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Land-based sources of pollutants to coastal waters of southern Belize: Comparison of predictive model with empirical data

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Land-Based Sources of Pollutants to Coastal Waters of Southern Belize –
Comparison of Predictive Model with Empirical Data

by

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A thesis submitted in partial fulfillment of the requirements for the degree of Master’s in Science
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Victor Eduardo Alegria

ABSTRACT

A Level III fugacity-type model was applied to southern Belize (Stann Creek and Toledo Districts) to predict which of the pesticides most heavily used in banana and citrus farms are most likely to end up in streams and coastal waters via surface runoff. Concentrations of all target pesticides in coastal waters of southern Belize were then measured during two sampling campaigns (dry season and rainy season) in 2008. Several pesticides were measured in significant levels, including some as far out as waters overlying coral reefs. The presence of these pesticides in the coastal waters indicates that agricultural activities in southern Belize may have a potential impact on coral reefs offshore. Results of the predictive model were compared with the empirical data to determine how well the model works in a tropical region such as southern Belize. Overall, there is considerable agreement between the two, indicating that the model employed herein can be applied to other tropical areas. Concentrations of mercury and lead were also measured in the same study area. Mercury levels were uniform and low, suggesting natural sources. Lead levels varied and are most likely explained by the presence of unregulated and illegal waste dumps near streams in the region. An analysis was carried out to examine government policy on pesticide use. Findings indicate a lack of a coherent governmental policy on the sale and use of pesticides, most likely because
of too many agencies/ministries being involved and the lack of national standards for these pesticides in the environment.
Chapter One

Introduction

Background

Pesticides are used in huge quantities globally in order to ensure sufficient agricultural productivity. As a result, the issue of environmental contamination from these chemicals is still an active area of research. Once applied, pesticides may be quickly degraded microbiologically, physically, or chemically. In most cases, however, pesticides are persistent enough that they are subject to movement away from application sites. Pesticides have been shown to be transported away from application sites by volatilization into the atmosphere, leaching and movement through soil and into groundwater, and surface runoff to streams and coastal waters. The predominant transport mechanism is determined by a variety of factors, including the chemical’s physical-chemical properties, the quantities employed in the field, the method of application, prevailing weather conditions, and the type of soil in which pesticides are employed. Consequently, determination of fate and transport of pesticides is a very complex endeavor. As a result, most studies in this field concentrate on potential movement of pesticides in one media or via one mechanism at a time. That is, studies focus on soil-air exchange and atmospheric transport, or percolation through soil into underground aquifers or laterally to surface waters, or surface runoff into surface waters, etc. Fewer studies attempt to look at movement of pesticides in all media simultaneously.
Regardless of approach, it has been shown that significant quantities of pesticides can be removed from sites of application via all mechanisms into all media. For example, volatilization of pesticides into the atmosphere after application (as opposed to spray drift during application) can remove large fractions of pesticides from agricultural fields (Qiu et al., 2004). One study documented loss of over 50 percent of DDT applied to a field within one month. Sieber et al. (1996) have documented significant pesticide loss via spray drift during aerial application. Other studies have documented significant loss of pesticides from agricultural fields via surface runoff, especially with rainfall. Studies have calculated pesticide loss from runoff ranging from <0.01 to >10 percent of the pesticide applied (Southwick et al., 2003; Senseman et al., 1997). Although these fractions may seem small, if very large quantities are actually applied the amounts lost via surface runoff can be significant. When rainfall occurs soon after pesticide application, losses may be more significant (Senseman et al., 1997). Ultimately, the concentrations of pesticides from runoff may reach concentrations in surface waters that are detrimental to flora and fauna that inhabit those waters. In a similar manner, many studies have documented the leaching of pesticides from soils and contamination of groundwater (Geisler et al., 2004 and ref 1-4 therein).

In areas with farms near coastal areas, surface runoff of pesticides into coastal waters is a major concern (Hapeman et al., 2002; Scott et al., 2002; Alegria et al., 1999). Coastal waters constitute a very sensitive ecosystem, with important habitats that can be adversely affected by pesticides. Loss of important species in coastal waters has both ecological as well as economic repercussions since fisheries as well as tourism and recreation are adversely affected.
In general, there are two strategies to determine the transport and fate of pesticides from agricultural fields to the environment. One is through field studies and direct measurements of pesticides in the various compartments available (that is, soil, air, water). The second is via the use of models that may predict the transport and fate of pesticides into these various compartments. Direct measurement of pesticides in the environment is cost- and time-intensive. Therefore, this strategy is often not feasible. This is especially true in developing countries, which usually lack the finance, equipment and trained personnel to carry out such studies. Even when some direct measurements are feasible, models are useful to screen pesticides so as to refine the potential target list. This approach will enable limited resources to be focused on the most likely transport mechanism of pesticides as well as on the pesticides most likely to present environmental problems.

Many different types of models have been developed to assess movement of pesticides from application sites. Some focus on particular transport pathways while some attempt to provide an overall picture of the movement of pesticides into all possible compartments. Models such as the Pesticide Root Zone Model (PRZM), Groundwater Loading Effects of Agricultural Management Systems (GLEAMS), and Chemical, Runoff, and Erosion from Agricultural Management Systems (CREAMS) have been extensively used to simulate pesticide transport at field scale (Ramanarayan et al., 2005; Carsel et al., 1985; Leonard et al., 1987; Knisel, 1980). Other models have been designed to study transport of pesticides from soils into selected compartments. For example, some models have been developed to simulate the volatilization of volatile pesticides from soil into air (Reichman et al., 2000; Jury et al., 1990; Chen et al., 1995;
Baker et al., 1995; Wang et al., 1998; Woodrow et al., 1997). Other models simulate pesticide loss via runoff into surface waters (Guo et al., 2004; Verro et al., 2002).

Models differ in their complexity and they differ on how well they simulate what really happens in the field. The simpler the model, the less input parameters needed to run it. However, simpler models are less likely to simulate field conditions accurately. There is still a great need for developing models to predict the fate of pesticides in the environment. Recently, the Canadian Environmental Modeling Center (CEMC) released a new model called Level III which attempts to predict the fate of pesticides in the environment.

**Research Project**

Detailed herein are the results of a research project we have carried out that had as its main objectives: (1) application of the CEMC Level III Model to predict the environmental fate of pesticides used in citrus, bananas and aquaculture farms in southern Belize, with a special focus on predicting which pesticides are more likely to end up in coastal waters via surface runoff; (2) measuring pesticide and selected heavy metal concentrations in coastal waters of southern Belize to determine the extent of contamination from agriculture and garbage dumps; (3) comparing the empirical results with those predicted by the CEMC Level III model in order to validate the model; and (4) analysis of pesticide legislation in Belize. The project also had as an important component the generation of recommendations on pesticide usage to farmers as deemed appropriate by the results of the empirical data.
Research Setting

The southern part of Belize, specifically the southern Stann Creek District, is home to the citrus and banana industries, as well as most of the major aquaculture farms. Most citrus and banana farms are located in coastal areas, and for obvious reasons all aquaculture farms are in coastal waters. All three industries are known to be heavily dependent on the use of pesticides (I. Fabro, per. comm.). The Toledo District is also home to some citrus farms.

The entire coast of Belize is lined with the world’s second-longest system of coral reefs (generally referred to as the Barrier Reef). This barrier reef is located close to the coast, anywhere from ~5km to ~20 km offshore. There is therefore great concern that pesticides from agriculture/aquaculture may be transported to coastal waters and adversely affect the coral reefs, especially since coastal waters and the coral reefs are important sources of income for the country (from fisheries and tourism). There are several rivers that flow through banana and citrus farms and empty into the southern coast of Belize. There are also some rivers that flow through areas with less intensive agricultural practices prevalent (subsistence farming mostly, although there is one area with some significant area under rice cultivation). These rivers can potentially transport pesticides into coastal waters in the region. Previous studies have documented the input of pesticides from coastal agricultural fields via rivers/streams to coastal waters in other regions of the world (Alegria et al., 2000a,b; Hapeman et al., 2002; Scott et al., 2002). In recognition of these and other similar problems, the United Nations, through its United Nations Environmental Programme (UNEP), has identified land-based sources of pollutants as a research focus in the wider Caribbean, including Belize.
Research Methodology

Chapters 2 – 4 will discuss in more detail the exact approaches used to carry out the research project. Briefly, we documented the types and amounts of pesticides used in citrus and banana farms and application protocols/strategies used. This information allowed us to rank pesticides in terms of quantities used in southern Belize.

From the list of pesticides used in citrus, banana and aquaculture we selected those for which 250 kg or more are used annually in southern Belize as target pesticides. We applied the CEMC (Canadian Environmental Modeling Centre) Level III model to this list of pesticides. This model requires input parameters on pesticide name, pesticide properties, application rates, types of soil, amount of rainfall, and soil type. Chapter 2 will detail the results of applying this predictive model to the study region. We were especially concerned with identifying those pesticides predicted to be most susceptible to surface runoff since these would be the ones most likely to be found in coastal waters. To a lesser extent, those that are most likely to volatilize into air have the potential to also impact coastal waters. Previous studies have shown that pesticides that volatilize into air may be deposited into coastal waters by dry or wet deposition (Alegria et al., 1999).

During 2008 we carried out two campaigns to measure the concentrations of pesticides in coastal waters of southern Belize (Stann Creek and Toledo Districts). This allowed us to compare the results of the predictive model with actual empirical data. Chapter 3 will detail the results of this part of the project. Briefly, we selected 8 rivers in the study region. Four were selected because they flow through citrus and banana farmlands, two were selected because they flow through areas that are used for other less-intensive agricultural activities (with the possible exception of some rice farms), one was
selected as a reference site since it flows through protected areas, and one was selected because it forms the boundary between Belize and Guatemala and we were interested in how similar or different its signature would be compared to the other rivers (Figure 1).

We collected water samples from transects laid out from the river mouths in all eight cases and moving out offshore until we reached waters overlying coral reefs. In a couple of cases we could not sample in a transect parallel to the coast or all the way out to where the major coral reefs are located because of maritime borders between Belize, Guatemala and Honduras or because the reefs are located too far offshore (see Figure 1). Water samples were processed on-shore and transported to our laboratories at USFSP for analysis. Most pesticides were measured using gas chromatography – mass spectrometry (GC-MS), but a couple had to be measured using high-performance liquid chromatography (HPLC).

The results of the empirical study have been compared to those of the predictive model, as detailed in chapter 3. Chapter 3 also discusses levels of mercury and lead in coastal waters of southern Belize. While carrying out our first sampling campaign in 2008, our local partners in Belize mentioned concerns about the presence of heavy metals in coastal waters, especially mercury and lead. As a result, during the second sampling campaign we incorporated sampling for heavy metals. Mercury in these samples was measured using graphite furnace – atomic absorption spectrophotometry (GFAAS) while lead was measured using inductively-coupled plasma mass spectrometry (ICPMS). Results will be discussed in detail in chapter 3, including potential sources of these metals.
Chapter 4 will discuss the results of an analysis of pesticide policy in Belize. This chapter will also include an analysis of potential flaws in the way the government of Belize oversees the sale, use and application of pesticides in the country.

**Significance of the Project**

There are several reasons why the results of this research project are important. First, we have documented for the first time the extent to which pesticides and metals are present in coastal waters of Belize. This information is important in the country’s efforts to protect sensitive coastal ecosystems, especially coral reefs, from degradation due to agriculture and unauthorized waste dumps. Second, we have applied the relatively new Level III Model to a tropical area for validation for the first time, to our knowledge. This will add significantly to the body of knowledge on the use of such models. Finally, we will generate the first analysis of policies governing chemicals, and specifically pesticides, in Belize. This analysis will be very useful to help the relevant authorities develop improved chemical/pesticide management strategies.

**Conclusions**

The results detailed in this thesis show conclusively that I have achieved the objectives set out for my M.S. degree in Environmental Science and Policy. The results contribute to increasing the body of knowledge regarding land-based sources of pollutants to coastal waters in tropical regions in general, and southern Belize in particular. The validation of the Level III model is also important and also represents a significant contribution to science. Finally, the results have been used to generate useful
recommendations to farmers in the citrus and banana industries in Belize, which should benefit all concerned stakeholders.
Chapter Two

Application of Level III Fugacity Model to Southern Belize

Background

Understanding the fate of pesticides is extremely important because they are designed to have a biological effect (i.e. they are toxic to at least some organisms) and because they are released into the environment deliberately and in significantly large quantities (Muir et al., 2004). There is particular interest in understanding the impact of pesticides on non-target organisms and non-agricultural ecosystems.

In general, there are two approaches to studying the fate and transport of pesticides in the environment. One is to carry out empirical studies to trace the movement and eventual fate of pesticides once they are applied. These studies must be long-term and in-depth. As such, they require funds, trained personnel and analytical laboratory capabilities to accomplish. The second approach is to use a modeling approach. This approach involves essentially computer simulations that mimic what occurs in the environment. As such, the extent to which they mimic reality is governed by input parameters. Some models are simple, with relatively simple input parameters. These are easier to use and understand, but their realism is limited. More complex models require more and more complex input parameters. They are more difficult to manipulate and understand but their results more closely match reality.

The agrochemical industry is a multi-billion one and new pesticides are introduced on a yearly basis. As a result, it is very difficult to study the fate and transport
of every pesticide in existence. This is where modeling becomes an extremely valuable tool. Pesticides may be divided by properties such as structure, mode of action, etc. If the fate and transport of members of a given family of pesticides is known, then it may be possible to predict the fate and transport of other members of that family of pesticides via modeling. The process may actually be applied in the reverse whereby the results of modeling may be used to prioritize which pesticides should be empirically studied in the environment. One approach would be to apply sophisticated models to pesticides and then develop a tiered system where priorities are based on the likelihood of a pesticide having a significant impact on the environment, as indicated by the modeling results. Another approach is to determine via modeling which of the various environmental media may be most impacted by pesticides; that is, is a given pesticide more likely to be volatilized into air and be atmospherically transported and deposited, or is it more likely to be transported via surface runoff into nearby streams, etc? Thus, depending on which ecosystem is prioritized in terms of protection, only the relevant pesticides may be empirically studied.

