated water; and inhalation, by up taking contaminants through the gills during respiration (Johnson and Finley, 1980).

Fish are chronically exposed to a variety of pesticides in their natural environment. Many of these chemicals also have the potential to accumulate in their tissues. Several studies have shown that most fish sampled from the agricultural areas contained detectable levels of pesticides. In particular, high levels were detected in fish from the Los Angeles and San Diego harbours, parts of the San Francisco Bay, and the Sacramento and San Joaquin Rivers (US EPA, 1992).

Pyrethroids are metabolized and eliminated at a significantly slower rate in fish when compared to birds and mammals. This may explain the higher toxicity of pyrethroids in fish when compared to other animals (Bradbury and Coats, 1989). Laboratory investigations have proved that pyrethroids are absorbed at a high rate

by gills and these factors into the vulnerability of fish to aqueous pyrethroid. Fish also metabolizes and eliminates these chemicals at a very low rate. The half-lives are greater than 48 hours for the elimination of several pyrethroids by trout, whereas the half-lives of the same compounds are between 6-12 hours in birds and mammals (Bradbury and Coats, 1989).

Fish are deficient in the enzymes that hydrolyze pyrethroids. Metabolism of deltamethrin, cypermethrin or cyhalothrin is largely oxidative in fish, whereas in rats/mice the main reaction is the ester cleavage by carboxyesterase (Demoute, 1989).

Deltamethrin may also disturb phosphate and calcium homeostasis which may impact the reproductive state of the fish (Srivastav et al., 1997).

Fish primarily metabolize pyrethroids by oxidative degradation, with ester hydrolysis being a secondary reaction. Glickman et al. (1981) and Glickman and Lech (1981) reported that the oxidation and hydrolysis of permethrin in *Oncorhynchus mykiss* tissues were comparatively slower than in mammalian tissues. Mulla et al. (1978) reported the permethrin toxicity in 48 hours with LC₅₀ of 0.005, 0.006, and 0.097 mg/L for adult Desert pupfish (*Cyprinodon macularius*), Rainbow trout (*Oncorhynchus mykiss*), and Western mosquitofish (*Gambusia affinis*), respectively.

Deltamethrin is a pyrethroid widely used in agricultural areas. Koprucu and Aydin (2004) investigated the effects of deltamethrin on embryos and larvae of *Cyprinus carpio* and reported that the number of dead embryos significantly increased in response to deltamethrin concentrations of 0.005, 0.05, 0.5, 5, 25, and 50 µg L⁻¹ ($p < 0.05$ for each cases). While dose-response decreases in hatching success were recorded as 75.2, 64.6, 47.4, 26.0, 14.4, and 9.0%, respectively. Exposure to the lowest concentration of deltamethrin (0.005 µg L⁻¹) resulted in significantly reduced numbers of dead larvae when compared to the higher concentrations ($p < 0.05$). Based on experimental results, deltamethrin may affect the development and reproduction of *Cyprinus carpio*. Therefore, deltamethrin must not be used in agricultural areas near the aquatic ecosystems.

Exposure to deltamethrin at a concentration of 2mg/l caused an inhibitory effect on the monooxygenase system of the Carp liver (*Cyprinus carpio* L.), whereas a faster metabolism of deltamethrin occurred when the Carp liver was exposed to a low concentration of 0.2 mg/l. The faster metabolism was due to an induction of hepatic microsomal cytochrome P450-dependent monooxygenases (Dee' r et al., 1996).

Viran et al. (2003) conducted a study on deltamethrin's effects on behavioural responses of the fish *Poecilia*

reticulata for 8 consecutive hours and then every 12 hours during the acute toxicity tests. Exposure to the lowest concentration of 1.00 mg/l had close to normal behaviour response, while less general activity and loss of equilibrium was observed at the highest concentration of 4mg/l when compared to the control group. The changes in behavioural response started an hour after the dosing of deltamethrin in all concentrations tested.

The exposure of deltamethrin to freshwater fish, *Channa punctatus* showed a significant ($P < 0.01$) decrease in the activity of all organs. The decreased activity observed was 45% in liver, 43% in kidney and 33% in gills. A significant ($P < 0.01-0.001$) increase was recorded in the activities of Glutathione S-transferase (GST) and Glutathione Peroxidase (GPx) in the liver and kidney, while there was a significant decrease ($P < 0.001$) in the activities of GST and GPx in the gills (Sayeed et al., 2003).

Cypermethrin is extremely toxic to bees (WHO, 1992) and vertebrates, with fish being the most sensitive of all vertebrates (Edwards et al., 1986). Several studies have already shown the LC₅₀ of between 0.93 and 21.4 µg/l in many fish species (Carrquiriborde et al., 2007; Polat et al., 2002; Stephenson, 1982).

