University of São Paulo
"Luiz de Queiroz" College of Agriculture

HYDRUS 2D simulation of atrazine movement in tropical and temperate soils under corn cultivation

Luciano Alves de Oliveira

Thesis presented to obtain the degree of Doctor in Science. Area: Agricultural Systems Engineering.

Piracicaba
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versão revisada de acordo com a resolução CoPGr 6018 de 2011

Advisor:
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DEDICATORY

I dedicate,

To my wife, Isabella Cardoso Ferreira da Silva Condotta, who have been by my side in the personal way and professional way, being the love and the light of my life;

To my parents, Ana Maria Alves de Oliveira e Claudemir César de Oliveira, from whom I received unconditional support, comprehension and love;

To my relatives, who always support and collaborate with me and help me to be who I am;

To my friends, who were always by my side at the good and the bad moments, and they made the basis for everything;

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EPIGRAPH

Someone asked a question:

- What does surprise you more at Humanity?

Then there was an answer:

- Humankind, they lose their health to earn Money and after that, they lose Money to recover their health. Moreover, they think too much in the future, but they forget the present in a way that they do live neither the present nor the future. In addition, they live as they never would die but they die as if they have never lived before.

Jim Brown

SUMMARY

RESUMO

Simulação da dinâmica da atrazina pelo modelo HYDRUS 2D sob cultivo de milho em regiões de solo tropical e temperado

O aumento de produtividade dos cultivos, na maioria das vezes, está associado a um aumento na utilização de insumos agrícolas, dentre eles, os herbicidas. Quando esses produtos são aplicados de uma maneira desordenada ao solo, processos de lixiviação podem ocorrer e, dessa forma, provocar algum tipo de contaminação ambiental, alcançando, assim, águas subterrâneas. Nesse sentido, em termos de aplicação de herbicidas, a atrazina é um exemplo dessa classe, que é intensamente utilizada no Brasil e no mundo e é frequentemente considerada como sendo um dos principais poluentes orgânicos, revelando-se, também, como um dos potenciais contaminantes do lençol freático. Visando maior controle de riscos de um possível impacto ambiental aliado à necessidade de aumento de produtividade, faz-se necessário o conhecimento com maior detalhamento sobre a dinâmica desses elementos no perfil do solo. Dessa forma, buscou-se como objetivo principal dessa pesquisa, simular a dinâmica da atrazina em um perfil de solo utilizando-se, para tal, o modelo HYDRUS 2D, sob condições de cultivo de milho, em regiões de solos tropicais e temperados e obter parâmetros de uma equação que transforme dados de indução eletromagnética (EMI) em parâmetros do movimento da atrazina. Deste modo, a pesquisa foi conduzida em dois locais distintos: Local 1 - Escola Superior de Agricultura “Luiz de Queiroz” (ESALQ/USP), junto ao Departamento de Engenharia de Biossistemas e Laboratório de Ecotoxicologia (CENA/USP) ambos em Piracicaba, SP (Brasil) e Local 2 - U.S. Meat Animal Research Center (MARC/ARS/USDA), em Clay Center, Nebraska (EUA). No Brasil, um cultivo de milho usando-se três tratamentos de atrazina foi conduzido em estufa experimental a fim de se obter dados de concentração do herbicida na solução do solo. Em seguida, amostras do mesmo solo foram coletadas para realização de curvas de eluição (BTC) para se obter os parâmetros de movimento da atrazina através do software STANMOD. Após a obtenção de tais parâmetros, simulações de movimento da atrazina no solo foram realizadas através do modelo HYDRUS 2D. Por fim, índices estatísticos de comparação foram utilizados para avaliar este software. Nos Estados Unidos, dados de EMI foram coletados num campo de cultivo de milho antes da aplicação de atrazina. Em seguida, amostras de solo deste campo foram coletadas para realização de BTC’s para se obter os parâmetros do movimento da atrazina. Após a obtenção de tais parâmetros, foram gerados modelos correlacionando dados de EMI com os parâmetros do movimento do herbicida. Posteriormente, índices estatísticos de comparação foram utilizados com o objetivo de se comparar os dados reais obtidos com os dados obtidos pelo novo modelo gerado. Por fim, simulações do movimento da atrazina foram feitas com o intuito de avaliar a contaminação do subsolo. Além disso, mapas com dados interpolados foram gerados, facilitando a visualização dos locais mais suscetíveis à contaminação. No experimento realizado no Brasil, os parâmetros do movimento da atrazina encontrados foram: $R = 1,604$, $\beta = 0,82$ e $\omega = 2,5$ h-1. Com tais parâmetros, o modelo HYDRUS 2D simulou o movimento da atrazina com precisão ($r = 0,9815$) e acurácia ($d = 0,9906$), quando a planta de milho não está inclusa no sistema. Quando a planta é considerada, o modelo prevê o movimento da atrazina com precisão ($r = 0,8609$), porém sem precisão ($d = 0,4449$). No experimentos realizado nos EUA, os parâmetros do movimento da atrazina encontrados foram: $R = 7,45$, $\beta = 0,47$ e $\omega = 5,56$ h-1. Modelos para obtenção dos parâmetros de movimento da atrazina utilizando-se EMI como dado de entrada foram gerados e seus índices estatísticos de comparação foram: R2 = 0,9012, $r = 0,9311$ e $d = 0,9589$. Deste modo, o modelo HYDRUS 2D é uma ferramenta para simular o movimento da atrazina no solo. No entanto, mais pesquisas devem ser feitas no que se refere à presença da planta no sistema solo-planta-atmosfera, pois os parâmetros que controlam a absorção de água e solutos podem estar obsoletos. A técnica de obtenção de EMI também foi bem sucedida na previsão dos parâmetros do movimento da atrazina e, portanto, deve ser utilizada para monitoramento, não só da própria atrazina, mas também de outros contaminantes.

Palavras-chave: Modelagem computacional; Engenharia de água e solo; Dinâmica de solutos no solo; Modelagem de contaminação ambiental; Dinâmica de herbicida no solo

ABSTRACT

HYDRUS 2D simulation of atrazine movement in tropical and temperate soil region under corn cultivation

The crop productivity increase is often associated with an increase in the use of agricultural products, including herbicides. When these products are applied in an untidy way, leaching may occur and cause environmental contamination either at the soil or at the groundwater. Regarding herbicides, atrazine is widely used in Brazil and around the world. It is also considered as the main organic pollutant, and a potential contaminant of the water table. According to that, it is necessary to build a detailed knowledge about the dynamics of these molecules through the soil with the objective to better control the contamination risks. Thus, the main goal of this research was to simulate the atrazine's movement through both tropical and temperate soils under corn cultivation using HYDRUS package models, and to obtain equation parameters to transform electromagnetic induction (EMI) signal data in atrazine's movement parameters. Thus, the research was conducted in two different places: 1 – "Luiz de Queiroz" College of Agriculture (ESALQ/USP) at the Biosystems Engineering Department and at the Ecotoxicology Laboratory (CENA/USP) both in Piracicaba, SP (Brazil), and 2 – at the Meat Animal Research Center (MARC/ARS) from the United States Department of Agriculture (USDA) in Clay Center, NE (US). In Brazil, a corn crop using three treatments of atrazine was conducted in a greenhouse to obtain the herbicide concentration data from the soil solution. Then, soil samples were collected to run breakthrough curves (BTC) to obtain atrazine's movement parameters through STANMOD model. After that, atrazine's movement simulations were taken through the HYDRUS 2D model. In the end, statistical indexes were used to compare observed and modeled data aiming the evaluation of HYDRUS 2D model for the movement of atrazine. In US, EMI data were collected in a corn field before atrazine application. Then, soil samples from this field were collected for BTC's to obtain atrazine's movement parameters. After obtaining such parameters, models were generated correlating EMI signal data with atrazine's movement parameters. Subsequently, statistical comparison indexes were used to compare the actual data obtained with the data obtained by the new model generated. Finally, simulations of the movement of atrazine were made with the purpose of evaluating the contamination of the subsoil. In addition, maps with interpolated data were generated, facilitating the visualization of sites most susceptible to contamination. In Brazil, the atrazine's movement parameters were $R = 1.604$, $\beta = 0.82$ e $\omega = 2.5$ h^{-1}. Then, HYDRUS 2D simulations were precise ($r = 0.9815$) and accuracy ($d = 0.9906$) when the corn plant is not in the system. However, with the presence of the corn, HYDRUS 2D still predicted atrazine with precision ($r = 0.8609$) but the accuracy was low ($d = 0.4449$). In US, the atrazine's movement parameters were $R = 7.45$, $\beta = 0.47$, and $\omega = 5.56$ h^{-1}. Further, models using EMI signal data to predict atrazine's movement parameters were generated. The statistical indexes to these models were $R^2 = 0.9012$, $r = 0.9311$, and $d = 0.9589$. Overall, HYDRUS 2D is a model to predict atrazine's movement through the soil. However, more researches need to be carried out considering the plant as part of the system and the parameters which account water and solutes absorption need to be improved. The EMI technique to obtain atrazine's movement parameters was also well succeeded. Thus, it should be broadly used to monitor atrazine and other contaminants.

Keywords: Computational modeling; Water and soil engineering; Soil solutes dynamics; Environmental contamination modeling; Soil herbicide dynamics

1 INTRODUCTION

It has been estimated the world's population will reach 10 billion by 2050. This increase in population will require increases in food production to meet the nutritional needs of this population. With a limited amount of arable land, productivity of the land will have to meet this need.

Corn (Zea mays) is in Poaceae family and is an important world crops because it can be used by humans and animal (poultry and swine) as a food source. This result in 1074.4 million of tons corn consume worldwide annually. Approximately 65% of the annual worldwide corn consumption is supplied by these major corn-producing countries: United States (320 millions of tons grains), China (241 millions of tons grains), 28-Europe Union (76 millions of tons grains), Brazil (62.5 millions of tons grains). In addition, corn ethanol production is an importance transportation fuel additive in United States accounting for 30% of the U.S. corn produced. It is important to note the material remaining after ethanol production (distiller's grains) is used as an animal feed.

One tool used to help increasing crop yield is yield prediction. These predictions allow producers to more efficiently use input. Computer modeling can be a powerful tool to manage pesticide inputs once the solute dynamic in soil was understood. These models provide cost-effective predictions resulting from management choices on production as well as environmental consequences. Models and simulations are the best way to predict agriculture. This way, modeling and agriculture go hand in hand. Mankind has always used models to gain a better understand of nature. Thus, it is a necessity to continue improving agricultural models to improve agriculture.

Computer modeling has evolved over the years with the advancement of computer hardware and better understanding of physical, chemical and biological processes in the environment. One area of improved prediction is with soil systems. Soil systems are very dynamic and complex systems. This complexity is driven by the many components that comprise soil such as, nutrients, chemical elements, and microorganisms. Among these elements, there exist important interactions: water and nutrient absorbing, microbiologic transformations, water and nutrients leaching, etc. Modeling these interactions and their effects throughout the soil is part of an important part of agriculture modeling. More accurate soil modeling leads to more accurate crop modeling. Nowhere is this more apparent than in HYDRUS.

HYDRUS is a software package, which includes several models of water and solute movement through the soil. It uses boundaries conditions to numerically predict soil conditions. Several studies were done using HYDRUS and proved that the model was extremely accurate and precise. HYDRUS is widely used in many industrial and environmental applications, as well as for addressing many agricultural problems. Examples of existing agricultural applications include irrigation management, drip and sprinkler irrigation design, studies of root water and nutrient uptake.

One possibility of HYDRUS is to model atrazine's fate. This herbicide can have a detrimental impact on the environment, humans and animals. Atrazine is synthesized chemically and CIBA-GEIGY Company registered it for the first time in 1958. Its intense use and its soil mobility contribute to atrazine be considered as one of the most water-detected herbicide in Europe and US. Atrazine is also classified as toxic agent, which deregulate the hormonal balance, and C carcinoma agent, which are potentially carcinogenic to humankind. This herbicide can also retard the mammal glandules development and induce abortion in lab rats. It can also affect the embryo development in lab rats, even when low exposition levels are used.

Another tool widely used is electromagnetic induction (EMI) sensors, which collects soil apparent electrical conductivity. This soil characteristic is influenced by several factors as water content, soluble salts, mineralogy, organic matter, and other soluble molecules. The EMI sensors are powerful tools because they are robust and can acquire signals from shallow soil layers and even deep soil layers. They are easily pulled through the field which makes the data acquisition also easy. However, they cannot have any interference from metal when acquiring data. Thus, several studies are being made to correlate EMI signal data with agricultural concerns as soil moisture, soil salinity, nitrate content, organic contaminants, etc.

Under these circumstances, this research aimed to evaluate the HYDRUS package (STANMOD and HYDRUS 2D) simulating atrazine's movement through different soils as well to apply a EMI model to obtain atrazine's movement parameters looking towards atrazine contamination at deep soil layers.

2 OBJECTIVES

2.1 General objective

The main object of this research was to simulate the atrazine's movement through different soils (tropical and temperate regions) during corn development using the HYDRUS package (STANMOD and HYDRUS 2D). Moreover, the research aimed to evaluate a possible atrazine contamination at deeper soil layers.

