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Assessing the Impacts of Unrestricted Pesticide Use in Small-Scale Agriculture on Water Quality and Associated Human Health and Ecological Implications in an Indigenous Village in Rural Panam[aacute]

Sarah Louise Watson

University of South Florida, sarah_watson@utexas.edu

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Assessing the Impacts of Unrestricted Pesticide Use in Small-Scale Agriculture on Water Quality
and Associated Human Health and Ecological Implications in an Indigenous Village in Rural
Panamá

by

Sarah Louise Watson

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Civil Engineering
Department of Civil and Environmental Engineering
College of Engineering
University of South Florida

Major Professor: Qiong Zhang, Ph.D.
James R. Mihelcic, Ph.D.
Ismael Hoare, Ph.D.

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Key words: fate and transport, risk assessment, ecotoxicity, rural gravity-fed water systems,
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ABSTRACT

In 2014, the global pesticide industry's projected worth is \$52 billion and by 2020, the developing world will make up one-third of the world's chemical production and consumption. Pesticides can have unintended negative consequences for human health and the environment, especially in the developing world where regulations are loose or nonexistent. One country with unrestricted use of pesticides is Panamá, especially in Santa Rosa de Cucunatí. In this indigenous village, small-scale farmers and ranchers spray paraquat, glyphosate, picloram, and 2,4-D at higher elevations than the spring water source of a gravity-fed water system, the river, and the village. The objective of this study was to estimate the concentration of these pesticides in the water system and the river and to perform a human health and ecological risk assessment.

Pesticide fate and transport models in the graphical user interface EXAMS-PRZMS Exposure Simulation Shell (EXPRESS), which was developed by the United States Environmental Protection Agency, were used to predict concentrations of the four mentioned pesticides in drinking water and the river using chemical properties, data from Food and Agriculture Organization and Smithsonian Tropical Research Institute, and the author's experience as a Peace Corps Volunteer. The results from Tier I model FQPA Index Reservoir Screening Tool (FIRST) were used to compare immediate and delayed rain events, noting minimal difference. The Tier II PRZM-EXAMS shell provided estimated drinking water concentration (EDWC) profiles. The paraquat profile was much lower than picloram, glyphosate, and 2,4-D, which had almost identical profiles with peak concentrations around 12 ppm and the average annual concentration 100 ppb.

Average Daily Dose (ADD) via drinking water was calculated for men, women, and children using model results and compared to the oral reference dose (RfD). ADDs only exceeded the RfD with maximum peak EDWCs, implying low risk. However, RfD was used to calculate a breakpoint concentration, the concentration at which each pesticide presents a risk to the consumer. This was then compared to the maximum peak (highest, i.e. worst-case scenario) and annual (lowest, i.e. best-case scenario) EDWC profiles. In the best-case scenario, glyphosate and picloram did not pose a threat, paraquat posed a moderate threat and 2,4-D posed a high threat, with the concentration exceeding the breakpoint for 90 percent of the years. With respect to the worst-case scenario, all four chemicals posed high threats to the consumer. Individual exposure via consumption of fish from the river was calculated using a calculated bioconcentration (BCF) factor and calculated breakpoint concentrations. For the best case scenario, picloram presented a low risk and 2,4-D presented a high risk but for the worst case, both of these chemicals presented a very high risk. An additive exposure of these two human health pathways found that for the best case scenario, exposure from most of the four chemicals did not approach the RfD. However, for the worst-case scenario the exposures were significantly higher than the oral RfD—therefore, between the lowest and the highest concentrations, the general population is at risk.

For the ecological risk assessment, the 96-hour peak profile was compared to the 96-hour lethal dose (LD50); glyphosate posed a high risk to fathead minnows and low risk to bluegills and 2,4-D presented a high risk to fathead minnows, low risk to channel catfish, and very high risk to bluegills. A more general risk assessment compared maximum peak and annual concentrations to the US EPA's aquatic life benchmarks. Glyphosate presented no threat and 2,4-D only presented a threat to plants. For picloram, fish were at very high risk at the chronic

level and low risk at the acute level, and plants were at moderate risk. Paraquat presented the most significant threat to aquatic life, exceeding benchmarks for all plants and invertebrates at the chronic level 100 percent of the time. It presented no threat to fish in the best-case scenario, but a high risk for fish at the chronic level in the worst case scenario, as well as very high risk for all invertebrates and plants. Improvements in application and watershed protection as part of a multi-disciplinary approach are proposed in place of technological mitigation strategies. Recommendations for future studies include the development of a developing-world context model and experimental studies in the developing world to compare to model results, where possible.

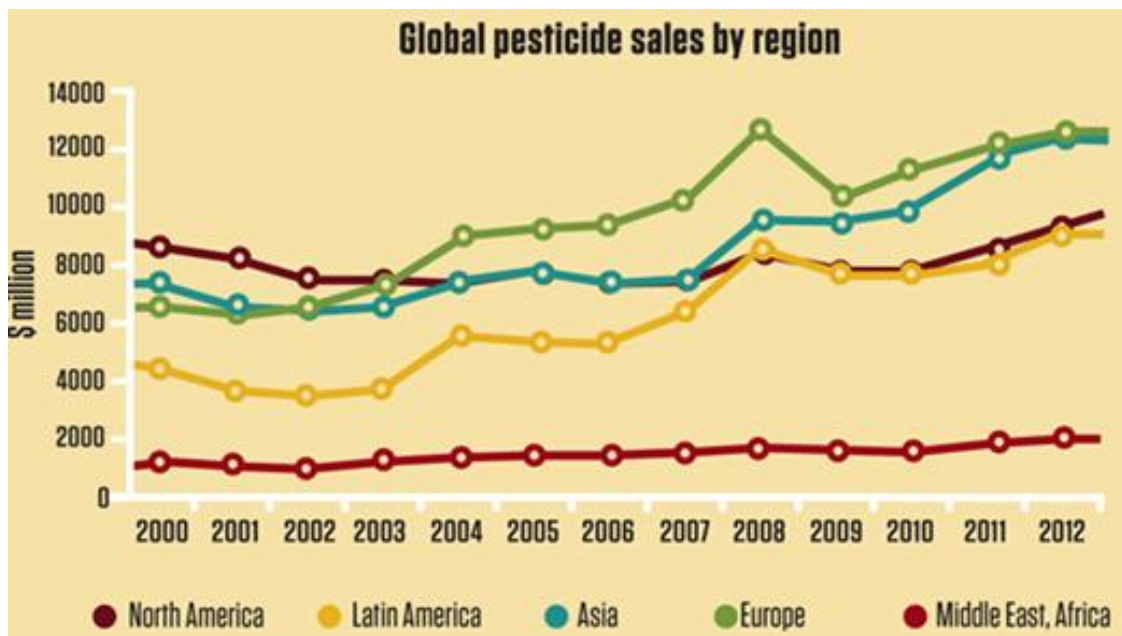
CHAPTER 1: INTRODUCTION

Worldwide, pesticides have helped achieve higher food productions, increased food security by reducing vulnerability of crops to plagues and pathogens, and lower morbidity and mortality rates for certain vector-borne diseases such as malaria. However, pesticides can have many adverse environmental impacts: persistence in soil can make once-rich soil unusable for farming, bioaccumulation can wipe out living creatures and sources of food, and runoff and groundwater infiltration can contaminate water, causing nutrient pollution (US EPA, 2005a). Additionally, pesticides have potential for various unintended negative consequences to human health ranging from respiratory issues, impairment to the central nervous system, developmental issues in babies and children, to types of cancer such as lymphoma (Bus & Hammond, 2007). Many of these unintended negative consequences are not yet fully understood.

In 2007, five billion pounds of pesticides were sprayed worldwide (US EPA, 2013) and in 2014 world demand is expected to reach \$52 billion (The Freedonia Group, Inc., 2010). In recent decades, the availability of pesticides has increased in developing countries, to the far-out reaches of the countryside where “subsistence” agriculture is still the lifestyle. Previously it was assumed that the poorest of the poor could not afford pesticides, but they are especially cheap in countries where regulations are loose. Sometimes they are given free of charge by government agencies (Mokhele, 2011; J. Girard, personal communication, April 11, 2011; Ruth Xochihua, personal communication, November 19, 2013) or are sold by agriculture supply stores that they are “pure medicine” for the crops, as it happens in Panamá (V. Quintero, personal communication, March 13, 2012). At times, pesticides that are banned or restricted for use in

developed countries are brought to developing countries for crops that are then shipped back to the developed world for sale (Wright, 1986) or return by atmospheric transport (Mihelcic, 1999)—this is referred to as “the circle of poison” (Wright, 1986).

Since 2000, pesticide sales in North America have only increased slightly and sales in Europe have increased by nearly \$6 billion (Figure 1). Sales in the Middle East and Africa have remained steady probably due to the fact that the majority of farmers in sub-Saharan Africa remain too poor to use pesticides on a regular basis. Pesticide sales in Asia have also increased substantially as they are highly dependent on pesticide use, which remains a significant public health issue. For example, in Sri Lanka in the 1990s, death by pesticide poisonings exceeded death by infectious diseases (Eddleston et al., 2002). Figure 1 shows that in the last five years, Latin America has started to approach North America in pesticide sales. This is alarming because pesticide use and sales in Latin America remain generally unregulated.



(Reproduced from Science, 2013)

Figure 1: Global Pesticide Sales by Region

By 2020, the developing world is projected to be responsible for one-third of the world's chemical production and consumption (including pesticides) (Rain, 2005). In the developing world, adverse environmental and health effects are typically greater due to laws that are non-existent or not enforced. Agricultural supply stores sell chemicals without restriction. Workers, who utilize agriculture chemicals, are typically untrained in chemical safety, do not wear personal protective equipment or know how to properly use or store chemicals, and sometimes are illiterate and unable to read the toxicity warning labels. In extreme cases, pesticides are used in suicide attempts.

Lack of regulation or sound chemical management for pesticides in developing countries is a critical issue that may hinder the sustainable development of those countries. Pesticide use can aid to achieve some of the Millennium Development Goals (MDGs), established in 2000 for international development and agreed upon by the United Nations (UN), such as eradicating extreme poverty and hunger and combating infectious diseases. However, unintended consequences of misuse of pesticides relate to all MDGs and have the potential to hinder their achievement (Table 1).

Table 1: How Pesticide Safety Pertains to the Millennium Development Goals

1	Eradicate Extreme Poverty and Hunger	Misuse by workers can impede their ability to work until death and overuse can hinder productivity of persons in poverty's farms.
2	Achieve Universal Primary Education	Chemical exposure can have serious, irreversible adverse effects on mental development, can lower aptitude and increase behavioral deficits.
3	Promote Gender Equality and Empower Women	Biologically, women absorb chemicals more in the body. Representing 60% of the agricultural workforce, women are more likely to be exposed.
4	Reduce Child Mortality	Children are most vulnerable to the adverse effects of misuse of pesticides, sometimes resulting in death.
5	Improve Maternal Health	Pesticides can cause reproductive issues and impede a mother's ability to fight off disease and increases maternal mortality.
6	Combat HIV/AIDS, Malaria, and other diseases	Pesticides may help to protect against vector-borne diseases, but if used incorrectly can do more harm than good and can cause disease.
7	Ensure Environmental Sustainability	Chemicals are already present in all ecosystems and will only increase with time, causing harm to plants, animals, and humans.
8	Global Partnership for Development	Existing and emerging sound chemical management policy is a global health concern in development platform.

(Adapted from Rain, 2005)

The World Health Organization's (WHO) International Program on Chemical Safety (IPCS), founded in 1980, rates hazardous pesticides as one of the top ten chemical or groups of chemicals of major public health concern worldwide (WHO, 2010). Around the same time as the founding of the IPCS, the Food and Agriculture Organization (FAO) of the UN released the International Code of Conduct on the Distribution and Use of Pesticides, intended to reduce negative impacts associated with pesticide use, specifically in developing countries. The proclamation is considered "the globally accepted standard for pesticide management" (Wesseling et al., 2005) and includes standards for national governments to enforce regarding registration of pesticides. However, this document generally serves only as recommendation, as registration of pesticides and poisonings in Central America do not comply with the code (Wesseling et al., 2005). Furthermore, most countries in Central America do not have their own legislation pertaining to pesticides but rather refer to the international legislation. In Central America, 98% of all pesticide poisonings go unreported (Science, 2013). El Salvador, Nicaragua, and Honduras have initiated efforts to restrict certain chemicals at the legislation level, while many countries lag behind (Wesseling et al., 2005).

One country with seemingly nonexistent regulations in relation to pesticide safety is Panamá. The Panamanian government only has legislation pertaining to the exportation and commercialization of agricultural products, establishing upper limits on residues of certain pesticides used. Panamá has a population of 3.8 million, approximately 75% of which live in urban areas (World Bank, 2014). Although Panamá has the highest GDP in Latin America and currently has ongoing high-profile projects such as the expansion of the Panamá Canal and an underground metro, it is home to the second worst wealth distribution of the region (CIA, 2014) and still has 27% of the population living below the poverty line (World Bank, 2014). One

group especially vulnerable to wealth inequality is the Emberá indigenous peoples (Table 2), which are the local peoples at the study site. One of the top environmental issues is water contamination by agricultural runoff, which kills marine life and contaminates drinking water with inadequate or often no treatment system at all (CIA, 2014). The WHO Guidelines for Drinking Water (2004) recently emphasized the importance of protecting drinking water in the developing world from chemicals, especially pesticides from agricultural runoff.

Table 2: Development Inequality between the Emberá and the National Averages (Ministerio de Salud, 2013)

	Emberá	Nationwide
Poverty	73.7%	25.8%
Access to Improved Water	28%	92.9%
Access to Improved Sanitation	58%	94.5%
Illiteracy	22.9%	5.5%
Primary School Dropout	14%	1.7%
Population Density (person/km²)	2.3	45.9
Life Expectancy (years)	66-69	76-79

The most rural and most impoverished workers remain the least regulated and most vulnerable to adverse effects of pesticide use. In the Darién province of Panamá, there is no industrial agriculture and the majority of the people dedicate themselves to subsistence agriculture, cattle farming, or fishing. In the rural areas, farmers and their families are exposed because pesticides are sold without restrictions and with no safety training on proper use of agricultural chemicals. Herbicides, such as paraquat, glyphosate, picloram, and 2,4-D, are sold and used in an area that was once entirely primary rainforest. Although occupational exposure is significant, exposure via drinking water may impact all community members who utilize community managed water systems. The primary sources of drinking water in rural Panamá are gravity-fed water systems or nearby rivers, which are typically surrounded by agricultural areas,

so the rural populations are vulnerable to ingestion of water contaminated by pesticides, especially in the rainy season when pesticides are used the most.

This study is significant because no water quality studies have been performed for the Darién province of Panamá, and studies on fate and transport of pesticides in water are very few in the developing world context (Batiha et al., 2008; Sangchan et al., 2012). This is the first study that investigates the effect of pesticide use on gravity-fed water systems in the developing world. A study such as this is also significant because local agencies such as the Ministry of Agriculture (*Ministerio de Desarrollo Agropecuario, MIDA*) and Ministry of Health (*Ministerio de Salud, MINSA*) have no plans to perform these types of studies, nor do they disseminate information about the topic (V. Quintero, personal communication, March 13, 2012).

This research explores the impact of the use of pesticides in small-scale agriculture on water quality of a gravity-fed water system and its human health and ecological implications in an indigenous village in rural Panamá. Chapter 2 explains the location of the study and the motivations, objectives, and hypotheses of this study. Chemicals of interest and pesticide-related studies executed in the developing world are also discussed. After explaining the details of the study site and an overview of existing models used in the developed world, theory, model selection of EXAMS-PRZM Exposure Simulation Shell (EXPRESS), major assumptions and data inputs as well as the risk assessment methods are detailed in Chapter 3. In Chapter 4, the results from EXPRESS are presented for the four chemicals of interest: paraquat, glyphosate, picloram, and 2,4-D and the human health and ecological risk assessment are presented before a brief explanation of limitations and public health and policy implications. Chapter 5 provides final conclusions of the study and recommendations for future studies.

CHAPTER 2: STUDY BACKGROUND

2.1 Study Site

In the Darién province, and most other parts of Panamá, the majority of the rural population dedicate themselves to agriculture. The most produced crops are rice and corn, followed by several root plants including cassava and yams, and occasionally sugar cane, coffee, cacao, and other fruits. Vegetables and colder-weather crops (potatoes, carrots, onions, etc.) are mostly grown in the Chiriquí province in the mountains, where industrial agriculture is mainstream (this will not be discussed in this study). Cattle-farming is also widely practiced, especially in the Darién, where large areas of rainforest are deforested and chemicals are sprayed for monoculture grass.

In what is now considered “ancient times” by Emberá indigenous people, some integrated pest management (IPM) methods were utilized to combat plagues from destroying crops (G. Bacorizo, personal communication, November 17, 2011). However, this has changed over recent years, especially in the last 40 years when previously protected areas of the primary rainforests of the Darien province were opened up to whoever could mark and clear the land. People from all corners of the country came for the free land, much of which was deforested for ranching. Shortly thereafter, pesticides were introduced to the area and became widely available without restriction (J. Barrigon, personal communication, June 20, 2012).

Farming and ranching activities are typically held in higher-elevation areas, and populations reside in lower elevation areas. This is especially true with the Emberá indigenous peoples, who live down by rivers (often in flood plains). Additionally, most of the water systems

in Panamá are gravity-fed, which are also situated at higher elevations but typically at lower elevations than the farm fields. Therefore, if farms that use pesticides surround a gravity-fed water system at its source, there is significant potential for contamination through runoff. In the Darién province, there is a very distinct difference between the rainy and dry seasons—and agricultural activities only take place in the rainy season because the dry season is too dry for crop production. This means that there is potential contamination from runoff as far as all the way down to the village and the river.

The particular site of interest is Santa Rosa de Cucunatí in the Darién province (Figure 2).



(Adapted from Centers for Disease Control and Prevention, 2013; Public Domain)

Figure 2: Geographic Location of Santa Rosa de Cucunatí, Darién, Panamá

Santa Rosa de Cucunatí is a small Emberá indigenous community where the author lived and worked as a Peace Corps Volunteer for two years as part of the University of South Florida

Master's International Program. The gravity-fed water system (aqueduct) of interest is a spring source with a small forested area but mostly surrounded by cattle ranching and small-scale agriculture activities. In general, the pesticides paraquat and glyphosate are used as herbicides in the smaller-scale agriculture of crops for consumption and in the lawns around the huts of the village. Picloram and 2,4-D are the two main ingredients in "Bulgrass", a herbicide sold in Panamá that is used extensively in pastures for livestock.

2.2 Motivations, Objectives, and Hypotheses

The motivation of this study is to reduce acute and chronic illnesses in men, women, and children caused by the unrestricted use of pesticides paraquat, glyphosate, picloram, and 2,4-D in the Darién province of Panamá and potentially in other developing world contexts.

The objectives of this study are to:

1. Estimate the concentrations of paraquat, glyphosate, picloram, 2,4-D in the gravity-fed water system and the river in the context of rural Panamá using the EXPRESS model
2. Explore the human health and ecological implications of the results of the model using standard risk assessment methods
3. Provide recommendations to reduce risk and therefore minimize negative human health and ecological impacts and for future studies

The hypotheses of this study are:

1. The pesticides in the gravity-fed water system of the study location are above the threshold concentrations for acceptable levels of drinking water.
2. The application of pesticides immediately before a rain event raises the concentration in the gravity-fed water system and the river more than if the rain event is delayed.

3. The concentrations of the pesticides in the river have the potential to kill off aquatic life in the river.
4. Due to the concentrations of pesticides in the river, eating fish and shrimp from the river present a risk to the villagers.
5. Alternative chemicals and alternative practices may help mitigate the adverse impacts of pesticide use on these sources of water.

2.3 Chemicals of Interest

The four chemicals of interest are herbicides—chemicals used to get rid of unwanted weeds before planting a crop or a monoculture grass. According to WHO, “the main trouble pesticides with regard to acute poisoning globally have been organochlorines (OC), organophosphates (OP), carbamates and paraquat” (Wesseling et al., 2005), and all four chemicals of interest fall into one of these categories. All chemicals of interest are on Pesticide Action Network International’s List of Highly Hazardous Pesticides (Pesticide Action Network).

2.3.1 Paraquat

1,1'-Dimethyl-4,4'-bipyridinium dichloride (paraquat), $C_{12}H_{14}Cl_2N_2$, is one of the most notorious pesticides in the world. Its toxicity has been studied for nearly 50 years (Clark et al., 1966): its ingestion can have adverse effects on the gastrointestinal tract, lungs, kidney, liver, heart, and brain (US EPA, 1997). Consequently, it is one of the top chemicals of choice for self-poisoning (suicides), a problem so severe that some developing countries have actually banned (Trinidad) or restricted sales (Samoa) of paraquat (Eddleston et al., 2002). More chronic health problems affect the central nervous system (CNS) and the brain, including Parkinson’s disease, gliomas, and neurobehavioral issues (McCormack et al., 2002; Lee et al., 2005; Brooks et al., 1998). A typical paraquat container is shown in Figure 3.



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Figure 3: Typical Container of Paraquat in the Developing World

Paraquat has been shown to partition into the organic matter in soil due to its high k_{oc} value ($k_{oc}=6,780$). It is resistant to both anaerobic and aerobic microbial degradation and does not photodegrade in aqueous solutions (US EPA, 1997). Therefore, it is a threat to biodiversity and surface water, especially via runoff. It has the seventh highest Environmental Impact Quotient (EIQ) out of hundreds of agricultural chemicals. EIQ is a parameter that combines farm worker exposure, a consumer component, and ecological toxicity, which include both groundwater and surface water factors. Paraquat scored very high in applicator effects and aquatic and ecological toxicity (Kovach et al., 1992). Additionally, several studies have documented paraquat's increasing resistance (Bishop et al., 1987; Fuerst & Vaught, 1990).