Cypermethrin is toxic to the freshwater fish *Colisa fasciatus*. Sub-lethal doses of cypermethrin altered the total protein, free amino acids, nucleic acids (DNA and RNA) and enzymes LDH, SDH and AChE in the fish (Singh et al., 2010). Smith and Stratton (1986) compiled the adverse effects of cis-cypermethrin on fish species as follows (exposure time and LC₅₀ in µg/l): Rainbow trout (*S. gairdneri*) 96-h 6.0, Atlantic salmon (*Salmo salar*) 96-h 2.0, Mosquito fish (*Gambusia affinis*) 24-h 9.0 and 48-h 8.0; Desert pupfish (*Cyprinodon macularius*) 24-h 10.0 and 48-h 6.0.

Alpha-cypermethrin is extremely toxic to fish and aquatic invertebrates but is non-toxic to birds. It is metabolized and eliminated slower in fish as compared to mammals and birds (Sarikaya, 2009).

Some Threatened Fish Species

The Atlantic Sturgeon (*Acipenser sturio*) (Fig. 1) was formerly found to inhabit areas in the North Sea, north-eastern Atlantic and Mediterranean coasts of Europe and the Black Sea. Due to pollution and river regulations, there has been degradation and destruction of many of their spawning sites. In the last three generations, the population has declined by 90% and has become extinct in most of its former areas. Currently in the Garonne River, France, the last remaining population is still declining (Kottelat et al., 2009).



Fig. 1. Atlantic Sturgeon (*Acipenser sturio*).

Populations of fish *Tilapia busumana* (Fig. 2) from Ghana are presently declining due to agricultural practise, leaching of pesticides and other agrochemicals (Entsua-Mensah and Lalèyè, 2006).



Fig. 2. *Tilapia busumana*.

Sahara Aphanius (*Aphanius saourensis*) (Fig. 3) is a species Endemic to Algeria. Due to water pollution and other threats this species has been listed as Critically Endangered (Azeroual, 2007).



Fig. 3. Sahara Aphanius (*Aphanius saourensis*).

Effects on Amphibians

Amphibians are an important part of aquatic ecosystems and are the good indicator of environmental stress (Blaustein, 1994; Blaustein and Wake, 1995). They have contact with water as larvae and both with water and land as an adult. Thus, they are exposed to the stressors in both

aquatic and terrestrial environments (Blaustein and Wake, 1990; Vitt, *et al.*, 1990; Khan *et al.*, 2009). Out of 6285 amphibians species, 1895 are in danger of extinction, this makes them the most threatened group of species known to date (IUCN, 2011).

Pesticides can affect frogs and other amphibians in different ways, as they destroy the natural biotic balance in agricultural fields' and reduce the diversity and abundance of biodiversity with cascading effects at higher trophic levels (Larson *et al.*, 1997; Khan and Ghazala, 2008). Pesticides can affect their behaviour and reduce their growth rates (Bishop, 1992; Carey and Bryant, 1995; Alford and Richards, 1999). Under the effects of pesticides, many frogs and toads grow extra legs and eyes and do not survive to adulthood (Kegley *et al.*, 1997).

Amphibians are known to be vulnerable to pesticides that are cholinesterase inhibitors. Several studies have reported that some pesticides reduce cholinesterase (ChE) activity in the frogs; *Rana tigrina* (Khan *et al.*, 2002a,b and 2003a) and *Rana cyanophlyctis* (Khan *et al.*, 2003b,c,d ; Khan and Yasmeen, 2005; Khan *et al.*, 2006; Khan *et al.*, 2007). There is some indication that field application of these pesticides may be deleterious to amphibians (Jolly *et al.*, 1978; Thybaud, 1990; Berril *et al.*, 1993; Materna *et al.*, 1995). In 1992, World Health Organization (WHO) recognized that cypermethrin is an alpha-cyano pyrethroid, whose primary target site in the vertebrate nervous system is the sodium channel of the nerve membrane. The behavioural response of twisting, writhing, and non-coordinated swimming in amphibians is an indication of cyano pyrethroid poisoning (Berril *et al.*, 1993; Greulich and Pflugmacher, 2003).

Khan *et al.* (2003c) studied the induced effects of lambda cyhalothrin on *Rana cyanophlyctis* and reported that this pesticide decreased cholinesterase levels up to 46.3% in liver, 57.1% in kidney and 50.7% in brain. In another study, Khan and Ghazala (2009) investigated the effects of beta cypermethrin on frogs and reported that the ChE activity decreased to 30.0% in the liver ($F_{2,6}=13.28$, $P=0.006$), up to 40.0% in the kidney ($F_{2,6}=6.80$, $P=0.029$) and to 44.44% in the brain, ($F_{2,6}=22.99$, $P=0.002$). In another study, Khan *et al.* (2003b), compared the effects of both lambda cyhalothrin and permethrin on cholinesterase in *R. cyanophlyctis* and *R. tigrina* and reported that amphibians in general are sensitive. *R. cyanophlyctis* is more sensitive to these chemicals than *R. tigrina*, and lambda cyhalothrin is most toxic among the pesticides tested.