2.2 Specific objectives

The specific objectives were to:

1) Obtain atrazine transport parameters using breakthrough curves by numerical adjustments with STANMOD model for both Brazilian and American soils.

2) Evaluate the HYDRUS 2D model performance by simulating atrazine's movement through the soils.

3) Apply electromagnetic induction (EMI) to monitor atrazine's movement parameters according to the soil variability.

3 LITERATURE REVIEW

3.1 Corn

3.1.1 Economic aspects

Corn (*Zea mays*) belongs to *Poaceae* family and is considered as one of the most important crops in the world. It is used for food for humans and animals (poultry and swine). Besides, it has an energy importance in United States where 30% of the corn is used to ethanol production.

According to Cardoso et. al (2011), corn has around 500 sub products as fat, glucoses, amid, ferment, drinks, sodas, liquors besides industrial plastic, animal food, enzymes, etc. Thus, it has a big scale socioeconomic importance.

The major countries in corn production are United States (371 millions of tons grains), China (216 millions of tons grains), Brazil (94.5 millions of tons grains), 28-Europe Union (61 millions of tons grains) being part of 1041.7 million of tons corn production in all over the world.

Regarding corn consume, the major countries are United States (320 millions of tons grains), China (241 millions of tons grains), 28-Europe Union (76 millions of tons grains), Brazil (62.5 millions of tons grains) being part of 1074.4 million of tons corn consume in all over the world.

The major exporting countries are United States (56.6 millions of tons grains), Brazil (35 millions of tons grains), Argentina (25 millions of tons grains), Ukraine (20 millions of tons grains) being part of 156 million of tons corn exporting all over the world.

Regarding world stock, the major countries are China (79.6 millions of tons grains), United States (54 millions of tons grains), Brazil (11.4 millions of tons grains), 28-Europe Union (7.1 millions of tons grains) being part of around 199 million of tons world stock.

The third report of CONAB (2018) says that Brazil produced 93 million of tons of corn grains. The planted area for this production was around 17 million of hectares that results in a 5.5 tons of grains per hectare. It is very important to say that the production come from two seasons in one year. According to the same report, Mato Grosso – MT, Mato Grosso do Sul – MS, Goiás – GO and Minas Gerais – MG are the main regions planting corn in Brazil.

3.1.2 Crop aspects

Corn presents five development stages. 1 – Emergence and germination, this period lasts for around 4 and 12 days because of the temperature and soil moisture. 2 – Vegetative growing, this period varies according to genotypes and climatic issues and classifies the crop as super-precocious, precocious and normal. 3- Flowering, which occurs between seeding and fructification. 4 – Fructification, this period lasts from 40 to 60 days. 5 – Maturity this period is short and indicates the plant's life end (Fancelli and Dourado-Neto, 2000).

Mangelsdorf (1974) describes corn as a specific plant for grain production. It depends on humans to survive, and it is annual, tough and tall. Its height is around one and four meters and its vital organs do not survive more than one vegetative cycle.

A 15-cm corn plant has all of its structures formed, grows up only in volume, and in cells number. To support that, the embryo develops creating a compact stalk with nodes. The sixth to the 10th nodes under the soil surface are those that generate root. They are responsible to root the plant and make the plant as a cone form. These roots also develop and create capillary that are responsible to absorb water and nutrients (GOODMAN & SMITH, 1978).

Corn requires 500 to 800 mm of water in its lifecycle to have a good production (DOOREMBOS & KASSAN, 1994). Another author, Shaw (1977), compiled several studies and concluded that the corn water need is around 400 to 600 mm. If irrigation is not possible to use, 300 to 350 mm water can provide a satisfactory production when the water is well distributed (FANCELLI, 1991).

The corn water necessity occurs at the emergency, flowering and grain formation (FANCELLI & DOURADO-NETO, 2000; BERGONCI & BERGAMASCHI, 2000). Then, the zygote formation and the grain growing with the high transpiration rate have their water demand supplied. Besides, large productivities demand large amounts of water combined with large sun light availability and temperatures around 25° C e 30° C.

Nitrogen (N) is the nutrient that corn needs more. It is the most expensive nutrient, but it is the one that most influence the production (AMADO et. al, 2002; SILVA et. al, 2005). The good amount of N is around 20 to 50 g per kg of dry matter (MALAVOLTA, 1980).

Some studies show that N influence the phosphorus (P) absorption even in soils with high P contents (TERMAN & NOGGLE; 1973; KAMPRATH, 1987). P acts in several plant processes as energy transfer, nucleic acids synthesis, glucose, respiration, enzymes activation and deactivation, carbohydrates metabolism, N_2 fixation (VANCE et. al, 2003).

Potassium (K) is the major positive ion nutrient in plants and its function is to store and to translocate carbohydrates. It maintains water in vegetal issues and the plant energetic state stabilization (MEURER, 2006).

3.2 Herbicides

Food, fiber and energy production have become large as fast as agriculture has used chemical substances. These substances help in the control of undesirable organisms as fungus, insects, weeds, and their consume increases 2.6 millions of tons per year (WILSON & TISDELL, 2001).

In 2005, among those substances, pesticides reached the mark of 5.8 million of tons consumed all over the world. Brazil was the main pesticide consumer followed by US (WILSON & TISDELL, 2001; CARVALHO, F. P. 2006; GRUBE et. al, 2011; PELAEZ et. al, 2013).

Weeds decrease corn production until 70% of its potential varying according to the species and infestation rate as well as the corn space, physiologic state (FANCELLI & DOURADO-NETO, 2000). Further, herbicide control is the main method to control weeds in agricultural systems all over the world. However, it can affect other organisms according its toxicity (ZINDAHL, 2013; SANTOS et. al, 2013).

Thus, both environmental and health safety are a concern because after pulverizing the product losses are around from 2 up to 90%(TAYLOR, 1995; LEU et al., 2004; SOUTHWICK et al., 2009).

One example of herbicide loss along the production system is leaching. According to United States Environmental Protection Agency (USEPA, 2016) criteria and GUS indexes (GUSTAFON, 1989), the leaching potential is the main herbicide characteristic related to subsurface water contamination.

However, it is very important to know the physics, biological and chemical molecule characteristics before applying it in the environment. These characteristics in addition with environmental and soil conditions condition the solute displacement in the soil (CHRISTOFFOLETI & LOPEZ-OVEJERO, 2005).

The main physical-chemical herbicide properties that control its behavior are steam pressure (SP), octane-water partition coefficient (Kow), acid/basis ionization constants (pka and pkb), Henry constant law (H), half-life ($T_{1/2}$) and solubility in water (S).

The steam pressure herbicide is the volatilization tendency in its pure state and it is temperature function. On another hand, octane-water partition coefficient tells the relationship between the pesticide in octane phase saturated in water and its concentration in water saturated in octane (LAVORENTI, et. al, 2003). The Henry constant law is the air-liquid partition. It is obtained dividing the partial pressure and the concentration in the interface air-water. As large the value is, large the volatilization potential (LAVORENTI, et. al, 2003).

The acid/basis ionization constants are the molecule ionization tendency. It indicates if the herbicide is ionic and in what pH it occurs (LAVORENTI et. al, 2003). Half-life is the herbicide capacity to get into a chemical reaction and become other products. Thus, the herbicide half-life is the time that the molecule takes to reduce its concentration by the half (LAVORENTI, et. al, 2003). Finally, the herbicide water solubility is the maximum concentration the water can dissolves the herbicide in a given temperature. This characteristic is directly related to leaching (KOLLMAN; SEGAWA, 1995).

3.3 Atrazine

Atrazine (2-chloride-4-ethylamino-6-isopropylamino-striazine) is an herbicide that control weeds at corn crop, which is significantly tolerant (NALEWAJA, 1968) (Figure 1).

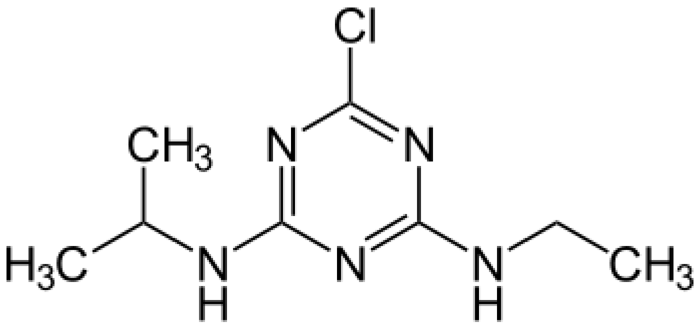

Figure 1 – Atrazine molecular form (2-cloro-4-2-chloride-4-ethylamino-6-isopropylamino-striazine).

Atrazine is part of the s-triazine family. These compounds contain a hexametric aromatic ring, symmetric, constituted by alternated three carbon atoms and three nitrogen atoms. Thus, it is a selective herbicide controlling weeds in pre and post-emergence in several crops.

The general method used is on the soil. However, the contact method is an option. The apoplastic path is the general method that atrazine is translocated inside the plant. Its action stops the electrons transport in the photosynthesis light phase. It stops the CO_2 fixation, which starts to decrease a couple of hours after the applying. The CO_2 fixation decreasing also decreases the carbohydrate production (TAIZ & ZIEGER, 2013).

Atrazine is synthesized chemically and CIBA-GEIGY Company registered it for the first time in 1958. Its intense use and its soil mobility contribute to atrazine be considered as one of the most water-detected herbicide in Europe (CEREJEIRA et. al, 2003) and US (BOYD, 2000). Atrazine is also classified as toxic agent which deregulate the hormonal balance (FRIEDMANN, 2002), and C carcinoma agent, which are potentially carcinogenic to humans (BIRADAR & RAYBURN, 1995).

This herbicide retards the mammal glandules development and induces abortion in lab rats. It also affects the embryo development in lab rats, even when low exposition levels are used. (NAROTSKY et. al, 2001).

Some atrazine properties are showed in Table 1.

Table 1 - Atrazine properties

Property	Atrazine value
Water solubility (Sw) a 25°C (mg L^{-1})	33
Density (g cm^{-3})	1,187
Molecular mass (g mol^{-1})	215
Steam pressure (mmHg)	3107
Fusion point (°C)	176
Log Kow a 25°C	2,68
pKa 21°C	1,7
Henry Law constant (atm m^3 mol^{-1})	$2{,}48x10^{-9}$

Source: Rodrigues & Almeida (1995).

Atrazine degrades in two compounds, desethylatrazine and hidroxiatrazine. These compounds have affinity with organic matter in a clay soil under direct plant and conventional plant, which retards leaching (KRAHEMBUHL et. al, 2005).

Nakagawa and de Andrea (2000) found atrazine is mineralized only in natural soil, it produces extractable metabolites in both natural soil (75%) and sterilized soil (67%). A study showed that the atrazine leaching contaminates the water table in medium texture soils and sandy soils (CORREIA & LANGENBACH, 2006). These authors found that leaching is from four to 11% of the atrazine lost in soil. Volatilizing is 0.33% and mineralizing is 0.25%. Queiroz and Monteiro (2000) tested 14-C atrazine in soil planted with corn. They found 36% of detached CO_2 was 14-C and this means 150 days of half-life for atrazine.

3.4 Water and solute dynamic in soil

Leaching is an example of water and solute transport in soil. Chemical and physical determine this movement. The water dynamic in soil is a continuous process and controls chemical elements that are responsible for soil evolution, nutrients availability and water demand (MACIEL NETTO et. al, 2000).

Water and solutes displacement are simultaneous movements and the solute transport is a consequence of water convection, water flux or water diffusion. Understanding these transport process is very important to establish control practices in solute transport in soils (BRESLER, 1981).

Atrazine is an example of solute and its balance mass should be described better understand the relationships with the soil. Thus, Richards's equation is one method to describe the water movement through the soil. It is a combination between Darcy's law and the continuity equation (eq.1).

$$\frac{\delta\theta(h)}{\delta t} = \frac{\delta}{\delta x}\left(K(h)\,\frac{\delta h}{\delta x}\right) + \frac{\partial K(h)}{\partial x} - s(h) \qquad (1)$$

where:

θ - volume water content in soil, $L^3\ L^{-3}$
h - water head, $M\ L^{-1}\ T^{-2}$
K - soil hydraulic conductivity, $L\ T^{-1}$
t - time, T
x - depth, L
s - sink, $L^3\ L^{-2}\ T^{-1}$

On another hand, Advection-Dispersion Equation by Fick's law determines atrazine movement. Van Genuchten & Wagenet (1989) demonstrated these equations.

3.4.1 Solute transport model including equilibrium kinetic adsorption ("two-site")

The two-site kinetic equilibrium model divides the soil in 2 phases, solid phase type 1, equilibrium adsorption, and solid phase type 2, kinetic adsorption. The models subscripts will be as in van Genuchten (1981) e Parker & van Genuchten (1984).

$$S_1 = fKC \qquad (18a)$$

$$S_2 = (1-f)KC \qquad (18b)$$

where,

S_1 - type 1 adsorption, $M\ L^{-3}$
S_2 - type 2 adsorption, $M\ L^{-3}$
f - changing fraction, dimensionless

Total adsorption (S) is in equation 19.

$$S = S_1 + S_2 \tag{19}$$

when in equilibrium it is similar to equation 7.