2.3.2 Glyphosate

N-(phosphonomethyl)glycine (glyphosate), $C_3H_8NO_5P$, is the world's highest selling agrochemical. Patented by the agricultural giant Monsanto, glyphosate is the main ingredient in Roundup, a common weed killer both in the developed and developing world. It is responsible for 10% of Monsanto's annual revenue, even after their patent expired in 2009. With genetically modified seeds that are glyphosate-tolerant, it makes up about half of Monsanto's \$14.8 billion net sales (Monsanto, 2013). Glyphosate is the only pesticide in this study that is not restricted by the US EPA and available for purchase and use in the United States. According to studies, glyphosate has relatively low acute dermal and oral toxicity. The most significant acute toxicity concerns are eye and skin irritation from splashes (US EPA, 1993). Although several long-term health studies conclude that glyphosate is non-carcinogenic, it is considered an endocrine-disrupting (ED) compound (McKinlay et al., 2007).

In 2012, the US EPA raised the acceptable amount of residue of glyphosate on food crops (RT USA, 2013). Glyphosate, like most agrochemicals, has documented resistance, requiring more and more each season to accomplish the same goal; eventually killing off all good bacteria and depleting the nutrients in the soil and making it extremely difficult to plant new crops (Aktar et al., 2009). Glyphosate has the lowest Henry's law constant and k_{oc} value of all four chemicals of interest, which means that it tends to partition to the aqueous phase rather than gas phase or organic phase. It presents a threat to surface water because it is not readily broken down by sunlight (photolysis) or hydrolysis. Because of its low k_{oc} and preference for the aqueous phase, it is a threat to groundwater via leaching. Additionally, it is toxic to many aquatic species and can cause fish kills (Kovach et al., 1992).

2.3.3 Picloram

4-Amino-3,5,6-trichloro-2-pyridinecarboxylic acid (picloram), $C_6H_3Cl_3N_2O_2$, is an ingredient in Agent Orange, a cocktail of herbicides sprayed during the Vietnam War from the years 1962 to 1971 over trees and dense foliage to destroy enemy cover (Institute of Medicine, 2012). As a result, millions of local Vietnamese and thousands of US soldiers were exposed, resulting in death, cancer, and developmental issues spanning multiple generations (Institute of Medicine, 2012). As a standalone pesticide, picloram can have acute toxicity via inhalation and the eyes. On a chronic level, it can be toxic to the liver, kidneys, and blood. It has only been classified carcinogenic by the US EPA due to an additive and presents low cancer risk to workers, which are required by law in the United States to wear chemical resistant gloves (US EPA, 1995). In other studies, it is classified as carcinogenic in rats to the adrenal and pituitary glands as well as the reproductive organs (Reuber, 1981). It is also classified as an endocrine disrupting compound (McKinlay et al., 2007).

It remains a restricted use pesticide by the US EPA as the main environmental threats are to surface water and groundwater. It is highly persistent, extremely resistant to hydrolysis and microbial degradation with very high half-lives: some experimental values range from 167 to 513 days (US EPA, 1995). It is relatively mobile due to low k_{oc} value and has been detected in groundwater in at least 10 states and has been found in 420 out of 744 surface water samples by the US EPA Office of Drinking Water (US EPA, 1995). It also has potential to kill aquatic species, with moderate toxicity to freshwater fish (US EPA, 1995).

2.3.4 2,4-D

(2,4-dichlorophenoxy)acetic acid, $C_8H_6Cl_2O_3$, commonly referred to as 2,4-D, is one of the two main ingredients in Agent Orange. In 2005, approximately 46 million pounds were

sprayed in the United States alone and although it is classified as “restricted” by the US EPA, it is available for use on home lawns (US EPA, 2005). It sits near the top of many of the most hazardous pesticides lists and studies (Swanson et al., 1997) and has been under medical review for decades, but with the conclusions of no cause to cancer or non-Hodgkins lymphoma (Bus and Hammond, 2007). Instead, it is classified as having low acute toxicity but is considered an endocrine-disrupting chemical with longer-term effects on reproductive organs, the eyes, kidney, adrenal, and thyroid glands (US EPA, 2005).

2,4-D is a slightly controversial chemical in the United States: recently the National Resources Defense Council (NRDC) has unsuccessfully petitioned to the US EPA to reconsider the chemical’s toxicity (NRDC, 2012). With regards to environmental fate, 2,4-D degrades relatively quickly in soil, and in aerobic aquatic environments but is highly persistent in anaerobic terrestrial and aquatic environments (US EPA, 2005b). Studies by the United States Geological Survey (USGS) determined 2,4-D to be the top detected pesticide in surface water nationwide, present in 12 out of 13 streams (Aktar et al., 2009). Other studies found 2,4-D in 19 out of 20 river basins, and has been detected in the air up to 3.9 ng/m^3 (Aktar et al., 2009).

2.4 Developing World Studies

2.4.1 Use and Understanding

Most literature about pesticides in the developing world are studies of use and availability, finding that they are widely available, widely used, and with little to no education on their dangers and restrictions of sale. Developing countries have increased use of synthetic chemical pesticides in recent decades due largely to their transitions from agricultural to industrial economies, but also to “eradicate insect-borne and endemic diseases” (such as malaria), and to increase crop yield and protection of one-product farming (Ecobichon, 2001).

Older, more acutely toxic and environmentally persistent pesticides are sold in developing countries than in developed nations (where they are banned) because they come non-patented, are less expensive, and sometimes manufactured in country or regionally.

Although small-scale use from subsistence farmers and cattle ranchers remains small in comparison to “agricultural giants”, their use should not be undermined: the World Health Organization estimates 3 million “acute, severe poisonings” with 220,000 deaths and perhaps more unreported cases (Ecobichon, 2001) and chronic effects remain unmonitored and undocumented. Although the majority of studies reporting self-poisoning come from Asia, a study detailed paraquat self-poisonings of Mexican farm workers (Tinoco et al., 1993). An epidemiological study in Panamá from February to July 1992 from Hospital Santo Tomas, the largest public hospital in Panamá City, documents 343 pesticide intoxications, of which only 26 were adults, with 10 total deaths, 6 of which were attributed to paraquat (Acosta de González et al., 1993).

A survey of farmers in a village in Venezuela found statistically significant difference in pesticide-related health problems of farmers versus non-farmers and found that farmers did not use personal protective equipment and commonly mixed pesticides (Rojas et al., 1999). In a survey of vegetable farmers in northern rural Tanzania, most report acute side effects of pesticide use yet are still increasing their use annually (Ngowi et al., 2007). In the Amazon basin of Ecuador, virtually all 111 farmers surveyed (99.1%) used pesticides (the most common being paraquat, organophosphates, and glyphosate), most (89.1%) knowing that they are dangerous. More than half also reported spraying in the house to eliminate insects and only 11.7% reported using personal protective equipment (Hurtig et al., 2003). The vast majority of studies show that at the most, sprayers wear long pants and rubber boots (which they typically wear to work in the

farm anyways), and the majority make no attempt to wear face or head coverings and gloves are not used (Mokhele, 2011), sometimes with extensive knowledge of the dangers of pesticides (Ngowi et al., 2007).

In a study of pesticide use in Egypt, 86% reported using these chemicals in the home, which is not the intended use of these chemicals and can be very persistent within the household (Ibitayo, 2006). Those from the study in Venezuela started farming as young as 7 years old, as children working in the family farms from an early age are very common in the developing world. In Trinidad, children are allowed to purchase pesticides and only 2% of pesticides used are on the approved national list (Pereira et al., 2007).

The top factors influencing occupational exposures mostly include poor safety practices attributed to little to no safety training and occupational regulations. The vast majority of developing country pesticide users lack secondary education and any safety training regarding its use (Mokhele, 2011). One study in Brazil found that even though the safety information on the containers was in the local language and included pictograms for illiterate users to understand the dangers of pesticides and proper safety procedures (Figure 4), safety measures were not observed (Waichman et al., 2007).



(Adapted from Waichman et al., 2007)

Figure 4: Common Safety Pictograms on Pesticide Containers

Mixing of pesticides is common in rural Tanzania and other developing countries and no information is disseminated on the consequences: mixing insecticides can almost guarantee

resistance (Metcalf, 1980). With regards to environmental persistence and toxicity, the majority of those surveyed in a study in Egypt revealed that they were unsure of whether or not pesticides left a residue on plants or contaminated nearby water sources (Ibitayo, 2006).

In rural Panamá, many subsistence farmers are illiterate. Often, the poorest of the poor work as day-wage laborers that are paid very little for an entire day's manual labor, which most often consists of spraying these chemicals in someone else's farm. It does not appear that most users read the labels or looked at the pictograms as personal protective equipment was not used. Ministry of Agriculture workers and those who sell the chemicals give no advice about pesticide safety. Workers eat and drink during spraying sessions and mix pesticides frequently. Sprayers are not washed or rinsed and containers are burned, littered, or used for other purposes. Chemicals and the backpack sprayers used are stored in the house often near food. The general population seems to understand that pesticide runoff can harm the river as fish kills have occurred at the study site but do not concern themselves with the runoff that is most likely entering the spring that feeds the gravity-fed water system (i.e. drinking water) for the community. Several developmental defects have been seen in children under 5 in the area, usually manifesting itself as a disfigured hand but the effect on children's motor skills was not obvious to the author as general literacy rates are low among both children and adults.

2.4.2 Occupational Exposure

The three main pathways of human exposure are inhalation, ingestion, and skin contact. Direct ingestion is rare except in the case of intentional pesticide poisoning, so the main pathway of ingestion is by water contaminated by pesticides, which is the main focus of this study. Inhalations from spraying and air drift are also noted pathways. A study of smallholder farmers in the Philippines tested for their exposure by putting water in their knapsack sprayers and water-

sensitive papers were placed in a test field and on the subjects. Their legs were by far the most exposed, 31 times higher than on their arms due to the nature of the equipment and crops, as well as the fact that farmers walk through sprayed rows of crops out of necessity (Snelder et al., 2008). Although similar findings occurred in the studies in greenhouses in Italy and Finland (Capri et al., 1999; Tuomainen et al., 2002), a study of greenhouse workers in Argentina found that the torso absorbed most of the chemical from spray drift (Flores et al., 2011).

A study created “the weight method” to calculate airborne drift and deposition potential from backpack sprayers based on a “water mass balance measured in high absorbent papers (HAP) under low evaporative conditions and unsaturated atmosphere” in Colombia. This method requires HAP and a drying oven to calculate exposure per unit area. This is calculated for different parts of the body under different weather conditions and an estimate for soil deposition is calculated (Garcia-Santos et al., 2011). Other experimental studies calculate personal dermal exposure (PDE) using tracers, such as fluorescent tracers or uranine, one comparing exposure as a function of the nozzle on the backpack sprayer for potato farmers in Colombia (Lesmes-Fabian et al., 2012). A more sophisticated study utilizing personalized exposure dynamics through spatial drift and half-life equations with GPS points estimates a personal exposure level of small-scale agricultural workers in developing countries (Leyk et al., 2009). A study among Malaysian rice paddy farmers using paraquat and 2,4-D found that wind speed had the largest effect on inhalation and PDE was extremely negatively correlated with the amount of personal protective equipment worn (Baharuddin et al., 2011).

The last noteworthy pathway is mother to baby. Although several survey studies show that it is mostly men who are spraying pesticides (e.g., Mokhele 2011; Rojas et al., 1999; Ngowi et al., 2007), a study of Yemeni women living farming communities show that the vast majority

have sprayed banned pesticides and without personal protective equipment and some have done so while pregnant (El-Zaemey et al., 2013). Additionally, women are typically washing the clothes with pesticide residues on them and caring for the children. A study potentially linking parental exposures to pesticides and childhood Leukemia in Costa Rica found that fathers working with picloram, benomyl, and paraquat had a positive correlation with risk of childhood Leukemia, though more studies are needed to link the two (Monge et al., 2007).

2.4.3 Modeling and Experimental Studies

Few studies were identified that assess the environmental fate and transport of pesticide use in the developing countries (as classified by the World Bank). A study in Thailand tested the validity of a common model, Agricultural Nonpoint Source (AGNPS), in watershed in a tropical environment. The study used two years of rainfall data and extensive mapping in Geographic Information Systems (GIS) to determine that the model was an accurate predictor of nutrient yields (total nitrogen and total phosphorus) and predicted runoff but over-predicted peak flow. However, this study did not choose to model pesticide environmental fate and transport or acknowledge any toxicity implications (Babel et al., 2004). A similar study in Rwanda sampled 11 sites for one year along the Akagera River (which feeds into Africa's largest lake, Lake Victoria) to model nonpoint source pollution and compare to land use to identify nutrient pollutants mostly in the form of nitrates, phosphates, ammonium (Wali et al., 2011). Batiha et al. (2009) simulated fate and transport of mancozeb, spinosad, and chlorosulfuron (pesticides) in Malaysia using the modified Equilibrium Criterion (EQC) model to include vegetation compartment in addition to model air, soil, sediment, and water. This study found that the degradation in vegetation is significant and should be incorporated into the model, but does not mention toxicity or risk assessment.

Another study in Thailand aims to understand pesticide dynamics in a river in a tropical watershed by sampling once per hour and analyzing with gas chromatography, finding that many pesticides, especially those with low k_{oc} values ($\log k_{oc} < 3$), have the ability to be transported during runoff peaks. Therefore, for an accurate profile of the fate and transport, “high temporal resolution” (sampling over short time periods) is necessary (Sangchan et al., 2012). Some studies in Argentina (Peruzzo et al., 2008) and Hong Kong (Tsui et al., 2007) utilized high-performance liquid chromatography (HPLC) to measure for glyphosate in the environment. Peruzzo et al. (2008) found that SoilFug model simulations were good predictions of glyphosate concentrations. Tsui et al. (2007) also used bioassays on river fish, but neither study explored risk implications. The previously mentioned study of rural farming in the Philippines (Snelder et al., 2008), most of the pesticides studied fall under the margin of exposure (MOE), indicating a serious threat to human health and the environment. Glyphosate does not have a determined MOE, which is noteworthy because it was present in high levels. Humans and aquatic species were determined to be at risk.

CHAPTER 3: WATER SYSTEM STUDIED AND METHODOLOGY

3.1 Location and Characteristics of Study System

The community in this study is Santa Rosa de Cucunatí, a small remote indigenous village in the Darién province of Panamá. The system of interest is the gravity-fed water system, a spring source that provides water for 135 villagers for all of their drinking, cooking, washing, bathing, and cleaning necessities. The spring is moderately protected with a constructed spring box, connected to a break pressure tank to relieve some of the pressure build-up during the rainy season.



Figure 5: Spring Source (left) and Distribution Line (right) of the Water System

The distribution line consists of 4" PVC pipe that spans approximately 3 kilometers. The distribution line connects to a storage tank that holds approximately 7,500 gallons and with a flow rate of 20 gallons per minute (typically overflowing), where the water is then distributed to the 33 taps through 1" PVC pipe.

The system has been operational since 1996 with few outages. Materials were donated by the Panamanian Ministry of Health and the people of Santa Rosa constructed the system. Throughout the years, the system has been threatened with increasing deforestation due to the increasing land use changes from rainforest to cow pasture. According to the local water committee, this has decreased the quantity of water throughout the system's history. However, it has been noted that climate change can have more of a projected impact on decrease in spring recharge than land use change (Fry et al., 2012). Additionally, water quality may be threatened due to increasing use of agrochemicals in both the cow pastures and the small-scale farms, which are at a higher elevation than the spring source of the gravity-fed water system. Therefore, when it rains the spring is potentially vulnerable to contamination from pesticide runoff.

3.2 Modeling Approach

Santa Rosa de Cucunatí is located 18 kilometers down a dirt road winding through primary rainforest and countless cow pastures to the nearest electricity, telephone signal, or basic necessities. The nearest laboratory to test water is in Panamá City, a one-day trip from Santa Rosa. Laboratories in this location are only able to test for basic water parameters: turbidity, fecal coliform, pH, etc. Santa Rosa's water has never been tested by the Ministry of Health, as technicians are typically overworked and with limited resources. More sophisticated methods such as Gas Chromatography (GC) and various types of assays are simply unavailable. Additionally, unlike *E Coli* and pH testing, there are less resource intensive field testing methods

for chemical pollutants. For these reasons, this study utilizes modeling to achieve its objectives and evaluate its hypotheses. The sources of model input, the methods used and the logic flow of the entire study is shown in Figure 6.

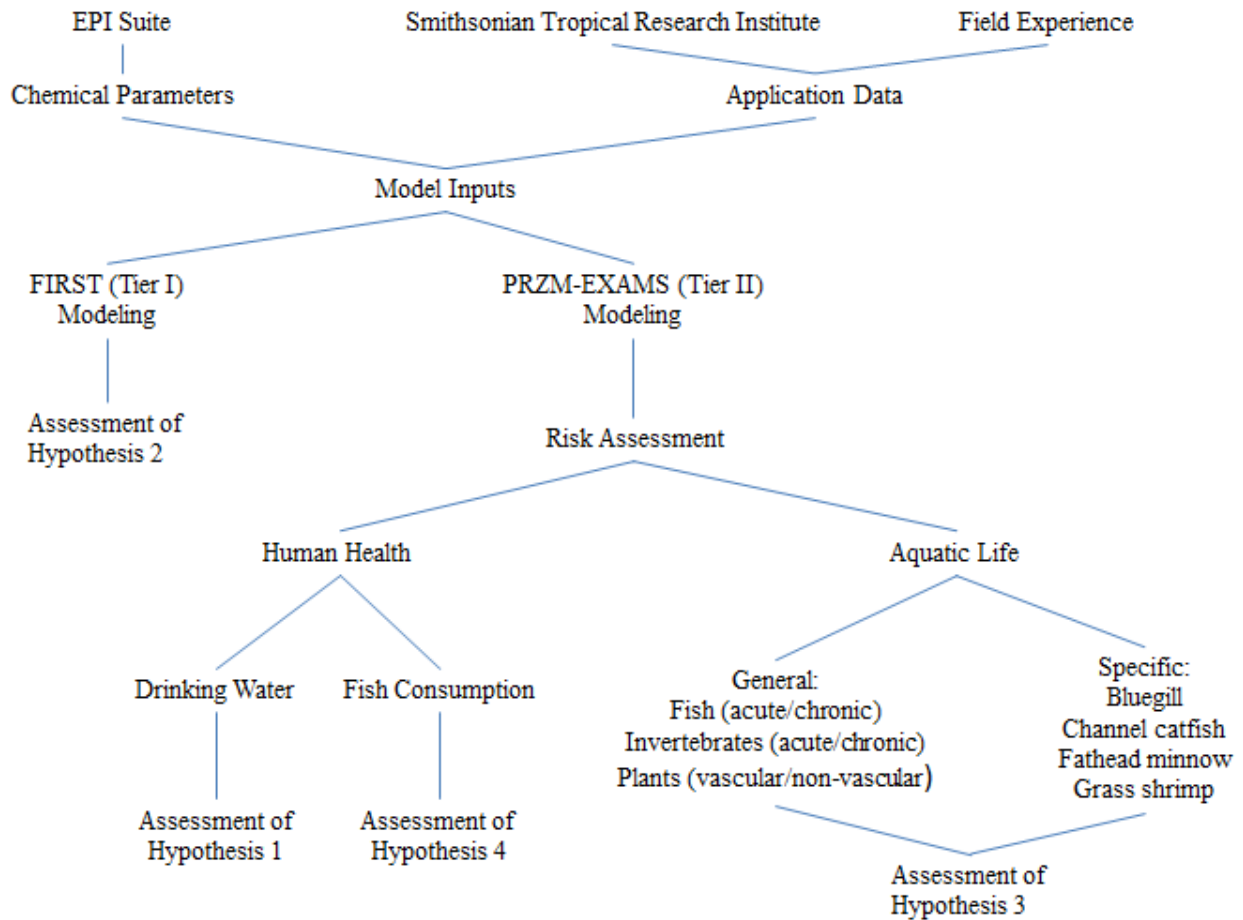


Figure 6: Process Schematic of Study Methodology

3.3 Overview of Existing Models

Because non-point source pollution from agricultural runoff is a global issue for the environment and human health, several models have been developed over the past several decades, including several by the US EPA and the United States Geological Survey (USGS). Fate and transport environmental models are typically divided into two categories: (1) watershed-scale, which aims to calculate the effects at a larger scale (an entire watershed) and (2)

catchment-scale, which aims to calculate the effects at a smaller scale, the field. For the purposes of this study, only catchment-scale models were considered. Generally, models incorporate or are paired with GIS for watershed-scale studies. Additionally, GIS data for this study site are not available; therefore, models utilizing GIS were not considered.

The Agricultural Chemical Transport Model (ACTMO), one of the first agricultural runoff models, was developed nearly 40 years ago, but was not determined in the literature review to being applied to any studies relevant to this research. The Pesticide Transport and Runoff (PTR) and the updated version Agricultural Runoff Management (ARM) models were also developed around the same time by the US EPA and are also not cited as being used to carry out simulations in published studies similar to the proposed research in this thesis. Similarly, the Water Sediment Chemical (WASCH) model was also developed over 40 years ago: no current versions of the model or publication citations were able to be located.

Watershed Regressions for Pesticides (WARP) are statistical models developed to predict concentration statistics for unmonitored streams. This model was first developed for atrazine and has evolved to include prediction maps for many chemicals in a USGS database, but only within the United States (Stone et al., 2013). They are not available for other countries nor can they be adapted for such purposes. The USGS has over 100 water quality models available for public use, some of which can simulate solute transport, but none are specifically designed to model pesticide fate and transport and the majority use GIS.

Chemicals, Runoff, and Erosion from Agricultural Management Systems (CREAMS) was developed by the United States Department of Agriculture (USDA), though it is now considered obsolete because the Groundwater Loading Effects of Agricultural Management Systems (GLEAMS) model was developed as an update to replace it and is one of the most

commonly used pesticide fate models (McCarthy et al., 2007). It is typically used for field-scale studies as it can over-predict in watershed-scale simulations and it predicts “runoff, percolation, and soil and chemical losses of a nutrient or pesticide at the edge of a field and from the root zone” (Shirmohammadi & Knisel, 1994). However, since it is a model intended for groundwater it was not considered for this study. The Agricultural Drainage and Pesticide Transport model (ADAPT) was developed as a combination of GLEAMS and DRAINMOD, a subsurface drainage model and is also intended for groundwater simulations. The Dynamic Watershed Model (DWSM) is a single storm event model which models storm water runoff, soil erosion, and has the capability to model non-point source chemical transport in a watershed. However, the watershed is divided into several sub-watersheds with further subdivisions of water channels and is used mostly for its hydrologic capabilities rather than its chemical transport capabilities (Boorah, 2010).