Berril *et al.* (2009) subjected embryos and larvae of three species of the *Rana* genus of frogs (*R. sylvatica*, *R. pipiens*, *R. Clamitans*), the toad (*Bufo americanus*) and salamander (*Ambystoma maculatum*) to one or both of the pyrethroid fenvalerate and permethrin. Concentrations of

0.01ppm to 2ppm were used and subjects were exposed for 22 or 96 hours. No significant mortality of embryos or larvae occurred during or following the exposure to these pyrethroids. Nevertheless, tadpoles showed delayed growth following the exposure. Affected tadpoles and larvae responded to prodding by twisting abnormally instead of darting away. These effects (slower growth and abnormal behaviour) may result in higher risk to predation.

Some Threatened Amphibian Species

In South Africa, Pickersgill's Reed Frog (*Hyperolius pickersgilli*) (Fig. 4) is an Endemic species. Due to habitat destruction, agricultural activities and pollutants such as pesticides, it has been listed as a Critically Endangered Species (SA-Frog, 2010).



Fig. 4. Pickersgill's Reed Frog (*Hyperolius pickersgilli*).

In addition, the population of Spotted Snout-burrowers (*Hemisus guttatus*) (Fig. 5) in South Africa is also facing habitat loss and agrochemical pollution threats (SA-Frog, 2010). A recent study (Khan *et al.*, 2010) indicated that three species of frog are at risk due to pesticide contamination. Tiger Frog (*Hoplobatrachus tigerinus*) (Fig. 6) found in Taiwan, throughout Southern China and the other mainland countries of South East Asia throughout most of the Indian Subcontinent, Northward to Nepal and Pakistan; Indian Burrowing Frog (*Tomopterna breviceps*) is distributed throughout India, West of the Ganges Delta and Nepal, Bangladesh, Myanmar, Sri Lanka and Pakistan, and Indian Cricket Frog (*Limnonectes limnocharis*) found in Southern Japan and the Riu-Kiu Islands through the Philippines and the Island of Indonesia East-Central China West to Nepal and Kashmir and Pakistan are now listed as Threatened Species in the Thatta districts of Sindh province due to the effects of agricultural pesticides and habitat destruction.



Fig. 5. Spotted Snout-burrower (*Hemisus guttatus*).



Fig. 6. Tiger Frog (*Hoplobatrachus tigerinus*).

Effects on Aquatic Mammals and Some Threatened Aquatic Mammalian Species

Many cases of adverse impact of pesticides affecting dolphins have been reported. Dolphins accumulate high concentrations of organic pollutants because they have a low activity of drug-metabolizing enzymes (Tanabe *et al.*, 1997). River dolphins are one of world's Threatened Species (Akhtar *et al.*, 2009). Critically Endangered Yangtze River Dolphin (*Lipotes vexillifer*) in China (Fig. 7), and 1331 remaining *Platanista minor* dolphins of the Indus River in Pakistan (Fig. 8) are already close to extinction (Perrin *et al.*, 1989; Reeves *et al.*, 1991; Reeves and Chaudhry, 1998; Khan, 2006).



Fig. 7. Yangtze River Dolphin (*Lipotes vexillifer*).



Fig. 8. Indus River Dolphin (*Platanista minor*).

In Bangladesh, the extensive use of fertilizers and pesticides for the “green revolution” has created major water-quality problems. The Ganges River Dolphin (*Platanista gangetica*) inhabits the Ganges, Meghna, Brahmaputra and Karnaphuli rivers and their tributaries in India (Fig. 9), Bangladesh, Nepal and Bhutan (Lal Mohan, 1989). A recent study has shown that Ganges River Dolphins or susu (*Platanista gangetica*) are unable to metabolize the chemicals found in pesticides (Kannan *et al.*, 1994).



Fig. 9. Ganges River dolphin, *Platanista gangetica*. (source: <http://euteachers.net/cms/index1.php>).

Another freshwater Gray Dolphin (*Sotalia fluviatilis*) is considered to be the world’s only exclusive freshwater delphinid (Fig. 10). It inhabits the Amazon drainage as far inland as southern Peru, south eastern Colombia and eastern Ecuador and is facing some threats including pollution (Secchi, 2010).



Fig. 10. Gray Dolphin (*Sotalia fluviatilis*). (source: www.iucnredlist.org).

Effects on Birds

Reduction in the population levels of several bird species has been linked to exposure to pesticides through ingestion and/or absorption (Mineau *et al.* 2005; Ortego *et al.* 2007).