The type-1 and type 2- mass balance are similar to equation 5.

$$\rho \frac{\partial S_1}{\partial t} = J_{a1} - \rho \mu_{s1} S_1 \tag{20a}$$

$$\rho \frac{\partial S_2}{\partial t} = J_{a2} - \rho \mu_{s2} S_2 \tag{20b}$$

where,

J_{a1} - solution transfer by adsorption type-1, M L^{-3} T^{-1}

J_{a2} - solution transfer by adsorption type-2, M L^{-3} T^{-1}

Adding the equations 20a and 20b into equation 4 results the mass transport equation for the whole system (eq.21).

$$\frac{\partial(\theta C)}{\partial t} + \rho \frac{\partial(S_1 + S_2)}{\partial t} = \frac{\partial}{\partial x}\left(\theta D \frac{\partial C}{\partial x} - qC\right) - \theta \mu_1 C - \rho \mu_{s1} S_1 - \rho \mu_{s2} S_2 \tag{21}$$

As type-1, it is always in equilibrium. Thus, adsorption occurs by the time derivative in equation 18a.

$$\frac{\partial S_1}{\partial t} = fK \frac{\partial C}{\partial t} \tag{22}$$

Using the first-order adsorption rate law, which is similar to equation 14 and using equation 18b, which is the mass balance equation for type-2, equation 23 appears.

$$\frac{\partial S_2}{\partial t} = \alpha[(1 - f)KC - S_2] - \mu_{s2} S_2 \tag{23}$$

Substituting equations 22 and 23 into equation 21 and using equation 18a to eliminate S_1 from degradation term in equilibrium phase, equation 24 appears.

$$\frac{\partial(\theta + f\rho K)C}{\partial t} = \frac{\partial}{\partial x}\left(\theta D \frac{\partial C}{\partial x} - qC\right) - \alpha\rho[(1-f)KC - S_2] - \theta\mu_l C - f\rho K\mu_{s1}C \tag{24}$$

The model two-site model is complete.

3.4.2 Solute transport model including two-region adsorption and degradation

Two-site model divides soil-liquid and soil-solid phases in two regions, mobile, m, and immobile, im. The convective-dispersive solute transport occurs in the liquid phase mobile region. On the other hand, the solute transport depends on diffusion occurring when it goes from the mobile phase through immobile phase. The transport also depends on the factor (f) which is responsible to equilibrate instantaneously the soil-solid phase in the mobile region of the liquid phase. Moreover, another factor (1-f) is responsible to equilibrate the immobile region of the soil-liquid phase.

Degradation is harder to model in two-region model than in two-site model according to van Genuchten & Wagenet (1989). It happens because the degradation rate inside the aggregates is different of that occurs at the aggregate surface due O_2 concentration variation and microbial activity. To maintain the equation in general mode, it is necessary to know the mobile and immobile degradation coefficients in the soil-liquid phase as well as the mobile and immobile degradation coefficients in the soil-adsorbed phase. Thus, two-region model contain four degradation coefficients instead of 3 that two-site model contain.

Using the same procedure that previous cases, solute transport equation in liquid-mobile phase (subscript m) is in equation 25.

$$\frac{\partial(\theta_m C_m)}{\partial t} = \frac{\partial}{\partial x}\left(\theta_m D_m \frac{\partial C_m}{\partial x} - qC_m\right) - J_{a1} - J_{a2} - \theta_m \mu_{lm} C_m \tag{25}$$

Where,

μ_{lm} - Degradation coefficient in liquid-mobile phase, dimensionless

J_{a1} - transfer rate from liquid phase to solid phase in mobile region, M L^{-3} T^{-1}

J_{a2} - Diffusion transfer rate from mobile liquid region to immobile liquid region, M L^{-3} T^{-1}

The mass balance (eq. 26) for adsorbed concentration in the mobile region (S_m) is similar to equation 5.

$$f\rho\frac{\partial S_m}{\partial t} = J_{a1} - f\rho\mu_{sm}S_m \tag{26}$$

where,

μ_{sm} - mobile-solid degradation coefficient, dimensionless

The mobile solute transport equation (eq. 27) appears when adding equations 25 ans 26.

$$\frac{\partial\theta_m C_m}{\partial t} + f\rho\frac{\partial S_m}{\partial t} = \frac{\partial}{\partial x}\left(\theta_m D_m\frac{\partial C_m}{\partial x} - qC_m\right) - J_{a2} - \theta_m\mu_{lm}C_m - f\rho\mu_{sm}S_m \tag{27}$$

The mass balance (eq. 28) is similar to soil-immobile region (subscript im) without the convective-dispersive terms.

$$\frac{\partial\theta_{im}C_{im}}{\partial t} + (1-f)\rho\frac{\partial S_{im}}{\partial t} = J_{a2} - \theta_{im}\mu_{lim}C_{im} - (1-f)\rho\mu_{sim}S_{im} \tag{28}$$

Equation 29 shows the changes between mobile and immobile regions in the liquid phase.

$$J_{a2} = \alpha(C_m - C_{im}) \tag{29}$$

Where, α is a mass transfer coefficient between mobile and immobile regions in liquid phase.

Equations 30a and 30b describe adsorptions inter and intra aggregates in the following regions.

$$S_m = KC_m \tag{30a}$$

$$S_{im} = KC_{im} \tag{30b}$$

Substituting equations 29, 30a and 30b in equations 27 and 28, it is possible to have two-region transport model equations including degradation for transient water flux in equations 31a and 31b.

$$\frac{\partial(\theta_m + f\rho K)C_m}{\partial t} = \frac{\partial}{\partial x}\left(\theta_m D_m \frac{\partial C_m}{\partial x} - qC_m\right) - \alpha(C_m - C_{im}) - (\theta_m \mu_{lm} + f\rho K \mu_{sm})C_m \qquad (31a)$$

$$\frac{\partial[\theta_{im} + (1-f)\rho K]C_{im}}{\partial t} = \alpha(C_m - C_{im}) - [\theta_{im}\mu_{lim} + (1-f)\rho K \mu_{sim}]C_{im} \qquad (31b)$$

3.5 Computer modeling

Computer modeling is great tool to model organic molecules once the solute dynamic in soil was understood. A computer modeling advantage is the time and money economy as Prata et. al (2003) showed. Thus, the HYDRUS models package helps in atrazine monitoring and displacement.

HYDRUS is widely used in many industrial and environmental applications, as well as for addressing many agricultural problems (ŠIMŮNEK et. al 2016). Examples of existing agricultural applications include irrigation management (BRISTOW et. al 2002; DABACH et. al 2015), drip and sprinkler irrigation design (BRISTOW et. al 2002; GÄRDEÑAS et. al 2005; HANSON et. al 2008; KANDELOUS et. al 2012), studies of root water and nutrient uptake (ŠIMŮNEK and HOPMANS, 2009; VRUGT et. al 2001a, b).

HYDRUS is physically-based, detailed hydrological model that simulates the relationships between soil, water, and weather, while using a sink term to account for water uptake by plant roots. The core of the model is the Richards one-dimensional equation, which combines the Darcy-Buckingham law for the fluid flux with the continuity equation.

It simulates soil water movement by considering spatial differences in the soil water potential in the soil profile. The governing equation is solved numerically using an implicit finite element scheme, which can be applied to both saturated and unsaturated conditions. The soil hydraulic functions are described using the analytical functions of van-Genuchten-Mualem (MUALEM, 1976; VAN GENUCHTEN, 1980).

The model also considers, as needed, the effects of heat on water flow and the fate and transport of solutes in soils. Numerical solutions are provided for both flux and pressure head controlling boundary conditions at the top and the bottom of the system. The Penman-Monteith equation is used to estimate potential evapotranspiration, ET_p. The HYDRUS model also use the leaf area index (LAI) or the soil cover fraction (SC) to separate potential evapotranspiration (ET_p) into potential plant transpiration (T_p) and potential evaporation (E_p) of a partially covered soil. Reductions in T_p and E_p are calculated using a physically-based approach. Reductions in T_p and E_p are obtained by using the Feddes et. al (1978) approach involving stress response functions, which depends of the type of crop. Reductions in E_p are obtained directly from the numerical solution of the Richards equation by switching from a flux to a pressure head boundary condition when some limiting minimum pressure head is reached. The effects of salinity and water/oxygen stress on actual transpiration can be either additive or multiplicative. Surface runoff is evaluated as infiltration-excess water calculated using the Richards equation for specified precipitation rates and soil hydraulic properties.

Field drainage to the tile drains can be simulated using the Hooghoudt or Ernst equations for homogeneous and heterogeneous soil profiles, respectively. The bottom flux is calculated according to the selected bottom boundary conditions.

HYDRUS 1D could obtain atrazine transport parameters in satisfactory response when used in Swiss, New Zealand and India (PERSICANI, 1993, CELESTINO LADU & ZHANG 2011 e KULLURU et. al 2010). Persicani, 1993 also showed that HYDRUS 1D is a complete software once it uses more input variables than other software as GLEAMS, BAM, MOUSE e TETrans. Celestino Ladu & Zhang (2011) showed that is not necessary to use STANMOD once HYDRUS 1D can adjust the input parameters. However, they said it is important to have accurate data input. Thus, it is easy to understand the necessity in use STANMOD.

The HYDRUS 2D input data are soil information (texture, retention curve, soil density, hydraulic conductivity) and solute data (dispersion coefficient, dispersivity, β e ω (ŠIMŮNEK & ŠEJNA, 2007).

The HYDRUS models have been considered as satisfactory and have been said like a robust model for processes simulations in temperate and tropical soils. Because of this, it is possible to reach a sustainable agriculture looking for preserve the environment.

3.6 EMI

Electromagnetic induction (EMI) is widely used by soil scientists to better understand the spatial variability of soils properties at field and landscape scales (Corwin, 2008; Toushmalani, 2010).

Recent improvements in instrumentation and integration with other technologies (global-positioning systems (GPS), data processing software, and surface mapping programs) have fostered the expanded use of EMI in soil applications. The impetus for this expanded use has been the need for more accurate soil maps than those provided by traditional mapping techniques (Batte, 2000; Brevik et. al 2003; 2012) and the demonstrated efficiency of EMI to improve the accuracy and reliability of soil maps and provide more detailed information on soils and properties.

Electromagnetic induction sensors commonly used in agriculture and soil investigations include the DUALEM-1 and DUALEM-2 meters (Dualem, Inc. Milton, Ontario); the EM31, EM38, EM 38-DD and EM38-MK2 meters (Geonics Limited, Mississauga, Ontario), and the Profiler EMP-400 (Geophysical Survey Systems, Inc., Salem, New Hampshire). These EMI sensors transmit a primary electromagnetic field, which induces electrical currents in the soil. These currents generate a secondary electromagnetic field, which is read by the sensor's receiver. Under conditions known as "operating under low induction numbers", the secondary field is proportional to the ground current and is used to calculate the "apparent" or "bulk" electrical conductivity (EC_a) for the volume of soil profiled. The dual-geometry configuration of the DUALEM-1 and DUALEM-2 meters, the dual orientation of the EM38-DD meter, and the dual receiver-transmitter spacings of the EM38-MK2 meter allow the simultaneous measurement of EC_a and/or apparent magnetic susceptibility (MS_a) iver two distinct depths. The depth of investigation (DOI) for EC_a measurements made with sensors developed by Dualem, Inc. and Geonics Limited is commonly taken as the depth of 70% cumulative response. The Profiler EMP-400 is a multi-frequency sensor and its DOI is assumed to be "skin-depth" limited and dependent upon the frequency and the conductivity of the profiled materials. All of the aforementioned sensors support GPS communication, data loggers, and proprietary software. Some EMI sensors, such is DUALEM-1, DUALEM-2S, and Profiler EMP-400, come with internal GPS receivers and display/keypads.

Possible applications for EMI are 1- a surrogate measure for the assessment of soil properties: 1a – soil salinity (Corwin, 2008; Johnston et. al, 1997; Mankin and Karthikeyan, 2002; van der Lelij, 1983). 1b soil texture (Heil and Schmidhalter, 2012; James et. al 2003; Saey et. al, 2012a), clay content (Cockx et. al 2009; Harvey and Morgan, 2009; King et. al 2005).

Woodbury et. al, 2009 tried to test the validity of using EMI survey data in conjunction with a prediction-based sampling strategy and ordinary linear regression modeling techniques to measure and predict spatially variable manure accumulation on a feedlot surface. They found excellent correlations between the EMI data and the $\ln(Cl^-)$, total N, total P and volatile solids. Each model can explain >90% of the constituent sample variations.

Another study of Woodbury et. al, 2011 tried to determine if EMI could be used to predict differences in volatile fatty acids (VFA) and other volatiles produced in vitro from feedlot surface material following a simulated rain event. They found that using EMI and mapping techniques as a tool provides understanding of manure accumulation patterns and zones for potential odorant emission from the feedlot surface.

