# FATE AND TRANSPORT OF HERBICIDES IN SOIL IN THE PRESENCE OF SURFACTANTS IN IRRIGATION WATER

**By**

**FAHMIDA NILUFAR**

Department of Bioresource Engineering
Macdonald Campus of McGill University
Montreal, Canada

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**Imagination is more important than knowledge,**
**For knowledge is limited while imagination embraces the entire world**

-Albert Einstein

*This work is dedicated to my beloved parents*
*Md. Firoz Uddin Shah & Doulatun Nesa*
*And also to my two adorable younger brothers*
*S.M. Toufiq and S. M. Shaikh*

# ABSTRACT

In many countries around the world, municipal sewage and industrial wastewaters are typically treated, or sometimes only partially treated, prior to their discharge into surface waters. A major anionic surfactant, Linear Alkyl benzene Sulfonate (LAS), and a degraded product of a non-ionic surfactant, Nonylphenol (NP), are frequently found in municipal wastewaters. When wastewater containing such surfactants and their degraded products is used for irrigation, it can have an effect on the sorption/desorption and movement of pesticides in soils. Therefore, a lysimeter study was conducted, in summer 2004, to assess the effect of LAS and NP on the movement of agricultural herbicides through a sandy loam soil. The degradation of the herbicides was studied in lysimeters over a ninety-day period. Irrigation water with a concentration of 12 mg $L^{-1}$ of LAS and NP was used to assess their effect on the leaching of atrazine, metolachlor, and metribuzin. Moreover, a laboratory sorption experiment was undertaken to estimate the partition coefficients ($k_d$) of the three herbicides with water containing the same concentrations of LAS and NP. Irrigation water containing low concentrations of surfactants (LAS and NP) did not increase leaching of the three herbicides. Therefore, these results would reduce the concerns regarding pesticide leaching through sandy soil brought on by LAS and NP in wastewaters for irrigation, which is becoming more important due to increasing water scarcity in the dry climate regions of the world.

Beside the lysimeter study, mathematical models can be used effectively and economically in a very short period of time for simulating herbicide concentrations into soil. PESTFADE, a one dimensional transient flow model, was used, in this study, to simulate the fate of the three herbicides in sandy soils. Another model, Artificial Neural Network (ANN), was also used over mathematical modeling due to its faster execution period and less input parameter requirements, for predicting the concentrations of the three herbicides in a sandy loam soil. The predicted concentrations, from both models were compared with the experimental results from the lysimeter study. Although slight overestimations and underestimations were observed, both models simulated herbicide concentrations in the soil profile satisfactorily.

# RÉSUMÉ

Dans plusieurs pays de par le monde, les eaux usées municipals et industrielles sont généralement traitées, ou bien partiellement traitées, avant leur evacuation aux eaux de surface. Un important agent de surface anionique, le benzènesulfonate d'alkyle à chaîne droite (BSA), ainsi que le nonylphénol (NP), un produit de dégradation d'un agent de surface non-ionique, se retrouvent fréquemment dans les eaux usées municipales. Lorsque des eaux usées contenant de tels agents de surface, ou les produits de leur dégradation servent à l'irrigation, elles pourraient avoir un effet sur la sorption/désorption et le mouvement de pesticides dans les sols. Une étude en lysimètres fut donc entreprise à l'été 2004, afin de déterminer l'effet du BSA et du NP du sur le mouvement d'herbicides agricoles dans un loam sableux. La dégradation des herbicides fut étudié dans ces lysimètres sur une période de 90 jours. Une eau d'irrigation ayant une teneur en BSA et NP de 12 mg $L^{-1}$ servit à évaluer leur effet sur le lessivage de l'atrazine, le métolachlore, et la métribuzine. De plus, une expérience de sorption en laboratoire fut visa à estimer les coefficients de partage ($k_d$) des trois herbicides dans de l'eau contenant ces mêmes concentrations en BSA et NP. Les eaux d'irrigation contenant de basses concentrations des surfactants BSA et NP n'augmentèrent pas le lessivage des trois herbicides. Ces résultats réduisent donc l'inquiétude qu'il aurait pu y avoir quant à un lessivage de pesticides causé par la présence de BSA et NP dans les eaux usées servant à l'irrigation ; un souci croissant étant donné les pénuries en eau dans les régions sèches du monde.

En plus des études en lysimètre, les modèles mathématiques peuvent rapidement s'avérer éfficaces et économiques pour la simulation des concentrations des herbicides dans le sol. PESTFADE, un modèle d'écoulement transitoire à une dimension, servit dans cette etude, à simuler le sort des trois herbicides dans des sableux. Une modélisation semblable, celle-ci par réseau de neurones formels, fut choisie devant la modélisation mathématique, étant donné son temps d'exécution plus court et le moindre nombre de paramètres d'entrée nécessaires. Les concentrations prédites par chacun des modèles furent compares aux données provenant des expériences en lysimètre. Quoique de petites sur- et sous-estimations furent notes, les deux modèles simulèrent de façon satisfaisante les concentrations d'herbicides dans le profil du sol.

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# LIST OF SYMBOLS AND ABBREVIATIONS

| | |
|---|---|
| APCI | Atmospheric Pressure Chemical Ionization |
| ANN | Artificial Neural Network |
| $^oC$ | Degree Celsius |
| CADD | Conduction Adsorption Diffusion Degradation |
| CESIO | Comite European Des Agents De Surface Et De Leurs Intermediaires Organiques |
| cm | Centimeter (100 cm=1 meter) |
| CMC | Critical Micelle Concentration |
| cmol | Centimole, unit for CEC (cation exchange capacity) |
| DAD | Diode Array Detector |
| DOE | Department of Environment |
| DW | Distilled water |
| CP | Coefficient of performance |
| EF | Model efficiency |
| EPA | Environmental protection agency (United States) |
| ET | Evapotransporation (millimeter) |
| EU | Europe |
| g | Gram |
| GUI | Graphical User Interface |
| HPLC | High performance liquid chromatography |
| ha | Hectare |
| i.e. | That is |
| IUPAC | International Union of Pure and Applied Chemistry |
| $k_d$ | Soil water partitioning coefficient |
| kg | Kilogram |
| $k_{sat}$ | Saturated hydraulic conductivity |
| $k_{oc}$ | Adsorption coefficient |
| L | Liter |
| LAS | Linear Alkylbenzene Sulfonate |

| | |
|---|---|
| LMS | Least Mean Square |
| mg | Milligram |
| min | Minute |
| ml | Milliliter |
| MS | Mass Spectrometry |
| NER | Near Eastern Region |
| NP | Nonylphenol |
| NS | Non-significant |
| P | Statistical probability |
| PAN | Pesticide Action Network |
| PESTFADE | PESTicide Fate and Dynamics in Environment |
| ppb | Parts per billion ($\mu$g $L^{-1}$) or ($\mu$g $kg^{-1}$) |
| ppm | Parts per million (mg $L^{-1}$) or (mg $kg^{-1}$) |
| $\mu$g | Microgram |
| $\mu$L | Microliter |
| OECD | Organization for Economic Co-operation and Development |
| r | Correlation coefficient |
| RMSE | Root Mean Square Error |
| rpm | Revolution per minute |
| RRMSE | Relative Root Mean Square Error |
| S | Significant |
| SD | Standard deviation |
| SE | Standard error |
| SWACROP | Soil Water Actual transpiration and Crop Production |
| Trt | Treatment |
| TW | Tap water |
| US | United States |

# CHAPTER I

# INTRODUCTION

Pesticides are being applied to agricultural lands all over the world for increased crop production, as well as for greater yield. The use of pesticides, therefore, continues to exist as world population and the demand for food production continues to grow. In 1994, Canada used 29.18 million kg of pesticides, which is equivalent to 0.94 kg *per capita*. In France, Italy, and Australia the use of pesticides was reported to exceed 1.8, 2.7 and 6.2 kg *per capita*, respectively (OECD, 1999). At present, the proportion of pesticides used in developing countries is one third of the total value (e.g.US $26 billion) of the world pesticide market (Karlsson, 2004). Also, in the United States, the overall usage of pesticides is 0.99 billion kg per year, which is roughly 4 kg *per capita* (Colborn et al., 1997).

Along with the extensive use of pesticides, concerns regarding potential adverse environmental effects have grown globally. Pesticides have been detected in surface and ground water bodies in many parts of the world. Several studies have shown that Canadian soils and ground waters are polluted with pesticide residue, and in many cases, the concentrations of pesticides exceed the maximum acceptable limit (Masse et al., 1994; Aubin et al., 1993; Patni et al., 1987). In 2003 and 2004, twenty-one pesticides were detected in water samples collected, out of the fifty-eight, from the mouth of the Nicollet, Saint-François, Yamaska and St. Lawrence rivers, of which atrazine and metolachlor were most frequently found (Hébert and Rondeau, 2004). In Europe, pesticide residues were found in 42% of samples collected in 2002, of which 5.1% were above the EU's maximum acceptable residue level for a specific pesticide in a particular food (PAN Europe, 2004). Furthermore, the USEPA (1998) reported that as a result of the agricultural use of pesticides, 46 different pesticides had been detected in ground water and 76 pesticides in surface water bodies.

It has been estimated that less than 0.1% of pesticides applied to crops reach their target pests; however, most of the pesticides enter to the environment, and contaminate soils, water and air, which eventually affects non-target organisms (Pimentel and Levitan, soils, water and air, which eventually affects non-target organisms (Pimentel and Levitan, 1986). Throughout the world, the accumulation of pesticides in food and drinking water has been generally recognized as dangerous, and the long-term persistence and toxicity of pesticides in groundwater is potentially responsible for causing various kinds of human illnesses (Mannion, 1995; Peralta et al., 1994). Studies have shown that 0.22 million deaths occur worldwide each year with 3 million cases of severe pesticide poisonings (Stangil, 2001). In the US, 35% of consumed food has detectable pesticide residues, however, laboratory analytical methods can detect only one-third of the total pesticides that could possibly be present in food due to lower concentrations (Colborn et al., 1997). Consequently, pesticide related illnesses in the US were estimated to occur 0.3 million times a year (Stangil, 2001). Therefore, the use of pesticides and their potentially undesirable effects on the environment and human health has been one of the major concerns of recent research.

## 1.1 Wastewater reuse and surfactants

Besides pesticide usage and their environmental impact, water shortages are a severe problem in several parts of the world. The majority of southern European countries, parts of North America, as well as other African and Asian nations situated on the Mediterranean coasts, are facing water deficits for agriculture (Nurizzo, 2003). As water scarcity is growing, decision makers and planners are considering non-traditional water resources in an attempt to reduce the gap between water supply and demand. As a substitute for fresh water irrigation, wastewater is taking its place in water resource management (Hansen and Kjellerup, 1994).

Wastewater, used for agricultural purposes, contains a variety of compounds; among them surfactants are the most common. These surfactants usually enter the wastewater from the daily use of domestic and industrial cleaning products (dish washing, personal cleaning, clothes and car washing, etc). Surfactants are the primary components in chemical formulations of these cleaning products. Different types of surfactants (anionic, non-ionic, ionic, synthetic, etc.) are being used in these products depending on their applications. Research has shown that the concentration of surfactants and their products in industrial wastewater varies from a few hundred to a few thousand mg $L^{-1}$ (Narkis and Ben-David, 1985), whereas, the concentration in municipal waste water varies from a few $\mu g\ L^{-1}$ to a few mg $L^{-1}$ (Narkis and Ben-David, 1985; Matthijs et al., 1999; Feijtel et al., 1999; Davi and Gnudi, 1999). Therefore, if these wastewaters are used for irrigation can reach agricultural fields.

## 1.2 Effect of surfactants on pesticides movement

Although the presence of surfactants in surface waters and wastewater was detected as early as the 1950's (Freeze and Cherry, 1979), the interaction of pesticides and wastewater used in agricultural fields has not been previously evaluated in much detail. The evidence from several studies indicates that surfactant could either reduce pesticide leaching by increasing the sorption (Valoras et al., 1969; Sanchez-Camazano et al., 1996; Cox et al., 1997; Abu-Zreig et al., 1999), or it could increase leaching potential by increasing mobility of pesticide (Mustafa and Letey 1969; Chiou et al., 1987; Lee and farmer, 1989; Abu-Zreig et al., 2000; Sanchez-Camanzano et al., 2000). Most of these experiments were done in the laboratory using high ranges (500-20,000 mg $L^{-1}$) of anionic and non-ionic surfactant concentrations. However, the hydro-physical properties of soil as well as on the leaching and adsorption of pesticides are depended upon the type of surfactants and the amount used.

Therefore, it is also important to evaluate the fate and transport of pesticides through the agricultural soil profile, after irrigation with municipal wastewater bearing anionic and non-ionic surfactants and their degraded products at concentrations in the order of a few mg $L^{-1}$. Therefore, although the mobility of the three most common agricultural herbicides, atrazine, metolachlor and metribuzin, has been studied under different conditions in several studies (Singh and Kanwar, 1991; McDonald et al., 1999; Heatwole et al., 1997; Jebellie, 1997) the fate of these three herbicides in soils irrigated with municipal wastewater is unknown and needs to be investigated. However, a lysimeter study can be conducted to investigate the interaction between low concentration of surfactants and pesticides in soils that receive untreated or partially treated wastewater.

## 1.3 Mathematical modeling

Field, lysimeter and laboratory experiments are the most effective and practical way to investigate pesticide transport phenomenon in soils, their use permits thorough investigation of selected parameters for a given soil type in a controlled or uncontrolled manner. However, sometimes it is hard to conduct field, lysimeter or laboratory experiment due to lack of research facilities, greater time requirements, and high expenses. As well, these experiments produce site-specific results only (Li et al., 1999). So, mathematical models can also be used effectively as a tool for predicting the extent of pesticides in the environment and their adverse effects on natural resource systems (Liestra, 1973; Mackay et al., 1986; Smith et al., 1991; Lewis et al., 1995; Clemente et al., 1998; Kalita et al., 1998; Kumar et al., 1998; Li et al., 1999; Azevedo et al., 2000; Bakhsh et al., 2004). A wide variety of computer models are available that can quantitatively simulate pesticide leaching in the soil profile and runoff in the aqueous phase. The USEPA's PRZM3 (Carsel et al., 1984), GLEAMS (Leonard et al., 1987), LEACHM (Wagnet and Hutson, 1987), and RZWQM (USDA-ARS, 1992) models are widely used. These models simulate leaching, runoff potential of pesticides, and field-scale drainage patterns. Some of them are also able to make watershed-scale assessments.

PESTFADE is one such model developed by Clemente et al. (1993) and further modified by Li et al. (1999), was used in this study to simulate pesticide transport in the soil profile. PESTFADE is one dimensional model that simulates simultaneous movement of water and solute in unsaturated and homogeneous soils. This model differs from other models because it predicts adsorption/desorption and chemical-microbial degradation under normal/controlled drainage conditions for agricultural fields in arid, semi-arid and humid regions. Also, PESTFADE considers macropore flow and kinetic sorption phenomenon, which makes it an appropriate choice for simulating herbicide concentrations in soil. The model is also user friendly and well tested under various field conditions (Clemente et al. 1998; Li et al., 1999).

## 1.4 Artificial Neural Networks

Along with conventional mathematical models, the search to find an alternative method for fast, simple, and accurate pesticide simulation modeling remains of interest. Mathematical models involve too many input parameters and require long simulation period. A thorough understanding of governing processes is very important for mathematical model, which is sometimes very difficult to simulate. Moreover, various uncertainties arise due to spatial variability of hydraulic conductivities in soil, incorrect input parameters, consideration of macropore flow, which often produce inaccurate predictions. Artificial Neural Networks (ANNs)—which do not require explicit specifications of relationship between inputs and outputs—can be used as an alternative to conventional mathematical models. They can perform complex tasks like pattern recognition, and processes information in a way similar to the human brain. Due to their remarkable ability to derive meaning from complicated or imprecise data by learning from examples, ANNs can be used to extract patterns and detect trends that are too complex to be noticed by either humans or other conventional computer models.

In recent research in the fields of hydrology, agriculture, surface, and subsurface water quality, ANNs have gained remarkable ground for prediction purposes (Hsu et al., 1995; Maier and Dandy, 1999; Schleiter et al., 1999; Ni et al., 2004). ANNs have been effectively used for simulating water table depths in subsurface-drained and subirrigated fields (Yang et al., 1996), and for simulating soil temperature and concentrations of pesticides in agricultural soils and wells (Yang et al., 1997; Sahoo et al., 2004). As well, ANNs have been used effectively to predict nitrate contamination levels in wells (Sahoo et al., 2004), saturated hydraulic conductivity in soils (Lebron et al., 1999), and annual nitrate loss in drain outflow (Salehi et al., 2000).

## 1.5 Objectives

The objectives of this research were to examine the influence of low surfactant levels, commonly present in semi-treated and untreated municipal wastewater, on the movement of three agricultural herbicides, atrazine, metolachlor, and metribuzin in soil. The study's findings could address the environmental acceptability of using municipal wastewater for agricultural irrigation. More specifically, the objectives of this study were:

1. To study the fate and transport of the three herbicides in the presence of anionic and non-ionic surfactants in irrigation water,
2. To perform laboratory studies on the sorption of the three herbicides to support the results of lysimeter findings,
3. To use a mathematical model to simulate the concentrations of the three herbicides in the soil profile, and
4. To use Artificial Neural Networks to simulate the fate and transport of the three herbicides in the soil profile.

### 1.6 Thesis organization

This study is divided into six chapters. The first chapter includes background on the extent of pesticide use, their environmental impact, wastewater reuse and its interaction with pesticides, as well as an overview on the use of mathematical modeling and ANNs, along with a presentation of the study's objectives.

In Chapter II, a detailed literature review is presented on the agricultural and environmental impacts of the three herbicides, atrazine, metolachlor, and metribuzin, as well as their chemical and physical properties. Also, a comprehensive overview of wastewater reuse is presented in this chapter. Out of the many components in wastewater, surfactants are highlighted in this study. Therefore, a comprehensive review of surfactant-soil-pesticide relationships is presented. As well, a review of mathematical modeling and Artificial Neural Networks is presented.

The methodology and results of the lysimeter study are presented in Chapter III. This chapter focuses on the influence of anionic and degradation product of non-ionic surfactants on the movement of the three herbicides in the soil profile. Also, the methodology and results of laboratory sorption studies, as well as numerical results of degradation studies are presented in this chapter for the three herbicides in presence of surfactants.

In Chapter IV, the mathematical model, PESTFADE, is described and employed. The calibration and validation results from the simulation studies are presented for the three herbicides. In Chapter V, an Artificial Neural Network model, using a Cascade

Correlation Algorithm, is described and employed for simulating the herbicide concentrations in the soil profile.

Finally, the thesis is concluded with Chapter VI which summarizes the entire work including lysimeter, laboratory and models studies to investigate the fate and transport of the three herbicides. Also, the major findings of this study are summarized and recommendations for future work are given.

# CHAPTER II

# LITERATURE REVIEW

This chapter reviews previous studies that have investigated the use of pesticides and their fate in the environment. As well, the reuse of wastewater and surfactants in wastewater are reviewed. The effects of wastewater surfactants on the hydro-physical properties of soils, upon which such waters are applied, are reviewed, particularly in the context of their effects on pesticides translocation. Also, mathematical modeling and artificial neural networks are discussed as means to simulate the transport behavior of pesticides into soils.

## 2.1 Pesticide use and their fate

Pesticides are applied to the agricultural fields, all over the world, to promote better crop production. Basically, pesticides were developed as means to produce more food to nourish the growing population; therefore, modern conventional agriculture is heavily depended upon the chemical inputs. There are different groups of pesticides that have been developed depending on the target organism, such as insecticides: control of insects; fungicides: control of fungi; and herbicides: control of weeds. Most of these pesticides are mobile in the environment and this movement is beneficial if the pesticides are used effectively and carried only to a specific target area. However, during the last few decades, concerns have been raised over the impact of agricultural use of pesticides on the environment due their extensive use throughout the world (Yang et al., 2003).

In 1982, pesticide use in United States was about 0.3 billion kg (Kalita et al., 1992). However, it has been reported in 1997 that United States uses 0.99 billion kg of pesticides per year, which is roughly around 4 kg *per capita* (Colborn et al., 1997), and the average farm spent nearly $4200 per year on chemical pesticides (USEPA, 1997).The quantity used by the US represents 20% of the total pesticide used globally, of which herbicides accounted for the largest segment of the pesticide market. In 1994, Canada used 29.2 million kg of pesticides, which was equivalent to 0.94 kg per *capita*. In France, Italy, and Australia the use of pesticides was reported to exceed 1.8, 2.7 and 6.2 kg *per* *capita*, respectively (OECD, 1999). At present, pesticide use in developing countries amounts to one-third of the total money (US $26 billion) spent on pest control products in the world (Karlsson, 2004). These figures of pesticide usage reveal a stable trend in pesticide use throughout the world.

Pesticide contamination of groundwater represents a problem, not only because their chemical toxicity for specific organisms, but also because they are widely and heavily applied in the environment (Canada used approximately 35 thousand tons of pesticides in 1991). In Canada, there is more water underground than on the surface. About eight million people (26% of the population) depend on groundwater. Approximately two-thirds (five million) of these users live in rural areas (The atlas of Canada, 2004). Moreover, most pesticide usage occurs in agricultural areas where over 90% of rural residents obtain their drinking water from wells (Crowe and Milburn, 1995).

According to the briefing of Canadian Water and Wastewater Association in 2000, pesticide contamination of drinking water is becoming a major issue (EDS, 2000). Although concentrations did not exceed recommended Canadian standards, pesticide residues were detected in wells by government monitoring teams across the country. Between 1989 and 1994, 30% of Quebec drinking water systems were found to contain residues of atrazine or its metabolites (EDS, 2000). Atrazine is one of the pesticides most frequently found in surface and groundwater in Quebec, Ontario, British Columbia, Nova Scotia and Saskatchewan. Between 1985 and 1986, Health Canada detected the pesticide aldicarb in 80% of samples, and aldicarb and its metabolites are highly persistent in groundwater. In Prince Edward Island, concentrations sometimes exceeded the recommended standards for drinking water (EDS, 2000). In 1998, an Ontario well survey detected atrazine in one sample to be at 210 ppb, some 40 times the Canadian guideline of 5 ppb. Also, between 2003 and 2004, twenty-one pesticides of fifty-eight analyzed pesticides have been detected in water samples taken from the St. Lawrence River and its tributaries (Hébert and Rondeau, 2004). In the U.S., public attention was first captured when pesticide residues were found in Love Canal in New York (Logan, 1993). Atrazine has also been found in 30% of water samples in Europe. In the United States, over 273 thousand tones of pesticides enter the environment every year (Stevenson et al. 2003). In 68,000 wells in 45 states of the US, 16,000 wells in 42 states were found to contain pesticides. Approximately 10,000 of these wells contained pesticide concentrations which exceeded EPA drinking water standards (EDS, 2000). Agricultural pesticide use has set off a continuously ringing alarm in developing countries for the past 30-40 years, and these countries are also experiencing negative human-health and environmental side effects (Karlsson, 2004). Therefore, the extensive use and detection of pesticides has led scientists to study the fate of pesticides so as to define the processes by which surface and ground water is getting contaminated.

### 2.1.1 Atrazine in the environment

The chemical name of atrazine is *2-chloro-4-ethylamine-6-isopropylamino-S-triazine* (Kidd et al., 1991) and the chemical structure is shown below:

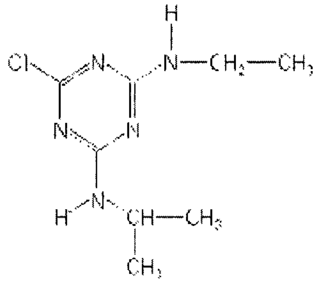


**Figure 2.1 Chemical structure of atrazine** (Worthing and Hance, 1991)

Atrazine is a selective triazine herbicide used to control broadleaf and grassy weeds in corn (*Zea mays* L.), sorghum, sugarcane, pineapple, Christmas trees and others crops. This is available as dry, liquid, water dispersible granular and wettable powder formulation. In 1990, over 24 million hectares of crop land were treated with atrazine in the U.S (EXTOXNET, 1996).

Atrazine is highly persistent in soil. Most of the breakdown usually occurs by chemical hydrolysis and degradation by soil microorganisms. The rate of hydrolysis increases in proportion to the organic material in the soil. Hydrolysis is rapid in acidic or basic environments, but slower at neutral pH. Atrazine is moderate to highly mobile in soil and does not adsorb strongly to soil particles. The half life of atrazine is 60 to 100 days and it has a high potential for groundwater contamination (Wauchope et al., 1992). In private wells and in community wells, atrazine is found to be the second most common pesticide (U.S. National Library of Medicine, 1995). In 1990 the National Survey of

Pesticides in drinking water found atrazine in about 1% of all wells. Furthermore, concentrations of atrazine exceeding the EPA's maximum contamination level (MCL) have been detected from the Mississippi, Ohio and Missouri Rivers and their tributaries (US Department of the Interior, 1991). Atrazine is one of the most frequently detected herbicides in the St. Lawrence River and its tributaries in Canada. In the Yamaska River, atrazine loading rate was estimated to be 27.7 kg day$^{-1}$; which is approximately 54% of the total atrazine loading in Quebec City (Hébert and Rondeau, 2004).

Standards and guideline values (GV) for atrazine residues in drinking water for different countries (IUPAC technical report, 2003) are listed below

**Table 2.1 Concentration level of atrazine residues ($\mu$g L$^{-1}$)**

| | WHO | USA | New Zealand | Australia | Canada |
|---|---|---|---|---|---|
| | *GV* | *MCL* | *MAV* | *GV* | *MAC* |
| Atrazine | 2 | 3 | 2 | 0.5 | 5 |

MAC-Maximum Accepted concentration MAV- Maximum Accepted value MCL- Maximum concentration level

### 2.1.2 Metolachlor in the environment

The chemical name of metolachlor is *2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide* and the chemical structure is as follows:

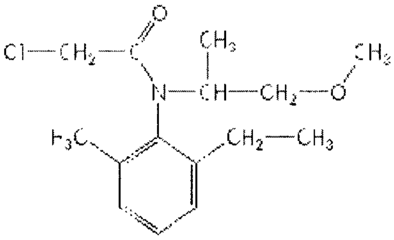


**Figure 2.2 Metolachlor chemical structure** (Worthing and Hance, 1991)

Metolachlor is used in the control the broadleaf weeds in field corn, soybeans, peanuts, grain sorghum, potatoes, pod, highway right-of-ways and woody ornamentals. It is usually applied on the field before crop emergence.

Metolachlor is mobile in the soil, easily leached, and resists breakdown for long periods of time. The factors affecting the breakdown of the compound are temperature, moisture, microbial activity, soil type, nitrification, oxygen concentrations and sunlight.

The half-life has been found 30-50 days in northern areas and 15-25 days in southern areas (American Conference of Governmental Industrial Hygienists, 1991). Metolachlor is stable to breakdown in acidic water and at 20°C, the half life is more than 100 days, and in highly basic waters, the half life is 97 days (Cummings et al., 1992). Because of its slow microbial and anaerobic degradation rates, metolachlor has the potential to contaminate the groundwater by leaching through the soil. Metolachlor was detected in about one percent of the wells (about 60,000 wells) at concentrations ranging from 0.1 to 1 ppb (Lu, 1995; U.S. EPA, 1985). Metolachlor has also been found in surface water at maximum concentration of 138 ppb in 14 states in the U.S. (Lu, 1995). In the St. Lawrence River and its tributaries in Canada, metolachlor is also one of the most frequently detected herbicides (Hébert and Rondeau, 2004). In 2003, IUPAC reported the guideline values (GV) for metolachlor for different countries (Table 2.2).

**Table 2.2 Concentration level for Metolachlor residues ($\mu$g $L^{-1}$)**

| Pesticide | WHO | USA | New Zealand | Australia | Canada |
|---|---|---|---|---|---|
| | *GV* | *HA* | *MAV* | *GV* | *MAC* |
| Metolachlor | 10 | 100 | 10 | 2 | 50 |

MAC-Maximum Accepted Concentration MAV- Maximum Accepted Value HA-Health Advisory

### 2.1.3 Metribuzin in the environment

Metribuzin is a triazine herbicide which inhibits the photosynthesis in susceptible plant species. Usually, it is used to control annual grasses and broadleaf weeds in field and vegetable crops, in turfgrass and on fallow lands. The chemical name of metribizin is *4-amino-6-tert-butyl-4, 5-dihydro-3-methyltio-1, 2, 4-triazin-5-one* (Kidd et al., 1991) and chemical structure is as follows:

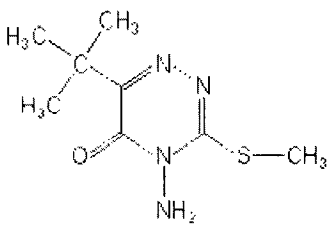


**Figure 2.3 Metribuzin chemical structure** (Worthing and Hance, 1991)

Metribuzin is of moderate persistence in the soil. The half life of metribuzin is approximately 60 days and varies according to the soil type and climatic conditions (Wauchope et al., 1992). Metribuzin is soluble in water, and poorly bound to most soils, which confers upon it a strong potential to leaching down towards the ground water. Metribuzin has been detected in Ohio Rivers and Iowa wells and in groundwater (USEPA, 1985, 1988). Soil microbial degradation is the major mechanism for the loss of metribuzin over volatilization and photo-degradation. Guideline values (GV) for metribuzin in drinking water as reported by IUPAC (2003) are given in Table 2.3.

**Table 2.3 Concentration level for Metolachlor residues ($\mu$g L$^{-1}$)**

| Pesticide | USA | New Zealand | Australia | Canada |
|---|---|---|---|---|
| | *HA* | *MAV* | *GV* | *MAC* |
| Metribuzin | 200 | 70 | 1 | 80 |

MAC-Maximum Accepted Concentration MAV- Maximum Accepted Value HA-Health Advisory

## 2.2 Reuse of wastewater

Fresh water, once used for an economical or beneficial purpose, is generally discarded as waste. In many countries, these waste waters are discharged, as untreated waste or as treated effluent, into natural watercourses from which they are abstracted for further use after undergoing dilution and some degree of degradation within the stream. Thus, indirect reuse of wastewater may have occurred up to a dozen times or more through this system before being discharged to the sea. Such indirect reuse is common in the larger river systems of Latin America and many other countries (Cavallini and Young, 2002).

