An Experimental Time-Dependent Method for the Study of Atrazine Sorption onto a Characterized Soil

by

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DEDICATION

To:

My Parents:

Muhyialdeen Malibari and Zohra Mohammed

My Brothers and Sisters:

Adnan, Abeer, Afaf, Awateef, Atef, Aziza, Shareef, and Manal

My Husband:

Yusry Malibari

My Children:

Sara and Mohammed

ABSTRACT

An Experimental Time-Dependent Method for the Study of Atrazine

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This work focused on the sorption/desorption of atrazine in aqueous soil suspensions. Soil used in this study was extracted from Northport (N.S.) and was chemically and physically characterized in-house. The soil acidity was determined to be at pH 4.7 and mass percent concentration of carbon, hydrogen, and nitrogen was 1.86%, 0.48%, and 0.34%, respectively. The mineral composition of the Northport soil consisted mainly of silica (SiO_2, 67%). Scanning Electron Microscopy analysis showed that the most abundant elements were Si (30.61%), O (47.94%), Al (9.80%), Fe (5.68%), and Mg (2.06%). Time-dependent sorption curves of atrazine were measured at constant temperature of 20°C using an off-line and an on-line separation technique with High Performance Liquid Chromatography. The sorption experiment showed that 66% of atrazine remained in solution, 6% of atrazine was labile sorbed onto the soil, and 28% of atrazine was unrecoverable and lost from solution during the first hour of sorption. Sorption kinetics results shows that after one full day of sorption, 20% of atrazine remained in solution, 32% was labile sorbed or extractable, and 48% of atrazine was unrecoverable.

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LIST OF ABBREVIATIONS

SEM	Scanning Electron Microscopy
EDS	X-ray Energy Dispersive Spectroscopy
XRD	X-Ray Diffraction
BET	Brunauer–Emmett–Teller
HPLC	High Performance Liquid Chromatography
CHN	Carbon Hydrogen Nitrogen
CEAR	Center for Environmental Analysis and Remediation
PEI	Prince Edward Island
ATSDR	Agency for Toxic Substance and Disease Registry
AT	Atrazine
EPA	Environmental Protection Agency
EU	European Union
K_D	Distribution Coefficient
Θ_C	Labile Sorption Capacity
K_{OC}	Distribution Coefficient
K_{OH}	Octanol-Water Coefficient
$t_{1/2}$	Total Loss Half Life
BET	Surface Area
k	Rate constant
M_T	Initial concentration
min	Minute
h	Hour

w	Week
PDA	Photo-diode Array Detector
(W/V)	Weight of Suspended Soil per Volume of Sample (g/L)
Θ_{a0}	Empty Sorption Sites
M_1	Solution-Phase Pesticide
Θ_{a1}	Filled Sorption Sites
Θ_{d1}	Amount Diffused into Particle Interiors

CHAPTER ONE

1.1 Introduction

1.1.1 Pesticides

Agricultural crops need protection from pests. Agricultural pesticides have emerged as environmental problems; its clean up remains a challenge. For the use of chemical pesticides to be as safe as possible, their persistence, physical states, and leaching from soil and in water have to be quantitatively determined.

Pesticides are organic chemicals used in agriculture to protect agricultural crops from pests such as weeds, fungus, or insects. For instance, weeds affecting corn include Lambsquarters, Morning Glory, Nightshade, Pigweed, Cocklebur, Velvetleaf and Foxtail.[1] Moreover, pesticides, such as herbicides, insecticides, and fungicides, are meant to be effective against a particular pest. The suffix "-cide" derives from Latin, "to kill," [2] (i.e., herbicides kill weeds, insecticides insects, fungicides fungi, and rodenticides rodents).[3]

Pesticides protect principal crops, such as sugar cane, maize, soybean, and citrus fruits.[4] Pesticide use on agricultural crops has been shown to increase agricultural yield by 100%, as pesticides kill pests that spread before they spread. Although pesticides are harmful; their use in agriculture continues despite the risks because they help to increase crop yields.

Agriculture crops are essential for human and animal survival. Prior to the use of pesticides, global food production was low because pests limited crop growth. The use of

pesticides improved crops yield, creating surpluses of food, such as fruits and vegetables. Pesticides have the advantage of increasing the amount of crop yields year over year.

However, pesticides are a source of animal health problems, including adverse effects on human health. Pesticides, after use, behave with soil in several ways: they can remain for short or long periods of time; can move to other places by rain; and leach into the ground, depending on the type of pesticide. If some pesticides are distributed across a field, for example, some are then taken up by plants, and some stay in the soil. Issues then arise about those pesticides that remain in soil. This study focuses on the interaction between soil and pesticides, since pesticides have advantages and disadvantages. Also, this study provides better predictions about pesticide damage before applying it to an agricultural field.

1.1.1.1 Atrazine

Modern agriculture uses large amounts of organic chemicals, such as herbicides. Herbicides, used to kill weeds and broad-leaved trees, are a heterogeneous class of chemicals.[4] Their persistence and transport in the environment raise questions of environmental and human safety. Some herbicides can have long half-lives or are suspected to be carcinogenic. The improper application of herbicides can result in direct contact with humans and wildlife, which is problematic because they cause a range of health problems, from skin rashes to cancer. Under some conditions, some herbicides can be transported by water via leaching or surface runoff, which contaminates groundwater or distant surface water sources.

Atrazine (AT), synthesized in 1958 by Novartis Laboratories, is a common herbicide, generally used to control broadleaf and grassy weeds in corn yield and for general weed control. The chemical structure of atrazine is shown in Figure 1.1.1

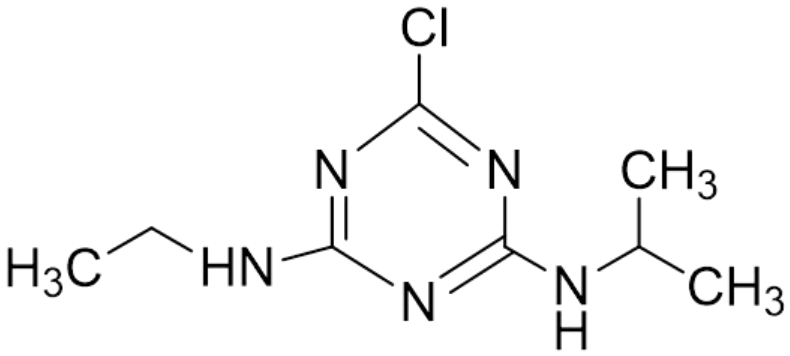

Figure 1.1.1 Atrazine chemical structure.

Atrazine is one of the most widely used herbicides in the US, with 76 million pounds applied to crops each year. Atrazine (or its by-products) is one of the most frequently detected pesticides in ground and surface water.[3,4] It can remain active for long periods of time.

Atrazine contamination incidents have been reported in nearly all of Canada. Since 2004, atrazine has been forbidden in Europe, but it is still largely used in regions such as Brazil and the US. [1,2,3] Even though the US Environmental Protection Agency (EPA) accepted its continued use in October 2003, in the same month, the European Union (EU) announced a ban of atrazine usage due to water contamination.[5]

As an example, most pesticide use on Prince Edward Island (PEI) potato crops are contact fungicides, which protect potato plants from contracting Late Blight. PEI potato farms are affected by pesticides, especially in summer.[6] Heavy rains wash pesticides off

fields and into waterways, where chemicals kill aquatic animals over many years. According to the Agency for Toxic Substance and Disease Registry (ATSDR), when atrazine is applied to soil, it can remain for a long time, such as days or months before it is broken down. However, after a while, any atrazine that enters the groundwater by run-off or leaching could remain for a longer period since atrazine is broken down in water more slowly.[7] This study is important because of the potential harm of atrazine to human health.

The circumstances that encourage herbicide transport are forceful storm events (generally soon after application) and soils with limited capacity to adsorb or maintain the herbicides. Therefore, the determination of atrazine kinetics and its mechanism is critical to understand its behaviour in the soil. The study of the atrazine kinetics and sorption mechanism will allow us to understand better the root causes of problems associated with pesticides being present and remaining in soil and ground water, and to study the ways to minimize the effects of herbicides on the environment. Finally, using pesticides is essential for weed control, but it has to be limited by a specific amount, which does not harm people or the environment.

1.1.2 Agricultural Soil

Agricultural soil is an example of a heterogeneous system[8] since it is a mixture of very complicated components, which contain minerals such as Silica, Anorthite, and Albite. Northport soil, which is the test soil sample for this work, is a typical example for agricultural soil. Northport soil was physically and chemically characterized and the results are reported in chapter three under section "1.3. Northport soil characterization"

In Northport, Cumberland County, Nova Scotia, the surrounding agricultural land consists of watersheds with marshes that drain into the Northumberland Strait, Nova Scotia. This hydrological landscape allows for farm chemicals (including pesticides) to wash directly into the nearby lobster fishery when there are heavy rain events. A similar issue was addressed by the Federal Government's Great Lakes Program during the 1980's. This work will focus on the interaction between a known pesticide used in Nova Scotia, Atrazine, with a soil sample from Northport, Nova Scotia, which was collected from the edge of a marsh that drains into the Northumberland Strait.

1.1.3 Theory

1.1.3.1 Interactions between Pesticides and Agricultural Soil

Currently, research involving soil has been based on equilibrium methods; however, these methods do not consider chemical reactions in soil that occur over an extended period of time.[9] Kinetics methods study chemical reactions between pesticides and soils over a certain length of time. The time-dependent actions between pesticides and soil can include desorption, sorption, and intraparticle diffusion. Sorption kinetics is one of the main approaches used to determine the persistence and transport of pesticide in subsurface soil environment. However, this procedure is complex and mostly unpredictable.[10]

The sorption mechanism of an analyte species onto a soil is either described using an equilibrium or kinetic approach. The equilibrium approach suggests that the analyte concentration remains constant over time after a while and that analyte sorption has stopped whereas the kinetic approach (or dynamic approach) suggests that the analyte concentration is never constant and that sorption/desorption is continuously taking place over time. The

sorption process for equilibrium and kinetic involves the same kind of sorption sites for both but each with a different chemical retention/sorption time. First, there is a labile sorption site on the soil surface and, second, a kinetic approach that describes a molecule moving from the surface to the centre of a particle. This dynamic model describes the behaviour of pesticide adsorption-desorption on the surface of the soil, and focuses on a second order reaction kinetic method.[11]

To simulate sorption kinetics, various models have been developed, such as one-box model, two-box model, and diffusion model.[8,12] Several kinetics models have been used to describe the kinetics of chemical reaction on natural materials, such as zero-order, first-order, second-order, fractional-order, Elovich, power function, and parabolic diffusion models.[13] However, some of these kinetic models are approximations due to the limited time range used in these kinetic studies.[13] Moreover, they might not be applicable models to describe reactions in a heterogeneous system, such as soils and soil components. This study focused in the last type, i.e., sorption kinetics of analytes in a heterogeneous system. This work endeavours to gain a better understanding of the pesticide molecule atrazine when it moves from the land surface to the middle of the agricultural soil (Northport soil) particle which defined an intraparticle diffusion theory. When there are a variety of particle sizes and multiple retention sites, chemical kinetics and transport phenomena take place at the same time, and usually a fast reaction is followed by a slower reaction.[13] Many kinetic studies on organic chemical sorption/desorption with soil have shown that sorption/desorption is observed as a rapid reversible phase followed by slower phase, non-reversible phase which is called the intraparticle diffusion.[14] Figure 1.1.2 shows two types of sorption processes, the sorbed type (blue square), and the intraparticle type (green

triangle).[11] One can see that the sorbed and intraparticle sorption processes are evolving in opposite direction.

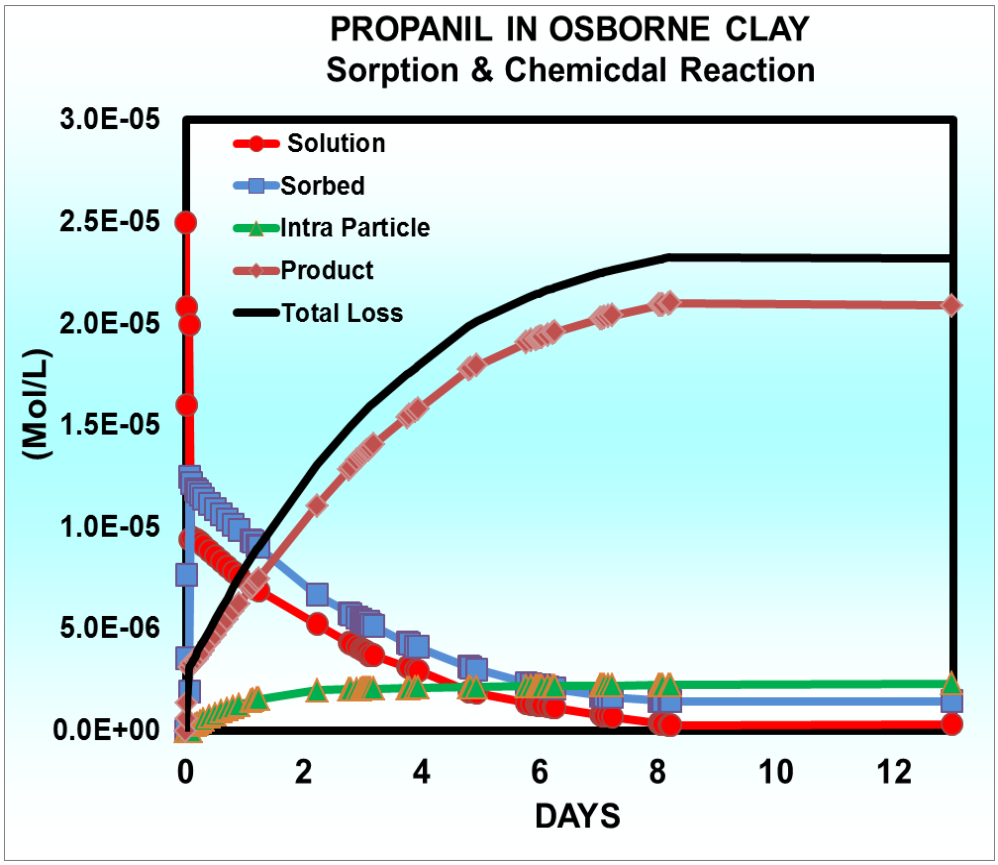

Figure 1.1.2 Kinetics curves of Model #5. Standard deviation: solution, labile sorbed, chemical reaction, and intraparticle diffusion. (Reprinted from reference 11 with permission)

Atrazine uptake is observed to have a fast labile surface sorption followed by slower intraparticle diffusion.[15] In the equilibrium condition, the sorption of chemical on a solid from a water solution could be as a result of a reversible reaction for sorption-desorption, which reaches an extreme equilibrium situation between the concentration of the chemical

in two phases.[13] But in soils, labile sorption from solution onto the solids is not usually attained in equilibrium processes. In extreme cases the sorption might go to completion.

1.1.3.2 Dynamic Behavior between Agricultural Pesticides in Soil

Many studies report the dynamic behaviour of pesticides in soils.[16,17,18] For example, Figure 1.1.2 shows that the sorption, desorption, and chemical reaction in the interaction propanil in Osborne clay sample are dynamic.[9]

1.1.4 Conventional Chemical Kinetics

Chemical kinetics depends on a chemical stoichiometry calculation based on empty and filled sorption sites as products and reactants mol/g. The distribution coefficient, K_D, which implies equilibrium, was usually used to explain the sorption-desorption process. The assumption behind this is the equilibrium condition of the two processes. However, some researchers have shown this is not true for environmental samples due to its dynamic and non-specific nature, since the agricultural soil nature is defined as a mixture.[16] The K_D is incorrect for at least three reasons. Equilibrium usually is not attained (or attainable); K_D does not account for all of the reactants and products, and does not account for chemical stoichiometry.

There are two different experimental conditions to consider: first, the labile sorption capacity of the soil, Θ_C (W/V), is larger than the analyte solution concentration; and the

second condition, which is the opposite of the first, i.e. that Θ_C is less than the analyte solution concentration. This information could be useful to determine if the analyte sorption onto the soil is controlled by a pseudo first order sorption kinetics.