Fig. 11. Baikal Teal (*Anas Formosa*). (source: BirdLife International, 2011).



Fig. 12. Marbled Teal (*Marmaronetta angustirostris*) (source: BirdLife International, 2011).

Synthetic pyrethroids have a relatively low acute toxicity in birds but can destroy a bird’s food supply. Waterfowl that feed on aquatic insects and insectivorous birds are especially vulnerable to pyrethroids (Mueller-Beilschmidt, 1990).

Egrets and herons are at the top of the aquatic food webs, and thus particularly susceptible to pollutant bioaccumulation (De Lucca-Abbot *et al.*, 2001). However in the case of cypermethrin, the birds are affected without being exposed directly to the pesticides. This usually occurs when pesticides are applied to birds’ food sources such as bugs/insects and rodents. Some studies have indicated that the growth of young birds can be stunted in areas where insecticides have been used heavily, resulting in insect populations too low to meet young birds’ protein growth demands (Facemire, 1991).

Cypermethrin has shown no toxicity to birds. The acute oral LD₅₀ in mallard ducks is greater than 4,640 mg/kg. The dietary LC₅₀ is > 20,000ppm for mallards and Bobwhite Quail. No adverse reproductive effects have been observed in mallards or Bobwhite Quails given 50 ppm, the highest dose tested (US EPA, 1989). Cypermethrin is used in killing insect larvae which are normally eaten by birds, thus birds are indirectly affected by this compound as their food source is affected. A study on Blue Tits’ (*Parus caeruleus*) nesting success showed a

100% mortality of caterpillars (eaten by Blue Tits) after an aerial application of cypermethrin in an oak forest. An increase in nestling fatality, a decrease in successful nests and a decrease in weight of the surviving nestling was observed when exposure to cypermethrin coincided with egg hatching and early nestling stage (Pascual and Peris, 1992).

Some Threatened Bird Species

In China and South Korea, birds were indirectly affected by poisoned grain and pollution from agricultural and household wastes. The Baikal Teal (*Anas Formosa*) (Fig. 11) is now listed as a threatened bird species. This bird breeds in eastern Siberia, Russia and is found mainly on passage in Mongolia and North Korea. It winters mainly in Japan and South Korea (BirdLife International, 2011). Another species, the Marbled Teal (*Marmaronetta angustirostris*) (Fig. 12) found in Russia, Uzbekistan, Turkmenistan, Tajikistan, Kazakhstan, Afghanistan, China, Iraq and winters in Iran, Pakistan and north-west India is also listed as a threatened species due to agricultural and industrial pollution (BirdLife International, 2011).

CONCLUSION

Pesticides have harmful effects on species biodiversity. These compounds can have adverse effects either directly or indirectly on the normal life cycles of animals and their habitats. Different species of fish, amphibians, birds and aquatic mammals have been listed as endangered because of chronic exposure to pyrethroids and other related agrochemicals. Measures can be taken to lower the level of exposure to animals and their habitat. Flow of energy is disturbed when any level of the food chain/web is affected by compounds such as pesticides and other agrochemicals. This can lead to widespread adverse effects causing an imbalance in the ecosystem.

REFERENCES

Alford, RA. and Richards, SJ. 1999. Global Amphibian Declines: A Problem in Applied Ecology. *Annu. Rev. Ecol. Syst.* 30:133-165.

Azeroual, A. 2007. *Aphanius saourensis*. In: IUCN 2010. IUCN Red List of Threatened Species. Version 2010.4.

Akhtar, MW., Sengupt, D. and Chowdhury, A. 2009. Impact of pesticides use in agriculture: their benefits and hazards. *Interdisc Toxicol.* 2(1):1-12.

Bradbury, SP. and Coats, JR. 1989. Toxicokinetics and toxicodynamics of pyrethroid insecticides in fish. *Environmental Toxicology and Chemistry.* 8(5):373-380.

Bradbury, SP. and Coats, JR. 1989. Comparative toxicology of the pyrethroid insecticides. *Rev. Environ. Contam. Toxicol.* 108:133-177.

Blaustein, AR. and Wake, DB. 1990. Declining amphibian populations: a global phenomenon? *Trends in Ecol. Evol.* 5:203-4.

Bishop, CA. 1992. The effects of pesticides on amphibians and the implications for determining causes of declines in amphibian populations. In *Declines in Canadian Amphibian Populations: Designing a National monitoring Strategy*. Canadian Wildlife Service. Occas. Pap. No. 76:67-70.

Berril, M., Bertram, S., Wilson, A., Louis, S., Brigham, D. and Stromberg, C. 1993. Lethal and sub-lethal impacts of pyrethroid insecticides on amphibian embryos and tadpoles. *Environ. Toxicol. Chem.* 12:525-539.