A study conducted found sequential measurement of profile-weighted soil electrical conductivity (EC_a) was effective in identifying the dynamic changes n plant-available soil N, as affected by animal manure and anhydrous ammonia fertilizer treatments during four corn growing seasons (Eigenberg et. al, 2006).

Lastly, Jaynes et. al, 1995 found electromagnetic induction measurements failed to predict the observed high Kd values but the advantage of using EMI measurements to map K_d was rapid, easy, and inexpensive method once it has been calibrated.

4 Main Results and Discussion

Two articles were developed in this work. The first one involved the comparison of HYDRUS 2D simulations for atrazine movement and comparing with real data in a corn cultivation. Comparison indexes were calculated between the simulated data for atrazine movement and real concentration obtained through the soil solution in the environment of corn crop. Based on the results obtained in this research, the second paper was possible to be developed.

This first aimed to evaluate how precise and accurate HYDRUS 2D simulate atrazine concentration using real data for atrazine concentration at 20, 40, and 60 cm depth It was found that data obtained by the software can be used to have an idea in how atrazine movement behave through the soil. It was also noticed that atrazine concentration is higher at the shallow depth of the soil, increasing when the atrazine concentration applied is higher. The model also shows this pattern through the soil profile indicating that it can be used as a tool to provide information without running expensive analyses.

The second experiment of this work aimed to evaluate EMI sensor to predict regions of a corn field atrazine could reach the groundwater. To do this, EC_a was collected with GPS coordinates and Breakthrough curves were running to obtain atrazine's movement parameters.

It was obtained good correlations between the EC_a and the atrazine's movement parameters and it was found that the EMI sensor can be used to predict atrazine concentration, through movement parameters and HYDRUS 2D simulations. Coupling the two tools, HYDRUS 2D and EMI sensor is a good way to pursue sustainability and find where atrazine will be a potential contaminant of groundwater.

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5 A COMPARISON BETWEEN REAL AND MODELED DATA FOR ATRAZINE MOVEMENT THROUGH TROPICAL SOIL REGION UNDER CORN CULTIVATION

Abstract

Atrazine is used world-wide and is known to be mobile in the soil. HYDRUS package has been used to model atrazine's fate and transport. Thus, the objective of this work was to evaluate the HYDRUS 2-D model for accurately predicting atrazine transport under corn production. The research was conducted in a greenhouse at Biosystems Engineering Department of "Luiz de Queiroz" College of Agriculture (ESALQ/USP) and at Ecotoxicology laboratory owned by Nuclear Energy in Agriculture Center (CENA/USP). The research was conducted in three distinct stages: an experimental greenhouse with corn plantation and soil solutions collection, atrazine transport parameters obtained by Breakthrough Curves and numerical adjustments using STANMOD model, and numerical simulation of solution distribution (water and atrazine) using HYDRUS 2D model to compare observed and modeled data. Atrazine concentration is higher at 20-cm soil layer. Explanations for that are the root system activity makes atrazine bonds to this soil layer. HYDRUS 2D overestimates atrazine's concentration both at topsoil as well as subsoil. Interactions between atrazine and root exudates were not considered in the model. The degradation parameter may change with the dynamic system where the plants were inserted. The model presents high precision predicting atrazine movement pattern, thus contamination can be followed by farmers. The model weaknesses were found at two critical points. The atrazine's sink parameters should be considered at a real and dynamic corn crop situation including roots liberating exudates, and active microorganisms. The evapotranspiration modeling underestimate water uptake. More researches taking crops in account need to be done.

Keywords: Computational modeling; Water soil engineering; Soil solutes dynamics; Environmental contamination modeling; Soil herbicide dynamics

5.1 Introduction

Estimations for the world's population are to reach 10 billion by 2050 (United Nations, 2017). Feeding this population will require increases in food production to meet critical nutritional needs (FAO, 2009). With a limited amount of arable land, substantial productivity increases of this land will have to be achieved to meet these nutritional needs (Ray et. al., 2012).

Corn (Zea mays) is an important world crop because it can be used by humans and animal (beef, poultry and swine) as a major food source. This result in 1074.4 million tons corn consumes world-wide annually (FAO, 2017). Approximately 65% of the annual world-wide corn consumption is supplied by these major corn producing countries: United States (320 millions of tons grains), China (241 millions of tons grains), 28-Europe Union (76 millions of tons grains), Brazil (62.5 millions of tons grains). In addition, corn ethanol production is an importance transportation fuel additive in United States accounting for 30% of the U.S. corn produced. It is important to note the material remaining after ethanol production (distiller's grains) is used as an animal feed.

Tools used to increase input use efficiency while improving crop yield are prediction models. These models allow producers to more efficiently use inputs (Ewert et. al., 2015). Computer modeling can be a powerful tool to manage pesticide inputs once the solute dynamic in soil is understood. These models provide cost-effective predictions resulting from management choices on production as well as environmental consequences (Prata et. al 2003).

Computer modeling has evolved over the years with the advancement of computer hardware and better understanding of physical, chemical and biological processes of the environment. One area of improved prediction is with soil systems. Soil systems are very dynamic and complex systems comprise of many components such as, nutrients, chemical, mineral and biological elements. Among these elements, there exist important interactions: water and nutrient absorbing, microbiologic transformations, water and nutrients leaching, etc. (Verecken et. al, 2016).

Modeling the interactions of these elements and their effects on contaminant transport throughout the soil profile is critical for accurate predictions. As our understanding of these processes improves, models need to reflect these advancements. Thus, it is a necessity to continue updating agricultural models to improve their usefulness (Dourado Neto et. al, 1998).

HYDRUS is a software package, which includes several models of water and solute movement through the soil. It uses boundaries conditions to numerically predict soil conditions. Studies have documented the efficacy of HYDRUS (Simunek et. al., 2007). HYDRUS is widely used in many industrial and environmental applications, as well as for addressing many agricultural problems (ŠIMŮNEK et. al 2016). Examples of existing agricultural applications include irrigation management (BRISTOW et. al 2002; DABACH et. al 2015), drip and sprinkler irrigation design (BRISTOW et. al 2002; GÄRDEÑAS et. al 2005; HANSON et. al 2008; KANDELOUS et. al 2012), studies of root water and nutrient uptake (ŠIMŮNEK and HOPMANS, 2009; VRUGT et. al 2001a, b).

HYDRUS has been used to model atrazine's fate and transport because studies have shown this pesticide can have detrimental impact on the environment, humans and animals (Mendonça et. al., 2016; Walters et. al., 2014; Lind et. al., 2004; Neuman-Lee and Janzen, 2011). Atrazine is used extensively world-wide and is known to be mobile in the soil. This mobility results in atrazine being considered one of the most detected herbicide in European surface waters (CEREJEIRA et. al, 2003) and US (BOYD, 2000). It is reported atrazine affects human health by irritation of eyes and skin and cause effects on central nervous and immune systems (Hayes et al. 2002; Zaya et al. 2011). It is also classified as toxic agent which deregulate the hormonal balance (FRIEDMANN, 2002), and C carcinoma agent, which are potentially carcinogenic to humans (BIRADAR & RAYBURN, 1995). Also, Atrazine has been shown to retard mammal glandules development and induce abortion in lab rats. It can also affect the embryo development in lab rats, even when low exposition levels are used. (NAROTSKY et. al, 2001).

The objective of this work was to evaluate the HYDRUS 2-D model for accurately predicting atrazine transport under corn production. To evaluate accuracy, we determined the concentration for atrazine application passing through a tropical soil and compared these values with predicted values generated by the HYDRUS model.

5.2 Material and Methods

The research was conducted in a greenhouse managed by the Biosystems Engineering Department of "Luiz de Queiroz" College of Agriculture (ESALQ/USP) and at the Ecotoxicology laboratory owned by Nuclear Energy in Agriculture Center (CENA/USP). Both are in Piracicaba-SP with C_{WA} climate as determined by the Köppen classification (22° 43' 33" S, 47° 38' 00" W, and 511m of altitude).

The research was conducted in three distinct stages. First, an experimental greenhouse had corn plantation and soil solution was collected. Then, atrazine transport parameters were obtained by Breakthrough Curves (BTC's) and numerical adjustments using STANMOD (HYDRUS package). Finally, numerical simulation of solution distribution (water and atrazine) using HYDRUS 2D model was done during the development of the crop.

To validate the atrazine movement simulations in region tropical soil, ten boxes were filled with Udox soil sandy loam Sertaozinho phase representing typical soil layering. The soil was compacted to a density, 1.45 g cm^{-3}. To facilitate drainage the compacted soil was placed on a bed of gravel covered with a landscape fabric. Once the boxes were filled, three tensiometers, and three ceramic cup extractors were installed. The tensiometers and extractors were installed at 20, 40 and 60 cm depth.

Once the equipments were installed, soil samples were collected for physical and chemical analyses. Analysis was completed by a commercial laboratory (PiraSolos – Piracicaba – SP, Brazil) and are included in Table 1.

Table 2 – Texture analysis for Oxisol.

depth (cm)	Clay <0,002 mm	Silt 0,053-0,002 mm	Sand Total	Coarse sand 2,00-0,210 mm	Fine sand 0,210-0,053 mm
	----------	----------	g/kg	----------	----------
0-20	210	40	750	340	410
20-40	211	39	750	360	390

Approximately 1,500 kg ha^{-1} dolomite was applied into the soil based on the chemical analysis requiring Ca^+ to be added to the soil. The soil pH was adequate for growing corn (Malavolta et. al 2006).

A meteorological station was installed inside the greenhouse to record climatic data. The meteorological data collected were maximum temperature (ºC), minimum temperature (ºC), wet bulb temperature, solar radiation (W m^{-2} e MJ m^{-2} day^{-1}) and wind velocity (m s^{-1}). The temperatures were collected by a forced aspiration psychrometer as described by Marin et. al (2001). Solar radiation was collected by a pyranometer LI200X, Campbell Scientific®. And the wind velocity was collected by an anemometer 03001, Campbell Scientific®. Climatic data were stored in a CR1000 datalogger from Campbell Scientific®.

The relative humidity (%) and the reference evapotranspiration, ET_o, (mm d^{-1}) were calculated according to Penman-Monteith equation described by Allen et. al (1998).

$$ETo = \frac{0.408\,\Delta\left[(Rn - G) + \gamma \frac{900}{Ta + 273}\, u_2(e_s - e_a)\right]}{\Delta + \gamma(1 + 0.34\, u_2)} \tag{1}$$

Where, ET_o is the reference evapotranspiration (mm d^{-1}); R_n is the net radiation (MJ m^{-2} d^{-1}); G is the soil heat flux (MJ m^{-2} d^{-1}); (es - ea) represents the vapor pressure deficit of the air (kPa), γ is the psychrometric constant (kPa °C^{-1}),u_2 is the wind velocity (m s^{-1}) and T_a is the average air temperature (°C).

A germination test was done to evaluate the viability of corn seeds. The corn variety selected was Pioneer® 30F35VYHR Leptra® technology for bugs protection and Roundup ReadyTM. The test was performed using 128 cells and it was determined to have a 94.5% of successful germination at the end of 7 days.

A starter fertilizer was applied to the soil using single superphosphate (100 kg ha^{-1}), potassium chloride (100 kg ha^{-1}) e urea (100 kg ha^{-1}). Potassium and nitrogen were split in 3 phases, 30 kg ha^{-1} at rate of 70 kg ha^{-1} each one at V4 and V8, according to Fancelli e Dourado

Neto (2000). Corn was planted on 10/26/2017 at a rate of 66,666 corn plants per hectare or 8 plants per box.

To ensure soil moisture was non limiting, the soil should be wet to provide reasonable amounts of solution. Then, two days before collecting this solution, 20 mm irrigation depth were applied.

Atrazine, or Primóleo by Syngenta®, was applied in 11/7/2017 in post-emergence according recommendations to field conditions applying. It was applied in three treatments, (T1) as the provider recommends (240 mg L^{-1}), (T2) two times (T1) (480 mg L^{-1}) and (T3) three times (T1) (720 mg L^{-1}). All the treatments were applied in the same day. The amount applied was 5 (T1), 10 (T2) e 15 (T3) L ha^{-1} as distributed in an entirely casual experiment (Figure 1).

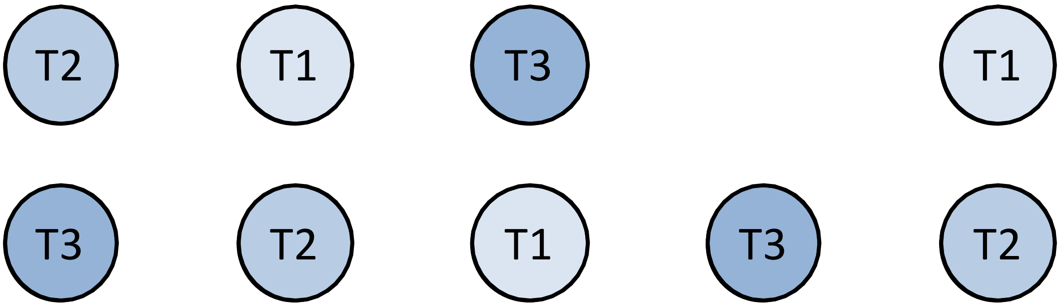

Figure 3 – Entirely casual experiment with their respectively treatments.