The Belizean Situation

Belize, as is the case in most developing countries, does not possess the analytical capabilities to carry out research on the fate and transport of pesticides in the environment. In addition, there is a lack of funding for such research. As a result, there has never been, to our knowledge, any comprehensive study on the fate and transport of pesticides in the environment, only a few limited studies on specific media (Alegria et al.,
2000; Wu et al., 2006). There is concern, however, that some ecosystems may be adversely affected by the presence of pesticides in them.

In Belize, the banana and citrus industries are concentrated in the southern Stann District and to a lesser extent the Toledo District (Figure 1). These industries are heavily-dependent on pesticide usage. Lying offshore in Belize is the world’s second longest barrier reef. This system of coral reefs lies an average of approximately 15 km offshore. The health of the barrier reef has been in decline in recent years and there exists the possibility that agrochemicals may be partly responsible for this.

**Research Project**

We have carried out modeling studies in which we have applied a fugacity model developed by the Canadian Environmental Modeling Centre (CEMC) to southern Belize with the objective of determining its effectiveness at predicting which pesticides are most likely to end up in surface waters in the region.

**Environmental Fate Modeling of Pesticides in Belize**

*Defining Equilibrium*

The environmental fate of a chemical, as determined by the Mackay Level I and Level II models, describes the behaviour of a substance in a steady-state system that is at equilibrium. This implies that conditions within the system do not change with time, and that inputs and outputs are equal (Mackay et al., 1996). The environment is a closed
system that is composed of different environmental media, such as air, water, soil, sediment, aerosols, fish, etc., which have fixed volumes (Mackay, 2001). Thus the partitioning behaviour of a chemical that is introduced to such an environment will have a mass balance expression in which the total amount of chemical present, $M$, will equal the sum of amounts in each compartment, as described by:

$$M = \sum C_i V_i$$

(1)

where $C$ is the concentration in units of mol m$^{-3}$, $V$ is the volume in units of m$^3$, and the subscript $i$ is the environmental compartment in question (Mackay, 2001). Assuming that the volumes in a closed system are constant, and are not affected by the input of a chemical, it becomes necessary to determine the concentration of a substance in the various compartments in order to calculate a chemical mass balance within that system.

This can be accomplished by considering the concentration ratio at equilibrium, as described by Nernst’s Distribution Law,

$$K_{12} = C_1/C_2$$

(2)

where $K_{12}$ is a constant referred to as the partition coefficient. Thus, by knowing the concentration of a substance in one compartment, it is possible to calculate the concentration of a substance in another compartment by using the appropriate partition coefficient (Mackay, 2001). Generally there are two partition coefficients that can be determined with relative ease, experimentally, for most organic compounds. These partition coefficients are $K_{ow}$ and $K_{aw}$, where,

$$K_{ow} = C_o/C_w$$

(3)

and

$$K_{aw} = C_a/C_w$$

(4)
where the subscripts $a$, $o$ and $w$ refer to air, octanol and water respectively.

The partition coefficient described by equation 3 is commonly referred to as the octanol-water partition coefficient. It is perhaps one of the most frequently used descriptors of chemical behaviour in the environment, and is a measure of a chemical’s hydrophobicity, or degree to which a chemical partitions out of water (Mackay, 2001). As the value for $K_{ow}$ increases the tendency for the chemical to partition out of water also increases.

Meanwhile, the partition coefficient described by equation 4 is known as the air-water partition coefficient and is essentially the ratio of vapour pressure to water solubility, which is also referred to as the Henry’s law constant, $K_H$.

$$K_H = \frac{P^s}{RTC_w^s}$$  \hspace{1cm} (5)

where the superscript $s$ denotes saturation, $P^s$ is the vapour pressure (Pa), and $C_w^s$ is the solubility in water (mol m$^{-3}$) (Mackay, 2001). Values for the constants given in equation 3 and 5 for a number of organic chemicals can be obtained from a variety of sources, including the handbooks of Mackay et al. (2006), Howard (1990), and Lyman (1990), or they may be estimated as described by Boethling and Mackay (1999), or through the use of the EPIWIN suite of programs (Meylan, 1999).

Although the partition coefficients defined in equations 3 and 5 have been studied for a large number of substances, there are other partition coefficients that need to be determined if one wishes to calculate the mass balance of a substance in an environmental system. Given the number of environmental compartments that might exist in a particular system, it could prove to be difficult, if not impossible, to define partition coefficients between all of the pairs of media that might exist. For instance a
system with 6 compartments will require 30 different partition coefficients to determine the concentrations in each compartment at equilibrium. However, it is possible to calculate the concentration of an organic chemical in various environmental media by utilizing another approach that has been described extensively by Mackay (2001). This approach uses the concept of fugacity as the criterion for equilibrium.

**The Concept of Fugacity**

In a system that is in thermodynamic equilibrium, the laws of thermodynamics must be obeyed. For a closed system of constant composition there exists the thermodynamic properties of temperature $T$, internal energy, $U$, and entropy, $S$, as introduced by the zeroth, first, and second laws, respectively (Mackay, 2001). In addition, there is the property of Gibbs free energy, $G$, which is defined in terms of the thermodynamic properties listed above. For a reversible process in a closed system of constant composition that can only perform pressure-volume work, the first and second laws of thermodynamics may be combined to yield

$$dU = T \, dS - P \, dV \quad (6)$$

This equation is often referred to as the fundamental equation for a closed system, and may be expressed in terms of Gibbs free energy as,

$$G = U + PV - TS \quad (7)$$

The differential to this equation is,

$$dG = dU + P \, dV + V \, dP - T \, dS - S \, dT \quad (8)$$

Substitution of equation 6 into equations 8 leads to

$$dG = -S \, dT + V \, dP \quad (9)$$
Equation 9 shows that a change in Gibbs free energy is proportional to changes in pressure and temperature, and thus suggests that $G$ may be best regarded as a function of $P$ and $T$. Since environmental systems at equilibrium are found to be at constant temperature and pressure, minimization of the Gibbs free energy is the equilibrium criterion that the system is striving towards (Mackay, 2001). The derivative of the differential shown in equation 9 is,

$$\left( \frac{\partial G}{\partial T} \right)_P = -S \quad (10)$$

$$\left( \frac{\partial G}{\partial P} \right)_T = V \quad (11)$$

These relations show how the Gibbs energy varies with temperature and pressure. For a pure substance, at constant temperature and pressure, the molar Gibbs energy, $G_m$, is equivalent to the chemical potential, $\mu$, for that substance, and is defined as

$$\mu = \left( \frac{\partial G}{\partial n} \right)_{T,P} \quad (12)$$

As it happens, at equilibrium, the chemical potential of a substance is the same throughout a system, regardless of how many compartments there are (Mackay, 2001). To see the validity of this statement, consider a system in which the chemical potential of a substance is $\mu_1$ at one location and $\mu_2$ at another location. When an amount $dn$ of the substance is transferred from one location to the other, the Gibbs energy of the system changes by $-\mu_1 dn$ when material is removed from location 1, and changes by $+\mu_1 dn$ when that material is added to location 2. The overall change is therefore $dG = (\mu_2 - \mu_1)dn$. If the chemical potential at location 1 is higher than that at location 2, the transfer is accompanied by a decrease in $G$, and so has a spontaneous tendency to occur. Only if $\mu_1 = \mu_2$ is there no change in $G$, and only then is the system at equilibrium. Thus chemical
potential could be used as a criterion for equilibrium in determining the direction of mass diffusion (Mackay, 2001).

However, since chemical potentials are logarithmically related to pressure, as seen in the equation,

\[ \mu = \mu^* + RT \ln \left( \frac{P}{P^*} \right) \]  

(13)

and since chemical potentials are difficult to measure, their use in calculating the concentration of a substance in various media is limited (Mackay, 2001). It is possible to adapt equation 13, which represents the chemical potential for an ideal gas, by replacing \( P \) by an effective pressure, referred to as fugacity, \( f \), and rewrite equation 13 as,

\[ \mu = \mu^* + RT \ln \left( \frac{f}{P^*} \right) \]  

(14)

The term ‘fugacity’ comes from the Latin for ‘fleetness’ in the sense of ‘escaping tendency’ (Mackay, 2001). Fugacity has the same units as pressure, and at low partial pressures, under ideal conditions, fugacity is equal to the partial pressure of a substance, and is therefore linearly related to concentration (Mackay, 2001). In addition, fugacity is logarithmically related to chemical potential, thus, it is a measure of the molar Gibbs energy, and as such can replace chemical potential as a criterion for equilibrium (Mackay, 2001).

Given that fugacity is linearly related to concentration, the following relation can be used,

\[ C_i = Zf \]  

(15)

where \( Z \) is a proportionality constant, referred to as the fugacity capacity, having units of \( \text{mol m}^{-3} \text{ Pa}^{-1} \), and is analogous to heat capacity (Mackay, 2001). Substitution and rearrangement of equation 15 into equation 1 yields,
\[ f = M / \Sigma V_i Z_i \]  
(16)

thus the fugacity of a substance can be readily obtained given that the total mass of a substance, and the volume of individual environmental compartments are known constants. It is possible to determine the \( Z \) value for a particular environment by recalling the relationship that exists for partition coefficients, as seen in equation 2. Substitution and rearrangement of equation 2 into equation 15 thus leads to (12)

\[ K_{12} = C_1/C_2 = Z_1 f / Z_2 f = Z_1 / Z_2 \]  
(17)

and

\[ Z_1 = Z_2 K_{12} \]  
(18)

Since the \( Z \) value for air is equal to \( 1/RT \) for systems in which the ideal gas law applies, \( Z \) values for other compartments can therefore be readily obtained. For instance, the \( Z \) value for water is equal to \( Z_a K_{aw} \), since it can be seen from equation 18 that \( K_{aw} = Z_a / Z_w \) (Mackay, 2001).

In order to determine the overall persistence of a substance it is important to recognize that the calculations shown above merely describe how a substance will partition in an environmental system, essentially describing a Level I approach. To evaluate the length of time a substance will persist in that system it is necessary to consider processes that are responsible for removing it from the system. Generally there are two removal processes that are considered: removal by advection, and removal by degrading reactions. Since overall persistence is a measure of how long a chemical will remain unchanged in an environment, processes involving removal by advection are not considered. Thus, advection residence times can be made to be infinity, implying that the substance never flows out of the closed system.
In a steady-state system at equilibrium, in which a chemical is being discharged at a constant rate into the system, the rate at which a chemical is being input to the system must equal the output rate (Mackay et al, 1996). For a first-order reaction of the form
\[ A \rightarrow B \]  
(19)
the rate equation is
\[ -\frac{d[A]}{dt} = k[A] \]  
(20)
where \( k \) is the first order rate coefficient, having units of L mol\(^{-1}\) h\(^{-1}\). Rearrangement and integration of equation 20 yields
\[ \ln \frac{[A]_0}{[A]} = k(t_n - t_0) \]  
(21)
Since \( t_0 = 0 \) h, equation 21 can be rewritten as
\[ \ln \frac{[A]_0}{[A]} = kt \]  
(22)
The rate at which a substance is removed from an environmental system is related to its half-life. The half-life \( t_{1/2} \) of a reactant is defined as the time required for the concentration of the reactant to decrease to halfway between its initial and final values. Thus, at the half-life, where \([A] = [A]_0/2\), equation 22 can be rewritten as
\[ \ln \frac{[A]_0}{([A]_0/2)} = kt_{1/2} \]  
(23)
or
\[ t_{1/2} = \frac{\ln 2}{k} \]  
(24)
The residence time (\( \tau \)) of a reactant in a system is defined as
\[ \tau = \frac{M}{E} \]  
(25)
where \( E \) is the efflux of the reactant, which describes the rate of removal of a chemical from a system. In a perfectly mixed closed system the following relationship exists between residence time and half-life
\[ t_{1/2} = \ln 2 \tau \]  
(26)

For simplifying purposes, environmental degradation processes are considered to proceed following pseudo-first order reaction kinetics. Thus the relations described in equations 24 and 26 are referred to in carrying out Level II type calculations, which incorporate a degradation \( D \) value, having units of mol/Pa·h, and defined as (12)

\[ D_i = V_i Z_i k_i \]  
(27)

Values for \( Z_i \) are obtainable from equation 18, while values for \( k_i \) are obtainable from equation 24 using media specific half-lives. When a \( D \) value is multiplied by the fugacity of a substance a transport rate is obtained in terms of mol h\(^{-1}\), and is therefore similar to the rate constant seen in equation 20 (Mackay, 2001). The fugacity for a substance in which degradation processes are being considered can be written as

\[ f = I / \Sigma D_i \]  
(28)

where \( I \) is the input rate and has units of mol h\(^{-1}\). Thus, using equation 15, it is possible to determine the concentration of chemical in an environmental compartment while taking degradation processes into consideration. From the concentrations present in each compartment, a value for the total amount of chemical present in the system can be determined, from which the residence time, using equation 25 can also be evaluated. Finally, the overall persistence, or overall half-life, of a substance is determined by equation 26.
Degradation Processes

The persistence of a chemical in an evaluative environmental system is essentially described in terms of its half-life. The half-life is the time it takes for half of the amount of chemical to be removed from the environment. The actual rate of disappearance of a chemical from the environment will depend on the processes available for removing it. These processes, which will have different importance for different environmental compartments and in different parts of the globe, determine the overall persistence, and thus the persistence of the chemical. Therefore a brief discussion pertaining to the various mechanisms involved in removing a chemical from an environmental system is warranted.