Gamble and co-workers presented the opportunity for the application of conventional chemical kinetics to the ultimate examples of different sorption substrates, natural soils by using numbers of empty and filled sorption sites.[11] According to Gamble *et.al.*[9], weighted averages are the experimental rate coefficients for the mixtures of sites. These authors further showed that rate coefficients are decreasing functions of the reaction time.[9,19] Moreover, Gamble mentioned that, in the past, the numbers of mol/g of sorption sites were unknown.[11] The rate coefficient is time dependent and decreases over time.[16,20] Figure 1.1.3 and Figure 1.1.4 show that the rate coefficient is decreasing as a function of time.[11]

The sorption of an organic chemical onto the surfaces of an immersed soil is known to be directed by second-order kinetics.[20] By using conventional chemical kinetics based on stoichiometry, quantitative predictions have been proven to work for pesticide sorption in soil slurries.[21] The reaction mechanism is explained with conventional chemical kinetics by using the experimental values of the numbers of empty and filled sorption spots as reactants and products.[11]

1.1.4.1 Sorption Sites Stoichiometry

The chemical stoichiometry calculations based on empty and filled sorption sites as products and reactants mol/g is the basis of the chemical kinetics. The labile sorption stoichiometry for herbicide on immersed soils had been determined successfully for some soils and herbicides.[22,23,24] Quantitative predictions have been established for pesticide

sorption in soil slurries by using the conventional chemical kinetics based on stoichiometry.[9]

(A)

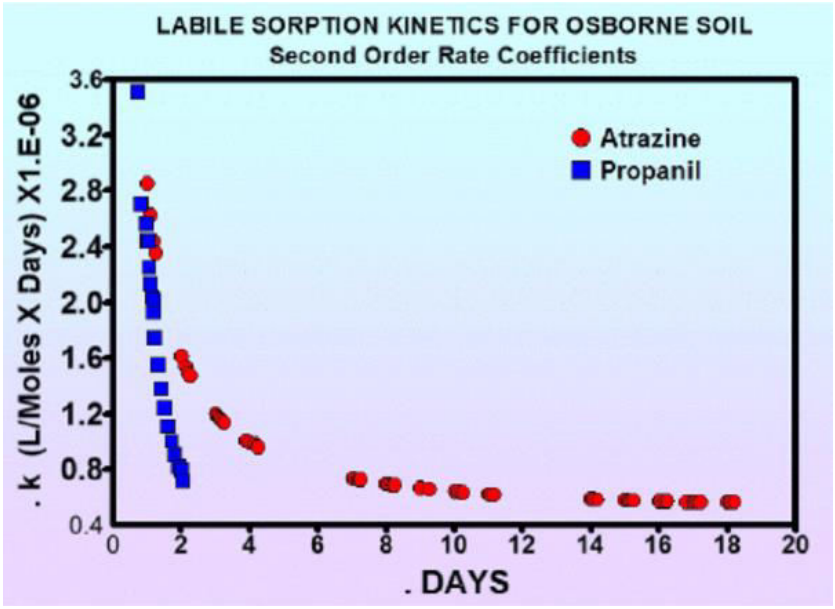

Figure 1.1.3 (A) Second order kinetic rate coefficients from spreadsheet calculations with experimental data. (Reprinted from reference 11 with permission)

(B)

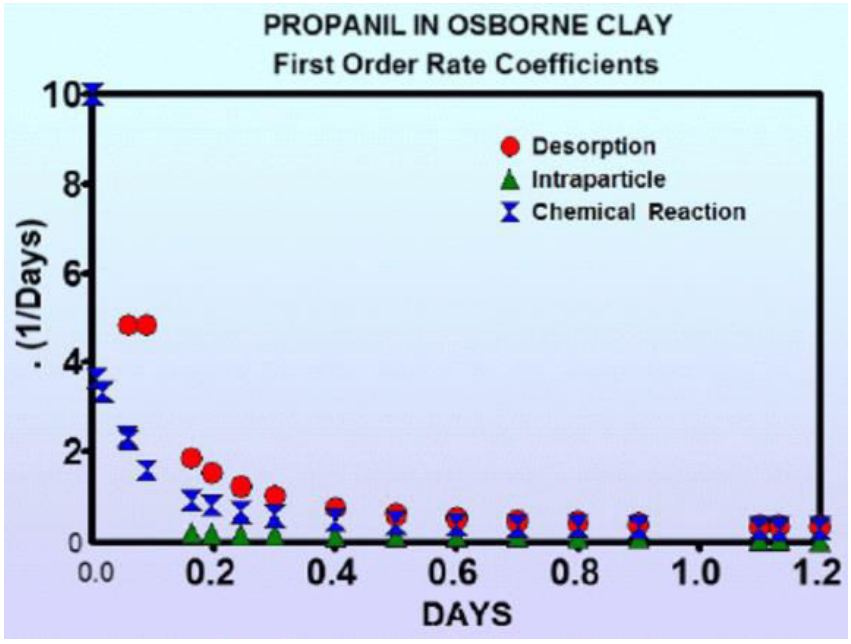

Figure 1.1.4 (B) First order kinetic rate coefficients from spreadsheet calculations with experimental data. (Reprinted from reference 11 with permission)

1.1.4.1.1 Labile Sorption Capacity Θ_C (Filled and Empty Sites)

Any mixture of pesticide and soil will have different distribution of the absorbed pesticide among the soil components, known as labile sorption capacities.[9] It is affected by the presence of humic material, its molecular weight range and some of its ionized and unionized carboxyl group, and the number of phenolic OH group in the humic material.[9] The numbers of mol/g on each sorption site is generally unknown.[11] Determining the saturation sites of the total number of labile sorption sites, which are the labile sorption capacity, Θ_C (mol/g), becomes possible with HPLC technique.[11] The labile sorption capacity has been defined as a saturation limit, Θ_C[25]; it measures the number of labile sorption sites. The following equation (1.1) gives the material balance of the labile sorption capacity[26]:

$$\Theta_C = \Theta_0 + \Theta_1 \qquad (1.1)$$

Where

Θ_C labile surface sorption capacity (mol/g)

Θ_0 unoccupied active sorption sites of solid

Θ_1 occupied active sorption sites of solid

Some reports show the existence of labile sorption capacity, Θ_C that are not mentioned by others.[11] However, the labile sorption capacity is second-order kinetics.[11]

For instance, the total number of sorption sites from which propanil could be readily desorbed was measured by site saturation, which is the labile sorption capacity Θ_C.[11]

There is a possibility of using the numbers of empty and filled sorption sites as reactants and products for the use of conventional chemical kinetics calculations for cases of irregular sorption substrates and natural soils.[11,27] This research focused on the use the number of sorption sites as reactants and products in kinetics. Table 1.1.1 shows that in the sorption process, the empty sites and the dissolved chemical are reactants and the filled sites are products that follow the second order kinetic.[11] Labile sorption capacities (the number of sorption sites) are the first parameter used in this work's spreadsheet calculation model.

The general description of the sorption model is in equation 1.2 [9]

$$\Theta_{a0} + M_1 \Leftrightarrow \Theta_{a1} \rightarrow \Theta_{d1} \qquad (1.2)$$

Θ_{a0} = Empty sorption sites

M_1 = Solution-phase pesticide

Θ_{a1} = Filled sorption sites

Θ_{d1} = Amount diffused into particle interiors.

Table 1.1.1 Sorption and reaction kinetics for propanil in Osborne clay. (Reprinted from reference 11 with permission)

Process	Reactants	Products	Kinetic rate law
Sorption	Empty sites and dissolved propanil	Filled sites	Second order
Desorption	Filled sites	Empty sites	First order

Intraparticle diffusion	Filled sites	Empty sites and intraparticle propanil	First order
Chemical reaction	Propanil, dissolved+ sorbed	3,4-Dichloroanaline and propanoic acid	First order

1.1.4.1.2 Time-Dependent Rate Coefficients

Several studies report interaction between pesticide and soils changed over experimental time.[11,16] Experimental rate coefficients for the mixtures of sites are weighted averages. The rate coefficients are decreased function of reaction time.[11] If equilibria exist, the law of mass action calculations yields weighted average equilibrium functions.[11,28] When equilibrium does not exist due to the dynamic behaviour of the sorption process, kinetics calculations produce weighted average rate coefficients.[11,29] Figure 1.1.3 and figure 1.1.4 shows that the rate coefficient is variable, decreasing over time. The numerical weight for the weighted average rate coefficients is the reaction time.[18] For sorption to reach equilibrium, it could require a long time, possibly weeks to a few months.[11] The rate coefficient is the second parameter to use in the spreadsheet model.

1.1.4.2 Empirical Parameters

Simple distribution coefficients are not useful for the foundation of kinetics chemistry. In equilibrium condition, it is important to describe the kinetics between pesticide and soil only by some form of the law of mass action, which accounts for all

reactants and products. By this correct description, quantitative predictions can be expected to be realistic if equilibrium exists.

For pesticide sorption from solution inside immersed surfaces, the distribution coefficient, K_D, is not an applicable parameter for two reasons.[11] First, it accounts only for one side of the two reactants instead of both. K_D fails to describe a reactant of empty sorption sites. It does not recognize correctly the product that is the set of filled sorption sites. Unclear sorption data are used, lacking for the capability of describing the difference between labile sorption and total sorption.[11] Second, a distribution coefficient appears to be unable to describe the labile sorption sites when they have become saturated. The consequence of this is that sorption becomes unresponsive to this solution concentration, which makes it inapplicable for predicting the kinetic behaviour (i.e. how quick) and sorption capacity (how much) of soil sorption sites.[11]

Nevertheless, when the equilibrium condition is in the incorrect state, dynamic conditions are commonly used in this situation, and kinetics can only explain accurately these conditions and equilibrium usually does not exist, so that K_D is not relevant.[11] Many studies report the dynamic behaviour of pesticide in soils.[30,31] These studies confirm that using these parameters for kinetic behaviour determination is not appropriate due to the dynamic response and non-equilibrium condition of the soil.

Some studies describe the difficulty of using the empirical parameters (K_D, K_{OC}, and K_{OH}) for pesticide behaviour in the soil, since soil has a dynamic behaviour and does not have equilibrium condition.[17,18] For example, experimental curves for propanil in Osborne clay in Figure 1.1.2 shows that sorption, desorption, and chemical reaction were all powerfully dynamics.[11] Only kinetics explanation could be used for the experiment by

conventional stoichiometry.[16] Without equilibrium condition, kinetic calculations need to use weighted average rate coefficients.[9] Table 1.1.2 shows the common empirical parameters used for the pesticide in the soil.[32] For example, the number of sorption sites is important, not the surface areas because of the difficulty of measuring the surface soil area when cracks and holes appear on the surface.

1.1.5 Second Order Sorption Kinetics

Second order kinetics was defined mathematically as the speed of the reaction between two reactants. Nevertheless, for pesticides and immersed fields, the second-order reactant is the number of unpopulated labile sorption sites.[11]

Table 1.1.2 The common empirical parameters used for pesticide in soil. (Reprinted from reference 32 with permission)

Distribution Coeffici	K_D	(L mg^{-1})
Distribution Coeffici	K_{OC}	(L mg^{-1})
Octanol-Water Coeff	K_{OH}	Dimensionless
Total Loss Half Life	$t_{1/2}$	Days
Surface Area	BET	m^2

In some studies, a second-order kinetics process appears in pesticide sorption from solution onto immersed soils.[11]

Assuming that the sorption reaction proceeds as follows:

$$A + B \rightarrow P \qquad (1.3)$$

In the sorption case:

A = the molecules in solution.

B = the sorption sites in surface which is also the empty sites.

P = the products which is also the filled sites.

The rate law for the second order differential form is

$$\frac{d[A]}{dt} = -k\,[A]\,[B] \qquad (1.4)$$

where k is the rate constant.[33]

The second-order kinetic theory for the sorption process has been recently established in the laboratory.[27] Many studies show that the presence of intraparticle diffusion proceeds from surface sites into particle interiors.[34] The sorption of the organic chemical onto the surfaces of an immersed soil is recognized experimentally to be directed by second-order kinetics.[11] Table 1.1.1 shows the reactants for the sorption are the empty sites and the dissolved chemical (Propanil).[11] The products are the filled sites which both follow the second order kinetics.

If the labile sorption capacity exists for hydrophobic molecules at solution-solid interfaces, this theory will be useful for labile sorption.[32] Furthermore, based on the stoichiometry of labile sorption, it is better to use the second-order kinetics instead of pseudo-first-order kinetics.[32] All literature mentioned above confirmed that the second-order kinetics theory is useful for pesticide sorption kinetics. In addition, above mentioned

studies required measuring the concentrations of the reactants and the numbers of sorption sites.

The sorption-desorption of organic material with soil is characterized generally by fast, reversible phase sorption, followed by a slower sorption phase.[35] The rapid stage describes the organic chemical in a labile form, which can be easily desorb; the slower step describes the chemical in a nonlabile form, which is difficult to desorb when diffused into the organic material and inorganic soil components.[36] Figure 1.1.2 shows the reactants and the products, and the kinetics law for sorption, desorption, intraparticle diffusion, and chemical reaction.

1.1.6 Desorption Kinetics

Table 1.1.1 presents an adsorption process when the reactants are the filled sites and the products are the empty sites, which follows first order kinetics.[11] In the adsorption process, a chemical molecule moves from the sorption sites since the chemical reaction is moving the molecule from solution and sorption sites. In nature, adsorption was determined to be kinetic.[11] Atrazine adsorption was proven by using a batch equilibration technique.[11]

1.1.7 Intraparticle Diffusion

Intraparticle diffusion describes diffusion of a molecule from the surface area to the middle of particle which makes the bound residue. The bound residue is that which could be physically trapped within the solid particles by intraparticle diffusion.[37,38] Figure 1.1.2

shows intraparticle diffusion (green triangle). It the first few days when a reaction is fast, the intraparticle diffusion increases. In this case, the filled sites are present as reactants, and empty sites and intraparticle of the chemical are present as the products, which follow the first order kinetics (see Table 1.1.1). Many studies have confirmed the existence of intraparticle diffusion goes from surface sites into particle interiors.[11]

1.1.8 Bound Residue Formation

Soil-bound pesticide residue has been defined as unextractable and caused by intraparticle diffusion. The bound residue was defined as a part of an organic chemical that cannot be recuperated by the online HPLC microextraction technique.[39,40] Some studies report examples of pesticide-bound residues in plants and foods.[41,42,43,44] Several studies have defined bound residue formation by intraparticle diffusion with first-order kinetics.[11] In the general reaction, the bound residue formation uses the experimental values of labile sorption, Θ_{a1} (W/V)

$$aA + bB + \ldots \rightarrow yY + zZ + \ldots \quad (1.5)$$

The rate law is

$$-\frac{1}{a}\frac{d[A]}{dt} = k\,[A] \quad (1.6)$$

where k is a positive number that does not depend on any concentrations, but depends (usually strongly) on temperature.[45]

Also, the rate expression for a first-order reaction is

$$\frac{dX}{dt} = -kX \qquad (1.7)$$

where X is a concentration.[13] In the reactant, the concentration decreases over time, t, which is dependent on the rate constant, *k*. The rate law is a differential equation that describes the rate of change on a reactant (or product) concentration over time. By integrating the rate law, an expression for the concentration as a function of time could be obtained, which is the experimental data.[45] But, experimentally, in the case of whole soil or some components of soil, which is a complicated system, *k*, it is not constant with decreasing function over time, as showed in Figure 1.1.3 and figure 1.1.4.

1.1.9 Chemical Reaction

Table 1.1.1 shows sorption and the chemical reaction for propanil in Osborne clay. In this case of chemical reaction, the reactants are the dissolved and sorbed chemical (Propanil). The products are 3, 4- Dichloroanaline and propanoic acid. Figure 1.1.2 shows the sorption chemical reaction of propanil with Osborne clay. Figure 1.1.2 shows the chemical reaction as product (dark red diamond), increasing over time. Figure 1.1.5 presents an example of humic acid structure which has many carboxyl groups.

