Chapter 3: Background on pesticides

3.1 Definition and classification

According to Cunningham, *et al.* (2003), a pesticide is "*any chemical that kills, controls, drives away, or modifies the behavior of a pest*". There are different types of pesticides and a classification is offered according the target organism. A biocide is a chemical that kills a wide range of living organisms. More specific substances are named after their target organism. Herbicides are designed to kill plants, fungicides kill fungi, and insecticides kill insects. Specific pesticides include: acaricides, nematicides, rodenticides and avicides.

Another classification of pesticides is based on their chemical structure. The groups are:

Inorganic pesticides They include arsenic, copper and mercury compounds. Highly toxic biocides have the ability of remaining in the environment for extended periods of time. They are generally neurotoxins and even a single dose may cause permanent damage [Cunningham *et al.*, 2003].

Natural organic pesticides Mainly plant extracts. Some examples are nicotine and nicotinoid alkaloids from tobacco, rotenone from the roots of derris and cubé plants and pyrethrum, a complex of chemicals extracted from *Chrysanthemum cinerariaefolium*. [Cunningham *et al.*, 2003]. Even if natural, many of these compounds are toxic to humans and other life forms, recently rotenone has been linked to nerve damage and Parkinson's disease [IPM of Alaska, 2003].

Fumigants Generally small molecules such as carbon tetrachloride, carbon disulfide, ethylene dichloride, ethylene dibromides that gasify easily and penetrate rapidly into some materials. They are used to sterilize soil and prevent degradation of stored grain. These compounds are very dangerous for workers, and their use has been severely restricted or banned. [Cunningham *et al.*, 2003].

Chlorinated hydrocarbons They are synthetic organics containing chlorine. They inhibit nerve membrane ion transport and block nerve signal transmission. They may be persistent in the environment and are subjected to bioaccumulation. Many have been banned or restricted throughout the world, but some continue to be actively used. They include DDT, chlordane, aldrin, paradichlorobenzene, 2,4-dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid [Cunningham *et al.*, 2003].

Organophosphates Synthetic organics containing phosphorus complexes. They inhibit cholinesterase, an enzyme that regulates the peripheral nervous system. Extremely toxic to mammals, birds and fish (generally 10-100 times more poisonous than most chlorinated hydrocarbons) [Cunningham *et al.*, 2003]. They degrade easily, so their bioaccumulation is rare. Some examples are parathion, malathion, dichlorvos, dimethyldichlorovinylphophate (DDVP) and tetraethylpyrophosphate (TEPP).

Carbamates Derivatives of carbamic acid, they act in the same way as organophosphates and have low bioaccumulation rates. Generally toxic to bees. They include carbaryl, aldicarb, aminocarb and carbofuran.

Microbial agents/biological controls Living organisms that control pests. Bacteria, viruses and insects have been used as “natural” controls. They can act in 4 ways: as parasites of the pest, as predators, as pathogens or as weed feeders [Weeden *et al.*, 2005].

3.2 Pesticide history

Humans have used mechanisms to control pests since the beginning of agriculture. Smoke, salt, and animals are some of the ways in which bothersome organisms were controlled in the past. The earliest pest control strategies were conducted by the Summerians in 2500 B.C. who used sulfur compounds to control insects and mites. Greeks and Romans used oil sprays, ash and sulfur ointments and lime to protect themselves and their crops [Cunningham *et al.*, 2003].

In the early 1930's the chemical pest control era as we know it began. DDT was discovered as an effective insecticide in 1934 by the Swiss chemist Paul Müller. DDT was used in Switzerland to control potato beetles in 1939 and commercial production began in 1943 [Cunningham *et al.*, 2003]. DDT made a revolution in the world, it was an efficient and stable compound that was easily spread over a wide area. It was effectively used in tropical countries to combat the *anopheles* mosquito, which transmits malaria. In 1944, the first hormone based pesticide, 2,4-D, was introduced. Two years later, Switzerland reported the first case of pesticide-resistance, houseflies were not being affected by DDT anymore [Dent]. During the 1950's and 1960's there were numerous reports on DDT resistant plagues, and in 1962, Rachel Carson published "Silent Spring". This book created an awareness revolution by pointing out pesticides as the reason for the systematic poisoning of the ecosystem, ultimately reducing the bird population due to eggshell defects. In the following years, new types of pesticides were developed (1973-1975, synthetic pyrethroids, [Dent]). During this time, new approaches such as "integrated pest management" were developed and adopted throughout the world to reduce pesticide consumption and increase efficiency in the control of pests.