Bryan, B., Marrs, T. and Turner, P. 1993. *General and Applied Toxicology* (vol. 2). Macmillan Publishers Ltd., New York, USA.

Berril, M., Bertram, S., Wilson, A., Louis, S., Brigham, D. and Stromberg, C. 1993. Lethal and sublethal impact of pyrethroid insecticides on amphibian embryos and tadpoles. *Environ Toxicol Chem.* 12:525-539.

Blaustein, AR. 1994. Chicken Little or Nero's fiddle? A perspective on declining amphibian populations. *Herpetologica.* 50:85-97.

Blaustein, AR. and Wake, DB. 1995. The puzzle of declining amphibian populations. *Sci. Am.* 272:52-57.

Brown, CD., Holmes, C., Williams, R., Beulke, S., Beinum, W., Pemberton, E. and Wells, C. 2007. How does crop type influence risk from pesticides to the aquatic environment? *Environmental Toxicology and Chemistry.* 26(9):1818-1826.

Berrill, M., Bertram, S., Wilson, A., Louis, S., Brigham, D. and Stromberg, C. 2009. Lethal and sublethal impacts of pyrethroid insecticides on amphibian embryos and tadpoles. *12(3):525-539.*

BirdLife International. 2011. IUCN Red List for birds. <http://www.birdlife.org>

Carey, C. and Bryant, CJ. 1995. Possible inter-relationships among environmental toxicants, amphibian development, and decline of amphibian populations. *Environ. Health Perspec.* 103(4):13-17.

Carriquiriborde, P., Diaz, J., Mugni, H., Bonetto, C. and Ronco, EA. 2007. Impact of cypermethrin on stream fish populations under field use in biotech-soybean production. *Chemosphere.* 68:613-621.

Demoute, JP. 1989. A brief review of the environmental fate and metabolism of Pyrethroids. *Pest. Sci.* 27:375-385.

Dee r, KA., Banka, L., Nemcsok, J. and Abraham, M. 1996. Effects of deltamethrin on hepatic microsomal cytochrome P450-dependent monooxygenases in carp. *J. Environ. Sci. Health. B* 31 (3):637-644.