Typical removal processes for a substance are associated with biological and chemical degradation processes. The most important environmental reaction processes are typically associated with biodegradation, hydrolysis, oxidation, and photolysis.

Biodegradation

Biodegradation refers to the transformation of an organic compound into other compounds through microbial action, which can occur in the environmental compartments of water and/or soil and sediment. The agents of biodegradation are primarily bacteria and fungi. Each group is remarkably diverse, although the metabolic capabilities of bacteria as a group tend to be greater (Hemond and Fechner, 1994). Bacteria are active under both aerobic and anaerobic conditions, while fungi are active under only aerobic conditions.
Generally, the chemical transformations for which bacteria and fungi are capable can be described by two important principles. First of all, microbes generally mediate biotransformations that are energetically favourable (Hemond and Fechner, 1994). In other words, reactions involving microbial activity result in a net decrease in the Gibbs free energy of the chemical system, with the microbes utilizing the released energy for their own use. This can result in a significant increase in the microbial population, which could dramatically affect the rate at which a chemical compound is transformed (Mackay, 2001). This principle also suggests that if a chemical is present at a concentration that is too low to provide sufficient energy to the microbes, that it may essentially be ignored, and not transformed (Mackay, 2001).

Secondly, most chemical transformations are accomplished by means of enzymes, which are proteins synthesized by organisms that act as a catalyst in the biotransformation of an organic compound (Hemond and Fechner, 1994). The role of an enzyme is to bind reactants and hold them in such an orientation that they are more readily available to react. The products of the reaction are then released, making the catalyst available to facilitate another transformation. Individual organisms will produce different enzymes, suggesting that some microbes can accomplish a certain chemical transformation, while other microbes cannot (Hemond and Fechner, 1994). Generally, enzymes are well adapted to chemically transforming most naturally occurring organic compounds. However, most microbes have yet to evolve the capability of transforming many of today’s synthetic organic compounds, which do not naturally occur (Mackay, 2001). These include compounds containing a large number of branched carbon chains,
ether linkages, meta-substituted benzene rings, chlorine, amines, methoxy groups, sulfonates, and nitro groups.

Given these factors, the rate at which a chemical is transformed will depend on the nature of the chemical compound, on the amount and condition of enzymes which may be present in various organisms in various states of activation, and which are available to perform the chemical transformation, on the availability of nutrients such as nitrogen, phosphorous, and oxygen, as well as temperature and the presence of other substances which might help or hinder the transformation (Mackay, 2001). Thus the biotransformation of organic compounds can be extremely complex, and difficult to predict.

In order to assign a rate constant for reactions involving microbes a number of simplifying assumptions have been made. These include the assumption that biodegradation occurs following first-order kinetics, which, given the number of factors which are necessary to facilitate the biodegradation of a compound is highly inaccurate. Thus by making estimates of what the first order rate constant or half-life is based on experiment and experience is the biodegradation rate of a compound assigned.

*Hydrolysis*

The process of hydrolysis involves the addition of water to a chemical species as a result of reaction with water, hydrogen ion, or hydroxyl ion (Mackay, 2001). There are two classes of organic compounds that are likely to undergo hydrolysis. The first class includes alkyl halides, which are straight-chain or branched hydrocarbons in which a
hydrogen has been replaced by a chlorine, fluorine, bromine, or iodine atom. The reaction with water proceeds as follows:

$$\text{H}_2\text{O} + \text{R-X} \rightarrow \text{R-OH} + \text{H}^+ + \text{X}^-$$

The second class of compounds that may undergo hydrolysis includes esters and ester analogs (Hemond and Fechner, 1994). Esters are compounds containing a modified carboxylic acid group, in which the acidic hydrogen atom has been replaced by some other organic functional group. Hydrolysis converts esters into the parent organic acid, plus an alcohol. For instance, ethyl acetate hydrolyzes to acetic acid and ethanol according to the overall reaction:

$$\text{H}_2\text{O} + \text{CH}_3\text{COOC}_2\text{H}_5 \rightarrow \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$$

The intermediate steps that occur during the hydrolysis of alkyl halides and esters may involve a number of chemical species, including H₂O, OH⁻ and H⁺. Where hydroxyl and hydrogen ions are involved as part of the rate-limiting step, the hydrolysis reaction rate will be very sensitive to the pH of the water (Mackay, 2001). Thus, one method of testing if a compound might be subject to hydrolysis is to subject the chemical to pHs of 3, 7 and 11, and observe the rate of decay (Mackay, 2001). From this test it will then be possible to assign rate constants for acid, base and neutral hydrolysis, which can be combined to give an expression for the rate at any given pH (Mackay, 2001).

**Oxidation**

A chemical may react with oxygen, an activated form of oxygen, such as singlet oxygen, with ozone, with hydrogen peroxide, or with various free radicals, most notably with hydroxyl and nitrate radicals (Mackay, 2001). The rapid reaction of hydroxyl
radicals with many trace gases in the atmosphere places it at the center of much of the daytime atmospheric chemistry (24). This is because sunlight plays a critical role in the formation of hydroxyl radicals as seen in the following reactions:

\[ \text{(1)} \quad \text{O}_3 + h\nu \rightarrow \text{O}(^1\text{D}) + \text{O}_2 \]

\[ \text{(2)} \quad \text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH} \]

with the hydroxyl radical going on to react with a large number of chemical species, including organic compounds.

At night, atmospheric chemistry is dominated by the nitrate radical, which can be formed due to reaction with ozone as follows:

\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \]

The nitrate radical then acts as a hydrogen atom abstractor in much the same way as the hydroxyl radical.

\[ \text{CH}_4 + \text{NO}_3 \rightarrow \text{CH}_3 + \text{HNO}_3 \]

It should be noted that the atmosphere is a highly reactive medium, and that the examples shown above only represent a small fraction of the number of reactions that might be possible. Rates involving these reactions can be estimated by performing kinetic experiments in which the rate of decay at which a substance in contact with an oxidant is monitored, and a rate constant established (Mackay, 2001).

*Photolysis*

A molecule may absorb electromagnetic radiation and, in the process, break down into its atomic or molecular components. Such chemical reactions are referred to as photochemical, and the process by which a photochemical reaction occurs is called
photolysis. The rate constant for a photochemical reaction may be of second order. For instance, the reaction rate for NO₂ can be written as \(-d[NO₂] / dt = k' [h \nu][NO₂]\).

However, this expression is not very useful, since the second-order rate constant would vary significantly with the energy of the photon involved in the reaction. Thus, it is simpler if a pseudo first-order process could be used to describe the rate of reaction. This can be done by assuming that there is a constant flux of photons with a fixed distribution with respect to wavelength. Thus, the rate expression given above would become

\[-d[NO₂] / dt = j [NO₂],\]

where \(j\) is the pseudo first-order rate coefficient that accounts for the absorption coefficient of the reactant, the quantum efficiency of the reaction in question and the solar spectrum and intensity at the altitude and latitude under consideration. With a little information on the spectral characteristics in which the molecule absorbs light and the amount of incoming radiation, it is relatively simple to make estimates of \(j\) for a number of compounds, from which the rate constant or half-life can be determined.

Using Partitioning Data to Identify Key Half-lives

Recognizing the need to minimize physical-chemical and reactivity data requirements, Gouin et al. (2000) have proposed an approach that would use partition coefficients as a means of establishing the compartment to which a substance is most likely to partition. This method is similar to the Level I approach, in that it uses an equilibrium, steady-state mass balance model to determine the overall persistence of a substance by first identifying the relevant half-lives. The advantage of this approach is that the method focuses on the mass fractions of a chemical in each medium, which can
be useful in assessing to which compartment a particular substance is most likely to partition. To this end, Gouin et al. (2000) have categorized the environment into compartments of air, water and octanol, where the octanol compartment represents the organic carbon content associated with both the soil and sediment compartments. An assumption has been made that suggests that the half-life in soil for a substance is equivalent to its half-life in octanol. This has been justified by demonstrating that 97.8% of the equivalent volume of octanol comes from soil, with the remaining 2.2% coming from sediment. Since the soil compartment represents the medium from which the octanol is largely derived, it can be assumed that the degradation processes a substance undergoes in the soil will be equivalent to those that the substance undergoes in the organic fraction of the soil.

Knowing the volume ratios of each environmental compartment, the air-water partition coefficient, $K_{AW}$, and the octanol-water partition coefficient, $K_{OW}$, it is possible to determine the mass fraction of a chemical in each medium by,

$$F_i = \left( \frac{V_i K_{iw}}{K_{ww} V_w + K_{AW} V_A + K_{OW} V_O} \right)$$  \hspace{1cm} (36)

where the subscript $i$ is air, water, or octanol and $K_{ww}$ is 1.0 (29). If a substance is found to have a mass fraction in a particular compartment that is greater than 99%, then it is unlikely that the half-lives for the other compartments will be required in determining the overall half-life. Using equation 36 to determine the partitioning behaviour of 233 chemicals, Gouin et al. (2001) observed that 60% of the substances were found to require a minimum of 2 half-lives, with the remaining 40% being identified as multimedia. Chemicals that are found to be multimedia would require information regarding mode of entry, which could affect the overall half-life of these substances, more so than those
partitioning primarily to one environmental medium. Using the identified key half-lives of the remaining substances, the overall half-life is then determined by,

$$1/\tau_R = F_A / \tau_A + F_W / \tau_W + F_O / \tau_O$$  \hspace{1cm} (37)

Thus, the highlight of this method is its ability to identify multimedia substances, which are known to require mode of entry data in assessing their persistence. In addition to this, the identification of key half-lives also leads to a reduction in reactivity data needed to assess a chemicals’ persistence in a steady state system that is at equilibrium. The accuracy of the results, however, is ultimately limited by the accuracy of the partition coefficients used, as well as the assumptions made pertaining to the rates of degradation in octanol. Generally this method is simple to understand, easy to use, requires minimal data input and produces reliable results. Given these attributes, it is believed that this method can provide a valuable screening tool for assessing how substances might partition in an environmental system. This information can be useful in defining the fate of a chemical, and can furthermore be used to better define which parts of an environmental system that the chemical is most likely to be found.

*Application of Level I and II modeling to pesticides commonly used in Belize*

Table 1 shows the main currently-used pesticides (CUPs) in the banana and citrus industries in Belize. Physical-chemical property data for these chemicals have been obtained from Mackay et al.(2006), or have been estimated using the EPIWIN suite of programs (Meylan, 1999), largely due to a paucity of property data available for these compounds. In many instances, where data are available, a wide range of values exist, and where data are not available the estimation methods used may or may not be
appropriate. Thus, caution is recommended when interpreting results. Nevertheless, it is believed that the property data should be sufficient to qualitatively predict the likely environmental fate of the pesticides listed in Table 1.

Table 1: Physical-chemical property data for selected CUPs used in Belize. Data are taken from various sources, including Mackay et al. (2006) and estimated using the EPIWIN software package (Meylan, 1999).

<table>
<thead>
<tr>
<th>CAS No</th>
<th>Chemical Name</th>
<th>MW g/mol</th>
<th>MP deg C</th>
<th>Input Data P^S Pa</th>
<th>S g/m3</th>
<th>log K_{OW} (298 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13194-48-4</td>
<td>Ethoprop</td>
<td>242.34</td>
<td>20</td>
<td>0.0465</td>
<td>7.00E+02</td>
<td>3.59</td>
</tr>
<tr>
<td>1897-45-6</td>
<td>Chlorothalonil</td>
<td>265.91</td>
<td>250</td>
<td>0.133^C</td>
<td>6.00E-01</td>
<td>2.64</td>
</tr>
<tr>
<td>1563-66-2</td>
<td>Carbofuran</td>
<td>221.25</td>
<td>151</td>
<td>8.00E-05</td>
<td>3.51E+02</td>
<td>2.32</td>
</tr>
<tr>
<td>1071-83-6</td>
<td>Glyphosate</td>
<td>169.074</td>
<td>230</td>
<td>4.00E-05^H</td>
<td>1.20E+04</td>
<td>&lt;0^D</td>
</tr>
<tr>
<td>13071-79-9</td>
<td>Terbufos</td>
<td>288.431</td>
<td>-29.2</td>
<td>0.0427</td>
<td>5.00E+00</td>
<td>4.48</td>
</tr>
<tr>
<td>1910-42-5</td>
<td>Paraquat</td>
<td>257.16</td>
<td>300</td>
<td>1.34E-05</td>
<td>6.20E+05</td>
<td>&lt;0^D</td>
</tr>
<tr>
<td>95465-99-9</td>
<td>Cadusafos</td>
<td>270.39</td>
<td>20</td>
<td>0.120</td>
<td>2.48E+02</td>
<td>3.9</td>
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<tr>
<td>23135-22-0</td>
<td>Oxamyl</td>
<td>219.26</td>
<td>109</td>
<td>0.0306</td>
<td>2.82E+05</td>
<td>&lt;0^D</td>
</tr>
<tr>
<td>22224-92-6</td>
<td>fenamiphos</td>
<td>303.36</td>
<td>49</td>
<td>0.000133</td>
<td>3.29E+02</td>
<td>3.23</td>
</tr>
<tr>
<td>34256-82-1</td>
<td>acetochlor</td>
<td>269.77</td>
<td>0</td>
<td>0.00373</td>
<td>2.23E+02</td>
<td>3.03</td>
</tr>
<tr>
<td>70585-38-5</td>
<td>Bitertanol</td>
<td>337.415</td>
<td>118</td>
<td>1.00E-06</td>
<td>5</td>
<td>4.1</td>
</tr>
<tr>
<td>215934-32-0</td>
<td>azoxystrobin</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>119446-68-3</td>
<td>difenoconazole</td>
<td></td>
<td>406.27</td>
<td>2.43E-06</td>
<td>1.50E+01</td>
<td>4.3</td>
</tr>
<tr>
<td>116-06-3</td>
<td>Aldicarb</td>
<td>190.25</td>
<td>99</td>
<td>0.004</td>
<td>6.00E+03</td>
<td>1.1</td>
</tr>
<tr>
<td>133855-98-8</td>
<td>epoxiconazole</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>141517-21-7</td>
<td>trifloxystrobin</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2921-88-2</td>
<td>Chloropyrifos</td>
<td>350.6</td>
<td>41</td>
<td>0.00227</td>
<td>7.30E-01</td>
<td>4.92</td>
</tr>
<tr>
<td>121-75-5</td>
<td>Malathion</td>
<td>330.36</td>
<td>2.9</td>
<td>0.001</td>
<td>1.45E+02</td>
<td>2.8</td>
</tr>
<tr>
<td>1861-32-1</td>
<td>Daclthal</td>
<td>332</td>
<td>156</td>
<td>0.0066</td>
<td>2.92E+02</td>
<td>4.24</td>
</tr>
<tr>
<td>333-41-5</td>
<td>Diazinon</td>
<td>304.36</td>
<td>25</td>
<td>8.00E-03</td>
<td>6.00E+01</td>
<td>3.3</td>
</tr>
<tr>
<td>86-50-0</td>
<td>Azinphosmethyl</td>
<td></td>
<td>317.324</td>
<td>73</td>
<td>3.00E-05</td>
<td>2.7</td>
</tr>
</tbody>
</table>