Eighty-eight developing countries, housing close to one-half of the world's population, already experience water deficits, with resulting constraints on human and environmental health, as well as economic development. In near eastern region (NER), out of 29 member states, 16 are classified as under water deficit, with less than 500 m$^3$ person$^{-1}$ yr$^{-1}$ renewable fresh water resources (FAO, 1997a). In rural and pre-urban areas of most developing countries, the use of sewage and wastewater for irrigation is a common practice (e.g. across Asia, Africa, Latin America, etc). Wastewater is often the only source of water for irrigation in these areas, even in areas where clean water sources exists; small farmers prefer wastewater because of its high nutrient content which reduces the need for expensive chemical fertilizers (IWMI, 2003). The USEPA (1992) reported that the world's population has grown 1.5 times over the second half of the 20th century and urban populations have grown 3 times. As the population growth increases, it eventually leads to greater domestic water use; therefore, good-quality water resources available for agricultural use tend to decrease. Global water use has increased ten times between 1900 and 2000, and on a global scale, about 70% of water from available sources is used for agricultural purposes, primarily for irrigation (FAO, 1997a). Haruvy (1997) reported that within the next four decades, treated sewage effluent will become the main source of water for irrigation in Israel. The effluent will meet 70% of the agricultural water demand, and play a dominant role in sustaining agricultural development. In Palestine, to meet future irrigation demand recycled wastewater will be used as the primary water source in the forthcoming decades (Sbeih, 1996). As well, Fedler et al. reported an interesting case study with increasing commercial demand for wastewater that had originally been land applied as a disposal mechanism (Fedler et al., 1987). Moreover, 42 countries across the world were listed by Scott et al. (2000), as having done some research on wastewater reuse for agricultural purposes.

Standards for wastewater reuse for irrigation in many countries have been influenced by the USEPA (1992), NRC (1996), OAS (1997) and Environment ACT (1999) guidelines. The use of wastewaters for irrigation, containing several chemicals may have an effect on the movement of pesticides into and through the soil. One of the most common chemicals in wastewater is surfactants, which come from the use of detergents, hand washes, and from several personal cleaning agents.

### 2.2.1 Surfactants in the Environment

Municipal wastewater is the aggregate of all water used and disposed off in a community. The mean per capita domestic waste water flow rate for the United States is 200-500 L person$^{-1}$ day$^{-1}$ (Barber et al., 1995). The synthetic-organic chemical composition of municipal wastewater is a function of the various products consumed by individual households and the contribution of industrial effluents. In most developing countries, municipal wastewater is partially treated or may remain untreated prior to their discharge into surface waters.

The land application of wastewater and sludges has been an important management option, particularly in arid regions, where water is scarce and where waste water can serve as a source for irrigation. The transport of water and chemicals through the soil is usually governed by factors such as the type of solute, moisture content of soil, and the chemical, physical and hydraulic properties of the soil. Irrigation with wastewater and land application of sludge can add large amount of organic chemicals to the soil-water system, eventually resulting in an increased amount of dissolved organic chemical in the infiltrating water (Hutchins et al. 1985). The highest concentration of organic chemicals discovered in wastewater and sludges, originate from detergents containing anionic and non-ionic surfactants (Field, 1990; Field et al., 1992; Wild et al., 1990). These surfactants have been recognized as the most abundant group of organic chemical in municipal wastewater (Brunner et al., 1988). In the United States, about 7 million tons of biosolids are produced annually in wastewater treatment plants and several million kilograms of surfactants could be potentially released to soil through land application of wastewater (Xia, 2001). Therefore, the long-term application of waste water will result in an increase of the less biodegradable surfactants in the soil-water system (Abu-Zreig, 2003).

There are several kinds of surfactants used in personal cleansing, household and industrial cleaning products, such as anionic, non-ionic, cationic and amphoteric (SDA, 2004). Among them, anionic and non-ionic surfactants are the most commonly found surfactants in the environment, and are described briefly below.

#### 2.2.1.1 Anionic surfactant: Linear alkylbenzene sulfonate

Anionic surfactants (negatively charged) are used in laundry and hand dishwashing detergents, household cleaners, and personal cleaning products. They ionize in solution and have excellent cleaning properties. There are various kinds of anionic surfactants available such as linear alkyl benzene sulfonate (LAS), alcohol ethoxysulfates, alkylsulfates and soap. Among them, LAS is the most important class of anionic surfactants with an estimated world consumption rate of 1.8 million metric tons

(Terzić and Ahel, 1994). In Denmark and Western Europe, consumption was 485 metric tons and 7000 tons, respectively (Berth et al., 1989; Borglum et al. 1994). The consumption of LAS in the United States is about 300,000 metric tons year$^{-1}$ (Schirber, 1989). More than 60% of these LAS are used in domestic and industrial cleaning agents. Once they are used in a detergent or personal cleaning agent, eventually they enter the sewage system and will lead them to the treatment plant before their discharge to the environment. They are shown to be common contaminants in municipal and industrial wastewaters and in the rivers as well (Terzić and Ahel, 1994). The LAS and their byproducts are nontoxic to humans, but aquatic organisms can be sensitive to concentrations ranging from 10-1000 μg L$^{-1}$ (Kimerle and Swisher, 1977; Kimerle, 1989).

In 1994, the research from the Council for LAB/LAS Environmental Research (CLER) measured LAS concentrations in different rivers around the world (Table 2.4). At present up to 3.1 × 10$^{5}$ km of rivers in United States have less than 4 μg L$^{-1}$ of LAS. It has been found that the presence of surfactants in surface waters causes extensive foaming in some cases. In particular, the highly branched anionic surfactants cause foams at concentrations 0.5 mg L$^{-1}$ in wastewater (Green et al., 2003; Richard, 2003). In Nepal, if the worst case scenario is assumed, such that all of the wastewater generated by laundry washing was discharged into the Bagmati River, the resulting total concentration would be about 0.2 mg LAS L$^{-1}$ (Richard, 2003).

**Table 2.4 Concentration of LAS in different rivers**

| Countries/Rivers | LAS concentration | Year |
|---|---|---|
| Illinois River, USA | 0.54 mg L$^{-1}$ | 1959-1964 |
| Rhine River, Germany | 0.01 mg L$^{-1}$ | - |
| Tama River, Japan | 2.5 mg L$^{-1}$ | 1968 |
| Chao River, Thailand | 0.34 mg L$^{-1}$ | 1983 |
| Mississippi River, USA[a] | 0.1-10 μg L$^{-1}$ | 1995 |

[a] Barber et al., 1995

One of the LAS biodegradation studies found LAS concentration in wastewater of about 5.2 mg L$^{-1}$ (Matthijs et. al., 1999). Feijtel et al. (1995) reported concentration in the inlet to wastewater treatment plants (WWTP's) was around 15 mg LAS L$^{-1}$. In 1999, 12.5 mg $L^{-1}$ LAS were predicted in terms of the conventionally low sewage flow of 200 L $person^{-1}$ $day^{-}$ in the Netherlands (Feijtel et al., 1999). The raw sewage concentrations of LAS recorded from eight Swiss sewage treatment plants ranged from 0.95-3.9 mg $L^{-1}$ and the effluent concentrations from secondary clarification ranged from 7-330 $\mu g$ $L^{-1}$ (Brunner et al., 1988). The input and distribution of linear alkylbenzenesulphonates (LAS) in the Kirka river estuary were studied in 1990-1991. It was found that municipal wastewaters contained LAS at total concentrations of 285-1041 $\mu g$ $L^{-1}$ and at the most polluted part of the estuary, Ŝibenik Harbour, the total LAS input via wastewaters was 12.6 kg $day^{-1}$ (Terzić and Ahel, 1994).

### 2.2.1.2 Non-ionic surfactant: NonylPhenol ethoxylate

*Non-ionic* surfactants (not charged) are typically used in laundry and automatic dishwasher detergents and rinse aids. They do not ionize in solution and they are resistant to water hardness and clean well. The non-ionic surfactants hold the second place in the worldwide surfactants consumption, amounting to over 8 million tons a year in the 1990s. Out of the non-ionic surfactants, the polyoxyethelene alcohols which are often synonymous with non-ionic surfactants hold the third place after soaps and alkylbenzene sulphonates (LAS). Alkylphenol ethoxylate (APEO) surfactants have been used for more than 40 years in a variety of industrial processes and cleaning products. It has been estimated that the net worldwide production of APEOs exceeds 500,000 tons annually, consisting of approximately 80% nonylphenol ethoxylates (Bennett and Metcalfe, 1998; Ahel et al., 1996; Hawrelak et al., 1999). A majority of APEO surfactants currently in use in North America are the nonylphenol polyethoxylates (NPEOs).

Nonylphelol Ethoxylates (NPEs) are an important class of non-ionic surfactants that have been widely used in detergent formulations, both industrial and domestic. Due to their suitability for liquid detergents, the domestic use of nonylphenol ethoxylate-based detergents has increased in the USA and many other countries. The global demand for alkylphnol ethoxylate (APE) in household detergents is estimated at 0.45 million tons. In the US, APEs used in laundry and industrial applications include ethoxylated octyl, nonyl and dodecylphenols. Among them, nonylphenol ethoxylate (NPE) is the largest volume product used almost exclusively in household detergent applications (Canada Gazette, 2001). It is important to specify in this review that NPEs are also used as wetting agents and as dispersants or emulsifiers in some pesticide formulations and also agrochemicals (Evangelou, 1998).

Because surfactants are most widely used in aqueous solutions, these compounds are discharged directly into the environment via industrial and municipal wastewater treatment systems (Ahel et al., 1994a, 1994b). NPEs most common degradation product is nonylphenol (NP), which enters the environment via industrial and municipal wastewater. Several transformations occur to NPEs when it enters the sewage systems. Initially, the ethoxylate (EO) groups are removed and NPEs end up as less biodegradable compounds, such as NP, NP1EO, and NP2EO. Many surfactants commonly used in household and commercial cleaners are not tested for in effluent discharge by municipal wastewater plants, even though they represent significant percentage of surfactants entering the wastewater plants. Around populated centers, environmental concentrations of surfactants and their degraded products in the inland waters range between 0.005 mg $L^{-1}$ and 2 mg $L^{-1}$ (www.enviro-solution.com). The concentration of NP in the sediments of Lake Ontario is 37 $\mu g$ $L^{-1}$ and >300 $\mu g$ $L^{-1}$ in the sewage sludge. The NP concentrations in sewage treatment plants of Canada are generally in the range of approximately 100-500 $\mu g$ $L^{-1}$ (Bennie et al., 1997; Bennett et al., 1998), where as, the sewage treatment plant of Switzerland has shown that the NP concentration ranged from <0.5-419 $\mu g$ $L^{-1}$ in municipal wastewater (Veŝtak and Ahel, 1994). A concentration of 7-12 mg $L^{-1}$ of non-ionic surfactants has been found in the effluents from a municipal sewage treatment plant in Israel (Narkis and Henefeld-Furie, 1977). Veŝtak and Ahel (1994) reported the concentrations of NP varied from 0.5-419 μg $L^{-1}$ in municipal wastewaters of Croatia. In 2001, 200 μg NP $L^{-1}$ was found in the influent wastewaters and up to 23 μg $L^{-1}$ of NPE parent compounds and their metabolites were detected in the WWTPs effluents discharged into the Kansas River (Xia, 2001). The concentration of NP in the secondary effluent and digested sludge at the Zurich-Glatt WWTP in Switzerland were found to be 2.7 mg $L^{-1}$ and 78 mg $kg^{-1}$ (dry weight basis) (Brunner et al., 1988; Ahel et al., 1994). Rudel et al. (1998) found a total concentration of 30 mg $L^{-1}$ for nonyl / octylphenol and polyethoxylates in ground water immediately down gradient from septic systems and leach fields in the Cape Cod area of Massachusetts. Total alkylphenol levels were reported to be as high as 80 mg $L^{-1}$ in an Italian river and were attributed to domestic and industrial waste discharges (Davi and Gnudi, 1999). Other researchers have also investigated the occurrence and distribution of alkylphenol compounds in Great lakes sediments (Hawrelak et al., 1999), as well as the aquatic environment of the rivers and estuaries in England and Wales (Blackburn and Waldock, 1995). The concentrations of APE degradation products, especially NP, in treated waste water effluents in the US ranged from 0.1-369 μg $L^{-1}$, in Spain from 6-343 μg $L^{-1}$ and in UK up to 330 μg $L^{-1}$ (Ying et al. 2002). The Environment Agency for England and Wales (1998) showed that 46% of the bulk of NPEs is reaching the soil, through sludge from the polluted sewer system being spread on agricultural land, in the form of less biodegradable product NP.

Right from the above review, it is clear that surfactants, especially anionic and non-ionic, are being used widely in detergents throughout the world. Therefore, the extensive use of detergents, and eventually their presence in wastewater, led the scientists to carry out experiments to investigate their effects on soil properties, as well as on organic chemical movements, when wastewater is used for irrigation purposes.

## 2.3 Effect of surfactants on soil properties

Surfactants possess a large hydrophobic hydrocarbon chain with a hydrophilic polar end that may contain either an anion or cation or have neutral properties. The hydrophobic portion reacts slightly with water molecules, whereas the hydrophilic polar end interacts strongly with water molecules and may cause a decrease in surface tension and increase water penetration into the soil. To artificially improve soil structure and infiltration capacity, surfactants have been used as soil conditioners since the 1960's (Mustafa and Letey, 1969). The purposes of these wetting agents are to decrease the solid liquid contact angles and improve water flow and hydro-physical properties of soil (Pelishek et.al., 1962; Miyamoto, 1985). These surfactants are similar to those detected in municipal wastewater in their chemical group but differ in chemical structure, chemical characteristics and physical properties. Usually the qualities of detergent surfactants are evaluated in terms of detergency in water and the effect on soils. The effects of detergent surfactants, which eventually come to be present in wastewater as organic chemicals, on the physical properties of soils are of interest. Very little information is available regarding the effect of surfactants present in municipal wastewater on soil properties and as well as on organic chemical transport into soil (Abu-Zreig, 2003; Foy, 1992).

Miyamoto (1985) studied six wetting agents, three non-ionics and three anionics, on infiltration through loamy sand, clay loam, and silty clay soils. He found that anionic surfactants were more efficient in improving infiltration than non-ionic surfactants. The addition of polyvinyl alcohol (PVA) and polyacrylamide (PAM) resulted in an increase of hydrophobicity in sandy soil and decrease in hydrophobicity in silty loam soils (Hartmann et al., 1976). Similar results were observed by El-Asswad and Groenevelt (1985) and Kijne (1967). An increase in hydraulic conductivity may cause an increased infiltration rate. The main factors that affect the soil hydraulic properties in presence of surfactants could be the solution surface tension and solid-liquid contact angle (Pelishek et al., 1962). Poiseuille's law describes the quantity of water that can be infiltrated into the soil in terms of surface tension and solid-liquid contact angle:

$$Q = \frac{nr(\rho rgh - 2\sigma \cos \theta)}{8L\mu}$$

Where

| | |
|---|---|
| $Q$ | depth of water entering into the soil per unit time (L T$^{-1}$) |
| $n$ | soil porosity(L$^{3}$ L$^{-3}$) |
| $r$ | effective pore radius (L) |
| $\rho$ | liquid density (M$^{3}$ L$^{-3}$) |
| $g$ | gravitational acceleration (L T$^{-2}$) |
| $h$ | distance from water surface to wetting front (L) |
| $\mu$ | liquid viscosity (M T$^{-2}$) |
| $\sigma$ | surface tension |
| $L$ | distance from soil surface to wetting front (L) |
| $\theta$ | solid liquid contact angle |

Surface tension, $\sigma$, and solid liquid contact angle, $\theta$, have received attention in surfactant studies. A decrease in liquid solid contact angle would increase infiltration, whereas the opposite would happen when there is a decrease in the liquid surface tension. The net effect of a surfactant on infiltration depends on the value of $\sigma \cos\theta$ (Pelishek et al., 1962; Mustafa and Letey, 1971). Furthermore, when the depth of the wetting front is small, surface tension and contact angle has their greatest influence on infiltration rate.

However, the influence of surface tension and contact angle becomes smaller when the wetting front gets deeper (Pelishek et al., 1962).

## 2.4 Surfactants and pesticides

Surfactants have been added to various agrochemicals to improve their efficacy as some downward movement of these agrochemicals is desirable (Chow et al., 1992; Hill et al., 1972). However, few studies have been conducted on the movement of pesticides in presence of surfactants (Bayer, 1966; Pitblado, 1972), and very little work has been done on the effect of surfactants commonly present in partially treated or untreated municipal wastewater.

Surfactants, present in wastewater, can increase, decrease or cause no effect on the movement of pesticides. It depends on the type and concentration of surfactants, type of pesticides, soil type, and soil-water conditions. Bayer (1967) studied the effect of 23 surfactants, 4 anionic, 6 cationic and 13 non-ionic, on the depth of leaching of urea herbicides in a sandy clay loam soil. According to his results a 1% concentration of each surfactants (1 anionic, 11 non-ionic, and 2 cationic) increased the depth of leaching of diuron. Increasing the amount of anionic surfactants up to 10%, resulted in further increases in the depth of leaching. In the case of cationic and non-ionic surfactants the movement of pesticides was decreased.

The application of anionic surfactant (sulphonic) decreases the capillary rise and penetrability and increases the solid-liquid contact angle and sorptivity (Abu-Zreig et al., 2003). An anionic surfactant with a concentration of about 3000 mg $L^{-1}$ resulted in sorption of atrazine and an significant increase of $K_d$ (partition coefficient) in a sandy loam soil (Abu-Zreig et al., 1999), while the application of non-ionic (Rexol and Rexonic) surfactants increase leaching (Abu-Zreig et al., 2000). In contrast, the effect of surfactants on the adsorption and movement of atrazine has been reported as being negligible (Huggenberger et al., 1973). Other studies have shown that non-ionic surfactants at a concentration of 0.2% could increase the adsorption of liadane and diuron. At higher concentrations of 0.5% to 1.0%, the surfactants led to a decrease in adsorption of those two pesticides (Pitblado, 1972; Huggenberger et al., 1973; Foy, 1992). Furthermore, the alkyl sulfate anionic surfactants (sodium dodecyl sulfate, SDS) were shown to decrease adsorption and actively desorb pollutants from soil and eventually allow the cleaning up of the contaminated soil (Dentel et al., 1993; Sanchez-Camazano et al, 2000). Among the findings research has also shown that surfactants can cause contaminants to move more rapidly through the vadose zone and reach the water table more quickly than if no surfactants was used (Henry and Smith, 2003). Pitblado (1972) concluded that the anionic surfactants had a greater effect on herbicide movement than do non-ionic surfactants.

A study with 3 non-ionic surfactants at a concentration of 2% resulted in increased movement of trifluralin and oryzalin in sandy soil. The addition of surfactants in dry soil had more effect on herbicide movement than in wet soil (Koren, 1972). Foy (1992) found that atrazine movement went deeper when the soil was pre-leached with water.

These above experiments mostly focused on the effects of high concentrations of surfactants, as are usually found in industrial wastewater. A few laboratory experiments have shown that at low concentrations surfactants did not have any significant effect on organic chemical movement through soil (Huggenberger et al., 1973). The relation among surfactant, pesticide and soil-water system is nonconforming and it is difficult to predict the total effect of surfactants on pesticide movement.

Referring to the review of literature, it seems that experiments on pesticide leaching have been done using a wide range of surfactants. Most experiments were done using high concentration of surfactants in the laboratory. However, very few studies have been carried out to evaluate the fate and transport of pesticides through soil after irrigation with municipal wastewater or water from surface water bodies (rivers, lakes, ponds, etc), which contains surfactants in lower concentrations (few mg $L^{-1}$).

## 2.5 Mathematical modeling

Computer simulation modeling offers an alternative approach to laboratory, lysimeter and field experiments, to study the impact of various farming practices on the fate and transport mechanism of herbicides from agricultural areas. Several mathematical models have been developed in last two decades coinciding with the rapid increase in the use of agrochemicals. Generally, mathematical models do not give a complete picture of the various aspects of the complex processes occurring in the soil. A necessary aspect of a mathematical model is over-simplification, which may lead unrealistic responses of the model in certain cases. In contrast, computer modeling can be more economical, faster, and environmentally safe in comparison with large field-scale experiments, when characterizing the contamination potential from pesticide usage (Jaynes and Miller, 1999).

To assess the effects of agricultural chemicals on water quality, various models such as GLEAMS (Leonard et al., 1987), PRZM3 (Carsel et al., 1984), OPUS (Smith and Ferreira, 1986), LEACH-P (Wagnet and Hutson, 1986, 1987) have been developed.

**GLEAMS:** The Groundwater Loading Effects of Agricultural Management System (GLEAMS) model (Leonard et al., 1987; Knisel et al., 1993) is a functional model used to simulate processes affecting water quality events on an agricultural field. It is a modified version of the well-validated CREAMS (Knisel, 1980) model. The GLEAMS model is used to simulate water quality events on an agricultural field. GLEAMS has been used to evaluate the hydrologic and water quality response under several scenarios, considering different cropping systems, wetland conditions, subsurface drained fields, agricultural and municipal waste application, nutrient and pesticide applications, and different tillage systems. Three submodels included are, hydrology, erosion/sediment yield, and chemical transport. The hydrology component simulates runoff due to daily rainfall using a modification of the SCS curve number method. Hydrologic computations are determined using a daily time step. A modified Universal Soil Loss Equation (USLE) is used to estimate inter-rill and rill detachments. Different topographic configurations and surface flow processes were taken into account to properly assess the sediment detachment and deposition on the land surface. The chemical transport submodel is further subdivided into nutrient and pesticide components. The pesticide component of the GLEAMS incorporates the surface pesticide response of CREAMS with a vertical flux component to route pesticides into, within, and through the root zone. Characteristics of pesticide adsorption to soil organic carbon are used to partition compounds between solution and soil fractions for simulating extraction into runoff, sediment, and percolation losses. Pesticide dissipation in soil and on foliage is treated as a first-order process with a different apparent half-life for each. The nutrient component of the GLEAMS is a multifaceted submodel and considers both nitrogen and phosphorus cycles. Tillage algorithms are also included in the model to account for the incorporation of crop residue, fertilizer and animal waste.

Prediction of atrazine concentrations, conducted by Ma et al. (2000), using GLEAMS model was found to be within two orders of magnitude of the observed values. Connolly et al. (2001) conducted a study to investigate the effect of different management scenarios on the transport of endosulfan by using GLEAMS model. It was concluded that due to an increase in infiltration and reduction in erosion, the transport of endosulfan was minimized. But high rainfall event could possibly result in severe endosulfan leaching. A 50-year simulation was carried out by Gorneau et al., (2001) to test the effect of different herbicide and tillage practices. The GLEAMS model was found to perform well in simulating subsurface drain water quality (Baksh et al., 2001). The model considers simple linear adsorption, and does not consider preferential flow, two-site sorption kinetics and volatilization (Vanclooster et al., 2000).

**PRZM:** EPA's PRZM3 (Carsel et al., 1984) links two models, PRZM and VADOFT. PRZM is a one dimensional dynamic, compartmental model used to simulate chemical movement in unsaturated soil system and can simulate as many as three chemicals simultaneously. It has two major components, hydrology and chemical transport. Hydrologic component calculate and simulate runoff and erosion by SCS and USLE equation, evapotranspiration by empirical equation or pan evaporation data, water movement using soil parameters, field capacity, wilting point, saturation water content. Chemical transport component simulates pesticide concentrations in soil as dissolved, adsorbed and vapor phase; also the transport and transformation of nitrogen induced by atmospheric decomposition can be simulated. Transport equations are solved by a backward-difference implicit scheme or with a characteristics algorithm that eliminates numerical dispersion. VADOFT is a one dimensional finite element model, which solves for flow in the vadoze zone. These two models are linked together to a flexible execution supervisor that allows building a model that is tailored to site specific situations. PRZM3 incorporates soil temperature simulation, volatilization and vapor phase transport in soil, irrigation simulation, and microbial transformation (Malone et al., 1999). The model is capable of estimating probabilities of concentrations in or from various media. Monte Carlo pre- and post-processors are provided to perform probability based exposure analysis. One of the limitations of this model is over simplification, where first-order rate constant is assumed to be fixed value. Also, the flow of solute in fractured porous media, preferential flow, two-site sorption kinetics and volatilization are not considered by the model (Vanclooster et al., 2000).

PRZM has been well tested using field data (Kaluli et al., 1997; Ma et al., 1999; Ma et al., 2000; Chu et al., 2000). Vischetti et al. (1995) used PRZM2 model to predict the fate of napropamide and pendimethalin in soils. High discrepancies in model simulation were observed in this case. GLEAMS, Opus, PRZM2β, and PRZM3 were used by Ma et al. (2000) to predict atrazine losses in a loamy sand soil under convention tillage practice. PRZM2β overestimated the atrazine concentrations, which was might be due to an unrealistic mixing model. However, the predictions by GLEAMS and PRZM3 were within two orders of magnitude of the observed concentrations. Also, Ma et al. (1999) used GLEAMS and PRZM2 to simulate 2, 4-D in a small turf plot. Underestimations were observed for both the models, which was thought to be due to the inaccurate calculations involved in the partitioning of the compounds. The transport of metribuzin was conducted by Malone et al. (1999) using GLEAMS and PRZM3 under three field conditions. Underestimations in metribuzin concentrations were observed at 75 cm and at 15-75 cm soil depth by both the models. In the subsurface soil regions, PRZM3 provided better prediction and GLEAMS gave good prediction in the sediment runoff. However, Malone et al. (1999) concluded that the model performance could have been improved by adding macropore component in both the models.

**LEACHP:** Leaching estimation and Chemistry (Wagnet and Hutson, 1986, 1987) is a simulation model to simulate non-volatile pesticides in the unsaturated soil profile. With a high level of sophistication and flexibility, LEACHP model can simulate water and solute movement with a great accuracy. Three different versions of the model are available, which are capable of calculating instantaneous and reversible pesticide sorption. The convection-dispersion equation is used to simulate pesticide movements.

However, the runoff, management practices, crop yield, macropore flow and degradation products of applied pesticides are not included in LEACHP model (Clemente et al., 1993). Smith et al. (1991) used PRZM and LEACHP models to predict the fate of atrazine in a soil column study and concluded that underestimations, in both models, were due to simplistic approach for adsorption of pesticides calculation and non-consideration of preferential flow.

Based on the above review, it can be stated that most of these models possess some limitations, such as preferential flow and non-equilibrium sorption have not been considered in GLEAMS, LEACHP, or PRZM. PRZM is limited to non-volatile pesticides since the vapor phase partition coefficient has not been considered. The runoff, erosion, drainage systems, and agricultural management practices have not been considered in LEACHP, which represents a limitation of this model.

To improve all the above mentioned limitations Clemente et al. (1991, 1993) developed the Pesticide Fate and Dynamics in the Environment model (PESTFADE), which can simulate water and solute movement simultaneously in the unsaturated soil profile. The special features of the model are: it includes macropore flow based on two-site non-equilibrium sorption kinetics, state-of-the-art mathematical expressions for pesticide transport model, heat flow, moisture flow and runoff as well as water table management practices in arid and semi-arid regions. Also, instead of treating $K_d$ as constant, PESTFADE adjusts $K_d$ according to changes in soil temperature, sorption capacity of soil, and soil tortuosity (Li et al., 1999). PESTFADE has been validated against field data (Clemente et al., 1993; Clemente et al., 1998; Li et al., 1999). GLEAMS and PESTFADE model were used to determine atrazine movement in a clay loam soil by Kaluli et al. (1997). It was concluded that PESTFADE results were improved with lower standard error when macro pore component and two-stage sorption kinetics were incorporated. Therefore, macro pore flow component and two-site kinetic sorption approach make PESTFADE unique and appropriate for pesticide simulations in soil. Moreover, Tafazoli (2003) made a graphical user interface for PESTFADE which make the model user-friendly and interactive.

## 2.6 Artificial Neural Networks

Mathematical modeling usually needs a numerous input parameters and in many cases, these inputs parameters are not readily available. To be able to make an accurate simulation the thorough understanding of physical and chemical transport phenomenon is a prerequisite. Also, the over-simplified assumptions for the mathematical models sometimes made the model to predict the real situation inaccurately; as well these models require longer time for execution. Nevertheless, an artificial neural network (ANN) can be a substitute for mathematical modeling in simulating herbicide concentrations in soil. ANNs are an information processing system, which processes information in a manner similar to that of the human brain, learning from examples, and which are composed of highly interconnected processing elements (neurons) involved in solving a specific problem. This field was established before the advent of modern computers, but this field initially met with great frustrations and was poorly regarded. Currently, ANNs are an important and successful new field of interest.

Neural networks work in a manner similar to the human brain, but due to the complexity of human neurons and limited computing power, neural networks may differ considerably from the human brain in detail. However, the following minimum characteristics of neural networks are common to the human brain. An artificial network is a basic processing unit including many inputs and one output (Figure 2.4). Inputs are fed to the neural network from another processing unit or from outside. All the inputs are *weighted* and the execution is dependent on the weight of a particular input. The summation function provides the *weighted sum* of input values and is compared with the pre-set threshold values. The *threshold value* indicates if the sum reaches the threshold; if so, the signal will be transmitted, otherwise the signal will not transmit. Two operations are involved with processing unit, training and using mode. In the training mode, the neural network is trained, repeating the process of transmission for specific inputs, to learn certain patterns. When the trained input pattern is found, the related output becomes the current output in the using mode. Neural network can adapt to a particular situation by changing the *weights* or *thresholds*. Among various existing algorithms that cause the neural network to *adapt*, *Delta rule* and *back error propagation* are the most common. Generally, delta rule is used in *feed-forward* networks and back error propagation is used for *feedback networks* (Stergiou and Siganos, 1996). Also *feed forward back propagation* can be used in ANN models (Sahoo et al. 2004). In a feed-forward network, the signals travel one way from input to output (Figure 2.5). On the other hand, in feed-back networks the signals can travel in both directions, which introduce a loop into the network.

