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PESTICIDE CHARACTERISTICS THAT AFFECT WATER QUALITY

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Introduction

Humankind has come to view pure water as a privilege of modern society. Technology makes it possible to expect to turn on the faucet and have clean, clear water readily available. However, the technology that makes this possible also creates stress on the very water resources that are now taken for granted.

Clean, quality water can be preserved through an understanding of the products and processes that endanger this valuable resource. Pest control agents and fertilizers represent only a portion of the contaminants introduced into our water systems that affect quality. However, the use of these products is under our control as individual citizens. We can do much to keep these products from adversely affecting water quality. A knowledge of pesticide behavior in the environment is essential to a comfortable understanding of these dangers that these productsmay or may not possess. This publication will outline and explain several factors that need to be considered when assessing a pesticide's potential for affecting water quality. With a better understanding of the processes that endanger water resources, protection of water quality is possible.

The standards determining water quality depend on its intended use. Drinking water standards are higher than irrigation water or water used in industry. Laws such as the Clean Water Act and the Safe Drinking Water Act provide specific standards of quality for water used in various ways.

Throughout this text several words are given as bold-faced text. These words are defined in a glossary at the end of this manual.

Why is Water Quality Important?

Water is a part of everyday life, yet it is not an unlimited resource. Fresh water accounts for less than 2.5 percent of earth's water. The other 97.5 percent is salty, which is found mostly in oceans and inland seas. Of all freshwater present on earth, nearly 80 percent is ice in the polar ice caps and glaciers of the world. This leaves only about 0.2 percent of earth's fresh water available for our use (this represents 1/500th of all water on earth). Another way of thinking about this is imagining that if all of earth's water was represented by a gallon jug of milk, less than 1/4 an ounce (only a few drops) would be available for use (Environmental Protection Agency 1990).

Most of the available fresh water is found in **groundwater** with a much smaller percentage in rivers, lakes, soil moisture, and the atmosphere. This might appear as an inadequate amount of water to support life on earth, however, if it is of high quality, the amount present is sufficient. Presently, only about two percent of groundwater in the United States is **polluted**, but an increasing amount of surface waters is now at least somewhat contaminated (Environmental Protection Agency 1990).

Water quality is important in our lives because it is essential to all life. We rely on water not only to sustain our lives, but to do the same for pets, livestock, yards and crops. If the quality of water is changed by the presence of **toxins**, it is potentially harmful to these life forms, instead of sustaining them.

To understand what changes water from being beneficial to harmful, you must understand what makes water polluted, or of poor quality. Many substances that cause pollution are chemicals that are toxic, at least in certain quantities. For example, pesticides are designed to kill certain pests, called target pests. The components of pesticides that enable them to kill animal pests (including insects) are normally not designed to be **species specific**. Instead pesticides have characteristics or application methodologies that make them more likely to come in contact with the **target pest** and not a **non-target** animal. These target pests, however, are simply species of animals that share many of the same characteristics of other animals. One of these characteristics is a susceptibility to certain toxins. In other words, a chemical that is toxic to one animal also may be toxic to other forms of animal life. Although it might take a larger dose of **pesticide** to harm humans than pests such as insects, many pesticides are still **toxic** to humans. The doses needed to kill a pest might not kill us, but may still harm us. Many pesticides classified as herbicides are designed as species specific to the target plant pest. The exceptions to this are broad spectrum herbicides that are designed to kill a wide variety of plants. A herbicide that is specific to one or more species of plants does not insure that it is safe to enter the water system. Some of the dangers from these chemicals are yet to be fully understood. Caution should therefore be used to insure that these products do not unnecessarily enter the water system. Using safe, well-planned applications of materials, such as pesticides, the risk to humans and other animals is minimal. If these same products enter the water system, they may reach **non-target** animals and pose a hazard to other animal life (including humans and domestic animals) and non-target plant life. Along with pesticides, there are many other materials that can cause the same type of dangers to our waters and ultimately to us. Many of these materials are mentioned in this manual, but they cannot all be covered. A good way to deal with the problem of water pollution is by striving not to introduce any hazardous materials into waters without reason, because the result may be a deterioration of water quality.

The overall picture is not as bleak as you might be imagining. There is reason for optimism that these important water resources are available now and will be in the future. Because the threat to water systems and the mechanisms that cause water to become **polluted** are now better understood, steps have been taken to protect the quality of our water. This manual provides ideas and guidelines that can be used in everyday life to help ensure this.

Sources of Water Pollution

Water pollution refers to changing of the chemical and physical properties of water from a beneficial state to one that is dangerous to organisms relying on water for their well being. There are two basic forms of water pollution; (1) changing the types and amounts of materials carried by water, and (2) altering the physical characteristics of a body of water. This manual will attempt to make you aware of some of the sources of water pollution.

Water pollution comes in many forms, from a wide range of sources. Agriculture may contribute to water pollution from feedlots, pastures, and croplands. Mining, petroleum drilling, and landfills may also be major sources ofwater pollution. Otherwater pollution sources, related to humans, are sanitary sewers, storm sewers, industry, and construction.