^A Data obtained from EPIWIN software
^B No data available for these compounds
^C Data reported have large variability, selected value to be used with caution
^D Values of log K_{OW} are negative, a value of 0 is assumed for illustrative purposes for Figure 1.
Using the method described by Gouin et al. (2000) the Level I partitioning behaviour of each of the chemicals listed in Table 1 has been calculated. Results are illustrated in Figure 1. Figure 1 is a plot of log $K_{AW}$ vs log $K_{OW}$ including points representing the partitioning properties of the target pesticides in this study. The 45° diagonals are lines of constant log $K_{OA}$, the octanol-air partition coefficient, because $K_{OA}$ is $K_{OW}/K_{AW}$ or log $K_{OA}$ is log $K_{OW}$ - log $K_{AW}$. Lines of constant $F_A$, $F_W$, and $F_O$ are drawn in Figure 1 using the above volume ratios. The lines corresponding to one-third in each compartment converge at the point where log $K_{OW}$ is 3.1; log $K_{AW}$ is -2.74; and $V_W$, $K_{AW}V_A$, and $K_{OW}V_O$ are equal, i.e., $K_{AW}$ is $V_W/V_A$ or 1300/650 000 or 0.002 and $K_{OW}$ is $V_W/V_O$ or 1300/1. If the ratios of the volumes change, for example, if the water volume is increased, the location of this central point will move upward along the 45° diagonal changing the location of the lines of constant $F_i$. The 1% and 99% lines divide the $K_{AW}/K_{OW}$ space into regions in which partitioning is predominately into one medium and in which it is likely that degradation in that medium is most important. In the region to the upper left, where more than 99% is in air, the air half-life probably controls the persistence, and it is unlikely that half-lives in water, soil, or sediment are required. To the lower right of the 99% octanol line, substances are strongly sorbed, and only data for soils and sediments are likely to be needed. To the lower left, water is the dominant medium of partitioning. Half-lives in air are generally shorter than those in water, soil, and sediment, largely because of relatively rapid hydroxyl radical reactions. As a result, even 0.5% partitioning to air can represent an appreciable fraction of the overall degradation. The 0.1% air line (also shown) may be a better limit. Substances with more than 1% in each medium are classified as “multimedia.” For these substances, all half-
lives will be required. Similarly there are regions where only two half-lives may be required.

**Figure 1:** Environmental partitioning of CUPs listed in Table 1 in an environmental system that is at steady-state and equilibrium, consistent with the model environment described by Gouin et al. (2000).
Oxamyl, glyphosate, paraquat, and aldicarb all show a strong propensity for partitioning to the aquatic environment, whereas mancozeb, acetochlor, malathion, ethoprop, azinfosmethyl, fenamiphos, carbofuran, bitertanol, and difenoconazole are found to largely partition equally between octanol and water (Table 2). For these substances their mode-of-entry into the environment may influence their overall fate. For instance, if emitted to soils they may likely remain largely sorbed to the organic carbon content found in the soil, and if degradation in soil is relatively fast in comparison to advection from soil to water, they would remain in the soil compartment. For the remaining substances the mass fraction in the air becomes increasingly important, suggesting the potential for transport away from sites of use due to surface-air exchange processes. For these substances mode-of-entry will also likely be important.

In Table 2 estimates regarding reactivity processes in air, water, soil, and sediment have been assessed, and the overall half-life of each of the substances calculated based on the partitioning behaviour of the substance, using equation 37. The results suggest that the majority of substances will have an overall environmental half-life that is <1000 h or about 6 weeks. The data reported in Table 2, however, is based on Level II calculations, which assume the model environment is steady-state and at equilibrium. To assess the fate of these CUPs in an environment that is steady-state but non-equilibrium, a Level III model calculation was carried out. For simplification, an assumption has been made that 80% of the substance is emitted to soil, 10% to water, and 10% to air. The model environment has also been parameterized to more closely resemble the environment of Belize. Environmental parameters used and results for each of the substances are illustrated in Figures 3 – 21.
Table 2: Estimated reactivity data based on Mackay et al. (2006) and the EPIWIN software package, mass fractions in air, water, and octanol and overall environmental half-life.

<table>
<thead>
<tr>
<th>CAS No</th>
<th>Chemical Name</th>
<th>HL air hours</th>
<th>HL water hours</th>
<th>HL soil hours</th>
<th>HL sed Hours</th>
<th>FA</th>
<th>FW</th>
<th>FO</th>
<th>Overall Half-life (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8018-01-7</td>
<td>Mancozeb</td>
<td>1.21</td>
<td>480</td>
<td>1680</td>
<td>3360</td>
<td>0.08%</td>
<td>49.42%</td>
<td>50.49%</td>
<td>4.95E+02</td>
</tr>
<tr>
<td>13194-48-4</td>
<td>Ethoprop</td>
<td>3.72</td>
<td>360</td>
<td>720</td>
<td>3240</td>
<td>0.08%</td>
<td>24.89%</td>
<td>75.03%</td>
<td>5.13E+02</td>
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<tr>
<td>1897-45-6</td>
<td>Chlorothalonil</td>
<td>170</td>
<td>170</td>
<td>550</td>
<td>1700</td>
<td>89.88%</td>
<td>7.56%</td>
<td>2.56%</td>
<td>1.73E+02</td>
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<tr>
<td>1563-66-2</td>
<td>Carbofuran</td>
<td>5</td>
<td>170</td>
<td>550</td>
<td>1700</td>
<td>0.00%</td>
<td>86.06%</td>
<td>13.94%</td>
<td>1.88E+02</td>
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<tr>
<td>1071-83-6</td>
<td>Glyphosate</td>
<td>170</td>
<td>1700</td>
<td>1700</td>
<td>5500</td>
<td>0.00%</td>
<td>99.92%</td>
<td>0.08%</td>
<td>1.70E+03</td>
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<tr>
<td>13071-79-9</td>
<td>Terbufos</td>
<td>1.06</td>
<td>900</td>
<td>1800</td>
<td>8100</td>
<td>2.00%</td>
<td>4.02%</td>
<td>93.99%</td>
<td>5.16E+01</td>
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<td>1910-42-5</td>
<td>Paraquat</td>
<td>12.1</td>
<td>900</td>
<td>1800</td>
<td>8100</td>
<td>0.00%</td>
<td>99.92%</td>
<td>0.08%</td>
<td>9.00E+02</td>
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<tr>
<td>95465-99-9</td>
<td>Cadusafos</td>
<td>2.14</td>
<td>360</td>
<td>720</td>
<td>3240</td>
<td>0.37%</td>
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<td>85.71%</td>
<td>3.04E+02</td>
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<td>23135-22-0</td>
<td>Oxamyl</td>
<td>11.4</td>
<td>900</td>
<td>1800</td>
<td>8100</td>
<td>0.00%</td>
<td>99.92%</td>
<td>0.08%</td>
<td>9.00E+02</td>
</tr>
<tr>
<td>22224-92-6</td>
<td>Fenamiphos</td>
<td>3.3</td>
<td>900</td>
<td>1800</td>
<td>8100</td>
<td>0.00%</td>
<td>43.17%</td>
<td>56.82%</td>
<td>1.25E+03</td>
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<td>Acetochlor</td>
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<td>1440</td>
<td>2880</td>
<td>13000</td>
<td>0.05%</td>
<td>54.60%</td>
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<tr>
<td>70585-38-5</td>
<td>Butertanol</td>
<td>5.79</td>
<td>900</td>
<td>1800</td>
<td>8100</td>
<td>0.00%</td>
<td>9.30%</td>
<td>90.70%</td>
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<tr>
<td>215934-32-0</td>
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<td></td>
<td></td>
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<td></td>
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<tr>
<td>119446-68-3</td>
<td>Difenoconazole</td>
<td>11.9</td>
<td>4320</td>
<td>8640</td>
<td>38900</td>
<td>0.00%</td>
<td>6.07%</td>
<td>93.93%</td>
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<tr>
<td>116-06-3</td>
<td>Aldicarb</td>
<td>5</td>
<td>550</td>
<td>1700</td>
<td>17000</td>
<td>0.00%</td>
<td>99.03%</td>
<td>0.97%</td>
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<td>133855-98-8</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>2921-88-2</td>
<td>Chloropyrifos</td>
<td>17</td>
<td>170</td>
<td>170</td>
<td>1700</td>
<td>33%</td>
<td>1.52%</td>
<td>98.14%</td>
<td>1.65E+02</td>
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<tr>
<td>121-75-5</td>
<td>Malathion</td>
<td>17</td>
<td>55</td>
<td>55</td>
<td>550</td>
<td>0.03%</td>
<td>67.14%</td>
<td>32.83%</td>
<td>5.50E+01</td>
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<tr>
<td>1861-32-1</td>
<td>Dacthal</td>
<td>291</td>
<td>206</td>
<td>412</td>
<td>1338</td>
<td>51.13%</td>
<td>3.38%</td>
<td>45.49%</td>
<td>3.31E+02</td>
</tr>
<tr>
<td>333-41-5</td>
<td>Diazinon</td>
<td>550</td>
<td>1700</td>
<td>1700</td>
<td>5500</td>
<td>0.32%</td>
<td>39.15%</td>
<td>60.53%</td>
<td>1.69E+03</td>
</tr>
<tr>
<td>86-50-0</td>
<td>Azinphosmethyl</td>
<td>1.7</td>
<td>900</td>
<td>1800</td>
<td>8100</td>
<td>0.00%</td>
<td>72.02%</td>
<td>27.97%</td>
<td>1.02E+03</td>
</tr>
</tbody>
</table>
## ENVIRONMENTAL PARAMETERS

### Dimensions and Densities

<table>
<thead>
<tr>
<th></th>
<th>Area m²</th>
<th>Depth m</th>
<th>Volume Fraction</th>
<th>Volume m³</th>
<th>Density kg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air: Bulk</td>
<td>2.30E+10</td>
<td>1000</td>
<td>-</td>
<td>2.30E+13</td>
<td>101</td>
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<tr>
<td>Air Vapour</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>Aerosol</td>
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<td>-</td>
<td>0.0500</td>
<td>1.15E+12</td>
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<td>Water: Bulk</td>
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<td>-</td>
<td>8.00E+09</td>
<td>1000</td>
</tr>
<tr>
<td>Water</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.00E+09</td>
<td>1000</td>
</tr>
<tr>
<td>Susp. Particles</td>
<td>-</td>
<td>-</td>
<td>5.00E-06</td>
<td>40000</td>
<td>1500</td>
</tr>
<tr>
<td>Fish</td>
<td>-</td>
<td>-</td>
<td>1.00E-06</td>
<td>5000</td>
<td>1000</td>
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<td>Soil: Bulk</td>
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<td>-</td>
<td>2.14E+09</td>
<td>1500</td>
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<tr>
<td>Air</td>
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<td>-</td>
<td>0.200</td>
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<td>Water</td>
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<td>Solids</td>
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<td>-</td>
<td>0.500</td>
<td>1.07E+09</td>
<td>2400</td>
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<td>Sediment: Bulk</td>
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<td>Water</td>
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<td>-</td>
<td>0.800</td>
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<td>Solids</td>
<td>-</td>
<td>-</td>
<td>0.200</td>
<td>1.60E+07</td>
<td>2400</td>
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### Organic Carbon and Advection

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<thead>
<tr>
<th>Organic Carbon Mass Fractions g/g</th>
<th>Advection Residence Times</th>
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<tr>
<td>Soil Solids</td>
<td>Air 100, 4.17</td>
</tr>
<tr>
<td>Sediment Solids</td>
<td>Water 1000, 41.7</td>
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<tr>
<td>Susp. Particles</td>
<td>Soil -</td>
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<td>Fish Lipid</td>
<td>Sediment 50000, 2083</td>
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### Transport Velocities

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<tr>
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<th>m/h</th>
<th>m/y</th>
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<tr>
<td>Air side air-water MTC</td>
<td>5.00</td>
<td>43800</td>
</tr>
<tr>
<td>Water side air-water MTC</td>
<td>0.0500</td>
<td>438</td>
</tr>
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<td>Rain rate</td>
<td>3.00E-04</td>
<td>2.63</td>
</tr>
<tr>
<td>Aerosol dry deposition velocity</td>
<td>10.0</td>
<td>87600</td>
</tr>
<tr>
<td>Soil air phase diffusion MTC</td>
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<td>175</td>
</tr>
<tr>
<td>Soil water phase diffusion MTC</td>
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</tr>
<tr>
<td>Soil air boundary layer MTC</td>
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<td>43800</td>
</tr>
<tr>
<td>Sediment-water MTC</td>
<td>1.00E-04</td>
<td>0.876</td>
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<tr>
<td>Sediment deposition velocity</td>
<td>5.00E-07</td>
<td>4.38E-03</td>
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<tr>
<td>Sediment resuspension velocity</td>
<td>2.00E-07</td>
<td>1.75E-03</td>
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<tr>
<td>Soil water runoff rate</td>
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<td>0.438</td>
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<tr>
<td>Soil solids runoff rate</td>
<td>1.00E-08</td>
<td>8.75E-05</td>
</tr>
</tbody>
</table>

| Scavenging ratio (unitless)    | 1.00|

Figure 2: Environmental parameters used in Level III calculations.
Figure 3: Level III results for mancozeb.
Level III

Version 2.80.1
Simulation Identifier:

![Diagram of Ethoprop in Belize](image)

**Legend**
- EMISSION
- REACTION
- ADVECTION
- INTERMEDIA
- EXCHANGE

Soil
- 8.67E+05 kg (94.3%)
  Fug = 0.697 µPa
  Conc = 335 ng/g solids
  Residence Time
  Total = 919 h
  Reaction = 1009 h
  Advection = 10234 h
  Total Emissions = 1000 kg/h
  Total Mass = 9.19E+05 kg
  All emission, transfer, and loss rates have units of kg/h.