Toxic Substances in Surface Waters (TOXSWA), was developed in the Netherlands to describe the fate of pesticides entering field ditches to calculate edge-of-field pesticide predicted environmental concentrations in surface water. However, since sedimentation and suspended solids are not programmed into the model it is only able to be used for time periods less than one month (Adriaanse, 1996). SHETRAN is a spatially-distributed hydrologic model that was developed in the United Kingdom. It has been used in studies in over 100 cited publications but its main concern and capabilities are soil erosion, land use changes, and catchment hydrology (SHETRAN, 2013). Hydrological Simulation Program-Fortran (HSPF) is a Fortran-based model that simulates effects from hydrologic changes, is particularly useful in mixed urban and non-urban locations, but requires extensive input, e.g. hourly rainfall (CWEMF, 2007).

SoilFug was developed by the Canadian Centre for Environmental Modeling and Chemistry to assess potential degradation, evaporation, and leaching of pesticide to a surface soil (CEMC, 1996). The required inputs are various chemical properties, dosage rates, and various soil properties. Outputs include system fugacity, D values (the time required to kill 90% of the microorganisms in the soil), concentrations in soil and basin water, and pesticide losses by runoff, degradation, and volatilization. SoilFug takes into account different transport processes (e.g. degradation, runoff) with the assumption of phase equilibrium (Calamari & Zhang, 2002). It has been used mainly to calculate the concentration in the runoff water (Guardo et al., 1994, Tremolada and Paola, 1996), which is then assumed to be as the same concentration in a drainage basin (Calamari & Zhang, 2002). Calamari and Zhang (2002) recommend using SoilFug for developing world contexts due to the fact that most of the inputs are chemical and soil properties and not experimentally measured data. Another model developed by the Canadian Centre for Environmental Modeling is ChemCAN, but it comes pre-loaded with 24 regions of Canada (CEMC, 2003). Another model with geographic specificity is ChemGL, a multi-compartment model developed to simulate chemical fate and transport in the Great Lakes (Zhang et al., 2003).

The US EPA has been involved in environmental fate and transport modeling for decades and the Office of Pesticide Programs (OPP) has developed several models with specific interest in pesticide fate and transport. Surface water pesticide fate and transport models include Pesticide Root Zone Model (PRZM), Exposure Analysis Modeling System (EXAMS), EXAMS-PRZM Exposure Simulation Shell (EXPRESS), k_{ow} Aquatic Bioaccumulation Model (KABAM), FQPA Index Reservoir Screening Tool (FIRST), Generic Estimated Environmental Concentration (GENEEC2), Tier I Rice Model, and Pesticides in Flooded Application Model

(PFAM). KABAM consists of a bioaccumulation model that estimates pesticide concentrations in aquatic organisms and a risk assessment from the consumption of those organisms by birds and mammals, intended for use for non-ionic organic chemicals with a $\log K_{ow}$ value between 4 and 8 (US EPA, 2009), which does not pertain to any of the four chemicals of interest of this study. PFAM is intended to estimate pesticide concentration in any sort of agricultural flooded field. The Tier I Rice Model is specifically intended to model pesticide concentration in rice paddies. Tier I models require less input and give fewer results: they are typically more of a cursory, conservative estimation. Tier II models aim to give a more comprehensive analysis, which require more inputs and provide more results.

EXPRESS is the combination of two Tier I models (FIRST and GENEEC2) and two Tier II models (PRZM and EXAMS). Because FIRST and GENEEC2 are Tier I models that do not provide extensive results, they are not cited in literature. The Tier II models, PRZM and EXAMS are combined into one model in EXPRESS. EXAMS has been used extensively since its development. The first published study modeled phalate esters (chemicals mainly used as plasticizers) in four different aquatic environments: a pond, an oligotrophic lake, a eutrophic lake, and a river and was carried out by the Environmental Research Laboratory of the US EPA (Wolfe et al., 1980). In 1986, a study assessing EXAMS' prediction of volatilization of three herbicides in a flooded rice field found EXAMS simulations to agree with measured data to be a good predictor when compared to lab experiments (Seiber et al., 1986). Sato and Schnoor (1991) then compared EXAMS to two other chemical fate models, concluding that all three models can be "useful tools for assessing long-term fate of persistent chemicals", as long as the user is aware of limitations of each model. EXAMS was also used to assess the environmental fate of anti-foulants in seawater (Jacobson & Willingham, 2000) and accurately predicted levels of estrogen

in a river (Balam et al., 2010). An adapted version of EXAMS was used to predict fate of herbicide atrazine in a small tidal estuary in North Carolina (McCarthy et al., 2006). PRZM has also been cited extensively in literature; most of the studies deal directly with the pesticide in root zone soil. However, Chiovarou and Siewicki (2007) combined EXAMS with PRZM to model various agrochemicals' behavior in a lake in Oregon and a creek in Florida to assess their relative aquatic risk.

3.4 Model Selection

An appropriate model is chosen with the objectives and hypotheses of the study in mind. The hypotheses are interested in investigating fate and transport of pesticides in surface water (the river) and groundwater (a spring), the impact on drinking water and fish consumption, and the effect of rainfall on these two at the field scale. FIRST and GENEEC2 are Tier I models and PRZM and EXAMS are Tier II models; the integration of all four with graphical user interface is EXPRESS (Figure 7).

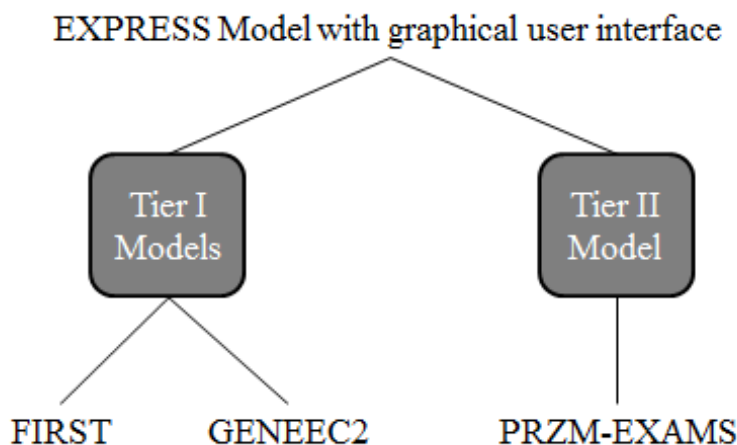


Figure 7: The EXPRESS Model Contains Multiple Models

EXAMS was developed by the US EPA to assess the fate, exposure, and persistence of pesticides in surface water systems (Burns, 2007). PRZM was developed by the US EPA to simulate chemical movement within and immediately below the plant root zone (Burns, 2007).

EXAMS and PRZM are established models and have been widely used for several years. They were linked together so often to provide a more comprehensive exposure assessment of pesticides in aquatic environments, with specific interest in impacts on drinking water, that the US EPA developed a model linking the two with a graphical user interface, EXPRESS.

3.5 Theory

Once a pesticide is sprayed, there are various transport pathways by which it partitions to the various environmental compartments. There are also physical, chemical, and biological processes that determine its persistence and fate. Persistence is a measure of how long the chemical remains in exposed particular compartment. Fate can be defined by the expected environmental concentrations (EEC) of the chemical in various compartments, which ultimately relates to risk. Transport and transformation processes of pesticides in the environment are described below.

3.5.1 Transport Processes

When the pesticide is applied, plant uptake occurs and the pesticide accumulates in the plant as intended. This raises concerns to the consumer if they are continually consuming foods with pesticide residue. Emission refers to pesticide losses to air during application, which is more significant when the pesticide is applied with a sprayer, as it is in this study. Volatilization is the transport of a compound from liquid or solid phase to gas phase (Mihelcic, 1999) and with respect to this study refers to the diffusion of the chemical from the surface of the plant, soil and water up into the air. Volatilization is highly dependent on the chemical's vapor pressure. Wash off is the process that occurs when water hits the sprayed plant and transport it to the soil. Surface runoff is when the pesticides are carried by rain, rolling off the ground surfaces to be deposited in surface water bodies. Leaching is when the pesticide infiltrates the soil layer and

goes all the way down to the water table, affecting the groundwater. The pesticide transport processes of this study are summarized in Figure 8.

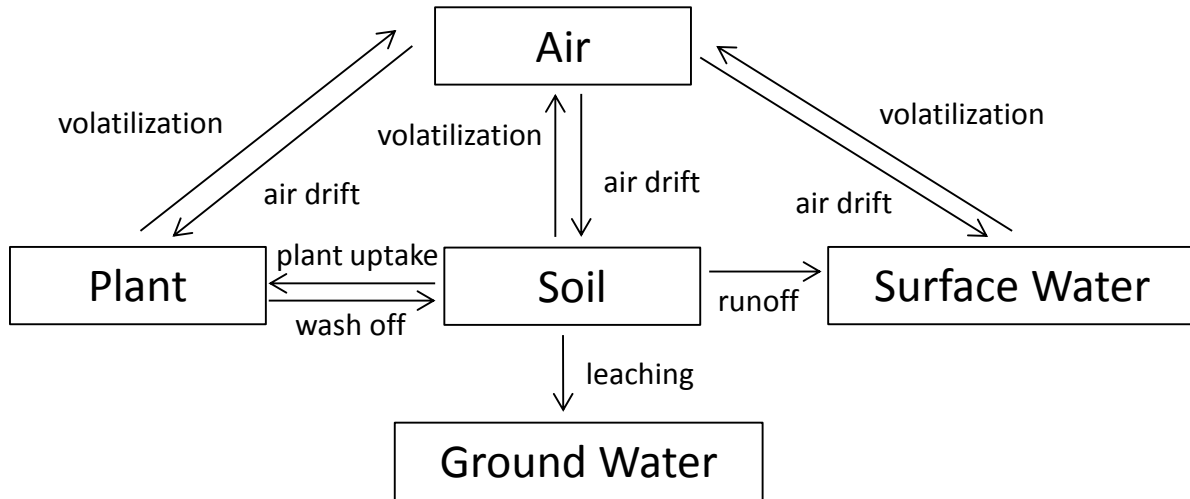


Figure 8: Transport Pathways of Pesticides in this Study

3.5.2 Transformation Processes

Degradation refers to the breakdown of pesticides in the environment and is the major process of pesticide loss after application. The breakdown of the “parent” compound convert into intermediate products and eventually simple products such as CO₂, H₂O, nitrogen, phosphorus or sulfur (Cheng & Lehman, 1985). Photolysis is the breaking down of chemicals via sunlight, which in water depends on various circumstances such as light intensity, turbidity of water, and depth in the water column. Direct photolysis occurs when the molecules absorb the light photons directly and indirect photolysis occurs when the energy from the molecule that has absorbed the light photon affects another molecule.

Biodegradation comes from the microbial metabolism of pesticides and depends on many factors such as the presence of enzymes and bacteria, temperature, pH, moisture, and

bioavailability¹ of pesticides. For example, 2,4-D has been observed to degrade faster when the pH is above 6.0 (Kells et al., 1980).

Chemical degradation processes include hydrolysis and ionization. Hydrolysis is the process of breaking bonds in a chemical due to a reaction with water, which is highly dependent on the pH of the water. Ionization refers to the transfer of ions; an ionized compound behaves differently than its neutral version. For example, an ionized organic acid can be adsorbed to the sediment much more readily than its neutral form and the solubility of the ionized form of an organic compound is higher than its neutral form (PMM, 2002).

3.6 Model Inputs, Outputs and Assumptions

The EXPRESS graphical user interface provides reproducible simulations quickly for an unlimited number of crop scenarios. EXPRESS actually contains four separate models: FQPA Index Reservoir Screening Tool (FIRST) and Generic Estimated Environmental Concentration (GENEEC2) are both Tier I analyses and the PRZM-EXAMS shell is the Tier II Analysis. Because the PRZM and EXAM models are combined into one model, EXPRESS can be considered a “3-in-1” model. The FIRST and GENEEC2 Tier I models require most of the same inputs (Table 3), most of which pertain to the crop, application of the pesticide, and pesticide chemical properties. The FIRST model gives only two outputs: peak day untreated drinking water concentration and average annual untreated drinking water concentration. GENEEC2 was not considered in this study because it is based on a farm pond rather than the drinking water reservoir that is pre-programmed in FIRST and the PRZM-EXAMS shell. FIRST simulations were run twice for each of the four chemicals to compare the results from immediate versus delayed rain events.

¹ Bioavailability refers to the extent to which a toxic contaminant can be transformed in biological media or actions in an aquatic environment (Hammelink et al., 1992).

The PRZM-EXAMS shell requires substantially more inputs than FIRST and GENEEC2 as it is more complex, but the inputs are still chemical properties and field and farming properties. Both the original pesticides and degradation products are simulated. The model provides tabular and graphical outputs for each individual scenario and the water column and benthic zone for both a farm pond (no flow) and a drinking water index reservoir (with flow).

Table 3: EXPRESS Models' Inputs and Outputs

Model	Inputs	Outputs
FIRST	crop, application rate and timing, percent cropped area, k_{oc} , soil aerobic half-life, wetting, type of spray, depth of incorporation, solubility, aerobic aquatic half-life, hydrolysis half-life	peak day concentration (acute), average annual drinking water concentration (chronic)
GENEEC2	crop, application rate and timing, k_{oc} , soil aerobic half-life, wetting, type of spray, high/low boom, fine/medium droplet size, width of no-spray zone, depth of incorporation, solubility, aerobic aquatic half-life, hydrolysis half-life	Estimated Environmental Concentrations (EECs): peak, max 4-day, max 21-day, max 60-day, max 90-day
PRZM-EXAMS	crop/weather scenario, presence of metabolites, chemical name, molecular weight, partition coefficient, soil aerobic half-life, vapor pressure, flow/no flow, water column half-life, benthic sediment half-life, hydrolysis by temperature profile, photolysis, % crop cover, spray method, application rate and timing	upper 10th percentile soil and water concentration profiles, annual hydrology summary at bottom of soil column, water balance (leaching/evapotranspiration/runoff), dissolved EECs in drinking water reservoir and sediment

Because EXPRESS was developed to predict concentrations of pesticides in drinking water sources systems that are near agricultural activities in the United States, the user interface comes pre-loaded with more than 160 farm scenarios within the United States. These crop scenarios list the crop (e.g. tomatoes, alfalfa, and potatoes) and the city and state which is loaded with multiple decades of weather data. Because EXPRESS is user-friendly, it has simplified many of its parameters. There are only two environments to choose from: the water system is automatically modeled as both a farm pond (no flow) and a flowing index reservoir, based on a typical Midwest drinking water reservoir. The model does not allow the users to design their own environment. Therefore, another important assumption to note is that the spring source for

the gravity-fed water system in Panamá is modeled as the default index reservoir in EXPRESS for both Tier I and Tier II simulations. Therefore, the most significant difference in the inputs in this study is the difference in chemicals themselves (i.e. relative toxicities and associated risk).

3.7 Data Input Sources for Modeling

There are three categories of data inputs for the Tier I simulations in FIRST: farm field parameters, pesticide application parameters, and pesticide chemical properties (Table 4).

Table 4: Inputs for FIRST Simulations in EXPRESS

	Paraquat	Glyphosate	Picloram	2,4-D
Crop¹	Rice	Rice	Rice	Rice
Application (lb/acre)²	16.745	16.745	16.745	16.745
Applications/year¹	10	10	10	10
Interval b/t Applications (d)¹	15	15	15	15
Crop Cover (%)¹	87	87	87	87
k_{oc}⁴	6,780	1.0	38.77	29.63
Soil Aerobic Half-Life (d)⁴	75	30	120	75
Immediate Rain?	<i>yes/no</i>	<i>yes/no</i>	<i>yes/no</i>	<i>yes/no</i>
Nozzle Height (in)¹	20-50	20-50	20-50	20-50
Droplet Size¹	fine	fine	fine	fine
Width of No-Spray Zone (ft)¹	0	0	0	0
Depth of Incorporation (in)¹	0	0	0	0
Solubility (mg/L)³	6.20E+05	1.05E+04	430	677
Aerobic Aquatic Half Life (d)⁵	150	60	240	150
Photolysis Half Life (d)³	0	0	7	13

¹Field observations

²Smithsonian Tropical Research Institute

³EPI Suite, experimental

⁴EPI Suite, modeled

⁵As per model instructions, aerobic aquatic half-life used was double the soil aerobic half-life

All farm field parameters (crop, crop cover, width of no spray zone, depth of incorporation) and the majority of the application parameters were gathered from the author's personal observational experience in the field. The national annual average of pesticides used per acre given by the Smithsonian Tropical Research Institute was used as the application rate because

application rates were not measured in the field. Due to common overuse of pesticides at the study site, this most likely provides conservative model results. Chemical property parameters were provided by the Estimation Program Interface (EPI)-Suite developed by the OPP of the US EPA. Experimentally-based parameters were used as they were available.

Inputs for Tier II PRZM/EXAMS simulations are similar to those of the Tier I simulations. Inputs are broken down into design, PRZM-Efate, EXAMS-Efate, and application parameters, and are provided in Table 5.

Table 5: Summary of Inputs for PRZM/EXAMS Simulations

	Paraquat	Glyphosate	Picloram	2,4-D
Crop Scenario ¹	FL sugarcane	FL sugarcane	FL sugarcane	FL sugarcane
Molecular Weight	257.16	169.07	241.46	221.04
Solubility (mg/L) ³	6.20E+05	1.05E+04	430	677
k_{oc} ³	6,780	1.0	38.77	29.63
Soil Aerobic Half-Life (d) ⁴	75	30	120	75
Vapor Pressure (mmHg) ⁴	1.00E-07	1.25E-09	3.20E-07	2.79E-05
Farm Pond? (no flow) ¹	no	no	no	no
Index Reservoir? (flow) ¹	yes	yes	yes	yes
Aquatic Aerobic Half-Life (d) ⁴	150	60	240	150
Hydrolysis Half-Life (d) ³	0	0	0	38
Aquatic Direct Photolysis (d) ³	0	0	7	13
Application Rate (lb/acre) ²	16.745	16.745	16.745	16.745
Crop Cover (%) ¹	87	87	87	87
Applications ¹	10	10	10	10
Days b/t Applications ¹	15	15	15	15
Application Method ¹	ground spray	ground spray	ground spray	ground spray

¹Field observations

²Smithsonian Tropical Research Institute

³EPI Suite, experimental

⁴EPI Suite, modeled

⁵As per model instructions, aerobic aquatic half-life used was double the soil aerobic half-life

The most significant difference between the Tier I and Tier II models is that the PRZM-EXAMS model requires the user to choose one of the pre-loaded 160 crop-and-weather scenarios. The chosen crop scenario is a sugar cane farm in West Palm Beach, Florida. Sugar cane was chosen because with respect to the height above the ground, roots belowground, and shape of the crop is

the mostly similar to rice crops that are available in the study area; they are both grasses (Chastain, 2013). Figure 9 also details that the West Palm Beach area in the southernmost part of Florida has the same ecological classification as the Darién province of Panamá: tropical moist deciduous forest.



(Image adapted from FAO)

Figure 9: South Florida and Eastern Panamá are Ecologically Comparable

Weather data from south Florida is also pre-programmed in the model simulations, including rainfall data. The Pacific side of the Darién province experiences lower average annual rainfall than the Caribbean side, around 70 inches per year (UNESCO), which is slightly higher than the average annual rainfall in West Palm Beach, Florida. The dominant soil type in south Florida, however is inceptisol and in the Darién, Panamá it is ultisol, also known as red clay soil (USDA) (Table 6).

Table 6: Comparison of Soil and Weather Data for Panamá and South Florida

	Darién, Panamá	West Palm Beach, Florida
FAO Climate Classification	tropical moist deciduous forest	tropical moist deciduous forest
Average Annual Rainfall (in)	70.87	62.45
USDA Soil Classification	ultisol	inceptisol

3.8 Risk Assessment Methodology

3.8.1 Human Health Risk Assessment Methods

Risk to human health is determined by toxicological parameter and the exposure.

Exposure is a function of concentration over time depending on the exposure pathways. In this study, two exposure pathways are considered.

3.8.1.1 Risk Associated with Drinking Water

Because the study's main interest is the exposure of humans through drinking water from the gravity-fed water system that is near pesticide spraying, the method of quantifying exposure is through the average daily dose (ADD), which is defined by the concentration, intake rate, a person's body weight, exposure duration, and averaging time.

$$\text{Average Daily Dose (mg/kg * d)} = \frac{\text{Concentration (mg/L)} \times \text{Intake Rate (L/d)} \times \text{Exposure Duration (d)}}{\text{Body weight (kg)} \times \text{Averaging Time (d)}}$$

Equation 1

ADD was calculated for men, women, and children due to differing body weights and consumption habits. The average daily dose is then compared to the toxicology parameter oral reference dose (RfD), which is defined as “an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without deleterious effects during a lifetime” (US EPA, 2011).

The oral RfDs for the chemicals of interest in this study are shown in Table 7. It should be noted that the Joint FAO/WHO Meeting on Pesticide Residue have their own database of Acceptable Daily Intake values (mg/kg*d), but there is no value for picloram. The value for 2,4-D is identical to the oral RfD and for paraquat, the values are nearly identical. The oral RfD differs significantly only for glyphosate, which is three times higher than the US EPA's oral RfD value.

Table 7: Oral RfDs for Chemicals of Interest (US EPA, 2012c)

	Paraquat	Glyphosate	Picloram	2,4-D
RfD (mg/kg*d)	4.5E-03	1.0E-01	7.0E-02	1.0E-02

Because different groups of the population are more vulnerable to illness and disease, such as children and the elderly, it is important to perform separate calculations for each group. Therefore, these calculations were performed for men, women, and children. The average body weight of an adult male in the United States is about 80 kilograms (US EPA, 2011), but as Panamá is a developing country it is much lower. The average weight for an adult male in Panamá is 61.8 kilograms and an adult female is 55.4 kilograms (de Bermudez et al., 1984).

Additionally, for a more comprehensive risk profile, the oral RfD was then set to the ADD in order to back calculate the concentration at which the pesticide poses a threat to the consumer, named “breakpoint concentration”. Breakpoint concentrations were calculated for each chemical of interest as well as for men, women, and children in order to compare to the estimated drinking water concentration (EDWC) profiles, which are modeled over 30 years’ meteorological data in order to see the percentage of years exceeding breakpoint concentrations and therefore presenting a risk to the consumer.