To further our examination of sources of water pollution, let's look at how much pollution comes from various sources. The 1990 EPA report on national water quality suggests that pollution of streams and rivers comes mostly from agriculture (more than 50%). The next highest source was municipal sources (about 12 %). **Groundwater** contamination is from several sources, including agricultural activities, storage tank leakage, industrial waste, sewer and septic leakage, leaching from landfills, mining, and many other sources (Environmental Protection Agency 1990).

The remainder of this section describes some of the most common forms of water pollution:

Organic Waste Products

Organic waste products are materials that result from the natural processes of both plants and animals. There are far too many forms of organic waste products to mention all of them here. Examples of some organic products that commonly enter waters are; sewage, runoff from livestock wastes, food waste, decomposing plants and animals, and grass clippings. The danger to water quality is due to byproducts formed from organic materials in water. This process uses up dissolved oxygen in the water needed by aquatic life. This process may also yield **toxic** levels of nutrients such as nitrates. Small amounts of organic products may enrich life but largeramounts are a detriment to the well being of the aquatic environment.

Habitat modification

When the habitat changes in or around bodies of water, effects can occur that change the quality of water. Examples of habitat modifications that have the potential to compromise water quality are loss of stream side vegetation, **siltation**, smothering bottom dwelling organisms, increased water temperature, and changing of other physical properties of the water. One or more of these alterations can cause a shift of the natural balance in the aquatic environment. This natural balance provides a system that maintains water quality for living organisms.

Fertilizers

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High levels of nitrate, from NO_3 and NH_4, in surface or ground water and excess phosphate, from PO_4, in surface water are common pollutants associated with fertilizers. Nitrates from fertilizers and several **pesticide** chemicals have begun to show up in some of the larger aquifers in the United States. Figure 1 shows areas of ground water in the U.S. Recent changes in regulation of fertilizers and chemicals have come about due to concern about the nation's ground water. **Water pollution** associated with fertilizers usually occurs because of adding more nutrients to the soil than can be taken up by the crop. These materials travel from fields to ground water or surface water, by water, by the process of **leaching** or runoff. Another common source of pollution by nitrates and phosphate is from sewage systems.

Nitrates are not highly toxic to animal life, but they may easily convert to more **toxic** nitrites in the stomachs of ruminant animals, and under certain conditions in humans. Nitrogen applied to the soil is usually in the form of NH_4, NO_2, or NO_3. In typical temperate climate soil, NH_4 tends to leach slowly and is not much of a threat to the **groundwater**, except when there is excess rainfall or irrigation. However, even nitrogen applied as NH_4 is readily converted by some soil bacteria to NO_2, or NO_3. These two forms of nitrogen compounds may travel more rapidly through the soil if there is an excess amount that is not taken up by plants.

The more common problem is when these nitrogen products travel into surface waters by way of runoff. Nitrogen is often the limiting element in **eutrophication** of coastal marine waters. The missing element for a large increase in growth of algae in these waters becomes present when nitrogen products reach coastal waters. This in turn can cause a cut off of oxygen and sunlight from other inhabitants of that water.

Phosphate is often used by agriculture in forms that are very water soluble. In a period of a few weeks or months, phosphate added to the soil converts to less soluble forms if it has not been taken up by plants. Unused phosphate often precipitates with calcium, iron, and aluminum, or is incorporated into organic matter and is essentially insoluble. At this point, phosphate poses little danger to the water system. The exception to this situation occurs in very sandy soils, where some **leaching** may take place. A more serious problem connected with phosphate is when it enters surface waters by way of runoff. Phosphate is often the limiting compound in **eutrophication** of freshwater, as nitrogen is in marine waters. The result of large amounts ofphosphate reaching surface waters is often a great increase in growth of algae and the reduction of other life forms in these waters.

The real dangers from the compounds outlined above is in misuse rather than in their use. If applications of fertilizers are in amounts that plants use, there is really little danger to our ground waters. The only danger with proper application amounts is, therefore, from runoff. This should be taken into account when applying fertilizers to areas that are prone to runoff into surface waters.

Nutrients found in fertilizers (and some soap and detergents) such as nitrates and phosphates may become major sources of **water pollution**. Initial thoughts might tell us that if fertilizers wash into the water system, they are just transported to other plants found downstream. This would not appear to cause problems, but these nutrients also come in contact with aquatic plants. The result of fertilizing aquatic plants, such as algae, is an unusual growth of **non-target** plants. This can lead to choking water ways, using up dissolved oxygen, and cutting off light to deeper waters. This results in the elimination of vital resources to invertebrates, fish and other plants living in the over-fertilized body of water. This can cause poisoning of the affected water and additional pollution from sudden die-off and subsequent decomposition of large numbers of aquatic organisms.

Toxic chemicals: Heavy metals

There are many **toxic** chemicals that can enter the water system, most commonly by the actions of humans. Heavy metals, such as mercury, lead, selenium, and cadmium, are of particular interest because they can be very hazardous to humans, even in very small amounts. These metals are a byproduct of industrial life, but when they enter bodies of water, they are often taken up by aquatic organisms and passed up the food chain. This process is known as **bioaccumulation**, in which these materials are taken up by animal life and not eliminated. This accumulation occurs until lethal levels are reached or the animal is eaten by another animal higher up the food chain (sometimes humans). These materials also can come directly from our faucets, if the water is from a contaminated source. In this case the metals accumulate in our bodies, until toxic levels are reached. There are also other toxic chemicals that are byproducts of human activities and are hazardous to us when they enter our waters. Some of these include

PCBs, dioxin, and petroleum products.