- De Lucca-Abbott, SB., Wong, BSF., Peakall, DB., Lam PKS., Young, L., Lam, MHW. and Richardson, BJ. 2001. Review of effects of water pollution on the breeding success of waterbirds, with particular reference to ardeids in Hong-Kong. *Ecotoxicology*. 10:327-349.
- Edwards, R., Millburn, P. and Hutson, DH. 1986. Comparative toxicity of cis-cypermethrin in Rainbow trout, frog, mouse and quail. *Toxicol Appl Pharmacol*. 84:512-522.
- Ewing, RD. 1999. Diminishing Returns: Salmon Decline and Pesticides. Biotech Research and Consulting, Inc., Corvallis, OR. pp 55.
- Entsua-Mensah, M. and Lalèyè, P. 2006. *Tilapia busumana*. In: IUCN 2010. IUCN Red List of Threatened Species. Version 2010.4. <www.iucnredlist.org>
- Facemire, FC. 1991. Impact of agricultural chemicals on wetland habitats and associated biota with special reference to migratory birds. B 780, SDSU, Brookings, SD. pp 65.
- Glickman, AH., Hamid, AAR., Rickert, DE. and Lech, JJ. 1981. Elimination and metabolism of permethrin isomers in rainbow trout. *Toxicol. Appl. Pharmacol*. 57:88-98.
- Glickman, AH. and Lech, JJ. 1981. Hydrolysis of permethrin, a pyrethroid insecticide, by rainbow trout and mouse tissues in vitro: A comparative study. *Toxicol. Appl. Pharmacol*. 60:186-192.
- Greulich, K. and Pflugmacher, S. 2003. Differences in susceptibility of various life stages on amphibians to pesticide exposure. *Aquat Toxicol*. 65:329-336.
- Gibbs, KE., Mackey, RL. and Currie, DJ. 2009. Human land use, agriculture, pesticides and losses of imperiled species. *Diversity and Distributions*. 15(2):242-253.
- IUCN. 2011. Why is biodiversity in crisis? www.iucn.org
- Johnson, W. and Finley, MT. 1980. Handbook of Acute Toxicity of Chemicals to Fish and Aquatic Invertebrates. US Fish and Wildlife Service Publication 137. Washington, DC, USA.
- Jolly, AL. Jr., Avault, JW. Jr., Koonce, KL. and Graves, JB. 1978. Acute toxicity of Permethrin to several aquatic animals. *Trans. Am. Fish Soc*. 107:825-827.
- Kannan, K., S. Tanabe, and R. Tatsukawa. 1994. Biodegradation capacity and residue pattern of organochlorine in the Ganges river dolphins from India. *Toxicological and Environmental Chemistry*. 42:249-261.
- Kegley, S., Neumeister, L. and Martin, T. 1997. *Disrupting the Balance: Ecological Impacts of Pesticides in California*. Pesticide Action Network, USA. pp. 99
- Kim, DE. 1998. Endocrine disruption in fish. Kluwer Academic Publishers, London. IUCN. The Asian amphibian crisis. http://www.iucn.org/about/union/secretariat/offices/asia/regional_activities/asian_amphibian_crisis/
- Khan, MZ., Fatima, F. and Ahmad, I. 2002^a. Effect of Cypermethrin on Protein Contents in Lizard *Calotes versicolor* in comparison to that in Frog *Rana tigrina*. *Online Journal of Biological Sciences*. 2(12):780-781.
- Khan, MZ., Shah, EZ., Ahmed, I. and Fatima, F. 2002^b. Effects of agricultural pesticides permethrin (pyrethroid) on protein contents in kidney and liver of lizard species *Calotes versicolor* in comparison to that in frog *Rana tigrina*. *Bull. of Pure & App. Sc.* 21A (2):93-97.
- Khan, MZ., Tabassum, R., Naqvi, SNH., Shah, EZ., Tabassum, F., Ahmad, I., Fatima, F. and Khan, MF. 2003^a. Effect of Cypermethrin and Permethrin on Cholinesterase Activity and Protein Contents in *Rana tigrina* (Amphibia). *Turk. J. Zool.* 27: 243-246.
- Khan, MZ., Nazia, M., Fatima, F., Rahila, T. and Gabol, K. 2003^b. Comparison of the effect of Lambda cyhalothrin with permethrin on cholinesterase activity in *Rana cyanophlyctis* and *Rana tigrina* (Ranidae: amphibian). *Bull. of Pure & App. Sc.* 22A (1):43-49.
- Khan, MZ., Maria, Z. and Fatima, F. 2003^c. Effect of Lambda Cyhalothrin (Pyrethroid) and Monocrotophos (Organophosphate) on Cholinesterase activity in liver, kidney and brain of *Rana cyanophlyctis*. *Korean J. Biol. Sciences*. 7(2):165-168.
- Khan, MZ., Fatima, F., Mahmood, N. and Yasmeen, G. 2003^d. Comparison of Cholinesterase activity in the brain tissue of lizard *Calotes versicolor* with that of frog *Rana cyanophlyctis* under the effect of Cypermethrin, Lambda Cyhalothrin, Malathion and Monocrotophos. *Bulletin of Pure and Applied Sciences*. 22 A (2):105-112.
- Khan, MZ. and Yasmeen, G. 2005. Pesticide dependent cholinesterase activity in brain of *Rana cyanophlyctis* (amphibian). *J Exp. Zool. India*. 8 (1):135-140.
- Khan, MZ. and Law, FCP. 2005. Adverse Effects of Pesticides and related Chemicals on Enzyme and Hormone Systems of Fish, Amphibians and Reptiles. *Proc. Pakistan Acad. Sci.* 42(4):315-323.
- Khan, MZ. 2006. Current Status and Biodiversity of Indus Dolphin Reserve and Indus Delta Wetlands (Ramsar Sites). *Proc. 9th International River Symposium*, Brisbane, Australia. 1-26.
- Khan, MZ., Yasmeen, G. and Hamid, S. 2006. Effect of Sundaphos (Organophosphate) and beta-cypermethrin (Synthetic Pyrethroid) on Cholinesterase Activity in Liver and Kidney of *Euphlyctis cyanophlyctic*. *Hamadryad*. 30(1&2):176-180.
- Khan, MZ., Rais, M. and Yasmeen, G. 2007. Inhibitory effects on cholinesterase activity produced by the two