Soil solutions were collected approximately every other week to measure the actual atrazine concentration in the soil profile. Approximately 24 hours following each irrigation, an 80 kPa vacuum was applied to the extraction tubes to collect soil water for analysis. Extractions of soil solution were after the irrigation.

The corn crop cycle took approximately 4 months. Tasseling occurred at the week 9 (12/25/2017) and manual pollination occurred from week 10 to week 12. Harvest occurred on 02/26/2018 with a total of 80 corncobs harvested.

Atrazine concentration was analysis using a commercial laboratory (CENA/USP Ecotoxicology Laboratory, Piracicaba-SP, Brazil. Samples were analyzed using liquid chromatography with mass spectrometry (LC-MS/MS) (Agilent Technologies 1200 series with a binary pump equipped and a G1367C automatic sampler). The LC-MS/MS used a C18 Zorbax column (100 mm x 3.0 mm, 3.5 μm) (Agilent Technologies, Santa Clara - CA, United States). The mobile phase was a 40/60 ratio of water to acetonitrile at a constant flow rate of 0.6 mL min^{-1}. The water phase was comprised of 0.1% formic acid and 5 mmol ammonium formate. The injection volume was 10 µL with a run time of 6 minutesThe MRM mode (Multiple Reactions Monitoring) was used to detect atrazine by the electrospray in positive mode ionization.

For the breakthrough curves, leachate was collected after passing through three laboratory soil columns. The soil columns were glass cylinders (30 cm length and 5 cm diameter) that were filled with soil to a depth of 20 cm and packed to 1.45 g cm^{-3} similar to those measured under field conditions. A 10 mL $CaCl_2$ solution was applied in each column to obtain steady-state conditions. After that, distillated water was applied to leach $CaCl_2$ through the column. Water by itself can be used to condition the soil once the clay existent does not swell.

Once the steady-state was achieved with the distilled water, 500 mL of 14C-atrazine solution (13.62 µg L^{-1}) was applied to each column in 48 hours to established atrazine break-through-curves (BTCs). To establish these BTCs, leachate was collected at 12-hour interval until the sample contained 10% of the initial atrazine concentration. A 10 mL subsample from each of the collected samples was mixed with scintillation solution. These samples were analyzed using a liquid scintillation spectrometry (LSS) (Packard TR 2500) as described by Mendes et al. (2016). With the estimates of the resident concentration and effluent concentration, displacement parameters for atrazine were obtained for each column using STANMOD model CXTFIT (Toride et. al, 1995).

Next, atrazine's transport parameters were determined numerically using equation 2a and 2b. These simulations were determined using CXTFIT model existent on STANMOD.

$$\beta R\frac{\partial C_1}{\partial T}+(1-\beta)R\frac{\partial C_2}{\partial T}=\frac{1}{P}\frac{\partial^2 C_1}{\partial x^2}-\frac{\partial C_1}{\partial x} \tag{2a}$$

$$(1-\beta)R\frac{\partial C_2}{\partial T}=\omega(C_1-C_2) \tag{2b}$$

Where:

$$\beta=\frac{\theta_m+\rho f_m K_D}{\theta+\rho K_D} \tag{3}$$

$$P=\frac{v_m L}{D_m} \tag{4}$$

$$R=1+\frac{\rho K_D}{\theta} \tag{5}$$

$$\omega=\frac{\alpha_m L}{q} \tag{6}$$

$$C_1 = \frac{C_m}{C_0} \tag{7}$$

$$C_2 = \frac{C_{im}}{C_0} \tag{8}$$

Where, R is the retardation factor; C is the relative solute concentration; T is the relative time; P is the Peclet number; x is the relative distance; ϱ is the bull density (g cm^{-3}); θ is the volumetric soil-water content (cm^3 cm^{-3}); C_0 is initial concentration; v is the average pore water velocity (cm h^{-1}); q is the Darcy flux (cm h^{-1}); L is the column length (cm); C_m and C_{im} are concentrations in the mobile and immobile regions, respectively; θ_m is the mobile water content; f_m is the fraction of the soil in equilibrium with the mobile water; v_m is the pore water velocity in the mobile region; D_m is the mobile pore water hydrodynamic dispersion coefficient; α_m is the first order mass transfer coefficient (h^{-1}); β is the fraction of solute in the mobile region; and ω is the dimensionless mass transfer coefficient.

Three undisturbed soil samples were collected to determine the soil- water potential. Volumetric water content were determined for nine pressures. To facilitate the range in pressures, two chambers were used. Tensions for 1, 2, 4, and 10 kPa were done using a Buchner funnel fitted with a porous plate and a known hanging column of water and 30, 50, 100, 500, and 1500 kPa using a pressure plate (KLUTE, 1980). The volumetric moisture values allowed the obtaining of the parameters for soil's water retention curve (Table 2) through a numerical approach by the model retention curve (RETC) (van GENUCHTEN, 1980). This program allows several numerical approaches to obtain soil's water retention curve and hydraulic conductivity (van GENUCHTEN et. al 1991).

Table 2 – Retention curve parameters for Latossolo Vermelho Amarelo - Sertãozinho.

depth (cm)	θs (cm^3 cm^{-3})	θr (cm^3 cm^{-3})	α (cm^{-1})	n (-)	Ks cm h^{-1}	l (-)
0-20	0.54497	0.10879	0.09242	1.55771	12.18	0.5
20-40	0.54856	0.11012	0.09451	1.55741	12.17	0.5
40-60	0.54782	0.11245	0.09745	1.55987	12.17	0.5

The soil's water retention curve, modeled by van Genuchten is presented at the following equation.

$$\theta(\varphi_m) = \theta_r + \frac{\theta_s - \theta_r}{[1 + (\alpha|\varphi_m|)^n]^m} \tag{9}$$

Where, θs is saturated volumetric moisture, L^3 L^{-3}; θr is residual volumetric moisture, L^3 L^{-3}; α is retention function parameter, L^{-1}; n and m are retention function parameter, dimensionless; φm is matric potential, L.

To simulate the water absorption and nutrient uptake by a crop, a procedure developed by Feddes et. al (1978) was used. HYDRUS models present a database for root water uptake for different plants based on Wesseling (1991) and Taylor and Ashcroft (1972). Geographical positions data used were: latitude (22° S); altitude (547 m); Angstrom coefficients (a = 0.26 and b = 0.51) for Piracicaba – SP (OMETTO, 1968).

Numerical simulations for water and atrazine were made by HYDRUS 2D model, which is a model for simulating water, heat and solute in two or three dimensions. The model is supported by an interface based in interactive graphics for pre-processed data, mesh for structure and non-structure finite elements. The geometry information was chosen for two dimensions, unity in cm and the initial size was (x = 60 cm and z = 50 cm). It was also determined that the simulations were for water flux, solute transport and water and solute root uptake.

The time unit chosen was days with minimum interval of 0.001 day for model operation. The output time unit was average by day. The hydraulic model used was van Genuchten-Mualem from van Genuchten (1980). The dual-porosity model with two-site sorption in the mobile zone (physical and chemical non-equilibrium) was chosen. The solute parameters and reactions parameters were set as obtained before.

The model was evaluated by statistics analyses, which compare real data to simulated data. The parameters used were Root Mean Square Error (RMSE (eq. 10)), Willmot agreement index (d (eq. 11)), Pearson correlation coefficient (r (eq.12)).

$$RMSE = \frac{\sqrt{\sum_{i=1}^{N}(m_i - s_i)^2}}{N} \tag{10}$$

$$d = 1 - \frac{\sum_{i=1}^{N}(m_i - s_i)^2}{\sum_{i=1}^{N}(|s_i - m_a| + |m_i - m_a|)^2} \tag{11}$$

$$r = \frac{\sum_{i=1}^{N}[(m_i - m_a)(s_i - s_a)]}{\sqrt{\sum_{i=1}^{N}[(m_i - m_a)^2]\sum_{i=1}^{N}[(s_i - s_a)^2]}} \tag{12}$$

Where, RMSE is root mean square error; s_i is simulated value; N is number of comparison; d is Willmott agreement index; r is Pearson correlation coefficient; m_a is average observed value; s_a is average simulated value.

5.3 Results and Discussion

Atrazine's movement parameters from three replicates of breakthrough curves are presented at the up part of table 4. In average, the water velocity (v) through the pores was 21.6 cm h^{-1}. Second, the partition coefficient between the mobile and immobile phases (β) was 0.82. Third, the transfer coefficient (ω) was 2.5 h^{-1}.For last, the degradation coefficient was considered 0.5 as obtained from Queiroz & Monteiro (2000).

Also, statistical indexes are presented in table 3. In average, the RMSE (ug L^{-1}) was 0.0293. The model accuracy is d = 0.9844, and precision is r = 0.9836. Evidently, for soil columns and predictions made out of that, the model works great.

Table 3 – Atrazine`s movement parameters and modeling indexes comparing observed modeled data for three replicates of breakthrough curves.

parameter	A	B	C
v (cm h^{-1})	21.80	21.40	21.60
β	0.790	0.830	0.840
ω (h^{-1})	2.420	2.530	2.550
μ	0.500	0.500	0.500
index	**A**	**B**	**C**
RMSE (μg L^{-1})	0.0270	0.0312	0.0298
d	0.9906	0.9863	0.9763
r	0.9815	0.9845	0.9848

Figure 2 shows the pulse breakthrough curve for atrazine movement through the soil used for the experiment for each column. The predicted data follows the observed data reasonably well with the exception of the breakthrough time for the peak. The peak for the observed data presents was at 1.6 pore volumes while predicted data was slightly later at 1.8 pore volumes.

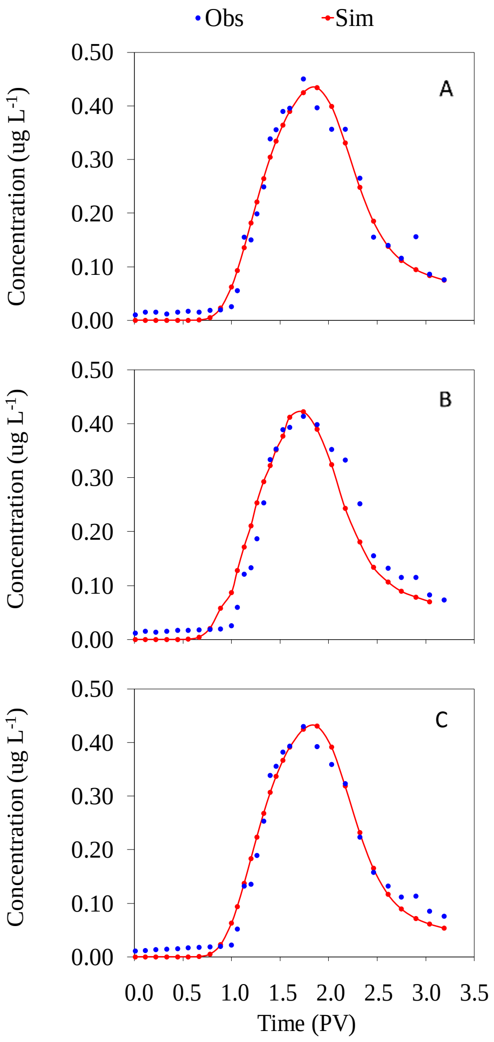

Figure 2 – Atrazine's breakthrough curves obtained for three replicates of a tropical soil.

One possible explanation for this could be preferential flow along the column wall. The interface of the soil with the experimental column results in a less tortuous path when compare to the bulk soil. Care was taken to minimize this preferential flow but it could not be eliminated thereby skewing the curve to the left.

After the breakthrough curves being done and the collections of soil solution in the experiment, atrazine concentration analyses were done in order to evaluate HYDRUS 2D simulations. But first, a statistical mixed procedure evaluating the 3 different treatments was done.

Table 5 – Mixed procedure for statistics analyses evaluating differences among treatment (trt), depth, and days after atrazine application (daa).

Effect	DFDen	DFF	ValuePr>F
trt	2198414	66.7	<.0001
depth	2198801	96	<.0001
daa	1019814	239	<.0001
trt*depth	4198137	47.6	<.0001
trt*daa	2019815	89.24	<.0001
trt*depth*daa	6019889	13.92	<.0001

According to the statistical tests (table 5), there are significant differences (Value Pr < 0.05) among the three treatments along the cycle and depth. Also, the same test show that there are differences among the treatments, among the depths, and among the days after atrazine application (daa). Moreover, interactions between the treatments and depth, and between the treatment and the daa were also significant.

For T1 and T2, there are statistical differences until 70 daa when comparing the treatment at the three depths. After that, there are no significant differences in the analyzed atrazine concentration through the soil profile. For T3, 20-cm depth is always different from the other depths. However, this treatment does not show significant differences after 70 daa at 40 and 60-cm depths.

Comparing the treatments at the same depth (Figure 3) shows that all the three treatments are statistically different for every daa at the 20-cm depth. However, for 40-cm depth the statistical differences start at 35 daa and go until 56 daa. From 63 daa until 84 daa, there are no statistical differences along the treatments. Last, at 60-cm-depth, the statistical differences start at 35 daa when T1 and T2 are different from T3. From 42 daa until 56 daa, there are significant differences among the three treatments. For 63 and 70 daa, T1 is considered significantly different from the other two treatments. For 77 and 84 daa there are not significant differences among the treatments anymore.