Toxic chemicals: Pesticides

Pesticides are products used to kill pest species, such as insects (insecticides), nematodes (nematicides), rodents (rodenticides), fungi (fungicides) and plants (herbicides).

Table 1. Approximate volumes of the most used insecticides in the United States in 1991 and 1992 (Source of this information is the Untied States Environmental Protection Agency 1992).

PESTICIDE	Usage in Million Pounds Active Ingredient (ave. 1991-1992)
Chlorpyrifos	15.0
Carbaryl	12.5
Malathion	12.5
Terbufos	10.0

Pesticides are an area of concern for maintaining water quality because of their widespread use. These chemicals are used in both urban areas and agricultural settings. Pesticides are used by a wide spectrum of users, from individuals, to companies, to municipalities. Table 1 gives an example of the amount of pesticides used in the United States. This table shows only four of the many insecticides used, but should give an example of the large amount of insecticide being applied. Insecticide use does not represent pollution being introduced into waters, but instead represents potential for **water pollution** if this insecticide is not used properly.

Table 2. Properties of some of the most commonly used insecticides in Texas (Texas Agricultural Extension Service 1993 and Ware 1992.

CHEMICAL	1990 USE[1]	SOLUBILITY[2]	K_{OC}[3]	HALF-LIFE[4]
Carbaryl (Sevin®)	595,225	low	high	10 days
Chlorothalonil (Bravo®)	204,342	very low	low	30 days
Diazinon	39,308	low	low	40 days
Disulfoton (Di-Syston®)	360,714	low	medium	30 days
Malathion	314,365	low	low	1 day
Methamidophos (Monitor®)	11,932	high	very high	6 days
Methyl Parathion (Penncap-M	676,037	low	low	5 days

®)				
PCNB (Terraclor®, Turfcide®)	393,137	very low	low	21 days
Phorate (Thimet®)	75,134	low	low	60 days

[1] Total Pounds active ingredient used in Texas

[2] Danger of leaching due to low solubility

[3] Danger of leaching due to soil adsorption properties

[4] Half-life in days under normal field conditions

A list of a few commonly used pesticides and their potential as water pollutants is presented in Table 2. This list should indicate the relative dangers of some of the pesticides that are available for use. Note that Table 2 does not include all chemicals that are available, but instead serves to show properties of some pesticides in common use.

This manual is not trying to persuade you to use only pesticides that pose little danger as potential water pollutants. There are some instances where few choices exist to control a **target pest**. If the only material available for control of an unwanted pest is a **pesticide** with high potential to become a water pollutant, then there is really no option but to use it, if the pest must be eliminated. However, with information about the **water pollution** potential of pesticides, you can plan its use to minimize the chance of these pesticides actually becoming water pollutants. Guidelines are given at the end of this manual that should be followed when using any pesticide, especially those with a high potential to become a source of pollution.

Pesticide Properties

Before continuing any further, the question of why there is concern about pesticides entering the water system needs to be answered. The role of pesticides is to kill pests, but the properties that make these pesticides efficient at controlling pests may also pose a danger to other animal life, including humans. Many pesticides (especially animal pesticides such as insecticides, nematicides, and rodenticides) are not specific to their target pest, making them potentially at least somewhat dangerous to other animal life. The difference is often a matter of quantity. A certain amount of a given **pesticide** will kill a **target pest**, but may be within the limits of human tolerance. However, constant exposure may still cause chronic problems that are often more severe than acute, short term exposure problems. Even if humans are able to tolerate the levels used to kill pests, these substances are still toxins that can have a detrimental effect to the health of **non-target** animals, such as pets and livestock. The real danger begins when these pesticides do not remain in the area of application, but instead move into other areas, such as water, where they become a source of exposure to other organisms. Once water contamination has occurred it is very difficult and expensive to clean-up.

There are several properties of pesticides that allow understanding of what they contain and how dangerous they are to humans. These concepts are given in the rest of this section. An understanding of what these concepts mean allows for the evaluation of the dangers presented by specific chemicals.

Active Ingredient

The active ingredient is the chemical or chemical compound that performs the intended purpose of a substance. In the case of a **pesticide**, the active ingredient is the material intended to kill the **target pest**. It is the active ingredient that is **toxic** to the pest and has the potential to be dangerous to other animals. The other substances in a pesticide are usually **inert** (not reactive) and are used to carry the **toxin** (active ingredient) while making its application easier. The activeingredient is usually a very small percentage of the total ingredients in a pesticide. An example of this concept is a simple insecticide bait made with boric acid and sugar water that can be used to kill several insect pests. The actual amount of boric acid (active ingredient) might be as low as 1 percent. The other 99 percent is a carrier for the active ingredient. This carrier is sugar water, which also acts as an attractant for the insect target pest. Sugar water does not function as a killing agent for the target pest but allows delivery of a small, but effective amount of toxin.