Ethoprop in Belize
- Air
  5099 kg (0.555%)
  Fug = 3.51E-07 µPa
  Conc = 222 ng/m³

- Water
  36621 kg (4.20%)
  Fug = 0.320 µPa
  Conc = 4828 ng/L

- Sediment
  6245 kg (0.597%)
  Fug = 0.218 µPa
  Conc = 209 ng/g solids

Date: 2/3/2009, Time: 11:20:01 AM

**Figure 4:** Level III results for Ethoprop
Figure 5: Level III results for chlorothalonil
Figure 6: Level III results for carbofuran
Figure 7: Level III results for glyphosate
Level III

Version 2.80.1
Simulation Identifier:

Figure 8: Level III results for terbufos
Figure 9: Level III results for paraquat.
Figure 10: Level III results for cadusafos.
Figure 11: Level III results for oxamyl.
Level III

Version 2.80.1
Simulation Identifier:

Figure 12: Level III results for fenamiphos.
Figure 13: Level III results acetochlor.
Figure 14: Level III results for bitertanol.
Figure 15: Level III results for difenoconazole.
Figure 16: Level III results for aldicarb.
Figure 17: Level III results for chlorpyrifos.
Figure 18: Level III results for malathion.
Figure 19: Level III results for daetathal.
Figure 20: Level III results for diazinon.
Figure 21: Level III results for azinphosmethyl.
Table 3: Summary of results from Level III calculations regarding fractions in air, water, and soil, as well as Level III overall half-life. Note: assumed that emissions are 80% to soil, 10% to water, and 10% to air.

<table>
<thead>
<tr>
<th>CAS No</th>
<th>Chemical Name</th>
<th>$F_A$</th>
<th>$F_W$</th>
<th>$F_{soil}$</th>
<th>Overall Half-life (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8018-01-7</td>
<td>Mancozeb</td>
<td>0.26</td>
<td>3.62</td>
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<tr>
<td>13194-48-4</td>
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<td>4.2</td>
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<tr>
<td>1897-45-6</td>
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<td>2.81</td>
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<td>13071-79-9</td>
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<td>Paraquat</td>
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<td>95465-99-9</td>
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<td>5.16</td>
<td>94.1</td>
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<td>0.95</td>
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<td></td>
</tr>
<tr>
<td>141517-21-7</td>
<td>Trifloxystrobin</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2921-88-2</td>
<td>Chloropyrifos</td>
<td>0.07</td>
<td>0.32</td>
<td>93.9</td>
<td>11384</td>
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<td>121-75-5</td>
<td>Malathion</td>
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<td>Azinphosmethyl</td>
<td>0.27</td>
<td>7.96</td>
<td>91.4</td>
<td>1924</td>
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</tbody>
</table>
Conclusions

The Level III calculations for this group of CUPs indicates that the majority of substances when emitted 80% to soil, 10% to water, and 10% to air, will remain primarily in the soil compartment to which they are emitted, with the overall environmental half-life being largely influenced by estimates regarding their biodegradation in soil. Similar to the Level II calculations, four of the CUPs, oxamyl, glyphosate, paraquat, and aldicarb all show a strong propensity for partitioning to the aquatic environment, however, not to the same extent as the Level II calculation. In this case, because the substances are emitted largely to soils a significant fraction of the pesticide will remain in that compartment, although almost half will partition to the water phase. For these substances, both the water and soil half-life will influence both their environmental fate and overall environmental half-life. It is also notable that in the Level III calculations both malathion and chlorothalonil show significant fractions in the air phase, approximately 6% for each compound. For these substances assumptions regarding the air half-life become increasingly important for assessing their overall environmental half-life and environmental fate. For malathion, the relatively short air half-life (17 h), strongly influences its overall half-life, whereas the longer air half-life for chlorothalonil (170 h) will likely influence its ability to undergo long-range transport, while similarly influencing the overall half-life. Both chlorpyrifos and difenoconazole have mass fractions <1% in water, thus their environmental fate and overall persistence will be strongly influenced by their reactivity in soils and sediments.

In general, it is likely that the majority of CUPs investigated here will have detectable amounts in surface and ground water near to where they are being used. This
can be quickly assessed by examining the molecular structure of these compounds, which
tend to have polar functional groups associated with them. The Level I, II, and III model
calculations presented here help to better quantify their environmental fate. Combined
with empirical measurements, model output can be compared with field data, and sources
of error in the model calculations better defined. Currently, in the absence of empirical
data, the model output should be interpreted with some caution, particularly given the
largely unknown uncertainties associated with the physical-chemical properties of each
the CUPs, errors associated with assumptions regarding their environmental degradation
and mode-of-entry information, and assumptions relating to the parameterization of the
physical environment used in the Level III model, which has been adjusted to better
resemble the Belize environment.

Because mobility of pesticides through soil profiles is dependent upon water
movement it is essential that the hydrology be simulated accurately. Having reliable data
from the field on hydrological characteristics of soil is obviously of great importance.
Having parameterised the model it is then necessary to develop a realistic simulated
water balance (distribution of incoming precipitation between evapotranspiration, surface
run-off, plant uptake and groundwater recharge). Once a realistic water balance is
obtained it is then necessary to consider the behaviour of the chemical within this
hydrological regime. Generally, the most sensitive environmental fate parameters are the
rate of degradation (which attenuates the concentration of pesticide in the soil profile)
and the sorption coefficient (which controls the relative rate of transport through the soil).
For the CUPs studied these variables are indeed highly uncertain. Thus, where sufficient
hydrological data are available and it is possible to duplicate water balances and transport
of water through soil with reasonable accuracy there is a much greater chance of correctly predicting chemical transport. It is therefore essential that characterization and parameterization of soil hydrology be carried out with great care.

Numerous exercises have demonstrated that where it is possible to calibrate against observed hydrology data the accuracy of pesticide leaching simulations can be significantly increased. It must be recognized that each model has its own limitations - a chromatographic flow model, for instance, cannot be used to accurately simulate leaching in cracking clay soils where preferential flow dominates. It is the recognition of model limitations that is one of the keys to advancing higher quality modeling - essentially a matter of choosing the right tools for the job. In this modeling exercise we have used evaluative models to assess the likelihood that the CUPs listed will accumulate in surface waters in Belize. Simplified assumptions have been made regarding mode-of-entry, assuming that the majority of the chemical is applied directly onto the soil surface, with a fraction (10%) being emitted to air and surface waters as a result of spray drift, and model output has been based largely on estimated physical-chemical property data, which are likely to be reasonable but not accurate. It is thus important to appreciate how these assumptions influence the output of the model.

It is suggested that the modelling work with the Mackay-type models thus provides a first tier, of a tiered approach, with respect to assessing the environmental fate of CUPs in Belize. In this instance, the results suggest that a small fraction of the chemical applied to agricultural lands will migrate to surface waters. The next step would be an attempt to accumulate field data, reporting levels in the air, water, and soil, as well as the collection of other important parameters, such as soil organic carbon.
content, information pertaining to soil hydrology, application rates, and meteorological information such as temperature and rain rates. This information can then be used to assess the performance of the model, and hopefully to improve parameterisation. If the field and model data show good agreement, the third step in the process would be an attempt to better assess environmental fate and transport, providing insight regarding environmental risk.
Chapter Three

Levels of Pollutants in Coastal Waters in Southern Belize

Introduction

Previous studies have shown that coastal waters are susceptible to contamination from land-bases sources (Saison et al., 2008; Hapeman et al., 2002; Leonard, 1990; Wauchope, 1978). Pollutants in coastal waters may originate from agricultural areas (pesticides, excessive nutrients, pathogens), urban areas (pesticides, polycyclic aromatic hydrocarbons, metals, polychlorinated biphenyls, flame retardants, hydrocarbons, etc.), industrial parks (organic solvents, flame retardants, fuel, polycyclic aromatic hydrocarbons, metals, etc.), vehicles (hydrocarbons, oils, etc.) and a myriad other sources (Jeong et al., 2008; Hou et al., 2006; Southwick et al., 2002; Dietrich and Gallagher, 2002).

Coastal areas are also known for their tremendous value, both ecologically and economically (Cooper et al., 2009; Burke et al., 2008). They are important areas for spawning of many valuable species of fish and also serve an important function for recreation and tourism (Cooper et al., 2009; Burke et al., 2008). As a result, protection of coastal areas is at the top of the environmental agenda of all countries with coastlines. In fact, the United Nations, through its United Nations Environmental Programme (UNEP), has made coastal protection one of its key initiatives. In the Wider Caribbean countries it has set up a programme to fund research on Land-Based Sources of Pollutants to Coastal Waters.
In countries such as those in the wider Caribbean, there is special concern about the presence of pollutants from land-based sources because many of these countries have coral reefs in their coastal waters. The health of coral reefs has been in decline for several years, and although coral bleaching due to warming waters has been implicated as the main culprit, there exists the distinct possibility that pollutants from land-based sources may at the very least be contributing to coral reef decline.

Unfortunately, in most countries of the Caribbean very few studies have been carried out to document the extent of pollution in coastal areas. This is due in part to scarce resources for scientific research and a lack of analytical facilities and trained personnel to carry out such studies. Such is the case in Belize.

**Research Project and Objectives**

As an initial effort to remedy the situation in Belize, we have carried out a campaign to document the extent of pollution in coastal waters of southern Belize with respect to pesticides and selected heavy metals. Our major objectives were: (1) Measure levels of selected agricultural pesticides in coastal waters. (2) Determine if any pesticides are transported as far out as areas containing coral reefs. (3) Compare the results of the sampling campaign with the results from the predictive Level III fugacity model. (4) Measure levels of mercury and lead in coastal waters and determine potential sources.
Research Area

Since both the banana and citrus industries in Belize are concentrated primarily on the fertile, flat lands along the southern coastal areas of Belize and, in the case of citrus, on the Stann Creek Valley, Geographic Information Systems (GIS) was used to visualize and focus our research area. Using the information gathered during interviews with stakeholders (chapter 2) and ArcGis 9.0, the major watersheds that were potentially affected by these industries were identified and targeted for sampling. A total of eight rivers were selected for sampling, starting with North Stann Creek River which empties directly in front of Dangriga Town on the north and going as far south as the Sarstoon River, which borders Belize with Guatemala (Figure 4). The three northernmost rivers, North Stann Creek River, Sittee River and South Stann Creek River, were identified as the primary water source for the citrus industry with a couple banana farms also using the latter river. In the case of North Stann Creek River, several incidences of fish kills have been reported to the Department of Environment in the past, with claims that agrochemicals were to blame (Mai, pers. comm.).

Identified further south were Mango Creek and Big Creek which were categorized as one for purposes of forming a transect they empty within 200 m of each other within a lagoon and Monkey River, both of which drain areas dominated by banana farms. Over 60% of the banana plantations use as their only water source the Swasey and Bladden Rivers, which join to form Monkey River (see Figure 4). These rivers are intensively used by the banana plantations for a variety of purposes including chemical preparation, irrigation and processing. Further south was our reference river, Swasey River, whose
watershed has protected status as a biological corridor managed by Yax’che Conservation
Group and TIDE.

The last two rivers in the research area include the Rio Grande and the Sarstoon
Rivers. Rio Grande River was selected because it flows through areas characterized by
low impact agriculture such as small scale rice and citrus plantations and subsistence
farming. A particular point of interest with this river is that it has a dump site only a
couple miles from the river mouth. Punta Gorda Town (the main urban centre in the
Toledo District) and neighboring communities dump all categories of waste in this site.

The southernmost river, Sarstoon River, was selected since it borders Belize with
Guatemala, which has large-scale livestock rearing and agriculture.