Typically, artificial neural networks consist of three layers: input layer, hidden layer, output layer (Figure 2.5). Neural networks with *error propagation* incorporated, have certain characteristics: (i) one or more hidden layer(s), (ii) all units within a layer are connected to all units of the next layer, and (iii) there are no connections between non-successive layers (Braspenning et al., 1995). Input layers contain the data or examples that are fed to the network. The starting values of input nodes are multiplied by the weight associated to those nodes and they move to the hidden layer. The weighted sum is then transmitted towards output layer by an appropriate transfer function (Shaoo et al, 2004; Zhang et al., 1999). The general principle for all training prototype in ANN is to minimize the differences between output values obtained from the output layer and known values that were fed as input through certain number of epochs (runs).

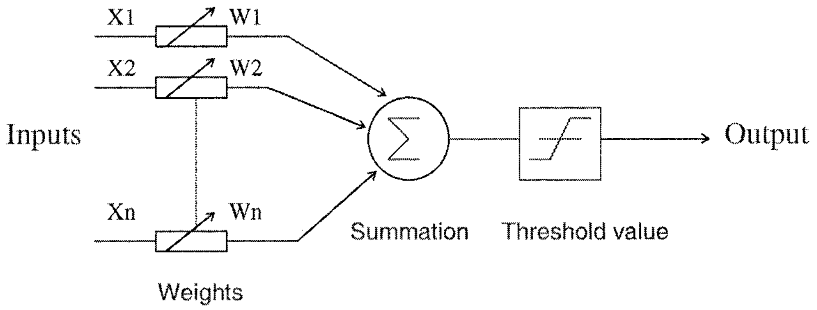


**Figure 2.4 The components of processing unit**

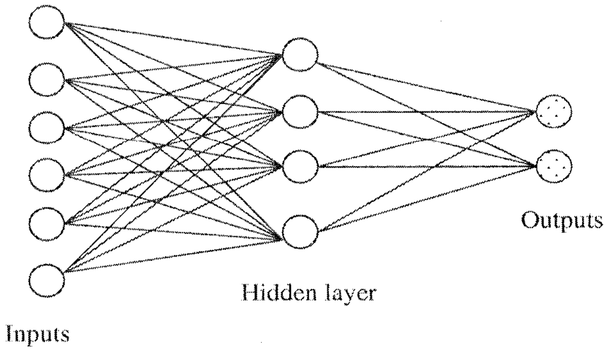


**Figure 2.5 Feed-forward neural networks**

Neural networks have the capability to derive meaning from complex dataset, and also can be able to obtain patters from the dataset to detect trends, which are too complex to notice either by humans or by conventional computers. Pattern recognition is one of the popular applications of neural networks, which is implemented by using a feed-forward neural network. While training or learning, neural networks are trained to relate outputs with the given input patterns and neural network gives the output corresponding to the trained input pattern that is almost similar to the given pattern. The other advantages of neural networks reported by Stergiou and Siganos (1996) are: adaptive learning, self-organization, real-time operation, and fault tolerance via redundant information coding. Due to the ability to identify patterns or trends in any datasets neural networks are successfully and widely used in sales forecasting, industrial process control, customer research, data validation and also in medical fields (Stergiou and Siganos, 1996). In recent decades the uses of neural networks has extended to the fields of agriculture, hydrology, and water quality prediction (Yang et al., 1997; Yang et al., 1998; Salehi et al., 2000; Yang et al., 2000; Ni et al., 2004; and Sahoo et al., 2004).

## 2.7 Concluding Remarks

Pesticides are the most extensively used agrochemicals in the agricultural fields throughout the world. Along with the use, concerns regarding potential adverse environmental effects of these pesticides have grown globally. Also, water shortage is another severe problem in most of the arid and semi arid regions. Consequently, decision makers and planners are considering non-traditional water resources in an attempt to reduce the gap between water supply and demand. As a substitute for fresh water irrigation, wastewater is smetimes being used to irrigate agricultural fields. Wastewater usually contains a variety of compounds and among them; surfactants are the most commonly found compounds. When agricultural fields are receiving wastewater and pesticides simultaneously, surfactants may affect the pesticide mobility in soil due to their effect on soil adsorption/desorption properties. Numerous studies have been conducted concerning pesticide mobility in the presence of surfactants. However, most of these studies were done in the laboratory. Very little work has been done to investigate the effect of surfactants present in municipal wastewater, on pesticides movement. An outdoor lysimeter study can be useful to investigate the effect of surfactants on pesticide movement into soil, considering spatial variability, soil heterogeneity and climatic variability.

Beside the lysimeter experiment, mathematical modeling is the most economical method to study the fate and transport of pesticides into soil. These models provide a rapid means to simulate the extent of pesticide, risk assessment, and may also save time. PESTFADE can be a good choice for pesticide simulation since it incorporates pesticide sorption mechanisms and preferential flow.

One problem with mathematical modeling is that they often require a number of input parameters, which are usually not easily measurable. Also, some models take a long time to execute, which may become a critical factor while defining or evaluating new management practices or strategies. ANN models can be used for modeling pesticide movement in such cases. They are generally very fast and require considerably less input parameters.

# PREFACE OF CHAPTER III

Pesticides' fate in the environment and the effect of surfactants on pesticide leaching and adsorption were reviewed in the preceding chapter (Chapter II). Due to the increasing water scarcity throughout the world, the use of wastewater for irrigation is becoming popular. In many countries, municipal wastewater is being discharged into the surface water bodies as treated, partially treated or untreated and is eventually being used for irrigation. The most abundant organic chemicals present in wastewater are surfactants; therefore, when wastewater or water from effluent-rich rivers is used for irrigation they might increase or decrease the mobility of pesticides, depending on the surfactants' properties. Thus it is important to understand the behavior of pesticides in the soil profile when wastewaters containing surfactants are being used. Therefore, a lysimeter study was undertaken to determine the fate and transport of three agricultural herbicides (atrazine, metolachlor and metribuzin) in the presence of irrigation water bearing surfactants. The experimental procedure and results of an experiment conducted in the summer of 2004 are presented in this chapter (Chapter III).

The role of the candidate, as the main author of the manuscript, was to investigate the effect of surfactants on movement of the three herbicides in agricultural soil. The author was also responsible for performing all analytical and statistical analyses.

**Research paper based on the chapter:**

Nilufar, F. and S.O. Prasher. Fate and transport of herbicides in agricultural soils in the presence of surfactants in irrigation water. (Manuscript to be submitted to the *Transactions of the ASAE*).

# CHAPTER III

## FATE AND TRANSPORT OF THREE HERBICIDES IN AGRICULTURAL SOIL IRRIGATED WITH MUNICIPAL WASTEWATER

### ABSTRACT

In many countries around the world, municipal sewage and industrial wastewater are treated to some degree prior to their discharge into surface water bodies. Frequently found in municipal wastewater are Linear Alkyl benzene Sulfonale (LAS), a major anionic surfactant, and the degraded product of non-ionic surfactant Nonylphenol (NP). When wastewater containing surfactants and their degraded products is used for irrigation, it can affect the sorption/desorption and movement of pesticides in soils. Therefore, a lysimeter study was conducted to assess the effect of LAS and NP on the movement of three agricultural herbicides through a sandy soil. Nine lysimeters, irrigated with water containing LAS and NP, at a concentration similar to those commonly found in municipal wastewater or highly effluent reach river, were used to evaluate the fate and transport of three common herbicides, atrazine, metolachlor and metribuzin. The fate and transport of the three herbicides was studied over a ninety-day period. The results show that the herbicides leached down to 0.2 m of the soil profile, for the three treatments, with considerable concentrations and degraded faster over time. Irrigation water with a concentration of 12 mg $L^{-1}$ of LAS and NP had almost no effect on the leaching of atrazine, metolachlor, and metribuzin. The herbicide concentrations found in leachates, taken 0.9 m below the soil surface, were less than 0.02 $\mu$g $L^{-1}$. To measure the sorption behavior, a laboratory experiment was undertaken to estimate the partition coefficients ($k_d$) for the three herbicides with water containing the same concentration of LAS and NP. In the presence of LAS, increase in $k_d$ values were observed for atrazine and metribuzin, however, the sorption was not significantly altered for the three herbicides in the presence of NP. Hence, these results should help to reduce the concerns regarding pesticide leaching brought on by wastewaters containing LAS and NP for irrigation.

**Keywords.** Linear alkylbenzene sulfonate, nonylphenol, wastewater, atrazine, metolachlor, metribuzin.

## 3.1 Introduction

Land application of wastewater and sewage sludge is an important management option in many countries, where wastewater is being discharged, untreated or semi-treated, into natural watercourses and on the land surfaces (Bauer, 1974). The use of wastewater for irrigation has became more important due to increasing water scarcity; it has been found to already be a common practice in rural and pre-urban areas across the Asia, Europe, Africa, and Latin America (IWMI, 2003).

Municipal wastewater usually contains a variety of compounds, both organic and inorganic; the most abundant organic chemicals are surfactants and their degraded products (Brunner et al., 1988). Anionic and non-ionic surfactants are the most common type of surfactants used in domestic and industrial detergents, which end up in municipal and industrial wastewater as well as in rivers (Painter, 1992, Field, 1990; Wild et al., 1990). The presence of surfactants in surface water was detected in the 1950's (Freeze and Cherry, 1979; Twelfth Progress Report, 1977). At present, environmental attributes for surfactants often receive much attention for their technical properties and economic aspects, and the surfactants are designed to remain stable for short period of time before breakdown into its components, despite the fact that foaming has been observed at sewage treatment plants (Stratton, 2005) and on effluent rich rivers and streams, and has not been faded completely (Britton, 1998).

In 1991, the estimated use of detergents in the United States was more than 2.2 million tons (Greek, 1991). The U.K. consumption in 1990 was in the range of 16 to 19 thousand tons (DOE, 1993). In 2003, the global surfactant market was estimated about 12 billion tons. In developed countries, the use of surfactants is forecasted to increase by 20% within 2001-2012, whereas in Asia, the demand could increase by 70% (CESIO, 2004). Research has shown that concentration of surfactants and their products in the industrial wastewater varies from a few hundred mg $L^{-1}$ to few thousand mg $L^{-1}$ (Narkis and Ben-David, 1985), whereas in municipal wastewater, the concentration varies from a few $\mu g\ L^{-1}$ to few mg $L^{-1}$ (Narkis and Ben-David, 1985; Matthijs et al., 1999; Feijtel et al., 1999; Davi and Gnudi, 1999).

Surfactants have indigenous adsorption/desorption properties and are good solvents for organic compounds (Liu et al., 1991). Surfactants are amphibilic molecules having two components, a hydrophilic or water soluble head group and a hydrophobic or water insoluble tail group. At low concentrations, surfactants stay as monomers, however, at high concentrations, surfactants form self-aggregates (micelles) and surface tension tends to reduce. After a certain concentration, surface tension becomes constant, which is known as the critical micellar concentration (CMC). Surfactants above the CMC level may greatly increase the solubility of less hydrophilic organic pollutants, as shown in the figure 3.1 (Sanchez-Camanzano, et al., 2000).

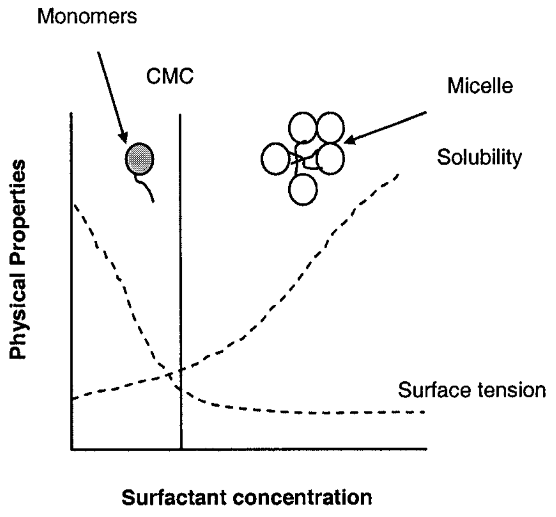


**Figure 3.1 Schematic diagram of organic chemical solubility with surfactant concentration.**
[Source: Mulligan et al., 2001]

When surfactants come in contact with solids, they may also decrease/increase liquid-solid contact angles, which can affect liquid infiltration into a soil according to Poiseuille's law:

$$Q = \frac{Cr^2 \rho g h}{8 L \eta} + \frac{2 C \gamma \cos \theta}{8 L \eta} \qquad (1)$$

where,

| | |
|---|---|
| Q | is the quantity of liquid entering the soil per unit surface area per unit time ($L\,T^{-1}$) |
| C | is the volume fraction of the wet soil ($L^3\,L^{-3}$) |
| r | is the effective pore radius (L) |
| $\rho$ | is the liquid density ($M^3\,L^{-3}$) |
| g | is the gravitational constant ($L\,T^{-2}$) |
| L | is the distance from soil surface to wetting front (L) |
| $\eta$ | is the liquid viscosity ($M\,T^{-2}$) |
| $\gamma$ | is the liquid surface tension, and |
| Cos $\theta$ | is meant for the liquid-solid contact angle. |

From the equation, it can be seen that the increase in surface tension ($\gamma$) may result in the increase of infiltration; conversely, an increase in the liquid-solid contact angle ($\theta$) would decrease infiltration. The increase/decrease in liquid-solid contact angle would increase/decrease the soil aggregate dispersion. When the depth of the wetting front (L) is small, surface tension and contact angle would have an influence on infiltration; this is not the case when the depth is large (Pelishek et al., 1962).

In 1960s, surfactants were used to improve the physical conditions of water-repellent soils to control erosion and for water management by increasing the water infiltration (Pelishek et al., 1962). Mustafa et al. (1969) reported that surfactants not only increased the dispersion of soil aggregates, but also decreased the aggregate stability of soil. Moreover, herbicide formulations contain surfactants in order to accentuate downward movement in the soil (Jansan et al., 1960). Several studies have been carried out by using surfactants with herbicides in the spray system, and it has been observed that high concentrations of surfactants enhanced herbicide mobility and decreased adsorption of herbicides, with the reverse holding true for low concentrations of surfactants (Huggenberger et al., 1973; Bayer, 1966; Hill et al., 1965).

When wastewater is used for irrigation, its prolonged use may result in the leaching of the less biodegradable surfactants to ground water (Freeze and Cherry, 1979; Field et al., 1992). Therefore, surfactants might also influence the downward movement of pesticides by increasing their solubility (Dentel et al., 1993). Agricultural lands receiving municipal wastewater and pesticides simultaneously might lead to increased leaching and/or increased adsorption of pesticides. Studies have been done to evaluate the effect of high concentrations of surfactants on the hydro-physical properties of soil as well as on the leaching and adsorption of pesticides (Abu-Zreig et al., 1999; Sanchez-Camanzano, et al., 2000). However, little work has been conducted to evaluate the fate and transport of pesticides through the agricultural soil profile, after irrigation with municipal wastewater, which contains amounts of surfactants and their degraded products in the order of a few mg $L^{-1}$.

Although the mobility of three agricultural herbicides, atrazine, metolachlor and metribuzin, has been studied under different conditions (Singh and Kanwar, 1991; Weber et al., 1993; Heatwole et al., 1997; Jebellie, 1997; McDonald et al., 1999) the fate of these three herbicides in soils irrigated with municipal wastewater is unknown. Thus, the objective of this research is to examine the influence of low surfactant levels, commonly present in semi-treated and untreated municipal wastewater, on the movement of three agricultural herbicides, atrazine, metolachlor, and metribuzin. The findings from this study could be used to ascertain the environmental acceptability of the use of municipal wastewater for agricultural irrigation, especially when fresh water is scarce.

## 3.2 Materials and Methods

### 3.2.1 Experimental design

The experiment was conducted in nine outdoor lysimeters, which were set up at the Macdonald Campus of McGill University, Ste-Anne-De-Bellevue, Quebec. The PVC lysimeters (0.45 m diameter × 1 m high), sealed at the bottom using 0.6 m × 0.6 m PVC sheets, were packed with sandy soil in layers to a bulk density of 1350 kg $m^{-3}$. A 0.05 m diameter drainage pipe was installed at the bottom portion of each lysimeter. Four 0.01 m soil sampling holes (laterally) were made in each lysimeter at 0.1, 0.2, 0.4, and 0.7 m depths from the surface. To simulate the worst case scenario for pesticide movement and to avoid plant uptake, no crop was planted. All lysimeters were placed under a rain cover so as not to allow rainfall.

The experiment was conducted in triplicate with three different types of water applications: tap water, anionic surfactant with water, and a degraded product of non-ionic surfactants with water. Wastewater was prepared in the laboratory by using only the surfactant and degraded product in water at a concentration of 12 mg $L^{-1}$. Anionic surfactant (Alkylbenzene Sulphonic acid) and the degraded product (Nonylphenol) of non-ionic surfactant were supplied by Huntsman Corporation (Houston), and their physical and chemical properties are presented in table 3.1.

**Table 3.1 Physical and Chemical characteristics of surfactants used in the study**

| Property | Anionic surfactant | Non-ionic surfactant |
|---|---|---|
| Chemical name | Alkylbenzene sufonic acid | Nonyl Phenol |
| Product code and name | SALS Sulfonic Acid LS | MNP Nonylphenol |
| Appearance | Liquid | Viscous liquid |
| Water solubility | > 10% | <0.1 |
| Specific gravity | 1.05 | 0.95 |
| Viscosity | not determined | 400 cSt at 37.8°C |
| pH | 2 | 7.1 |
| Molecular weight, gmol$^{-1}$ | 317 | 220 |
| Vapor pressure, mmHg | 0.002 | <1 at 20°C |
| Boiling point, °C | 330 | 293.3 |
| Odor | not determined | Phenolic |

Reference: HUNTSMAN 2002

### 3.2.2 Soil characteristics

The soil belongs to the St. Amble complex, obtained from a field at Macdonald College of McGill University. Table 3.2 shows the physical properties of the soil. The metrological data was collected from Environment Canada (Ste-Anne-De-Bellevue station). Throughout the study period, the average air temperature, humidity and evaporation were 19.8°C, 71.85% and 3.93 mm day$^{-1}$, respectively. Irrigation was simulated by pouring the amount required for corn fields under no rainfall and high evapotranspiration. On days 2, 10, 20, 30 and 90, 44 mm irrigation was applied and then 70 mm irrigation was applied on days 40, 50, 60, 70 and 80, according to the corn (*Zea mays* L.) water requirement in the dry climate region (Benham, 2004).

**Table 3.2 Physical properties of soil**

| | | | |
|---|---|---|---|
| Sand | 92.20% | Organic Matter Content | 2.97% |
| Silt | 4.30% | Hydraulic conductivity | 3.68 m day$^{-1}$ (SD[a]=0.87) |
| Soil type | Sand | pH | 5.5 |
| Bulk Density | 1350 kg m$^{-3}$ | CEC | 4.9 cmol kg$^{-1}$ |

[a]SD=standard deviation

### 3.2.3 Pesticide application

Three herbicides, atrazine (*2-chloro-4-ethylamine-6-isopropylamino-S-triazine)*, metolachlor (*2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide*), and metribuzin(*4-amino-6-tert-butyl-4, 5-dihydro-3-methyltio-1, 2, 4-triazin-*

*5-one*) were sprayed on all lysimeters once on July 22, 2004. The three herbicides were applied at the locally recommended rate of 2.5 kg active ingredient $ha^{-1}$, 1 kg active ingredient $ha^{-1}$ and 2.75 kg active ingredient $ha^{-1}$, respectively.

### 3.2.4 Sampling method

After the application of herbicides, soil and leachate samples were taken from each lysimeter on days 0, 2, 5, 10, 21, 30, 50 and 90. Before each sampling, the stagnant water in the sampling tube at the bottom port of the lysimeters was emptied to take representative samples. The leachate samples were taken after each irrigation, and to inhibit the microbial reactions in the leachate samples, 10 ml of methelene chloride was added to each sample bottle prior to refrigeration. About 7 g of soil samples were taken after each irrigation from the soil surface and each of the four sampling ports. The soil samples were frozen until the extraction and analysis were done.

### 3.2.5 Extraction of pesticide residues

The water samples were mixed with 100 ml of dichloromethane (methylene chloride) in a separatory funnel. The mixture was hand shaken for few minutes, and the accumulated organic phase was collected from the bottom of the funnel; this process was repeated twice. The extracted organic phase was evaporated to separate dichloromethane from the herbicides. The residues were then dissolved in about 2 ml of hexane and stored in the refrigerator prior to liquid chromatography (LC) analysis. For the analysis of soil samples, each soil sample was mixed with 100 ml of methanol for 1 hour using a mechanical shaker. The mixture was transferred to a vacuum flask (Buchnel flask), and filtered under partial vacuum. The collected organic phase was evaporated in a water bath for 15 minutes and rinsed with 2 ml of hexane. The organic phase was then stored in a 5 ml glass vial in the refrigerator prior to LC analysis.

### 3.2.6 Analysis of soil extracts and water samples

Pesticide residues in soil and water samples were analyzed with an Agilent 1100 series Liquid Chromatograph with Mass Spectrometa (LC/MS), equipped with a column, an injector, an auto sampler, a Diode Array Detector (DAD), and an Atmospheric Pressure Chemical Ionization (APCI) detector. A C-8 column (4.6 × 150 mm) was used for the retention of organic compounds, and the column temperature was maintained at 40°C. Methanol, buffer, water, and acetonitryle were used as mobile phases. The buffer was prepared with 1 g of ammonium acetate in 1 L of distilled water. The method used to seperate the three herbicides in one run is summarized in the Tables 3.3 and 3.4. One mL of each sample was transferred to mini-vials, and the injection volume was set to 5 $\mu$L. Calibrations were performed with analytical standards for each herbicide within the concentration ranges of $10^{-2}$ to $10^{2}$ $\mu$g L$^{-1}$, and the correlation coefficient was determined by linear regression, typically with $r^2 \geq 0.95$. The machine (HPLC) detection limits were 0.5 $\mu$g L$^{-1}$ for atrazine, and 1 $\mu$g L$^{-1}$ for both metribuzin and metolachlor.

**Table 3.3 The LC flow rate and the mobile phase percentages**

| LC Flow rate | | Mobile Phase | | | |
|---|---|---|---|---|---|
| Time, min | Flowrate, ml min$^{-1}$ | Buffer % | Water % | Methanol % | Acetonytrile % |
| 0-20 | 0.4 | 40 | 20 | 15 | 25 |
| 20-40 | 1 | 0 | 0 | 22.5 | 37.5 |

**Table 3.4 The spray chamber parameters**

| | | | | |
|---|---|---|---|---|
| Dry gas flow | 6 L min$^{-1}$ | Dry gas temperature | 355°C ~ | 0-20 min |
| Nebulizer pressure | 60 psig | | 325°C ~ | 20-30 min |
| Mode of analysis | SIM | Vaporizer temperature | 275°C ~ | 0-20 min |
| | | | 400°C ~ | 20-30 min |
| | Positive | Negative | | |
| Capilary voltage | 4500 | 4500 | | |
| Corona current, μA | 10 | 10 | | |

Statistical analysis of herbicide concentrations at four depths observed over time was done for atrizine, metalochlor, and metribuzin, separately, using spatio-temporal analysis (SAS Institute, 1990). There were three replicates for each treatment, of which two replicates were taken into account for SAS analysis. The third replicate was taken off from the analysis because of the discrepancy in concentrations of the three herbicides due to the low hydraulic conductivity in those lysimeters. In this regard, the detailed information of the three herbicides in soil, at different depths, as well in leachate is presented in the Appendix (Table 1-3).

### 3.2.7 Sorption studies

The laboratory sorption test was carried out to assess the sorption behavior of atrazine, metolachlor and metribuzin in soil with LAS and NP. The dry sandy soil was sieved through a 2 mm sieve. The percent moisture was determined by oven dry method at 105° C for 24 hours. In a 60 mL centrifuge tube, 5 g of soil was added to 10 mL (*3, 15, 30, 60 mg* $L^{-1}$) of each herbicide solution and 20 ml of DW, LAS (*18 mg* $L^{-1}$) and NP (*18 mg* $L^{-1}$), separately. Therefore, the initial concentration of each herbicide was *1, 5, 10,* and *20 mg* $L^{-1}$, while initial concentration of LAS and NP solution was *12 mg* $L^{-1}$. The experiment was done in triplicate. Soil solutions with mixture were allowed to equilibrate for 24 hours, and were centrifuged at 4000 rpm for 20 minutes. After the completion of the centrifugation, the samples of the supernatant were collected and analyzed with LC/MS, which was taken as final concentration or equilibrium concentration. The adsorption coefficient, $k_d$ ($cm^3\ mg^{-1}$), for each herbicide was fitted using Freundlich relationship:

$$C_{ad} = k_d \times C_{sol}^{n} \qquad (2)$$

where, $C_{ad}$ *is* adsorbed concentration, mg $kg^{-1}$, $C_{sol}$ is concentration in equilibrium solution, mg $L^{-1}$, and n is Freundlich coefficient (n=1).

## 3.3 Result and Discussion

### 3.3.1 Effect of LAS and NP on herbicide residues in water

The leachate samples were analyzed to quantify the amount of atrazine, metolachlor and metribuzin leaching to the shallow ground water. The results for the three herbicide concentrations in leached water from the lysimeters are shown in Figure 3.2. The concentrations of all three herbicides, atrazine, metolachlor and metribuzin, were found to be very low in the water samples. This is most likely due to the adsorption of herbicides in the upper soil profile. Moreover, the lysimeters were exposed above the ground surface; therefore, high soil temperature would have also caused increased biodegradation and left less herbicide available for leaching. Although, throughout the ninety-day experimental period, the concentration of atrazine and metolachlor were found in trace amounts, metribuzin was not detected in the leachate at all after 20 days. This could be due to the high water solubility of metribuzin, which would have biodegraded faster at high temperatures, as compared to atrazine and metolachlor.

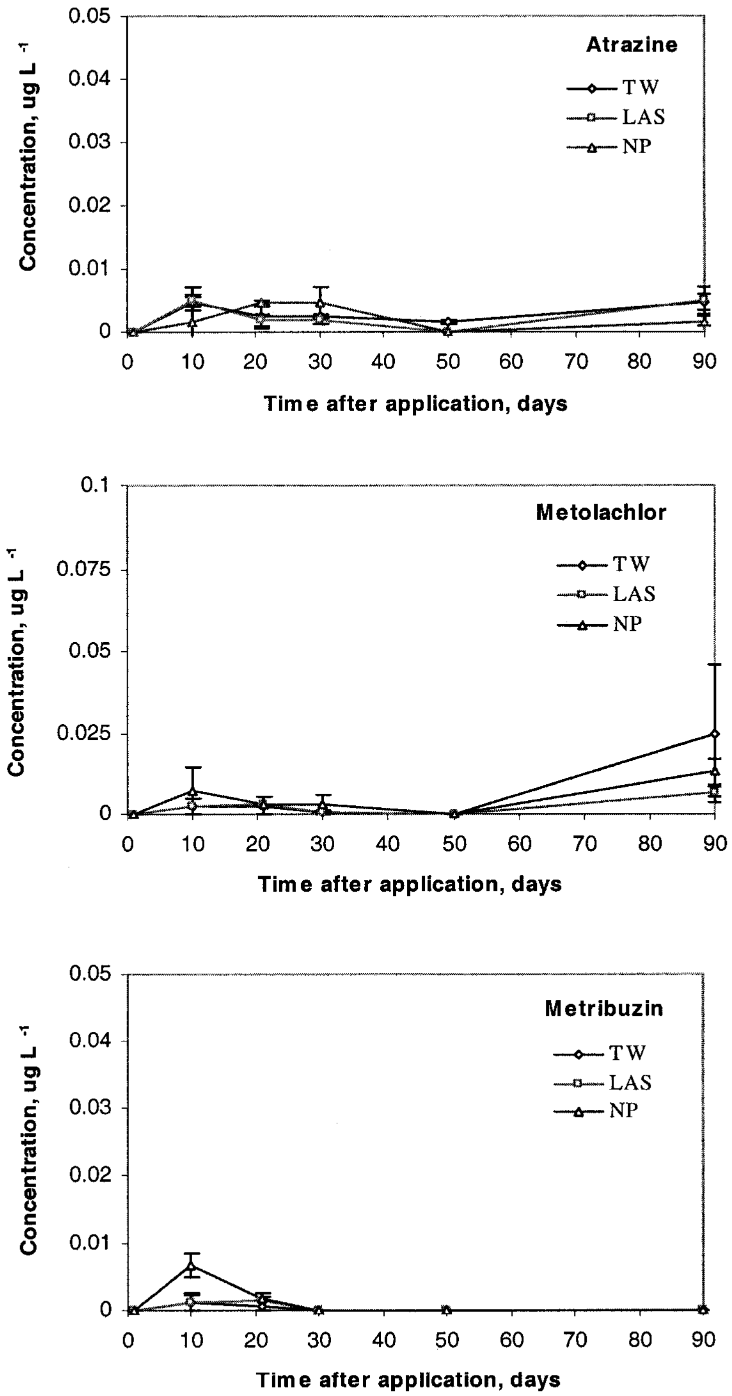


**Figure3.2 Atrazine, metolachlor and metribuzin residues in water samples (TW- tapwater, LAS- Linear alkylbenzene, and NP- Nonylphenol)**

The highest concentrations of atrazine, metolachlor, and metribuzin in the leachates were 0.005, 0.02, and 0.01 $\mu$g $L^{-1}$, respectively. These concentrations are much lower than the maximum allowable concentrations of 5, 50, and 80 $\mu$g $L^{-1}$, set by IUPAC (2003) for drinking water in Canada. Although slight variations in concentrations among the three treatments were observed, the concentrations of the herbicides were very low, and the relative variations between treatments were of little importance for practical purposes. Therefore, it can be concluded that there was no remarkable effect, either by LAS or NP, in irrigation water on the concentrations of the three herbicides in the leachates.