It is important to highlight the peaks at each depth. At 20-cm depth, the peaks for T3 (~ 9 ug L^{-1}), T2 (~ 6 ug L^{-1}), and T1 (~ 2.5 ug L^{-1}) occur at 35 daa. At 40-cm depth, the peaks for T3 (~ 4 ug L^{-1}), T2 (~ 2.2 ug L^{-1}), and T1 (~ 1.6 ug L^{-1}) occur at 42 daa. And, at 60-cm depth, the peaks for T3 (~ 3.7 ug L^{-1}), T2 (~ 2 ug L^{-1}), and T1 (~ 1.5 ug L^{-1}) occur at 49 daa. The peaks move with a delay of 7 days through each depth showing how slow atrazine moves through the soil and indicates possible management decisions to avoid groundwater contamination. One best management practice that could be adopted maintain the concentration applied around the recommended dose avoiding reach more than twice. Another practice is to avoid areas where there are not weed infestation. In other words, applying the atrazine only when it is really necessary to control the weeds.

Taking into account the mass balance for the atrazine applied in the system, some of the atrazine could have been leached underneath the 60-cm layers (BOESTEN, 2016; DE PAULA, 2016), part of atrazine molecules could have been degraded (ERICKSON, 1989), and part of atrazine molecules could be absorbed by the corn plant (Davis et al. 1965; Roeth & Lavy, 1971; Montgomery & Fredy, 1961).

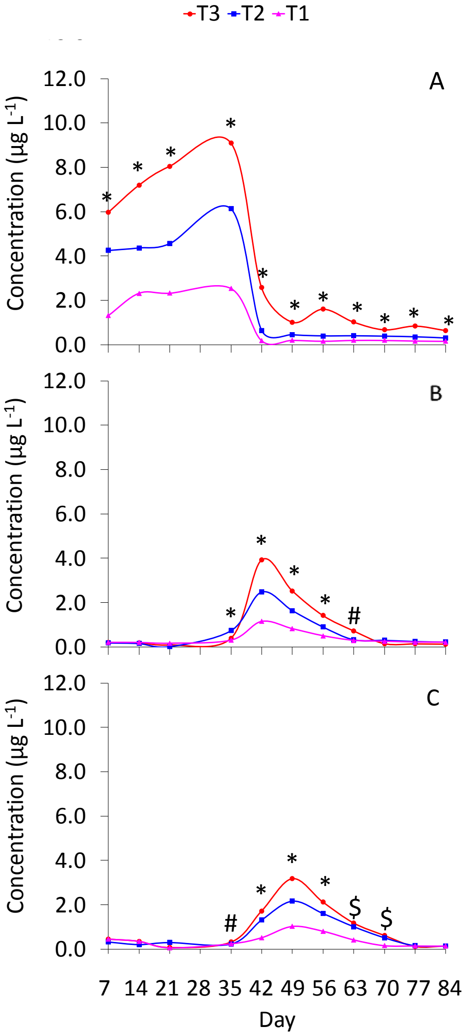

Figure 3 – Atrazine's concentration along days after atrazine application for T1, T2, and T3 at 20 (A), 40 (B), and 60 (C) cm depth. * - All the treatments are different; # - T3 is different from T2 and T1; $ - T1 is different from T2 and T3.

To help with the choice of best management practices and to allow the producer possible contaminations, HYDRUS 2D seems to be a useful software. Table 6 presents the indexes for comparison between observed and modeled data for atrazine concentration. The RMSE ranges from 0.0350 to 0.2372 ug L^{-1} and shows a pattern where 20-cm depth is always higher than the other two depths. This happen because the concentrations at 20-cm depth are also higher than the other two depths. Moreover, T3 presents the highest values for error once it is the treatment with the highest concentration. The Willmott coefficient values range from 0.8953 to 0.9684 what shows how accurate the model is. As it happened with the RMSE, the accuracy is higher when the atrazine concentration is lower. The same thing happens with the Pearson correlation coefficient, which values range from 0.9057 to 0.9323.

Table 6 – Indexes scores comparing observed and modeled data for atrazine concentration at three different treatments (T1, T2, and T3) at three different depths (20, 40, and 60 cm).

TRT	Depth (cm)	RMSE (ug L^{-1})	d	R
T1	20	0.1171	0.8981	0.9146
	40	0.0539	0.9629	0.9323
	60	0.0423	0.9684	0.9240
T2	20	0.1877	0.8953	0.9072
	40	0.0612	0.9377	0.9120
	60	0.0532	0.9543	0.9179
T3	20	0.2372	0.8995	0.9057
	40	0.0710	0.9136	0.9112
	60	0.0350	0.9267	0.9177

Figure 4 shows observed and simulated data for atrazine concentration during a period of 84 daa when the corn crop was being conducted.

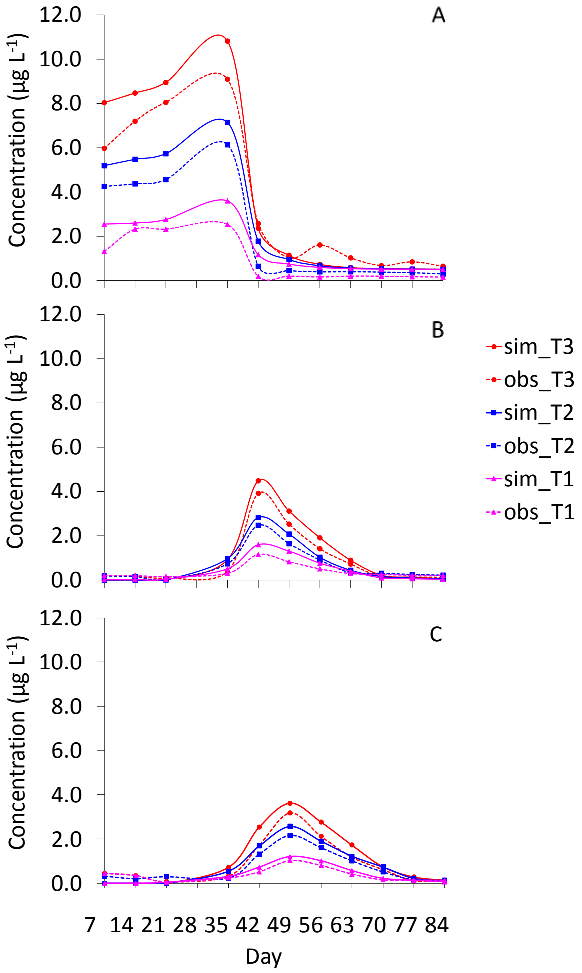

Figure 4 – Observed and simulated data for atrazine concentration (µg L^{-1}) according to days after atrazine application for 20 (A), 40 (B), and 60 (C) for T1 T2 and T3.

In general, the model overestimates what happen with the observed data and some explanations can be given. The atrazine's sink parameters should be considered at a real and dynamic corn crop situation where there are the roots liberating exudates, and active microorganisms living at the rhizosphere. Both situations can promote changes at atrazine concentration. Moreover, it needs to be evaluate the atrazine's absorbing by the plants. If there is this absorption, a new sink parameter should be estimated. Besides that, the evapotranspiration modeling underestimate water uptake, then more water stays at the arable layer. These parameters need to be corrected. And, finally, root uptake parameters need to be improved because they are old (1991) and nowadays hybrids are different.

HYDRUS 2D can be considered a powerful tool for producers and researchers because it can track atrazine concentration at the soil solution. Atrazine is a potential threat to soil ecosystem and environmental health (Fang et al. 2015; Freeman et al. 2011), thus it is necessary the development, the spreading and the use of tools like HYDRUS 2D.

5.4 Conclusions

Within the results and according to statistical indexes, HYDRUS 2D is a powerful tool to monitor atrazine's movement in a commercial corn plantation. The model presents high precision predicting atrazine movement pattern what means that the atrazine contamination can be followed by farmers. In addition to that, a high accuracy was presented, however the model overestimates the values for atrazine's concentration. The model weakness was found at two critical points. More researches taking crops in account need to be done.

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6 USING ELECTROMAGNETIC INDUCTION TECHNOLOGY TO PREDICT ATRAZINE LEACHING POTENTIAL.

Abstract

Atrazine is an herbicide commonly used to controls weeds in corn crop. Atrazine becomes an environmental concern when it moves offsite to surface water. Understanding how atrazine moves at the field-scale is important for developing management controls. Electromagnetic Induction (EMI) has been used to map certain contaminant transport at the field-scale. This study was developed to evaluate the efficacy of EMI technology for identifying surface soil atrazine concentration at the field-scale. The research was conducted in a silage corn field at the U.S. Meat Animal Research Center (USMARC), Clay Center, NE. The study was conducted in three stages i) first, EMI data collection and a response surface sampling design for collection of bulk soils and soil core samples, ii) atrazine transport parameters was obtained by Breakthrough Curves (BTC's) using the bulk soil and numerical adjustments using STANMOD (HYDRUS package), and iii) Modeling atrazine's parameters through EMI signal data with posterior atrazine's movement simulations through the soil using HYDRUS 2D. The parameters R, β, and ω measurements were strongly correlated. Additionally, the cross-correlation suggests each transport parameter exhibits a strong correlation EC_a measure from the EMI survey. The low values for RMSE and RRMSE and the high values for Willmott and Pearson coefficients indicates EMI technology can be used to predict atrazine movement parameters. HYDRUS 2D quantitatively present the atrazine concentration leaching and how bad the contamination would be. Combining both EMI technology with HYDRUS 2D modeling provides researcher with additional information for developing better management practices for controlling atrazine movement to surface water; however, further studies are needed determine the effectiveness of this approach for other soil types.

Keywords: Computational modeling; Water soil engineering; Soil solutes dynamics; Environmental contamination modeling; Soil herbicide dynamics

6.1 Introduction

A growing challenge facing many countries is meeting the demand for food to feed a growing population. Endemic with this increase in food production is the expectation to minimize the environmental impact (Pittelkow et al., 2015). Herbicides are a common tool used to control weeds and improve crop production around the world (Kniss, 2017). While herbicides are a powerful tool for weed control, these herbicides can become an environmental contaminant when they are transported off-site to surface waters.

Atrazine (2-chloride-4-ethylamino-6-isopropylamino-striazine) is an herbicide commonly used to controls weeds during corn production (NALEWAJA, 1968). Atrazine's mode of action for weed control is it stops CO_2 fixation thereby ceasing carbohydrate production (TAIZ & ZIEGER, 2013). Atrazine is also classified as toxic agent which deregulate the hormonal balance

(FRIEDMANN, 2002), and C carcinoma agent, which are potentially carcinogenic to humans (BIRADAR & RAYBURN, 1995).

One method for increase crop productivity while minimizing inputs is the use of precision agriculture (Anlauf et al.,2018). Precision agriculture attempts to use the specific types and amounts of production inputs for a given soil type. This is accomplished by increasing the number of correct decisions per unit area of land per unit time with associated net benefits (McBratney et al., 2005). Development and application of sensor data to improve information concerning each land unit is essential for precision agriculture to work effectively. One sensor that has been used effectively for identifying soil properties is electromagnetic induction (EMI) (Doolittle & Brevik, 2014).

Several studies have reported methodologies for using EMI to predict the spatial variability of soils. These studies are use soil properties such as salinity, subsurface water movement and soluble salts, soil water content, soil texture, clay content, lithology and mineralogy, soil compaction, CEC, soil pH, minerals to indicate changes(Cockx et. al 2009; Triantafilis et. al 2009; Sudduth et. al 2010; Al-Gaadi, 2012; Heil and Schmidhalter, 2012; Doolittle et. al, 2013). Jaynes et al (1995) tried to use electrical conductivity (EC_a) measured by EMI as a surrogate measure of soil-herbicide partitioning. They found that using EC_a to map the soil adsorption coefficient (Kd) is rapid, easy, and inexpensive once it has been calibrated. However, EMI failed to predict the observed high K_d values.

In order to assess a different approach to predict atrazine's movement through the soil, the objectives of this research were i) to determine the ability of EMI sensor data to predict atrazine's trasport parameters in a silage corn research field; ii) develop a model to converts EC_a into atrazine's movement parameters, and iii) use the software HYDRUS 2D coupled with the EMI model to predict atrazine movement through the soil profile.

6.2 Material and Methods

The site selected was a silage corn field at the U.S. Meat Animal Research Center (USMARC), Clay Center, NE, with D_{FA} climate according to the Köppen classification (40° 31' 20" N, 98° 3' 18" W, and 529m of altitude). The site transected a transition between two soil types resulting from a topographical relief. The largest area (approx. 85%) was a Hastings silt loam complex (table 1). The retention curve for the major component was considered and its retention curve parameters are presented in table 2.