Figure 22. Sampling region and sampling stations.
Materials and Methods

Sampling Sites

Obtaining both spatial and temporal data during the project lifespan was the major consideration in choosing the sampling scheme and sampling campaign times. Meteorological data, especially rainfall, was analyzed to select specific sampling periods for the rain and dry season. For purposes of this thesis two sampling campaigns were undertaken, one in late February – early March coinciding with the dry season and one in June at the start of the rainy season. This will allow us to determine any differences in surface runoff between the two seasons.

In order to obtain spatial resolution within the constraints of the project we decided to sample along transects parallel to the coastline starting from the mouths of all the rivers chosen for the study out to the areas containing coral reefs. Using a hand-held Global Positioning System unit transects were laid out from each river mouth and sampling sites were chosen to make them as equi-distant as possible. Most worked out to 2.5 – 3 miles apart. Table 4 has the exact coordinates of each station. Figure 22 indicates that it was not possible to always obtain nice transects parallel to the coast or to run the transects all the way to the areas containing coral reefs. The most extreme case of this was with the Sarstoon River. Due to the distance of the coral reef areas from the coast it was not possible to run a transect all the way out there. Because of the maritime borders existing between Belize, Guatemala and Honduras it was necessary to run the transect so as not to violate any border. Despite these limitations, Figure 22 shows fairly robust coverage of the study region.
Table 4. Coordinates of Sampling Sites.

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**Cleanup of Sampling Equipment and Material**

Prior to each sampling campaign all equipment and reagents were thoroughly cleaned to prevent sampling artifacts.

Stainless steel canisters were thoroughly washed with soap and warm water, followed by several rinses with Ultrapure water. Each canister was sealed and triple-wrapped in plastic bags. The plastic bottles for metal determination were washed thoroughly with soap and warm water, rinsed several times with deionized water, then washed with an acidic solution made by diluting ultrapure nitric acid with deionized water.

The stainless steel filter holder and the stainless steel columns for XAD-2 resin were thoroughly washed with soap and warm water, rinsed with Ultrapure water followed with pesticide-grade acetone. They were wrapped in solvent-cleaned Al foil and placed in a stainless steel case.

Glass fibre filters were baked at 500 °C in an oven overnight, wrapped in solvent-cleaned Al foil and stored in Ziploc bags. XAD-2 resin was cleaned by sequential Soxhlet extractions as follows: 24-h extractions in pesticide-grade methanol, followed by acetone, hexane, and dichloromethane. This is followed by sequential 4-h Soxhlet extractions with hexane, followed by acetone, and finally methanol. The methanol was displaced by several rinses with Ultrapure water. Finally, the resin was stored in an amber bottle under Ultrapure water.

Amber bottles were washed with soap and warm water, rinsed with distilled water, soaked in an acid bath for 3 days, and finally baked in a furnace at 450 °C.
Glass wool was Soxhlet-extracted overnight with pesticide-grade dichloromethane followed by petroleum ether.

**Sampling**

Water samples were collected in pre-cleaned stainless steel canisters from a small boat. Once a sampling was identified by GPS the boat was positioned so as to face the direction of the current and the engine was turned off. A 5-gal stainless steel canister was then dipped into the water from the bow of the boat, ensuring that water was collected from the surface (to account for any surface-microlayer artifact) and from a depth of approximately 1 m. Once full, the canister was immediately pulled out, capped and stored in the shadiest portion of the boat. At each station a water probe was used to measure temperature, pH, and salinity.

During the June sampling campaign samples were collected to measure concentrations of mercury and lead. At each station a pre-cleaned and pre-acidified 250-mL plastic bottles was dipped quickly from the bow of the boat from the side opposite the one where the stainless steel canister was dipped. Ultrapure concentrated nitric acid was added drop-wise to the water to take the pH to \(~1\). Each bottle was immediately placed in an ice cooler with ice.

**Processing**

Once on-shore, water for pesticide determination was filtered through glass fibre filters and XAD-2 resin as follows: Teflon-lined tubing from the stainless steel canister
to the top of a stainless steel filter holder containing a 135-mm glass fibre filter; the same
type of tubing was run from the bottom of the stainless steel filter holder to the top of a
stainless steel tube containing XAD-2 resin; the same type of tubing was run to a
peristaltic pump. The peristaltic pump pulled water through the assembly. The glass
fibre filter is designed to trap particulate matter with any associated pesticides while the
XAD-2 resin is designed to trap dissolved-phase pesticides. The filtration rate was set to
300 mL/min and was monitored frequently to adjust if needed to keep the rate as constant
as possible, thus allowing the calculation of volume processed based on processing time.
Samples collected from closer to shore often needed more than one glass fibre filter; in
such cases all the filters used in a given site were combined.

The steel column with XAD-2 resin was prepared as follows just before
processing each sample: a plug of clean glass wool was added at the bottom of the tube;
distilled water was added until it reached a height of approximately 20 cm; XAD-2 resin
was added until the slurry reached approximately 25 cm; another plug of glass wool was
added and the top cover of the column was secured.

Once processed, the glass fibre filters were wrapped in solvent-cleaned Al foil,
placed in a Ziploc bag and stored in a freezer until transported for analysis. The XAD-2
resin slurry was poured in small amber bottles with Teflon-lined lids and refrigerated
until transported for analysis. Both were transported to USFSP for analysis in an ice-
cooler with ice-packs.
Extraction

XAD-2 resin and glass fibre filters were Soxhlet-extracted overnight (16-18 h) using 200 mL of 25% DCM/hexane. Resin and filters for each sample were extracted together since our objective in this project was to obtain overall concentrations of pesticides and not to determine partitioning between the dissolved and particulate phases. Extracts were concentrated using a rotary evaporator followed by a gentle stream of ultrapure nitrogen to a final volume of approximately 1 mL after solvent-exchanging into pure hexane.

The concentrated extract was subjected to column chromatography using Florisil. A column was prepared by placing a plug of pre-cleaned glass wool at the bottom of the column, adding 8 g of Florisil (pre-baked at 450 °C) deactivated with 200 μL distilled water and overlaying with 1 cm pre-cleaned anhydrous sodium sulfate. The column was pre-eluted with 100 mL DCM followed by 100 mL hexane. The sample was placed on the top of the column and then eluted with 100 mL hexane followed by 100 mL DCM.

Both fractions were concentrated and solvent-exchanged into isooctane using a rotary evaporator followed by a gentle stream of nitrogen.

Analysis

Pesticides were analyzed in two groups. The first group consisted of acetochlor, cadusafos, carbofuran, azoxystrobin, ethoprophos, fenamiphos, bitertanol and oxamyl. The second group consisted of dacthal, chlorpyrifos, diazinon, chlorothalonil,
pendimethalin, azinphosmethyl, trifluralin, carbaryl, metribuzin, terbufos, dimethoate and malathion.

Analytical details for the first group are as follows: Instrument – Shimadzu; detector type – mass spectrometer, quadrapole type; transfer line temperature – 290 °C; injection temperature – 250°C; carrier gas – helium; injector type – split/splitless set at splitless mode; injection volume – 3uL; column – RTX-5MS from Restek – 15 meters long, 0.25um ID; detector settings – analyzing for ions 35 to 550; oven program - initially at 90 °C for 2.0 minutes, ramp 15 °C/minute to 250 °C, hold for 3.0 minutes; instrument was run in selective ion monitoring (SIM) mode to enhance sensitivity.

Analytical details for the first group are as follows: Instrument – Agilent 6890 GC – 5973; detector type – mass spectrometer, quadrapole type operated in electron capture negative ion mass spectrometry (GC-ECNI-MS); transfer line temperature – 250 °C; injection temperature – 250°C; reagent gas – methane; injector type – split/splitless set at splitless mode; injection volume – 2uL; column – DB5 – 30 meters long, 0.25um ID; oven program -initially at 90 °C for 1.0 minute, ramp 20 °C/minute to 160 °C, ramp 2 °C/minute to 200 °C, ramp 20 °C/min and hold for 15 minutes; instrument was run in selective ion monitoring (SIM) mode to enhance sensitivity.

Paraquat and Glyphosate

These herbicides are too polar to be sampled using the methodology detailed above. To sample for these herbicides we employed method-specific solid-phase extraction (SPE) cartridges. For paraquat we employed Ultraquat cartridges and for glyphosate we employed SAX (strong anion exchange), quaternary amine ion-exchange
cartridges (both purchased from Restek). We had the Ultraquat cartridges custom-made to hold 1g of adsorbent.

For paraquat, we collected 2L of water in pre-cleaned PVC bottles (following recommendations of EPA method 549.2). Bottles were stored in an ice-chest until further processing on-shore. Once on-shore, the Ultraquat SPE cartridges were conditioned by passing 4 mL ultrapure acetonitrile followed by 4 mL of deionized water. 1L of water was then filtered per cartridge so that 2 cartridges were used per sampling site. Filtration at a 25 mL/min was done using a six-position manifold attached to a vacuum pump. Cartridges were wrapped in pre-cleaned aluminum foil and refrigerated.

For glyphosate sampling, we collected 1L of water in pre-cleaned PVC bottles. Bottles were stored in an ice-chest during sampling. On-shore, the SAX cartridges were conditioned by passing through 12 mL of a pH 6 solution made by diluting ultrapure nitric acid with HPLC-grade water to the required pH. 1L of sample water was then filtered through the cartridge at 5 mL/min using a six-position manifold attached to a vacuum pump. Cartridges were wrapped in pre-cleaned aluminum foil and refrigerated.

Once each sampling campaign was completed, SPE cartridges were transported to our laboratories in a cooler with ice packs for analysis.

For paraquat, an acidic solution for elution was prepared by diluting 1 mL of 85% phosphoric acid to 1L with deionized HPLC-grade water. 2 mL of this solution was added to each cartridge and allowed to soak into the adsorbent bed for ~ 1 min. Then 4 mL of the solution was passed through the cartridge slowly (dropwise) into glass test-tubes. All test-tubes were previously deactivated with dichlorodimethylsilane as per instructions on the reagent. The pH of the eluent was checked and if it was acidic it was
neutralized with drops of concentrated ammonium hydroxide; then deionized HPLC-grade water was added to adjust the final volume to 5 mL. The extracts from the two cartridges per site were combined into one final extract.

For glyphosate, a pH 5 solution was prepared using ultrapure nitric acid and deionized HPLC-grade water. 2 mL of the pH 5 solution was added to each cartridge and allowed to soak into the adsorbent bed for ~1 min. Then 13 mL of the pH 5 solution was added and slowly (dropwise) passed through the cartridge and collected in deactivated glass test-tubes.

We initially planned to carry out the analysis for paraquat and glyphosate ourselves but our instrument is not equipped with the appropriate detector, so we had to have those samples analyzed by a commercial laboratory. Both herbicides were measured by HPLC, using a photodiode array detector with an absorbance wavelength of 257 nm for paraquat and derivatization followed by fluorescence detection for glyphosate. As part of our quality control, we spiked three PVC bottles containing deionized HPLC-grade water with glyphosate and three with paraquat to make solutions of known concentrations. These were filtered through the appropriate cartridges and processed and extracted as normal samples. They were also analyzed by the commercial laboratory to determine percent recovery. We also had solutions of both herbicides of known concentrations analyzed by the commercial laboratory for quality control purposes.
Metals

Due to a lack of instrumentation available we had to contract out the samples for mercury and lead analysis. Mercury and lead were measured in the water samples following EPA Method SW-846 and suitable procedures therein.

Quality Control

As part of our quality control, we spiked three PVC bottles containing HPLC-grade water with glyphosate and three with paraquat to make solutions of known concentrations. These were filtered through the appropriate cartridges and processed and extracted as normal samples. They were also analyzed by the commercial laboratory to determine percent recovery. Results were unsatisfactory. For one paraquat and one glyphosate solution percent recovery was in excess of 90%. However, for two paraquat solutions percent recoveries were below 25% and for two glyphosate solutions results indicated below detection limits. We also had two solutions each of both herbicides of known concentrations prepared in HPLC-grade water analyzed by the commercial laboratory for quality control purposes. Percent difference between laboratory values and known concentrations were 56.2% for paraquat and 65.5% for glyphosate. Limits of detection reported by the contract laboratory were 0.001 ppm for paraquat and 0.01 ppm for glyphosate.

For other pesticides we prepared solutions of known concentrations of labeled standards of azinphosmethyl, malathion, diazinon, carbofuran, and ethoprop. We spiked 6 samples from each sampling campaign each with 100 μL of each of the 5 pesticides and treated as samples from extraction through analysis. Percent recoveries of all 5 pesticides averaged over 90% and standard deviations were under 5%, indicating
excellent results. In addition, when running samples on the GC-MS, a solution of known concentration containing the target pesticides was run for every 10 samples to check that the instrument was working well. We also extracted four XAD-2 blanks and treated as samples. In all cases, blanks were below detection limits.

The contract laboratory that analyzed for metals also followed the QA/QC protocol set out by the method they employed (EPA Method SW-846).