### 3.3.2 Effect of LAS and NP on herbicide residues in soil

The movement of the three herbicides in the sandy soil was also assessed in the presence of LAS and NP in irrigation water and compared with tap water (TW) irrigation. Figures 3.3, 3.4 and 3.5 present the average values of the three herbicides concentrations in soil over a ninety-day period for the top soil, as well as for 0.1, 0.2, 0.4, and 0.7 m soil depths. As expected, at the soil surface, the concentrations (mg $kg^{-1}$) of the herbicides were high, as compared to the concentrations ($\mu$g $kg^{-1}$) at different depths of the soil profile. It was observed that the herbicides leached only up to 0.1 m soil depth with considerable concentrations, which reveals that herbicides would degrade by chemical and biological processes over time rather than leach down to lower depths. At the 10 cm depth, all three herbicide concentrations had an upward trend at the beginning of the ninety-day period, followed by a gradually decreasing trend (Figure 3.3, 3.4 and 3.5). At 0.2, 0.4, 0.7 m soil depths, the trend was similar to 0.1 m depth; however, concentrations were much lower, as compared to 0.1 m depth. Moreover, the concentrations of herbicides at 0.4 and 0.7 m were very low, and tended to be non-detectable. For metolachlor, the concentrations at 0.7 m depth were non-detectable, therefore, not shown in the figure (Figure 3.4). The decrease in concentrations of the herbicides over time and depth reveals that herbicides moved downwards as well as degraded over a period of time. Such decreases demonstrated a significant depth and time effect *($P \leq 0.05$)* for all the three herbicides (Table 3.5).

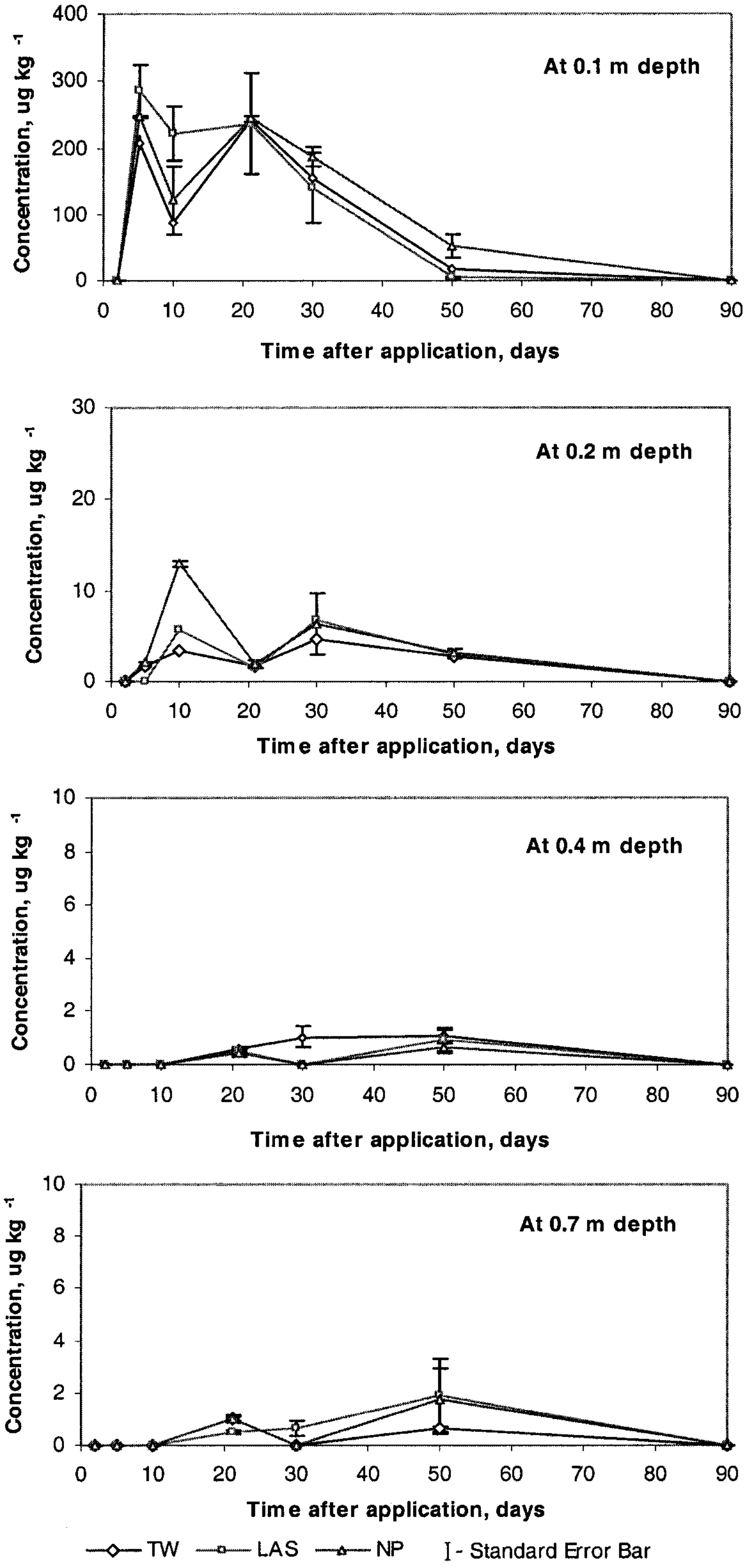


Figure 3.3 Atrazine concentrations at different depths of the soil profile over time (TW-tapwater, LAS- Linear alkylbenzene, and NP- Nonylphenol)

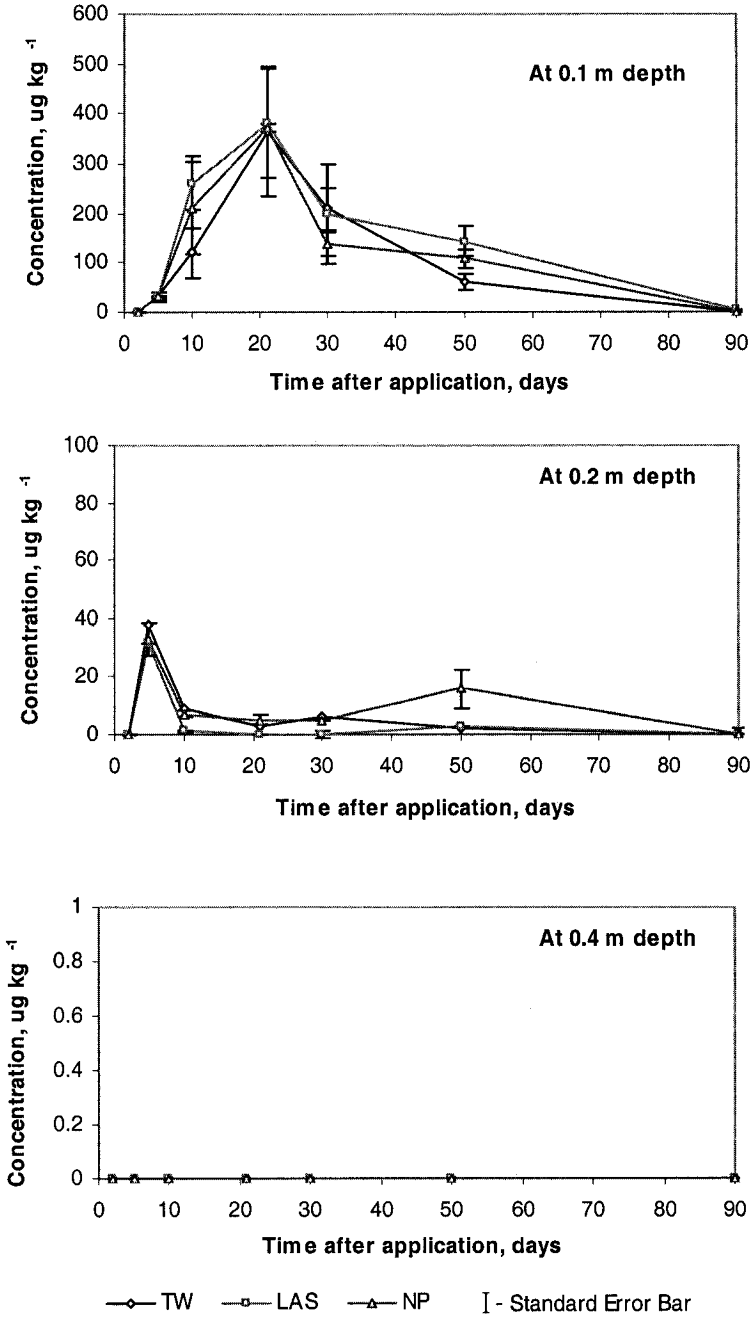


**Figure 3.4 Metolachlor concentrations at different depths of the soil profile over time time (TW- tapwater, LAS- Linear alkylbenzene, and NP- Nonylphenol)**

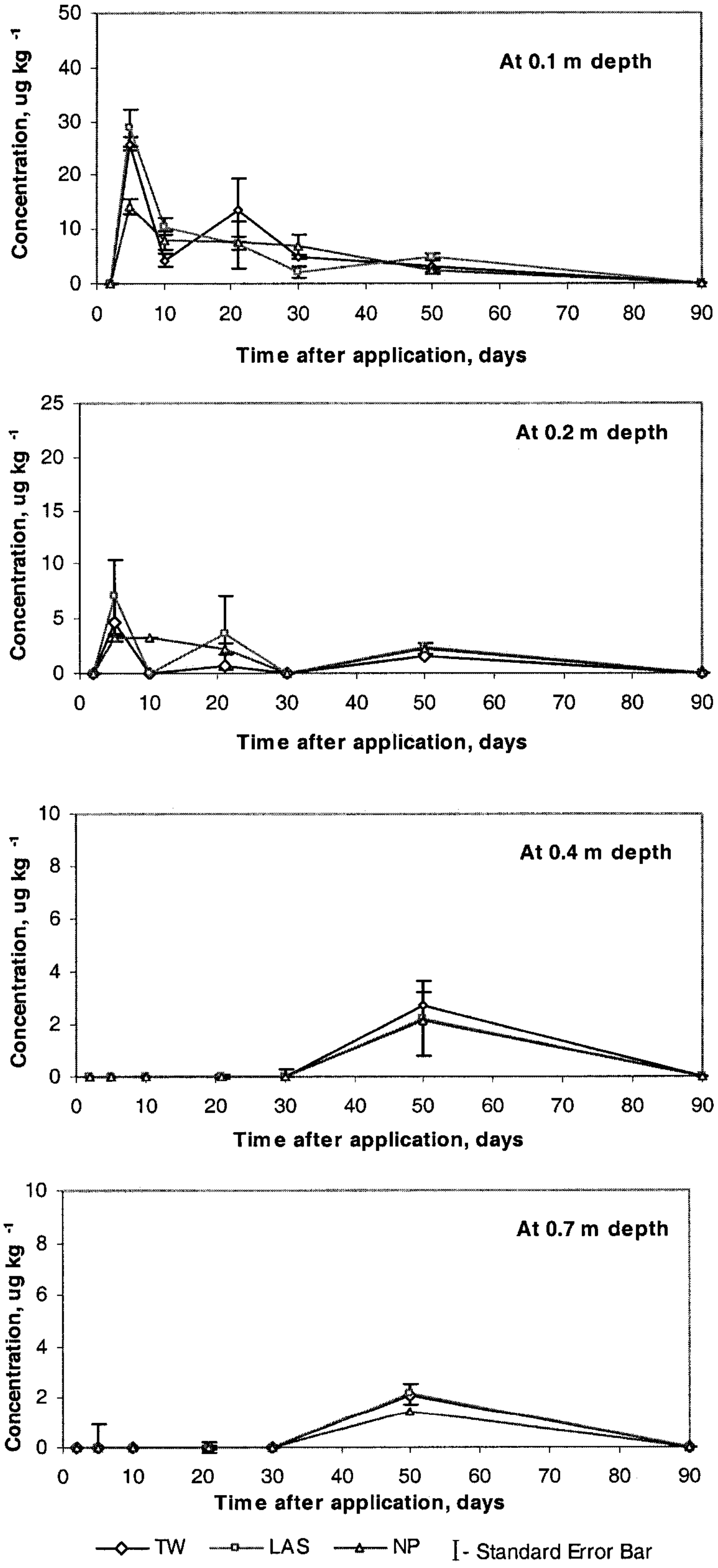


Figure 3.5 Metribuzin concentrations at different depths of the soil profile over time time (TW- tapwater, LAS- Linear alkylbenzene, and NP- Nonylphenol)

The results also showed that there were no significant $(P \leq 0.05)$ differences among the treatments for the three herbicides (Table 3.5). This indicates that there was no considerable effect of irrigation water, containing LAS or NP, on herbicide movement in the soil. However, although the overall treatment effects were not significant, it can be seen from Figures 3.3 and 3.5 that atrazine and metribuzin concentrations were slightly higher in the presence of LAS in irrigation water than the concentrations in the presence of NP in irrigation water and the control. Therefore, the results were analyzed for particular depths and times. On day 5 at 0.2 m and on day 10 at 0.1 m soil depths, atrazine concentrations were higher $(P \leq 0.1)$ in the presence of LAS in irrigation water, compared to the tap water treatment. Also, at 0.1 m soil depth on day 5, metribuzin concentration was higher in presence of LAS than in presence of NP in irrigation water and control. Metolachlor concentrations were higher $(P \leq 0.1)$ at 0.1 m depth on day 10 when irrigated with LAS-containing water, as compared to NP-containing water. These slightly higher concentrations of the three herbicides at 0.1 m and 0.2 m depths in the presence of LAS reveal that LAS in irrigation water increased the ionic adsorption of atrazine and metribuzin due to the sorption of LAS molecules by the soil constituents, and further enhanced site for adsorption of those herbicides. Anionic (LAS) surfactant seems to be adsorbed by the hydrophilic part with the soil particles, leaving hydrophobic part towards pore water, as reported by Abu-Zreig (2003,1999), which is called ionic adsorption, and ionic adsorption is stronger when the surfactants are present in lower concentrations. However, the differences in concentrations were not significant for all other lower depths over the ninety-day period.

**Table 3.5 Repeated Measures Analysis of Variance for the three herbicides**

| Herbicide | Source | Pr>F | Source | Pr>F |
|---|---|---|---|---|
| | Trt | NS | | |
| Atrazine | Time | * | Time×Trt | * |
| | Depth | * | Depth×Trt | NS |
| | Trt | NS | | |
| Metolachlor | Time | * | Time× Trt | NS |
| | Depth | * | Depth× Trt | NS |
| | Trt | NS | | |
| Metribuzin | Time | * | Time×Trt | NS |
| | Depth | * | Depth× Trt | NS |

NS- non-significant *- significant (at 5% significance level) Trt- Treatment

Also, a laboratory experiment was conducted to examine the adsorption behavior of the three herbicides. The adsorption isotherm for atrazine, metolachlor and metribuzin was developed by plotting the amount of herbicides adsorbed against the post-equilibration concentrations of herbicides in solution. From Figure 3.6, it is observed that a linear relationship exists between adsorbed and equilibrium concentrations of herbicides in aqueous solution. To measure the partition coefficient ($k_d$), linear regression was used. The result shows little variation in adsorptions of atrazine, metolachlor and metribuzin, as compared to the distilled water. The presence of LAS resulted in a 35% increase in $k_d$ for atrazine and 75% for metribuzin (Table 3.6). In the case of metolachlor, the influence of LAS was found to be minor, at around a 10% increase in $k_d$. The relative increase in $k_d$ might have been from increased dispersion of soil aggregates compared to the distilled water, which contributed to an adsorption of LAS with soil particles, further enhancing the sites for adsorption of the three herbicides. Low concentration of NP slightly increased the adsorption of metolachlor (an increase of 67% in $k_d$), and atrazine (increase of 6% in $k_d$). On the other hand, the presence of NP showed a decrease of 41% in $k_d$ for metribuzin. The adsorption of metolachlor was increased slightly in presence of NP, but metribuzin was desorbed in presence of NP. This might result in chemical interactions between NP and those two herbicides. For atrazine, the influence was very small, which might be due to minimal interaction between atrazine and NP. The sorption of atrazine and metribuzin were significantly higher ($P \leq 0.1$) in presence of LAS, compared to the control. Although slightly increased or decreased sorption of the three herbicides was observed with NP, as compared to the control, statistically the sorption was not significant ($P \leq 0.1$).

**Table 3.6 Partitioning coefficient $K_d$ for atrazine, metolachlor and metribuzin in presence of LAS and NP**

| | Partition coefficient, $k_d$ ($cm^3$ $g^{-1}$) | | |
|---|---|---|---|
| | Atrazine | Metolachlor | Metribuzin |
| With DW [†] | 1.09 | 1.06 | 0.36 |
| With LAS [†] | 1.47 | 1.17 | 0.63 |
| With NP [†] | 1.15 | 1.77 | 0.21 |

[†] DW-Distilled water; LAS- Linear alkylbenzene sulfonates; NP=Nonylphenol

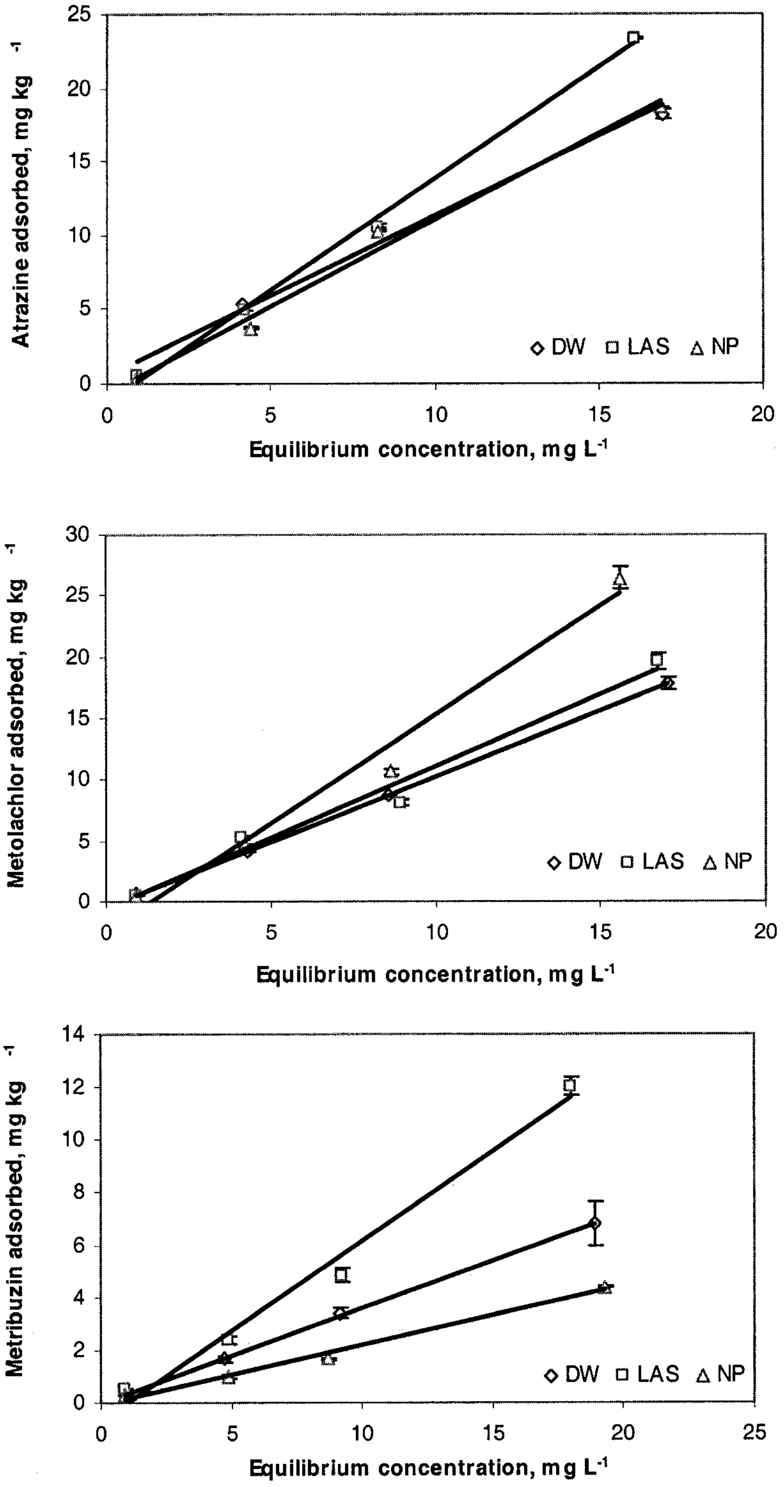


**Figure 3.6 Effect of LAS and NP on the adsorption of atrazine, metolachlor, and metribuzin time (DW- Distilled water, LAS- Linear alkylbenzene, and NP- Nonylphenol)**

The mechanism by which LAS might be influencing the herbicide movement in the soil profile is complicated to interpret. Although LAS can form foam at concentrations of *0.5 mg* $L^{-1}$ in distilled water (Richards, 2003) and slightly increase the solubility of pesticide, the effect on the movement of the three herbicides at concentration of *12 mg* $L^{-1}$ were not found. This was probably due to the fact that the concentration of LAS (*12 mg* $L^{-1}$) used in irrigation water was much lower than the CMC value of LAS, *433.5 mg* $L^{-1}$ (Ou et al., 1996). Usually at concentrations above the CMC value, surfactants increase the solubility of organic pollutants (Sanchez-Camazano et al., 2000) and consequently enhance leaching. However, LAS in irrigation water in this study was lower than its CMC level, and did not increase solubility and leaching of the three herbicides in this study, which is in agreement with previous works by Abu-Zreig (2003), Huggenberger et al. (1973), Mustafa and Letey (1969), and Bayer (1966).

Although the lysimeter experiment did not show a remarkable increase in sorption of the herbicides in the presence of LAS, laboratory experiments showed significant sorption of atrazine and metribuzin in the presence of LAS, as compared to the control. The observed slightly higher concentrations of atrazine during LAS treatment can be explained by slightly enhanced hydrodynamic dispersion. During the movement of LAS-contained irrigation water and herbicides through the soil profile, this is thought that LAS increased soil aggregate dispersion, which further increased the soil surface area and provided available sites for herbicides to be adsorbed with soil constituents (Abu-Zeirg et al., 1994, Huggenberger et al., 1973). Therefore, the herbicides were less prone to leaching.

In the lysimeter study, only a slight influence of LAS was observed at the upper soil profile. At low concentration, LAS strongly adsorbed to the topsoil and can be mobile up to 0.3-0.4 m into the soil (Kuchler et al. 1997, Figge et al. 1989). However, in this study the effect was observed down to 0.1 m, which could be because of the surface tension, liquid-solid contact angle, or because dispersion of soil provided by LAS in irrigation water did not influence the deeper soil profile (Pelishek et al., 1962). As a result, LAS did not have an effect on the herbicide concentrations at lower soil depths. Slight variations in concentrations of the three herbicides at the lower soil profile might have resulted from the variations in hydraulic conductivity and macropore flow in the lysimeters. The dissipation time of LAS in the lysimeter was reported to be 3 days due to rapid degradation of LAS at low concentration (Kuchler et al. 1997, Knaebel et al. 1990, Elsgaard et al. 2001b). Therefore, the accumulation of LAS was not expected, which could effect the movement of the herbicides at later stages of this study.

The concentration of 12 mg $L^{-1}$ of NP in irrigation water hardly influenced the movement of atrazine, metolachlor and metribuzin, as compared to the control and LAS-containing irrigation water. NP (nonylphenol) was a waxy substance and does not dissolve very well in water. Moreover, NP is a biodegraded product of nonylphenol ethoxylate (NPE) and cannot form micelle in water because it does not have an ethoxylate group in its chemical structure, where the ethoxylate group is responsible for forming micelle. When irrigation water containing NP was applied on the surface of the soil, the NP mostly remained on the surface rather than moving downward along with infiltrating water. Hence, interactions between herbicides and NP were not present, and the influence of NP on leaching or sorption of the herbicides seemed to be absent. Slight increase and decrease in sorption of the three herbicides were found in the laboratory experiment, however, in the lysimeters, the influence of NP-containing irrigation water on the herbicides were negligible.

### 3.3.3 Mass balance study

Herbicide residues in the soil profile (lysimeter), as well as in the leachate, were considered for a mass balance study. The numerical results were calculated with MATLAB 7.0 (1992) and are illustrated in Figure 3.7. The amounts of atrazine, metolachlor and metribuzin in the soil were reduced by 42%, 37% and 57%, respectively, following the irrigation shortly after the application of the herbicides. As well, a rapid depletion in total residues of the herbicides in soil was observed in this study. This might have resulted due to the high temperature of the soil in above-ground lysimeters causing rapid degradation of the three herbicides within 30 days (Figure 3.7). Also, the rain shelter used over the lysimeters might have contributed an additional increase in temperature of the soil profile, which might cause the herbicides to degrade faster than usual. The herbicide losses were found to be similar for the three treatments in this study, which suggests that LAS and NP added to the irrigation water did not increase degradation of these herbicides (Figure 3.7).

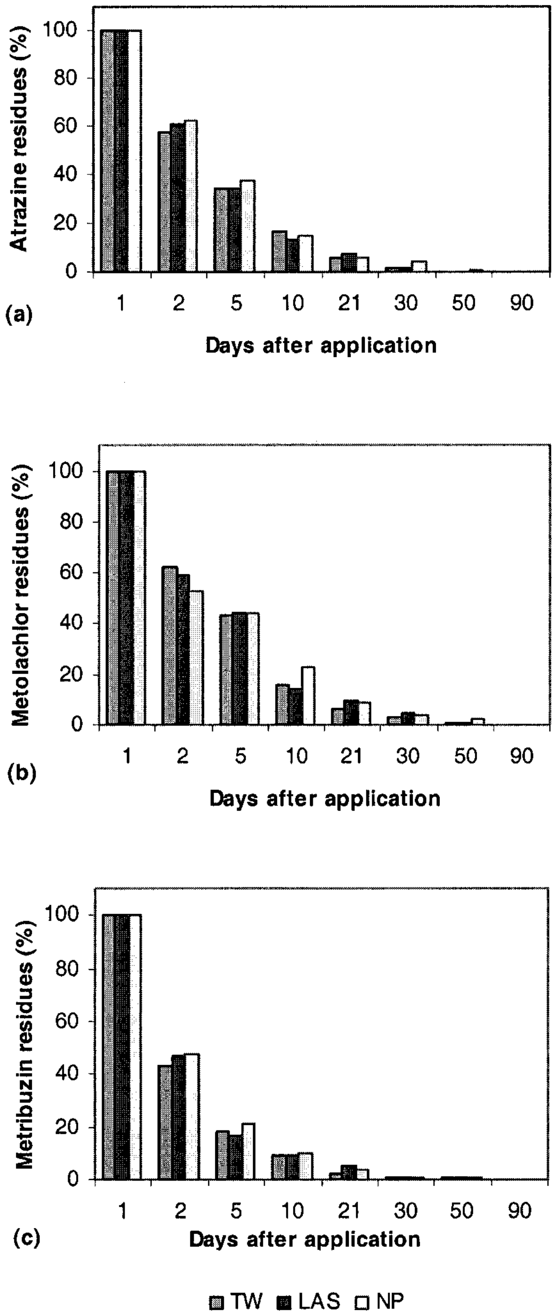


**Figure 3.7 Degradation and remaining residues of (a) atrazine, (b) metolachlor and (c) metribuzin in soil over time under three different treatment conditions**

### 3.4 Conclusions

The application of anionic (LAS) and degraded product (NP) of a non-ionic surfactant in irrigation water at low concentrations insignificantly increase the solubility of atrazine, metolachlor and metribuzin, and these herbicides did not leach in considerable concentrations beyond 0.2 m. However, a slight increase in adsorption of the three herbicides was observed in the upper soil profile under irrigation water containing LAS, which might be due to slightly enhanced hydrodynamic dispersion of soil; this delayed the mobility of the herbicides due to increased adsorption. The laboratory adsorption test demonstrated that the adsorption of atrazine and metribuzin were increased in the presence of low concentrations of LAS due to dispersion of soil, rather than its interaction with herbicides. In the presence of NP, the effects on the adsorption of the three herbicides were negligible. The presence of NP in irrigation water showed a slight increase in adsorption for metolachlor, but showed decrease in adsorption for metribuzin, whereas the effect was almost negligible for atrazine. Although the results showed little variations in the presence of NP for metolachlor and metribuzin, compared to control, statistically the adsorption/desorption were not significant. Therefore, the results from this study showed that the presence of anionic (LAS) and degraded product (NP) of a non-ionic surfactant, at low concentrations in irrigation water, should not cause any increased hazard by promoting greater mobility of herbicides to ground water.

# PREFACE OF CHAPTER IV

Pesticide transport models are used to minimize environmental pollution, risk assessments, and in the selection of appropriate management practices. A number of pesticide transport models can simulate pesticide movement in the soil profile. PESTFADE is a recent one-dimensional model, which is capable of providing a better estimation of pesticide sorption in the soil profile. In the following chapter (Chapter IV), the description of the PESTFADE model and its application to simulate the transport of three agricultural herbicides (atrazine, metolachlor, and metribuzin) is presented. This chapter also compares the simulated fate of the three herbicides in the lysimeter against the field data collected from a lysimeter study in the summer of 2004. The study described in previous chapter (Chapter III) showed that no significant differences in leaching of atrazine, metolachlor and metribuzin occurred in the presence of anionic and non-ionic surfactants at low concentrations in irrigation water, compared to surfactant-free water. Therefore, in this study, the treatment conditions in the lysimeter studies were assumed to be single (tap water) treatment condition.

The role of the candidate, as the main author of the manuscript, was to run and validate the mathematical model, PESTFADE. Also, the author was responsible for performing statistical analysis to validate the model. Dr. Shiv. O. Prasher, Professor of Bioresource Engineering, McGill University and supervisor of the candidate, offered his proficient supervision to the author.