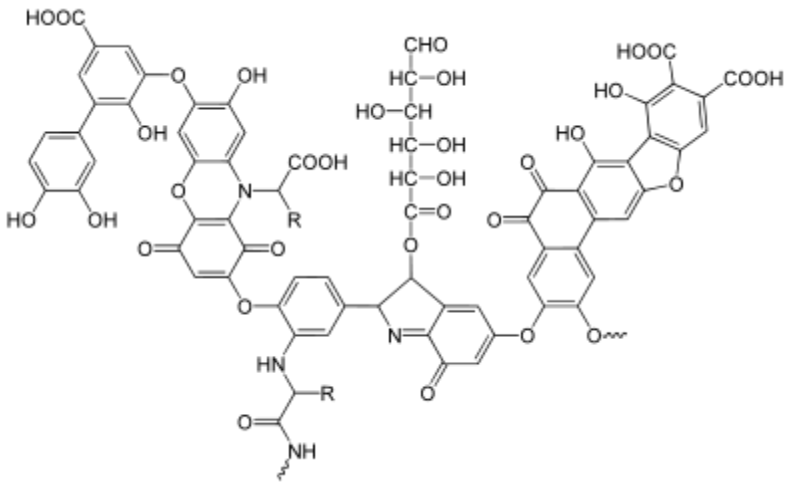

Figure 1.1.5 An humic acid structure.[46]

1.1.10 Spreadsheet Models

Through the use of environmental models, it is now possible to predict the transport, distribution, accumulation, and fate of the chemical. The aim of any chemical model is to offer a correct mechanistic image, at the molecular level, and to be able to predict events built on the known properties of the sorbent.[16] Models are established for diverse purposes and created in many ways and use different kinds of data.[11] For example, models for screening biosolides for hydrophobic organic chemicals are used for replacing the monitoring of the solids and for agricultural pesticides, such as PRZM and PEARL. [11,13]

Pesticide field trials are more expensive and require more work time than laboratory tests. By using predictive models, some costs are minimized.[11] Instead of empirical parameters that have nothing to do with mechanisms, there is a need for the introduction of models for molecular level mechanisms.[32] This agrees with Sparks' statement about the need of chemical kinetics in soil process models.[8] An interactive spreadsheet model was

created for quantitative predictions of the time-dependent physical states and chemical reaction for herbicide (Propanil) in a slurried, Manitoba clay soil.[11] A computer-based interactive spreadsheet model revealed curves according to the amount of chemicals used in order to kill only weeds, as well as overkill. Such models can be predictive using some control.

For quantitative predictions, model mechanisms are needed. A spreadsheet has been used and adapted from Gamble *et.al.*[9,11] which calculates the various outputs such as labile sorption types and atrazine sorption rate coefficients which are needed for the development of the kinetic sorption model. The spreadsheet used in this work has mathematical functions and graphics already encoded and therefore expensive software development is not required.[16] For example, the herbicide propanil in a slurried clay soil has been used to create an interactive spreadsheet model for the quantitative prediction of the time-dependent physical conditions and chemical response.[16] The interactive spreadsheet model has a graphical user sheet with a block of input cells shown in Figure 1.1.6. In the model, there are two categories of parameters, labile sorption types, Θ_C, and the kinetic rate coefficients.[11] By changing the original experimental values, predictions are made. The number of the yellow cells represents the design of the experiment.[9] By entering any changes into the yellow cells, it will produce predictions that are instantly seen in a set of graphs.[11]

The model can rapidly present predictions for variations in soil loading that might happen during pesticide mobilization by surface runoff.[9] These spreadsheet models are helpful in predicting a better amount of pesticide to be used on agricultural crops to be safe as possible. In this project, possibility of pesticides behaviours were studied such as if it would only kill the pests or stay for a long time and cause other problems or go to another place and case a problem there.

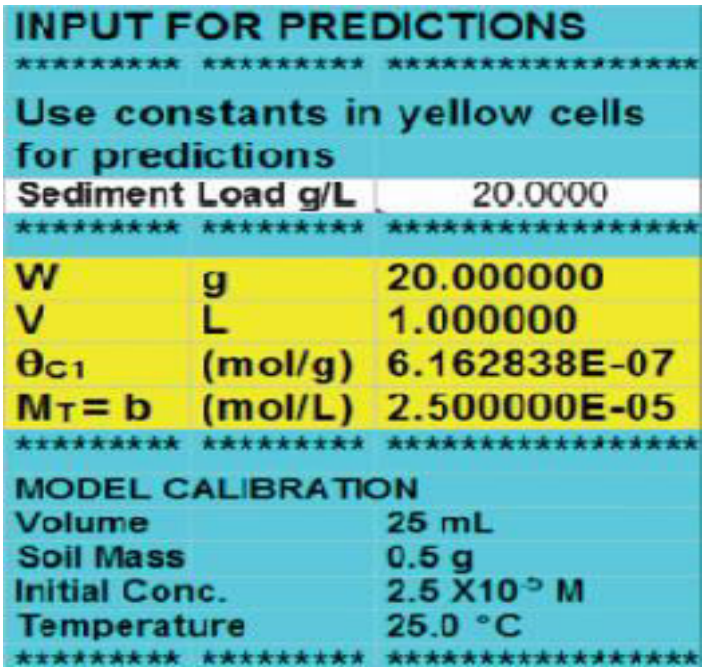

Figure 1.1.6 The user interface columns in Model#5. The graphs respond with predictions, to changes of input data for the yellow cells. W, g of slurried soil. V, L of solution. $\Theta_{C1,}$ (mol/g) of labile sorption capacity, M_T, (mol/L), initial concentration of pesticide. (Reprinted from reference 11 with permission)

1.1.11 Model #5

The kinetics model #5 is a mathematical description of the sorption-reaction mechanism. This model will be used to investigate the sorption reaction mechanism and kinetics of atrazine with a soil from Northport. Using the Model #5 spreadsheet, predictions over time of the sorption behaviour of atrazine in contact with Northport soil will be possible.

CHAPTER TWO

2.1 Research Objectives

The goal of this study is to apply physical chemistry to soil contamination problems. Table 1.1.2 presents some of the typical empirical parameters used to describe the kinetics between pesticides and soil. The safe and efficient use of agricultural pesticides requires that their reaction mechanisms in soil be quantitatively predicted.

The problem being investigated is the reaction kinetics and mechanisms of a hydrophobic organic chemical in a physically and chemically irregular mixture. The chemical is an herbicide (atrazine), and the irregular mixture is an agricultural soil (Northport soil). Prediction of leaching and persistence of pesticides and other hydrophobic organic molecules in the soil is an environmental problem.

In this project, kinetic experiments for pesticides in soils were studied for two reasons. First reason is to determine the number of sorption sites (mol/g in soil) via HPLC microextraction method, which are the labile sorption capacity, Θ_C, and the kinetic rate coefficients. These kinetic parameters are used for quantitative model predictions. Second reason is to develop a method of using online and offline HPLC microextraction to determine the time-dependent concentration kinetics of atrazine in the dissolved, labile-sorbed, and bound residue fractions. Kinetic curves will be developed for sorption, desorption, chemical reaction and inter-particle diffusion of atrazine in aqueous soil suspensions followed by the time-dependent kinetic rate coefficients determination.

In this thesis, it is intended to relate labile sorption capacities and kinetic rate coefficients to types of materials in the soil. The research project investigated the kinetics

and mechanisms of atrazine with Northport soil components. The first task was to collect information about the interactions of pesticides or other hydrophobic organic molecules at the solution-solid interface.

A physically and chemically analysed soil was used. This is significant because the kinetic parameters, which are the number of sorption sites, that is, the labile sorption capacity, Θ_C, and the kinetic rate coefficients, need to be related to the types, amounts, and properties of the soil components. The specific information required is the effect of types of solids and molecular structures on labile sorption capacities, Θ_C, and kinetic rate coefficients to make the predictions more general. These kinetic parameters are used for quantitative model predictions. The experimental procedure will be a sorption and reaction kinetic experiment of the herbicide atrazine in the Northport soil.

Moreover, conventional chemical kinetics was used for the predictions of pesticides and soils. The primary objective was to use the collected information to generalize the types of the interactive spreadsheet models. They were created for the quantitative prediction of the time-dependent physical states and chemical reaction of the pesticide, atrazine, in a slurried Northport soil. The determination of the pesticide's kinetic behaviour and mechanism is essential for understanding and predicting persistence and risks.

Chapter Three presents the HPLC methodology to analyze and study atrazine in Northport soil. In *Chapter Four,* the results for the application of the online HPLC microextraction and the offline separation for investigating the kinetics and mechanism of atrazine in contact with an aqueous slurry of Northport soil.

CHAPTER THREE

3.1 Analytical Methods

3.1.1 Northport Soil Characterization

Northport soil is found on the shore of the Northumberland Strait, Nova Scotia, Canada. Appendix 3.1 provides information about the sampling location of the Northport soil and time of collection. Chemical and physical characterizations used elemental analyzer and x-ray fluorescence which was done by Dr. Donald Gamble. Further chemical and physical characterizations were performed to complement information presented in Appendix 3.1 and Appendix 3.2.

3.1.1.1 Scanning Electron Microscopy (SEM)

The surface chemical composition of the Northport soil was analyzed in-house using an X-ray Fluorescence Spectrometer [Philips, PW2400]. A Scanning Electron Microscope (LEO-1450VP) was used to collect electron micrograph of the soil, and an X-Ray Energy Dispersive Spectrometer (INCA 250 EDS) was used to obtain a semi-quantitative analysis of the chemical composition of the soil. The work was done at The Electron Microscopy Centre at Saint Mary's University.

3.1.1.2 X-Ray Diffraction (XRD)

To identify crystalline compounds inside soil particles, an x-ray powder diffraction diffractometer [SIEMENS, D500] was used to collect the x-ray diffraction lines of the Northport soil. The x-ray diffractometer is located and operated by Dalhousie University.

3.1.1.3 Soil pH

Soils are affected by acidity, which usually comes from acid rain.[47] Measuring soil pH is an essential part in this research to identify the Northport soil kinetics behaviour. All pH measurements were done using a pH meter [CORNING, pH meter 320]. The pH meter was calibrated using pH 4 and 7 buffer solutions.

3.1.1.4 CHN Analyzer for the Northport Soil

The Perkin Elmer 2400 Series II CHN Elemental Analyzer can be used for a rapid determination of the carbon, hydrogen, and nitrogen in organic compounds. The CHN model is focused on the classical Pregl-Dumas technique where samples are combusted in a pure oxygen environment with the following combustion gases measured in an automated mode. The 2400 Series II system is comprised of four major zones: combustion, gas control, a separation, and a detection zones.

The CHN analysis for the Northport soil sample was done at The Centre for Environmental Analysis and Remediation (CEAR) at Saint Mary's University.

3.1.1.5 Soil Fractions

Fifty milligrams of Northport soil was added to 20 mL of water. After one hour from shaking the bottle, separated layers appeared.

3.2 Sorption Experiment

3.2.1 Materials and Samples Preparation

Sorption-reaction experimental samples were done by preparing the atrazine stock solution to contain 1.00 x 10^{-4} mg Atrazine/L. This was done by dissolving 0.0215 g of atrazine in 500 mL water with stirring for two hours. Continual stirring was needed to ensure the representative sampling in both the online and offline samplings.[26] The atrazine standard solutions with ten different concentrations (1.00 x 10^{-6} M − 1.00 x 10^{-5}) were prepared by the dilution of the stock solution in water. Three slurry samples and three solution sample were prepared by adding 0.0500 g Northport soil to 1.00 x 10^{-6} M atrazine standard solution and kept in 30 mL amber glass vials capped with Mininert® syringe valves to avoid decomposition and evaporation during the kinetic sorption experiment. Three soil blanks samples were prepared also by adding 0.0500 g Northport soil to 20 mL of water. The pre-wetting for all the soil samples was done for 48 hours. It permits the soil to have all its natural physical and chemical features.[26] The vials were placed in 50 mL jacketed beakers at 20 °C, by using a water bath with constant stirring for four weeks.

Sampling was done each hour for the six samples, including 3 Northport soil blanks, to have it run in the HPLC instrument daily for four weeks. There are two HPLC systems, the online HPLC analyses and the offline HPLC analyses. Table 3.2.1 shows a timetable for sampling the solutions. Table 3.2.2 shows a timetable for sampling the slurries. This procedure was done for all the nine samples.

Table 3.2.1 The solutions sampling timetable.

weeks	Day1	Day2	Day3	Day4	Day5
First week	5 min, 1h,2h,4h,8h,	24h,32h	48h,56h	72h,80h	96h,104h
Second week	1w	1w+24h, 1w+32h	1w+48h, 1w+56h	1w+72h, 1w+80h,	---------
Third week	----------	----------	3w	----------	----------
Fourth week	----------	----------	4w	----------	----------

Table 3.2.2 The slurries sampling timetable.

Weeks	Day 1	Day2	Day3	Day4	Day5
First week	Uptake1	Uptake2	Uptake3	Uptake4	Uptake5
Second week	Uptake6	----------	Uptake7	----------	Uptake8
Third week	----------	----------	Uptake9	----------	----------
Forth week	----------	----------	Uptake10	----------	----------

3.2.2 Temperature Control of Samples

To keep all the samples at the same temperature, a temperature controlled reaction vessel was used. It contains a water bath connected to 50 mL jacketed beakers by tubing. The samples maintained in 30 mL amber glass vials capped with Mininert® syringe valves to avoid decomposition and evaporation during the kinetic sorption experiment. The vials were set in the 50 mL jacketed beakers at 20 °C, by using a water bath with constant stirring. All the 50 mL jacketed beakers were covered with Styrofoam to maintain the temperature of the reaction vessel at a constant value. The inside of 50 mL jacketed beakers was also filled with water so that no gaps existed between the jacketed beakers and the amber glass vials to maintain the temperature constant. Finally, the temperature was measured by a temperature probe connected to a laptop which allowed temperature of the jacketed beakers to be continuously monitored. Figure 3.2.1 shows the temperature controlled reaction vessel for this experiment. Figure 3.2.2 shows the schematic representation of mixing vessel.

Figure 3.2.1 The temperature controlled reaction vessel for this experiment.

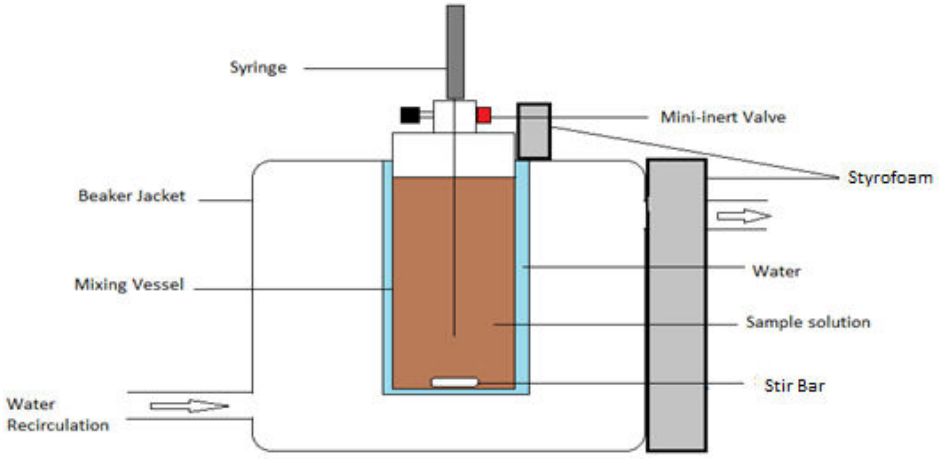

Figure 3.2.2 Schematic representation of mixing vessel.

3.2.3 High Performance Liquid Chromatography (HPLC) Microextraction for the Analysis of Soil Sample and Atrazine

High Performance Liquid Chromatography (HPLC) is an analytical technique that can used to measure the distribution of pesticide between a solution and suspended soil phase.[3] The online HPLC μ-extraction method for sorption-reaction kinetics in soil slurries has been previously described.[48,49,50,51,52,53,54,55] Figure 3.2.3 is a diagram of the online-HPLC instrument. HPLC and microscopy techniques were used together for sorption mechanisms in both environmental and pure crystal systems.[22] HPLC, which can resolve the total sorption into recoverable and unrecoverable fractions of pesticides in soils, revealed as labile sorption capacities.[16] Figure 3.2.4 shows the actual online HPLC instrument. In other words, HPLC can only resolve the total extractable chemical into dissolved, labile sorbed and bound residue fractions.[16,19]

An online HPLC microextraction technique has not been used to study whole natural soils.[1] Two sets of measurements were done by HPLC, the offline for the solutions, and the online for the whole aqueous slurry. Table 3.2.3 shows HPLC conditions in the experiment.