3.3 Health/environmental problems associated with pesticide use

Human health has been one of the most discussed issues related to pesticide use worldwide. The possibility of intoxication can come from three sources: 1)by consuming food cultivated with agrochemicals, 2) by exposure during their application and 3) the consumption of intoxicated species. Cunningham *et al.* (2003) divides human health problems into two categories:

1) Short-term effects, including acute poisoning and illnesses caused by relatively high doses and accidental exposures.

2) Long-term effects of chronic exposure to low dosage. Some suspected diseases linked to this exposure include cancer, birth defects, immunological problems and Parkinson's disease.

According to the United Nations "An estimated 1 to 5 million cases of pesticide poisoning occur every year, resulting in several thousand fatalities among agricultural workers." (Northoff and Williams, 2004). Pesticide toxicity depends in factors such as the route of exposure (inhaled, drank, skin contact), concentration and time of exposure.

The environmental fate of all chemical substances depends on their physical and chemical characteristics. Their solubility in water, size, and physical state are all properties that determine whether a pesticide will be persistent,(i.e if it will stay in the soil, water or air) and if it will be available to organisms. Table 3-1 shows the physico-chemical properties and environmental fate of pesticides.

Table 3-1. Physico-chemical properties and environmental fate of pesticides [INE, 1996]

Properties	Implications
Water solubility	Pesticides with an aqueous solubility greater than 500 mg/L are very mobile in soils and other elements of the ecosystems. Their largest concentration is found in aquatic ecosystems. Pesticides with an aqueous solubility greater than 25 mg/L (generally the organophosphates) are not persistent in living organisms. Pesticides with an aqueous solubility of less than 25 mg/L (organochlorides) tend to be immobilized in soils and concentrate in living organisms.
Lipid / water partition coefficient	This coefficient indirectly gives information about the solubilization and distribution of a pesticide in a living organism. Pesticides with a coefficient greater than 1 (aldrin and DDT) are liposoluble and can be easily absorbed by biological membranes and accumulated in fatty tissue, thus contributing to bioaccumulation.
Vapor pressure	Pesticides with a vapor pressure greater than 10^{-3} mm Hg at 25°C are very volatile. They have great mobility and disperse towards the atmosphere. The ones with a vapor pressure between 10^{-4} and 10^{-6} mm Hg at 25°C are less mobile. Compounds with vapor pressures lower than 10^{-7} are more persistent in soils and water. (i.e. herbicides and triazines)
Dissociation and ionization	When compounds solubilize, they may or may not dissociate. The ones that do not dissociate are non-ionic compounds, without charge. The ones that do are ionic and may be either cationic (positively charged) or anionic (negatively charged). Anionic pesticides (like the phenoxyacetics) and the non-ionic are mobile in soils, while the cationic are adsorbed in the soil, and inmobilized (such as paraquat).
Degradability	This property (by chemical, biological or photo degradation) gives information on the compound's ability to degrade and diminish its activity. Malathion, parathion and pyrethrines degrade diminishing activities.

With the information in Table 3-1, the environmental fate of pesticides may be assessed. Other important features include the mode of application (liquid, solid, aerosol), toxicity to organisms, and its concentration. Ecosystem disruption depends on these factors, so each active ingredient must be considered individually for different scenarios. Some environmental problems associated with pesticides are:

Contamination of food with pesticides.

Negative effects to non-target organisms.

Bioaccumulation.

Creation of resistant strains of plagues.

3.4 Mexico and pesticides

In recent years, Mexico has increased its consumption of agrochemicals in general. Statistics provided by the *Instituto Nacional de Estadística, Geografía e Informática* (*INEGI*) show, in particular, a growth of pesticide use of 74.35% from 1997 to 2002. Table 3-2 shows the increase in the usage of these types of chemicals and tendencies of use of other agrochemicals.

Table 3-2. Fertilizer and pesticide production by type of product. 1997-2002 [INEGI, 2003].