**Research paper based on the chapter:**

Nilufar, F. and S.O. Prasher. Simulation of three herbicides in agricultural soil using the PESTFADE model. (Manuscript to be submitted to the *Journal of Environmental Quality*)

# CHAPTER IV

# SIMULATION OF THREE HERBICIDES IN AGRICULTURAL SOIL USING THE PESTFADE MODEL

## Abstract

PESTFADE (PESTicide Fate And Dynamics in Environment) is a one-dimensional transient mathematical model that predicts the simultaneous movement of water and solutes in an unsaturated, homogeneous soil profile. In this study, the model was used to determine the fate of three herbicides in a sandy agricultural soil. Herbicide concentrations at different depths of the soil profile over predetermined time intervals after application were simulated. Field data on atrazine, metolachlor, and metribuzin concentrations from a lysimeter experiment, carried out in the summer of 2004, were used to calibrate and evaluate the model. In the field experiment, the lysimeters were sheltered from rain and so irrigation was applied. The model was calibrated with the soil surface data, and validated with the data from the 0.1, 0.2, 0.4, and 0.7 m soil depths. Calibration of the model showed the rate constant (day$^{-1}$) of the herbicides was the most sensitive parameter for obtaining simulated concentrations close to those measured. The model performance was analyzed using the following statistical approaches: root mean square error (RMSE), relative root mean square error (R-RMSE), linear correlation coefficient (r) and coefficient of performance (CP). The predicted concentrations of the three herbicides at the 0.4 and 0.7 m depths were in close agreement with the observed concentrations; RRMSE values were satisfactory and the correlation coefficient was good. Although the model performed poorly at the 0.2 m depth, the simulated herbicide concentrations at shallower depths followed the trend of measured data quite well for the three herbicides, as indicated by the low RMSE. Thus, the model performed well near the soil surface and also below 0.4 m, where the herbicide concentrations were respectively high or very low.

**Keywords.** PESTFADE, atrazine, metolachlor, and metribuzin.

## 4.1 Introduction

The contamination of ground and surface water bodies constantly increases with the increased use of pesticides in crop production. Reliable predictions of the environmental behavior of pesticides are one of the biggest challenges for pesticide scientists and regulatory agencies. Therefore, the ability to accurately predict the fate and transport of pesticides in the environment has become imperative. After application, redistribution of pesticides applied on soil is very complex to predict, given that the chemical processes varies from one soil to another under different environmental conditions as well as with spatial variability in soil characteristics. However, understanding the extent and specificity of flow transport phenomena of pesticides under field conditions would facilitate the reduction in ground water pollution. Although a number of studies have been carried out at different levels, such as field (Crisanto et al., 1995; Cox et al., 1997; McDonald et al., 1999; Azevedo et al., 2000; Andreu & Picó, 2004), lysimeters (Jebellie, 1997; Renaud et al., 2004), and laboratory(Sánchez-Camanzano et al., 1996; Abu-Zreig et al., 1999; Guo et al., 2000; Sánchez-Camanzano et al., 2000; Sánchez, 2004), to determine pesticide behavior in the soil environment, the long term effects of these pesticides in soil are still not clear. It is difficult to investigate the many possible behaviors of these pesticides in the environment given limitations of time, research facilities, the wide range of their chemical properties, and climatic variability. However, experimental limitations can be circumvented by using fast and accurate mathematical models.

Mathematical models are the most effective tools for predicting the extent of pesticides in the environment and their adverse effects on natural resource systems. In recent decades, considerable advances in such models have been made in terms of their ability to predict agricultural chemicals in the environment. Models are typically physical, conceptual, or mathematical representations of reality. They provide estimations of required time for chemical degradation, leaching and sorption of chemicals in soil, thus helping farmers to design effective crop, soil, and chemical management plans (Wagenet and Huston, 1986). A wide variety of computer models are available that can quantitatively simulate pesticide leaching in the soil profile and runoff in the aqueous phase. The USEPA's PRZM3 (Carsel et al., 1984, 1985), GLEAMS (Leonard et al., 1987), LEACHM (Wagnet and Hutson, 1987), and RZWQM (USDA-ARS, 1994) are widely used models. These models simulate leaching, runoff potential of pesticides, field-scale drainage patterns, and are thus able to make watershed-scale assessments. PESTFADE a model developed by Clemente et al. (1993) and further modified by Li et al. (1999), was used in this study to simulate pesticide transport in the soil profile. PESTFADE, is a one dimensional model, which simulates the simultaneous movement of water and solutes in unsaturated, homogeneous soils. This model differs from other models since it predicts adsorption/desorption and chemical-microbial degradation under controlled/uncontrolled drainage conditions for agricultural fields in arid, semi-arid and humid regions. A Graphic User Interface (GUI) was implemented by Tafazoli (2003), which makes the model more user-friendly and interactive.

One of the important features of computer simulation models is their ability to evaluate the contamination potential of a specific pesticide for several sites and to evaluate several pesticides at one site. Alternatively, these models can be calibrated to fit the results of any field study at one site in order to predict scenarios for different field conditions in terms of time and soil depth. It is desirable to understand the variability in natural field conditions; therefore, under different climatic conditions, model validation and calibration is necessary.

Consequently, this study was undertaken to:

(i) employ the PESTFADE model to simulate the movement of herbicides through the soil profile, and

(ii) calibrate and evaluate the PESTFADE model by comparing the predicted herbicide concentrations with measured concentrations obtained from a lysimeter study.

## 4.2 Model description

PESTFADE is a one dimensional, transient mathematical model to simulate the fate of pesticides in soil (Clemente et al., 1993). PESTFADE combines five different modules: SWACROP (Soil Water Actual transpiration and Crop Production), RUNOFF, MOISTE, HEAT and CADD (Conduction Adsorption Diffusion Degradation). SWACROP (Wesseling et al., 1989) is used to estimate evapotranspiration and simulate water flow in the heterogeneous soil root systems under humid arid and semi-arid regions. The RUNOFF (Haith, 1980) model analyzes and determines the pesticide status at the surface of the soil on each day by considering climate and tillage practices based on runoff depth and soil loss estimated by using the US Soil and Conservation Service Curve Number Method and Universal Soil Loss Equation to evaluate runoff depth and soil loss. The outputs, from the RUNOFF model, are then used to model degradation, volatilization, or leaching of pesticides, depending on soil properties, climatic and hydrologic conditions, and management practices. The MOISTE model in PESTFADE converts the moisture distribution to a nodal-point basis, which were obtained from SWACROP on a compartmental basis. The HEAT model analyzes the conduction of heat, temperature distribution and thermal conductivity in the soil profile according to Walker (1981a, 1981b). Finally, CADD model uses the moisture content from MOISTE, and the temperature profile from HEAT to simulate the solute transport, as a function of interacting process of convection, adsorption, volatilization, and microbial degradation (Clemente et al., 1991).

The PESTFADE model is applicable to different boundary conditions, tillage practices, and it takes into account the accidental spill, salt movement, oxygen diffusion, and the presence or absence of drainage and subirrigation systems. In PESTFADE, macro-pore flow, heat flow and the effect of different water table management systems on pesticides leaching are also taken into account. Although most existing models consider the soil water partitioning coefficient $k_d$ as a constant (Carsel et al., 1984, 1985; Wagenet and Hutson, 1987), PESTFADE adjusts the $k_d$ according to changes in soil pH, temperature, sorption capacity of soil, and soil tortuosity. PESTFADE has been modified by Li et al. (1999), by incorporating a new model for sorption kinetics, which takes into account the intra-particle diffusion of pesticides within the soil matrix, the sorption capacity of soil, and variable pesticide distribution coefficients. The PESTFADE model was validated against analytical solution, as well with laboratory and field experiments (Clemente et al., 1993; Clemente et al., 1998; Li et al., 1999). A study was conducted by Kaluli et al. (1997) to investigate atrazine movement in a clay loam soil in Quebec by using three models, PRZM, GLEAMS and PESTFADE. The study showed that PESTFADE model performed better with minimum standard error than the other two models since it considers two-stage sorption kinetics and macropore components. A graphical user interface (GUI) has been added to PESTFADE to make the model user friendly and more interactive (Tafazoli, 2003).

## 4. 3 Materials and Methods

### 4. 3.1 Field experiment

Field data for this study was taken from a lysimeter experiment carried out during the summer of 2004 at Macdonald Campus of McGill University, Sainte Anne-de-Bellevue, QC, Canada. The experiment consisted of nine PVC lysimeters (1 m long × 0.45 m diameter) packed to a bulk density $\rho = 1.35$ kg m$^{-3}$. The physical properties of the soil are presented in Table 4.1. Lysimeters were filled up to within 0.1 m of the top, and four different holes were made laterally at depths 0.1, 0.2, 0.4, and 0.7 m from the soil surface to allow the collection of soil samples. The lysimeters were equipped with a drainage pipe at the bottom to allow free drainage. The study area was covered so as not to allow rainwater into the lysimeters during the experiment. No plants were grown in the lysimeters so as to avoid any plant uptake, as well to simulate worst case scenario. Three herbicides, atrazine *(2-chloro-4-ethylamine-6-isopropylamino-S-triazine)*, metolachlor *(2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide)*, and metribuzin *(4-amino-6-tert-butyl-4, 5-dihydro-3-methyltio-1, 2, 4-triazin-5-one)*, were sprayed on the soil surface of each lysimeter, at the field recommended rates (2.5, 2.75, and 1 kg ha$^{-1}$). Irrigation was applied in consideration of the fact that no rainfall reached the lysimeters and that evapotranspiration was high. After the application of pesticides, 44 mm irrigation was applied on days 2, 10, 20, 30, and 90, and 70 mm was applied on days 40, 50, 60, 70, and 80 according to corn (*Zea mays* L.) water requirement. The soil samples were collected from the four different depths on days 0, 1, 2, 5, 10, 21, 30, 50, and 90 after the application of pesticides. Extractions of the soil samples were done in the laboratory and pesticide concentrations were analyzed with a LC/MS (Liquid Chromatography with Mass Spectrometry).These concentrations were used for the evaluation of the PESTFADE model.

**Table 4.1 Physical properties of soil**

| | | | |
|---|---|---|---|
| Sand | 92.2 % | Organic Matter | 3.0 % |
| Silt | 4.3 % | Hydraulic conductivity[†] | 3.68±0.87 m $day^{-1}$ |
| pH | 5.5 | Bulk Density | 1.35 kg $m^{-3}$ |
| Soil type: Sandy | | CEC | 4.9 cmol $kg^{-1}$ |

[†] mean ± standard deviation

### 4.3.2 Model Simulation and validation

#### 4.3.2.1 Model execution

To begin a simulation, the SWACROP model was used to calculate potential evapotransporation and water balance in the soil profile for the particular experimental conditions. Meteorological data, air temperature, wind speed and direction, humidity and evaporation, were collected from the Ste. Anne-de-Bellevue station of Environment Canada. Instead of rainfall data, irrigation data was used as the water source in the model. These data were required to execute the SWACROP model to simulate available moisture content in the soil profile. The outputs from the SWACROP model were imported into the PESTFADE model for predicting solute transport. Four modules in PESTFADE were executed sequentially as the output from one module was used as input for the next module.

The initial concentrations of the herbicides, soil parameters, and the other general input parameters used in the PESTFADE model are presented in Table 4.2. The model specifications were set for transient water and solute flow, variable dispersivity, Neumann upper boundary, solute flux dependent lower boundary, conventional adsorption mechanism and constant initial concentrations with depth. The depth of the soil profile was 1.0 m. The number of nodal points set into PESTFADE was 201 giving an internal nodal distance of 5 mm. To compare simulated herbicide concentrations with measured lysimeter data, the concentrations from the 0, 20, 40, 80 and 140 nodal points were taken, which were equivalent to the 0, 0.1, 0.2, 0.40 and 0.7 m soil depths.

**Table 4.2 Input parameters for PESTFADE model**

| Parameter | Value | Parameter | Value |
|---|---|---|---|
| Soil profile depth | 1.0 m | Application rate † | 2.2, 2.5,0.81 kg $ha^{-1}$ |
| Soil bulk density | 1.35 kg $m^{-3}$ | Solubility † | 33,530,1220 mg $L^{-1}$ |
| Organic matter content | 3.0 % | Henry's constant | $2.5\times10^{-7}$ |
| Porosity | 0.49 | Mass transfer coefficient | 0.15 $day^{-1}$ |
| Available moisture content | 0.25 $cm^3$ $cm^{-3}$ | Sorption capacity | 108 mol $L^{-1}$ |
| Curve number | 80 | Activation energy | 12200 cal $mol^{-1}$ |
| Drainage area | $1.58\times10^{-5}$ ha | Soil erodibility | 0.2 |
| Contouring factor | 1.0 | Time step | 90 days |

† The three values are for atrazine, metolachlor and metribuzin, respectively

### 4.3.2.2 Model calibration

The model was calibrated with the concentrations of herbicide at the soil surface. The data from the soil surface were taken for calibration, because the herbicides in the soil profile would depend on the quantity of herbicides present on the soil surface after the application. The quantity of herbicides on the soil surface depends on the irrigation rate, runoff (zero in this experimental condition), evaporation, photo degradation and also biodegradation, all of which contribute to herbicide losses at the soil surface.

The driving force behind calibrating the model was to minimize the difference between predicted and observed pesticide concentrations in the soil profile during the ninety-day period (i.e. June to September, 2004). An iterative process was used to determine the best values of the input parameters. Among the input parameters, rate constant, half life, and sorption coefficient ($k_d$) are known to be sensitive to pesticide movement in the soil (Bakhsh et al., 2004). The calibration was carried out for the three herbicides, atrazine, metolachlor and metribuzin, separately.

### 4.3.2.3 Model validation

The model was validated with the concentrations at different depths in the soil profile. To validate the model, the predicted concentrations of atrazine, metolachlor and metribuzin at soil depths of 0.1, 0.2, 0.4, and 0.7 m were compared with observed values obtained from the lysimeter experiment. Herbicide concentrations measured immediately after their application to soil surface were used as the initial concentrations for the simulation model. Simulations of the three pesticides were done separately for each simulation model. Simulations of the three pesticides were done separately for each herbicide for the ninety-day experimental period. The root mean square error (RMSE), relative root mean square error (RRMSE), coefficient of performance (CP), model efficiency (EF), and correlation coefficient (r) were used to assess the model performance (James and Burges, 1982). The following equations were used to calculate the statistical parameters:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{i=N}\left(\hat{Y}_i - Y_i\right)^2}{N}} \qquad (4.2)$$

$$RRMSE = \frac{RRMSE}{\overline{Y}} \qquad (4.3)$$

$$CP = \frac{\sum_{i=1}^{i=N}\left(\hat{Y}_i - Y_i\right)^2}{\sum_{i=1}^{i=N}\left(Y_i - \overline{Y}\right)^2} \qquad (4.4)$$

$$EF = 1 - CP \qquad (4.5)$$

where,

$\hat{Y}_i$ Predicted pesticide concentration, for sample size $N$,

$Y_i$ Measured pesticide concentration, for sample size $N$,

$\overline{Y}$ Mean measured pesticide concentration.

## 4.4 Result and Discussion

### 4.4.1 Model calibration parameters

Herbicide properties are very important parameters while simulating pesticide concentrations in the soil profile. A list of calibrated input parameters needed for the PESTFADE model is presented in Table 4.3. $K_d$ values, set in the PESTFADE model during calibration, were taken from a laboratory experiment (Chapter III). The degradation and persistence of the herbicides in soil are strongly affected by their decay rate. Decay rate constants of 0.17, 0.15, and 1.0 day$^{-1}$, were determined for atrazine, metolachlor and metribuzin, respectively, by calibrating the model. These rate constants are higher than those found in the literature (Bakhsh et. al., 2004). The higher rate constants indicate shorter half-lives for the three herbicides, which could be due to the high temperature in the soil profile, since the lysimeters were kept above the ground surface, speeding up the herbicide degradation. The rain cover over the lysimeters could have also contributed to an additional increase in the soil temperature.

The calibration of atrazine, metolachlor and metribuzin concentrations were done with the measured soil surface data from the lysimeter study. Fitted linear regressions for the simulated concentrations against the measured concentrations for the three herbicides are shown in Figure 4.1. The correlation coefficient (r) was found to be 0.99 for the three herbicides. Moreover, the regression analysis, done using t-test, showed that the slope and intercept values were not significantly ($P \leq 0.05$) different from the ideal values of 1 and 0 for the three herbicides (Table 4.4). The high correlation coefficient and regression analysis results reveal that calibration was performed very well. The RRMSE for atrazine, metolachlor and metribuzin were 0.23, 0.27, and 0.26, respectively, and the EF for the three herbicides was high. Consequently, low values of RRMSE and EF suggests that there was little variation between the simulated and measured concentrations, as far as calibration is concerned. After calibrating the model, simultaneous simulations were done for the herbicide concentrations at the soil surface, and 0.1, 0.2, 0.4, and 0.7 m depths.

**Table 4.3 Calibrated values for the three pesticides simulation by the model**

| Pesticide | $K_{sat}$, m day$^{-1}$ ‡ | Rate constant (day$^{-1}$) | $K_d$ † (cm$^3$ g$^{-1}$) | $K_{oc}$ † |
|---|---|---|---|---|
| Atrazine | 3.68 | 0.17 | 1.23 | 71 |
| Metolachlor | 3.68 | 0.15 | 1.33 | 76 |
| Metribuzin | 3.68 | 1.00 | 0.4 | 23 |

‡ Ksat- saturated hydraulic conductivity, † $K_d$ partition coefficient,
$K_{oc}$ sorption coefficient

**Table 4.4 Calibration results for the three herbicides**

| Calibration | r | Slope | Intercept | RMSE, mg kg$^{-1}$ | RRMSE | EF |
|---|---|---|---|---|---|---|
| Atrazine | 0.99 | 1.08 | 0.03 | 1.14 | 0.23 | 0.97 |
| Metolachlor | 0.99 | 1.08 | 0.35 | 1.47 | 0.27 | 0.96 |
| Metribuzin | 0.99 | 1.09 | 0.24 | 0.36 | 0.26 | 0.97 |

r- correlation coefficient; RMSE- Root Mean Square Error; RRMSE- Relative Root Mean Square Error; EF- Model Efficiency.

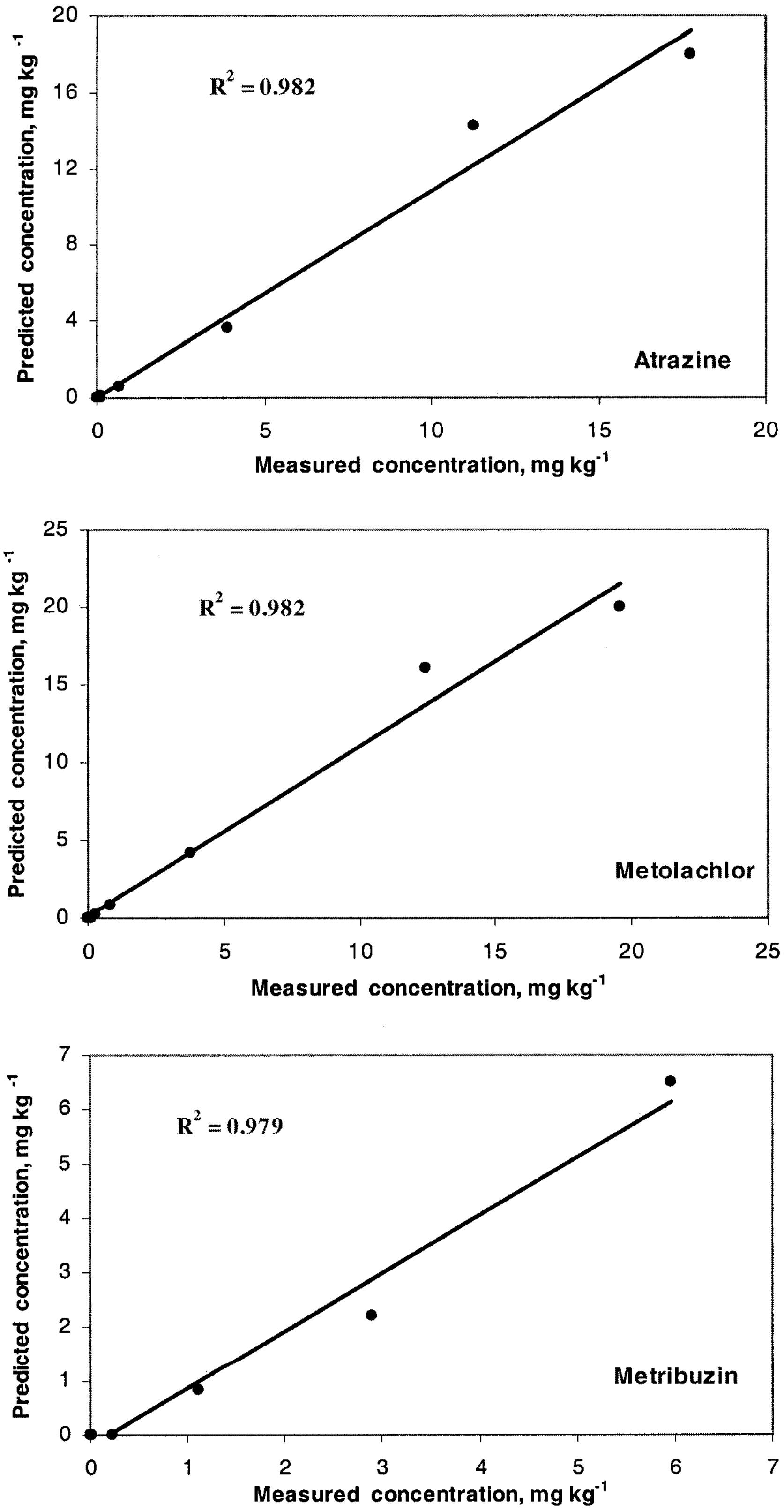


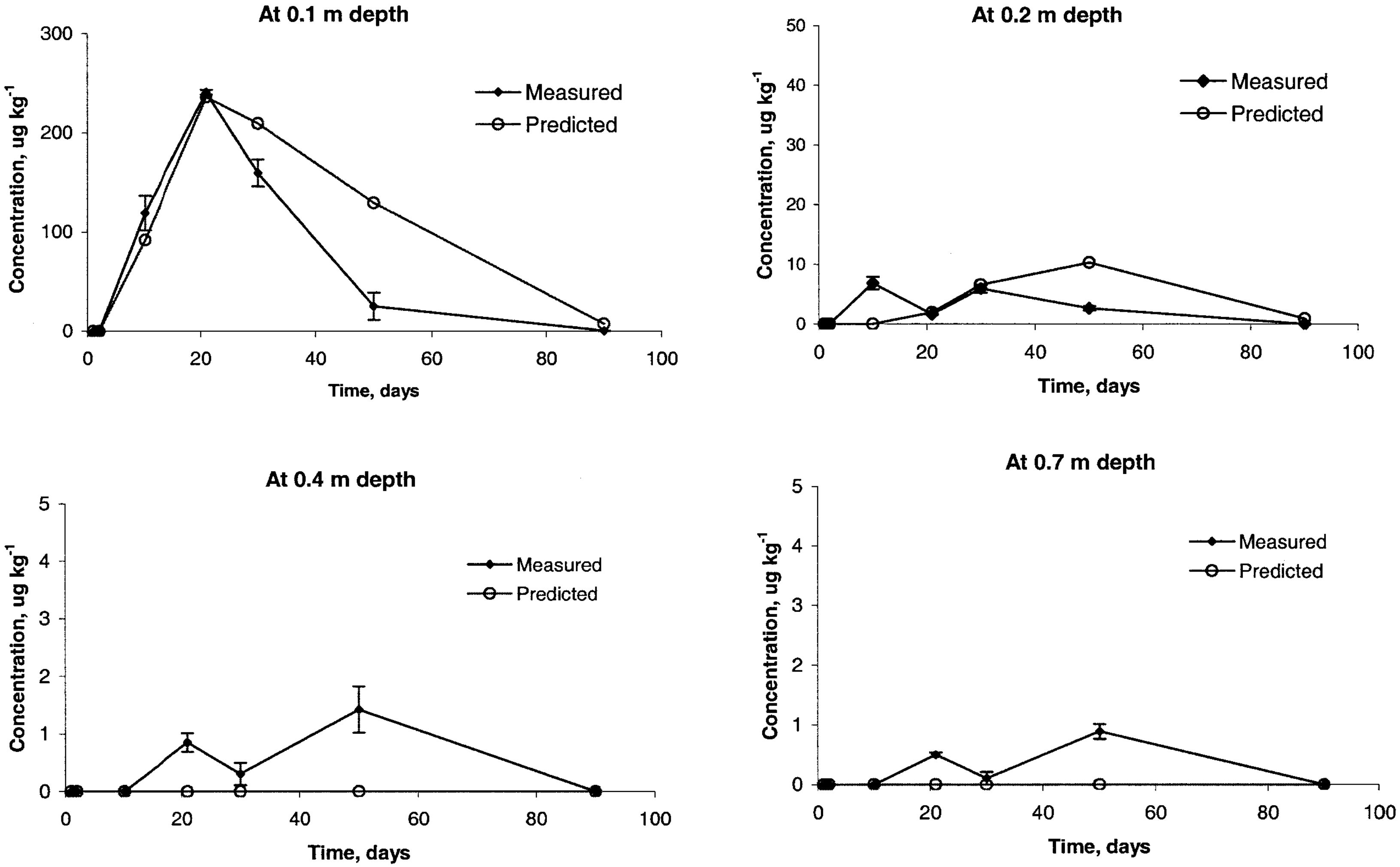
**Figure 4.1 Fitted regressions between simulated and measured herbicides concentrations at the soil surface**

### 4.4.2 Atrazine simulation

At evaluation depths (0.1, 0.2, 0.4, and 0.7 m), simulated and measured atrazine concentrations over time are presented in Figure 4.3. At the 0.1 m soil depth, at the beginning of the ninety-day period, the model was in close agreement with measured concentrations; however, at the middle to end of the period, the model slightly overestimated the concentrations of atrazine. Although a slight overestimation (AMD = –18.48 μg kg$^{-1}$) was observed, the correlation coefficient, RMSE, RRMSE and EF were 0.89, 45.02 μg kg$^{-1}$, 0.58 and 0.75 (Table 4.5). This revealed that simulated atrazine concentrations were in good agreement with measured data, and showed reasonably low discrepancies. The regression analysis showed that the slope was close to 1, but intercept was not significantly ($P \leq 0.05$) different from the ideal value, however, this method of evaluation is known to be quite stringent, and in field conditions the values are liable to be different from their ideal values (Bera et. al., 2005).

At the 0.2 m soil depth, the model initially underestimated and then overestimated the concentrations of atrazine compared to the measured concentrations (Figure 4.2). Overall, the model overestimated (AMD = –0.4 μg kg$^{-1}$) atrazine concentration at this depth. The correlation coefficient, RMSE and RRMSE were 0.3, 3.9 μg kg$^{-1}$ and 1.6, respectively (Table 4.4), which revealed wide discrepancies between simulated and measured concentrations. A negative EF value revealed that the differences between the observed and the predicted pesticide concentrations were quite high.

At the lower depths of 0.4 and 0.7 cm, the model simulated the concentrations as zero, which were almost the same as the measured concentrations at these depths, where the concentrations were either very low or non-detectable. Due to the lack of non-zero simulated values, correlation coefficients could not be determined, however, RMSE was calculated for these depths. The RMSE were 0.63 and 0.38 μg kg$^{-1}$ at the 0.4 and 0.7 m depths, respectively, showing the model performance to be satisfactory. Thus, it can be concluded that although the model performance was poor at the 0.2 cm depth, the model simulated well near the soil surface and also at or below 0.4 m, where the herbicide concentrations were reasonably high or very low.


At 0.1 m depth

At 0.2 m depth

At 0.4 m depth

At 0.7 m depth

Figure 4.2 Simulated vs. measured atrazine concentration at the soil surface and at different depths over time

### 4.4.3 Metolachlor simulation

The observed and simulated metolachlor concentrations over time at different soil depths are presented in Figure 4.3. At the 0.1 m depth, the model slightly underestimated the leaching of metolachlor in the first half of the 90-day period and then slightly overestimated it in the second half of the period. Overall the model underestimated (AMD = 2.2 μg $kg^{-1}$) the herbicide concentration at this depth. However, the correlation coefficient was 0.88 with and RMSE of 59.35 μg $kg^{-1}$, RRMSE of 0.48, and EF of 0.77, indicating good agreement between simulated and measured concentrations. At the 0.2 m depth, the model also underestimated (AMD = 2.3 μg $kg^{-1}$) metolachlor concentrations. The correlation coefficient and RMSE were 0.45 and 7.3 μg $kg^{-1}$, respectively. The RRMSE was high and EF was low (Table 4.5), which indicates greater discrepancies between simulated and measured concentrations at 0.2 m depth than at a 0.1 m depth. At the 0.4 and 0.7 m depths, the observed concentrations were well matched those simulated by the model. Although the EF was negative, the RMSE was 0.17 at the 0.4 cm depth, which indicates that the discrepancies were very little between simulated and measured concentrations (Figure 4.3). At the 0.7 m depth the concentrations were non-detectable in measured data, and model simulated concentrations as zero. Thus, the model performed in a pattern similar to that for atrazine.

### 4.4.3 Metribuzin simulation

Simulated metribuzin concentrations are presented in Figure 4.4. At the 0.1 m soil depth, the correlation coefficient was 0.97, which indicates very close agreement between simulated and measured concentrations. The RMSE, RRMSE and EF were 1.35 μg $kg^{-1}$, 0.37 and 0.85, respectively (Table 4.5), which indicates little discrepancy between simulated and measured concentrations. At the 0.2 m depth, the model underestimated (AMD = 0.89 μg $kg^{-1}$) soil metribuzin concentrations, and the correlation coefficient was 0.45 (Table 4.5). High values of RRMSE and low values of EF indicate that the model poorly predicted the concentrations at the 0.2 m depth, probably due to the complex physiochemical behavior in soil. At lower depths, measured metribuzin concentrations were very low as metribuzin is a highly water-soluble compound, and degraded readily because of high temperature in the soil profile; however, the model performed fairly well at these depths as the simulated metribuzin concentrations were very close to the measured concentrations. The RMSE were 0.89 and 0.72 μg $kg^{-1}$ for the 0.4 and 0.7 m depths (Table 4.5). Although the performance of PESTFADE model was less than desirable at the 0.2 m depth, the model performed well at other depths.