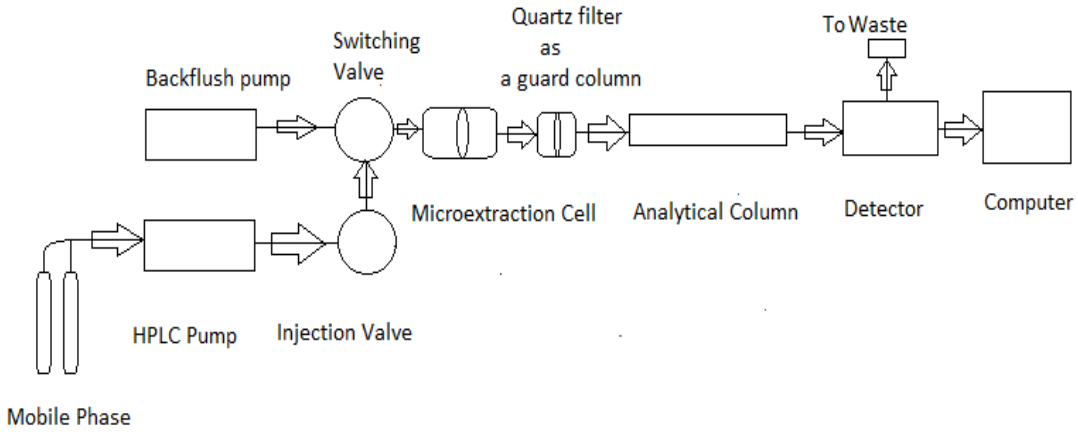

Figure 3.2.3 Diagram of the online-HPLC instrument.

Figure 3.2.4 Online HPLC instrument.

Table 3.2.3 HPLC conditions in the experiment.

Conditions	**Value**
Mobile phase	50% Acetonitrile - 50%Water
Flow rate	1.0 (mL/min)
Sample loop volume	20 µL
Display wavelength	230 nm
Backflush flow rate	10 mL/min
Sample Temperature	20°C
column	Kinetex , 2.6µm C_{18} 100A, 50 x 4.6 mm Id

3.2.3.1 Offline Solution Analyses

The HPLC system consisted of the following components placed in series: HP G1313Aautosampler; an HP G1312A binary pump; an HP G1316A column thermostat set at 25°C; an HP G1322A degasser unit; and an HP G1315A diode array UV-Vis detector.[26] Reversed-phase analytical column [Kinetex, 2.6u C_{18} 100A] of 50 x 4.6 mm internal diameter was used for the chromatographic determinations. In the HPLC setting, a second microextraction cell was added for this experiment instead of the guard column connected to the central column. The manual injection valve was also used instead the autosampler due to the time dependence of the experiment. The offline HPLC was used to measure the dissolved atrazine in water. The solutions measurements were done as a function of time. Slurry aliquots were collected in disposable syringes and by 0.45 μm filters; the solution concentrations were measured by injecting the solutions into the HPLC instrument.[11,16,52]

3.2.3.2 Online Microextraction Analyses

The online HPLC was used to measure both the dissolved atrazine in water and the total atrazine sorbed into the soil. The instrumental assembly consisted of a ProStar 230 solvent delivery system, a ProStar 330 photo-diode array detector (PDA) and an injection system. The injection system was modified to carry out the microextraction of the sorbate online and to carry out the subsequent removal of the sorbent particles by forcing a solvent to flow by an HPLC ternary pump [Varian 9012] to do a backflush through the extraction cell.[26]

This injection system is comprised of two valves. The first is a two-position six port injection valve [Rheodyne 7125, Alltech] equipped with a 20 µL sample loop and a column inlet microfilter (i.e., the extraction cell) that contains a 0.5 µm stainless steel frit of 3 mm length [Rheodyne 7335, Alltech]. The second is a two-position, six-port switching valve [Rheodyne 7000, Alltech]. The HPLC ternary pump [Varian 9012] connected to one of the ports of the injection valve was used to backflush for the microextraction cell. A reversed-phase analytical column, 2.6µm C_{18} 100°A of 50 x 4.6 mm Id [Kinetex] was used.[26]

The total atrazine that was recoverable from the solution and from the soil was measured as a function of time. Hydrophobic organic chemicals sorbed by soils are often only partly recoverable. Aliquots of unfiltered slurries were directly filled into the HPLC 20 µL loop by 250µL glass syringe (Hamilton 725 RN, 250µL).[11] Both offline and online HPLC analysis instructions for injecting sample solutions and slurries are describe in Table 3.2.4

The following experimental settings were used to prevent high pressure in the online HPLC instrument due to a blockage by fine soil particles to the microfilter and sample loop.

First, a microfiber quartz filter (Whatman) was added to the microextraction cell with an existing screen filter. The microfiber quartz filter did not dissolve in the mobile phase, which was (50% acetonitrile - 50% water) but it did not catch fine soil particles. There was also a leaking of the mobile phase in the microextraction cell because the quartz filter was not properly fitted. This setting did not work well.

Second, a disposable guard column with a union was placed immediately after the microextraction cell was inserted. The backflush did not clean the disposable guard

column successfully, since the guard column is designed to work with the mobile phase flow in one direction only, in contrast to the microextraction cell that works with two-way mobile phase flow. As a result, the pressure increased, and the setting failed to work.

Table 3.2.4 Injection instructions for solutions (the offline) and slurries (the online) to HPLC instrument.

Action	The injection valve	The switching valve	The mobile phase pathway
Offline			
1- Load sample solution after filtration by the filter unit 0.45µm	load position	Position B	The mobile phase flows from HPLC pump to column (Configuration#1)
2-Inject the sample solution	Inject position	Position B	The mobile phase together with the sample solution flows from HPLC pump to sample loop, to the microextraction cell, and to the column. (Configuration#2)
Online			
1 - Open the connecting union. 2- Load slurry	load position	Position B	The mobile phase flows through HPLC pump to the microextraction cell and the column. (Configuration#1)
3-Inject slurry	Inject position	Position B	The mobile phase together with the sample solution will go through HPLC pump, to sample loop, to the microextraction cell and the column. (Configuration#2)
4-After 20 s of injection of the slurry	load position	Position A	The mobile phase flows from HPLC pump to column.

			(Configuration#3)
5-Close the connecting union 6- Backflush	load position	Position A	The solvent from the extra pump flows to the microextraction cell to the sample loop and then coming out from the injection port. (Configuration#3)

Third, a second microextraction cell containing the microfiber quartz filter (Whatman) was added to catch fine soil particles, which can easily pass through the first microextraction cell and cause an increase in pressure. The microfiber quartz filter was easily changed because the mobile phase flows from the HPLC pump directly to the column when a switching valve was in position (A) without passing the microextraction cell. Figure 3.2.5 shows a schematic description of the injection system for online microfiltration analysis. This was not useful due to a hole present in the microfiber quartz filter. Also, the screen filter in the first microextraction cell after the backflush was not cleaned either, due to the existing of the second microextraction cell with the quartz filter, and the pressure increased.

On the other hand, other filters, such as Fluoropore PHLP, (0.45 um, 37 mm), Cellulose nitrate membrane filter, and White GSWP (0.22um, 25mm), were used. The three filters were dissolved in the mobile phase (50% acetonitrile - 50%water) because they were made of cellulose; as a result, these were not used.

Finally, adding the second microextraction cell before the main column with the microfiber quartz filter, as a cheaper disposable guard column, was the first successful setting for this experiment, shown in Figure 3.2.5

Another appropriate setting for this research was connecting the waste port from the switching valve (port# 6) with the injection valve (port# 6) by a union to allow the solvents from the backflush pump to go through the microextraction cell and the sample loop to cleaning both of fine soil particles that could block the pathway and increase pressure on the system. Waste came through the injection port and was collected in a beaker.

In the injection position, the union was opened, and the previous sample was collected in a beaker. After 30-seconds of injection sample, by switching the injection valve to load position and switching valve to position (A) and by pumping the backflush pump, the solvents (acetonitrile 50% - water 50%) went through the microextraction cell to the sample loop, and came out of the injection port to a beaker. The screen filter and the quartz filter were changed daily. (See Table 3.2.4 and Figure 3.4.5)

3.2.3.2.1 The Back Flushing Efficiency of the Online Microextraction Cell

To obtain a correct amount of solvent to flow by backflush solvent (acetonitrile 50% - water 50%) through the microextraction cell, the experiment was performed by injecting the slurries through four filters. The first filter was a new filter without injections and was used as control (blank). This was used to compare to other filters. The second filter was used for ten injections of slurries without backflush (0 mL/min). The third filter was used for ten injections of slurries with a backflush of 5 mL/min. The fourth filter was used for ten injections of slurries with a backflush of 10 mL/min. The four screen filters were then analyzed by SEM.

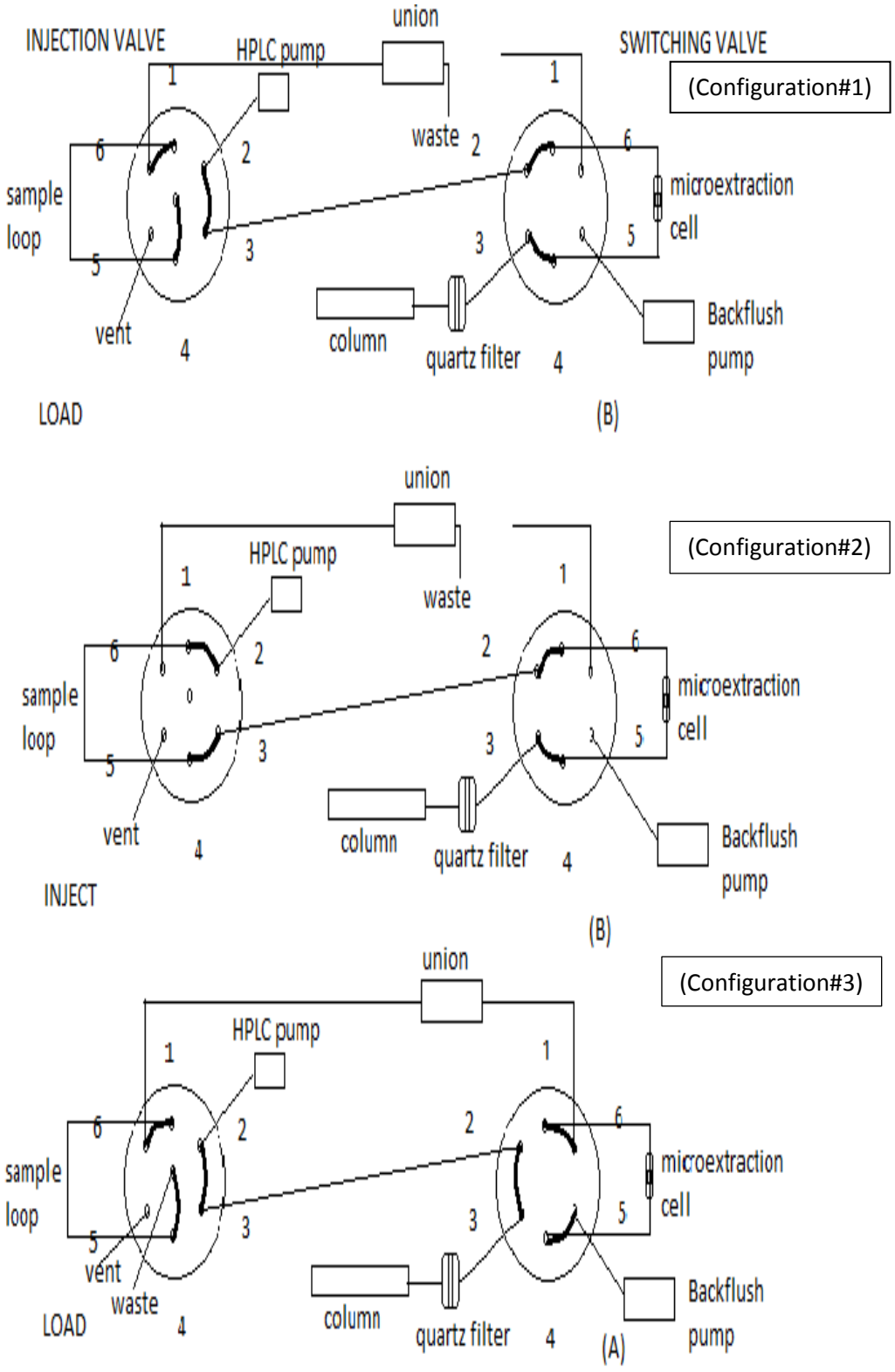

Figure 3.2.5 Schematic description of the injection system for online microfiltration analysis.

CHAPTER FOUR

4.1 Data, Results and Discussion

4.1.1 Northport Soil Characterization

There are two reasons for choosing or using the Northport soil. First, the exact date and location of the collected Northport soil sample have been recorded and reported in Appendix 3.1. Additionally, the location where the Northport samples were obtained is geographically nearby, so further samples could be easily obtained from the same location. Additionally, the Northport soil can be related to the climate, geology, and agricultural history of that area. Second, one could attempt to obtain the physical and chemical analyses data for the Northport soil that might be related to the labile sorption capacities and the kinetic rate coefficients, which are essential parameters for this study.

4.1.1.1 Scanning Electron Microscopy Method for the Northport Soil Sample

By the SEM method, the Northport soil surface was found to have some minerals, such as quartz, orthoclase, albite, illite, and hercynite. Also, the following elements were found: (Si, 30.61%), (O, 47.94%),which are the highest percentages of the Northport soil sample, (Ti, 1.21%), (Al, 9.80%), (Fe, 5.68%), (Mg, 2.06%), (Mn, 0.51%), (Ca, 0.33%), (Na, 1.80%), (P, 0.41%), (S, 0.24%), and (K, 1.68%). Further, the following oxides were found: (SiO_2, 65.48%), (Al_2O_3, 18.51%), which are the highest percentages, (TiO_2, 2.01%), (FeO, 7.31%), (MnO, 0.65%), (MgO, 3.421%), (CaO, 0.46%), (Na_2O, 2.43%), (K_2O, 2.0%),

($P_2\ O_5$, 0.94%), and (SO_3 0.60%). Table 4.1.1 shows the SEM results for the Northport soil sample. (For more Northport soil SEM results see Appendix 4.1 to Appendix 4.5)

Table 4.1.1 Scanning Electron Microscopy results for the Northport soil.

content		%
Minerals	Quartz, Orthoclase, Albite, Illite, Hercynite	
Elements		
	Si	30.61
	O	47.94
	Ti	1.21
	Al	9.80
	Fe	5.68
	Mg	2.06
	Mn	0.51
	Ca	0.33
	Na	1.80
	P	0.41
	S	0.24
	K	1.68
Oxides		
	SiO_2	65.48
	TiO_2	2.01
	Al_2O_3	18.51
	FeO	7.31
	MnO	0.65
	MgO	3.421
	CaO	0.46
	Na2O	2.43
	K_2O	2.0
	P_2O_5	0.94

	SO_3	0.60

4.1.1.2 X-Ray Diffraction Method for the Northport Soil Sample

X-ray diffraction results showed that the Northport soil consists of some minerals such as Silica (SiO_2, 67%), the most abundant, Anorthite ($CaAl_2Si_2O_8$, 19%), and albite ($NaAlSi_3O_8$, 14%). The Silicate containing minerals, together with carboxylic groups containing humic acid (see Figure 1.1.5), may help to understand the effects of soil components on pesticide reaction kinetics and mechanisms as in section 3.1.1.3 Soil pH. Table 4.1.2 shows the results for the Northport soil X-Ray Diffraction.

From the SEM, XRD, HPLC methods, it is possible to determine the number of sorption sites on the soil surface. Moreover, it may be possible to determine the location of sorption sites in the soil surface; for example, how much of the sorption sites go to a clay, and how much of go to humic materials. It might provide better kinetics predictions.

Table 4.1.2 Northport soil results by X-ray powder diffraction analysis.