Product (tons)	1997	1998	1999	2000	2001	2002 P/
Nitrogen-based fertilizers	2,333,867	1,901,547	1,261,766	542,296	484,513	387,109
Ammonium sulfate	889,616	725,016	589,068	444,669	484,513	387,109
Ammonium nitrate	402,506	368,729	330,271	90,725	NA	NA
Urea	1,041,745	807,802	342,427	6,902	NA	NA
Phosphate-based fertilizers	847,460	901,192	917,480	963,432	774,892	253,712
Superphosphated	NA	NA	NA	414,226	334,368	242,268
Triple superphosphated	270,846	273,141	248,305	NA	NA	NA

Formulas and Complexes	576,614	628,051	669,175	549,206	440,524	11,444
Insecticides	19,453	18,852	23,064	18,878	15,226	16,273
Liquid for agriculture	9,173	8,504	9,150	10,051	7,256	6,864
Dust for agriculture	10,280	10,348	13,914	8,827	7,970	9,409
Pesticides	12,321	16,554	17,002	19,760	19,906	21,482
NA	*Not available*					
P/	*Preliminary data*					

According to information provided by the *Asociación Mexicana de la Industria Fitosanitaria A.C.* (AMIFAC) in Mexico approximately 40 million agrochemical containers are used per year, which represents 4000 tons/year. Of these, 80% are plastic, 15% metal and 5% paper [AMIFAC, 2005]. They are mainly used in corn, sugarcane and sorghum.

3.5 2,4-D

The common name for 2, 4-dichlorophenoxyacetic acid is 2,4-D, typically formulated as the amine salt or ester form of the compound. Figure 3-1 shows its chemical structure.

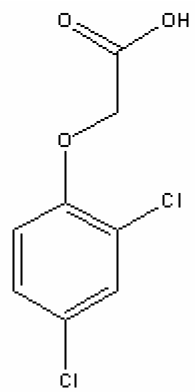

Figure 3-1. Chemical structure of the herbicide 2,4-diphenoxyacetic acid.

According to the US Department of Agriculture (USDA), Forest Service's pesticide fact sheet, 2,4-D is used to control broadleaf weeds, grasses and other monocots, woody plants, aquatic weeds and non-flowering plants. Furthermore, the USDA informs that 2,4-D degrades rapidly in soil and its capacity to contaminate ground-water is limited, because even if it has high mobility through the soil, microorganisms are able to degrade it. In water systems, 2,4-D may be detected up to six months later in still water, but dissipates quickly in moving water. In humans, acute exposure to 2,4-D has caused death, and in chronic intoxication liver, kidney, digestive, muscular and nervous system damage has been reported. [USDA, 2005].

2,4-D was the first mass-use herbicide introduced in 1946, and since then, has become the most widely used herbicide worldwide [Industry Task Force, 2005]. In Mexico 2,4-D is one of the most widely used pesticides; according to the *Instituto Nacional de Estadística, Geografía e Informática* and the *Secretaría de Medio Ambiente, Recursos Naturales y Pesca*, in 1995, 2,4-D accounted for 16.09% of all the active ingredients present in herbicides [INEGI and SEMARNAT, 1997]. Meanwhile, 2,4-D has been banned in Denmark, Norway and Kuwait, while Sweden cancelled it [PAN, 2005].

Commercial names in Mexico for 2,4-D are given in Appendix B. They include 31 brands for the active ingredient alone and 19 names for combined active ingredients products that contain 2,4-D. These sum 50 different forms in which this herbicide may be purchased in Mexico.

3.6 Atrazine

Atrazine is a selective herbicide used to control broadleaf plants and grassy weeds. Its chemical name is 2-Chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine. Figure 3-2 shows its chemical structure.

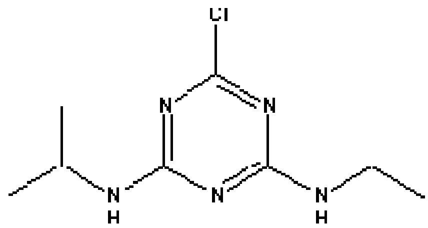

Figure 3-2. Chemical structure of the herbicide atrazine.

According to the U.S. Environmental Protection Agency (EPA), atrazine "is persistent in soil with a half-life exceeding 1-year under some conditions. Atrazine is also mobile since it can be transported to surface water via runoff, spray drift and atmospheric transport and is frequently detected in rainfall. It can also leach into groundwater. These characteristics, together with atrazine's level of use, contribute to widespread water contamination" [EPA, 2002]. Furthermore atrazine may represent contamination in water systems due to "the resistance of atrazine to abiotic hydrolysis and to direct aqueous photolysis, its moderate susceptibility to biodegradation, and its limited volatilization potential" [EPA, 2002].

Atrazine is now banned in Angola, Denmark, Germany, Norway and Sweden; Austria cancelled it [PAN, 2005]. In Mexico, atrazine is the third most widely used active ingredient, making up 12.8% of the market [INEGI and SEMARNAT, 1997].

Commercial names in Mexico for atrazine are given in Appendix B. They include 16 brands for the active ingredient alone and 16 names for combined active ingredients products that contain atrazine. This sums up 32 different forms in which this herbicide may be purchased in the country.