Toxicity

There are several terms that deal with the toxicity of a pesticide. These terms are defined for toxicity to specified animals after exposure of a specified time. These toxicity terms can apply to target pests or **non-target** animals, including humans. The most common of these toxicity terms are LD_{50} and LC_{50}.

LD_{50}

The LD_{50} is a measure of the a substance's toxicity. LD_{50} stands for the dose of a substance, such as a **pesticide**, that kills one-half of the animals tested. The LD_{50} for a specified animal is the amount that must be in or on the body of that type of animal to kill half of the affected population within a given amount of time. Comparing the LD_{50} of chemicals in animals gives a relative ranking of the toxicity to each animal. For example, the LD_{50} for ethyl alcohol in rats is 1400 mg/kg, which is less **toxic** than DDT, with an LD_{50} in rats of 113 mg/kg (the term "mg/kg" refers to the number of milligrams of **toxin** per kilogram of the animal tested). LD_{50}'s are often calculated using rats, because humans cannot be tested in a way that will test how many are killed, given a certain dose. Using rats as a test standard for LD_{50}'s is common but other animals such as trout, bluegill, and daphnia are also sometimes used. The information from LD_{50} is calculated for rats and can be used to estimate the LD_{50} for humans by multiplying by 70 (the average kilogram mass of humans). This assumes, of course, that humans are sensitive to the same substances as rats. Substances that are toxic to one mammal are often toxic to another. This conversion is an estimate that might not accurately calculate limits for human exposure. Table 3 gives a comparative toxicity of pesticides. Nearly ever substance has an LD_{50} at a certain dose, even substances such as sugar (LD_{50} =34,600 g/kg body weight) can be lethal at extreme doses. In examining LD_{50}'s the question to be asked is: How likely are humans and other animals to come in contact with a dangerous amount of a particular substance?

Table 3. Comparative toxicity of pesticides and natural products (1995 Farm Chemicals Handbook; Gosselin et al. 1984; SIPRI 1973).

PESTICIDE	LD_{50} (Rat) in mg/kg	Other Product With About Equal Toxicity
TCDD (Dioxin®)	0.0002	Ricin, pure (castor bean extract)
Flocoumafen (Storm®)	0.25	Strychnine
Sarin (GB nerve gas)	0.2	Black widow spider venom
Aldicarb (Temik®)	0.9	Nicotine alkaloid (free base)
Phorate (Thimet®)	1.0	Heroin
Parathion	2.0	Morphine
Carbofuran (Furadan®)	8	Codeine
Nicotine sulfate(Black leaf 40®)	50	Caffeine
Paraquat (Gramoxone®)	150	Benadryl (antihistamine)
Carbaryl (Sevin®)	250	Vitamin A
Acephate (Orthene®)	833	Salt substitute (KCl)
Allethrin (Pynamin®, Raid®)	1,160	Gasoline
Diazinon	1,250	Tobacco
Malathion	5,500	Caster oil
Ferbam (fungicide)	16,900	Mineral oil
Methoprene (Altosid®, Precor®)	34,600	Sugar
Pheromones (Checkmate®)	103,750	Water

LC_{50}

LC_{50} is another measure of toxicity. LC_{50} stands for the lethal concentration of a material to kill one-half of the animals tested in a specified amount of time. LC_{50} is the amount of a material that comes in contact with the animal being tested that will kill one-half the population affected. This lethal concentration may be in a medium such as the air or a body of water. In the context of this manual, it will deal with the amount of a substance in water that would kill animals that live in that body of water. In other words, if the LC_{50} is present for a type of fish, then the concentration of a **toxin** in the water is at a level that will kill one-half of that type of fish that are present in that body of water. Some commonly used insecticides are given with their properties and LC_{50} for fish in Table 2. Fish, such as bluegill, are often standards for tests of LC_{50}'s but other animals such as daphnia are also commonly used.

Formulation

Pesticides may be in several physical forms or formulations. They may be water dispersible granules, dusts, aerosols, emulsifable concentrates, flowable concentrates, solutions, solid baits, or liquid baits. They are sold in these forms because of advantages they offer to their application. Formulations influence the deposition on the soil or plant surface. In turn, they may regulate or influence its uptake by the plant or its movement into the upper soil profile. Formulations also determine the washoff or runoff characteristics of a **pesticide** in rain or irrigation water.

Effective dose

The effective dose is the amount needed to kill a **target pest**. Amounts less than the effective dose will likely not kill the target pest. In this case, the pesticide is applied without the ability to achieve the intended results, elimination of the pest. Instead, this pesticide is added to the environment for no gain. Amounts greater than the effective dose will not necessarily kill the target pest better. Instead, this larger dose may kill more **non-target** pests, cost more money to apply, and pollute the environment.

Half-life

The half-life is one measure of the **persistence** of a chemical. The half-life of a substance is the time required for that substance to degrade to one-half its previous concentration. In other words, if a pesticide has a half-life of 10 days, half of the pesticide normally breaks down by 10 days after application. After this time, the pesticide continues to break down at the same rate. In general, the longer the half-life, the greater the potential for movement, simply because it is present in the environment for a longer time. The half-life of a material such as a pesticide is not an absolute factor, however. Soil moisture, temperature, available oxygen, microbial populations, soil pH, photo degradation and other factors may cause the half-life of a substance to vary.