Minerals	%	Unknown Peaks
Silica (SiO_2)	67	19.85
Anorthite ($CaAl_2Si_2O_8$)	19	48.17
Albite ($NaAlSi_3O_8$)	14	58.73
Total	100	

4.1.1.3 Soil pH

Appendix 4.6 (see appendices section) from US Department of Agriculture Natural Resources Conservation Service (formerly, Soil Conservation Service) classifies soil pH ranges as follows: the Northport soil sample is acidic due to a pH of 4.7. Therefore, the acid H^+ reacts as a catalyst and replaces the chlorine with hydroxyl group OH^-. In other words, in a low pH soil, H^+ could catalyze Atrazine, and convert it to Hydroxyatrazine. Figure 4.1.3 presents the mechanism of producing Hydroxyatrazine from atrazine by acidic hydrolysis.[56] Figure 1.1.5 presents the example of humic acid structure, which may the Northport soil has; shows several Carboxyl groups were could catalyse atrazine to be Hydroxyatrazine by the acidic catalysis. By the titration, hydroxyl group was titrated in the Northport soil. Hence, atrazine concentration amount could be decreased due to the chemical reaction from soil acidity.

Atrazine Hydroxyatrazine $C_8H_{15}N_5O$

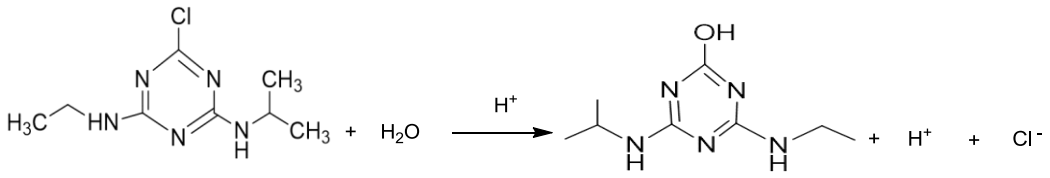

Figure 4.1.1 Mechanism of converting atrazine to Hydroxyatrazine by soil acidity.

4.1.1.4 CHN Analyzer for the Northport Soil

The Northport soil consists mainly of 1.86% Carbon, which is the highest, 0.48% Hydrogen, and 0.34% Nitrogen. Table 4.1.3 shows the CHN results for the Northport soil. (See Appendix 4.7. for more CHN analyzer results)

Table 4.1.3 The CHN analyzer results for the Northport soil.

Sample results	Weight (mg)	Carbon %	Hydrogen %	Nitrogen %
NPS01	7.164	2.08	0.49	0.29
NPS02	7.235	1.82	0.48	0.29
NPS03	7.216	1.68	0.43	0.34
NPS04	6.559	1.84	0.48	0.46
Average		1.855	0.47	0.345
Standard Deviation		0.16	0.027	0.08

4.1.1.5 Soil Fractions

Figure 4.1.4 shows the Northport soil fractions in contact with an atrazine containing solution. The first layer is sand and clay. The second one is organic and humic matter that might have caused a fast chemical reaction that resulted in the unrecovered part of the atrazine during the first 5 minutes of the experiment. (See section 1.1.9 chemical reaction) and also see Figure 1.1.5

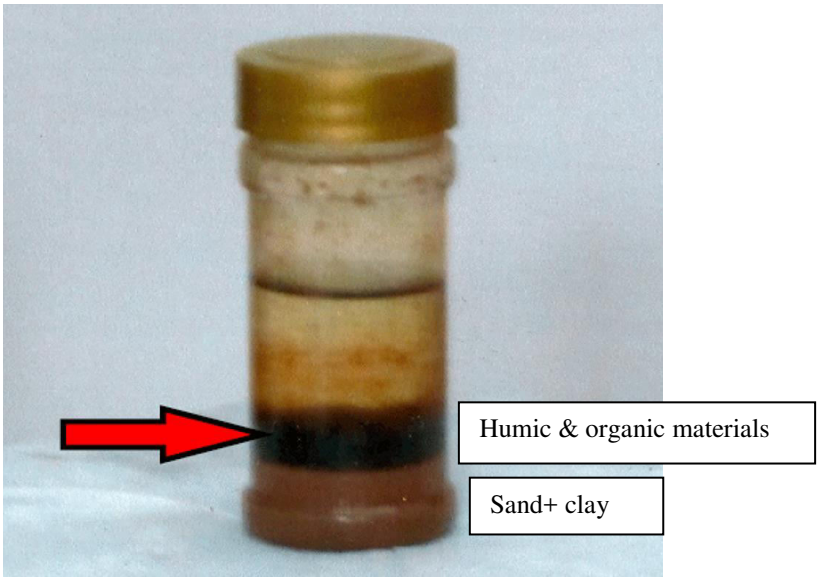

Figure 4.1.4 Northport soil fractions

4.1.1.6 The Back Flushing Efficiency of the Online Microextraction Cell

In order to determine what the optimum flow rate for the backflush, the following experiment was carried out. Four screen filter positions, which put in the microextraction cell, were tested followed by SEM analyzation. The first filter was a new filter without any injections or backflush. Figure 4.1.5 shows the SEM result for the unused filter. It is clean and was not used to filter the slurry. Figure 4.1.6 shows the SEM result for a second filter with 10 injections of slurry and without any backflush. It had collected a large quantity of soil particles, and it appeared to be very dirty. Figure 4.1.7 shows the SEM result for 10 injections of slurry with a backflush of 5 mL/min of solvent between each injection. The filter showed the presence of some soil particles at the surface. Figure 4.1.8 shows the SEM result for 10 injections of slurry with a backflush of 10 mL/min of solvent between each injection. The filter showed no presence of soil particles at the surface. It was very

clean and looked similar to the new screen filter in Figure 4.1.5. Therefore, the 10 mL/min backflush between injections was chosen, since it had better cleaning for the mobile phase

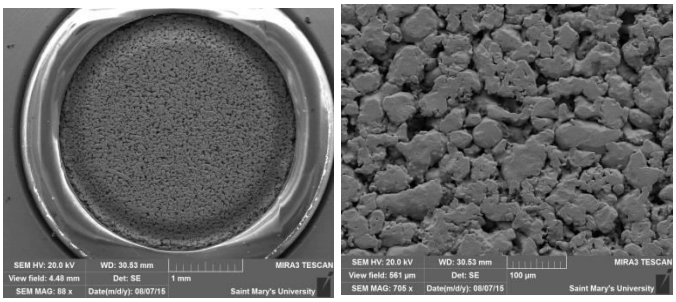

Figure 4.1.3 A new filter by SEM.

pathway. In this way, the pressure did not increase.

Figure 4.1.6 The second filter with ten injections of slurry without backflush 0 mL/min by SEM.

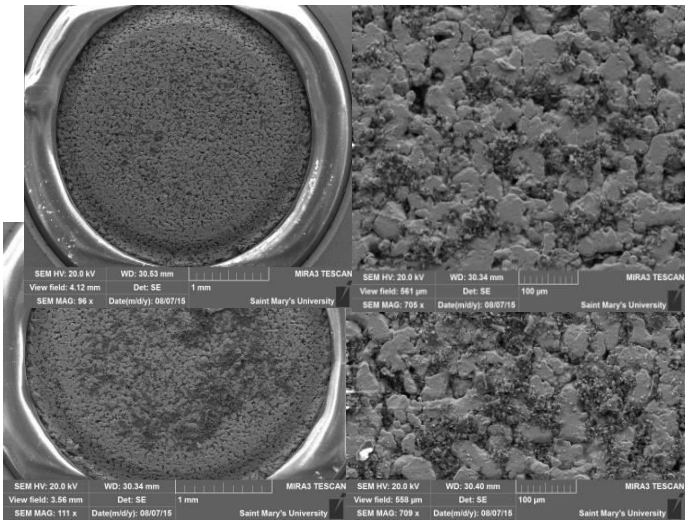

Figure 4.1.7 The third filter with ten injections of slurry with backflush 5 mL/min by SEM.

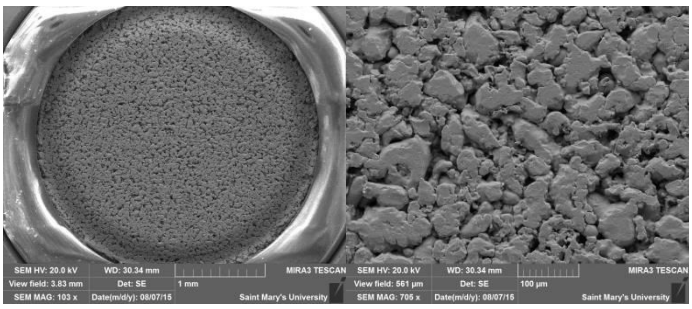

Figure 4.1.8 The fourth filter with ten injections of slurry with backflush 10 mL/min by SEM.

4.2 Calibration Curve

A series of ten atrazine standards solutions from 1.00 x 10^{-5} M to 1.00 x 10^{-6} M were prepared and analyzed by HPLC instrument daily to obtain atrazine calibration curve. Figure 4.3.1 presents an example of the atrazine calibration curve (peak area vs time) used to convert the HPLC peak area signal to concentration for the solution and slurry of atrazine with Northport soil on the first and second days of the sorption experiment. Appendix 4.8 presents daily atrazine calibration curves equations.

4.3 Kinetics of Dissolved Atrazine

Experimental method can be affected by several conditions such as temperature effects; effects of contaminant chemical structure; effects of the types and amounts of soil materials; effects of soil water content, and effects of catalysts including microbial enzymes. These could affect experimental results.

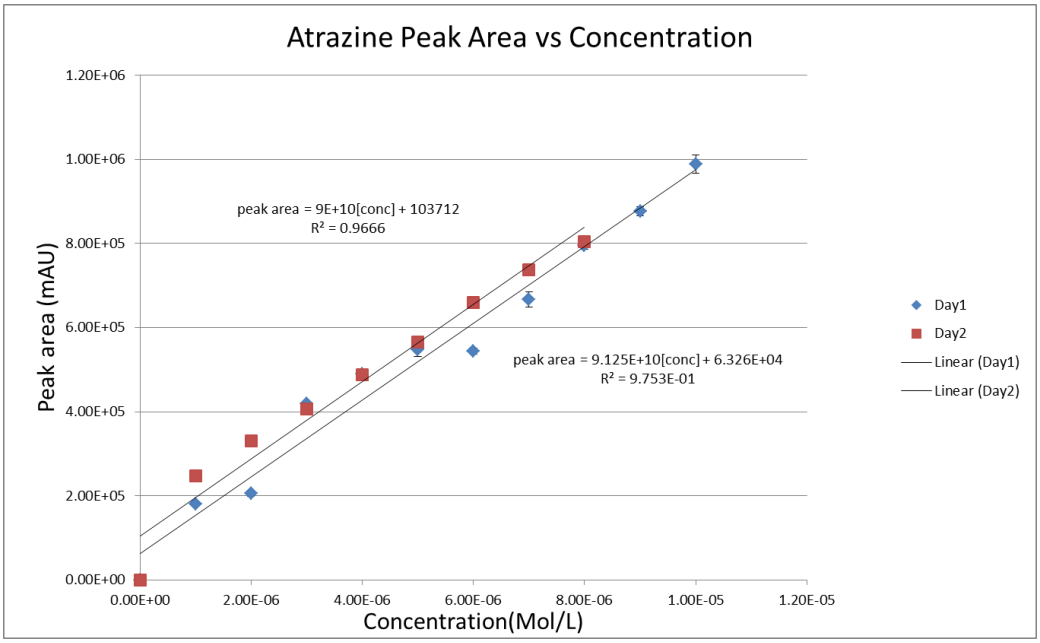

Figure 4.3.1 Calibration curve atrazine standard solution. Varian ProStar HPLC. Online microfiltration setup.

Figure 4.4.1 shows an example of the offline HPLC peaks for atrazine solution (Retention time 2.04 min) and water (Retention time, 0.92 min). The atrazine dissolve fractions are obtained from the solution measurements which is red line in Figure 4.4.2. Figure 4.4.4 presents an analysis curve for atrazine in Northport soil during 30 days. Moreover, the solution analysis had more experimental scatter than the slurry analysis. Support is needed for the improvement of the analytical chemistry methods, to reduce the experimental scatter. From Figure 4.4.2 and figure 4.4.4, atrazine solution concentration was 2.00 x 10^{-7} M during 30 days with Northport soil. Table 4.4.1 shows the experimental conditions and resulting fractions. In this Table values of 0.0 are cases in which actual values are outside the observable limits. Moreover, apparent irregularities might indicate control by kinetics instead of by equilibria.

4.4 Kinetics of Labile Sorbed Atrazine

The labile sorbed fractions are obtained from subtracting the solutions measurements from the slurry measurements. Figure 4.4.3 shows solution, labile sorbed, unrecovered curves for atrazine in Northport soil during 30 days. During the first 5 minutes there was an approximately 32% loss of recoverable Atrazine. There could have been a chemical reaction and it was too fast for intraparticle diffusion. Moreover, if there were any slow loss from intraparticle diffusion, it was not observable due to experimental scatter.

Table 4.4.1 Experimental conditions and resulting fractions.

Experiment	Initial Atrazine		Final Fractions %		
	(Moles/g)	(Moles/L)	Solution	Labile Sorbed	Unrecovered
A	$0.40X10^{-6}$	$1.0X10^{-6}$	20.0	31.6	48.4
B	$1.0X10^{-5}$	$1.0X10^{-5}$	2.5	0.0	97.
C	$1.2X10^{-5}$	$6.0X10^{-6}$	11.2	0.0	87.5
D	$2.0X10^{-4}$	$1.0X10^{-5}$	100.	0.0	0.0

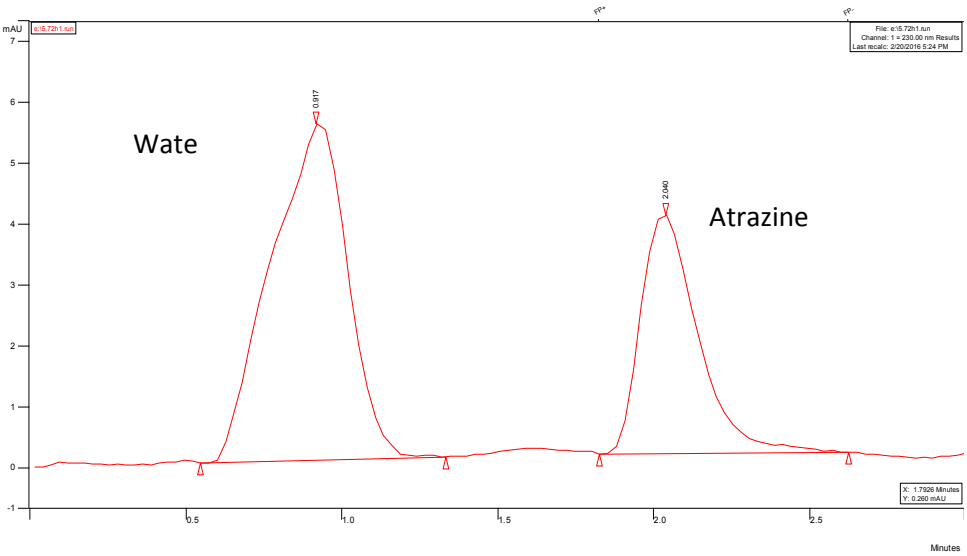

Figure 4.4.1 HPLC peaks of atrazine and unknown compound. Aliquot offline from 1.00 x 10^{-6} M atrazine-spiked Northport slurry at contact time t = 4.0 day. Retention time (R_t): 2.04 min; unknown peak: 0.92 min.