Table 3-3 has a brief summary of the characteristics of the target pesticides.

Table 3-3. Summary of target herbicides information

Common name	Type of pesticide	Environmental toxicity	Human toxicity	% of use in Mexico	Banned/restricted in other countries[1]
2,4-D	Herbicide	Unlikely to represent hazard to water systems.	Moderately hazardous	16.09	5 countries
Atrazine	Herbicide	May represent hazard to water systems.	Unlikely to be hazardous	12.8	8 countries

[1]Pesticide Action Network, Pesticides Database. 2005

3.7 Container management

Currently, Mexico has no legislation over the specific management and disposal of pesticide containers. On october 8th 2003, the *Ley para la Prevención y Gestión Integral de los Residuos* [(LPGIR) Law for the Prevention and Integral Management of Residues] was published in the *Diario Oficial de la Federación*. It states (article 55) that: “ the containers that carried hazardous materials and that are not used for the same purpose and with the same substance will be considered as hazardous, except those that have been subjected to treatment for their reuse, recycling or final disposal". It also asserts (article 31, fraction IX) that: "pesticides and containers with pesticide residue are subjected to a [disposal] management plan".

In many instances pesticide containers are left in the fields together with other rubbish (Fig 3-3). Many peasants lack education in the hazards of pesticide use and container disposal. This creates contamination hot spots in the Mexican countryside (Figs 3-4, 3-5 and 3-6). In Mexico AMIFAC has launched disposal management education campaigns following precepts recommended in other countries like Canada, the United States, some European states and the United Nations. This method of disposal includes rinsing the container (triple or pressure), separately collecting the packaging and finishing with either high temperature incineration or recycling. In the United States, 27,215.52 tons of pesticide plastic has been recycled since 1989 [Ag.Professional Weekly, 2005].

Figure3-3. Pesticide bottles thrown in the field. Morelos Mexico.

Figure 3-4. Pesticide and soda bottle lying side by side on a field in Morelos state.

Figure 3-5. Pesticide bottle leaking into the ground. Morelos Mexico.

Figure 3-6. Empty plastic pesticide containers on the side of a rural road. Morelos Mexico.

3.7.1 Triple rinsing

Triple rinsing is the basic method for cleaning pesticide containers. The technique can be summarized as:

1. Remove the cap from the container, and drain remaining product into the spray tank for 30 seconds.
2. Fill the container 10% to 20% full of water or rinse solution and secure the cap back on.
3. Shake liquid inside the container to cleanse all the inside surface.
4. Remove the cap and add the rinsate to the spray tank, allowing it to drain for 30 more seconds.
5. Repeat steps 2 through 5 two more times, always allowing for 30 second drains.

6. Allow to dry and replace cap.

3.7.2 Pressure rinsing

1. Remove cap from the pesticide container. Empty the leftover into the spray tank allowing 30 seconds to drain.
2. Insert the pressure-rinser nozzle by puncturing through the lower side of the pesticide container.
3. Hold the container upside down over the spray tank so rinsate will slide into the tank.
4. Rinse for 30 seconds or more rotating the nozzle to reach all inside surfaces.
5. Rinse caps in a bucket of water for 1 minute or more and pour this water into the tank.
6. Let dry and replace the cap.

3.7.3 High temperature incinerating

Incineration in industrial furnaces can reach temperatures of 1500°C, where complete oxidation of elements occurs, thus effectively destroying materials without sub-products. In Mexico cement kilns are an option, though costly. In an interview with Eng. Alejandro Galindo Betancourt, coordinator of AMIFAC's program of agrochemical container management (PLAMEVA), the cost of incineration in a special furnace is of $3,500 MXN per ton, and in cement kilns is of $250 USD per ton [AMIFAC, 2005]. These quotations do not include transport or logistics expenses.

3.7.4 Recycling

Recycling of materials may only be done to perfectly rinsed and dry containers. Labels and caps should be removed since they are often made of different plastics or materials. Pesticide containers should only be recycled into other agrarian products such as: other containers, fence poles, road sign poles, pellets and others [AMIFAC, 2005]. The *Plan de Manejo de Envases Vacíos de Agroquímicos* (PLAMEVA) (Management plan for empty agrochemical containers), conducted by AMIFAC promotes recycling as the most efficient option for the end-of-life of agrochemical containers, and 66.87% of all the collected containers have had this end. Currently, they are giving cleansed rigid containers to two recycling companies: one in the state of Jalisco, the second in the state of Mexico.