ADI

ADI is an old term that stands for *Acceptable Daily Intake*. This is now a defunct term for a reference dose that produces negligible toxicological effects. It is used to establish a neglible residue level for **pesticide** tolerances on human food or animal feed products. Although the term

ADI is still in use by many professions, it is no longer in official use by pesticide regulators. It has been replaced by the term *neglible residue*.

The term *negligible residue* means any amount of a pesticide chemical remaining in or on a raw agricultural commodity or group of raw agricultural commodities that would result in a daily intake regarded as toxicologically insignificant on the basis of scientific judgment of adequate safety data. Ordinarily this will add to the diet an amount which will be less than 1/2,000th of the amount that has been demonstrated to have no effect from feeding studies on the most sensitive animal species tested. Such toxicity studies shall usually include at least 90-day feeding studies in two species of mammals.

MCL

MCL stands for *Maximum Contaminant Level*. This term refers to toxic chemicals regulated as contaminants under the Safe Drinking Water Act (SDWA). Although MCLs do not apply to pesticides specifically, they apply in a general sense. Under SDWA, pesticides are grouped with a larger collection of **toxic** chemicals that can affect human health when found at certain specific concentrations above established MCLs in drinking water. The Safe Drinking Water Act and the associated regulations try to prevent contamination of drinking water from reaching MCLs through continuous monitoring of water supplies. Regulations under the SDWA establish MCLs in much the same way FIFRA, FDCA, and the Food Quality Protection Act of 1996 establish pesticide tolerances with neglible residues.

Classes of Pesticides

Insecticides

There are several categories of pesticides designed to control different groups of animals. These categories include insecticides (insects), nematicides (nematodes), and rodenticides (rodents). This manual refers to characteristics of insecticides, but pesticides designed to kill animals other than insects have similar characteristics and properties. Therefore, when talking about insecticides, we also cover properties of pesticides for other animals.

Insecticides applied to crops and in urban areas do not just disappear. It's true that these pesticides break down after a given time, but some of these pesticides are very persistent and remain in the environment for long periods. **Persistence** is a good quality for some pesticides because it means that it remains effective in killing pests for a long time. However, this attribute means that pesticides are around long enough to enter water sources under some conditions. This also means that pesticides entering water may remain **toxic** longer. Rainfall and irrigation can wash pesticides from sites of application into the water system. These pesticides can accumulate in invertebrates and fish; and pass through the food chain to birds, mammals, and even humans.

Herbicides

Herbicides are substances that cause disruption or stoppage of normal plant growth. The extent to which a plant suffers from the effects of a herbicide ranges from extremely little to the plant being highly sensitive, resulting in overall plant death. This range of susceptibility is often referred to as "selectivity". In other words, given herbicides will harm some plant but not others. Some herbicides are referred to as "non-selective" in that they are hazardous to most forms of plant life if applied at dosages recommended for weed control. However, herbicides, for the most part, work by affecting inherent processes to plants, not mammals or insects. This is the reason for their relatively low order of mammalian toxicity. The plant processes affected by herbicides require a great deal more discussion than what this manual will provide. Herbicides generally work by altering one or more of the following processes: Seedling growth, transport of water and nutrients, production of plant foods (photosynthesis), plant cell development, and plant protein synthesis.

The **persistence** of some herbicides can be looked upon as either a detriment or advantage. Obviously, the longer these materials remain active in the soil, the less appealing they are environmentally. However, to the farmer, weed control throughout the crop growing season (generally three to six months) is essential to ensure harvestability and his economic survival.

Table 4. Characteristics of some commonly used insecticides along with their relative toxicity to fish (Source of information is the U. S. Environmental Protection Agency 1992).

INSECTICIDE	Relative Runoff Potential	Relative Leaching Potential	Half-life in Days	Relative Toxicity to Fish[1]
Hydrdamethinon (Amdro®)	large	small	10	high
Diazinon	medium	large	30	high
Chlorpurifos (Durisban®)	large	small	30	very high
Malathion	small	small	1	very high
Acephate (Orthene®)	small	small	3	very low
Carbaryl (Sevin®)	medium	small	10	medium
Dimehoate (Cygon®)	small	medium	7	medium
Trichlorfon (Dylox®)	small	large	27	high
Dicofol (Kethane®)	large	small	60	high
Propargite (Omite®)	large	small	56	high

[1] Fish Toxicity based on catfish and bluegill. LC_{50} categories are rated as follows: very low = more than 100 mg/l, low = 10 to 10 mg/l, medium = 1 to 10 mg/l, high = 0.1 to 1 mg/l, very high = less than 0.1 mg/l.

It should be noted that the herbicide itself may not be as **toxic** as the **inert** materials in the herbicide formulation. Therefore, the formulation chosen for use may have more impact on the toxicity of the product than the active herbicide ingredient. Characteristics of some commonly used herbicides are given in Table 5.