- different pesticides on brain, liver and kidney of *Euphlyctis cyanophlyctis*. J. Exp. Zool. India.10(1):89-93.
- Khan, MZ. and Yasmeen, G. 2008. Effects of Sandaphose and beta-cypermethrin on Cholinesterase and Alkaline Phosphatase activity in liver, kidney and brain of *Euphlyctis cyanophlyctis*. CJPAS. 2(3):511-519.
- Khan, MZ. and Yasmeen, G. 2009. A study on the induced effect of beta-cypermethrin on skin of *Euphlyctis cyanophlyctis*. CJPAS. 3(3):937-941.
- Khan, MZ., Nazia M., Ghalib, SA., Hussain, B., Saima, S., Shahnaz, P. and Darakhshan, A. 2010. Impact of Habitat Destruction on the Population of Amphibians with Reference to Current Status of Frogs and Toads in Karachi and Thatta, Sindh. Canadian Journal of Pure and Applied Sciences. 4(3):1257-1265.
- King, KC., Gendron, AD., McLaughlin JD., Giroux, I., Brousseau, P., Cyr, D., Ruby, SM., Fournier, M. and Marcogliese, DJ. 2008. Short-term seasonal changes in parasite community structure in Northern Leopard froglets (*Rana pipiens*) inhabiting agricultural wetlands. J Parasitol. 94(1): 13-22.
- Koprucu, K. and Aydin, R. 2004. The toxic effects of pyrethroid deltamethrin on the common carp (*Cyprinus carpio* L.) embryos and larvae. Pesticide Biochemistry and Physiology. 80(1):47-53.
- Kottelat, M., Gesner, J., Williot, P., Rochard, E. and Freyhof, J. 2009. *Acipenser sturio*. In: IUCN 2010. IUCN Red List of Threatened Species. Version 2010.4. <www.iucnredlist
- Lal Mohan, RS. 1989. Conservation and management of the Ganges river dolphin, *Platanista gangetica* in India. In: Biology and Conservation of the River Dolphin. Eds. Perrin, WF., Brownell, RL. Jr., Zhou, K. and Liu, J. Occasional papers of the IUCN Species Survival Commission (SSC). 3:64-69.
- Larson, SJ., Capel, PD. and Majewski, MS. 1997. Pesticides in surface waters: Distribution, Trends, and Governing Factors. Ann Arbor, Inc., USA.
- Lloyd, J. 2010. Encyclopedia of Earth. Biodiversity. (Washington, DC, USA. Environmental Information Coalition, National Council for Science and the Environment). Retrieved April 26, 2011.
- Mulla, MS., Navvab-Gojrati, HA. and Darwazeh, JA. 1978. Toxicity of mosquito larvicidal pyrethroids to four species of freshwater fishes. Environ. Entomol. 7:428-430.
- Murphy, SD. 1986. Toxic effects of pesticides. In: Casarett and Doull's Toxicology, The Basic Science of Poisons (3rd ed.). Eds. Klassen, CD. et al. New York. pp. 519-581.
- Mueller-Beilshmidt, D. 1990. Toxicology and environmental fate of synthetic pyrethroids. J. Pesticide Reform. 10(3):32-36.
- Materna, EJ., Rabeni, CF. and La Point, TW. 1995. Effects of synthetic pyrethroid insecticides, esfenvalerate, on larval leopard frogs (*Rana* spp.) Environ. Toxicol. Chem. 14:613-622.
- Mineau, P., Downes, CM., Kirk, DA., Bayne, E. and Csizy, M. 2005. Patterns of bird species abundance in relation to granular insecticide use in the Canadian prairies. Ecoscience. 12(2):267-278. doi:10.2980/i1195-6860-12-2-267.1.
- Oudou, HC., Alonso, RM. and Bruun, HC. 2004. Voltammetric behaviour of the synthetic pyrethroid lambda-cyhalothrin and its determination in soil and well water. Anal. Chim. Acta. 523(1):69-74.
- Ortego, J., Aparicio, JM., Munoz, A. and Bonal, R. 2007. Malathion applied at standard rates reduces fledgling condition and adult male survival in a wild lesser kestrel population. Anim. Conserv. 10(3):312-319. doi:10.1111/j.1469-1795.2007.00114.x.
- Perrin, WF., Brownell, RL Jr., Kaiya, Z. and Jiankang, L. 1989. Biology and conservation of the river dolphins. In: Proceedings of the Workshop on Biology and Conservation of the Platanistoid Dolphins. Eds. Perrin, WF., Brownell, RL Jr., Kaiya, Z. and Jiankang, Wuhan, L. China.
- Pascual, JA. and Peris, SJ. 1992. Effects of forest spraying with two application rates of cypermethrin on food supply and on breeding success of the Blue Tit (*Parus caeruleus*). Environ. Toxicol. Chem. 11:1271-1280.
- Philip, GH., Reddy, PM. and Sridevi, G. 1995. Cypermethrin-induced in vivo alterations in the carbohydrate-metabolism of freshwater fish, *Labeo rohita*. Ecotoxicol. Environ. Safety. 31(2):173-178.
- Polat, H., Erkoç, FU., Viran, R. and Koçak, O. 2002. Investigation of acute toxicity of beta-cypermethrin on guppies *Poecilia reticulata*. Chemosphere. 49(1):39-44.
- Reeves, RR., Chaudhry, AA. and Khalid, U. 1991. Competing for water on the Indus plain: Is there a future for Pakistans River Dolphins? Environ Conserv. 18:341-350.
- Reeves, RR. and Chaudhry, AA. 1998. Status of the Indus River Dolphin *Platanista minor*. Oryx. 32:35-44.
- Rand, GM. 1995. Fundamentals of Aquatic Toxicology: Effects, Environmental Fate and Risk Assessment. 2nd ed. Washington, DC, USA.
- Stephenson, RR. 1982. Aquatic toxicology of cypermethrin. I. Acute toxicology to some freshwater fish