Table 1 - Texture and Organic Matter analyses for the 12 soil cores throughout the corn field

site	Clay (%)	Silt (%)	Sand (%)	OM (%)	Texture
2641	25	51	24	4.4	Silt Loam
3268	35	43	22	4.2	Clay Loam
3335	29	49	22	3.9	Clay Loam
3451	29	47	24	3.8	Clay Loam
4147	25	51	24	4.1	Silt Loam
4462	33	49	18	3.7	Silty Clay Loam
4829	46	33	21	3.9	Clay
5042	29	49	22	4.4	Clay Loam
5530	33	49	18	4.8	Silty Clay Loam
5647	33	53	14	3.8	Silty Clay Loam
6359	39	39	22	4.0	Clay Loam
6452	29	53	18	4.3	Silty Clay Loam

Table 2 – Retention curve parameters for each site.

site	θs (cm^{3} cm^{-3})	θr (cm^{3} cm^{-3})	α (cm^{-1})	n (-)	Ks cm h^{-1}	l (-)
2641	0.4350	0.0747	0.0064	1.5627	0.4750	0.5
3268	0.4593	0.0874	0.0103	1.4401	0.5038	0.5
3335	0.4474	0.0809	0.0076	1.5201	0.5171	0.5
3451	0.4446	0.0803	0.0080	1.5100	0.5175	0.5
4147	0.4350	0.0747	0.0064	1.5627	0.5475	0.5
4462	0.4625	0.0871	0.0087	1.4849	0.5146	0.5
4829	0.4725	0.0937	0.0153	1.3109	0.4850	0.5
5042	0.4474	0.0809	0.0076	1.5201	0.5171	0.5
5530	0.4625	0.0871	0.0087	1.4849	0.5146	0.5
5647	0.4685	0.0884	0.0084	1.4969	0.5133	0.5
6359	0.4641	0.0902	0.0122	1.3872	0.4917	0.5
6452	0.4528	0.0821	0.0072	1.5351	0.5108	0.5

The research was conducted in three distinct stages. First EMI technology was used to collect EC$_a$ data from the plot. Response surface sampling design used this EC$_a$ data to select 12 sampling sites to represent the spatial variability of the plot. The GPS coordinates for the EC$_a$ data were used to navigate to the 12 sampling sites to collect bulk soil to a depth of 40 cm. Next, breakthrough curves for each site were determined for each sampling site. This data was used to determine transport parameters using STANMOD (HYDRUS package). Finally, these transport parameters were correlated with the EC$_a$ data to determine whether EMI was an effective tool for predicting atrazine's movement through soil.

The corn crop was planted on 5/7/18 and atrazine (5.7 L ha^{-1} Volley atrazine NXT) was applied post emergence on 6/12/18. Prior to planting, EMI was used to collect spatial EC_a data from the site using a method detailed in Woodbury et al., (2009). A brief description follows. A Dualem-1S meter (Dualem Inc., Milton, ON, Canada) was used to collect EC_a data from the corn field surface. The meter was positioned on a nonmetallic sled and pulled at approximately 1.5 m s 1 at 2-m intervals across the corn field. Path spacing was maintained using a Trimble EZ – Guide Global Positioning System (GPS) – Guidance System (Trimble Navigation LTD, Sunnyvale, CA). The Dualem 1-S meter simultaneously records both horizontal and vertical dipole modes; however, only the horizontal co-planer orientation was used for this study (centroid depth-measure approximately 0.75m). Simultaneously, GPS coordinates of the insturment's position were determined using an AgGPS 332 receiver using real-time kinematic (RTK) correction (Trimble Navigation Ltd). Coordinates and EC_a data were collected at a rate of five samples per second and stored in a Juniper System Allegro (Juniper Systems, Logan, UT) datalogger. Edge effects from metal fencing were clipped from the EC_a data set before the sampling designs were determined.

Response Surface Sampling Design (RSSD) software program contained in the USDA-ARS EC_e Sampling, Assessment and Prediction (ESAP) software package (Lesch et al.., 2000) was used to select 12 sites in the corn field. The GPS coordinates associated with the selected EC_a values were used to navigate back to these sites for collecting bulk surface soil.

ESAP software package contains a sampling approach specifically designed for use with ground-based EC_a signal readings (Lesch, 2005), based on the observed magnitudes and spatial locations of the EC_a data, a minimum set of calibration samples are selected. These sites are chosen in an iterative, nonrandom manner to optimize the estimation of a regression model, and simultaneously maximize the average separation distance between adjacent sampling locations. Lesch (2005) demonstrated that such a sampling approach can substantially outperform a probability-based sampling strategy with respect to a number of important model-based prediction criteria.

Once the sampling designs were generated, bulk soil samples were collected to a depth of 15 cm at all 12 sites to run breakthrough curves (BTC's) to determine atrazine movement parameters: R, β and ω. The soil was air dried and mechanically ground to pass through a 2-mm sieve.

The BTCs procedures were done to obtain atrazine transport parameters in the laboratory premises of the U.S. Meat Animal Research Center (ARS), Clay Center, Nebraska (ARS/USA).

The soil columns were saturated with $CaCl_2$ solution to preserve clay from swelling, by capillarity, aiming to expel the air contained in micro pores. The columns were placed in a bucket and water was added by dripping along the walls of the bucket until it reaches about 2/3 of the height of the soil column. The columns remained in the bucket for 24 hours to allow for complete saturation. After saturation, the columns were placed in an apparatus such that a constant head of $CaCl_2$ solution (3 mmol L^{-1}) was applied at the top of the soil column and a 80 kPa suction tension applied at the bottom. The $CaCl_2$ was passed through the soil columns for 24 hours to establish steady-state flow. Once steady-state flow was established, a two pore volume atrazine pulse (5 mg L^{-1}) was passed through. Following the atrazine pulse, the $CaCl_2$ solution was reintroduced. Steady-state flow conditions were maintained throughout the study.

After collection of the effluents, the concentration of Atrazine in each flask was determined by the determination method based on liquid-liquid extraction followed by Ultra Performance Liquid Chromatography (UPLC). A calibration curve was established prior to each analysis.

Atrazine's transport parameters were determined numerically using equation 1a and 1b. These simulations were determined using CXTFIT (TORIDE, et al. 1995) model existent on STANMOD.

$$\beta R\frac{\partial C_1}{\partial T}+(1-\beta)R\frac{\partial C_2}{\partial T}=\frac{1}{P}\frac{\partial^2 C_1}{\partial x^2}-\frac{\partial C_1}{\partial x} \tag{1a}$$

$$(1-\beta)R\frac{\partial C_2}{\partial T}=\omega(C_1-C_2) \tag{1b}$$

Where

$$\beta=\frac{\theta_m+\rho f_m K_D}{\theta+\rho K_D} \tag{2}$$

$$P=\frac{v_m L}{D_m} \tag{3}$$

$$R=1+\frac{\rho K_D}{\theta} \tag{4}$$

$$\omega=\frac{\alpha_m L}{q} \tag{5}$$

$$C_1=\frac{C_m}{C_0} \tag{6}$$

$$C_2 = \frac{C_{im}}{C_0} \tag{7}$$

Where

R is the retardation factor; C is the relative solute concentration; T is the relative time; P is the Peclet number; x is the relative distance; ϱ is the bull density (g cm^{-3}); θ is the volumetric soil-water content (cm^3 cm^{-3}); C_0 is initial concentration; v is the average pore water velocity (cm h^{-1}); q is the Darcy flux (cm h^{-1}); L is the column length (cm); C_m and C_{im} are concentrations in the mobile and immobile regions, respectively; θ_m is the mobile water content; f_m is the fraction of the soil in equilibrium with the mobile water; v_m is the pore water velocity in the mobile region; D_m is the mobile pore water hydrodynamic dispersion coefficient; α_m is the first order mass transfer coefficient (h^{-1}); β is the fraction of solute in the mobile region; and ω is the dimensionless mass transfer coefficient.

Hence, the following spatially referenced, multivariate LR model was used to describe the relationships between atrazine parameters (R, β and ω) and the EMI signal data (Equation 8).

$$y_{ij} = A + B(EMI_i) + \varepsilon_{ij} \tag{8}$$

where

y_{ij} = the value of the jth chemical property at the ith sampling location;

$A; B$= the unknown regression model parameters for the jth regression equation (j = 1 and 2).

ε_{ij}= the jth spatially uncorrelated random normal error component.

The models which presented regression coefficients higher than 0.5 were statistically significant below the 0.05 significance level and considered adequate for predicting movement parameters for atrazine. Additionally, models with regression coefficients higher than 0.70 were considered adequate for mapping spatially referenced atrazine`s movement parameters based on ECa survey data. The indexes Root Mean Square Error (RMSE (eq. 10)), Willmot agreement index (d (eq. 12)), Pearson correlation coefficient (r (eq.13)) were used to evaluate the EMI model.

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}(m_i - s_i)^2}{N}} \qquad (10)$$

$$d = 1 - \frac{\sum_{i=1}^{N}(m_i - s_i)^2}{\sum_{i=1}^{N}(|s_i - m_a| + |m_i - m_a|)^2} \qquad (12)$$

$$r = \frac{\sum_{i=1}^{N}[(m_i - m_a)(s_i - s_a)]}{\sqrt{\sum_{i=1}^{N}[(m_i - m_a)^2]\sum_{i=1}^{N}[(s_i - s_a)^2]}} \qquad (13)$$

Where,

RMSE = root mean square error;
mi = observed value;
si = simulated value by the model to be evaluated;
N = number of comparison;
d = Willmott agreement index;
r = Pearson correlation coefficient;
ma = observed value average;

Maps with different interpolated data were generated using natural neighbor interpolation (Sibson, 1981) through MATLAB to spatialize the atrazine's movement parameters in the corn field.

6.3 Results and Discussion

Figure 1 was generated after the EMI collection and represents the soil characteristics according to apparent electrical conductivity. Despite the soil is considered homogeneous and classified as silt loam in the whole area, different characteristics can be noticed mainly in the southeast region of the field. These differences were perceived by the EMI sensor and represent the clay horizon which appear in the surface after the erosion of the top horizon due a stream running by this area.

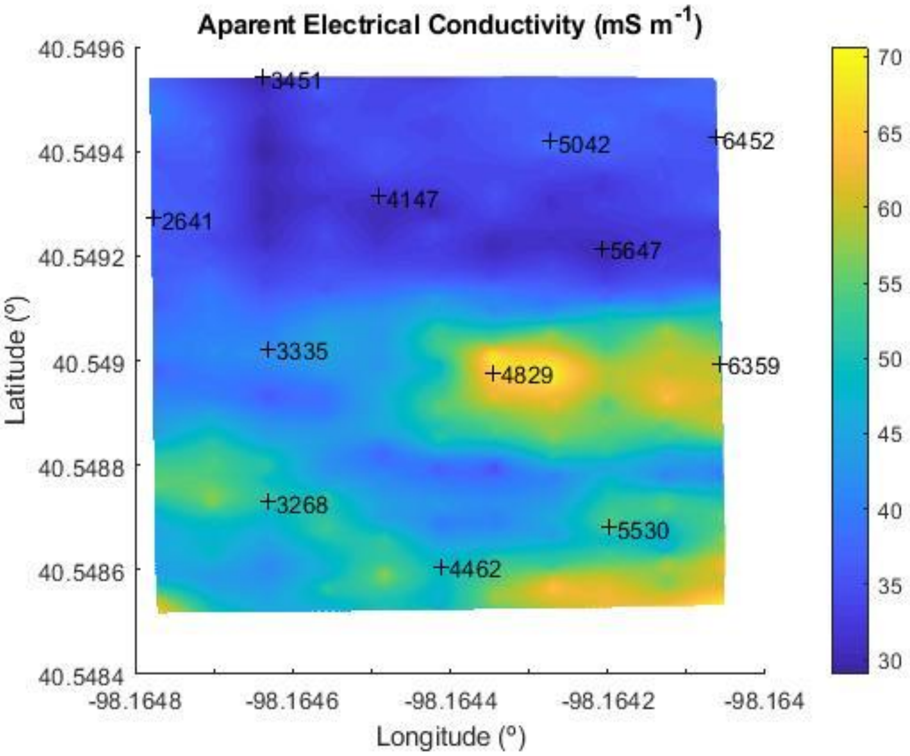


Figure 4 – EMI signal data spatialized along the sampling positions within the silage corn test site.

The basic EMI survey and atrazine parameters summary statistics are presented in Table 2. The shallow EMI signal data exhibited a mean of 43.021 mS m^{-1}, a standard deviation of 9.2651 mS m^{-1}, and a range from 28.914 to 70.885 mS m^{-1}. The retardation factor presented a mean of 7.45, a standard deviation of 4.3504, and a range from 1.95 to 16.48. This variation indicates that some portions of the soil are quite different and may interfere in atrazine movement. The parameter β exhibited a mean of 0.4734, a standard deviation of 0.1894, and a range of 0.11 to 0.8. Again, this quite variation may indicate that atrazine presents different behavior when passing from mobile to immobile soil phases. Lastly, parameter ω presented a mean of 5.56 h^{-1}, a standard deviation of 5.3764 h^{-1}, and a range of 0.2 to 17.46 h^{-1}. Following the previous parameters, the variation indicates that the changes between the mobile and immobile soil phases varies within the soil.