3.8.1.2 Risk Associated with Fish Consumption

Another major ingestion pathway is the fact that the villagers in Santa Rosa go fishing in the river almost daily in order to eat small river fish and/or shrimp as a major source of protein. The river is in the same watershed and more specifically and significantly, at an even lower elevation than the spring source of the gravity-fed water system. Therefore, for the purposes of further analysis, it is assumed that the EDWCs are also the concentrations of the pesticides in the river. However, to calculate the estimated individual exposure to each pesticide from ingesting

river fish (E_m , mg/kg*d), the concentration of the pesticide in the fish (C_m , mg/kg), the consumption rate (kg/d), and the body weight (kg) must be known.

$$E_m = \frac{C_m * CR}{BW}$$

Equation 2

Although there was no way to measure the chemical concentrations of the fish from the river in Santa Rosa, it was estimated using a bioconcentration factor (BCF). The BCF is the proportion of the chemical concentration in the fish to the concentration of the chemical in the surrounding water. The chemical concentration of the pesticide in the fish, C_m , has units of mg/kg. The commonly accepted method to estimate BCF (Veith et al., 1980) is based on the octanol-water partition coefficient, k_{ow} .

$$\log BCF = 0.76 \log k_{ow} - 0.23$$

Equation 3

As with all previous chemical properties used in calculations and for modeling inputs in this study, the octanol-water coefficient, k_{ow} , was taken from EPI suite. Similar to the drinking water risk assessment methods, individual exposure is compared to oral RfD. Breakpoint concentrations are calculated for concentrations of each pesticide in the river at which fish consumption presents a risk to the consumer. These are compared to the concentration profiles in order to see the percent years exceeding the breakpoint concentrations and therefore, presenting a risk to the consumer.

3.8.1.3 Additive Human Health Exposure Risk Assessment

As per standard risk assessment methods, the calculated human exposure from drinking water and fish consumption were added together for a more comprehensive ingestion exposure. Similar to the drinking water risk assessment methods, these additive exposures calculated using

both the highest concentration and lowest concentration from the PRZM-EXAMS concentration profiles. This was done in order to obtain a best- and worst-case human health additive risk assessment.

3.8.2 Ecological Risk Assessment Methods

Although the primary intention of this study is assessing the impacts of unrestricted pesticide use on the drinking water, there are ecological toxicological implications as well. The author of this study witnessed fish kills in the local river two times in two years, to which the local villagers attributed to overuse of pesticides. As previously mentioned, the PRZM-EXAMS concentration profiles are assumed to be the concentration of the stream in order to compare them to acute aquatic toxicity data, i.e. how much risk is present to the aquatic creatures due to the spraying of pesticides. The maximum 96-hour concentration profiles for all four chemicals of interest are compared to 96-hour LD50s for three fish species from the US Forest Service (Table 8) in order to see the percent of years' posing a threat to these specific species. The 96-hour LD50 concentration is an ecotoxicity parameter that shows at which concentration 96 hours after application that will kill approximately 50 percent of each respective species.

Table 8: 96-hour LD50, mg/L

	Paraquat		Glyphosate		Picoloram		2,4-D	
fathead minnow	unavailable		2.3	22°C	unavailable		2.7	20°C
channel catfish	<100	18°C	13.0	22°C	15.5	22°C	7.0	20°C
bluegill	13	24°C	5.6	22°C	23.0	22°C	0.54	22°C

(Adapted from Johnson & Finley, 1980)

The acute LD50 for grass shrimp was also compared to the river concentration profiles. Catfish and minnows are present in the river at the study site. Additionally, for a more general risk assessment, stream concentrations are compared to aquatic life benchmarks for general

aquatic life groups: fish, invertebrates, and plants (Table 9). This provides a risk assessment not only for the fish in the river, but also invertebrates and vascular and non-vascular plants.

Table 9: Aquatic Life Benchmarks (ppb)

	Fish		Invertebrates		Nonvascular Plants	Vascular Plants
	Acute	Chronic	Acute	Chronic		
Paraquat	6,000	< 369	600	< 36.9	0.396	71
Glyphosate	21,500	1,800	26,600	49,900	12,100	11,900
Picloram	6,500	550	34,150	11,800	4,900	—
2,4-D	12,075	14,200	12,500	16,050	3,880	13.1

(Adapted from US EPA, 2012d)

As with previous risk assessments, this was done with the minimum and maximum concentration profiles in order to provide a best- and worst- case scenario for aquatic life.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Model Results

4.1.1 Tier I Model (FIRST) Results

The primary goal of FIRST is to provide side-by-side concentration estimates in parts per million (ppm) for drinking water reservoirs near agricultural activities where pesticides are used. The model index reservoir used is a 427 acre watershed that feeds to a community water supply (CWS) in Shipman, Illinois. The simulations were run twice for each chemical in FIRST in order to compare the results from an immediate rain following spray events compared to a delayed rain following spray events (Figure 10).

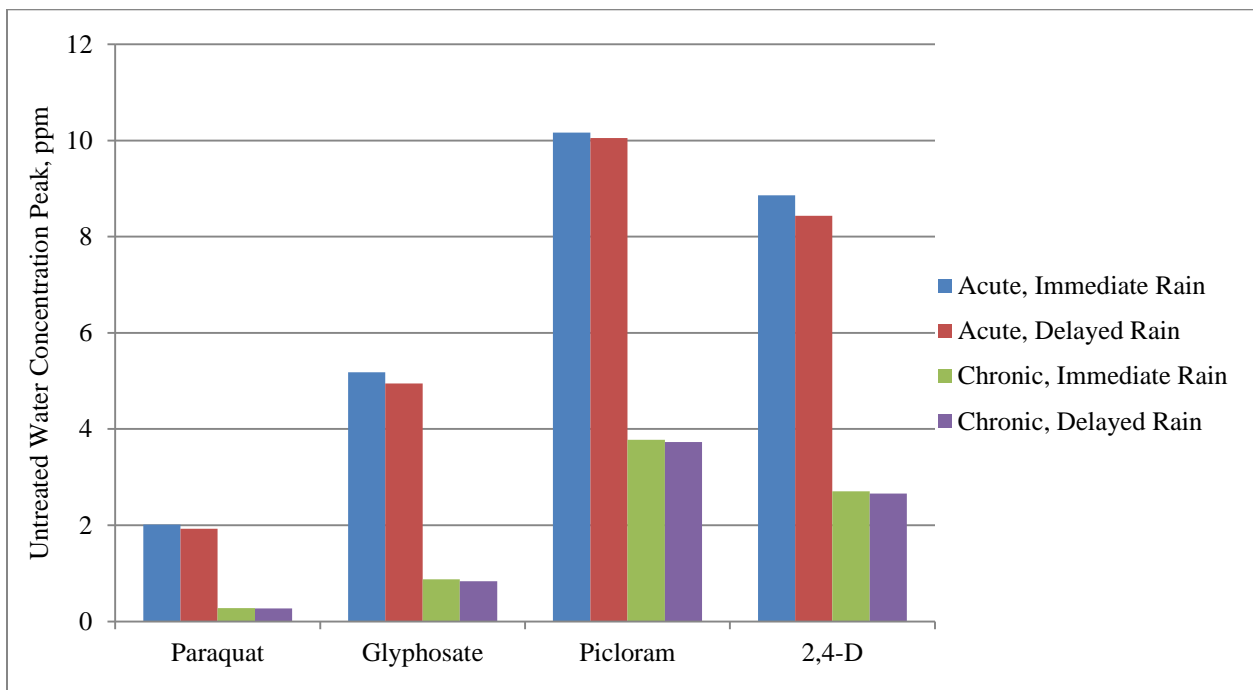


Figure 10: Summary of Outputs from Tier I Model Food Quality Protection Act Index Reservoir Screening Tool (FIRST)

Because the concentrations here are in the drinking water reservoir and not at the field itself, it is expected that concentrations with delayed rain event to be lower than those with immediate rain. However, the difference between the two is only between 1 and 5 percent for each output value.

The difference between the resulting concentrations between immediate and delayed rain events is surprisingly small. The program assumes “that rainfall and resulting runoff are sufficient to remove up to eight percent of the pesticide” from the field and a “portion of the chemical... flows into the reservoir and is dissolved in the reservoir water” (US EPA, 2012a). FIRST also assumes that the delayed rain event occurs two days after the spray event. Depending on how immediate and intense the rain event is, this may be too low of a proportion of that which is actually washed off and carried away by runoff. Additionally, the model is based off the assumption that rainfall is only sufficient for two reservoir turnovers per year, which is very low compared to the actual system studied.

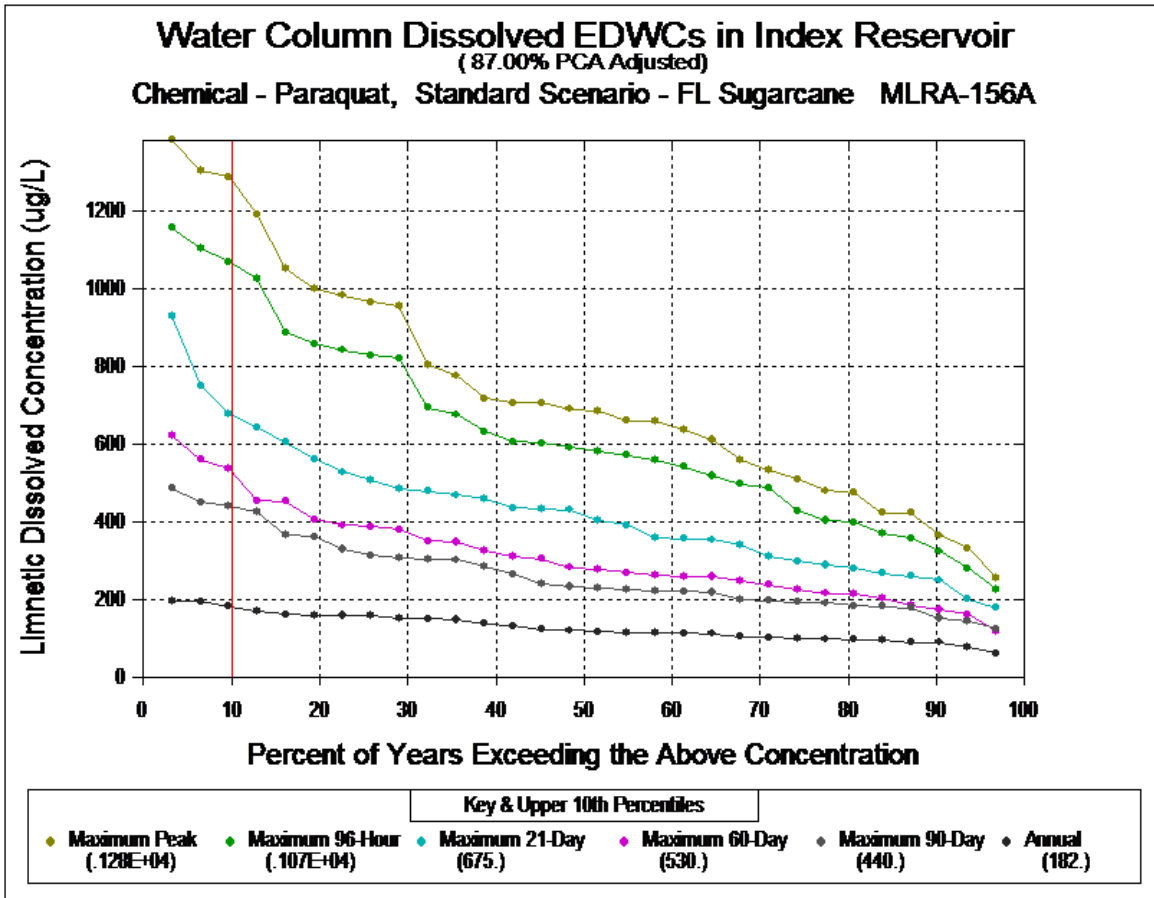
Based on the results from this model, it seems that picloram has the most impact on drinking water, with the highest acute and chronic concentrations for both immediate and delayed rain scenarios. This is probably due to its high half-lives in both soil and water. 2,4-D has the second highest concentrations in water which seems counterintuitive because it can be broken down by photolysis, implying faster degradation. However, the end concentration is highly dependent on k_{oc} value of the chemical (US EPA, 2012a). Paraquat has the lowest end point concentrations due to its high k_{oc} value. Since k_{oc} measures the proportion of the amount of the chemical sorbed to the soil to the amount of the chemical dissolved in solution, it is expected that paraquat would preferentially partition into soil instead of water.

4.1.2 Tier II Model (PRZM-EXAMS) Results

The primary goal of the PRZM-EXAMS shell is to provide a more refined (i.e., Tier II) prediction of the concentrations of pesticides in drinking water sources as well as aquatic ecosystems for exposure assessments (Burns, 2007). The PRZM component accounts for “climatic conditions, crop-specific management practices, specific soil properties, site-specific hydrology, pesticide-specific application and dissipation (fate and transport) processes” (Burns, 2007). The EXAMS component combines “subsequent hydrologic transport, volatilization, sorption, hydrolysis, biodegradation, and photolysis of the pesticide” (Burns, 2007).

The base index reservoir for the PRZM-EXAMS shell is the same reservoir as the aforementioned FIRST model. Unlike the Tier I models in EXPRESS, the PRZM-EXAMS shell does not allow for the adjusting of rainfall data. Since this model utilizes 30 years’ worth of historical meteorological data, side-by-side comparisons of the immediate versus delayed rain scenarios are not possible and were not simulated. The Estimated Drinking Water Concentrations (EDWCs) for the index reservoir for each chemical are shown in Figures 8, 9, 10, and 11, plotted against their percent of years exceeding the respective concentrations.

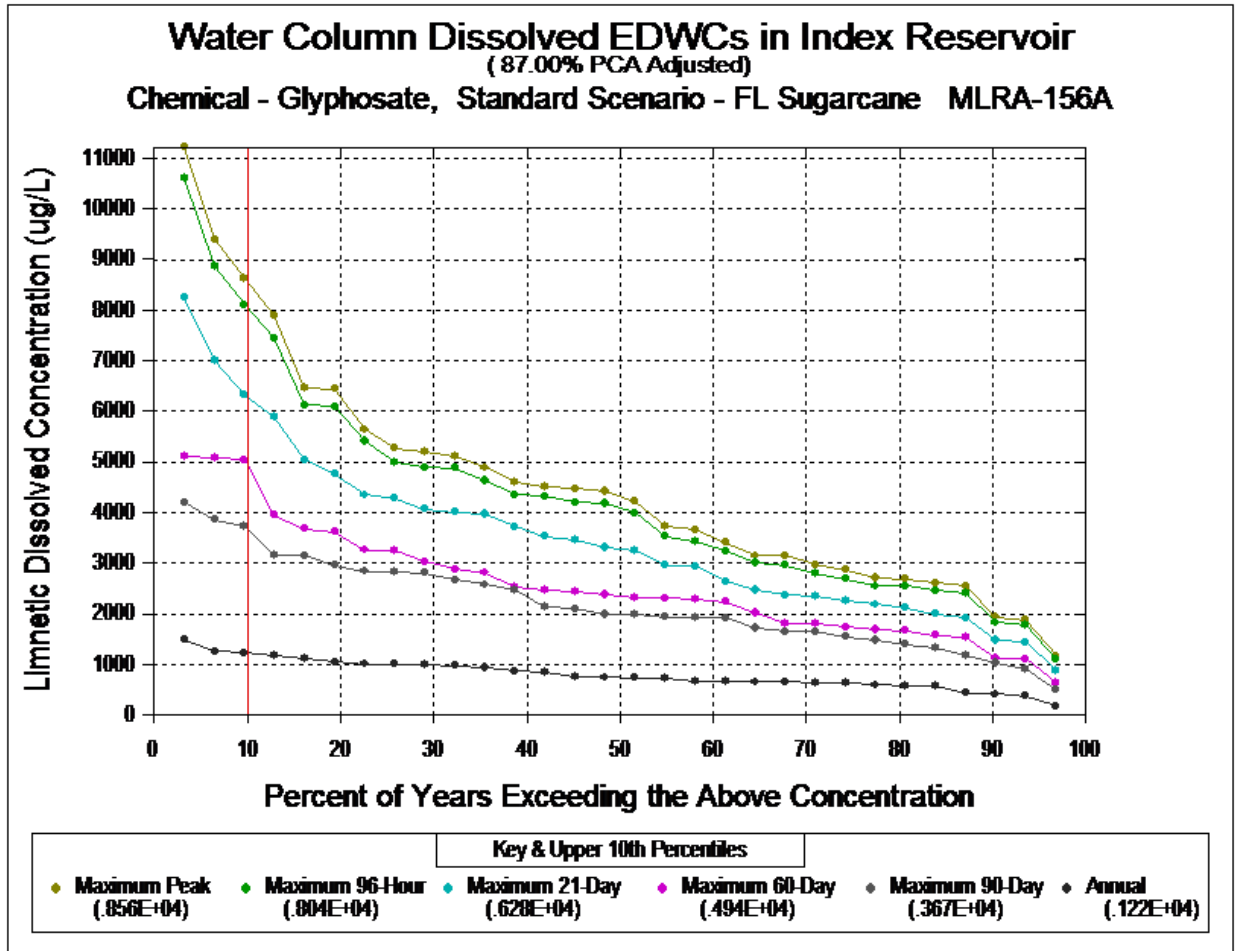
The maximum peak profile represents the maximum concentrations after pesticide application for each month averaged over a year; therefore its profile has the greatest value. The maximum 96-hour concentration profile (green) represents the maximum concentration 96 hours after application for each month averaged over a year. For example, Figure 11 shows that 50 percent of the years over 30 years the maximum 96 hour concentration exceeds 400 ppb. The maximum 21-day, 60-day, and 90-day profiles show the average of the maximum concentrations at 21, 60, and 90 days, respectively. Lastly, the annual concentration profile represents the average annual concentration versus the percent of years exceeding those concentrations.



Express v. 1.03.02 (2007-07-20) - Exams 2.98.04.06 with PRZM 3.12.2[48]

Figure 11: Profiles for Estimated Drinking Water Concentration, Paraquat

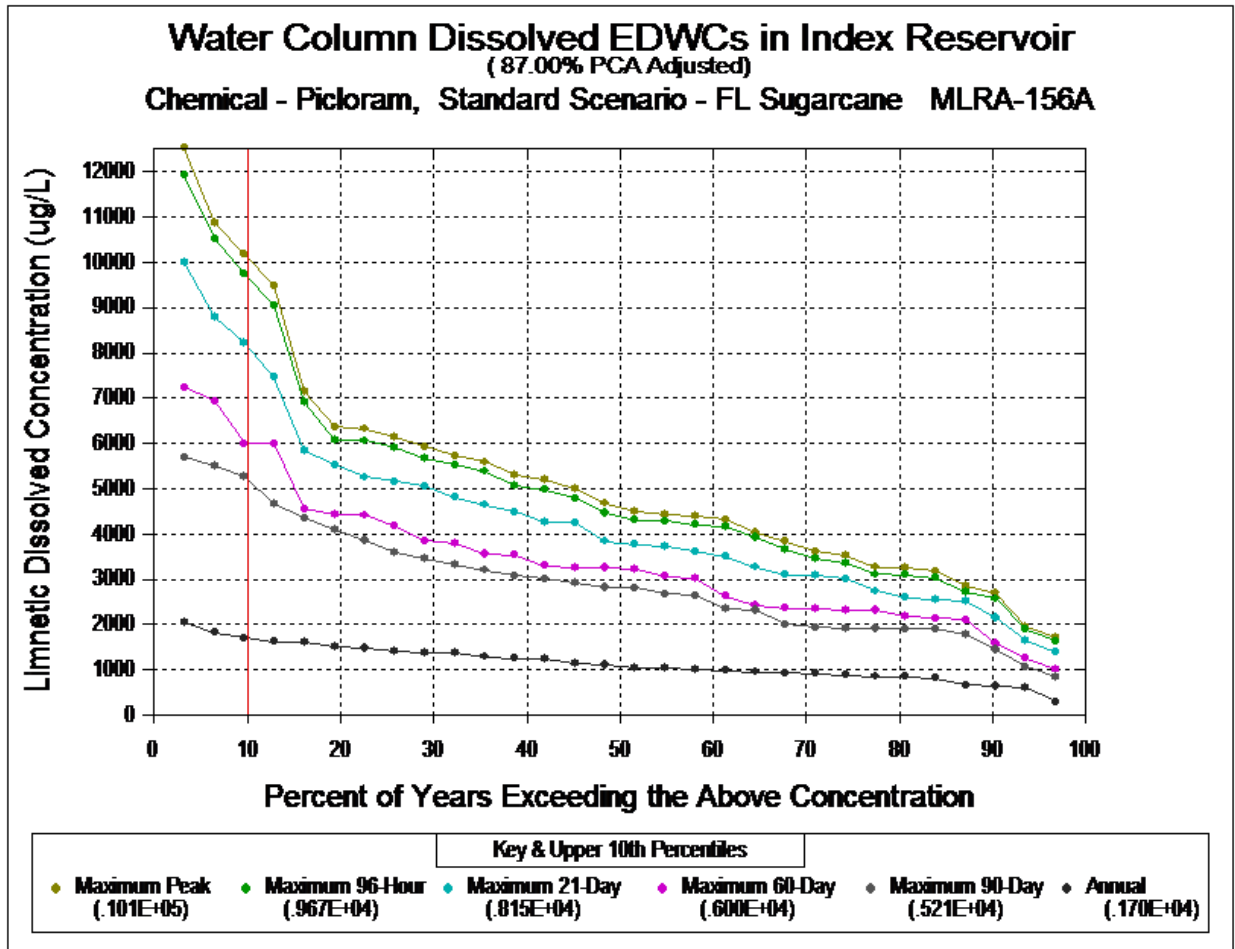
Paraquat's highest maximum peak concentration averaged over the 30 years of meteorological data is approximately 1,400 ppb. In contrast, its average annual mean concentration is approximately 85 ppb for almost 100 percent of the years. The maximum 96-hour profile is almost approaching the maximum peak profile; therefore, paraquat does not degrade much in the first 96 hours after application. The maximum 21-day profile shows significant degradation as it is much lower than the maximum 96-hour profile. The maximum 60- and 90-day concentration profiles even more so, with not much difference in their average concentrations. This implies that the third month after application there is not much degradation.