**Table 4.5 Model performance indicators for PESTFADE simulations of the three herbicides concentrations at different depths**

| Simulation | Depth, m | r | Slope | Intercept | AMD[†] | RMSE[‡] | RRMSE | EF |
|---|---|---|---|---|---|---|---|---|
| Atrazine | 0.1 | 0.89 | 0.93 | 23.8 | -18.48 | 45.02 | 0.58 | 0.75 |
| | 0.2 | 0.3 | 0.43 | 1.8 | -0.40 | 3.9 | 1.60 | -1.1 |
| | 0.4 | - | - | - | 0.37 | 0.63 | 1.73 | -0.5 |
| | 0.7 | - | - | - | 0.21 | 0.38 | 1.81 | -0.4 |
| Metolachlor | 0.1 | 0.88 | 0.82 | 19.7 | 2.2 | 59.35 | 0.48 | 0.77 |
| | 0.2 | 0.45 | 0.28* | 1.8 | 2.3 | 7.3 | 1.27 | 0.15 |
| | 0.4 | - | - | - | 0.07 | 0.17 | - | -0.2 |
| | 0.7 | - | - | - | 0 | 0 | - | 0 |
| Metribuzin | 0.1 | 0.97 | 1.14 | 0.42 | -0.93 | 1.35 | 0.37 | 0.85 |
| | 0.2 | 0.45 | -0.07* | 0.07 | 0.89 | 1.41 | 1.36 | -0.4 |
| | 0.4 | - | - | - | 0.33 | 0.89 | - | -0.1 |
| | 0.7 | - | - | - | 0.27 | 0.72 | - | -0.1 |

[†]AMD- Arithmetic Mean Difference (μg $kg^{-1}$) [-ve value for overestimation, +ve value is for underestimation]; [‡]RMSE- Root Mean Square Error (μg $kg^{-1}$); RRMSE- Relative Root Mean Square Error; EF- Model efficiency; * Significant.

Overall, the performance results indicate that PESTFADE performed satisfactorily in simulating herbicides concentrations. High model efficiencies were obtained for 0.1 m depth, however, the lower-depth performance were less satisfactory. The spatial variabilities in soil hydraulic properties could be the major reason for obtaining low performances by the PESTFADE model for some depths. Although the efficiencies at lower depths were negative, the predicted values were within an order of magnitudes to the values obtained from the lysimeters, which satisfies the criteria of model acceptance by Pesticide Exposure Assessment Workshop (1982), where the recommendation was that the model should replicate field data on concentration within an order of magnitude for screening applications (Clemente et al., 1998). The findings of this study also follow the findings by Clemente et al. (1998).

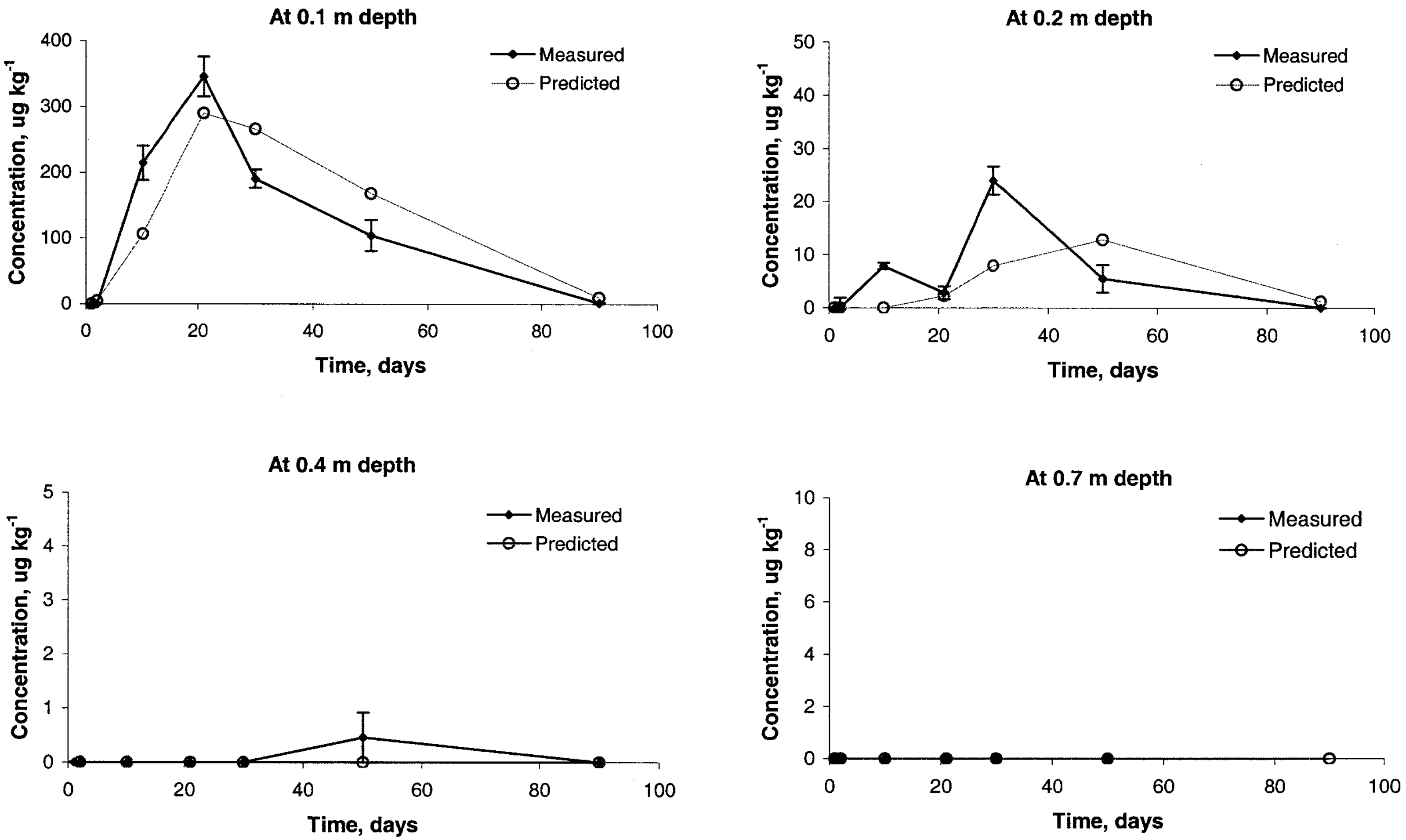


**Figure 4.3 Simulated vs. measured metolachlor concentration at the soil surface and at different depths over time**

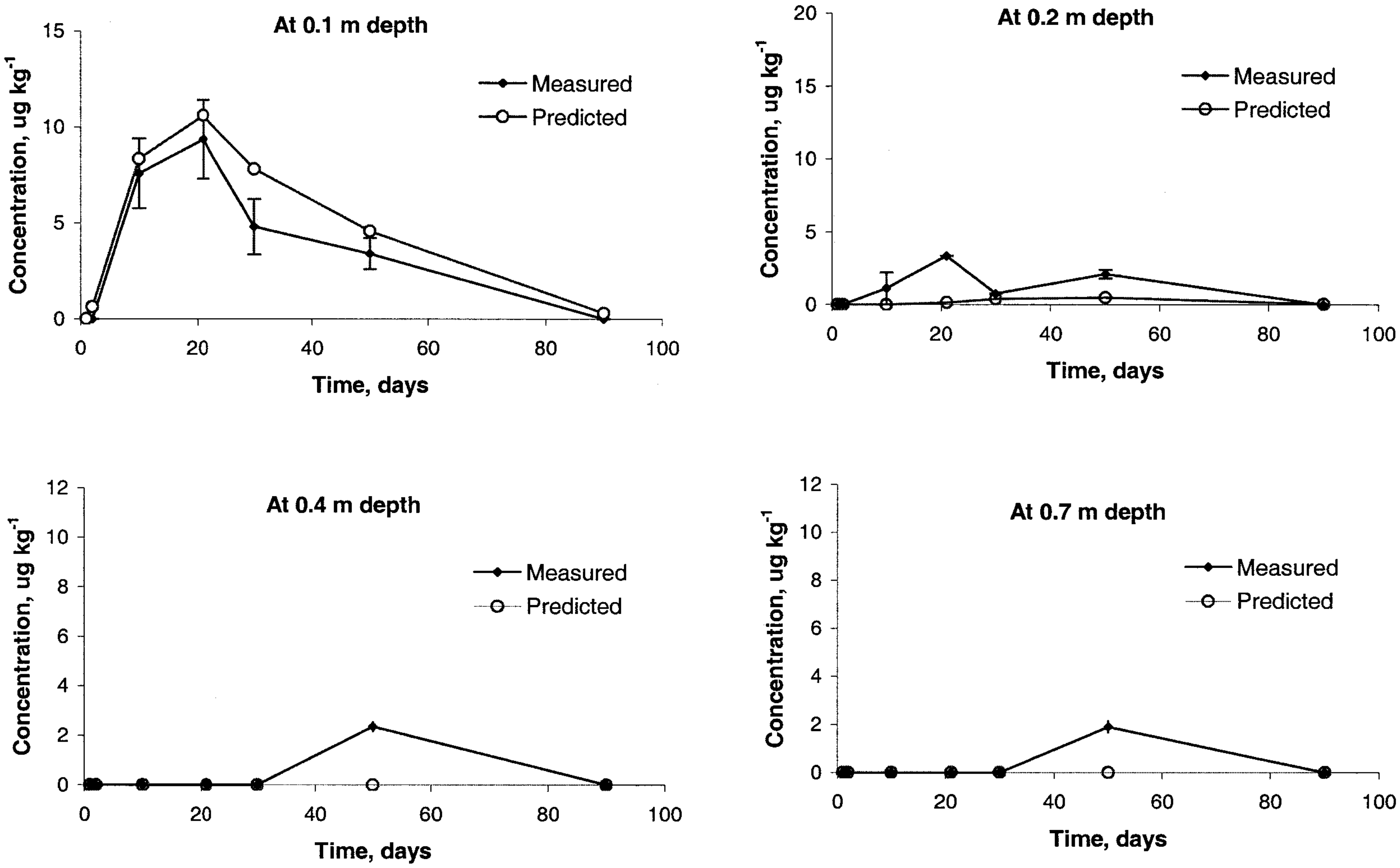


**Figure 4.4 Simulated vs. measured metribuzin concentration at the soil surface and at different depths over time**

## 4.5 Conclusions

Although to simulate herbicide concentrations in soil is not an easy task due to their complex physcio-chemical behavior in soils, the considerations of governing processes for pesticide movement and persistent, such as sorption phenomena, macropore flow, and simulation under different management scenarios in agricultural fields, can provide close-to-reality performance by a mathematical model. One such model, PESTFADE, was used in this study for simulating the concentration of three agricultural herbicides, atrazine, metolachlor, and metribuzin in the soil profile. The data consisted of pesticide concentrations that were obtained from a lysimeter experiment carried out in summer of 2004. The model was calibrated with the data at the soil surface and validated with the data from four different depths (0.1, 0.2, 0.4, and 0.7 m) of the lysimeter. While calibrating the PESTFADE model, the most sensitive parameter was found to be the rate constant (day$^{-1}$) for the three herbicides. The model predicted well with high accuracy at the 0.1 m soil depth, but at the 0.2 m soil depth the model did not make good predictions for atrazine and metribuzin, however, prediction for metolachlor were reasonable. At the 0.4 and 0.7 m depths, the model performed satisfactorily for the three herbicides with slight underestimations. The discrepancies between experimental and simulated results might be due to the measurement errors and variability in hydraulic conductivity in soils. Although the PESTFADE model slightly overestimated or underestimated the concentrations of the agricultural herbicides into soils, the simulated values for all depths were in an order of magnitude to that of lysimeter data. Therefore, it can be concluded that PESTFADE model performed well in predicting the concentrations at upper soil profile as well as at lower depths, for the three agricultural herbicides. Finally, it is recommended to test the model using wide varieties of field conditions, as well soil and chemical properties, which will establish the acceptability of the model for wide range of applications.

# PREFACE OF CHAPTER V

To continue the use of pesticides for better crop production, as well as to reduce their impact on the environment, it is important to understand the physical transport phenomena of pesticides and to model their concentrations under different field conditions. Although, conventional mathematical models have been used successfully used to simulate the complex physcio-chemical behavior of pesticides in the soil profile, the search to find an alternative method for simple, accurate, and fast simulation modeling remains of interest. Therefore, in the following chapter (Chapter V) Artificial Neural Networks (ANN) were used to simulate the three herbicide concentrations in the soil profile, given such models' remarkable ability to derive meaning from complicated or limited data. An ANN can be used to extract patterns and detect trends that are too complex to be noticed via conventional computer models. The data from a lysimeter study, carried out in the summer of 2004, was used in this study to develop and evaluate the ANN models. Based on the results presented in chapter III, the treatment conditions in the lysimeter study were assumed to be a single treatment condition.

The candidate, being the author of the manuscript, was responsible for carrying out the study, as well statistical analysis to ascertain the efficiency of the neural network model. Dr. Shiv O. Prasher, Professor of Bioresource Engineering and supervisor of the candidate, has provided his able guidance and has encouraged the author from the onset of the study.

**Research paper based on the chapter:**

Nilufar, F. and S.O. Prasher. Prediction of herbicide concentrations in agricultural soil using artificial neural network. (Manuscript to be submitted to the *Canadian Bioresource Engineering Journal*).

# CHAPTER V

# PREDICTION OF HERBICIDE CONCENTRATIONS IN AGRICULTURAL SOILS USING ARTIFICIAL NEURAL NETWORK

## Abstract

An Artificial Neural Network (ANN) model, using a cascade correlation learning algorithm was used to simulate concentrations of three commonly used herbicides – atrazine, metolachlor, and metribuzin– in agricultural soils. To examine between-sample variation in herbicide concentration predictions from small-sized datasets, a cross-validation approach was used. The model was built and trained with the following input parameters: accumulated daily irrigation, number of days after pesticide application, and soil temperature. The outputs of ANN model included the herbicide (atrazine, metolachlor, and metribuzin) concentrations in soil at 0, 0.1, 0.2, 0.4, and 0.7 m depths throughout the study period. The outputs from the ANN model were then compared with the experimental data obtained from a lysimeter study. The ANN model produced consistently good model prediction performance efficiency with a relatively low relative root mean square error, and with a good correlation coefficient for the three herbicides at different depths of the soil profile. The relative importance of the input parameters considered by the ANN model was also investigated. The time of sample collection and temperature of the soil profile were found to be the two most important parameters for predicting pesticide concentrations at different depths of the soil profile. Although irrigation was important in the upper soil profile, its importance was reduced in the lower soil profile. Therefore, the ANN model produced an effective input-output relationship and simulated herbicide concentrations with a small number of input parameters, as well with a small-sized dataset.

**Keywords.** Artificial Neural Network, cascade correlation algorithm, six-fold cross-validation, atrazine, metolachlor, and metribuzin.

## 5.1 Introduction

Pesticides applied to agricultural fields can potentially leach to the groundwater, depending on soil properties and the chemical properties of the pesticides (North Carolina Pesticide Board, 1997). Moreover, rainfall and irrigation are the main forces driving pesticides downwards through the soil. Consequently, in irrigated area or high rainfall regions, pesticides are being detected in deeper soil profiles as well as in ground water (Smith et al., 1995). The USEPA (1998) reported that as a result of the agricultural use of pesticides, 46 different pesticides had been detected in ground water and 76 pesticides in surface water bodies. Throughout the world, the accumulation of pesticides in food and drinking water has been generally recognized as dangerous, and the long-term persistence and toxicity of pesticides in groundwater is potentially responsible for causing various kinds of human illness (Mannion, 1995; Peralta et al., 1994). Therefore, potentially undesirable effects of pesticides on the environment and human health have been among the main concerns of recent research (Swancar, 1996; Colborn, et al., 1997; Stangil, 2001; Hébert and Rondeau, 2004).

To continue the use of pesticides for better crop production, as well as to reduce their impact on the environment, it is important to understand the physical transport phenomena of pesticides and to model their concentrations under different field conditions. Although several field (Crisanto et al., 1995; Cox et al., 1997; McDonald et al., 1999; Azevedo et al., 2000; Andreu & Picó, 2004), laboratory (Sánchez-Camanzano et al., 1996; Abu-Zreig et al., 1999; Guo et al., 2000; Sánchez-Camanzano et al., 2000; Sánchez, 2004), and lysimeter studies (Jebellie, 1997; Renaud et al., 2004) have been conducted to asses the transport behavior of pesticides, their scope have been limited by sparse knowledge about natural variability (macro pore flow, micro pore flow, soil types, microorganisms, various chemical properties, etc), and also due to the lack of field and analytical research facilities. To eliminate such limitations and to consider the convergence of all possible phenomena, conventional mathematical models have been used to simulate the complex physcio-chemical behavior of pesticides in the soil profile (Mutch et al., 1993; Nichols, 1994; Clemente et al., 1998). However, mathematical models need a number of input parameters, some of which are either difficult or tedious to obtain at a sufficient spatial or temporal density to cover the inherent variability in soil and the weather. Although, some models need less input parameters, the assumptions to simplify the models limit their use for variable field conditions, and produce inaccurate predictions. Nevertheless, the search to find an alternative method for simple, accurate, and fast simulation modeling remains of interest.

An Artificial Neural network (ANN) is an information-processing model inspired by the biological nervous system. It can perform complex tasks like pattern recognition, and processes information in a way similar to the human brain. ANNs—which do not require explicit definitions between systems inputs and outputs—are an alternative to conventional mathematical models. Conventional computer models use an algorithmic approach, i.e., to solve a problem, the computer follows a set of instructions. Until the specific steps to follow are known, the computer model cannot solve the problem. Due to its remarkable ability to derive meaning from complicated or imprecise data by learning from examples, an ANN can be used to extract patterns and detect trends that are too complex to be noticed by either humans or other conventional computer models. Moreover, the requirement for fewer input parameters and quick execution are additional advantages of ANNs.

In recent research in the fields of hydrology, agriculture, surface, and subsurface water quality, ANNs are increasingly being used for predictive purposes (Hsu et al., 1995; Maier and Dandy, 1999; Schleiter et al., 1999; Ni et al., 2004). ANNs have been effectively used for simulating water table depths in subsurface-drained and subirrigated fields (Yang et al., 1996); and for simulating soil temperature and concentrations of pesticides in agricultural soils and wells (Yang et al., 1997; Sahoo et al., 2004). As well, ANNs have also been used to asses nitrate contamination in wells (Sahoo et al., 2004), saturated hydraulic conductivity in soils (Lebron et al., 1999), and annual nitrate loss in drain outflow (Salehi et al., 2000). In this study the ability of ANNs to simulate pesticide fate in the soil is evaluated. The objectives are to:

i) simulate, by using an ANN model, the concentrations of three herbicides—atrazine, metolachlor, and metribuzin— over time at the soil surface as well at 0.1, 0.2, 0.4 and 0.7 m soil depths;

ii) compare predicted concentrations to those measured in a lysimeter study.

## 5.2 Methodology

### 5.2.1 Experiment details and data

An experiment was conducted in field lysimeters at the Macdonald Campus of McGill University, from June to September, 2004, to study the fate and transport of three commonly used pesticides in the soil. Nine PVC lysimeters (1 m high × 0.45 m diameter) were packed uniformly with a sandy soil ($\rho = 1.35$ kg $m^{-3}$) to a depth of 0.9 m. Table 5.1 gives the physical properties of the soil. A free drainage system was provided for all the lysimeters. The study area was covered with a shed to prevent the rainfall from reaching the lysimeters throughout the period of experiment. The experiment was conducted with three different types of water applications: tap water, anionic surfactant with water, and nonionic surfactant with water. Atrazine *(2-chloro-4-ethylamine-6-isopropylamino-S-triazine)*, metolachlor *(2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide)*, and metribuzin *(4-amino-6-tert-butyl-4, 5-dihydro-3-methyltio-1, 2, 4-triazin-5-one)* were sprayed only once during the experiment (July, 2004), at the locally recommended rate (2.5, 2.75 and 1.0 kg $ha^{-1}$, respectively) to all lysimeters. Sampling holes (laterally) were made at 0.1, 0.2, 0.4 and 0.7 m depths from the soil surface in all lysimeters for soil sampling. The soil samples were taken on days 0, 1, 2, 5, 10, 21, 30, 50, and 90 after the application of pesticides. The extractions of the soil samples were done in the laboratory and the concentrations of three herbicides were measured using LC/MS (Liquid Chromatography with Mass Spectrum). Since there were no significant differences found among the three water application treatments on the occurrences of herbicides in the soil profile, all the data were taken for neural network prediction assuming one (Tap water) treatment condition having six replicates, as far as water is concerned.

**Table 5.1 Physical properties of soil**

| | | | |
|---|---|---|---|
| Sand | 92.20% | Organic Matter Content | 2.97 % |
| Silt | 4.30% | Hydraulic conductivity | 3.68 m $day^{-1}$ (SD*=0.87) |
| Soil type : | Sand | pH | 5.5 |
| Bulk Density | 1.35 kg $m^{-3}$ | CEC | 4.9 cmol $kg^{-1}$ |

*SD=standard deviation

### 5.2.2 Artificial neural networks

Artificial Neural networks are analytical techniques, which can acquire information of a complex process from a set of observed data, sort the information of the fundamental process, and assemble the information to generate new observations (predictions) from same data types. While acquiring the knowledge of any situation from the observed data (training set), an iterative process is usually applied to a number of observed data to normalize the weights of the network and build the model. The typical structure of neural network technology is based on the computer-generated neuron showed in Figure 5.1. When any number of observed data (inputs) from an unknown environment is input to the neural network, the network processes the observed data to produce the network's predictions (outputs).

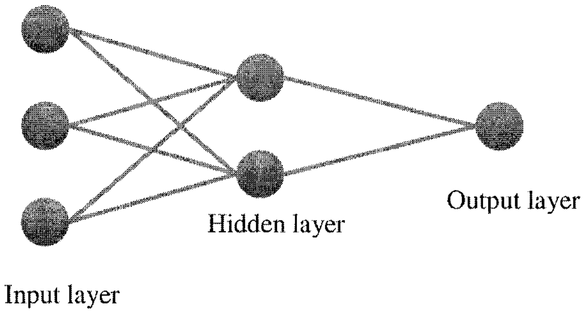


Figure 5.1 Network Structure

Neural networks are developed based on certain algorithms that allow a computer to make decisions based on past experiences. Although different types of neural networks are available, all of them function by imitating a human brain. The efficiency of a neural network is determined by how the network "learns." Supervised learning is the most widely used technique in the neural network held. The most popular supervised learning techniques used in the neural networks are back-propagation, radial-basis, and delta rule training algorithms. Although back-propagation was one of the first training algorithms, and is widely used for its simplicity, its learning rate is fairly slow. A simple network consisting of 2 inputs, 2 hidden and 1 output neuron, using back-propagation, can take thousands of epochs (epoch is one cycle through all the input data rows) to reach an acceptable error level. To overcome certain limitations of most popular back-propagation algorithms, Fahlman and Lebiere (1990) developed a new architecture for a supervised learning algorithm for artificial neural networks named the Cascade Correlation algorithm.

The main feature of the Cascade Correlation architecture is that the network begins with input neurons, output neurons and no hidden units. Hidden units are added to the network, one at a time, and connections of hidden units do not change after they have been added to the network (Figure 5.2).When the observed data are fed into an input neuron, the neurons starts activating. There is also a *bias* input, which is permanently set to +1 in the network and connected to every hidden or output unit, which can be learned just like other weights. In a given training set, always at least two equally logical, but totally opposite (true or false), generalizations could be made. However, bias is simply used to distinguish between these two logical outcomes. In neural networks, the value of the output neuron is a function of the sum of all input neuron values multiplied by the weight of the corresponding link to the output neuron, which can be written mathematically as:

$$y = f\left[\sum(x_1 w_1 + x_2 w_2 + x_3 w_3 + .......) + \beta\right] ........................ (5.1)$$

where,

$y$ = the output from neurons
$x_1, x_2, x_3...$ = input values
$w_1, w_2, w_3...$ = connection weights
$\beta$ = the bias value
$f(....)$= the transfer function = $\frac{1}{1+e^{-(...)}}$ (typical sigmoidal function)

The objective of a neural network is to generate an output value that is close to the observed value. At the beginning, the absolute difference between output from the network and the desired value (network error) can be high since the weights of the links are set randomly. But the network learns over time, which is called training, and sets new weights to each link, so as to give better prediction results. The absolute difference between the desired results and the network results are known as the network errors. The process is repeated for all the input data rows, fed to the network one by one. If the network error is too large, then one hidden neuron is added between the inputs and the outputs, and network is trained by transferring all the weighted inputs through the hidden unit towards the outputs (Figure 5.2). The hidden input weights are frozen at the time the unit is added to the network, and only the output connections are trained repeatedly using the delta rule, which is also known as least mean squares rule (Duong et al., 1996).

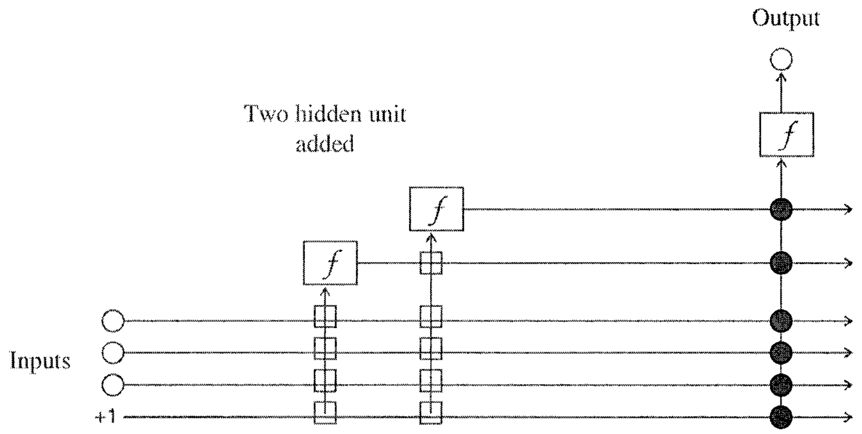


**Figure 5.2 Cascade Correlation architecture with 2 hidden units added, one after another (vertical lines summing up all the incoming activations). Node connections are trained repeatedly and box connections do not change.** [Source: Fahlman and Lebiere, 1990]

More hidden units are added, if necessary, one by one until the network performs adequately. Each hidden unit receives a connection from each of the input neurons and from any pre-existing hidden units resulting in a multilayered structure. The structure of the neural network becomes a deep net of cascaded hidden units, rather than a network with a wide hidden layer. For each hidden unit, the magnitude of the correlation between the new unit and output is maximized, and the residual error is eliminated using either a least mean square (LMS) rule or the Quickprop learning algorithm. The learning process is continued until an acceptable range of error is achieved.

The advantages of the Cascade correlation algorithm are that it requires only a forward pass, and that, at any given time, only one layer of weights are trained in the network, while the rest of the network doesn't change so the results can be cached. Therefore, it can serve as a high-order feature detector without a dramatic slow down, and can be used successfully for incremental learning. The Cascade correlation system learns very fast; the learning time in epochs grows roughly as N log N, where N is the number of hidden units added to solve the specific problem. The readers are referred to

Fahlman and Lebiere (1990) for further details about the cascade correlation algorithm and mathematical equations.

In this study, a commercial software package NeuroShell® Predictor 2.2 by Ward Systems Inc. was used to model and test the neural networks. Neuroshell Predictor is designed using TurboProp 2$^{TM}$, a proprietary variant of the cascade correlation algorithm, to simplify the conception of neural network applications to solve problems of forecasting and pattern recognition.

### 5.2.3 Model inputs and output

To simulate the herbicide concentrations in soil, neural network models were developed with inputs that are known to affect degradation, persistence and movement of herbicides, as well to be easily available in the field (Yang et al., 1997). Soil depth, irrigation, soil temperature, potential evapotranspiration and time (days after the pesticide application) were used as inputs to simulate soil pesticide concentrations with the ANN model. The outputs of the ANN model included the herbicide (atrazine, metolachlor, and metribuzin) concentrations in the soil at 0, 0.1, 0.2, 0.4, and 0.7 m depths. At the beginning the neural network had four inputs and one output, one such neural network for each depth. However, potential evapotranspiration is found to have minute effect on the movement of the herbicides (Yang et al., 1997), and thus was excluded from the input set.

### 5.2.4 Model development and validation

The quality of prediction depends on the data used in training the neural network and the design of the ANN itself. If all the inputs that affect the prediction are not included in building the neural network, good predictions are not possible. Typically, a large database is required to train a neural network model. However, only a limited number of data can be obtained from field studies. Cross-validation, one of the most commonly used resampling techniques (Stone, 1974), can be used to ensure the reliability of the model when the number of values in the dataset are few (Liu 1995; Derks et al., 1996; Yang et al., 1997; Prechelt, 1998; Zhang et al., 1999; Shaoo et al., 2004;). The principle of cross-validation is to divide the dataset into random training and test samples, where all the observations or patterns in the available samples are used for training the model. The training samples are used for fitting the model or parameter estimations, while the predictive effectiveness of the fitted model is validated using the test samples. A cross-validation method is able to examine the predictive validity of a neural network model by overlapping training samples and predicting exclusive test samples, when a small dataset is used for prediction purposes.

In this study, to split the available dataset evenly and to ensure the representative amount of data in the training and test sets, a six-fold cross-validation method was used. The total number of values in the dataset (herbicide concentrations at a particular depth) were randomized and then divided in to 6 subsets, with approximately the same number of samples. At any given time, five subsets were used as the training dataset, and the remaining subset (unseen data) was used for testing (Figure 5.3).