Table 5. Characteristics of some commonly used herbicides, with relative toxicity to fish (Source of this information is the United States Environmental Protection Agency 1992).

Herbicide	Relative Runoff Potential	Relative Leaching Potential	Half-life in days	Relative Toxicity for Fish[1]
MSMA (Arsonate®)Bueno®)	large	small	100	very low
Benelin (Balan®)	large	small	30	very high
Dicamba Soluble Salt (Barrvel®)	small	large	14	low
2,4-D Dimethylamine Salt (Weedar®)	small	medium	10	very low
MCPP Soluble Amine Salt (Mecoprop®)	small	large	21	low
Pendimethalin	large	small	90	high
Glyphosate Amine Soluble Salt (Rounduup®)Kleenup®)	large	small	47	very low
Metribuzin (Sencor®)	medium	large	40	medium

[1] Relative toxicity for catfish and bluegill. LC_{50} is based on the following levels: very low = more than 100 mg/l, low = 10 to 100 mg/l, medium = 1 to10 mg/l, high = 0.1 to 1 mg/l, very high = less than 0.1 mg/l

Herbicides vary widely in their potential to enter water supplies. Some herbicides are water soluble enough to enter into solution with rainfall or irrigation water. Their final destination is highly dependent upon the conditions under which they are applied.

They can leach downward or move with the erosion of soil particles if applied to a relatively bare soil surface. The extent to which either of these events occurs depends upon several physical and chemical properties of both the soil and the herbicide. Herbicide applied to emerged plants is either intercepted and absorbed by plants or deposited on the soil surface. Many herbicides are "inactivated" once they reach the soil surface due to tight bonds that form between them and the soil clay and/or organic matter. Further explanation of herbicide fate is given in other sections of this manual.

Fungicides

Fungicides are substances used to suppress or kill a variety of microorganisms. Most of the target organisms are members of the biological kingdom that includes fungi related organisms. However, the legal definition is much broader. FIFRA defines fungi as "any non-chlorophyll-bearing thallophyte (that is, any non-chlorophyll-bearing plant of a lower order than mosses and liverworts), as for example, rust, smut, mildew, mold, yeast and bacteria, except those on or in living man and other animals and those on or in processed food, beverages, or pharmaceuticals."

Although the legal definition is somewhat outdated scientifically, it gives a very adequate view of the broad group of chemicals loosely classified as fungicides through their registration under FIFRA.

Fungicides are among the most common chemicals used. They have broader use than insecticides or herbicides. They are included in a variety of industry applications as preservatives. Among the industrial uses of fungicides are textiles, plastics, rubber, paint, adhesives, emulsion polymers, wood, leather, etching and printing, cosmetics, pharmaceuticals, and concrete construction materials. These uses exist outside the normally recognized uses of fungicides in plant and animal protection.

Fungicides include as targets a range of pests broader than insecticides. They cut across three of the five recognized biological kingdoms. Among the targets of fungicides are true fungi, yeasts, monerans, phytoplasmas, slime molds, actinomycetes, and bacteria.

Fungicides are an area of concern for maintaining water quality because of their wide use by agriculture and home owners. Fungicides present a clear danger of pollution through their introduction into waters by improper application, storage and disposal. However, additional pollution hazards exist from drift, leeching, and runoff from treated areas where applications have been legal and proper.

A list of common fungicides and their potential as water pollutants is in Table 6. This list indicates the relative dangers of some of the fungicides available for use by home owners, farmers and industry. Table 6 does not include all fungicides, but simply presents examples of some very common farm and home fungicides.

Table 6. Risk factors of some commonly used fungicides.

Fungicide	Chemical type	Hazards
Mancozeb	EBDC1	Carcinogenic impurity (Ethylenethiourea, ETU) Heavy metal (manganese & zinc) accumulation
Thiram	TMTD2	Neurotoxic Contact dermatitis

		Teratogen Reproductive effects
Benomyl	Benzimidazole	Teratogenic effects Embryotoxic effects Chromosomal aberrations
Thiophanate	Thiophanate	Mutagen, Teratogen, Cytogenic effects Teratogenic effects
PCNB	Organochlorine	Biomagnfication Estrogenic effects
PMA3	Organomercurial	Heavy metal poisoning, Biomagnfication
Fixed Copper	Inorganic	Phytotoxic Phytoplanktonic effects
Kitazin-P	Organophosphate	Anticholinergic, Chitin inhibitor, Toxic to aquatic organisms
Streptomycin	Biofungicide	Allergin
Triadimefon	triazole (sterol inhibitor)	.

1.Ethylenebisdithiocarbamate

2.Tetramethylthiuram disulfide, bis(dimethylcarbamoyl) disulfides

3.Phenyl mercuric acetate

This manual is not attempting to persuade you to avoid the use of fungicides. This is not possible in many cases, if you want to save your lawn, a valuable tree or shrub, your crops, or your garden. However, with the information about **water pollution** potential of fungicides, you can plan their use and minimize chances of these chemicals entering surface and ground water.