Express v. 1.03.02 (2007-07-20) - Exams 2.98.04.06 with PRZM 3.12.2[48]

Figure 12: Profiles for Estimated Drinking Water Concentration, Glyphosate

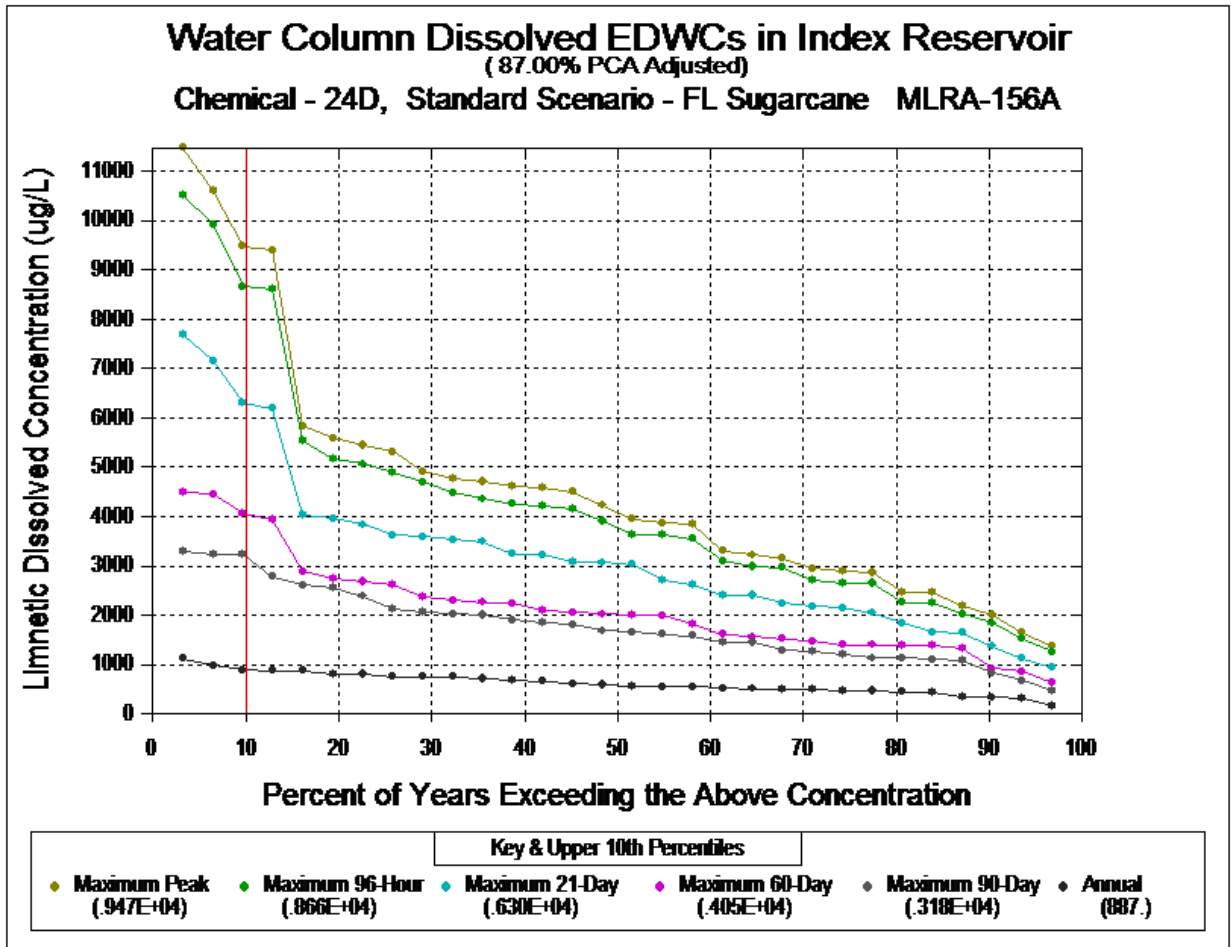
The EDWC profile for glyphosate (Figure 12) shows an average maximum peak concentration more than a magnitude greater than that of paraquat, which is a little more than 11 ppm. In the first 96 hours after application, glyphosate virtually does not degrade. Significant degradation in the index reservoir takes a couple months, as the maximum 60- and 90-day profiles are much lower than where the maximum peak profile. The annual concentration profile is relatively flat, which implies that for the 30 years that the annual concentrations were average, they were not very different. The average annual concentration is an estimated 160 ppb for almost 100 percent of the years.



Express v. 1.03.02 (2007-07-20) - Exams 2.98.04.06 with PRZM 3.12.2[48]

Figure 13: Profiles for Estimated Drinking Water Concentration, Picloram

The picloram EDWC profile (Figure 13) shows a similar degradation profile to that of glyphosate but with even slower degradation. Picloram has the highest average maximum peak concentration (more than 12 ppm) and also like glyphosate, virtually does not degrade within the first 96 hours after application. There is a very significant difference between the maximum 90-day profile and the annual concentration profile, signifying that most of the degradation within a year occurs in the latter nine months of the year. The annual concentration profile has a wider range, implying that the annual concentration was not as consistent and the average annual concentration is estimated at 270 ppb.

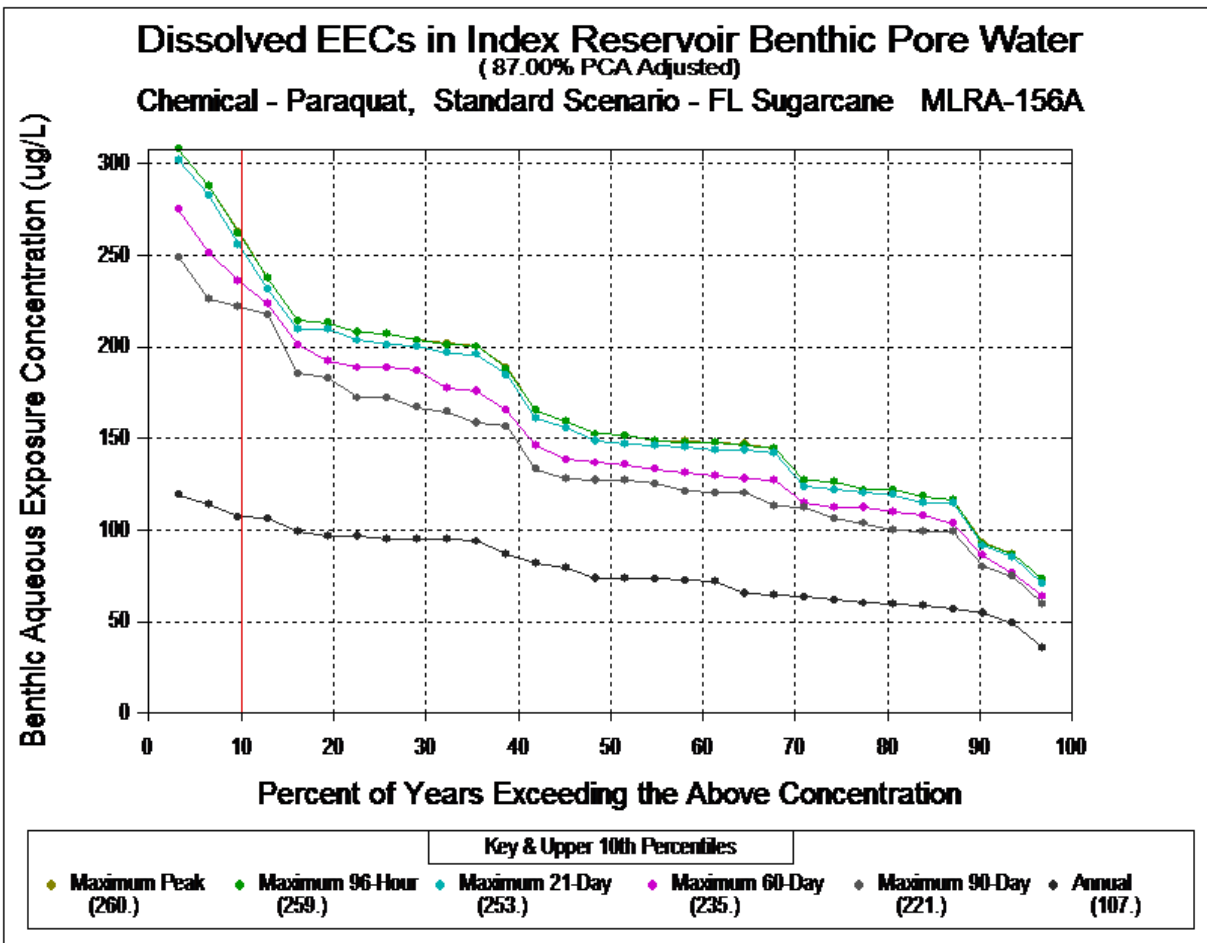


Express v. 1.03.02 (2007-07-20) - Exams 2.98.04.06 with PRZM 3.12.2[48]

Figure 14: Profiles for Estimated Drinking Water Concentration, 2,4-D

2,4-D shows a fairly evenly distributed degradation profile (Figure 14). Its maximum peak EDWC is very similar to that of glyphosate and picloram. The average annual concentration is roughly 90 ppb. Like the simulations in FIRST, picloram shows the highest peak EDWC. 2,4-D and glyphosate show similarly high average maximum peak EDWCs, around 11 ppm each. All three show significant differences between the maximum 60-day EDWC profile and maximum annual EDWC profile and slight difference between their maximum peak and maximum 96-hour EDWC profiles. Paraquat has a significantly different profile: a much lower peak and faster degradation.

Another important distinguishing feature of the Tier II model is that in addition to the estimated drinking water concentration profiles, dissolved EEC profiles in the benthic pore water are provided. The dissolved EEC profiles in benthic pore water for paraquat are shown in Figure 15.

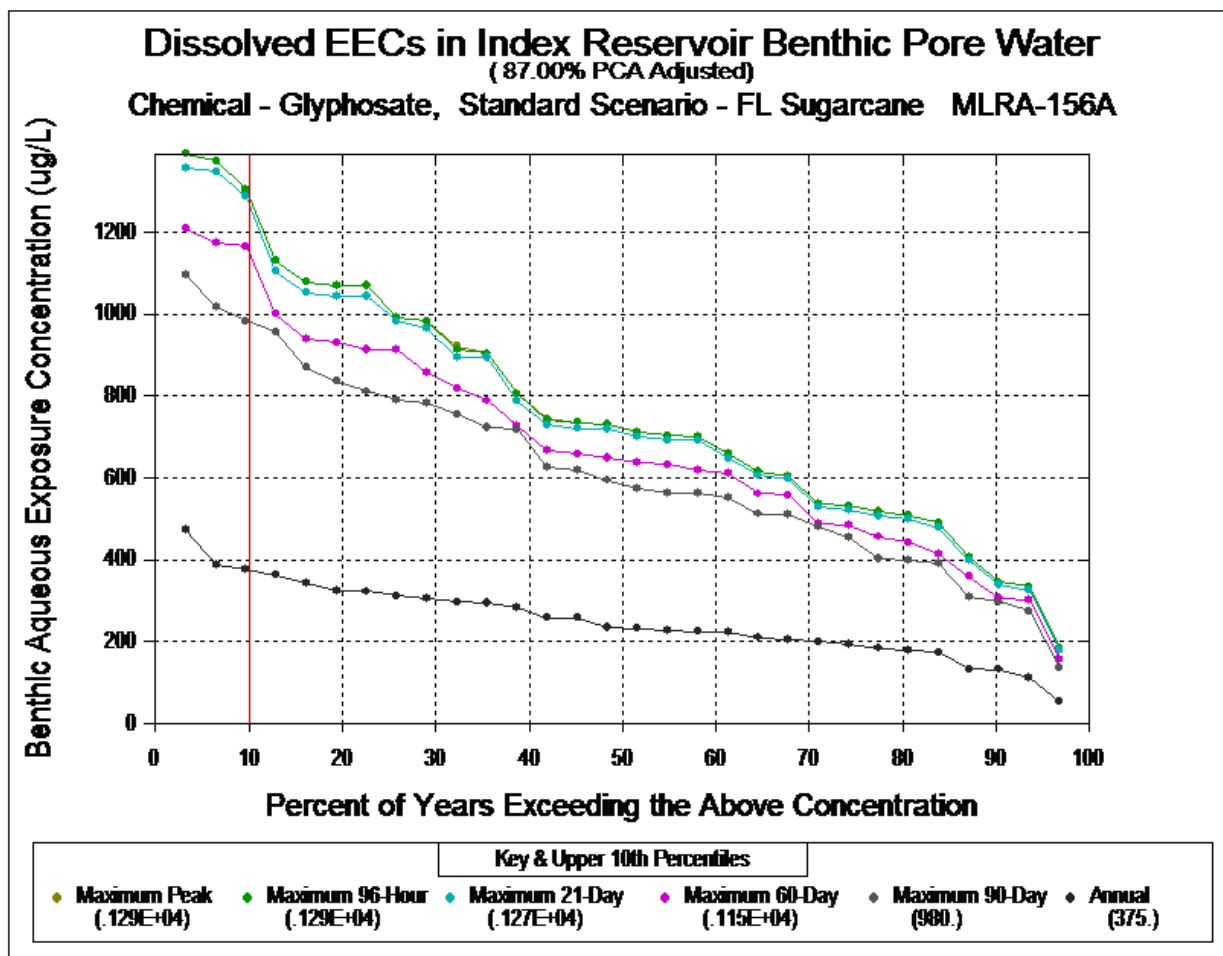


Express v. 1.03.02 (2007-07-20) - Exams 2.98.04.06 with PRZM 3.12.2[48]

Figure 15: Estimated Environmental Concentration Profiles in Benthic Pore Water, Paraquat

The highest average maximum peak concentration for paraquat is about 310 ppb. The similar profiles of all but the annual concentration signify that paraquat degrades slowly in the benthic pore water in the first 90 days, but degrades more rapidly in the latter part of a year. The average

annual concentration exceeds 40 ppb for nearly 100 percent of the modeled years, as seen by the lowest point on the annual concentration profile.

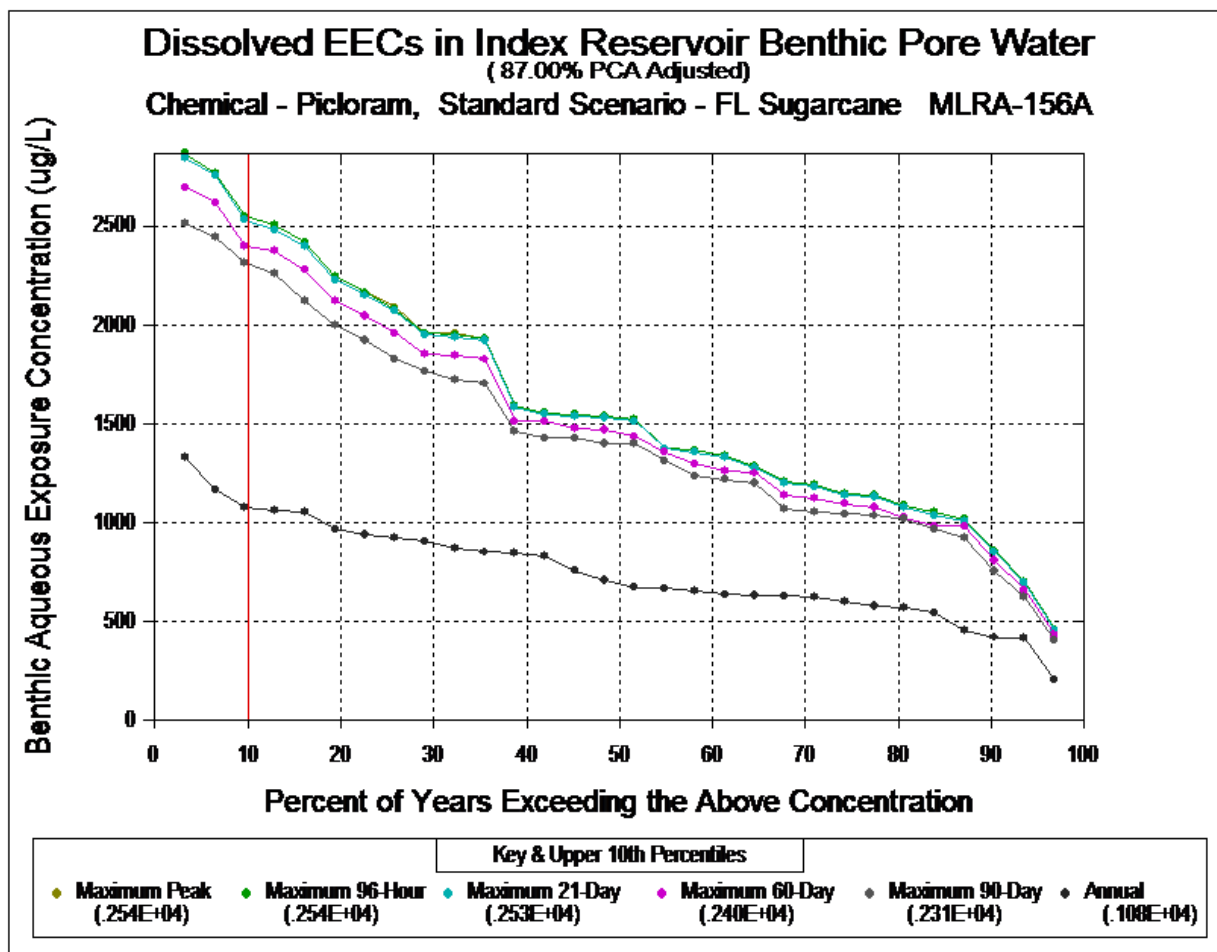


Express v. 1.03.02 (2007-07-20) - Exams 2.98.04.06 with PRZM 3.12.2[48]

Figure 16: Estimated Environmental Concentration Profiles in Benthic Pore Water, Glyphosate

Glyphosate’s highest average maximum peak benthic aqueous EEC is roughly 1400 ppb, much higher than that of paraquat (Figure 16), as seen by the highest point on the graph. This could be because paraquat has a very high k_{oc} so its EDWC and EEC profiles are lower than the other chemicals because it tends to move to the sediment. Similar to paraquat, glyphosate does not degrade readily in the first 90 days and the majority of the degradation occurs in the last nine months of the year. The annual concentration profile is fairly dynamic. Glyphosate’s average

annual benthic aqueous EEC is estimated as 65 ppb. The EEC profiles for picloram are shown in Figure 17.

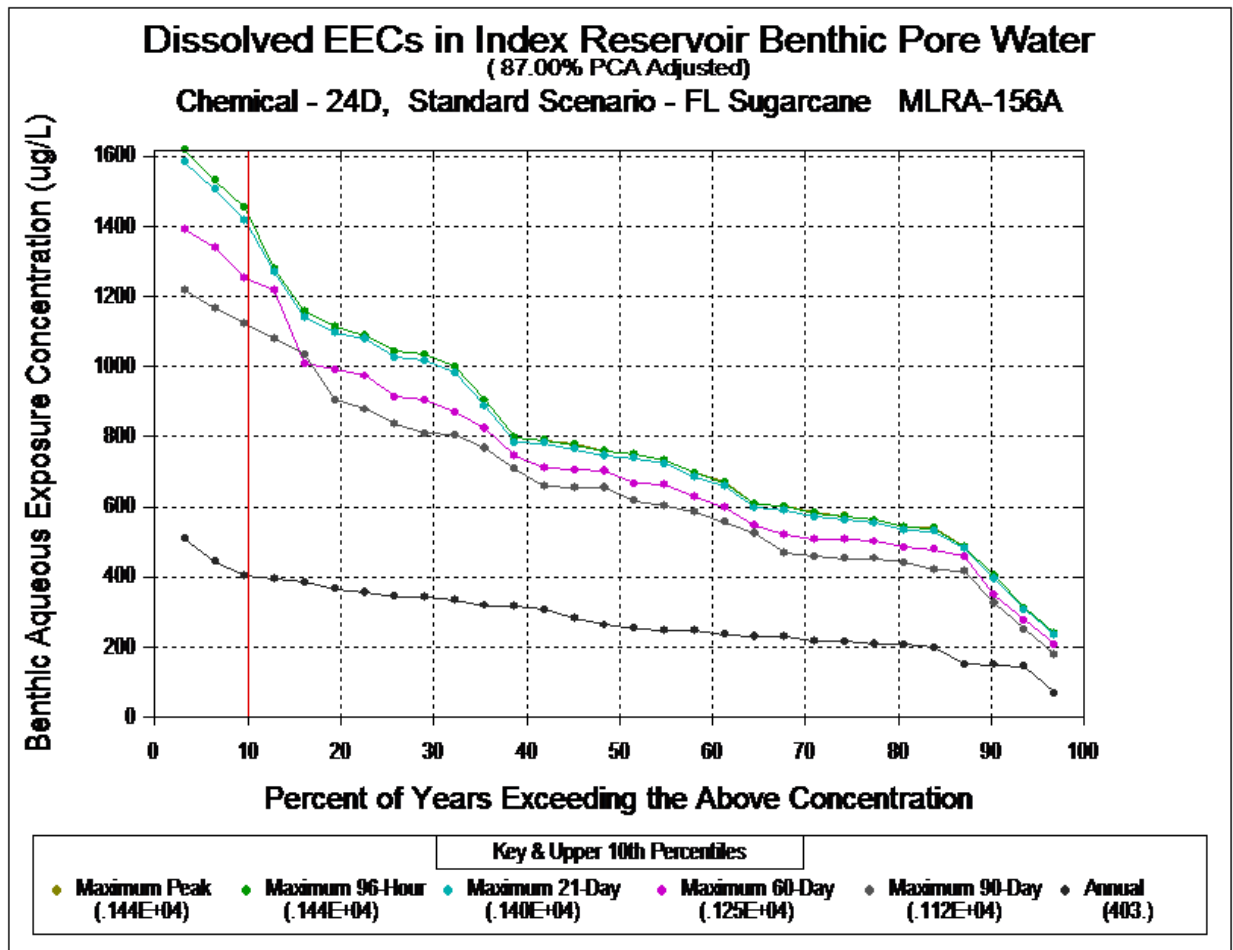


Express v. 1.03.02 (2007-07-20) - Exams 2.98.04.06 with PRZM 3.12.2[48]

Figure 17: Estimated Environmental Concentration Profiles in Benthic Pore Water, Picloram

The highest average maximum peak EEC for picloram is about 3000 ppb. It virtually does not degrade in the first 90 days after application. The annual concentration profile has the largest range out of all of the chemicals, starting around 1300 ppb and the average annual EEC is roughly 240 ppb for almost 100 percent of the years. The EEC profiles in benthic pore water for 2,4-D are shown in Figure 18. 2,4-D's highest average maximum peak concentration is much lower, around 1600 ppb. Similarly, it does not degrade in the first 90 days. Its annual EEC

profile has a much smaller range and the average annual EEC exceeds 80 ppb for nearly 100 percent of the modeled years.