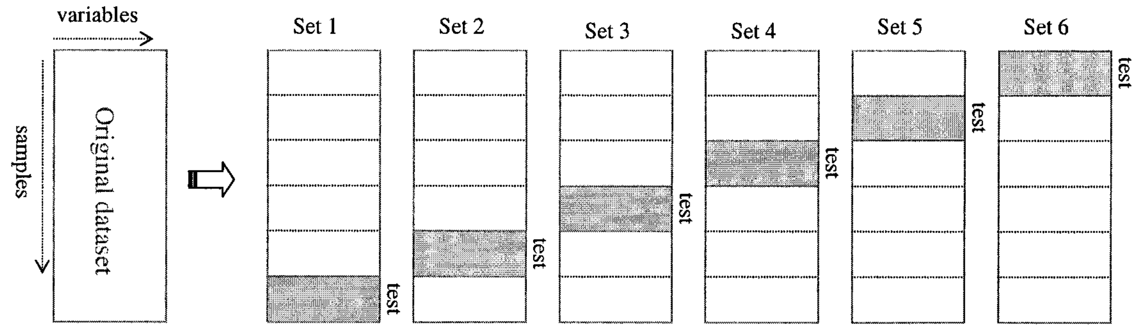


**Figure 5.3 Original data set is subdivided into six sets having different training and test sets.**
[Source: Derks et al., 1996]

Therefore, for each of the test datasets, a different prediction model was developed by the neural network, and those models were used to predict the unseen test datasets. The classical least square regression for the test sets was recorded for validation, and further evaluation was done using common statistical indices. This procedure was repeated to predict herbicide concentrations at different depths of the soil profile, for the three herbicides separately.

To retain available information to build a model and to compare the performance of six fold cross-validation method, another network was developed using the whole data set (trained and tested with same dataset). The errors from this network were compared with the cross-validation mean errors of the six models, proving the reliable performance of the cross-validation method with neural networks. Also, the relative importance of each input parameter, over the other inputs, was determined. This step would allow us to determine minimum input data required by the neural network to make predictions accurately.

### 5.2.5 Analysis of Results

To evaluate the predictive analysis of the model, the most common statistical indices, Root Mean Square Error (RMSE), Relative Root Mean Square Error (R-RMSE) and modeling efficiency (EF) were used for the validation of test datasets, and the formula used are briefly explained below:

RMSE The RMSE is used to measure estimator performance; it represents the expected accuracy under the simulated uncertainty conditions. The RMSE is expressed as (Fox, 1981):

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}\left(\hat{Y}_i - Y_i\right)^2}{N}} \tag{5.2}$$

where, $\hat{Y}_i$ is predicted pesticide concentration (μg $g^{-1}$), for sample size of N
$Y_i$ is measured pesticide concentration (μg $g^{-1}$), for sample size of N

RRMSE The RRMSE standardizes the RMSE, which represents the standard variation of the estimator. The RRMSE assigns equal weight to any overestimation or underestimation of the statistic. RRMSE is expressed as (Martin et al., 2003):

$$RRMSE = \frac{RMSE}{\overline{Y}} \tag{5.3}$$

where, $\overline{Y}$ is Mean of measured pesticide concentration (μg $g^{-1}$)

EF Modeling efficiency represents the overall model performance, and expressed as (Greenwood et al., 1985; Yang et al., 2000):

$$EF = 1 - \frac{\sum\left(\hat{Y}_i - Y_i\right)^2}{\sum\left(Y_i - \overline{Y}\right)^2} \tag{5.4}$$

where, $\hat{Y}_i$ is predicted pesticide concentration (μg $g^{-1}$), for sample size of N
$Y_i$ is measured pesticide concentration (μg $g^{-1}$), for sample size of N
$\overline{Y}$ is mean of measured pesticide concentration (μg $g^{-1}$)

## 5.3 Results and Discussion

Neural network model is used to predict the three herbicide concentrations at different depths of the soil profile. A six fold cross-validation method was used to develop the neural network models, and the variations among the six cross-validation models were evaluated for the three herbicides. The prediction performance of the neural network model is presented using the best and worst model results, out of the six cross-validation models, by comparing with the measured data obtained from the lysimeter experiment, for five different depths and for three herbicides. Also, the relative importance of the input parameters used by the neural network model is discussed.

### 5.3.1 Performance evaluation of six-fold cross-validation method

Figure 5.4 represents the variations among six neural network models developed for the three herbicides at different depths of the soil profile. Each column of points represents the RRMSE values obtained from six cross-validation models corresponding to the particular depths. The wider the distribution of the points in each column, greater the variations among the six cross-validation sets. For atrazine, at 0, 0.1 and 0.7 m depths, the figure shows less variation among the cross-validation subsets (Figure 5.4). Also for metolachlor, at 0 and 0.1 m depths, and for metribuzin, 0.1 and 0.7 m depths the cross validation models show less variations. The standard deviation of prediction errors, expressed as STD (RRMSE), also indicates a relatively small variation among the six cross-validation subsets at those depths, for the three herbicides (Table 5.2). Figure 5.4 also shows that for atrazine at 0.2 and 0.4 m depths, network predictions were varying widely (Figure 5.4). Similar behavior can be noticed at 0.2 m depth for metolachlor and 0, 0.2, and 0.4 m depths for metribuzin (Figure 5.4). Also, the STD (RRMSE) is relatively higher for these depths for the three herbicides (Table 5.2). This variation indicates the noise among the datasets at those particular depths and the variation might be due to highly complex input-output relationships. However, the RRMSE values change with the cross validation fold number and with depths. This indicates that neural network model is affected, to some extent, by the choice of the dataset.

Therefore, concerning the robustness of the prediction performance using a six-fold cross validation approach, a neural network model was developed using the whole dataset (same data for both training and testing). The average RRMSE of six cross-validation prediction models for atrazine, metolachlor and metribuzin are compared with the RRMSE of the network trained and tested with same dataset (Figure 5.5). The figure shows that, for atrazine, the average RRMSE of six fold cross-validation models had very little variation with the RRMSE of network developed with whole dataset for different depths of the soil profile. For metolachlor, the average cross-validation RRMSE were slightly higher than the network RRMSE with whole dataset. Similarly, for metribuzin, the average RRMSE of six cross-validation models were almost same as the network RRMSE with the whole dataset (Figure 5.5). Although the test sets were chosen in a completely randomized manner, the above comparison reveals that cross-validation subsets are also able to get, more or less, necessary information from the datasets used for training. Therefore, the samples in the six training and test sets were sufficiently representative for the appropriate input-output relationships to be made in the neural network model.

**Table 5.2 Mean RRMSE and standard deviation (STD) among six cross-validation models for the three herbicides at different depths**

| | Atrazine | | Metolachlor | | Metribuzin | |
|---|---|---|---|---|---|---|
| Depth, m | Mean | STD | Mean | STD | Mean | STD |
| 0 | 0.63 | 0.06 | 0.48 | 0.10 | 0.60 | 0.25 |
| 0.1 | 0.65 | 0.09 | 0.87 | 0.13 | 0.79 | 0.17 |
| 0.2 | 1.11 | 0.27 | 1.53 | 0.30 | 1.21 | 0.30 |
| 0.4 | 1.21 | 0.25 | - | - | 0.79 | 0.27 |
| 0.7 | 0.96 | 0.17 | - | - | 0.67 | 0.10 |

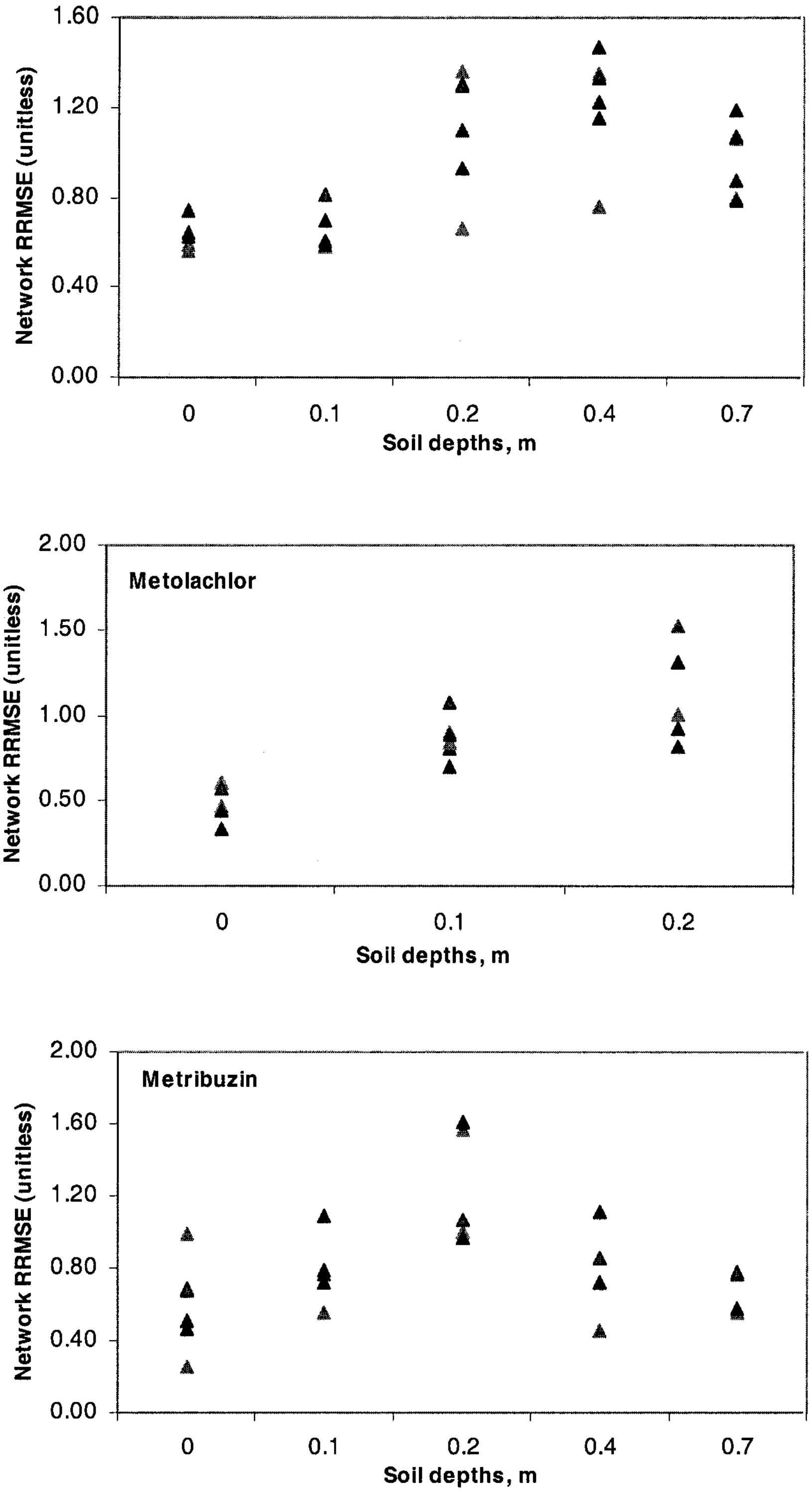


**Figure 5.4 Variations in network performance among six-fold of train-test datasets**

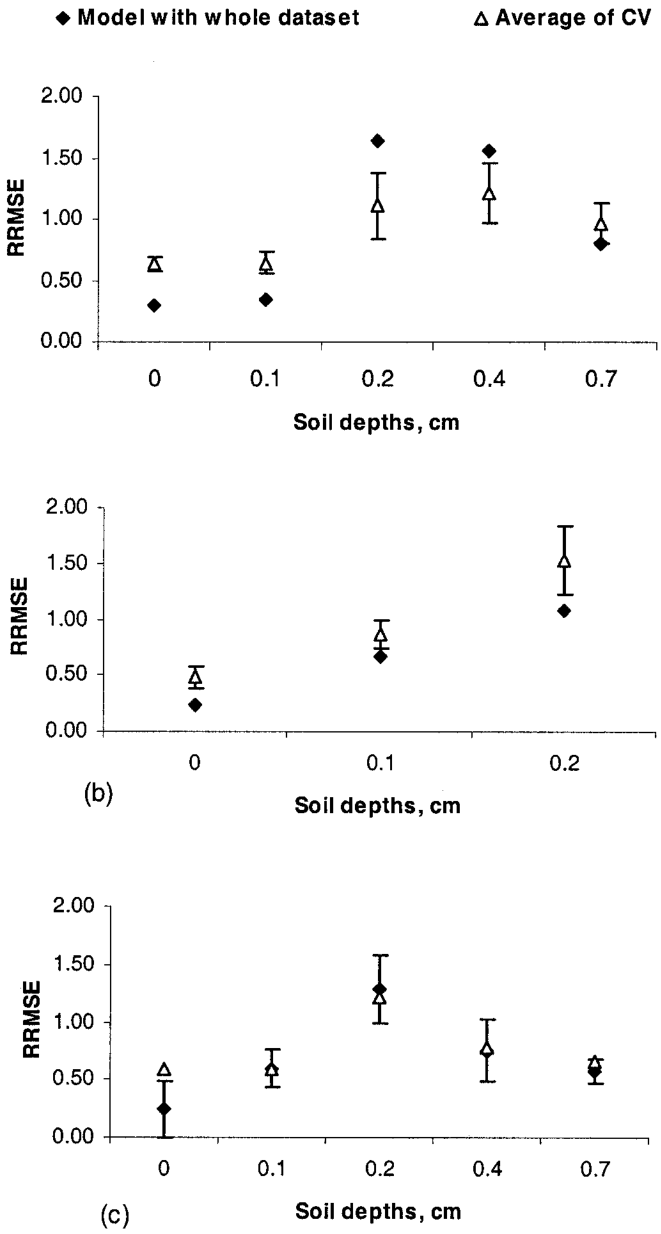


**Figure 5.5 Comparison between average RRMSE of six cross-validation (CV) sets and neural network trained and tested with same datasets (a) atrazine, (b) metolachlor, and (c) metribuzin**

### 5.3.2 Prediction performance of neural network model

To conceptualize the network's prediction performance, the best and worst prediction models among the six prediction models are summarized in Tables 5.3, 5.4, and 5.5, for the three herbicides at different soil depths. For visual interpretation, the predicted vs. measured concentrations for the three herbicides from the best and worst neural network prediction models are also shown in Figures 5.6, 5.7, and 5.8. The prediction for metolachlor concentrations were done for only three depths (0, 0.1, and 0.2 m) because the neural network could not be executed due to insufficient non-zero input data at the 0.4 and 0.7 m depths. One may notice that there are only a few points in the validation dataset (Figures 5.6, 5.7 and 5.8); this is because of the small set (6%) is used for testing since training is important for a network to develop an optimized input-output relationship and to check data for necessary information. Also, at lower depths (0.4 and 0.7 m), the lack of non-zero concentrations produced fewer points in the plot.

At the soil surface, for atrazine, there was a close concurrence between measured and predicted concentrations for the best model (Figure 5.6). The RRMSE and EF indicates the similarity of predicted and measured concentrations (Table 5.3). In the case of the worst model, the RRMSE was a little higher and the EF a little lower. Similar to atrazine, the predicted concentrations of metolachlor and metribuzin, for the best model, were in good agreement with measured concentrations, as can be seen from correlation coefficient (Figure 5.7 and 5.8), RRMSE and EF (Tables 5.4 and 5.5). However, the worst and best models for atrazine and metolachlor gave similar values of RRMSE and EF (Table 5.3 and 5.4), demonstrating the robustness of cross-validation approach in developing prediction models. For metribuzin, for the worst prediction model, although the RRMSE was high and EF was low, the correlation coefficient was good, and there were little variations between the magnitudes of predicted and measured dataset, (Figure 5.8). Nevertheless, the high *r* values and good EF for atrazine and metolachlor at the soil surface reveals that the neural network performed well in both worst and best models, as was the case for the best metribuzin prediction model.

**Table 5.3 Validation performance of the best and worst neural network for predicting atrazine concentrations at different soil depths**

| | Worst prediction | | | | Best prediction | | | |
|---|---|---|---|---|---|---|---|---|
| Depth, (m) | r | RMSE | RRMSE | EF | r | RMSE | RRMSE | EF |
| 0 | 0.94 | 1929.87 | 0.74 | 0.55 | 0.99 | 1276.19 | 0.59 | 0.74 |
| 0.1 | 0.82 | 56.99 | 0.81 | 0.44 | 0.96 | 33.24 | 0.59 | 0.70 |
| 0.2 | 0.40 | 6.62 | 1.35 | -0.59 | 0.97 | 0.29 | 0.66 | 0.66 |
| 0.4 | 0.49 | 1.80 | 1.22 | -0.04 | 0.95 | 0.13 | 0.76 | 0.68 |
| 0.7 | 0.75 | 0.28 | 1.06 | 0.12 | 0.97 | 0.13 | 0.78 | 0.63 |

r – correlation coefficient, RMSE – Root Mean Square Error (ug kg$^{-1}$), RRMSE- Relative Root Mean Square Error, EF- modeling efficiency

**Table 5.4 Validation performance of the best and worst neural network for predicting metolachlor concentrations at different soil depths**

| | Worst prediction | | | | Best prediction | | | |
|---|---|---|---|---|---|---|---|---|
| Depth, (m) | r | RMSE | RRMSE | EF | r | RMSE | RRMSE | EF |
| 0 | 0.98 | 968.37 | 0.46 | 0.76 | 0.99 | 610.22 | 0.33 | 0.90 |
| 0.1 | 0.73 | 144.33 | 0.89 | 0.23 | 0.94 | 47.57 | 0.70 | 0.50 |
| 0.2 | 0.11 | 6.29 | 3.59 | -3.88 | 0.92 | 4.90 | 0.92 | 0.58 |

r – correlation coefficient, RMSE – Root Mean Square Error (ug kg$^{-1}$), RRMSE- Relative Root Mean Square Error, EF- modeling efficiency

**Table 5.5 Validation performance of the best and worst neural network for predicting metribuzin concentrations at different soil depths**

| | Worst prediction | | | | Best prediction | | | |
|---|---|---|---|---|---|---|---|---|
| Depth, (m) | r | RMSE | RRMSE | EF | r | RMSE | RRMSE | EF |
| 0 | 0.94 | 163.73 | 0.98 | 0.11 | 0.99 | 207.38 | 0.26 | 0.92 |
| 0.1 | 0.77 | 5.36 | 0.79 | 0.21 | 0.97 | 1.89 | 0.56 | 0.78 |
| 0.2 | 0.07 | 3.41 | 1.57 | -0.12 | 0.78 | 0.66 | 1.07 | 0.36 |
| 0.4 | 0.92 | 0.45 | 0.85 | 0.61 | 0.99 | 0.13 | 0.46 | 0.88 |
| 0.7 | 0.95 | 0.24 | 0.77 | 0.67 | 0.98 | 0.14 | 0.55 | 0.83 |

r – correlation coefficient, RMSE – Root Mean Square Error (ug kg$^{-1}$), RRMSE- Relative Root Mean Square Error, EF- modeling efficiency

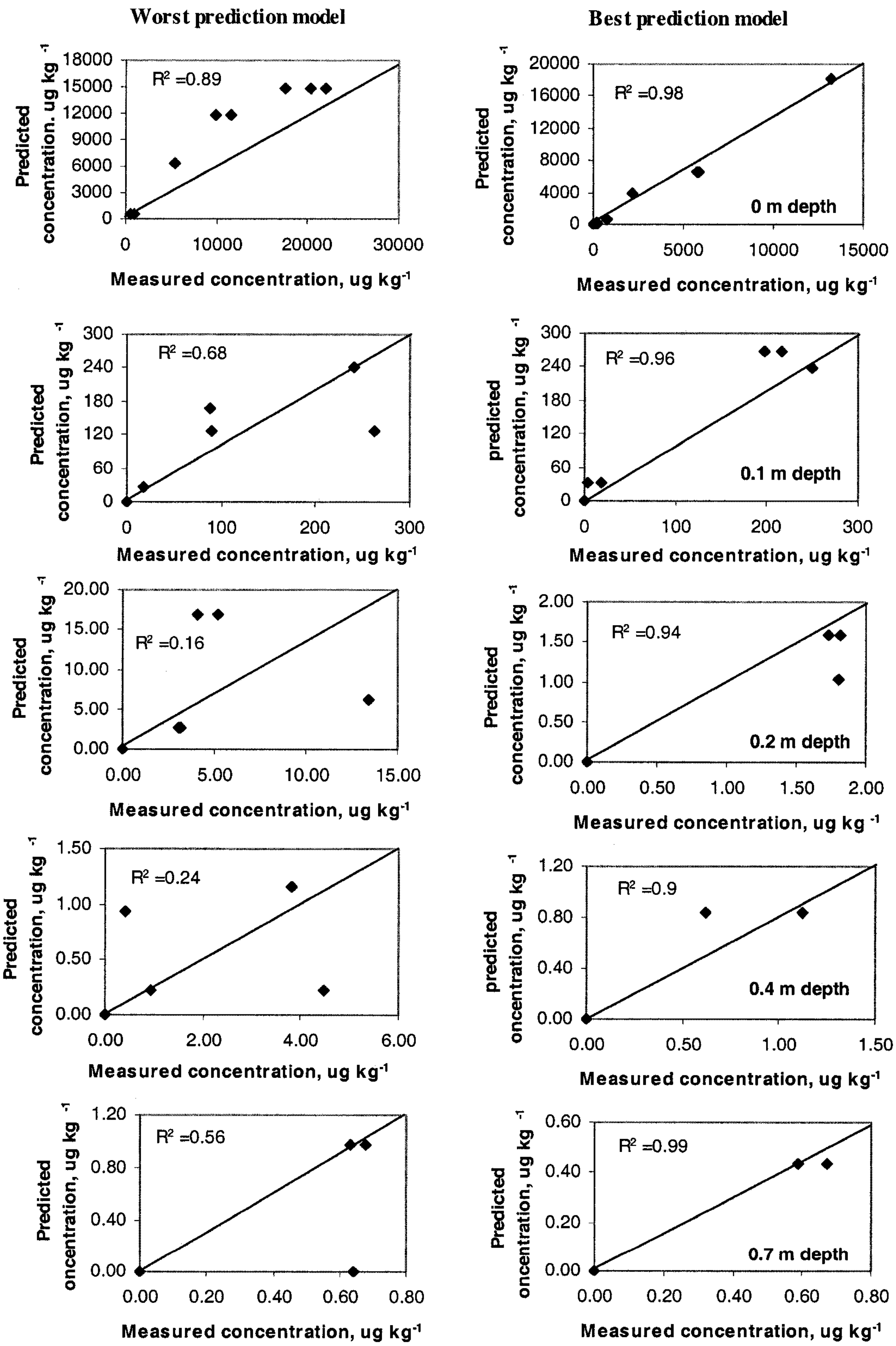


**Figure 5.6 Visual comparisons between best prediction model and worst prediction model for atrazine**

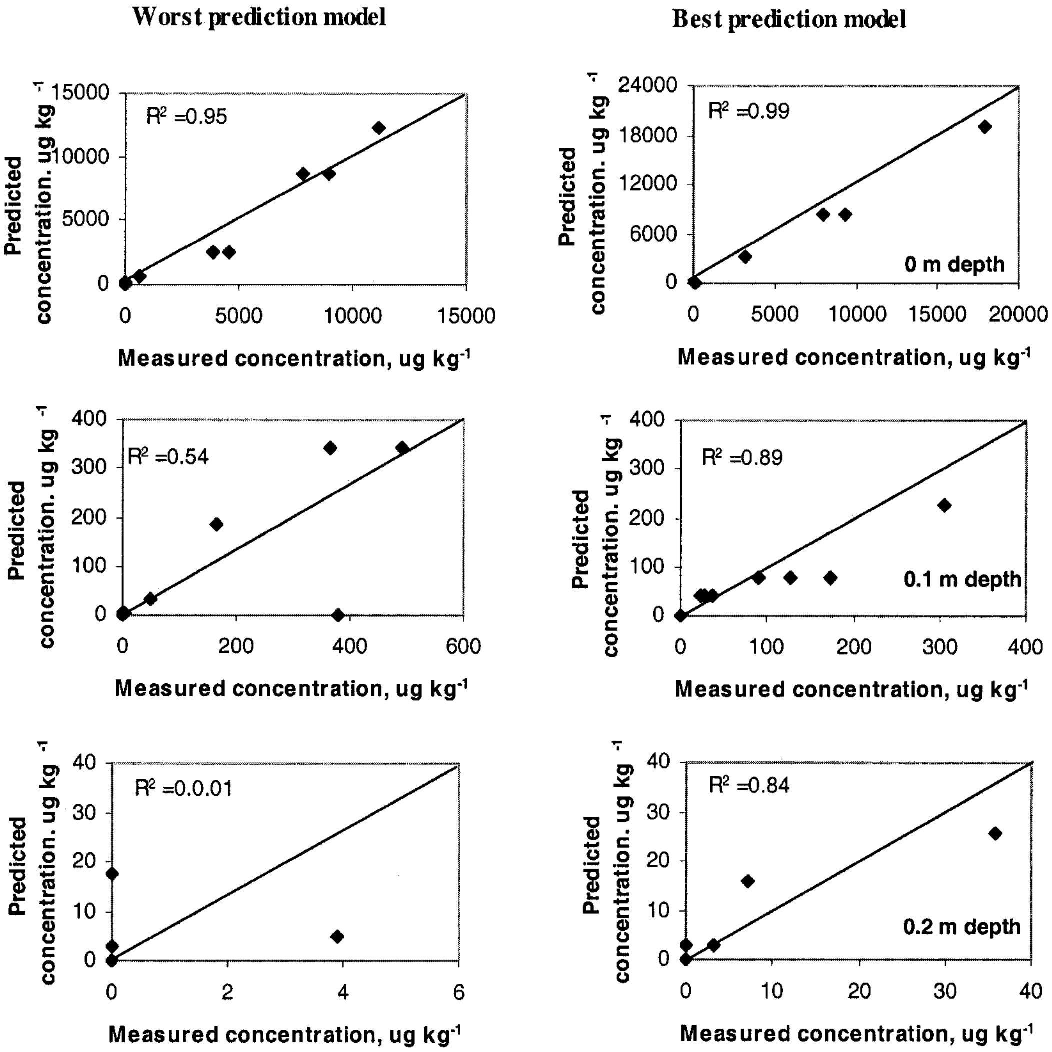


**Figure 5.7 Visual comparisons between best prediction model and worst prediction model for metolachlor**

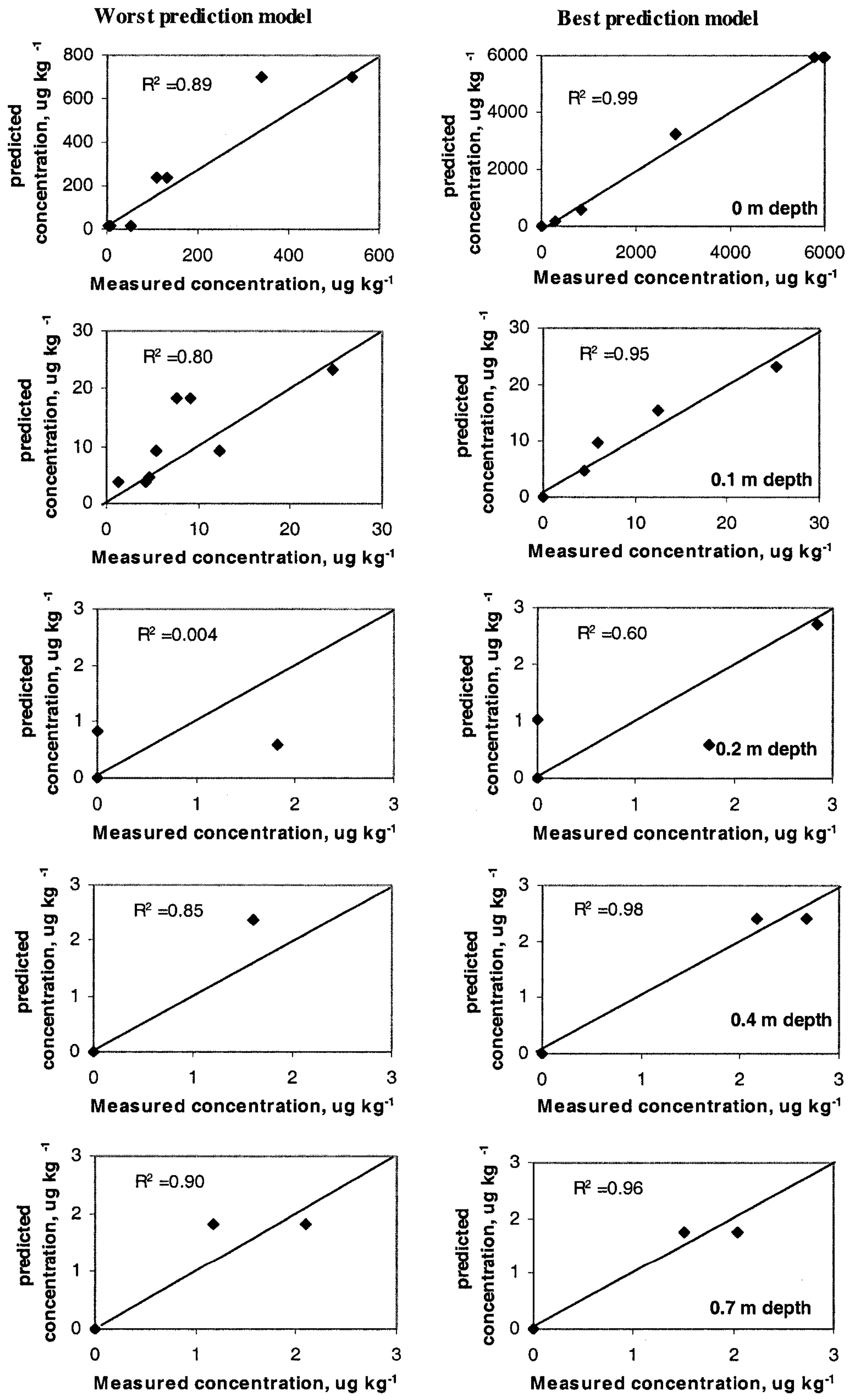


Figure 5.8 Visual comparisons between best prediction model and worst prediction model for metribuzin

At 0.1 m depth, predicted concentrations of atrazine were fairly close to the measured concentrations with a correlation coefficient of 0.96 for the best model, while the RRMSE and EF were 0.59 and 70%, respectively (Table 5.3). In the case of the worst model, the EF was lower, i.e. 44%, with a higher RRMSE. For metolachlor, the RRMSE and EF were 0.7 and 50%; while for metribuzin, the RRMSE was 0.56 and the EF 78%, in the case of the best model (Tables 5.4 and 5.5). However, the worst model performed poorly for metolachlor and metribuzin, showing a low EF (23% and 21%) and a relatively high RRMSE (Figures 5.7 and 5.8).