The processes affected by fungicides require a great deal more discussion than what this manual can offer. Fungicides work in a variety of ways. The ability of the target organisms to rapidly develop resistance has generated a wide variety of chemical actions. Fungicides generally target one or more biological processes in the target organisms. Generally they affect biochemical systems at the cellular level. Targets of fungicidal action include cell walls, enzyme and hormone systems, and the ability of the target organisms to grow and reproduce.

The **persistence** of some fungicides offers advantages and disadvantages to both the user and the environment. The more persistent fungicides present the hazard of remaining in the environment long enough to enter soil and water profiles. The most persistent fungicides, such as the mercurial compounds had the tendency to leave permanent residues in the soil that eventually entered surface and ground waters. These fungicides have largely disappeared.

It is also important to point out that the fungicide active ingredient may not be as **toxic** or as environmentally hazardous as some of the **inert** ingredients in the formulation. An example exists in many of the common seed treatments. A wide variety of fungicidal treatments are used in the prevention of seedling disease through seed treatment. A common inert ingredient in many of them is the pink dye, Rhodamine B. This dye is a toxic inert ingredient that EPA has placed on a special list of hazardous chemicals.

In view of the hazards presented by both active and inert ingredients in fungicide formulations, it is important to use care in selecting the formulation. The formulation chosen for use many have more impact on the toxicity or environmental effect of the product than the active ingredient alone.

How Pesticides Enter Waters

Pesticides can enter water through surface runoff or through **leaching**. These two fundamental processes are linked to the earth's hydrologic cycle. When we include urban water use in surface runoff, **pesticide** residues in municpal waste water fit the hydrologic model. Figure 2 shows the hydrologic cycle. This gives a graphic representation of the various routes water takes to reach a low point. When water enters an established body of water or backs-up behind a barrier, it carries with it the dissolved materials that it picked up in the media through which it flowed. Figure 3 shows the two routes pesticide pollutants may take to reach surface or ground waters.

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It is difficult to determine how materials that become water pollutants actually get into water sources. Often it is the action of water itself that causes pollutants to enter bodies of water. The source of water that transports pollutants may be natural, such as rainfall, or caused by humans, as in the case of irrigation or diversion of water. Pollutants also may enter bodies of water by wind or by their own passive movement.

Movement of pollutants is a complex system. To further complicate matters, pesticides can come from either point sources or non-point sources. Point sources are small, easily identified objects or areas of high pesticide concentration such as tanks, containers, or spills. Non-point sources are broad, undefined areas in which pesticide residues are present. Figure 4 shows graphic representation of both source types.

There are many factors that influence the potential for materials to move from one location to another. To make this problem even harder to understand, these factors must be considered together. Looking at only one factor is an over-simplification that will not lead to an accurate prediction of the movement of potential pollutants. There are several concepts that will help to understand the movement of pollutants into bodies of water. The following paragraphs review some of these concepts.

Surface runoff

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Any plumber will tell you that water always runs downhill. Water that flows across the surface, whether from rain, irrigation, or other water released onto the surface, always flows downhill until it meets with a barrier, a body of water, or begins to percolate into the soil. Some of these materials are those outlined in the previous section, which are potential water pollutants. Figures 1 and 2 show examples of surface runoff and how it can pick up and carry pesticides into surface or **groundwater**.

Leaching

Leaching is a process that occurs due to the movement of water because of precipitation or irrigation (Stiegler et al.).

This process takes place as water percolates from the surface through the soil until it either reaches a saturated soil layer, such as the **water table**, or attaches to soil particles (see Figure 5).

In the process of leaching, water soluble pesticides may be taken into solution and transported along with the percolating water (Figure 6). This is the same type of process used in making coffee. Water percolates through granules of coffee and as it makes its way through the coffee it carries with it materials that result in coffee. This water becomes coffee because of the water **solubility** of the material coming in contact with the water. The amount of materials transported through soils depends on several factors, including the amount of water applied or infiltrating; the adsorptive capacity of the soil; amount of organic matter in the soil; water solubility of the substances encountered; and permeability of the soil.

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Soil permeability is a function of soil texture; which depends on the sand, silt , and clay content. Water, and the products of **leaching**, reach the water table or are taken up by plants from the soil. When water reaches the **water table** with transported chemicals, the potential for **water pollution** occurs. The danger of this is that well water, which is the water source for many households, can be contaminated in this way.

Factors that Affect Pesticide Behavior in the Environment

Water solubility

The water **solubility** of a compound, such as an insecticide, is a measure of how easily it goes into solution with water. When these compounds go into solution they are capable of **leaching** or running off into bodies of water. Solubilities of materials, such as pesticides, are usually given in parts per million (ppm) or in some cases as milligrams per liter (mg/l). This is the number of milligrams that will dissolve in one liter of water at saturation.

Many systemic pesticides (Figure 7) are water soluble to allow them to be taken up into plants. Other pesticides are formulated in water soluble forms to facilitate their application in water mixtures or reduce their potential for damage to plant foliage. These water soluble pesticides can be readily dissolved in water and carried through the soil from one location to another (Figure 8).