**Results**

*Metals*

Mercury was found in all sampling sites (see Table 5 below). Concentrations were uniformly close to the method detection limit (0.001 ppm) suggesting natural sources for this metal. Lead was found in all samples (see table below). Concentrations varied at different rivers, suggesting point sources. An ongoing problem in Belize is the existence of illegal garbage dumps where people dispose of household goods, many containing metals. Of particular concern is the disposal of car batteries containing lead. We believe that the presence of lead is correlated with the presence of such garbage dumps. This is supported by the fact that levels are higher at river mouths and higher at the mouths of rivers that drain municipal areas (e.g. North Stann Creek traverses Dangriga Town, population ~ 10 000 and Monkey River passes near Monkey River Village, a village with a year-round population of around 4 000 people). Surprisingly, lead levels were significant at the mouth of Golden Stream, which drains mostly protected lands. One possibility is the presence of illegal dumpsites near this river.
**Glyphosate and Paraquat**

Glyphosate and paraquat were below detection limits for all samples. This is despite that these two herbicides are by far the most heavily used in citrus and banana farms. There are two possible explanations for these results. First, both paraquat and glyphosate are known to degrade very quickly in the environment. By the time water that flows through farms reaches the coast it is possible that enough time has elapsed to degrade all of these herbicides. However, a second explanation is that the methodology employed in this study was not suitable for the extraction and measurement of glyphosate and paraquat. This is supported by the lack of satisfactory results with regards to the samples and standards submitted to the contract laboratory for analysis. As discussed previously, recovery studies were poor and the results for the calibration solutions submitted were significantly different from the true values. As a result, we are unable to make definitive statements regarding the potential impact of these herbicides on offshore coral reefs. Until a reliable, reproducible method is used to produce reliable results results are uncertain. Further studies are certainly necessary in this area.

**Table 5. Metal concentrations in coastal waters of southern Belize.**

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Other Pesticides

Tables 6 and 7 below summarise the results for several pesticides that were detected in coastal waters of southern Belize. Due to analytical difficulties we were unable to analyse samples for all the pesticides targeted initially, but we were able to measure a sufficient number to draw preliminary conclusions and to compare with modeling results presented in Chapter 2 of this thesis.

The first observation made from the data is that generally levels of pesticides were higher in June than in February. February falls during the dry season in Belize
while June is right at the beginning of the rainy season, which generally runs from July to November but can start earlier. A study by Burke and Sugg (2006) indicates that total riverine discharge into coastal Belize is over four times higher in June compared to February. Thus, one would expect increased riverine input of pesticides in June, as observed in general in this study. In addition, in late May and early June at least two tropical storms affected Belize, Tropical Storms Alma and Arthur. Precipitation from these twin tropical storms caused the most severe flooding seen in Belize, especially southern Belize, in at least 50 years. As a result, higher concentrations of pesticides during June reflect increased input from flooded rivers flowing through agricultural lands.

The results indicate that the pesticides detected in at least one sample were cadusafos, ethoprop, acetochlor, fenamiphos, oxamyl, carbofuran, chlorpyrifos, dacthal, chlorothalonil, trifluralin, and malathion. Frequency of detection differed among these pesticides, as did levels. In terms of levels, the first six pesticides listed above were measured in significantly higher levels (several orders of magnitude) compared to the last five. However, there was no correlation between levels and frequency of detection. Thus, for example, carbofuran was detected only in six samples in February and five samples in May, but the concentrations in those samples were 6-7 orders of magnitude higher than levels of chlorpyrifos, a pesticide detected in almost all samples.

For some pesticides, namely oxamyl, cadusafos and chlorpyrifos, there is a general trend of decreasing concentrations from the river mouths extending offshore in each transect. This supports the hypothesis that the sources of these pesticides are the citrus and banana farms in southern Belize. However, this trend does not hold perfectly.
and does not hold for all pesticides. An interesting observation is that the middle stations in most transects seem to have elevated levels of pesticides, breaking the trend of decreasing levels as one moves offshore. An examination of the current systems in coastal Belize might explain this observation. It has been reported that in southern Belize there is a flow south along the coast until the currents meet in the Gulf of Honduras the western flow coming from the Caribbean Sea. This creates a current moving north some miles offshore near the coral reef. It is plausible to envision that this creates a mixing of pollutants in the coastal area, with some concentration in the middle of the area, which would match our results.

Due to analytical delays it was impossible for us to analyse the samples for all the target pesticides we chose at the beginning of the project. Therefore, it is possible that there still other pesticides that are being discharged into coastal waters of southern Belize. Further studies should help determine this. The data also shows that some pesticides are indeed transported far enough offshore that they are found in waters overlying the coral reefs. Thus, there is the potential that such pesticides may be adversely affecting coral reefs. As with metals, it should be a priority to measure levels of pesticides in the coral reefs to determine if there is any accumulation. This has been noted in previous studies (Glynn et al., 1989).
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Table 7. Pesticide levels in coastal southern Belize (pg).

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<th>ethoprophos Feb</th>
<th>ethoprophos June</th>
<th>acetochlor Feb</th>
<th>acetochlor June</th>
<th>fenamiphos Feb</th>
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<th>oxamyl Feb</th>
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<td>7.21E+10</td>
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|          | NSC2          | NSC3           | NSC4             | NSC5             | SR1           | SR2           | SR3             | SR4             | SR5         | SSC1         | SSC2         | SSC3         | SSC4         | SSC5         | MBC1         | MBC2         | MBC3         | MBC4         | MBC5         | MC3          | MC4          | MC5          | MR3          | MR4          | MR5          | RG1          | RG2          | RG3          | RG4          | RG5          | GS1          | GS2          | GS3          | GS4          | GS5          | SAR1         | SAR2         | SAR3         | SAR4         | SAR5         | 79           |
Comparison of Empirical Data and Modeling Results

Table 8 below ranks the pesticides that could be measured in this study in terms of their fractions predicted by the model to partition into water, their actual concentrations measured, and by their predicted overall half-lives.

Table 8. Comparison of empirical and modeling results.

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Rank by fraction predicted in water</th>
<th>Rank by concentrations measured in water</th>
<th>Rank by overall half-life (1=shortest)</th>
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<td>-</td>
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<td>Oxamyl</td>
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<td>1</td>
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<td>1</td>
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<tr>
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<td>3</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Acetochlor</td>
<td>4</td>
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<td>9</td>
</tr>
<tr>
<td>Fenamiphos</td>
<td>5</td>
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<tr>
<td>Ethoprop</td>
<td>6</td>
<td>5</td>
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<td>7</td>
<td>2</td>
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<td>Chlorothalonil</td>
<td>8</td>
<td>10</td>
<td>2</td>
</tr>
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<td>Dachthal</td>
<td>9</td>
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</tr>
<tr>
<td>Chlorpyrifos</td>
<td>10</td>
<td>7</td>
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The Level III fugacity model employed to predict which pesticides are most likely to partition into water correlates quite closely with empirical data. Assuming that the more a pesticide partitions into water the more likely it will be susceptible to runoff into nearby streams and into coastal waters, then the ranking done by the modeling and the empirical levels should correlate. This is indeed the case in general. Oxamyl is predicted to be the pesticide that partitions to the greatest extent into water and it is the pesticide measured in highest concentrations. Carbofuran is predicted to be third in partitioning into water and its measured concentrations were on average third highest. Acetochlor
was predicted fourth, and measured fourth. Fenamiphos was predicted fifth and measured sixth. Ethoprop was predicted sixth and measured fifth. Chlorothalonil was predicted eighth and measured tenth. Dacthal was predicted ninth and measured ninth. Chlorpyrifos was predicted tenth and measured seventh. Only two pesticides did not seem to correlate well, malathion and cadusafos. Malathion was predicted second and measured eighth and cadusafos was predicted seventh but measured second. Half-lives may help explain these anomalies between model and empirical data, especially for malathion. Even though it is predicted to partition heavily into water it is also predicted to have the shortest half-life. Thus, even if it partitions into water it may be degraded very quickly so that it is not found in high levels in coastal waters. In the case of cadusafos, its high concentrations may be due to usage patterns (that is, it may simply be that our sampling campaign coincided with the application time of this pesticide).

**Conclusions**

We have successfully carried out the first, to our knowledge, survey of levels of pesticides and metals in coastal waters of southern Belize. Our results indicate that there are some pesticides used in the banana and citrus industries that can be measured in coastal waters, and in some cases all the way out to waters overlying the barrier reef. Thus, there is the need for further studies to determine if any pesticides or metals are causing adverse effects on coral reefs. This would help in determining if alternative pesticide usage patterns are necessary in the banana and citrus industries. In the interim, it is recommended that care be exercised in the use of those pesticides measured in very
high levels in this study (for example, oxamyl, cadusafos, chlorpyrifos, dacthal, chlorothalonil).

Empirical results correlate very well with those predicted by a Level III fugacity model applied to the study region. This indicates that this model maybe applied to other areas in Belize and probably other tropical areas.
Chapter Four

Analysis of Pesticide Legislation in Belize

Background

Environmental management authority in Belize falls under several government ministries, quasi-governmental authorities and NGO institutions. Although the portfolio for environment currently rests with the Ministry of Environment, major responsibilities are held by the Ministries of Health (water and sanitation), Agriculture and Fisheries (fisheries, coastal zone management, pesticides control), and Natural Resources (forestry, national parks and protected areas, wildlife, water resource management, land use planning). Two quasi-government entities with specific responsibilities include Solid Waste Management Authority and Land Utilization Authority and several conservation NGOs managing natural resources on behalf of the Government of Belize.

This proliferation of institutions with environmental responsibilities gives rise to a number of implementation problems. For instance the current basis for resource allocation among institutions is not clear, and financial resources and technical capacity remain a problem. The primary institutions involved in environmental protection and natural resources management may be conveniently classified into environmental protection institutions (DOE, PCB and Public Health Bureau); resource management institutions (Forest Department, Fisheries Department); and land use planning institutions (Land Utilization Authority, Central Building Authority).
Belize’s Legislative Framework on Pesticides

In Belize, the legislative jurisdictions under which chemicals are managed lie within control of four principal organizations. These are: (i) Pesticides Control Board (PCB), (ii) Department of the Environment (DOE), (iii) Public Health Bureau (PHB)/Ministry of Health and, (iv) Belize Agriculture Health Authority (BAHA). These organizations are all government agencies. However, the main legal instruments used for controlling the use of chemicals, and specifically the pesticide chemicals, are the Pesticide Control Act (PCA) and the Environmental Protection Act (EPA). Both of these Acts would fall under the broad legal framework of Environmental Legislation.

The Pesticide Control Act (PCA)

The Pesticides Control Act (PCA) of 1985 (Chapter 216, Revised Edition 2000) provides authority to control the manufacture, importation, sale, storage and use of pesticides. The Pesticides Control Board (PCB) established by the Act carries out this function. To date prohibited, restricted and registered regulations have been completed. The Act itself identifies specific pesticides that are prohibited, restricted or registered. Registered pesticides are those pesticides that have been approved by the PCB for use in Belize. Sections 6 and 7 of the Act provide that the Board may grant a license for the manufacture or importation of any pesticides. Section 2 of the PCA provides for a “restricted use pesticide.” This refers to a pesticide which, if used in accordance with a widespread and commonly recognized practice, may generally cause, without additional regulatory action, unreasonable adverse effects on the environment, including the applicator and other people.
Several regulations have also been made for the proper use of registered pesticides. These regulations have been consolidated in the Pesticides Control Act, Chapter 216, R.E. 2003, showing the Subsidiary Laws as at October 2003. These regulations include: (a) Registered and Restricted Pesticides (manufacture, import and sale) Regulations, S.I 8 of 1989; (b) Registered and Restricted Pesticides (registration) Regulations, S.I. 77 of 1995; (c). Registered and Restricted Pesticides (manufacture, import and sale) Amendment Regulations, S.I. 30 of 1996; (d) Registered and Restricted Pesticides (certified user) Regulations, S.I. 112 of 1996 and (e) Pesticide Control (sale and confiscation) Regulations, S.I. 71 of 1998

These regulations provide the legal regiments for registration, labeling, importation, sale and use of pesticides. Additionally, regulations were recently enacted in order to expand the legal requirements of the PCA. These include the Restricted Pesticides (Certified User) Regulations, and the Pesticides Control (Sale and Confiscation) Regulations. These regulations demonstrate some concerns for the health and well being of workers. For example, S.I. no. 112 of 1996 (Restricted Pesticides (Certified User) Regulations) required that formal training of farmers, applicators and retailers be conducted on safe and efficient pesticide management. The enactment of S.I. No. 112, of 1996, required the pesticide user to pass a written or oral exam. Schedule III of this legislation required that the trainee comply with a number of stipulations including the ability to read and understand labels, safely and adequately prepare mixtures of pesticides, the proper calibration and use of equipment, among others. Additionally, with the enactment of S.I. No. 71 of 1998, Pesticides Control (Sale and Confiscation) Regulations the PCB was granted further powers to enforce S.I. no. 112 of 1996. This
S.I. required that establishments maintain a register of sales of restricted pesticides, and may only sell Restricted Use Pesticides (RUP’s) to persons in possession of a certified user’s license.

An application for registration of a pesticide should be submitted to the PCB prior to importation and should be accompanied by chemical, toxicological and environmental impact data. Any person wishing to register any pesticide must also submit details of the labels of packaging. This application is analyzed and a recommendation is made by the PCB’s Registration Committee and if approved, the conditions for such importation are detailed. This committee has for some time now been chaired by the Department of the Environment.

In terms of “Prohibited Pesticides”, the PCA defines these as any pesticide of which the possible effects on the environment, plant, animal or human being are considered by the Minister to be too dangerous to justify its use. Section 13 (1) provides that pesticides not registered as required in section 6 or listed under section 8, should be prohibited pesticides and accordingly shall not be brought into or used in Belize. Section 6 (1) provides that any person may, subject to the provisions of this Act, manufacture, import, advertise or sell a pesticide which is declared to be a registered pesticide. Section 6 (2) provides a list of registered pesticides which is given in the Second Schedule to this Act, and this schedule may be amended or replaced from time to time by order made by the Minister, in consultation with the Board.