Table 2 – Basic electromagnetic induction (EMI) survey data and atrazine parameters summary statistics.

variable	N	mean	SD	Min	Max
EMI , mS m^{-1}	2496	43.021	9.2651	28.914	70.885
R	12	7.45	4.3504	1.95	16.48
β	12	0.4734	0.1894	0.11	0.8
ω (h^{-1})	12	5.56	5.3764	0.2	17.46

Before the correlation between EC_a and the parameters, normality (w) and independence (score - Moran) tests were done. Both tests presented p-value > 0.05, thus were normal and independent for the parameters R, β, and ω (Table 3).

After the correlation and the model was created, indexes to evaluate the model were calculated. The RMSE for all the three parameters were considered low, around 5 – 7.5%. Regarding accuracy, the model presented Willmot agreement index higher than 0.95 which is considered accurate. Regarding precision, the model presented Pearson agreement index higher than 0.90 which is considered precise. Thus, the model is considered accurate and precise because the atrazine parameters are highly correlated to the clay amount contained in the soil. Once the soil presents clay variation, the atrazine's movement parameters also follow this variation.

Table 3 – Indexes for model evaluation for R, β, and ω

indexes	R	β	ω
RMSE	1.2755	0.0788	1.4821
r	0.9541	0.9040	0.9595
d	0.9760	0.9999	0.9815
w (p-value)	0.9468 (0.0677)	0.9529 (0.1291)	0.9493 (0.0520)
score (p-value)	1.2400 (0.0871)	0.9246 (0.2120)	0.9647 (0.1459)
R^2	0.9104	0.8172	0.9206

Figure 2A shows de model curve for Retardation factor and EMI signal data. The R^2 is 0.9104 indicating good correlation and as EMI data increase R also increases. Thus, the correlation is positive and means that as the soil present higher EMI, more interactions between atrazine and the soil occurs. On another hand, figure 2B shows the model curve between the parameter β and EMI signal data. The R^2 is 0.8172 indicating good correlation. However, the correlation is negative what means as the soil present higher EMI, more water molecules tend to be immobile than mobile, resulting in atrazine movement being slowed. At last, figure 30C shows the model curve for parameter ω and the EMI signal data. The R^2 is 0.9206 also indicating good correlation. The correlation is positive indicating that as higher EMI signal is, higher the changes between the mobile and the immobile phase. The changes between the two phases indicate the interaction grade between the solute and the soil.

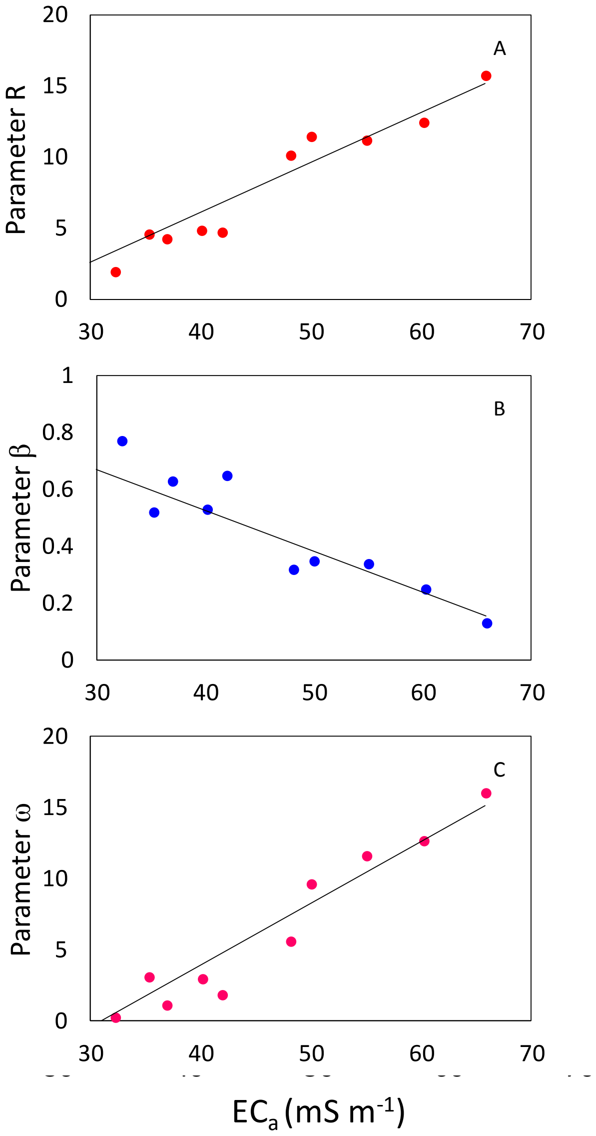
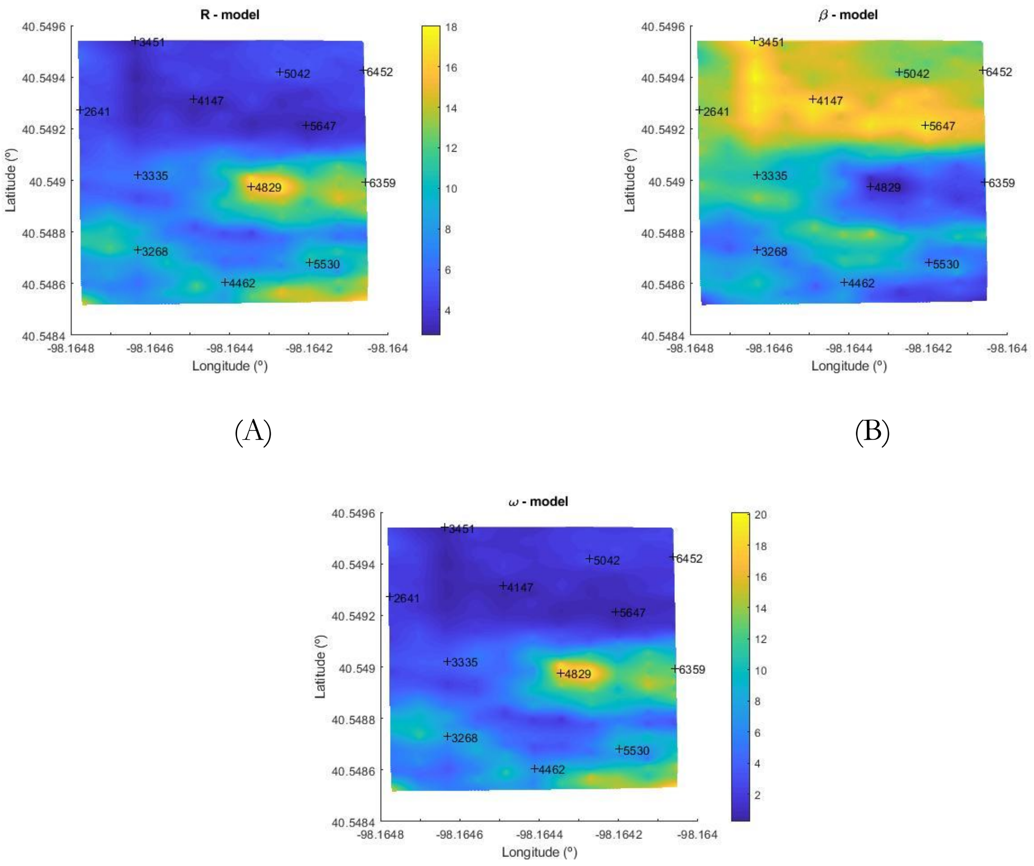


Figure 2 – Quadratic model to predict (A) R, and (C) ω, and exponential model to predict (B) β through EMI signal data.

As revealed by figure 3A, the spatialized retardation factor model shows the differences in value within the corn field. As the EMI signal data decrease (Figure 1), the retardation factor values also decrease. Also, figure 3B presents the spatialized parameter β model characteristics. As discussed before, β values increase as the EMI signal data decrease showing the inversely proportional behavior. Lastly, figure 3C presents the spatialized parameter ω model. In agreement with R, as the EMI signal data values increase, the values for ω also increase.

The maps facilitate the variation understanding about the atrazine's parameters. It is possible to say that despite the EMI signal data values do not vary a lot, the atrazine parameters vary and indicate different dynamics for its movement through the soil. It is necessary to remember that the atrazine concentration could scarcely be predicted. However, its behavior can be predicted through its movement parameters.



(A)

(B)

(C)

Figure 3 – EMI signal data spatialized (A), predicted spatial retardation factor (B), β (C), and ω (D) pattern across the corn field.

To evaluate atrazine's movement through the soil, four simulations were taken along the time corn was in the field. Figure 4 shows atrazine movement through the soil considering the average of parameters obtained (Figure 4A and the three different cores (Figure 4B - 5647, Figure 4C - 5530, and Figure 4D - 4829) to exemplify the differences found.

Using the parameters obtained through the soil core 5647, atrazine was more mobile than 4829. This characteristic occurred at 20-cm depth and 40-cm depth and atrazine might reach the groundwater. The explanation for that is the amount of clay contained in each soil region. At 4829, the clay amount was higher than 5647.

The soil core 5530, presented atrazine's movement similar to the average of the parameters through the corn field. The explanation for that is the clay amount at 5530 is median, thus the parameters for this soil core is similar to the average of all the soil cores.

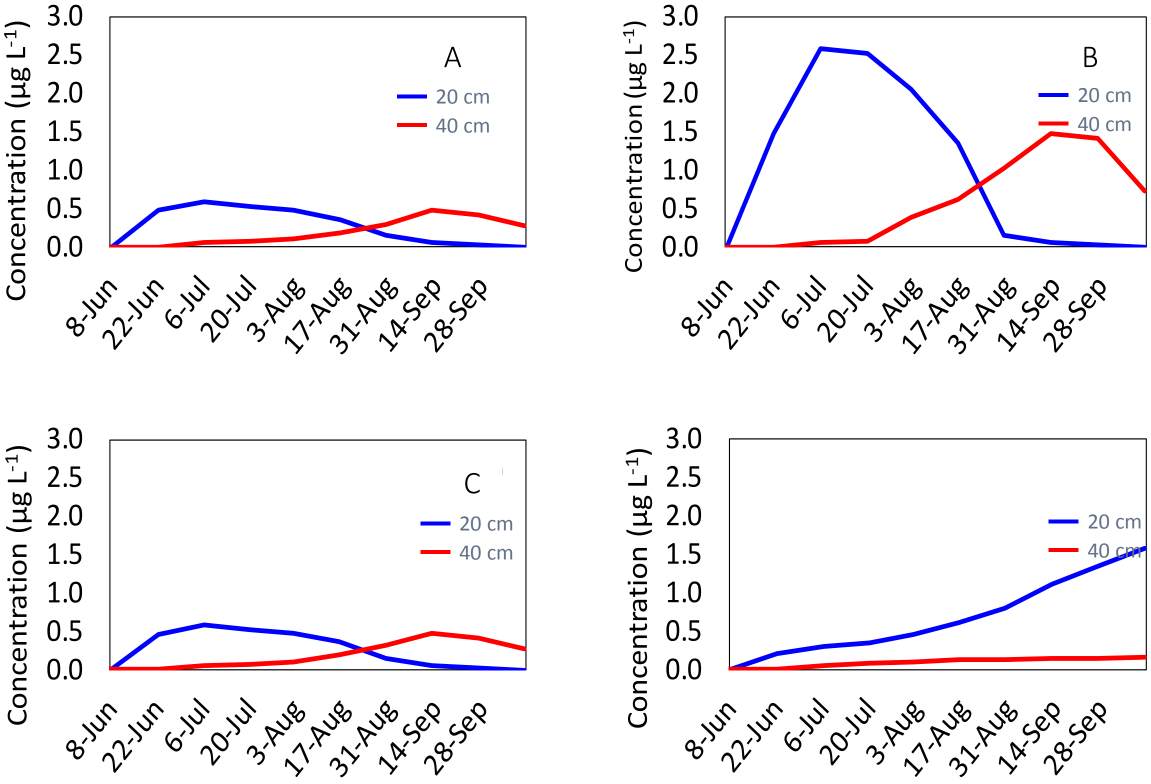


Figure 4 – HYDRUS 2D simulations for average (A), 5647 (B), 5530 (C), and 4829 (D).

6.4 Conclusions

The study evaluated the relationship between the atrazine's movement parameters and the EC_a values. For this particular setting, EMI appears to be an effective tool to use to better understand the spatially variable transport properties of the soil. Additionally, models to convert EMI signal data into atrazine's movement parameters (R, β, and ω) were suggested and they were totally reliable, according to the statistical indexes presented. Finally, the use of HYDRUS 2D to identify soil regions where atrazine leaches and reach the groundwater was presented. Combining it with the soil maps generated gives a new information about potential atrazine leaching occurs as well the order of the values for atrazine concentration leaching through the soil. In other words, working with both EMI sensor and HYDRUS models package can help to achieve a sustainable agriculture seeking to avoid groundwater contamination. Further studies should be carried out in order to expand the use of HYDRUS 2D coupled with the EMI sensor for other contaminants. It is also recommended deeper studies at the field scale using EMI signal to point possible differences that will influence the solutes movement.

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