At 0.2, 0.4, and 0.7 m soil depths, the best model predicted atrazine concentrations satisfactorily; RRMSE of 0.66, 0.76 and 0.78 and EF values of 66%, 68% and 63% at the 0.2, 0.4, and 0.7 m depths, respectively (Table 5.3). For the worst model, at 0.2 and 0.4 m soil depths, the model EF for atrazine was negative, and at 0.7 m depth, the model EF was also poor (Table 5.3 and Figure 5.6).The RRMSE and EF of 0.92 and 58% were found for the best model when predicting metolachlor concentrations at the 0.2 m depth (Table 5.4). For metribuzin, the best model performed poorly at 0.2 m depth, with an RRMSE of 1.07 and EF of 36% (Table 5.5). However, the model prediction for metribuzin concentrations at 0.4 and 0.7 m soil depths were fairly close to the measured concentrations, with higher EF (88% and 83%) and lower RRMSE (0.46 and 0.55). For the worst models, the model EF was negative for metolachlor and metribuzin at 0.2 m depth, along with a high RRMSE (Tables 5.4 and 5.5).The high values of RRMSE in the case of the worst models for the three herbicides reveal greater variations in the magnitudes between the predicted and measured concentrations, which were also the reason for poorer model efficiency.

The underestimation by the worst model might be attributable to having inadequate information regarding herbicide concentrations given the small number of samples available. Also, with the small available dataset, it was hard to create a large dataset for training and another dataset for testing. The RRMSE for the three herbicides increased at the 0.1 m and 0.2 m soil depth, compared to the soil surface, showing a greater discrepancy between the predicted and measured values. Moreover, too much noise in the training dataset, as a result of the variability in the transport of the herbicides at the 0.1 m soil depth, appears to have led the neural network to predict poorly. The general reason for these could be the variable hydraulic conductivity at different layers of the soil profile, macro pore flow, and also the typically complex chemical behavior of the herbicides. At the 0.4 and 0.7 m soil depths, herbicide concentrations in the training datasets were either very low or zero. Consequently, the lack of non- zero values could account for the neural network's poorer ability to predict the complex environmental information, and consequently the discrepancies between predicted and measured data.

Although underestimation was observed for the worst models, the best models performed well with a small number of records in the data set for all depths. Also, in some cases, less variation were found between the best and the worst model, which demonstrating similarity in model performance among the various cross-validation subsets. The mean performance, using the six-fold cross-validation approach, revealed a fairly good performance of the neural network at different soil depths for the three herbicide concentrations. Findings of this study were similar to those of Yang et al. (1997), Salehi et al. (2000), and Sahoo et al. (2004). Moderately high values of RRMSE were obtained for the three herbicides since small numbers of datasets were used (Limsombunchai, 2004). This can be reduced by using a larger dataset. Nevertheless, it is inspiring that limited amount of data and few input parameters were needed to develop the model in this study, and it provided good quality predictions. The execution time taken for each model development was less than one minute, which also demonstrated the simplicity and faster execution of the neural network model.

### 5.3.3 Relative importance of the input parameters

Another important aim in modeling herbicide concentrations with ANNs was to identify the role of different input parameters in the network prediction. The relative importance of the input parameters on herbicide concentrations at different depths were estimated by neural network during the development of the models. Figure 5.9 shows the mean relative importance of three input parameters, mean daily temperature, time after application of herbicides, and irrigation. Temperature of soil profile has an average importance on the concentrations of the three herbicides throughout the soil profile (Figure 5.9). In the field study, the lysimeters were placed above the ground, and seemed to have same average temperature throughout the lysimeter. Therefore, the temperature might affect the degradation of the three herbicides in a similar pattern in the soil profile. The importance of time increased from the soil surface to the lower soil depths, whereas the importance of irrigation decreased at deeper soil profile. This demonstrates herbicide degradation was also directly related to time, which affects the persistence and degradation, and irrigation, which affects mobility. When the herbicides were applied at the beginning, they degrade at a faster rate and, at the same time, they move downwards with irrigation water. When herbicides move to lower profile with time, they degrade at slower rates, and the time after the application of the herbicides plays an important role. Therefore, time crucially affects the persistence of the herbicides throughout the soil profile, and the simulated herbicide concentrations were affected moderately by time. On the other hand, irrigation water moves the herbicides better in the upper soil profile, however, when herbicide reaches to lower profile, the irrigation water might have less effect on their mobility. This is the reason the simulated herbicide concentrations were not much affected by irrigation at lower soil profile. These findings demonstrate the similarity of the results with those obtained by Yang et al. (1997). Therefore, it can be concluded that these input parameters can be used to build a neural network model and they may be sufficient to recognize the flow transport phenomena of the three herbicides in the soil profile.

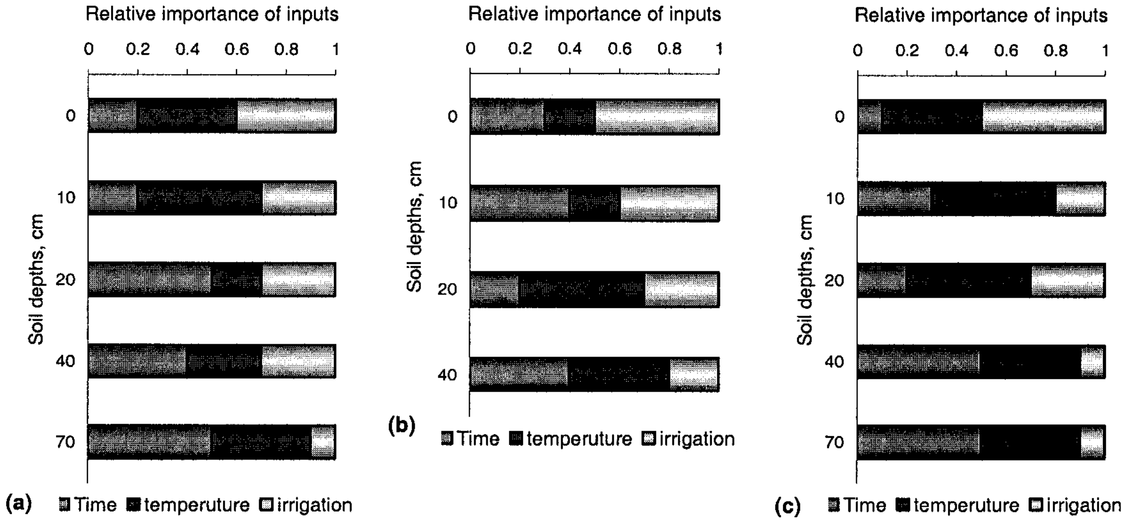


**Figure 5.9 Relative importances of input parameters at different depths for (a) atrazine, (b) metolachlor and (c) metribuzin**

## 5.4 Conclusions

Neural network model was used successfully in simulating the three herbicide concentrations in the soil profile with small amount of available data. A six fold cross-validation method was used to split the dataset randomly into training and test sets, while developing the models. Although in some cases, predictive performance of the neural network model was not good, the overall results still show the effectiveness of neural network modeling to simulate herbicide concentrations in agricultural soils. The input parameters used to develop the neural network model were temperature, time after application of herbicides and irrigation, which are easily measurable and affect herbicide degradation and mobility. Temperature seemed to have similar effect on the degradation of the three herbicides throughout the lysimeters, this might be because lysimeters were placed above the ground surface and the average temperature was same throughout the profile. The relative importance of time and irrigation varied differently at different depths of the lysimeter. The effect of irrigation seemed to have more effect on upper soil profile than lower soil profile, and herbicide degradation was directly related to the time after the application throughout the soil profile. Therefore, it can be concluded that neural network models yielded consistently good quality results with very few input parameters and small-sized datasets. However, the use of a large dataset is recommended, as it would increase the certainty of the neural network model.

# CHAPTER VI

# SUMMARY AND CONCLUSIONS

A lysimeter study was undertaken to evaluate the influence of surfactants on the mobility of the three agricultural herbicides, atrazine, metolachlor and metribuzin. Nine lysimeters (3 pesticides × 3 irrigation treatments), packed with a sandy loam soil, were used to conduct the study. The study area was covered with a rainfall shelter to prevent the lysimeters from being rained on. In order to simulate a worst case scenario, no crop was planted, and hence no plant uptake occurred. The three irrigation treatments consisted of tap water, water containing an anionic surfactant (LAS), and water containing degradation products (NP) of a non-ionic surfactants Soil and water samples were taken at pre-determined time intervals and were analyzed in the laboratory.

A laboratory sorption study was also conducted to quantify the partition coefficient ($k_d$) for the three herbicides in presence of LAS and NP. A mathematical model PESTFADE was used to simulate the mobility of the three herbicides in the soil profile. An Artificial Neural Network (ANN) was also employed for predicting the three herbicide concentrations in the soil profile. A cross-validation approach was used for splitting the datasets into training and test sets for the neural network model.

The following conclusions were drawn from this study:

i. The application of anionic (LAS) and degradation products (NP) of a non-ionic surfactant, at low concentrations, in irrigation water did not increase the mobility of atrazine, metolachlor and metribuzin.

ii. Slight deviations were observed in the distribution of all three herbicides in the upper soil profile under LAS-containing irrigation water, which could be due to LAS might have slightly enhanced the dispersion of soil aggregates. This would have delayed the mobility of herbicides due to increased adsorption.

iii. The laboratory adsorption test demonstrated that the adsorption of atrazine and metribuzin were increased in the presence of low concentration of LAS.

This was attributed to dispersion in soil aggregates, caused by the LAS, rather than the interaction between LAS and the herbicides.

iv. In presence of NP, the effects on the three herbicides were negligible in the lysimeter study. Slight variations in the concentrations in presence of NP were possibly due to the macro pore flow and non-equilibrium sorption of the herbicide in the lysimeters.

v. The presence of NP in the laboratory sorption test led to a slight increase in adsorption of metolachlor but decreased adsorption of metribuzin, whereas the effect was negligible for atrazine. The effects of NP on adsorption/desorption were not significant.

vi. The presence of anionic (LAS) and degradation products (NP) of a non-ionic surfactant at a low concentration in irrigation water should not cause any increased hazard by increasing the mobility of herbicides to ground water.

vii. The PESTFADE model was used to simulate three agricultural herbicides, atrazine, metolachlor, and metribuzin in the soil profile. While calibrating the model, the most sensitive parameter was found to be the rate constant ($day^{-1}$) for the three herbicides. The simulated results from the PESTFADE model showed a close agreement with the lysimeter data at the soil surface for the three herbicides. Model predicted well at a 0.1 m soil depth, but at 0.2 m soil depth, the model predicted the concentrations of atrazine and metribuzin poorly, while for metolachlor predictions were reasonable. At 0.4 and 0.7 m depths the model performed similarly for all three herbicides, giving slight underestimations.

viii. An ANN model was developed to simulate the concentrations of the three herbicides. At the upper soil profile the results of all cross-validation subsets were in close agreement with the predicted herbicide concentrations. For the lower profiles, the ANN prediction result was not as good. These variations in results, between cross-validation test sets, occurred when the samples were split into subsets. In some cases, the training sets provided limited necessary information for the model to use, when predicting test sets. Also, the limited number of data and the existence of non-zero values at lower soil profiles led to the poorer model predictions. This emphasizes the necessity of using good quality and large numbers of datasets to avoid poor ANN worst predictions and to obtain greater reliability.

ix. Three input parameters, temperature, irrigation and time (after pesticide application), were found to be important variables, as far as ANN modeling of the three herbicides is concerned. Temperature was found to have similar effect on the three herbicides behavior throughout all depths, since the lysimeters were placed above ground and temperatures were almost same in the soil profile.

# CHAPTER VII

# FUTURE RECOMMENDATIONS

Although the study was conducted successfully in the lysimeters and in the laboratory, and computer models and ANNs were employed effectively, a few shortcomings were encountered during the study. In this context, future recommendations are as follows:

i. The study was conducted in a sandy soil and with three herbicides. It is recommended to conduct similar experiments for other soil types. Also, the use of various other pesticides is suggested for future investigations.

ii. The wastewater was prepared in the laboratory using low concentrations of anionic and degradation products of non-ionic surfactants. A wide range of concentrations of those two surfactants should be used to evaluate their influence on herbicide movement. Wastewaters, obtained directly from sewage treatment plants or from an effluent-rich river, should be tested in further studies on pesticide fate and transport.

iii. Computer simulation models can play a very important role in simulating complex scenarios; however, well-documented computer models which can handle the complexities of soil and environmental variables should be tested.

iv. Although ANN models performed well in simulating the three herbicide concentrations in this study, the use of a large dataset is recommended to increase the reliability of their predictions.

# CHAPTER VIII

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# APPENDIX

**Table 1** Atrazine concentrations ( μg kg$^{-1}$) in soil samples under different treatment conditions, Tap water(TW), Linear alkylbenzene sulfonates(LAS) & Nonylphenol(NP)*

| | | Time, days | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Treatment | Depths, cm | 1 | 2 | 5 | 10 | 21 | 30 | 50 | 90 |
| TW1 | Top soil | 21757.38 | 11432 | - | 2850.00 | 1978.56 | 526.56 | 92.24 | 5.80 |
| | 10 | 0.00 | 0.00 | 79.00 | 18.43 | 45.63 | 20.15 | 21.69 | 0.00 |
| | 20 | 0.00 | 0.00 | 2.00 | 7.41 | 5.50 | 14.78 | 1.71 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 1.05 | 0.00 | 0.56 | 0.00 |
| | 70 | 0.00 | 0.00 | 0.00 | 0.00 | 0.67 | 1.44 | 1.50 | 0.00 |
| TW2 | Top soil | 14508.08 | 12320 | - | 1350.00 | 517.53 | 297.43 | 75.73 | 2.80 |
| | 10 | 0.00 | 0.00 | 218.04 | 86.47 | 249.46 | 150.31 | 17.28 | 1.20 |
| | 20 | 0.00 | 0.00 | 1.80 | 1.60 | 1.49 | 5.19 | 3.96 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.90 | 0.00 | 0.77 | 0.00 |
| | 70 | 0.00 | 0.00 | 0.00 | 0.00 | 0.55 | 0.64 | 1.14 | 0.00 |
| TW3 | Top soil | 16606.38 | 10504 | - | 2820.00 | 599.97 | 297.27 | 56.65 | 0.00 |
| | 10 | 0.00 | 0.00 | 198.00 | 89.30 | 234.59 | 156.76 | 18.14 | 0.00 |
| | 20 | 0.00 | 0.00 | 0.97 | 5.02 | 1.73 | 4.09 | 0.11 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 1.12 | 0.00 | 0.55 | 0.00 |
| | 70 | 0.00 | 0.00 | 0.00 | 0.00 | 0.59 | 0.00 | 0.61 | 0.00 |
| LAS1 | Top soil | 16914.75 | 11230 | - | 2150.00 | 1327.75 | 37.22 | 332.70 | 3.50 |
| | 10 | 0.00 | 0.00 | 1.80 | 2.23 | 4.35 | 0.00 | 5.51 | 0.00 |
| | 20 | 0.00 | 0.00 | 1.60 | 5.02 | 0.86 | 7.52 | 2.51 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.82 | 0.66 | 0.88 | 0.00 |
| | 70 | 0.00 | 0.00 | 0.00 | 0.00 | 0.78 | 0.00 | 0.66 | 0.00 |
| LAS2 | Top soil | 22014.26 | 9890 | - | 2150.00 | 785.72 | 79.69 | 138.14 | 12.70 |
| | 10 | 0.00 | 0.00 | 247.00 | 181.10 | 161.15 | 87.33 | 3.28 | 0.00 |
| | 20 | 0.00 | 0.00 | 0.00 | 6.33 | 1.08 | 4.17 | 3.28 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.43 | 0.40 | 0.96 | 0.00 |
| | 70 | 0.00 | 0.00 | 0.00 | 0.00 | 0.31 | 0.00 | 1.46 | 0.00 |
| LAS3 | Top soil | 13184.18 | 10230 | - | 1820.00 | 947.06 | 16.15 | 169.18 | 2.90 |
| | 10 | 0.00 | 0.00 | 323.70 | 262.02 | 312.16 | 192.32 | 5.98 | 0.00 |
| | 20 | 0.00 | 0.00 | 0.00 | 4.90 | 1.82 | 9.41 | 2.98 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.62 | 0.94 | 3.82 | 0.00 |
| | 70 | 0.00 | 0.00 | 0.00 | 0.00 | 0.67 | 0.00 | 0.67 | 0.00 |
| NP1 | Top soil | 17258.22 | 10230 | - | 6321.00 | 1267.56 | 318.50 | 254.40 | 3.40 |
| | 10 | 0.00 | 0.00 | 0.13 | 5.97 | 3.94 | 170.97 | 6.98 | 0.00 |
| | 20 | 0.00 | 0.00 | 2.50 | 0.71 | 1.18 | 2.89 | 1.97 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.65 | 0.00 | 4.18 | 0.00 |
| | 70 | 0.00 | 0.00 | 0.00 | 0.00 | 0.62 | 0.00 | 0.16 | 0.00 |
| NP2 | Top soil | 20399.36 | 11523 | - | 7523.00 | 708.61 | 253.85 | 198.26 | 33.10 |
| | 10 | 0.00 | 0.00 | 216.80 | 71.42 | 249.58 | 200.15 | 41.03 | 0.00 |
| | 20 | 0.00 | 0.00 | 1.70 | 12.63 | 2.24 | 9.82 | 3.07 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 1.17 | 0.49 | 1.77 | 0.00 |
| | 70 | 0.00 | 0.00 | 0.00 | 0.00 | 0.38 | 0.00 | 0.63 | 0.00 |
| NP3 | Top soil | 17579.39 | 13963 | - | 6502.00 | 434.34 | 162.25 | 109.82 | 8.60 |
| | 10 | 0.00 | 0.00 | 276.83 | 172.63 | 240.51 | 137.98 | 62.63 | 0.00 |
| | 20 | 0.00 | 0.00 | 2.44 | 13.41 | 1.50 | 43.84 | 3.11 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.87 | 4.49 | 1.75 | 0.00 |
| | 70 | 0.00 | 0.00 | 0.00 | 0.00 | 0.49 | 0.00 | 0.68 | 0.00 |

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* Zero concentration implies non-detectable level

**Table 2** Metolachlor concentrations ( $\mu g\ kg^{-1}$) in soil samples under different treatment conditions, Tap water(TW), Linear alkylbenzene sulfonates(LAS) & Nonylphenol(NP)*

| | | Time, days | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Treatment | Depth, cm | 1 | 2 | 5 | 10 | 21 | 30 | 50 | 90 |
| TW1 | Top soil | 21465.36 | 14230 | - | 3120 | 1201.78 | 387.89 | 155.11 | 1.20 |
| | 10 | 0.00 | 0.00 | 20.00 | 28.47 | 78.06 | 43.30 | 31.24 | 0.00 |
| | 20 | 0.00 | 0.00 | 40.00 | 11.01 | 2.57 | 2.89 | 0.00 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| TW2 | Top soil | 17257.67 | 10352 | - | 2300 | 585.74 | 15.64 | 82.26 | 3.60 |
| | 10 | 0.00 | 0.00 | 22.45 | 171.21 | 492.88 | 250.03 | 46.42 | 2.70 |
| | 20 | 0.00 | 0.00 | 37.10 | 3.90 | 0.00 | 9.82 | 4.75 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| TW3 | Top soil | 15548.83 | 11252 | - | 2350 | 643.69 | 16.65 | 39.65 | 0.00 |
| | 10 | 0.00 | 0.00 | 49.60 | 70.60 | 233.78 | 167.65 | 75.73 | 0.00 |
| | 20 | 0.00 | 0.00 | 35.80 | 7.33 | 2.70 | 43.84 | 0.00 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| LAS1 | Top soil | 23162.45 | 13630 | - | 2120 | 1036.06 | 412.18 | 124.75 | 2.70 |
| | 10 | 0.00 | 0.00 | 21.75 | 3.86 | 3.33 | 0.00 | 8.44 | 0.00 |
| | 20 | 0.00 | 0.00 | 31.20 | 7.33 | 0.00 | 0.00 | 1.81 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| LAS2 | Top soil | 17873.35 | 12300 | - | 2423 | 584.51 | 47.94 | 98.47 | 3.40 |
| | 10 | 0.00 | 0.00 | 37.60 | 445.10 | 272.14 | 98.60 | 112.30 | 3.20 |
| | 20 | 0.00 | 0.00 | 0.00 | 1.35 | 0.00 | 0.00 | 1.67 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| LAS3 | Top soil | 17599.57 | 13677.40 | - | 3850 | 935.56 | 5.53 | 90.89 | 4.50 |
| | 10 | 0.00 | 0.49 | 37.17 | 335.22 | 488.83 | 299.82 | 173.70 | 6.70 |
| | 20 | 0.00 | 0.00 | 31.68 | 1.18 | 1.78 | 18.69 | 5.16 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| NP1 | Top soil | 18179.87 | 12522 | - | 2310 | 953.44 | 102.13 | 231.96 | 3.80 |
| | 10 | 0.00 | 0.00 | 28.40 | 47.55 | 19.33 | 43.30 | 12.58 | 0.00 |
| | 20 | 0.00 | 0.00 | 38.90 | 1.07 | 0.85 | 0.00 | 0.00 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| NP2 | Top soil | 20143.41 | 11131 | - | 4533 | 728.46 | 290.88 | 172.20 | 23.30 |
| | 10 | 0.00 | 0.00 | 28.64 | 119.24 | 379.80 | 113.66 | 89.28 | 0.00 |
| | 20 | 0.00 | 0.00 | 35.80 | 8.30 | 6.81 | 8.15 | 9.36 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 2.76 | 0.00 |
| NP3 | Top soil | 24896.79 | 13652 | - | 3214 | 356.75 | 116.35 | 65.61 | 5.50 |
| | 10 | 0.00 | 378.45 | 36.51 | 304.88 | 364.56 | 163.24 | 127.67 | 0.00 |
| | 20 | 0.00 | 0.00 | 23.60 | 5.99 | 3.33 | 7.12 | 22.57 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

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* Zero concentration implies non-detectable level

**Table 3** Metribuzin concentrations ( $\mu g\ kg^{-1}$) in soil samples under different treatment conditions, Tap water(TW), Linear alkylbenzene sulfonates(LAS) & Nonylphenol(NP)[*]

| | | Time, days | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Treatment | Depth, cm | 1 | 2 | 5 | 10 | 21 | 30 | 50 | 90 |
| TW1 | Top soil | 5760.19 | 2853.00 | - | 560.00 | 390.56 | 103.62 | 28.17 | 3.20 |
| | 10 | 0.00 | 0.00 | 0.00 | 2.97 | 0.58 | 1.45 | 1.77 | 0.00 |
| | 20 | 0.00 | 0.00 | 4.09 | 1.02 | 0.64 | 0.00 | 1.48 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 1.90 | 0.00 |
| | 70 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 2.61 | 0.00 |
| TW2 | Top soil | 4204.94 | 2610.00 | - | 338.00 | 110.61 | 12.04 | 11.54 | 1.20 |
| | 10 | 0.00 | 0.00 | 27.00 | 5.43 | 7.57 | 5.27 | 2.55 | 0.00 |
| | 20 | 0.00 | 0.00 | 3.70 | 0.00 | 0.75 | 0.00 | 1.52 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 2.84 | 0.00 |
| | 70 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 1.60 | 0.00 |
| TW3 | Top soil | 5986.91 | 3380.00 | - | 540.00 | 174.95 | 17.45 | 16.80 | 0.00 |
| | 10 | 0.00 | 0.00 | 24.60 | 12.32 | 19.41 | 4.54 | 4.61 | 0.00 |
| | 20 | 0.00 | 0.00 | 6.15 | 0.00 | 0.00 | 0.00 | 1.50 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 3.38 | 0.00 |
| | 70 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 2.09 | 0.00 |
| LAS1 | Top soil | 5649.96 | 2850.00 | | 531.00 | 360.78 | 18.40 | 80.28 | 2.10 |
| | 10 | 0.00 | 0.00 | 0.30 | 0.90 | 0.77 | 7.33 | 0.00 | 0.00 |
| | 20 | 0.00 | 0.00 | 3.70 | 0.00 | 0.00 | 0.00 | 2.03 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 7.46 | 0.00 |
| | 70 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 2.35 | 0.00 |
| LAS2 | Top soil | 6572.04 | 3170.00 | - | 538.00 | 306.93 | 27.80 | 41.60 | 0.00 |
| | 10 | 0.00 | 0.00 | 25.40 | 11.98 | 8.07 | 0.79 | 5.66 | 0.00 |
| | 20 | 0.00 | 0.00 | 0.00 | 0.00 | 4.92 | 0.00 | 2.53 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 1.76 | 0.00 |
| | 70 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 2.12 | 0.00 |
| LAS3 | Top soil | 5969.66 | 2820.00 | - | 620.00 | 303.36 | 10.54 | 52.26 | 0.00 |
| | 10 | 0.00 | 0.00 | 32.40 | 8.95 | 12.56 | 3.27 | 4.27 | 0.00 |
| | 20 | 0.00 | 0.00 | 10.50 | 1.17 | 9.27 | 4.14 | 2.94 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 2.67 | 0.00 |
| | 70 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 2.04 | 0.00 |
| NP1 | Top soil | 6836.18 | 3220.00 | - | 991.20 | 321.25 | 10.59 | 5.56 | 2.10 |
| | 10 | 0.00 | 0.00 | 11.30 | 1.26 | 5.91 | 0.00 | 2.78 | 0.00 |
| | 20 | 0.00 | 0.00 | 3.17 | 0.00 | 0.00 | 0.00 | 2.78 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 2.70 | 0.00 |
| | 70 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 1.68 | 0.00 |
| NP2 | Top soil | 5771.90 | 3521.00 | - | 847.20 | 176.98 | 9.31 | 4.73 | 2.30 |
| | 10 | 0.00 | 0.00 | 15.66 | 5.94 | 32.84 | 4.60 | 2.72 | 0.00 |
| | 20 | 0.00 | 0.00 | 2.90 | 1.82 | 2.85 | 0.00 | 2.72 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 1.60 | 0.00 |
| | 70 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 1.18 | 0.00 |
| NP3 | Top soil | 6969.73 | 3532.00 | - | 798.00 | 131.59 | 10.69 | 3.12 | 0.00 |
| | 10 | 0.00 | 0.00 | 15.49 | 10.27 | 9.09 | 9.40 | 1.33 | 0.00 |
| | 20 | 0.00 | 0.00 | 3.78 | 1.75 | 1.60 | 0.00 | 1.33 | 0.00 |
| | 40 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 2.16 | 0.00 |
| | 70 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 1.50 | 0.00 |

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[*] Zero concentration implies non-detectable level

**Table 4** Atrazine, metolachlor and metribuzin concentrations ( μg $L^{-1}$) in Water samples under different treatment conditions, Tap water(TW), Linear alkylbenzene sulfonates(LAS) and Nonylphenol(NP)[§]

| Herbicides | Time, day | TW1 | TW2 | TW3 | LAS1 | LAS2 | LAS3 | NP1 | NP2 | NP3 |
|---|---|---|---|---|---|---|---|---|---|---|
| Atrazine | 1 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 10 | 0.005 | 0.006 | 0.008 | 0.006 | 0.003 | 0.005 | 0.004 | 0.005 | 0.021 |
| | 21 | 0.008 | 0.009 | 0.013 | 0.009 | 0.006 | 0.009 | 0.007 | 0.008 | 0.008 |
| | 30 | 0.003 | 0.002 | 0.003 | 0.001 | 0.003 | 0.002 | 0.002 | 0.003 | 0.009 |
| | 50 | 0.002 | 0.001 | 0.002 | 0.00 | 0.00 | 0.00 | 0 | 0.00 | 0.00 |
| | 90 | 0.005 | 0.007 | 0.003 | 0.008 | 0.006 | 0.001 | 0.0004 | 0.001 | 0.003 |
| Metolachlor | 1 | 0.00 | 0.00 | 0.00 | 000 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 10 | 0.00 | 0.00 | 0.007 | 0.007 | 0.00 | 0.00 | 0.00 | 0.00 | 0.022 |
| | 21 | 0.00 | 0.00 | 0.008 | 0.009 | 0.00 | 0.00 | 0.00 | 0.00 | 0.008 |
| | 30 | 0.00 | 0.00 | 0.002 | 0.002 | 0.00 | 0.00 | 0.00 | 0.00 | 0.009 |
| | 50 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 90 | 0.067 | 0.003 | 0.005 | 0.005 | 0.006 | 0.009 | 0.009 | 0.009 | 0.021 |
| Metribuzin | 1 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 10 | 0.00 | 0.00 | 0.003 | 0.004 | 0.00 | 0.00 | 0.00 | 0.003 | 0.017 |
| | 21 | 0.00 | 0.00 | 0.002 | 0.004 | 0.00 | 0.00 | 0.00 | 0.0004 | 0.005 |
| | 30 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 50 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 90 | 0.00 | 0.00 | 0.00. | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

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[§] Zero concentration implies non-detectable level