Express v. 1.03.02 (2007-07-20) - Exams 2.98.04.06 with PRZM 3.12.2[48]

Figure 18: Estimated Environmental Concentration Profiles in Benthic Pore Water, 2,4-D

Annual dissolved EECs in the benthic pore water are significantly lower than the EDWC profiles. The large difference between the maximum 90-day EEC and the maximum annual concentration implies that all four chemicals do not degrade significantly in the first 90 days after application, that the four chemicals are persistent in the benthic pore water. Again, the paraquat concentration is predicted as a magnitude lower than that of picloram. Glyphosate and 2,4-D have very similar EEC profiles.

EXPRESS is a self-proclaimed “screening-level” model, not a sophisticated “higher-tier application.” Additionally, the lack of experimental data due to the very remote study site forced many assumptions. Therefore, the estimated concentration profiles cannot be assumed to be completely representative of the gravity-fed water system in Santa Rosa, but environmental and ecological toxicity implications as well as human health implications can still be explored and discussed.

4.2 Risk Assessment for Human Health

4.2.1 Risk Associated with Drinking Water

The calculated ADDs for adult males are shown in Table 10. As per US EPA risk assessment standards, the daily intake rate of drinking water for adults was 2 liters per day for both men and women.

Table 10: Average Daily Doses for Adult Males (mg/kg*d)

	Paraquat	Glyphosate	Picloram	2,4-D
FIRST, acute	6.5E-05	1.7E-04	3.2E-04	2.8E-04
FIRST, chronic	9.1E-06	2.8E-05	1.2E-04	8.7E-05
PRZM-EXAMS, annual average	2.8E-03	5.2E-03	8.7E-03	2.9E-03
PRZM-EXAMS, max peak	4.5E-02	3.6E-01	4.0E-01	3.7E-01

Because the FIRST model predicted the lowest concentrations for all four chemicals of interest, the calculated ADDs were significantly lower than those of PRZM-EXAMS. Both acute and chronic ADDs calculated from concentrations in drinking water from the FIRST model are several magnitudes shy of the oral RfD for each chemical, implying that there is no associated risk. The only ADDs that exceeded the oral RfDs were using the worst-case scenario, the maximum peak of the PRZM-EXAMS profile, which implies an associated risk for all four chemicals of interest. The calculated ADDs for adult females are shown in Table 11.

Table 11: Average Daily Doses for Adult Females (mg/kg*d)

	Paraquat	Glyphosate	Picloram	2,4-D
FIRST, acute	7.2E-05	1.9E-04	3.6E-04	3.2E-04
FIRST, chronic	1.0E-05	3.2E-05	1.4E-04	9.7E-05
PRZM-EXAMS, annual average	3.1E-03	5.8E-03	9.7E-03	3.2E-03
PRZM-EXAMS, max peak	5.1E-02	4.0E-01	4.4E-01	4.1E-01

As expected due to their lower body weight, the ADDs for adult women calculated are slightly higher than those of adult men. The two concentrations used from the Tier II PRZM-EXAMS simulation shell are the highest and lowest predicted: the maximum peak concentration and the annual average for nearly 100 percent of the years, respectively. Because the average maximum peak for each chemical is the highest average maximum peak concentration for each chemical averaged over 30 years, it is not surprising that the ADDs calculated with these concentrations all exceed the oral RfD. In fact, the concentrations from the highest average maximum peak in PRZM-EXAMS were the only ADDs that exceeded the oral RfDs.

The body weight for a generic “child” was 25 kilograms for the purposes of this study. Also based on US EPA guidelines, the daily intake rate of drinking water for children was 1 liter per day. The calculated ADDs for children are shown in Table 12. Even though some ADDs come closer to approaching the oral RfDs, it is still only the highest average maximum peak concentrations from PRZM-EXAMS that exceed those values.

Table 12: Average Daily Doses for Children (mg/kg*d)

	Paraquat	Glyphosate	Picloram	2,4-D
FIRST, acute	8.0E-05	2.1E-04	4.0E-04	3.5E-04
FIRST, chronic	1.1E-05	3.5E-05	1.5E-04	1.1E-04
PRZM-EXAMS, annual average	3.4E-03	6.4E-03	1.1E-02	3.6E-03
PRZM-EXAMS, max peak	5.6E-02	4.5E-01	4.9E-01	4.6E-01

By these calculations, it can be assumed that the community members of Santa Rosa are not in danger of adverse effects of drinking from the untreated water of the gravity-fed water system. However, because the PRZM-EXAMS concentration profiles are quite detailed, it is worthwhile to investigate how often the ADDs are exceeding the oral RfDs by looking closer at the concentration profiles. In order to do this, a “breakpoint concentration” was calculated; that is to say, the concentration at which the ADD will exceed the RfD for men, women, and children. These values are shown in Table 13.

Table 13: Calculated Breakpoint Concentrations, ppb

	Paraquat	Glyphosate	Picloram	2,4-D
men	140	3,100	2,200	310
women	120	2,800	1,900	280
children	110	2,500	1,800	250

Once breakpoint concentrations are calculated, each value is compared to the EDWC profile for each chemical and for each subgroup of the population. Since the average annual concentration profiles have the most conservative estimations, this profile will have the lowest percentage of years exceeding the breakpoint concentration. The values for percent years exceeding breakpoint concentrations for average annual concentrations are shown in Table 14.

Table 14: Percent Years Average Annual Concentration Exceeds Breakpoint Concentrations (Drinking Water)

	Paraquat	Glyphosate	Picloram	2,4-D
men	38	0	0	90
women	60	0	0	90
children	70	0	0	90

The entire average annual concentration profiles over the 30 years’ time for glyphosate and picloram do not exceed the breakpoint concentrations. Therefore, if the consumer is only

concerned with the average annual concentration for these two chemicals, there is no risk. Paraquat shows moderate to high risk for the average annual concentration profile, and 2,4-D shows that nearly 100 percent of the time the ADD will exceed the oral RfD, which is alarming. The percent years that the highest average maximum peak concentration exceeds the breakpoint concentrations are shown in Table 15.

Table 15: Percent Years that the Highest Average Maximum Peak Concentration Exceeds Breakpoint Concentrations (Drinking Water)

	Paraquat	Glyphosate	Picloram	2,4-D
men	100	70	92	100
women	100	80	94	100
children	100	90	94	100

As can be expected, these percentages are much higher than the previous best-case scenario values. Paraquat and 2,4-D, the two chemicals that showed risk over average annual concentration now show that 100 percent of the years the highest average maximum peak concentrations are predicted to exceed the breakpoint concentration. Therefore, when the maximum peak concentrations of these two chemicals are considered to calculate the ADD, they will always exceed the oral RfD. Glyphosate and picloram show high risk at their peak concentrations, with very high percentages exceeding the breakpoint concentrations. This shows that at maximum peak concentrations, drinking the water from the gravity-fed water system almost always presents high levels of risk, implying a very high possibility of adverse human health effects.

4.2.2 Risk Associated with Consumption of Fish from the River

Bioconcentration factors (BCFs) are a ratio of the concentration of the chemical in a living organism divided by the concentration in an environmental medium (air, water, soil) (Mihelcic, 1999). The estimated BCFs are shown in Table 16.

Table 16: Calculated Bioconcentration Factors

	Paraquat	Glyphosate	Picloram	2,4-D
BCF	2.24E-04	1.53E-03	1.64E+02	8.05E+02

The BCFs for paraquat and glyphosate are small (less than 1) and the BCFs for picloram and 2,4-D are much higher, much greater than 1. BCF is related to the hydrophobicity of a chemical (represented by k_{ow}) but is also related to the lipid content as the chemicals tend to accumulate in the fatty tissue of a species (Mihelcic, 1999). Since BCF and concentration of each pesticide are the only differentiating factors, E_m for picloram and 2,4-D are much higher than that of paraquat and glyphosate (Table 17).

Table 17: Individual Exposure to Contaminant Due to Ingestion of Fish (E_m , mg/kg*d)

	Paraquat	Glyphosate	Picloram	2,4-D
men	7.20E-08	4.00E-06	4.70E-02	2.10E-01
women	6.00E-08	3.30E-06	3.90E-02	1.70E-01
children	4.10E-08	2.20E-06	2.60E-02	1.20E-01

The E_m for men, women, and children can then be compared to the oral RfD as was done with the ADD for the drinking water ingestion estimation. The values for the concentration of each pesticide in water were the highest average maximum peak from the PRZM-EXAMS Tier II model results, so they are high concentration values. Although the E_m for picloram is the same magnitude as its RfD, it is not above the RfD. Paraquat and glyphosate's predicted ingestion values do not come close to the oral RfD. However, the E_m values for 2,4-D for men, women, and children are significantly higher than the oral RfD, which means that all subgroups are at risk of adverse health effects from 2,4-D by eating the fish from the river.

As with the risk assessment for drinking water, the breakpoint concentrations were calculated for exposure from fish consumption (Table 18).

Table 18: Calculated Breakpoint Concentrations (Fish Consumption), ppb

Paraquat	Glyphosate	Picloram	2,4-D
8.7E+07	2.8E+08	1.9E+03	5.4E+01

It can be noted that the breakpoint concentrations for paraquat and glyphosate are very high. This is due to their low BCFs. Breakpoint concentrations were then compared to the EDWC profiles for the best- and worst-case scenarios (Tables 19 and 20).

Table 19: Percent Years Average Annual Concentration Exceeds Breakpoint Concentrations (Fish Consumption)

Paraquat	Glyphosate	Picloram	2,4-D
0	0	7	100

As can be expected, the breakpoint concentrations were not even close to presenting a risk for paraquat and glyphosate. Picloram presents a very small risk but 2,4-D presents a very high risk to the consumer via fish consumption for the best-case scenario.

Table 20: Percent Years that the Highest Average Maximum Peak Concentration Exceeds Breakpoint Concentrations (Fish Consumption)

Paraquat	Glyphosate	Picloram	2,4-D
0	0	95	100

For the worst-case scenario, both picloram and 2,4-D present a very high risk to the consumer while paraquat and glyphosate still present no risk. There are high uncertainties associated with the estimated risk due to uncertainties in the calculation of BCF and in model concentration estimations.

4.2.3 Additive Exposure and Risk for Human Health

The results of additive risk for human health for the best case scenario are shown in Figure 19.

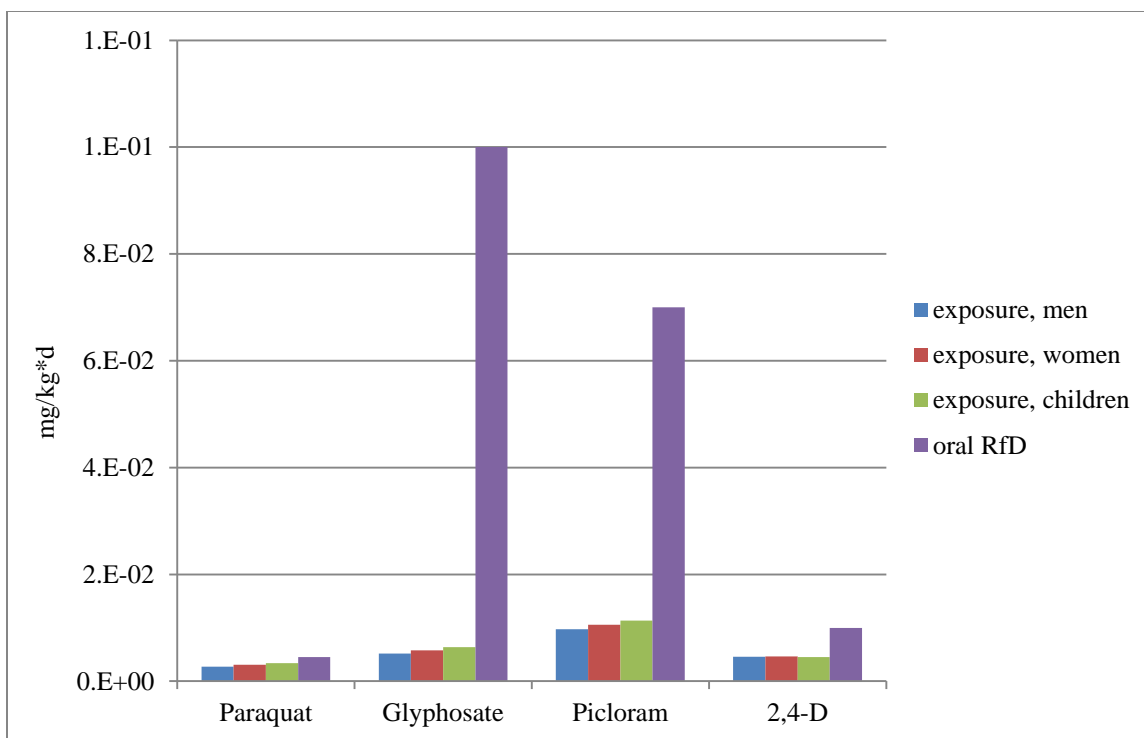


Figure 19: Additive Exposures Compared to Oral RfDs, Best Case Scenario

None of the additive exposures for men, women, or children exceed the oral RfD, implying zero risk in the best case scenario. The oral RfDs for glyphosate and Picloram are one magnitude higher than the calculated additive exposures. However, the additive exposures for 2,4-D is about one-half of the oral RfD. For paraquat, the additive exposures are approaching the oral RfD, which indicates that when the concentration of paraquat in water exceeds the minimum estimated values, it presents a risk to the consumer. The results from the worst case scenario are shown in Figure 20.

The additive exposures for men, women, and children all exceed the oral RfDs by several magnitudes for paraquat, glyphosate, picloram, and 2,4-D. This indicates a very high risk for all population groups from all four chemicals of interest. Additionally, these calculations do not take into account other ingestion pathways such as eating the sprayed crops, so exposure (and therefore risk) is most likely even higher.

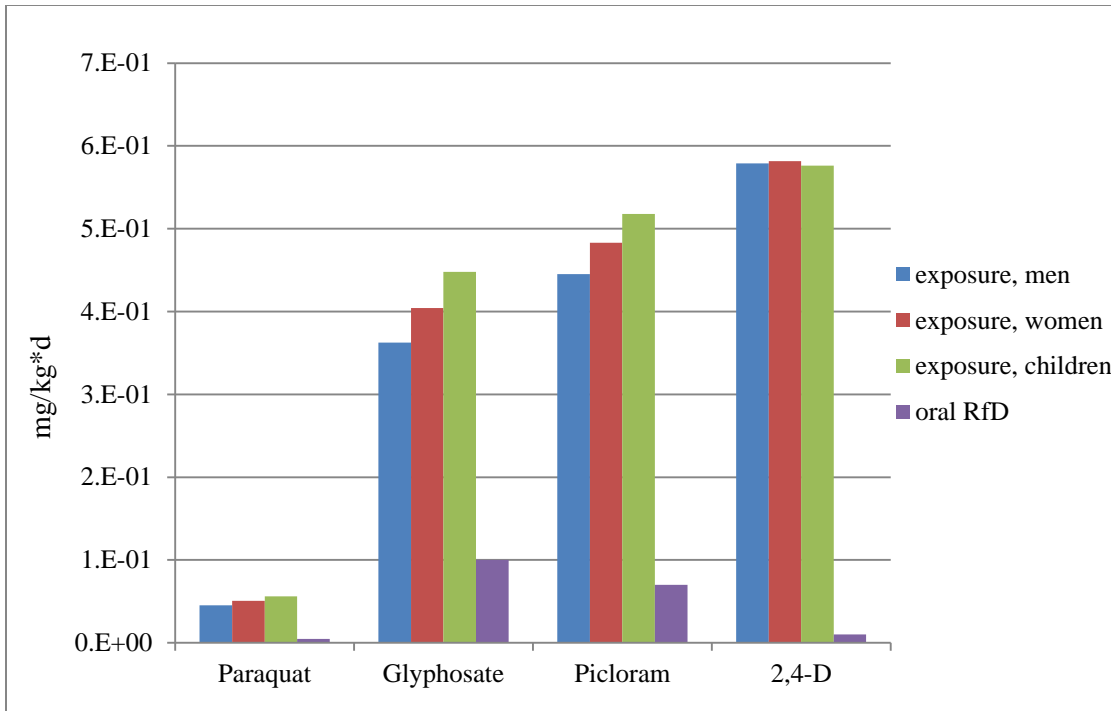


Figure 18: Additive Exposures Compared to Oral RfDs, Worst Case Scenario

4.3 Ecological Toxicity Implications

The comparison of the average maximum 96-hour concentration profiles to the 96-hour LD50s is shown in Table 21). The results show that in terms of acute aquatic toxicity, paraquat and picloram pose no threat (although two data points are missing). However, the assumed concentrations of glyphosate and 2,4-D in the stream pose a significant threat to fathead minnows and bluegills. Fathead minnows are the type of fish that are caught the most in the river.

Table 21: Percent Years Stream Concentration Exceeds 96-hour LD50

	Paraquat	Glyphosate	Picloram	2,4-D
fathead minnow	unavailable	87	unavailable	74
channel catfish	0	0	0	14
bluegill	0	22	0	100

Unfortunately, the only LD50 value found for freshwater shrimp, the aquatic species that is most common and most consumed in Santa Rosa, was for 2,4-D. The acute LD50 for grass shrimp is 0.092 mg/L or 92 ppb (US Forest Service, 2006), which the average annual concentration exceeds for nearly 100 percent of the years. Therefore, 2,4-D is considered to present a high level of risk to the shrimp in the local stream.

For a more general risk assessment, the assumed stream concentrations can be compared to the US EPA’s Office of Pesticides Program’s Aquatic Life Benchmarks. As before, these values were compared to the average annual concentration profiles in order to quantify the number of years for which the concentration exceeded the benchmark, therefore presenting a threat to a respective aquatic group in the best case scenario (Table 22).

Table 22: Percent Years Average Annual Concentration Exceeds Aquatic Life Benchmark

	Fish		Invertebrates		Nonvascular Plants	Vascular Plants
	Acute	Chronic	Acute	Chronic		
Paraquat	0	0	0	100	100	100
Glyphosate	0	0	0	0	0	0
Picloram	0	95	0	0	0	—
2,4-D	0	0	0	0	0	98

It seems that with respect to average annual concentrations, the only threats are to fish from picloram at the chronic time scale and that paraquat presents a significant chronic threat to invertebrates and all aquatic plants. Vascular plants are at risk by the assumed concentrations of 2,4-D in the river.

Considering the worst-case scenario, the average maximum peak concentrations are taken into account. Perceived risk becomes greater as the peak concentrations are higher than annual concentrations (Table 23).

Table 23: Percent Years Highest Average Maximum Peak Concentration Exceeds Aquatic Life Benchmarks

	Fish		Invertebrates		Nonvascular Plants	Vascular Plants
	Acute	Chronic	Acute	Chronic		
Paraquat	0	91	65	100	100	100
Glyphosate	0	93	0	0	0	0
Picloram	17	100	0	5	46	—
2,4-D	0	0	0	0	59	100

Concentrations of paraquat present moderate to very high risk on nearly all groups aquatic species. Glyphosate poses a threat only on fish at the chronic level, and 2,4-D threaten both nonvascular and vascular plants. Picloram presents maximum risk to fish on the chronic time scale and a low risk at the acute time scale, with moderate risk to nonvascular plants.

4.4 Study Limitations

All objectives of this study focus on the water quality aspect of unrestricted pesticide use, with special consideration to human exposure via drinking water and ingestion of contaminated fish/shrimp as well as the ecological impacts to aquatic life. However, there are several occupational and non-occupational exposure pathways that could not be considered due to lack of data and/or model limitations. These are summarized in Table 24.

Table 24: Summary of Non-Occupational and Occupational Exposure Pathways

Non-occupational	Occupational
Drinking Water	Spraying
Eating fish/shrimp from the river	Dermal
Eating sprayed crops (rice, corn, etc.)	Inhalation
Swimming in the river	Walking through sprayed fields
Walking/playing on the lawn	Mixing
Household storage	Disposal of containers
Residue on skin, clothes	
Washing contaminated clothes	
Pesticide container re-use	
Baby-to-mother (breastfeeding)	

The calculation for exposure from eating sprayed crops was not possible because there were no predicted concentration of pesticides in soil. The remaining exposure pathways are even less quantifiable, such as washing the contaminated clothes and pesticide container re-use, though they can be significant exposure pathways.

Sources of uncertainty due to the nature of pesticide fate and transport modeling are another limitation. The necessary assumptions equating the system studied with the index reservoir default in EXPRESS and the weather and soil data for the Florida sugarcane scenario are a very limiting factor of this study. Many chemical properties that came from the EPI Suite were estimated by models and have high uncertainty. Additionally, transport and transformation of pesticides in the environment can be affected by soil properties such as moisture content, fraction organic carbon; water properties such as temperature and pH; air properties such as humidity and wind speed; biological properties such as presence of microorganisms and plant physiology; and topography (Estevez et al., 2007). Another significant source of uncertainty is the fact that more often than not, these pesticides are being mixed together when they are applied. Sources of uncertainty in human health risk assessment lie with the variations from person to person ingestion of contaminated food and water and metabolism.