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A general rule is that solubilities of 1 ppm or less tend to remain at the soil surface and will not leach downward. However, materials with low solubilities may still move by surface runoff. Materials with solubilities greater than 30 ppm are likely to leach. Materials with solubilities between 1 and 30 ppm will often leach to some extent, depending on the influence of other factors, such as soil type. These general rules are not absolutes. Other factors, like soil properties and other properties of the **pesticide**, must be considered to accurately determine if a material will move from its area of application.

Soil adsorption

Soil **adsorption** is the tendency of materials to attach to soil particle surfaces. If a substance stays in, or on, the soil, because of high soil adsorption, it is less likely to move into the water system, unless soil erosion occurs. Soil adsorption characteristics are known for many materials, such as pesticides that might be introduced onto the land. One of the measures of soil adsorption is K_{oc}, the **octanol water partition coefficient**. K_{oc} values greater than 1000 indicate a substance that very strongly attaches to the soil and is not likely to move unless soil erosion occurs. Values of K_{oc} less than 500 indicate substances that might move with water in the **leaching** process or move off-site with surface runoff. Values between these two categories may rely on other influences to determine if they move or stay attached to the soil. These generalities for movement of substances through the soil are not absolute. Other soil characteristics and chemical properties of both the soil and chemical must be considered in making accurate predictions of movement.

Soil variability

A soil's texture, structure, and organic matter content will influence a material's **leaching** potential and runoff ability. This manual does not attempt to give leaching and surface and runoff indices for different soils, but instead gives general guidelines to follow regardless of the soil type. If you have an interest in analyzing your soil to determine the characteristics it possesses for water quality risks, these ratings are in a USDA publication called *Soil Ratings for Determining Water Pollution Risks for Pesticides*. The exact amount of variability of characters between soils can be difficult to determine because of differences in soil texture, soil structure, porosity, organic matter content, and soil moisture. This makes the effects of soil variability hard to account for in determining what influence it may have on movement of materials through the soil. Soil variability may be difficult to assess, but there are still simple guidelines to use by instead focusing on properties of the potential pollutant. These material properties are usually easy to obtain from data supplied by manufacturers. This information is often found on the label of the product.

Materials with one or more of the following values suggest the possibility of leaching or runoff problems regardless of the soil type: Water **solubility** greater than 30 ppm, soil **adsorption** less than 300-500 K_{oc}, or half-life greater than 21 days. However, keep in mind that there is large variability in soils that may affect the potential for pollution.

Other factors influencing pollutant movement

Several other factors affect **leaching** potential of materials. Two of these other factors are very important. One is depth to ground water. Another is permeability of the material in the unsaturated soil layer. These factors tell how far materials must travel to become water pollutants and how quickly they might move to the ground water layer. Amount of rainfall and irrigation are also important in moving potential pollutants.

Water Quality Protection

Most water pollution does not come from the normal, correct usage of materials such as pesticides and fertilizers. Problems often arise from misuse or careless use of these materials. A checklist is presented to help protect the quality of our water. This checklist should serve as a guideline to safeguard the future of our water quality.

- Read all product labels and adhere to the rate recommendations.
- When possible, use pesticides and fertilizers with less potential for surface runoff or leaching.
- Use integrated pest management (IPM) tactics to control pests when possible.
- Avoid applying pesticides when conditions are most likely to promote runoff or excessive leaching.
- Use current soil test information to establish fertilizer needs for a given crop.
- Store potential water pollutants away from water sources, such as wells, ponds, and streams.

- Exercise judgment in spraying pesticides when it is windy (over 4 mph).
- Calibrate all pesticide application devices to ensure accurate distribution and eliminate misuse.
- Calibrate spray equipment to insure application of correct amounts of products.
- Prevent spills and leaks from spraying equipment.
- Ensure that product containers are leak free.
- Do not dispose of unwanted materials by dumping them in drains or on the ground. Use responsible disposal practices.
- Use non-toxic products when a choice is possible.

Glossary

Adsorption - The adhesion of materials to the surface of a solid.

Bioaccumulation - The storage or accumulation of materials in the tissues of living organisms, instead of elimination.

Carcinogenic - A property that makes a material more likely to cause cancer in humans or animals that are exposed to it.

Eutrophication - Supplying with nutrition to allow the flourishing of affected organisms.

Groundwater - A region within the earth that is wholly saturated with water.

Inert - A substance that is not reactive in the environment and does not contribute to the action of the active ingredient. Inert materials often function as carriers and for dilution of active ingredients.

Leaching - Dissolving and transport of materials by the action of percolating water.

Non-target - An organism towards which an application is directed.

Octanol water partition coefficient - A unit of measure of the tendency of materials to be attached to soil particle surfaces (soil adsorption).

Persistence - The ability of a substance to remain in its original form, without breaking down.

Pesticide - A material used to kill an unwanted pest.

Polluted - With certain properties or characteristics changed which makes it potentially detrimental to the health of organisms that use the changed substance.

Siltation - To cover with silt or mud.

Solubility - The ability to be put into solution.

Species specific - Directed towards a unique species.

Target pest - An unwanted species that an application is directed towards.

Toxic - Poisonous to an organism with which it comes in contact.

Toxin - A substance that is poisonous to a given organism.

Water pollution - A detrimental change of the chemical or physical properties of a specified water.

Water table - the upper limit of the saturated level of the soil.

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