- and invertebrates in laboratory tests. *Aquat Toxicol.* 2:175-185.
- Smith, TM. and Stratton, GW. 1986. Effects of synthetic pyrethroid insecticides on nontarget organisms. *Res. Rev.* 97:93-119.
- Srivastav, AK., Srivastava, SK. and Srivastav, SK. 1997. Impact of deltamethrin on serum calcium and inorganic phosphate of freshwater catfish, *Heteropneustes fossilis*. *Bull. Environ. Contam. Toxicol.* 59(5):841-846.
- Sancho, E., Fernando, MD., Lleó, C. and Andreu-Moliner, E. 1998. Pesticide toxicokinetics in fish: Accumulation and Elimination. *Ecotoxicol. Environ. Saf.* 41(3): 245-250.
- Soderlund, DM., Clark, JM., Sheets, LP., Mullin, LS., Piccirillo, VJ., Sargent, D., Stevens, JT. and Weiner, ML. 2002. Mechanisms of pyrethroid neurotoxicity: Implications for cumulative risk assessment *Toxicology.* 171(1):3-59.
- Sayeed, I., Parvez, S., Pandey, S., Bin-Hafeez, B., Haque, R. and Raisuddin, S. 2003. Oxidative stress biomarkers of exposure to deltamethrin in freshwater fish, *Channa punctatus* Bloch. *Ecotoxicology and Environmental Saftey.* 56(2):295-301.
- Sarikaya, R. 2009. Investigation of Acute Toxicity of Alpha-Cypermethrin on Adult Nile Tilapia (*Oreochromis niloticus* L.). *Turkish Journal of Fisheries and Aquatic Sciences.* 9:85-89.
- Singh, SK., Singh, Sunil Kumar S. and Yadave, RP. 2010. Toxicological and Biochemical Alterations of Cypermethrin (Synthetic Pyrethroids) Against Freshwater Teleost Fish *Colisa fasciatus* at Different Season. *World Journal of Zoology.* 5 (1):25-32.
- Secchi, E. 2010. *Sotalia fluviatilis*. In: IUCN 2010. IUCN Red List of Threatened Species. Version 2010.4. <www.iucnredlist.org>. Downloaded on 27 April 2011.
- South African Frog Re-assessment Group (SA-FRoG) and IUCN SSC Amphibian Specialist Group 2010. *Hemisus guttatus*. In: IUCN 2010. IUCN Red List of Threatened Species. Version 2010.4. <www.iucnredlist.org>.
- South African Frog Re-assessment Group (SA-FRoG) and IUCN SSC Amphibian Specialist Group 2010. *Hyperolius pickersgilli*. In: IUCN 2010. IUCN Red List of Threatened Species. Version 2010.4. <www.iucnredlist.org>.
- Tanabe, S., Senthilkumar, K., Kannan, K. and Subramanian, AN. 1997. Accumulation features of polychlorinated biphenyls and organochlorine pesticides in resident and migratory birds from south India. *Arch Environ Contam Toxicol.* 34(4):387-397.
- Thybaud, E. 1990. Acute toxicity and bioconcentration of lindane and deltamethrin in tadpoles of *Rana temporaria* and the mosquito fish *Gambusia affinis*. *Hydrobiologia.* 190:137-146.
- US Environmental Protection Agency. 1992. Pesticide Fact Sheet Number 199: Cypermethrin. US EPA, Office of Pesticide Programs. Washington, DC, USA.
- US EPA. 2010. National Study of Chemical Residues in Fish, Volume I and II. Environmental Protection Agency, Washington, DC. <http://www.epa.gov/oppsrrd1/reevaluation/pyrethroids-pyrethrins.html>
- Viran, R., Erkoç, FÜ., Polat, H. and Koçak, O. 2003. Investigation of acute toxicity of deltamethrin on guppies (*Poecilia reticulata*). *Ecotoxicology and Environmental Safety.* 55(1): 82-85.
- Vitt, LJ., Caldwell, JP., Wilbur, HM. and Smith, DC. 1990. Amphibians as harbingers of decay. *Bio Sci.* 40:418-18.
- Wang, C. and Murphy, SD. 1982. Kinetic analysis of species to organophosphate insecticides. *Toxicology and Applied Pharmacology.* 66 (3):409-419.
- World Health Organization. 1992. Alpha-cypermethrin. Environmental Health Criteria.
- Zitko, V., Mcleese, DW., Metcafe, CD. and Carson, WG. 1979. Toxicity of permethrin, decamethrin, and realted pyrethroids to Salmaon and Lobster. *Bull. Environ. Contam. Toxicol.* 21(3):336-343.

Received: April 4, 2011; Revised: May 6, 2011;
Accepted: May 12, 2011