4.5 Risk Mitigation Strategies

There are several technological mitigation strategies in the form of best management practices (BMPs) or Integrated Pest Management (IPM). Reichenberger et al. (2007) reviewed mitigation strategies to reduce pesticide loads to ground- and surface water. Technological mitigation strategies include buffer strips, constructed wetlands, and subsurface drains. A buffer strip is typically a strip of vegetation at the edge of a field and/or by a body of water to intercept runoff. Because a small area immediately surrounding the spring source of the gravity-fed water

system is forested, it can be said that it already has a buffer strip. A focus on increasing the amount of vegetation between agricultural activities and the spring source of the gravity-fed water system should be considered as a form of source protection.

Constructed wetlands are man-made wetlands for habitat restoration or for the runoff of anthropogenic activities, e.g. wastewater discharge. They can help with load reduction and many studies find that they reduce pesticide loads to surface water (Reichenberger et al., 2007) but their placement must be deliberate and their design can be complicated if one is unfamiliar, i.e. they may not be appropriate technology for a small village in Panamá. For subsurface drains, the study found that there was no technology that could be implemented to mitigate these processes, but they could be reduced through “application rate reduction, product substitution and shift of the application date” (Reichenberger et al., 2007).

Changes in application are probably the most feasible mitigation strategies. As previously stated, pesticides are not only used in farming and ranching activities in and around Santa Rosa, but they are overused and abused. Simply reading and following the instructions on the pesticide containers would greatly reduce the application rate. The instructions detail how much water to add, how much should be sprayed per area of land, that it should not be mixed, human and environmental toxicity, and proper safety procedures. Product substitution could mean changing from the synthetic chemical pesticides to biological pesticides, or “biopesticides”, which are pesticides derived from biological material such as animals, plants, bacteria, and certain minerals. However, because the definition of biopesticide remains unclear and they are unavailable in most Latin American countries (US EPA, 2014), they are not currently recommended as a potential risk mitigation strategy.

4.6 Public Health and Policy Implications

Although technological mitigation strategies and BMPs have the potential to create a barrier between pesticides and humans and therefore decrease exposure and risk, they are not always the best fit to empower the community to improve or take preventative measures for their own health. At the community level, the most obvious intervention is pesticide education for the farmers and ranchers. The author noted that at the study site radio public service announcements (PSAs) seemed to have been effective teaching tool for villagers to learn (or be reinforced of the idea) to chlorinate their water. Therefore, a PSA that describes property safety equipment and handling and application procedures has the potential to increase safe use of pesticides. However, it cannot be assumed that education alone will change dangerous behaviors. With respect to non-suicidal negative health consequences, most can be mitigated or minimized simply by banning the most lethal pesticides, WHO class I and II pesticides. This also requires substituting these products with alternatives.

The aforementioned FAO International Code of Conduct on the Distribution and Use of Pesticides is the internationally accepted standard. This code “responded to growing concerns about inadequate controls on pesticides and the lack of regulatory infrastructure in developing countries”, but on a voluntary basis for both public and private interests (Jansen, 2008). The Prior Informed Consent (PIC) legislation was signed at the Rotterdam Convention in 1998 by Panamá and 152 other countries as well as the European Union (Rotterdam Convention, 2013), which includes a short list of hazardous chemicals that member countries must sign off on either allowing or banning these chemicals in the respective countries. None of the four chemicals of interest in this study are included on the short list, which includes the infamous DDT.

Legislation starting in the 1970s in Sri Lanka has been aimed at reducing the number of deaths from acute pesticide poisonings (most of them suicides). From the gradual ban of WHO class I organophosphate (OP) pesticides, poisoning and deaths from pesticides decreased. However, they were replaced with WHO class II chemicals, including endosulfan, which was eventually banned. The majority of deaths from pesticides continue to be from WHO class II OPs, which are less toxic than class I but still toxic enough for self-harm (Roberts et al., 2003).

A case study of Honduras argues for the banning of highly toxic pesticides over more complicated legislation that has been difficult to enforce (Jansen, 2008). It wasn't until 1995 that Honduras took interest in pesticide legislation via the *Organismo Internacional Regional de Sanidad Agropecuaria* (OIRSA), which was established to present a legal framework for Central American countries to comply with FAO code. In 1998 the German development agency (GTZ) helped establish concrete regulations, but they were later repealed. Although there is legislation, successful enforcement has still not been achieved (Jansen, 2008).

In 1991, the pesticide industry under the Global Crop Protection Federation (GCPF) initiated three voluntary pilot projects in Kenya, Thailand, and Guatemala, coined the Global Safe Use campaign. The pilot project in Guatemala consisted of three phases, the first of which was training and education. Eight hundreds government extension agents were trained, who then trained hundreds of thousands of farmers and housewives, school teachers, and children. Near the end of the first year of the campaign, the United States Agency for International Development (USAID) joined with its own \$4 million, three-year project, Pesticide Management Activity (PMA). The second phase focused on technical training of small vegetable growers. The final phase is "self-sustaining" control from the host country, in which a levy on imported pesticide active ingredients is collected to fund continuing education activities. Reported

pesticide poisonings between 1972 and 1997 have gone down dramatically, most trained children report not re-using pesticide containers (while most surveyed untrained children do) and most trained farmers read labels (while most untrained farmers surveyed do not) (Murray & Taylor, 2000).

In 2013, El Salvador, led by its Environmental Commission and the Movement for the Defense of Life and Natural Resources passed landmark legislation, banned 53 pesticides nationwide. Among the banned chemicals are paraquat, 2,4-D, DDT, and glyphosate. They plan to oust all of these pesticides within two years, giving them time to find alternatives. However, since the legislation is so new, it is unclear whether the bans are successfully being implemented (Sustainable Pulse, 2013).

A 2011 study by WHO surveyed 142 member countries and 113 of the countries completed the survey of pesticide legislation, regulation, and enforcement. Of those surveyed, 84 percent have national or regional legislation but are only enforced “to a large extent” by 41 percent. The Code calls for countries to document poisonings, but very few countries have a mechanism to do so. About half of the countries have no quality control facilities and report substandard or counterfeit pesticides to be a problem. Comprehensive legislation, registration, and enforcement practices are absolutely essential to mitigating potential risks from pesticide use (Matthews et al., 2011). It should also be noted that where capacity building activities are lacking is most likely due to the fact that the policy makers and their advisers have low levels of awareness of adverse unintended consequences from pesticide use and abuse (WHO, 2010).

Pesticide safety is not only a developing world public health issue. The US EPA recently amended the Agricultural Worker Protection Standard (WPS) with the intention of making pesticide use safer for farmers in the United States. Changes include annual mandatory trainings,

more mandatory no-entry signs for places where hazardous pesticides were sprayed, first-ever minimum age of 16 (except for family farms), new no-entry 25-100 foot buffer zones, first-ever accessibility to spraying and hazard information for farmworker advocates and medical personnel, and mandatory record-keeping to improve states' ability to follow up on compliance and enforce compliance (EPA Connect, 2014). This is important because in the United States more than 2 billion kilograms of pesticides are sprayed annually, about 77% from agricultural use (Rice et al., 2007). Understanding environmental fate and transport of pesticides is a global health issue. Ever-changing social, economic, and environmental pressures have the power to directly impact demand for pest management, (Rice et al., 2007) so the sustainability of pest management is an interdisciplinary issue and cannot be addressed by environmental engineering or public health studies alone.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

The objectives of this study were to review the studies of pesticides' effects on drinking and surface water in the developing world, existing models in the developed world, and to estimate concentrations of paraquat, glyphosate, picloram, and 2,4-D in drinking water and the river. The related hypotheses were that the pesticides in question were above concentrations in the gravity-fed water system and the river that pose a risk to the people of Santa Rosa via drinking water and ingestion of the fish from the river (hypotheses 1 and 4, respectively) and that the river fish were in danger of dying off (hypothesis 3). Also, the application of pesticides immediately before a rain event would result in higher concentrations than application followed by a delayed rain event (hypothesis 2). Additionally, alternative chemicals and alternative practices may help mitigate the adverse impacts of pesticide use on the environment and human health (hypothesis 4).

The EXAMS-PRZM Exposure Simulation Shell (EXPRESS) models FQPA Index Reservoir Screening Tool (FIRST) and Pesticide Root Zone Model-Exposure Analysis Modeling System (PRZM-EXAMS) shell were used for all modeling in this study. FIRST provided acute and chronic drinking water concentration estimations for the simulations, where picloram had the highest untreated drinking water concentrations. These Tier I models were used to assess hypothesis 2. Concentrations in water were higher for immediate rain events, but only by 1 to 5 percent. When the concentrations from FIRST were used for the risk assessment for human health via drinking water, the calculated Average Daily Doses (ADDs) were magnitudes below the oral Reference Doses (RfDs).

Simulations from the II PRZM-EXAMS shell provided Estimated Drinking Water Concentration (EDWC) and benthic pore water Estimated Environmental Concentration (EEC) profiles. The highest average maximum peaks and average annual concentrations were the main values used in the risk assessment, finding that only with the highest average maximum peak concentrations did the ADDs exceed the RfDs. However, when the breakpoint concentrations were calculated and compared to the concentration profiles, the annual concentration profiles presented moderate and high risks with respect to paraquat and 2,4-D with no risk associated with glyphosate and picloram but when compared to the maximum peak concentration profiles presented high risk to human health from drinking water for all four chemicals of interest (hypothesis 1).

Calculations were also carried out to assess the risk associated with consumption of fish from the river. Individual exposure to each pesticide was calculated and compared to RfDs and 2,4-D was the only chemical of interest that presented a threat to human health by this exposure route. When the RfD was set to the individual exposure, however, more risk was seen when compared to the stream concentration profiles. For the best case, picloram presented a low level of risk and 2,4-D presented a high risk but for the worst case both of these chemicals presented a very high risk to the consumer. Additive exposures from drinking water and fish consumption ingestion routes were also calculated and compared to the oral RfDs. For the best case, none of the four chemicals posed a threat to the consumer but for the worst case, exposure from all four chemicals greatly exceeded the oral RfDs, presenting a very high risk to the consumer.

Ecological implications were also explored by comparing concentrations of the pesticides in the river to aquatic life benchmarks. With regards to specific species, glyphosate and 2,4-D concentrations in the river exceeded 96-hour LD50s (lethal dose) for fathead minnows and

bluegills. With regards to the US EPA's aquatic life benchmarks, invertebrates at the chronic level and all plants were at risk due to paraquat concentrations with the average annual concentration. When the highest average maximum peak was considered, paraquat endangered nearly all fish, invertebrates, and plants at acute and chronic levels and fish at the chronic level were threatened by nearly all of the chemicals. This is in accordance with hypothesis 3 and observations made in the field by the author of this thesis.

Limitations of this study include the major assumptions that were necessary to perform model simulations and missing exposure pathways in the risk assessment. Additionally, the risk assessment due to the mixing of all four chemicals of interest could not be performed due to lack of methods and combined toxicity data points in literature of these chemicals. Technological mitigation strategies are not recommended but changes to application are feasible (hypothesis 4). Reducing occupational exposure by simply following instructions on pesticide containers and wearing personal protection equipment could minimize exposure to harmful chemicals can reduce overall exposure. Public health and policy implications conclude that this global public health issue is a multi-faceted problem that needs to be address at all levels and the solution will ultimately be a multi-disciplinary approach.

Recommendations for future studies include simulating pesticide concentrations using a model where the user can design their own environment, as one pre-loaded index reservoir in Illinois cannot be assumed to be identical to a gravity-fed water system in Panamá (or most other developing countries). Additionally, the ideal model would have weather data from all over the world, as the climate in Florida is very similar but the weather patterns are not the same as Panamá. The development of a fate and transport model for gravity-fed water systems with integrated human health and environmental risk assessment in the developing world context

could be useful. Additionally, low-cost field methods for testing for pesticides should be developed to monitor the pesticide concentration and compare the measured data to model results to validate the model.

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APPENDIX A: FIRST MODEL INPUT FILES

```
C:\express\progs\first.exe
FIRST
<F>QPA <I>NDEX <R>ESERVOIR <S>GREENING <T>OOL

ENVIRONMENTAL FATE AND EFFECTS DIVISION
OFFICE OF PESTICIDE PROGRAMS
U.S. ENVIRONMENTAL PROTECTION AGENCY

TIER ONE SCREENING MODEL
FOR DRINKING WATER PESTICIDE EXPOSURE

VERSION 1.1.0
January 1, 2007

THIS IS A PROGRAM TO ESTIMATE TIER ONE, ACUTE AND CHRONIC
CONCENTRATION VALUES FOR PESTICIDES IN DRINKING WATER BASED
UPON AN INDEX RESERVOIR LOCATED IN SHIPMAN, ILLINOIS

THE PROGRAM IS USED TO ESTIMATE CONSERVATIVE EXPOSURE
VALUES FOR PESTICIDES IN ANY AREA OF THE UNITED STATES

PLEASE ENTER A RUN NUMBER TO CONTINUE --->
```

Figure A.1: FIRST Model DOS User Interface

APPENDIX B: FIRST MODEL OUTPUT FILE

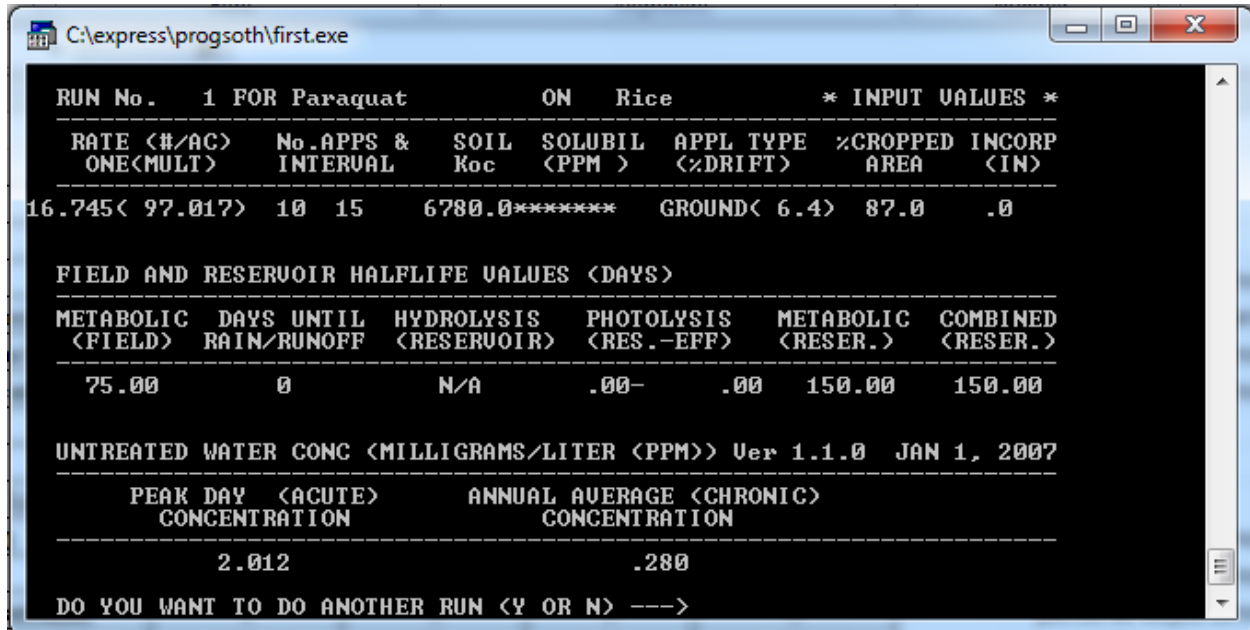


Figure B.1: FIRST Model Outputs

APPENDIX C: PRZM-EXAMS INPUT FILES



Figure C.1: PRZM-EXAMS Graphical User Interface

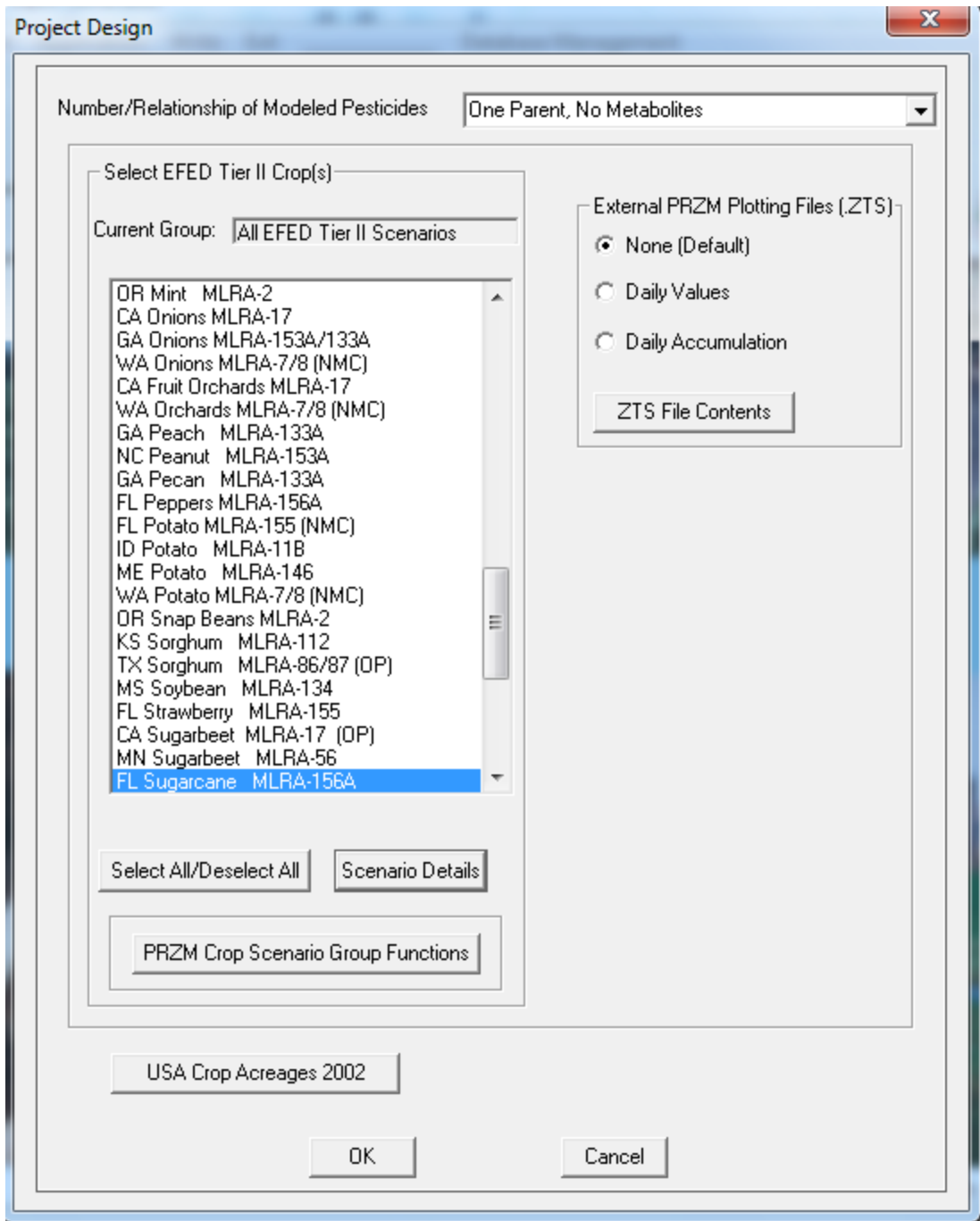


Figure C.2: PRZM-EXAMS Project Design Window

Enter PRZM Chemical Parameters

Chemical 1 | Chemical 2 | Chemical 3

PRZM 3.12 Tier II Standard Analysis

Chemical Name: Paraquat

Molecular Weight: 257.20

Solubility (mg/L): 0.62000E+06

Partition Coefficient Method: Soil Koc

Partition Coefficient Value: 6780.000

Aerobic Soil Half-life (days): 7.500E+01

Enter Chemical-Specific Foliar Process Data

Plant Uptake Factor: 0.0000

Foliar Half-life (days): 0.000E+00

Foliar Washoff Coefficient: 0.50000

Volatilization from Soil

Vapor Pressure: 1.00E-07

Units of Vapor Pressure: Torr (mm Hg)

Enter Chemical-Specific Data

Air Diffusion Coeff. (cm²/day): 4300.0

Enthalpy of Vaporization (kcal/mole): 20.000

OK Cancel

Figure C.3: PRZM Chemical Parameters Inputs

EXAMS Efate Input: Transport and Transformation Parameters

Farm Pond (no flow)

Index Reservoir (steady reservoir flow, m3/hr)

Chemical 1 | Chemical 2 | Chemical 3 | Pathways

Half-Lives (Whole-system "metabolism" must be manually corrected for interferences by hydrolysis etc. prior to entry.)