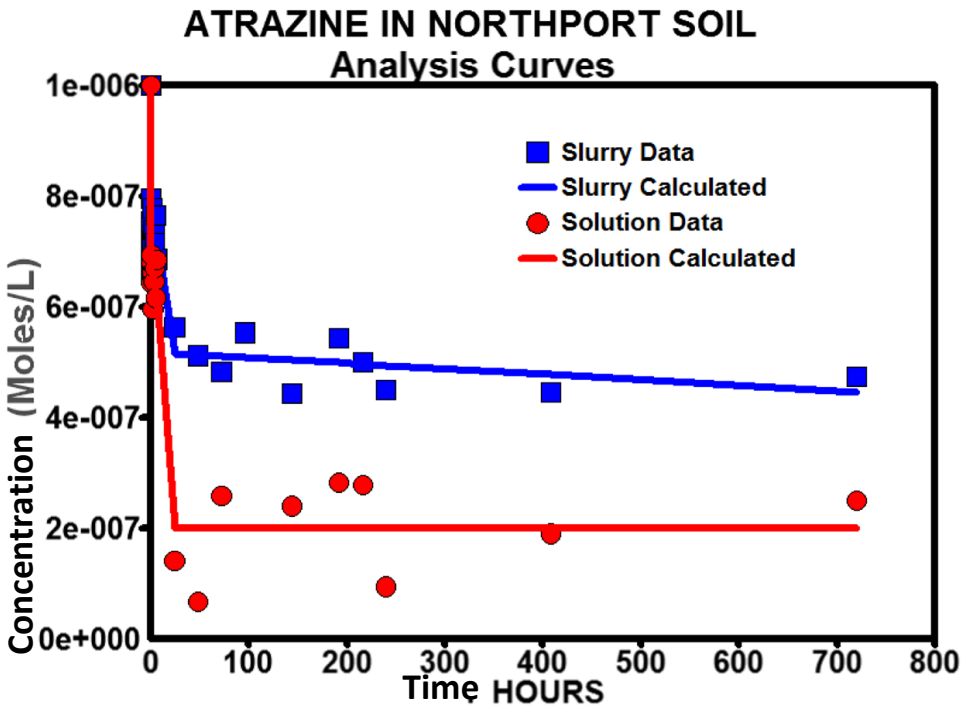

Figure 4.4.2 Slurries data, slurries calculated, solution data, and solution calculated analysis curve for atrazine in Northport soil during 30 days. Initial atrazine concentration: 1.00 x 10^{-6} M at 20.0°C.

Figure 4.4.3 shows that most of the sorption and chemical reaction happened during the first day. Also, the labile sorption sites were saturated during the first day. From Figure 4.4.4, two types of chemical reaction are possible causes of the loss of recoverable atrazine. One was the catalysed hydrolyses that would have produced Hydroxyatrazine. The other would have been chemical reaction with the soil organic matter. The curve will go down because chemical reactions are going off the sorption sites, which take atrazine away and cause the decrease of curve.

Labile sorption was observed outside experimental scatter after 1 hour. Data processing will determine whether or not it was observable outside experimental scatter during the first hour as observed in Figure 4.4.3. Data processing can yield better information about the reaction kinetics and mechanism for atrazine in Northport soil.

Figure 4.4.5 and Figure 4.4.6 show solution, labile sorbed and unrecovered kinetics curves for atrazine in Northport soil during the first hour and the first day of the experiment. The pie chart in Figure 4.4.5 shows 65.94% of atrazine was in solution, 6.12% of atrazine was sorbed, and 24.94% of atrazine was lost during the first hour. Moreover the pie chart in Figure 4.4.6 shows 20.02% of atrazine was in solution, 31.56% of atrazine was sorbed, and 48.42% of atrazine was lost during the first day. Moreover, Figure 4.4.7 shows that after 30 days, 20% of atrazine remained in solution, 25% was labile sorbed, and 55% of atrazine was lost or unrecovered. The spreadsheet columns for atrazine with Northport soil experiment shown in Appendices section (Appendix 4.9).

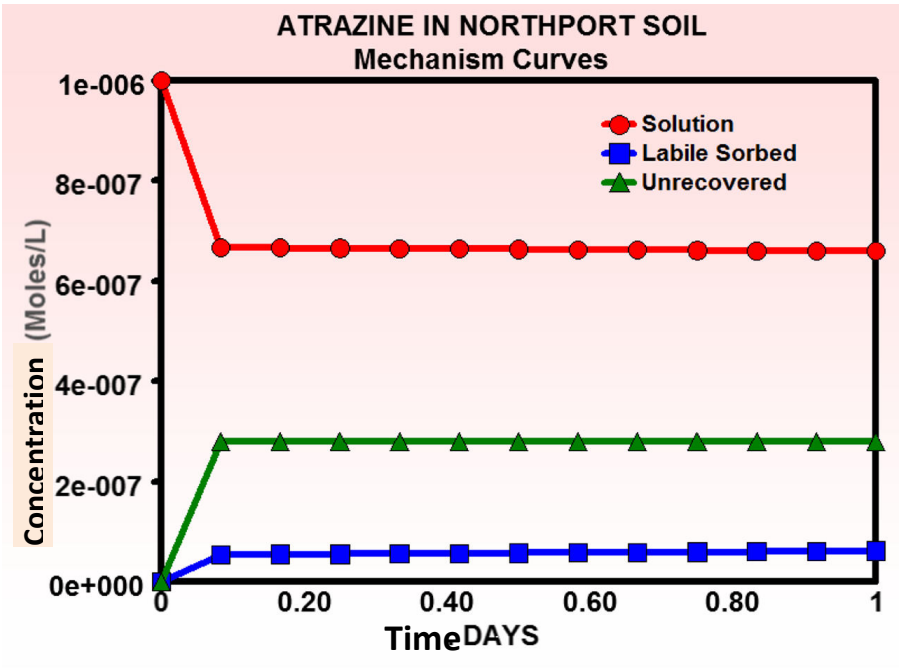

Figure 4.4.3 Solution, labile sorbed and unrecovered kinetics curves for atrazine in Northport soil during the first day of the experiment. Initial atrazine concentration: 1.00 x 10^{-6} M at 20.0°C.

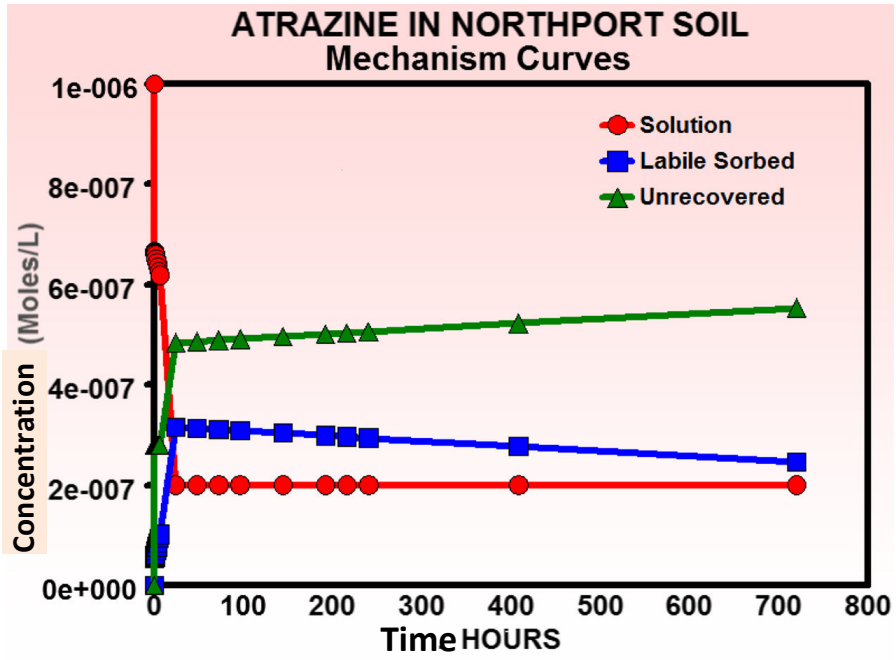

Figure 4.4.4 Solution, labile sorbed, unrecovered curves for atrazine in Northport soil during 30 days. Initial atrazine concentration: 1.00 x 10^{-6} M at 20.0°C.

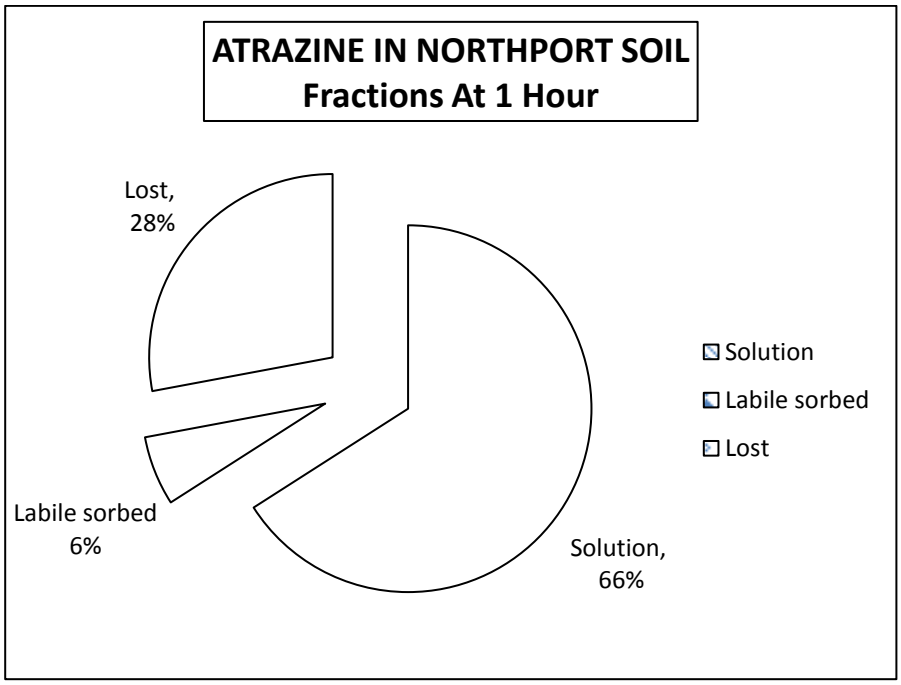

Figure 4.4.5 Atrazine in Northport soil fractions at first hour. Initial atrazine concentration: 1.00 x 10^{-6} M at 20.0°C.

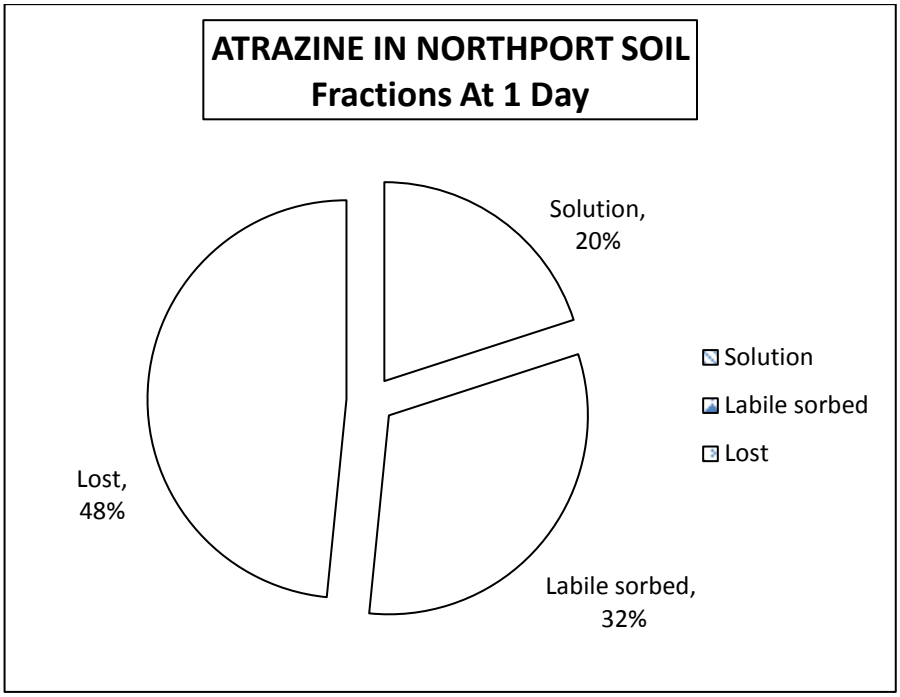

Figure 4.4.6 Atrazine in Northport soil fractions at first day. Initial atrazine concentration: 1.00 x 10^{-6} M at 20.0°C.

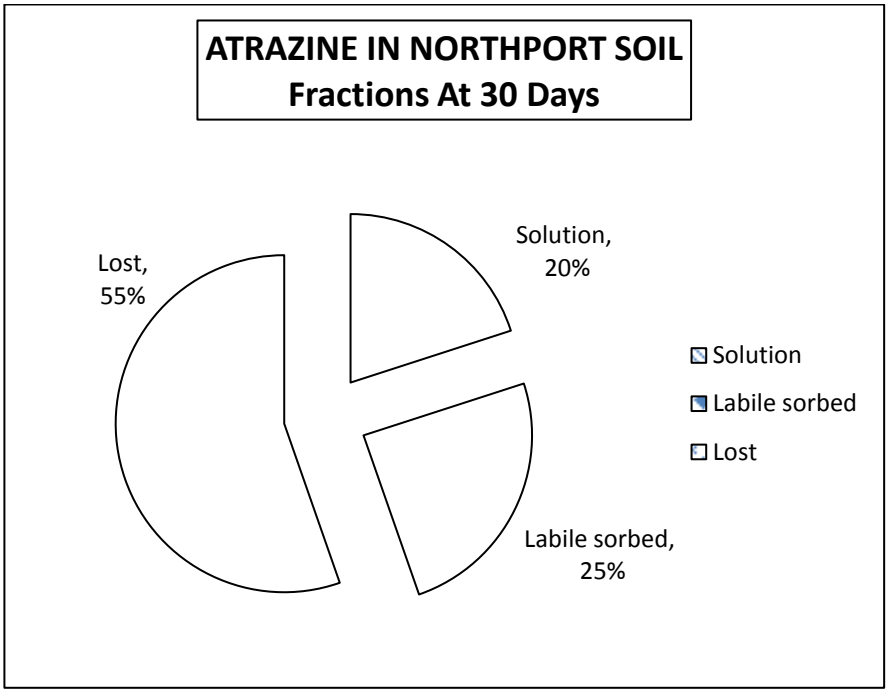

Figure 4.4.7 Atrazine in Northport soil fractions at 30 days. Initial atrazine concentration: 1.00 x 10^{-6} M at 20.0°C.

4.5 Kinetics of Atrazine Bound Residue

By subtracting the dissolved and labile sorbed measurements from the initial Atrazine concentration, which is 1.00×10^{-6} M, the bound residue could be estimated by the intraparticle diffusion.

Experimental data indicate that the half-life of atrazine catalysis by humic carboxyl groups at approximately pH = 4 would range from 18 hours to 2 days. This is too slow to explain the atrazine loss during the first 5 minutes of experiments with the Northport soil.[57] Intraparticle diffusion likely caused the slow loss of sorbed atrazine after the first day which was not observable during the first day. Also, a large excess of atrazine over labile sorption sites gave one type of pseudo first order kinetics for sorption. The large loss of recoverable atrazine implies that under field conditions this would reduce the amount of atrazine that could be leached to ground water or reach surface waters by runoff. The saturation of labile sorption sites would have caused pseudo zero order kinetics for intraparticle diffusion, as is indicated by the straight line. (See Figure 4.4.4)

CONCLUSIONS

This study is environmentally important because agricultural pesticides have to last long enough to protect crops but not so long that they become risks. By knowing some characteristics of Northport soil, the kinetics between this soil and atrazine is known.. Also, the spreadsheet model #5 proved to be useful for general use in the calculation of the various fractions of Atrazine.

This experiment with atrazine in the Northport soil was difficult for two reasons. First, large parts of the atrazine disappeared in less than 5 minutes without leaving reaction products in solution. Secondly, the reaction mechanism has two largely different time scales. The fast processes cannot be observed in the long time scale, and the slow processes cannot be observed in the short time scale. They are only measurable separately.

There are two reasons that cause a decrease or loss of atrazine concentration over time. First is the chemical reaction of the hydroxyl group that came from the soil acidity, which it would increase over time. Second is the sorption kinetics between Atrazine and Northport soil.

Finally, this research would be useful to use for The Pest Management Regulatory Agency and the United States Environmental Protection Agency. The incorrect empirical parameters that have traditionally being used can lead these Agencies to make prediction errors.

SUGGESTIONS FOR FUTURE RESEARCH

Further research might be focused on the following. First, studying the temperature affected in the kinetics behaviour between atrazine and Northport soil at different temperature at 10^{o}C, 30^{o}C. Second, the flushed waste from the online analysis (slurry) needs to be analyzed by alternative method to determine the bound residue. Third, studying the kinetics behaviour for Kaolinite as clay with atrazine and comparing the results with atrazine in Northport soil results. Fourth, from the SEM and XRD methods, it might be possible to determine the locations of the sorption sites and could have better predictions for the kinetics between the chemicals and agricultural soil. Moreover, because the solution analysis had more experimental scatter than the slurry analysis, support is needed for the improvement of the analytical chemistry methods, to reduce the experimental scatter. Moreover, more experimental data are needed to measure the labile sorption capacity for Northport soil with atrazine and to calculate the number of empty and filled sorption sites.