Section 8 (1) provides that no person shall sell a restricted pesticide unless, (a) he is authorized in the prescribed manner to do so; (b) the premises in which the sale is carried out have been registered in the prescribed manner for the purpose; and (c) the sale
is carried out in accordance with such other requirements as may be prescribed. Section 8 (2) provides another list of restricted pesticides and is given in the Third Schedule to this Act. This Schedule may be amended or replaced from time to time by order, by the Minister in consultation with the Board. The Act provides sufficient authority for enforcement if its provisions, authorizing a penalty for violation of the Act or regulations of a fine not exceeding five thousand dollars or to imprisonment for a term not exceeding five years or to both such fine and imprisonment.

The Environmental Protection Act (EPA)

Until the enactment of the Environmental Protection Act (EPA) in 1992, (Chapter 328, Revised Edition 2000), Belize had no comprehensive environmental protection legislation. Authority to prevent and control environmental pollution was contained in provisions of the Public Health Act, the Pesticides Control Act, and the older Dumping at Sea, and Water and Sewerage Acts. These Acts, however, were never effectively used to provide environmental protection, as the necessary supporting regulations, such as establishing environmental quality criteria and pollution control standards, were not established.

The EPA makes provisions for guiding the rational use of natural resources, for controlling environmental pollution, and for overall protection of the environment. Part I of the Act deals with preliminary matters of interpretation. It defines key terms including: “Environment”, “Environmental Pollution”, “Environmental Pollutant”, “Hazardous Substance”, “Waste”
Part II of the Act legally established the Department of Environmental (DOE), giving it the responsibility and authority to enforce the Act and its subsidiary legislation.

Part III of the Act provides for the prevention and control of environmental pollution and for the making of regulations. Under this Part and in section II (1) it is stated that: “No persons shall emit, import, discharge, deposit, dispose of or dump any waste that might directly or indirectly pollute water resources or damage or destroy marine life.”

Part IV provides for the prohibition on Dumping. In particular section 13(1) states that: “No person shall dump or dispose of or deposit any garbage, refuse, toxic substances or hazardous wastes in any place that may directly or indirectly damage or destroy flora or fauna, or pollute water resources or the environment.”

Part V provides for Environmental Impact Assessment (EIA) and regulations made there under. Section 20 (1) states: “Any person intending to undertake any project, programme or activity which may significantly affect the environment shall cause an environmental impact assessment to be carried out by a suitably qualified person, and shall submit the same to the Department of Environment for evaluation and recommendations.”

Part V Section 20 of the Pollution Regulations addresses the processing, storage, use and transportation of organic solvents and other volatile compounds. Through the Pollution Regulations, SI # 56 of 1996, mechanisms have been developed to establish the prohibition of industries operating and emitting contaminants into the environment, without a permit from the DOE (Regulation 4). These include emissions into the air from (1) industry (Regulation 4), (2) power generating installations, (Regulation 8), (3)
burning of refuse in urban areas (Regulation 13), (4) processing industries (Regulation 15), (5) gasoline or petroleum storage unit (Regulation 18), (6) storage containers for solvents, pesticides and other volatile compounds (Regulation 21), and (7) combustion engines such as motor vehicles (Regulation 25); and provide DOE with powers to require owners, occupiers and other agents to clean-up (Regulation 50) and abate pollution (Regulation 51). In order to encourage voluntary compliance, DOE is empowered to develop an environmental incentive programme (Regulation 58 (1)), as well as a "facility environmental audit programme" as a comprehensive investigation and evaluation system designed for detecting and preventing violations of environmental requirements or the commission of pollution related offences (Regulation 58 (3)).

**Governmental Policy on and Management of Pesticides**

Authority for environmental management as a whole in Belize is shared by a number of ministries, departments, quasi-governmental authorities and non-governmental institutions. The portfolio for environment now rests with the Ministry of the Environment (environmental planning, pollution), but major environmental responsibilities are also held by the Ministries of Health (water and sanitation), Agriculture and Fisheries (fisheries, coastal zone management, pesticides control), and Natural Resources (forestry, national parks and protected areas, wildlife, water resource management, land use planning). Quasi-governmental statutory authorities, such as the Solid Waste Management Authority and the Land Utilization Authority, were created to carry out specific responsibilities. Finally, several non-governmental organizations
(NGOs) are responsible for certain natural resources management functions for the Government of Belize.

This proliferation of institutions with environmental responsibilities gives rise to a number of implementation problems. For example, the current lack of clearly delineated roles and responsibilities results in unnecessary confusion and wasteful duplication of effort. Inter-ministerial coordination on environmental matters has not been fully institutionalized and needs urgent improvement. The current basis for resource allocation among institutions is not clear, and financial resources and technical capacity remain a problem.

The primary institutions involved in environmental protection and natural resources management may be conveniently classified into three categories: environmental protection institutions (Department of the Environment, Pesticides Control Board, and Public Health Bureau); resource management institutions (Forest Department, Fisheries Department, Office of Geology and Petroleum, National Hydrological Service, and Land and Surveys Department); and land use planning institutions (Land Utilization Authority, Central Building Authority, North Ambergris Caye Development Corporation and the various Town Boards that have been assigned planning functions).

It should be noted that there are a number of overlapping responsibilities between the various institutions and this problem has been compounded by the variety of statutory provisions. Part of the problem of overlapping responsibilities stems from the fact that some institutions (e.g. Forestry and Fisheries Departments) are comparatively old institutions while some (e.g. the Department of the Environment) are relatively new.
Another reason is that the various Departments and agencies have somewhat shifted their roles either to meet perceived needs or to deal with the realities of international funding.

**Rationalizing Legislative Amendments to Address Chemicals in Belize**

From an assessment of the above legislation, it is apparent that Belize has no comprehensive chemical management legislation. As reflected above, there are in fact two major legislations that significantly govern environmental “pollution” management. These are the Pesticides Control Act (PCA), and the Environmental Protection Act (EPA). The PCB Act governs agricultural chemicals including the POPs pesticides; and the Environmental Protection Act which, with its broad mandate to control, among other things, the volume, types, constituents and effects of waste, emission and discharges into the environment. The EPA can effectively control and minimize the trans-boundary movement of toxic and hazardous waste including the movement of PCBs and the unintentional releases of dioxins and furans into the environment. None of these Acts, however, make any reference to the control of exports of chemicals. Indeed, none of the Acts, or any other legislation address any of the following:

- Processes or procedures adopted to safely transport or export banned or obsolete chemicals;
- Environmental standards for dioxins or furans;
- Standards or procedures governing the burning of agricultural and other waste that would result in managing or reducing the release of chemical pollutants;
- Procedures for managing medical, pharmaceutical, veterinary or other biomedical waste;
• Provide capabilities to monitor source emissions of environmental and chemical pollutants;

• Determine acceptable standards of ambient chemical pollutants in air, soil, or water samples; and most importantly

• Provide responsibilities and capabilities to monitor the fate or impacts to pesticides being used in Belize upon its environment.

In an effort to address these issues the Department of the Environment recently developed new environmental legislations that have been submitted to Belize’s National Assembly for their approval. The new legislations include a Hazardous Waste Management Regulation, the Transporters of Hazardous Waste Regulations and, amendments to existing legislation such as Solid Waste Management Authority Amendment Act, Environmental Impact Assessment (Amendment) Regulations and the Effluent Limitations (Amendment) Regulations. It is anticipated that these regulations will become the formal basis for many of the global issues aimed at environmental protection. The Department has also recently initiated the development of Belize’s National Plan of Action (NPA) to address Land Based Sources of Marine Pollution. Prioritization of the major environmental issues has been done and a report has been prepared for cabinet’s endorsement.

While there is recognition of the value of assessing and re-evaluating the relevance of the legislation, as it relates to the management of chemicals, the outcome of previous initiatives are less than stellar. The initiatives boldly unfolded by the
Department of the Environment are yet to materialize as a result of constraints resulting from lack of funding and other resources.

For these reasons, the assertion is that clear outcomes will result only when an unambiguous strategy is developed to chart a pathway that will lead to legal instruments that will fill all the regulatory gaps and inconsistencies defined; and that will provide key government agencies with the power necessary to require – when needed – information from producers, importers, distributors, industrial consumers of chemicals and generators of waste.

**Belize’s Institutional Framework to Address Pesticides**

*Pesticides Control Board*

The Pesticides Control Board, established in 1985 under the Pesticides Control Act, (Ch. 216 of the Rev. Laws of Belize 2000) is responsible for the management of the use, importation, manufacturing and sale of Pesticides. The functions of the Board are to control imports or manufacturing of pesticides through a registration and licensing process, that also authorizes sale of these restricted pesticides and the process to follow (Registered & Restricted Pesticides (Manufacturing, Import & Sale Regulations, SI # 8 of 1988) and as amended in 1996 through SI #30 of 1996; as well as Pesticide Control (Registration) Regulations, SI # 77 of 1995; to register premises in which a restricted pesticide may be sold establishing the conditions that these establishments must comply with, as well as the cases where confiscation of pesticides are possible (Pesticide Control (Sale & Confiscation) Regulations, SI # 71 of 1998); to authorize pesticide applicators to use restricted pesticides (Pesticides Control (Certified Users) Regulations, SI # 112 of...
to classify any pesticide as a registered pesticide, restricted pesticide or a prohibited pesticide (Pesticides Control (Replacement Order), SI # 72 of 1988); and to deal with all aspects of the importation, manufacture, packaging, preparation for sale, sale, disposal and use of pesticides (Ch. 216, Rev. Laws of Belize, 2000). The Schedules to the Act contain a list of Registered, Restricted and Prohibited Pesticides and these have been recently revised by the Pesticides Control (Replacement of Schedules) Order, 1995 (S.I. # 100 of 1995). Regulations made under the Pesticides Control Act outline the mechanism for registering pesticides. Regulations made under the Act indicate that in the application for the registration of pesticides, applicants must complete a section that provides ecological information on the particular pesticide. This includes information on the persistence and alterations of the product in soil, water and air; the effects in terrestrial flora and fauna; the effects in aquatic flora and fauna and data on toxicity to beneficial insects; and data on mobility of the pesticide in the ecosystem. Information must also be included on the possible toxic effect of the pesticide oil human beings (S.I. # 77 of 1995, Schedule 1).

The Act makes provision for the appointment of a qualified technical person as an inspector who will have the power to enter any land or premises registered for the sale or manufacture of pesticide in order to carry out his functions which include inspecting, copying and examining relevant records or other documents; making examinations or inquiries and seizing and detaining any article which is related to the contravention of the Act (Sec. 17, Ch. 216, Rev. Laws of Belize, 2000).

The Pesticides Control (Amendment) Act on 2002, redefines “Pesticides” to incorporate and differentiate between restricted and prohibited pesticides; it grants the
Pesticides Control Board the power to establish Committees to assist in detailed technical works required by the Board; it repealed the post of Secretary in the PCB Secretariat and converts it into the “Registrar” of the Secretariat; it increased the Penalties for contravention of this Act; and it amends the First Schedule of the main Act (of 1985).

The Pesticides Control Board commissioned the Amendment of the Registration Regulations of 1995 (SI # 77 of 1995) in early 2003. This amendment to the Regulations was basically to differentiate between the various categories of registration of pesticides, with their corresponding fees; to provide for the Board’s ability to grant “provisional” registration to a pesticide for one year maximum for experimental purposes; for the repealing of schedules I and II of the 1995 Regulations for implementation of these amendments; and also to provide for the Minister of Agriculture to be granted with the power to “import a pesticide not registered in Belize, only during Emergency occasions.”

**Conclusions and Recommendations**

This study’s results indicate that the banana industry may be doing a better job with regard to being sensitive to environmental impacts of its pesticide activities compared to the citrus industry. The survey indicated clearly a greater knowledge of and interest in using environmentally-friendly methods. Considering that a significant of citrus farms are owned by owners of banana farms, it is possible that the difference in attention to environmental issues is due to a greater international pressure from the European Union on the banana industry.
Despite differences in the levels of interest and knowledge, results indicate that overall there exists a great degree of knowledge on environmental matters and interest on receiving training on such matters.

An analysis of Belize’s attempts to properly manage pesticides, years of strategies and media campaign focusing on ‘safe pesticide management’ have failed to bring about improvements. Thus, the most effective way to reduce human and environmental health risks in developing countries like Belize is to reduce pesticide use and/or switch to more environmentally- and health-friendly.

This study clearly indicates that the PCB is not actively engaged in stimulating interest in environmentally-friendly and other alternative pesticide management practices. There is also little on the way of training programmes for farmers.

It is recommended as a first step to better manage chemicals, including pesticides, in Belize that the appropriate agency (in our view DOE) carry out a comprehensive legislative study that would identify the strengths and gaps among existing legislation, especially the PCA and the EPA. The results of this study should lead to legislation encompassing comprehensive chemical management. It should incorporate control of persistent organic pollutants (POP) and other hazardous chemicals and it should detail a monitoring plan for the fate of these in the environment.

Also, since there is no one entity responsible for the management for chemical management in Belize, there is a need for the establishment of a single entity or established interagency with clear responsibilities for the management of all aspects of chemicals. This entity or interagency mechanism needs to be provided with adequate human resources, material and equipment and financial support. The human resource
should in this entity should be have the formal necessary skills to perform all aspects of chemical management from enforcement, monitoring and research, and translation of research findings to programmes, policies and finally to legislation.

There is an urgent need to enforce existing legislation on pesticide use and its effects on water quality, human health, flora and fauna.

Obtaining data on pesticides being used in Belize is challenging and to a large extend, what is made available can have huge discrepancies. It is therefore imperative that the regulatory body for chemical management establish an accessible organized system of pesticides.

It is definitely recommend that the Pesticide Control Board become active in setting up workshops and other training programmes for farmers to demonstrate alternative and more environmentally-friendly pesticide management practices. Certainly the results indicate a high degree of interest in further training on the part of farmers.
References