Water Column (Sediment-loaded study)

Aerobic "Metabolism" (days)

Benthic Sediment (Sediment-loaded study)

Anaerobic "Metabolism" (days)

Hydrolysis

Test Temperature (C)

Number of Different pH (3 or more)

	Test pH	Half-life (days)
1	5.00	0.000E+00
2	7.00	0.000E+00
3	9.00	0.000E+00

Aquatic Direct Photolysis (days)

Partition Coefficient Method

Partition Coefficient Value

OK Cancel

Figure C.4: EXAMS-Efate Input: Transport and Transformation Parameters

Pesticide Application Data

Current Crop and Status: Current Crop Number: Total Number of Crops:

Index Reservoir PCA (%)

Number of Applications

Application Timing Application Method

Application Units kg/ha lb/acre

	Days Rel.	Day	Month	CAM	Incorp. (cm)	Rate	Drift Pond %	Drift Res. %	Efficiency %
Application 1	1			2	4.00	16.745	1.00	6.40	99.00
Application 2	16			2	4.00	16.745	1.00	6.40	99.00
Application 3	31			2	4.00	16.745	1.00	6.40	99.00
Application 4	46			2	4.00	16.745	1.00	6.40	99.00
Application 5	61			2	4.00	16.745	1.00	6.40	99.00
Application 6	76			2	4.00	16.745	1.00	6.40	99.00
Application 7	91			2	4.00	16.745	1.00	6.40	99.00
Application 8	106			2	4.00	16.745	1.00	6.40	99.00
Application 9	121			2	4.00	16.745	1.00	6.40	99.00
Application 10	136			2	4.00	16.745	1.00	6.40	99.00

Figure C.5: Pesticide Application Data Input Interface

APPENDIX D: PRZM-EXAMS OUTPUT FILES

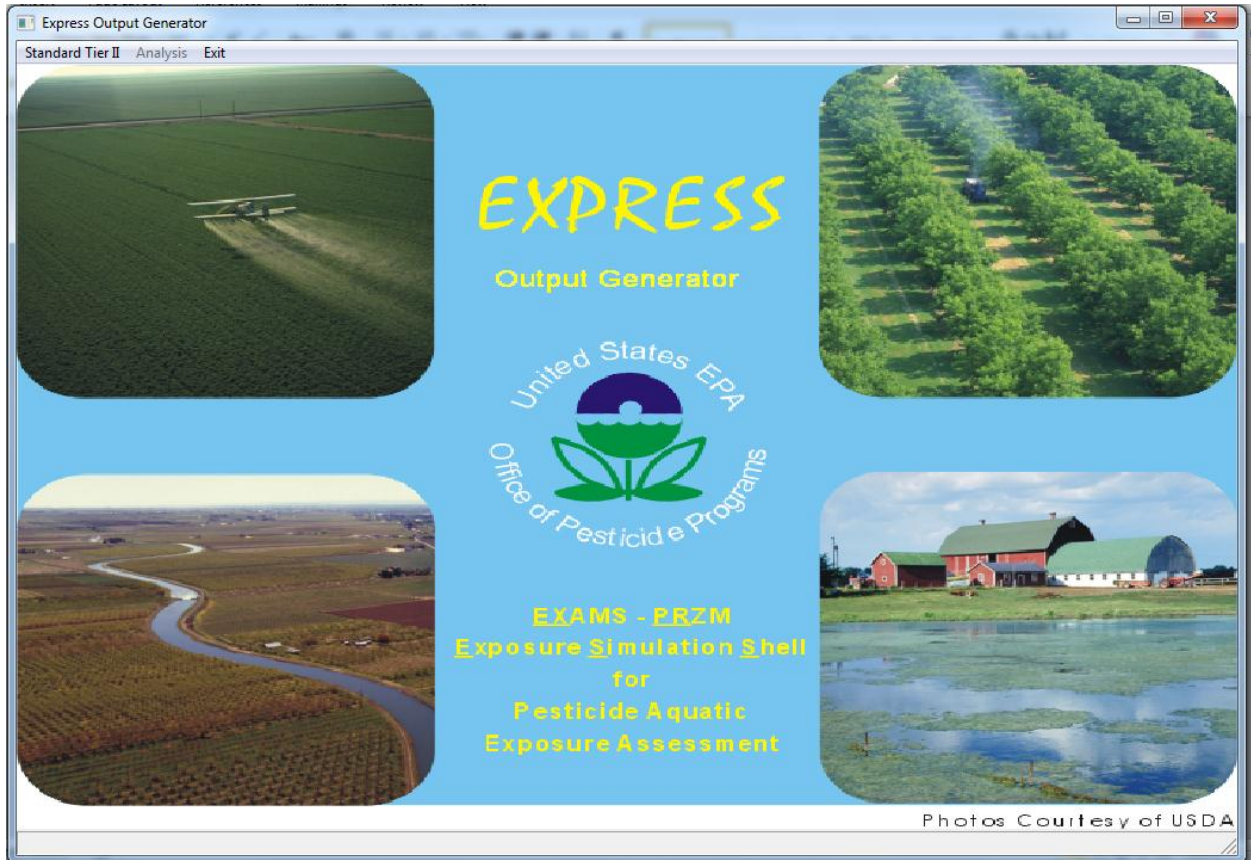


Figure D.1: EXPRESS Results Interface

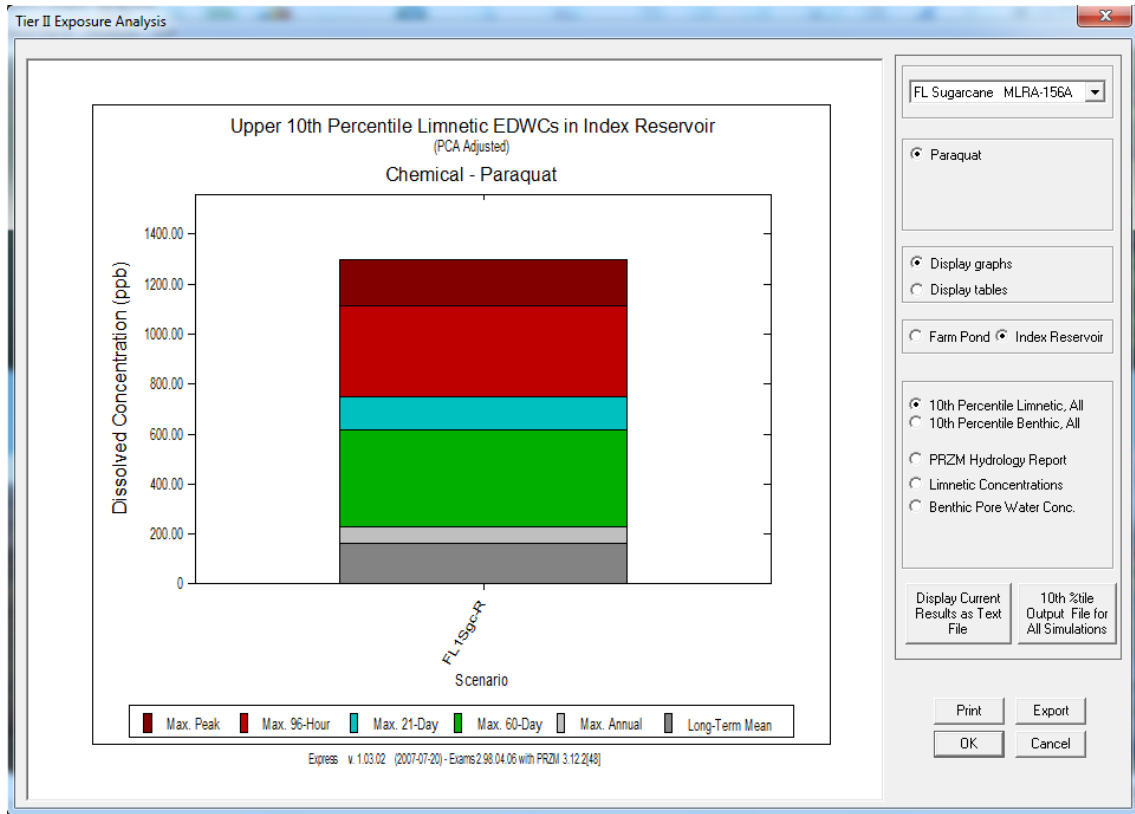


Figure D.2: Example Upper 10th Percentile Limnetic Estimated Drinking Water Concentration in Index Reservoir (Paraquat)

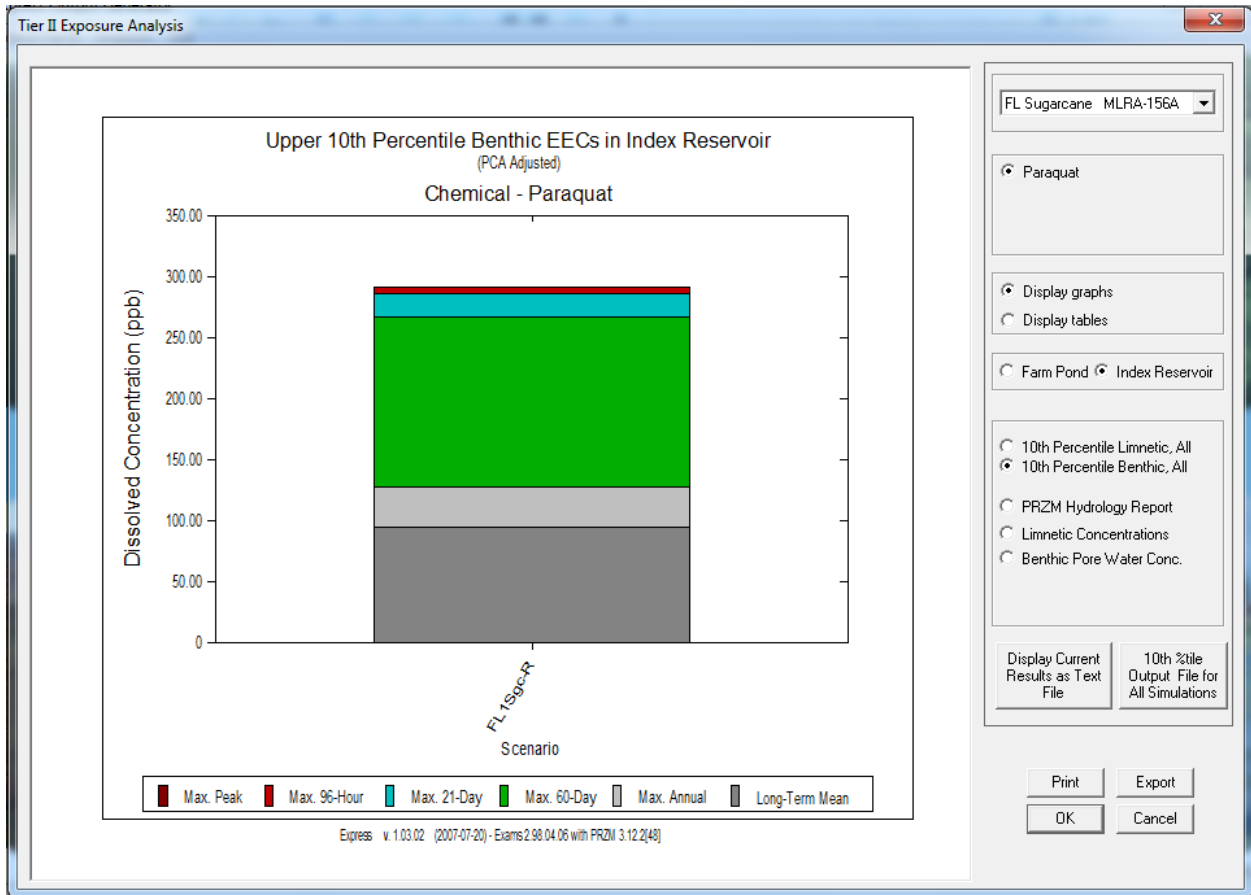


Figure D.3: Example Upper 10th Percentile Benthic Estimated Environmental Concentration in Index Reservoir (Paraquat)

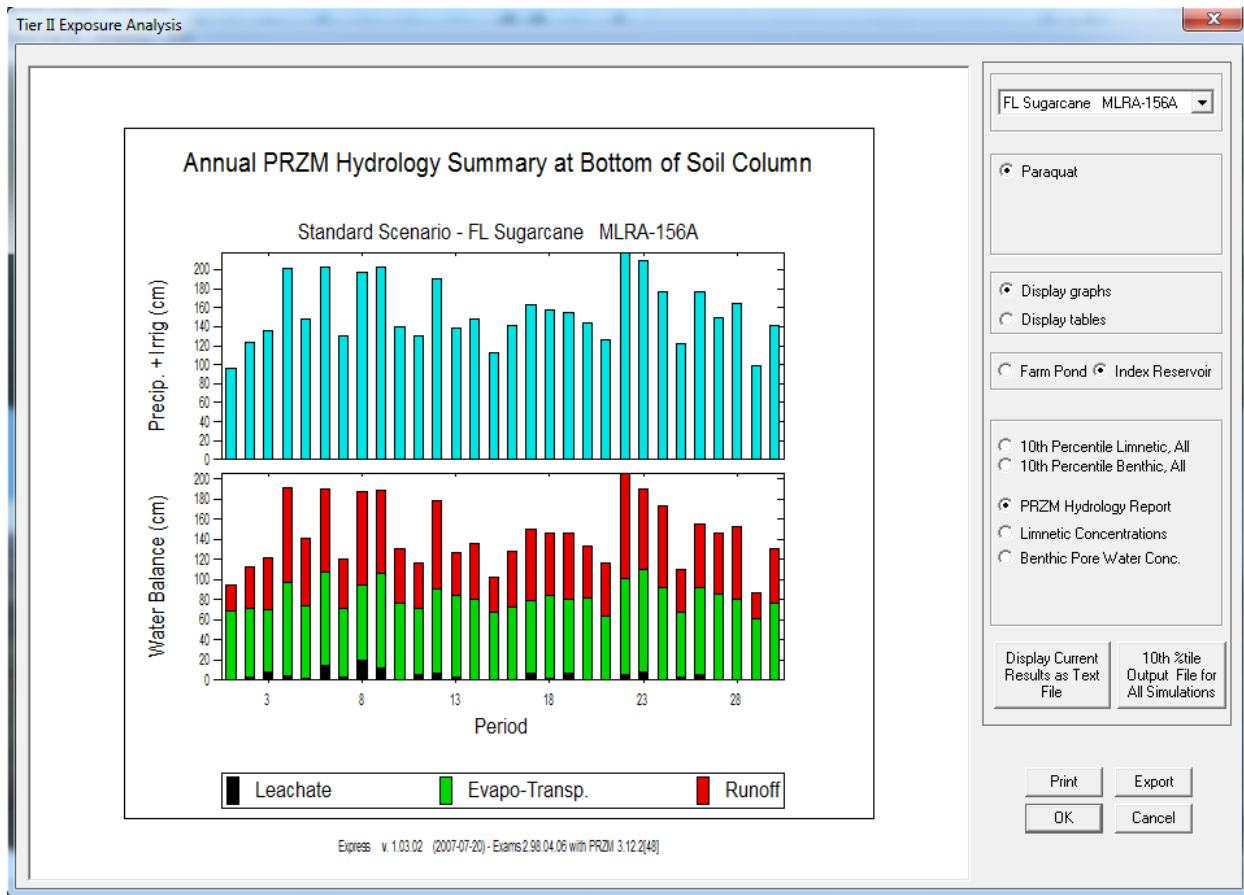


Figure D.4: Example Hydrology Summary Output (Paraquat)

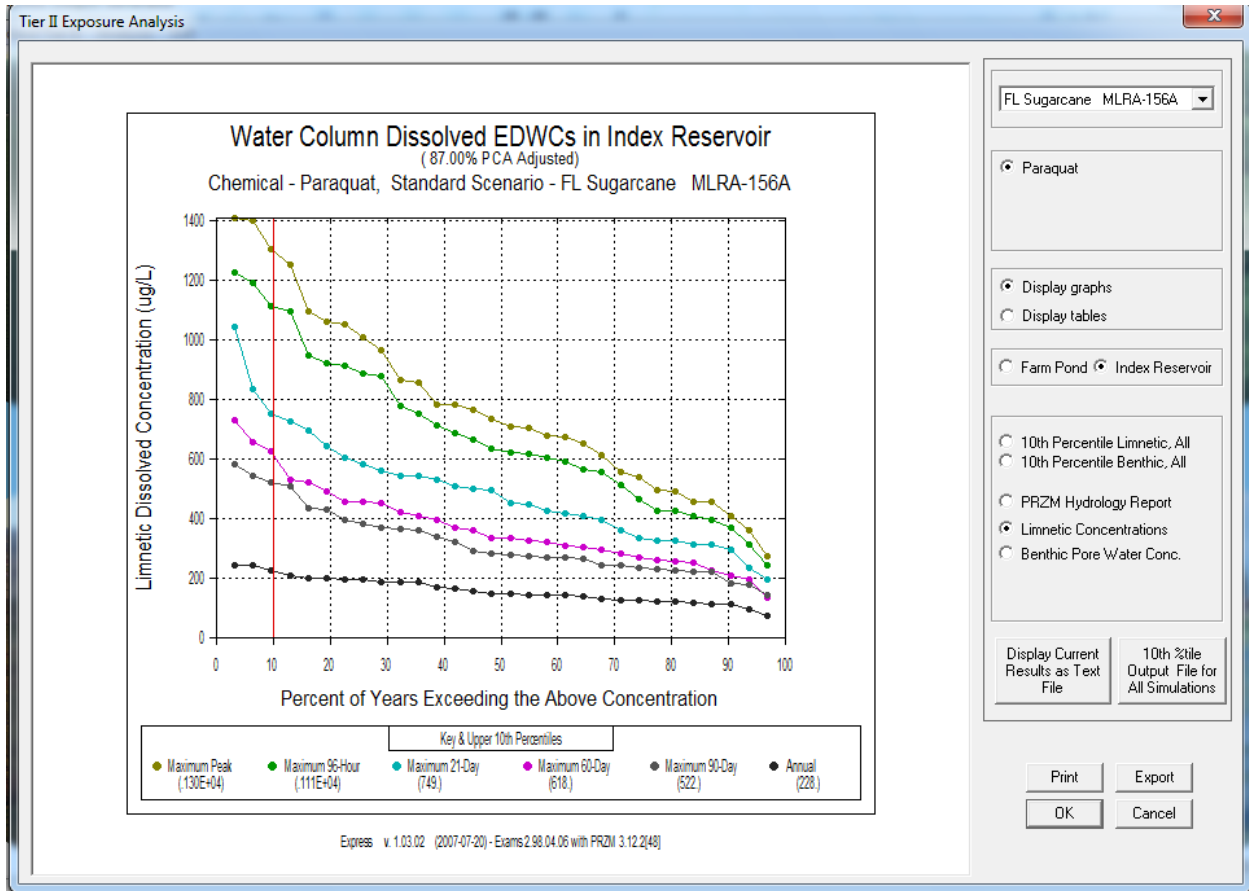


Figure D.5: Example Water Column Dissolved Estimated Drinking Water Concentration Profile in Index Reservoir (Paraquat)

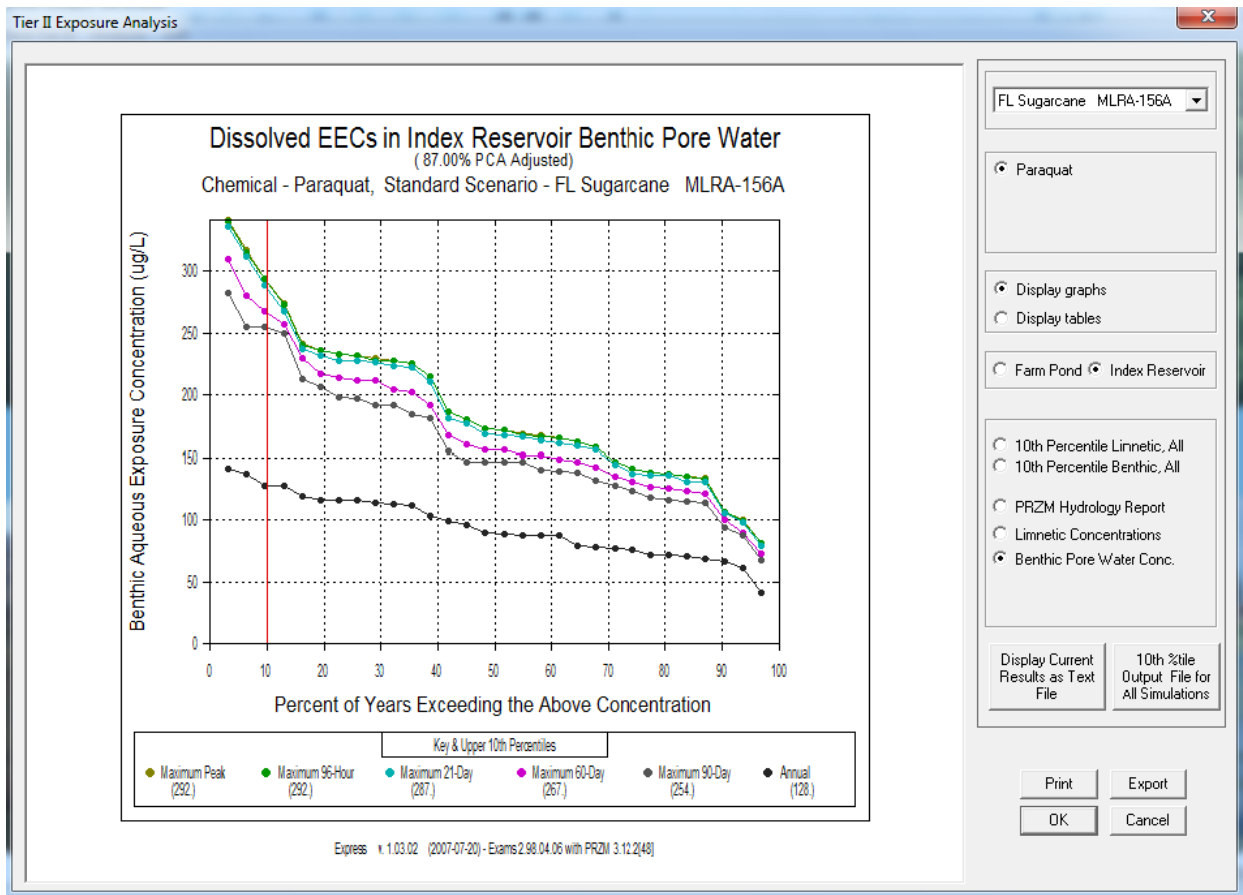


Figure D.6: Dissolved Estimated Environmental Concentration Profiles in Index Reservoir in Benthic Pore Water (Paraquat)


APPENDIX E: PERMISSION FOR REPRODUCTION OF FIGURE 4

request for permission to use figure of pictograms

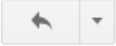


Inbox x



 **Sarah Watson** <sarahwatson@mail.usf.edu>
to awaichman

Feb 4 ☆



Dear Ms./Dr. Waichman,

I hope this email finds you well. I am currently writing a Master's thesis at the University of South Florida and I would like to use the pictograms from Table 3 of your paper about understanding of pesticide labels for a Figure in my thesis. Please reply to let me know if this is alright with you.

Thank you,
Sarah



 **Andrea Waichman** <awaichman@gmail.com>
to Sarah

Feb 4 ★



Dear Sarah,

I have no problem on using the pictograms from the Table 3.

I wish you success with you Master's thesis!!

All the best,

Andrea
Profa. Dra. Andrea Viviana Waichman
Diretora Técnico-Científica/Scientific Director

Fundação de Amparo à Pesquisa do Estado do Amazonas - FAPEAM
Travessa do Dera, s/nº - Flores CEP: 69058-793
Telefone/Phone: [0055 92 3878-4030](tel:00559238784030) – FAX [0055 92 3878-4030](tel:00559238784030)
Celular/Mobile: [0055 92 99623656](tel:00559299623656)
Homepage: www.fapeam.am.gov.br