More calculations are recommended to measure the kinetics parameters which are the labile sorption capacities, Θ_C, and the rate coefficient. Moreover, the number of empty and filled sorption sites would be successfully measured from the new model, Model#16, which is in progress. The future construction of a predictive spreadsheet model might require new experiments that do not saturate the labile sorption sites is recommended.

APPENDICES

Appendix 3.1 The Elemental Analyzer of Northport soil.

Collection Time:	4:20 PM November 30, 2009.
Collection Site:	* Geoposition reference point; N,S.C.M. #13688 N 5,088,133.238 m E 5,549,283.603 m * Collected 356.7 m East of the Geoposition reference site. * Site description; top 15 cm, root zone, bottom of a long grassy slope close to the swampy boundary of a brook. Former crop land.
Sample Description:	1 kg of dry fine brown powder. Air dried, screened twice and randomized.

Component	A0, 0 - 1in.	A2, 1 - 9in.
% coarse & fine gravel		0
% Sand (1.0 - 0.05 mm)		52

% Silt (0.05 - 0.005 mm)		35
% Clay (> 0.005 mm)		14
% Fine Clay (> 0.002 mm)		7
% Loss on ignition	64.7	1.3
pH	4.2	4.4
Available P_2O_5 (lb/acre)	224	16
% Total P_2O_5	0.19	0.04
% Total N	0.41	0.01
% Organic C	39.9	0.22
% Total SiO2	23.7	83.3
% Fe2O3	1.5	1.7
% Al2O3	5.2	12.5
SiO2/R2O3	7.9	10.6

Appendix 3.2. X-ray Fluorescence spectrometer for the Northport soil.

Major constituents	Units	Northport Soil
SiO_2	(%)	74.23
TiO_2	(%)	0.81
Al_2O_3	(%)	10.29
Fe_2O_3	(%)	3.26
MnO	(%)	0.063
MgO	(%)	0.93
CaO	(%)	0.25
Na2O	(%)	1.95
K2O	(%)	1.86
P_2O_5	(%)	0.131
LOI	(%)	6.01
Total	(%)	99.78
V	(ppm)	83.4
Cr	(ppm)	37
Co	(ppm)	11.3
Ni	(ppm)	25.3
Cu	(ppm)	15.4
Zn	(ppm)	54.4
Ga	(ppm)	12.1
Rb	(ppm)	79.6
Sr	(ppm)	71.4
Y	(ppm)	24.1
Zr	(ppm)	219.6
Nb	(ppm)	15.8
Ba	(ppm)	329.7
La	(ppm)	27.5
Pb	(ppm)	19
Th	(ppm)	11.4
U	(ppm)	3.3
Ce	(ppm)	48.4
Nd	(ppm)	25.4
Cs	(ppm)	5.2

*LOI: Loss on Ignition.

Appendix 4.1 SEM results for the Northport soil. (A)

Project: Project 1																
Owner: xiang																
Site: Site of Interest 1																
Sample: Sample 1																
Type: Default																
ID: Soil Sample																
Processing option : Oxygen by stoichiometry (Normalised)																
All results in weight%																
X and Y are beam positions																
Spectrum	In stats.	X (mm)	Y (mm)	Na	Mg	Al	Si	P	K	Ca	Ti	Fe	O	Total		
Spectrum 1	Yes	0.013	-0.003	3.21	1.72	8.94	28.79		1.13	0.15	5.93	2.22	47.9	100		
Spectrum 2	Yes	0.029	-0.056	1.61	1.05	8.58	32.16		2.34	0.34	0.54	5.36	48.02	100		
Spectrum 3	Yes	0.04	0.015	1.04	1.51	8.66	31.79	0.4	1.96		0.6	5.79	48.25	100		
Spectrum 4	Yes	0.112	-0.128	1	1.6	9.7	32.09		1.73	0.25	0.43	4.55	48.64	100		
Spectrum 5	Yes	0.211	0.073		0.21	1.22	44.98		0.23			0.65	52.7	100		
Max.				3.21	1.72	9.7	44.98	0.4	2.34	0.34	5.93	5.79	52.7			
Min.				1	0.21	1.22	28.79	0.4	0.23	0.15	0.43	0.65	47.9			
Project: Project 1																
Owner: xiang																
Site: Site of Interest 2																
Sample: Sample 1																
Type: Default																
ID: Soil Sample																
Processing option : Oxygen by stoichiometry (Normalised)																
All results in weight%																
X and Y are beam positions																
Spectrum	In stats.	X (mm)	Y (mm)	Na	Mg	Al	Si	P	S	K	Ca	Ti	Mn	Fe	O	Total
Spectrum 1	Yes	-0.056	-0.043	0.8	1.24	11.82	28.86			4.3		0.42		5.36	47.19	100
Spectrum 2	Yes	-0.045	-0.013	1.13	1.2	16	28.22			1.21	0.61	0.3		2.39	48.94	100
Spectrum 3	Yes	-0.014	-0.026			1.79	44.72			0.5				0.26	52.72	100
Spectrum 4	Yes	-0.003	-0.05	7.22	0.41	12.8	29.96			0.34	0.27			0.42	48.59	100
Spectrum 5	Yes	0.01	-0.02	1.04	1.55	14.3	27.74	0.37		1.87	0.22	0.8	0.12	3.68	48.29	100
Spectrum 6	Yes	0.025	-0.001		1.27	6.63	9.39			1.5			0.75	48.57	31.88	100
Spectrum 7	Yes	0.103	-0.051		3.11	15.88	25.07			3.86		0.24		4.78	47.06	100
Spectrum 8	Yes	0.075	0.026			12.06	23.28							21.3	43.36	100
Spectrum 9	Yes	-0.038	0.013	8.36	0.22	10.02	31.57			0.11		0.76		0.39	48.57	100
Spectrum 10	Yes	0.038	-0.022	7.98		10.21	31.72			0.42	0.37			0.83	48.47	100
Spectrum 11	Yes	0.03	-0.041		0.26	1.58	44.6			0.34				0.6	52.62	100
Spectrum 12	Yes	0.053	0.014	1.27	1.6	8.4	24.81			2.89	0.39	1.17	0.91	15.18	43.38	100
Spectrum 13	Yes	-0.065	-0.028	1.15	1.61	11.33	29.96			1.83	0.3	0.3	0.23	5.31	47.96	100
Spectrum 14	Yes	0.003	-0.002	1.55	1.64	12.8	26.98	0.5	0.23	1.7	0.43	0.64		6.11	47.42	100
Spectrum 15	Yes	0.064	-0.034	3.12	1.3	12.18	26.46			1.35	0.61	0.69	1.74	6.34	46.22	100
Spectrum 16	Yes	0.082	-0.023	2.45	0.61	7.38	34.71			1.13			0.84	3.93	48.96	100
Max.				8.36	3.11	16	44.72	0.5	0.23	4.3	0.61	1.17	1.74	48.57	52.72	
Min.				0.8	0.22	1.58	9.39	0.37	0.23	0.11	0.22	0.24	0.12	0.26	31.88	

Appendix 4.2 SEM results for the Northport soil. (B)

Project: Project 1																	
Owner: xiang																	
Site: Site of Interest 3																	
Sample: Sample 1																	
Type: Default																	
ID: Soil Sample																	
Processing option : Oxygen by stoichiometry (Normalised)																	
All results in weight%																	
X and Y are beam positions																	
Spectrum	In stats.	X (mm)	Y (mm)	Na	Mg	Al	Si	K	Ca	Ti	Mn	Fe	O	Total			
Spectrum 1	Yes	-0.025	-0.023	0.35	0.28	2.08	43.77	0.48				0.71	52.33	100			
Spectrum 2	Yes	-0.033	0.009	0.76	6.11	11.54	27.32	2.18		0.43	0.15	3.93	47.58	100			
Spectrum 3	Yes	-0.032	-0.008	0.31	1.38	15.91	24.87	5.25		0.23		5.69	46.36	100			
Spectrum 4	Yes	0.001	0.016		0.96	6.67	39.15	0.38				1.24	51.6	100			
Spectrum 5	Yes	-0.01	0.007	2.48	0.98	15.83	28.44	2.25		0.12		1.05	48.84	100			
Spectrum 6	Yes	-0.001	-0.004	0.8	0.92	6.11	17.68	1.79		0.74		34.71	37.26	100			
Spectrum 7	Yes	0.007	-0.016	0.68	0.79	12.07	29.18	3.92		0.35		5.63	47.38	100			
Spectrum 8	Yes	0.017	0	0.57	0.94	5.66	37.49	1.7		0.62		2.86	50.15	100			
Spectrum 9	Yes	0.021	-0.008	0.48	0.9	6.81	35.22	2.33	0.32	0.25		4.63	49.05	100			
Spectrum 10	Yes	0.032	-0.008	0.49	0.71	3.31	42.03	0.72				0.88	51.86	100			
Spectrum 11	Yes	0.042	-0.011	0.97	1.5	14.01	28.22	3.82		0.25		3.38	47.85	100			
Spectrum 12	Yes	0.004	-0.01		0.69	4.68	36.94	1.34		0.51		6.62	49.21	100			
Spectrum 13	Yes	0.031	0.002	0.97	4.82	10.54	27.84	2.17	0.19	0.64	0.41	5.25	47.17	100			
Max.				2.48	6.11	15.91	43.77	5.25	0.32	0.74	0.41	34.71	52.33				
Min.				0.31	0.28	2.08	17.68	0.38	0.19	0.12	0.15	0.71	37.26				
Project: Project 1																	
Owner: xiang																	
Site: Site of Interest 4																	
Sample: Sample 1																	
Type: Default																	
ID: Soil Sample																	
Processing option : Oxygen by stoichiometry (Normalised)																	
All results in weight%																	
X and Y are beam positions																	
Spectrum	In stats.	X (mm)	Y (mm)	Na	Mg	Al	Si	P	S	K	Ca	Ti	Mn	Fe	O	Total	
Spectrum 1	Yes	0.023	-0.003	0.71	0.51	3.36	42.06			0.72				0.78	51.86	100	
Spectrum 2	Yes	0.019	0.012	0.68	3.94	7.4	33.94			0.66		0.11		3.87	49.4	100	
Spectrum 3	Yes	-0.006	0.009	0.27		1.35	45.08			0.23				0.28	52.78	100	
Spectrum 4	Yes	0.043	-0.016	0.48	6.63	13.41	23.26			1.21		0.16		8.98	45.88	100	
Spectrum 5	Yes	0.053	0.024	1.69	3.33	14.63	25.31	0.51	0.25	1.83	0.33	0.26		4.3	47.57	100	
Spectrum 6	Yes	-0.042	-0.013		0.4	3.32	42.66			0.92				0.54	52.16	100	
Spectrum 7	Yes	-0.014	-0.014	1.22	4.89	14.86	23.57			1.27		0.76	0.24	6.71	46.48	100	
Spectrum 8	Yes	0.036	0.003	0.57	1.9	14.03	29.1	0.27		2.83		0.25		2.24	48.81	100	
Spectrum 9	Yes	0.056	-0.024	0.99	2.41	12.42	29.57			2.17		0.23		3.84	48.37	100	
Spectrum 10	Yes	0.003	-0.028		8.97	14	19.4			0.49			0.34	12.55	44.25	100	
Spectrum 11	Yes	-0.008	-0.003	1.64	1.1	16.38	27.11			4.43				1.31	48.03	100	
Spectrum 12	Yes	0.02	-0.016	6	0.48	10.87	32.19			0.25	0.2			0.88	49.13	100	
Spectrum 13	Yes	-0.023	-0.035	0.53	5.19	11.96	27.5			1.69	0.24	0.56	0.19	4.45	47.7	100	
Spectrum 14	Yes	-0.022	0.015		6.82	15.29	23.02			1.59		1.38	0.16	4.77	46.97	100	
Spectrum 15	Yes	-0.024	0.009		3.18	9.32	20.11			1.17		17.94		2.15	46.13	100	
Max.				6	8.97	16.38	45.08	0.51	0.25	4.43	0.33	17.94	0.34	12.55	52.78		
Min.				0.27	0.4	1.35	19.4	0.27	0.25	0.23	0.2	0.11	0.16	0.28	44.25		

Appendix 4.3 The Northport soil elements by SEM.

Sample	Site	Position	Mineral	Si	Ti	Al	Fe	Mn	Mg	Ca	Na	K	P	S	O	Total
Soil Sample	1	1		28.79	5.93	8.94	2.22		1.72	0.15	3.21	1.13			47.9	100
Soil Sample	1	2		32.16	0.54	8.58	5.36		1.05	0.34	1.61	2.34			48.02	100
Soil Sample	1	3		31.79	0.6	8.66	5.79		1.51		1.04	1.96	0.4		48.25	100
Soil Sample	1	4		32.09	0.43	9.7	4.55		1.6	0.25	1	1.73			48.64	100
Soil Sample	1	5		44.98		1.22	0.65		0.21			0.23			52.7	100
Soil Sample	2	1		28.86	0.42	11.82	5.36		1.24		0.8	4.3			47.19	100
Soil Sample	2	2		28.22	0.3	16	2.39		1.2	0.61	1.13	1.21			48.94	100
Soil Sample	2	3		44.72		1.79	0.26					0.5			52.72	100
Soil Sample	2	4		29.96		12.8	0.42		0.41	0.27	7.22	0.34			48.59	100
Soil Sample	2	5		27.74	0.8	14.3	3.68	0.12	1.55	0.22	1.04	1.87	0.37		48.29	100
Soil Sample	2	6		9.39		6.63	48.57	0.75	1.27			1.5			31.88	100
Soil Sample	2	7		25.07	0.24	15.88	4.78		3.11			3.86			47.06	100
Soil Sample	2	8		23.28		12.06	21.3								43.36	100
Soil Sample	2	9		31.57	0.76	10.02	0.39		0.22		8.36	0.11			48.57	100
Soil Sample	2	10		31.72		10.21	0.83			0.37	7.98	0.42			48.47	100
Soil Sample	2	11		44.6		1.58	0.6		0.26			0.34			52.62	100
Soil Sample	2	12		24.81	1.17	8.4	15.18	0.91	1.6	0.39	1.27	2.89			43.38	100
Soil Sample	2	13		29.96	0.3	11.33	5.31	0.23	1.61	0.3	1.15	1.83			47.96	100
Soil Sample	2	14		26.98	0.64	12.8	6.11		1.64	0.43	1.55	1.7	0.5	0.23	47.42	100
Soil Sample	2	15		26.46	0.69	12.18	6.34	1.74	1.3	0.61	3.12	1.35			46.22	100
Soil Sample	2	16		34.71		7.38	3.93	0.84	0.61		2.45	1.13			48.96	100
Soil Sample	3	1		43.77		2.08	0.71		0.28		0.35	0.48			52.33	100
Soil Sample	3	2		27.32	0.43	11.54	3.93	0.15	6.11		0.76	2.18			47.58	100
Soil Sample	3	3		24.87	0.23	15.91	5.69		1.38		0.31	5.25			46.36	100
Soil Sample	3	4		39.15		6.67	1.24		0.96			0.38			51.6	100
Soil Sample	3	5		28.44	0.12	15.83	1.05		0.98		2.48	2.25			48.84	100
Soil Sample	3	6		17.68	0.74	6.11	34.71		0.92		0.8	1.79			37.26	100
Soil Sample	3	7		29.18	0.35	12.07	5.63		0.79		0.68	3.92			47.38	100
Soil Sample	3	8		37.49	0.62	5.66	2.86		0.94		0.57	1.7			50.15	100
Soil Sample	3	9		35.22	0.25	6.81	4.63		0.9	0.32	0.48	2.33			49.05	100
Soil Sample	3	10		42.03		3.31	0.88		0.71		0.49	0.72			51.86	100
Soil Sample	3	11		28.22	0.25	14.01	3.38		1.5		0.97	3.82			47.85	100
Soil Sample	3	12		36.94	0.51	4.68	6.62		0.69			1.34			49.21	100
Soil Sample	3	13		27.84	0.64	10.54	5.25	0.41	4.82	0.19	0.97	2.17			47.17	100
Soil Sample	4	1		42.06		3.36	0.78		0.51		0.71	0.72			51.86	100
Soil Sample	4	2		33.94	0.11	7.4	3.87		3.94		0.68	0.66			49.4	100
Soil Sample	4	3		45.08		1.35	0.28				0.27	0.23			52.78	100
Soil Sample	4	4		23.26	0.16	13.41	8.98		6.63		0.48	1.21			45.88	100
Soil Sample	4	5		25.31	0.26	14.63	4.3		3.33	0.33	1.69	1.83	0.51	0.25	47.57	100
Soil Sample	4	6		42.66		3.32	0.54		0.4			0.92			52.16	100
Soil Sample	4	7		23.57	0.76	14.86	6.71	0.24	4.89		1.22	1.27			46.48	100
Soil Sample	4	8		29.1	0.25	14.03	2.24		1.9		0.57	2.83	0.27		48.81	100
Soil Sample	4	9		29.57	0.23	12.42	3.84		2.41		0.99	2.17			48.37	100
Soil Sample	4	10		19.4		14	12.55	0.34	8.97			0.49			44.25	100
Soil Sample	4	11		27.11		16.38	1.31		1.1		1.64	4.43			48.03	100
Soil Sample	4	12		32.19		10.87	0.88		0.48	0.2	6	0.25			49.13	100
Soil Sample	4	13		27.5	0.56	11.96	4.45	0.19	5.19	0.24	0.53	1.69			47.7	100
Soil Sample	4	14		23.02	1.38	15.29	4.77	0.16	6.82			1.59			46.97	100
Soil Sample	4	15		20.11	17.94	9.32	2.15		3.18			1.17			46.13	100

Appendix 4.4 The Northport soil oxidise by SEM.

Sample	Site	Position	Mineral	SiO2	TiO2	Al2O3	FeO	MnO	MgO	CaO	Na2O	K2O	P2O5	SO3	Total
Soil Sample	1	1		61.59	9.89	16.89	2.86		2.85	0.21	4.33	1.36			99.98
Soil Sample	1	2		68.8	0.9	16.21	6.9		1.74	0.48	2.17	2.82			100.02
Soil Sample	1	3		68.01	1	16.36	7.45		2.5		1.4	2.36	0.92		100
Soil Sample	1	4		68.65	0.72	18.33	5.85		2.65	0.35	1.35	2.08			99.98
Soil Sample	1	5	Quartz	96.22		2.31	0.84		0.35			0.28			100
Soil Sample	2	1	Orthoclase	61.74	0.7	22.33	6.9		2.06		1.08	5.18			99.99
Soil Sample	2	2		60.37	0.5	30.23	3.07		1.99	0.85	1.52	1.46			99.99
Soil Sample	2	3	Quartz	95.66		3.38	0.33					0.6			99.97
Soil Sample	2	4	Albite	64.09		24.19	0.54		0.68	0.38	9.73	0.41			100.02
Soil Sample	2	5	Illite	59.34	1.33	27.02	4.73	0.15	2.57	0.31	1.4	2.25	0.85		99.95
Soil Sample	2	6		20.09		12.53	62.48	0.97	2.11			1.81			99.99
Soil Sample	2	7	Illite	53.63	0.4	30.01	6.15		5.16			4.65			100
Soil Sample	2	8	Hercynite	49.8		22.79	27.4								99.99
Soil Sample	2	9	Albite	67.53	1.27	18.93	0.5		0.36		11.27	0.13			99.99
Soil Sample	2	10	Albite	67.86		19.29	1.07			0.52	10.76	0.51			100.01
Soil Sample	2	11	Quartz	95.41		2.99	0.77		0.43			0.41			100.01
Soil Sample	2	12		53.07	1.95	15.87	19.53	1.17	2.65	0.55	1.71	3.48			99.98
Soil Sample	2	13		64.09	0.5	21.41	6.83	0.3	2.67	0.42	1.55	2.2			99.97
Soil Sample	2	14	Illite	57.72	1.07	24.19	7.86		2.72	0.6	2.09	2.05	1.15	0.57	100.02
Soil Sample	2	15		56.6	1.15	23.01	8.16	2.25	2.16	0.85	4.21	1.63			100.02
Soil Sample	2	16		74.25		13.94	5.06	1.08	1.01		3.3	1.36			100
Soil Sample	3	1	Quartz	93.63		3.93	0.91		0.46		0.47	0.58			99.98
Soil Sample	3	2		58.44	0.72	21.81	5.06	0.19	10.13		1.02	2.63			100
Soil Sample	3	3	Illite	53.2	0.38	30.06	7.32		2.29		0.42	6.32			99.99
Soil Sample	3	4	Quartz	83.75		12.6	1.6		1.59			0.46			100
Soil Sample	3	5		60.84	0.2	29.91	1.35		1.63		3.34	2.71			99.98
Soil Sample	3	6		37.82	1.23	11.55	44.65		1.53		1.08	2.16			100.02
Soil Sample	3	7	Orthoclase	62.42	0.58	22.81	7.24		1.31		0.92	4.72			100
Soil Sample	3	8	Quartz	80.2	1.03	10.69	3.68		1.56		0.77	2.05			99.98
Soil Sample	3	9		75.34	0.42	12.87	5.96		1.49	0.45	0.65	2.81			99.99
Soil Sample	3	10	Quartz	89.91		6.25	1.13		1.18		0.66	0.87			100
Soil Sample	3	11		60.37	0.42	26.47	4.35		2.49		1.31	4.6			100.01
Soil Sample	3	12		79.02	0.85	8.84	8.52		1.14			1.61			99.98
Soil Sample	3	13		59.56	1.07	19.92	6.75	0.53	7.99	0.27	1.31	2.61			100.01
Soil Sample	4	1	Quartz	89.97		6.35	1		0.85		0.96	0.87			100
Soil Sample	4	2		72.6	0.18	13.98	4.98		6.53		0.92	0.79			99.98
Soil Sample	4	3	Quartz	96.43		2.55	0.36				0.36	0.28			99.98
Soil Sample	4	4		49.76	0.27	25.34	11.55		10.99		0.65	1.46			100.02
Soil Sample	4	5	Illite	54.14	0.43	27.64	5.53		5.52	0.46	2.28	2.2	1.17	0.62	99.99
Soil Sample	4	6	Quartz	91.26		6.27	0.69		0.66			1.11			99.99
Soil Sample	4	7		50.42	1.27	28.08	8.63	0.31	8.11		1.64	1.53			99.99
Soil Sample	4	8		62.25	0.42	26.51	2.88		3.15		0.77	3.41	0.62		100.01
Soil Sample	4	9		63.26	0.38	23.47	4.94		4		1.33	2.61			99.99
Soil Sample	4	10		41.5		26.45	16.15	0.44	14.87			0.59			100
Soil Sample	4	11	Illite	57.99		30.95	1.69		1.82		2.21	5.34			100
Soil Sample	4	12		68.86		20.54	1.13		0.8	0.28	8.09	0.3			100
Soil Sample	4	13		58.83	0.93	22.6	5.72	0.25	8.61	0.34	0.71	2.04			100.03
Soil Sample	4	14		49.24	2.3	28.89	6.14	0.21	11.31			1.92			100.01
Soil Sample	4	15		43.02	29.92	17.61	2.77		5.27			1.41			100

Appendix 4.5 The SEM coordinates for the Northport soil.

Sample	Site	Position	X (mm)	Y (mm)
Soil Sampl	1	1	0.013	-0.003
Soil Sampl	1	2	0.029	-0.056
Soil Sampl	1	3	0.04	0.015
Soil Sampl	1	4	0.112	-0.128
Soil Sampl	1	5	0.211	0.073
Sample	Site	Position	X (mm)	Y (mm)
Soil Sampl	2	1	-0.056	-0.043
Soil Sampl	2	2	-0.045	-0.013
Soil Sampl	2	3	-0.014	-0.026
Soil Sampl	2	4	-0.003	-0.05
Soil Sampl	2	5	0.01	-0.02
Soil Sampl	2	6	0.025	-0.001
Soil Sampl	2	7	0.103	-0.051
Soil Sampl	2	8	0.075	0.026
Soil Sampl	2	9	-0.038	0.013
Soil Sampl	2	10	0.038	-0.022
Soil Sampl	2	11	0.03	-0.041
Soil Sampl	2	12	0.053	0.014
Soil Sampl	2	13	-0.065	-0.028
Soil Sampl	2	14	0.003	-0.002
Soil Sampl	2	15	0.064	-0.034
Soil Sampl	2	16	0.082	-0.023
Sample	Site	Position	X (mm)	Y (mm)
Soil Sampl	3	1	-0.025	-0.023
Soil Sampl	3	2	-0.033	0.009
Soil Sampl	3	3	-0.032	-0.008
Soil Sampl	3	4	0.001	0.016
Soil Sampl	3	5	-0.01	0.007
Soil Sampl	3	6	-0.001	-0.004
Soil Sampl	3	7	0.007	-0.016
Soil Sampl	3	8	0.017	0
Soil Sampl	3	9	0.021	-0.008
Soil Sampl	3	10	0.032	-0.008
Soil Sampl	3	11	0.042	-0.011
Soil Sampl	3	12	0.004	-0.01
Soil Sampl	3	13	0.031	0.002
Sample	Site	Position	X (mm)	Y (mm)
Soil Sampl	4	1	0.023	-0.003
Soil Sampl	4	2	0.019	0.012
Soil Sampl	4	3	-0.006	0.009
Soil Sampl	4	4	0.043	-0.016
Soil Sampl	4	5	0.053	0.024
Soil Sampl	4	6	-0.042	-0.013
Soil Sampl	4	7	-0.014	-0.014
Soil Sampl	4	8	0.036	0.003
Soil Sampl	4	9	0.056	-0.024
Soil Sampl	4	10	0.003	-0.028
Soil Sampl	4	11	-0.008	-0.003
Soil Sampl	4	12	0.02	-0.016
Soil Sampl	4	13	-0.023	-0.035
Soil Sampl	4	14	-0.022	0.015
Soil Sampl	4	15	-0.024	0.009

Appendix 4.6 The soil pH ranges from The United States Department of Agriculture Natural Resources Conservation Service, formerly Soil Conservation Service classifies as follows.

Denomination	pH range
Ultra-acid	< 3.5
Extreme acid	3.5–4.4
Very strong acid	4.5–5.0
Strong acid	5.1–5.5
Moderate acid	5.6–6.0
Slight acid	6.1–6.5
Neutral	6.6–7.3
Slightly alkaline	7.4–7.8
Moderately alkaline	7.9–8.4
Strongly alkaline	8.5–9.0
Very strongly alkaline	> 9.0

Appendix 4.7 The CHN analyzer for the Northport soil.

Theoretical	Carbon %	Hydrogen %	Nitrogen %
Calibration: Acetanilide	71.09	6.71	10.36
Quality Control: LOAM-A	0.86	0.00	0.10
NorthPort Soil	0.00	0.00	0.00

Quality Control	Weigth mg	Carbon %	Hydrogen %	Nitrogen %
LOAM A	6.976	0.87	0.49	0.14
LOAM A	5.555	0.88	0.48	0.16
LOAM A	7.898	0.84	0.50	0.16

Sample results	Weigth mg	Carbon %	Hydrogen %	Nitrogen %
NPS01	7.164	2.08	0.49	0.29
NPS02	7.235	1.82	0.48	0.29
NPS03	7.216	1.68	0.43	0.34
NPS04	6.559	1.84	0.48	0.46

Note:
Combustion conditions: Oxyfill 1s; Extedend combustion 6s; Boost1 0s; Boost2 0s

Appendix 4.8 Daily atrazine calibration curves equations.

Day No#	Equations
1	Peak area= 3E+11[Conc]+28756
2	Peak area= 4E+11[Conc]-2575.7
3	Peak area= 4E+11[Conc]+5321.8
4	Peak area= 3E+11[Conc]+23932
6	Peak area= 4E+11[Conc]+16360
8	Peak area= 3E+11[Conc]+21832
9	Peak area= 4E+11[Conc]-7019.2
10	Peak area= 4E+11[Conc]+4517.4
11	Peak area= 4E+11[Conc]-5279.1
17	Peak area= 4E+11[Conc]-533.52
30	Peak area= 4E+11[Conc]+8557.3

Appendix 4.9 Spreadsheet columns experiment data.

Atrazine In Northport Soil
Mechanism Curves

April
March

Soil Wt. = 50.00 mg
Solution = 20.00 mL
Mo = 1.0000E-06 (Mol/L)

No.	Time Hours	Slurry (Mol/L) Calculated	Solution (Mol/L) Calculated
1	0.0000	1.0000E-06	1.0000E-06
2	0.0833	7.2056E-07	6.6683E-07
3	0.1667	7.2056E-07	6.6615E-07
4	0.2500	7.2056E-07	6.6548E-07
5	0.3333	7.2056E-07	6.6480E-07
6	0.4167	7.2056E-07	6.6412E-07
7	0.5000	7.2056E-07	6.6344E-07
8	0.5833	7.2056E-07	6.6277E-07
9	0.6667	7.2056E-07	6.6209E-07
10	0.7500	7.2056E-07	6.6141E-07
11	0.8333	7.2056E-07	6.6073E-07
12	0.9167	7.2056E-07	6.6006E-07
13	1.0000	7.2056E-07	6.5938E-07
14	2.0000	7.2056E-07	6.5125E-07
15	3.0000	7.2056E-07	6.4313E-07
16	4.0000	7.2056E-07	6.3500E-07
17	5.0000	7.2056E-07	6.2687E-07
18	6.0000	7.2056E-07	6.1874E-07
1	24.0000	5.1581E-07	2.0019E-07
2	48.0000	5.1342E-07	2.0019E-07
3	72.0000	5.1103E-07	2.0019E-07
4	96.0000	5.0864E-07	2.0019E-07
5	144.0000	5.0387E-07	2.0019E-07
6	192.0000	4.9909E-07	2.0019E-07
7	216.0000	4.9670E-07	2.0019E-07
8	240.0000	4.9431E-07	2.0019E-07
9	408.0000	4.7759E-07	2.0019E-07
10	720.0000	4.4654E-07	2.0019E-07

No.	Time Hours	Solution (Mol/L) (Mol/L)	Labile Sorbed (Mol/L)	Lost (Mol/L)
1	0.0000	1.0000E-06	0.0000E+00	0.0000E+00
2	0.0833	6.6683E-07	5.3732E-08	2.7944E-07
3	0.1667	6.6615E-07	5.4409E-08	2.7944E-07
4	0.2500	6.6548E-07	5.5087E-08	2.7944E-07
5	0.3333	6.6480E-07	5.5764E-08	2.7944E-07
6	0.4167	6.6412E-07	5.6441E-08	2.7944E-07
7	0.5000	6.6344E-07	5.7119E-08	2.7944E-07
8	0.5833	6.6277E-07	5.7796E-08	2.7944E-07
9	0.6667	6.6209E-07	5.8473E-08	2.7944E-07
10	0.7500	6.6141E-07	5.9150E-08	2.7944E-07
11	0.8333	6.6073E-07	5.9828E-08	2.7944E-07
12	0.9167	6.6006E-07	6.0505E-08	2.7944E-07
13	1.0000	6.5938E-07	6.1182E-08	2.7944E-07
14	2.0000	6.5125E-07	6.9310E-08	2.7944E-07
15	3.0000	6.4313E-07	7.7437E-08	2.7944E-07
16	4.0000	6.3500E-07	8.5565E-08	2.7944E-07
17	5.0000	6.2687E-07	9.3692E-08	2.7944E-07
18	6.0000	6.1874E-07	1.0182E-07	2.7944E-07
1	24.0000	2.0019E-07	3.1562E-07	4.8419E-07
2	48.0000	2.0019E-07	3.1323E-07	4.8658E-07
3	72.0000	2.0019E-07	3.1084E-07	4.8897E-07
4	96.0000	2.0019E-07	3.0845E-07	4.9136E-07
5	144.0000	2.0019E-07	3.0368E-07	4.9613E-07
6	192.0000	2.0019E-07	2.9890E-07	5.0091E-07
7	216.0000	2.0019E-07	2.9651E-07	5.0330E-07
8	240.0000	2.0019E-07	2.9412E-07	5.0569E-07
9	408.0000	2.0019E-07	2.7740E-07	5.2241E-07
10	720.0000	2.0019E-07	2.4635E-07	5.5346E-07

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