ATRAZINE TRANSPORT THROUGH A GLACIAL TILL AQUIFER IN NORTH-CENTRAL MISSOURI

A Thesis presented to the Faculty of the Graduate School

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Masters of Science

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by

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MAY 2009

The undersigned, appointed by the dean of the Graduate School, have examined the thesis entitled

ATRAZINE TRANSPORT THROUGH A GLACIAL TILL AQUIFER

IN NORTH-CENTRAL MISSOURI

presented by Steven Pagan,

a candidate for the degree Master of Science,

and hereby certify that, in their opinion, it is worthy of acceptance.

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Dr. Robert Lerch

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ABSTRACT

Although the claypan of North Central Missouri is traditionally believed to protect the groundwater from contamination, low concentrations of the herbicide atrazine have been detected in a shallow glacial till aquifer. The fate of the atrazine in the aquifer is not well known. With the continued use of atrazine, the concentration in the aquifer could increase to levels of concern or decrease if the conditions are not favorable for persistence. Beginning in the Fall 2007 and continuing through the Fall 2008, concentrations of atrazine and its degradation products deethylatrazine (DEA) and deisopropylatrazine (DIA) were measured at a typical field in Northeast Boone County, Missouri. The concentration ratio of DEA to atrazine (DAR) supports the concept that preferential flow paths within the claypan allow for direct transport of atrazine to the aquifer. These data were also necessary for constructing computer based flow models of the aquifer. Using the programs MODFLOW and MT3DMS within GMS 6.0, a groundwater flow model was produced that was coupled with a solute transport model of atrazine within the saturated zone. The model was constructed using constraints of historical use of atrazine since 1991. The model results were similar to those measured in the field and predictive simulations did not indicate an increase of atrazine concentration to alarming levels.

Chapter 1 – Introduction

Atrazine

The herbicide atrazine, 2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine (Figure 1), has become one of the most regularly used herbicides worldwide since its introduction in 1958. Atrazine is a member of the triazine family of herbicides structured around a heterocyclic ring containing nitrogen atoms at the 1, 3 and 5 positions (*s*-triazine ring). The structure includes a chlorine attached to the carbon in the second position of the *s*-triazine ring, and the carbons in position 4 and 6 have attached side chains of an ethylamine and an isopropylamine, respectively.

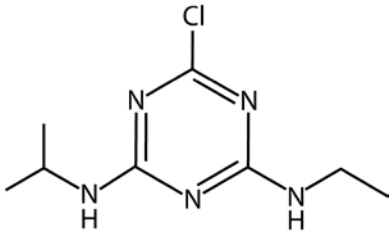

Figure 1. The structure of atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine).

In the United States atrazine is most commonly used on crops such as corn and sorghum, while worldwide it is also used for sugarcane and fruit, such as pineapple (Montgomery, 1997; Verschueren, 2001). Approximately 27-36 million kilograms of atrazine are applied to crops annually in the United States with 85% used for corn production in the Midwest states (Figure 2) (Sass and Colangelo, 2006). A variety of manufacturers produce atrazine and it is sold under numerous trade names such as Aatrex, Atrazine, Candex, Weedex A and many more including mixtures with other

herbicides (Montgomery, 1997; Vencill, 2002). Atrazine is available as a powder, suspension concentrate or granules, and is often combined with other herbicides such as alachlor, acetochlor, or metolachlor in order to control a variety of weeds.

As an herbicide, atrazine is used for pre and post-emergence control of broadleaf and grassy weeds. The herbicide is mainly absorbed by plants through the roots but can be taken in through the leaves when applied post-emergence. Once inside the plant, the herbicide accumulates within the shoots and leaves where it acts as a photosynthesis inhibitor. Within the photosystem II protein complex, atrazine occupies the quinone-B binding site of the subunit protein D1 preventing the flow of electrons needed for photosynthesis (Vencill, 2002). The agricultural use of atrazine has generated numerous environmental health concerns. The solubility of atrazine, 33 mg L^{-1} at 22°C (Vencill, 2002), with a long half life and low sorption allow for transport into both surface and ground water sources. Most of the atrazine applied to the field that is lost is from runoff to surface water systems, yet the portion of atrazine infiltrating the subsurface is also of concern because it has a longer residence time. The detection of atrazine in groundwater is widespread as indicated by the United States Geological Survey's National Water-Quality Assessment Program, which indicates that atrazine is the most common pesticide detected in streams and groundwater (Figure 3) (Gilliom et al., 2006). As a precaution the United States Environmental Protection Agency has set the maximum contaminant level to 3 µg L^{-1} for drinking water and 12 – 38 µg L^{-1} for aquatic environments.[1]

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[1] From the Envrionmental Protection Agency's websites, http://www.epa.gov/safewater/contaminants/dw_contamfs/atrazine.html and http://www.epa.gov/oppsrrd1/reregistration/atrazine/atrazine_update.html, accessed 30 April 2009.

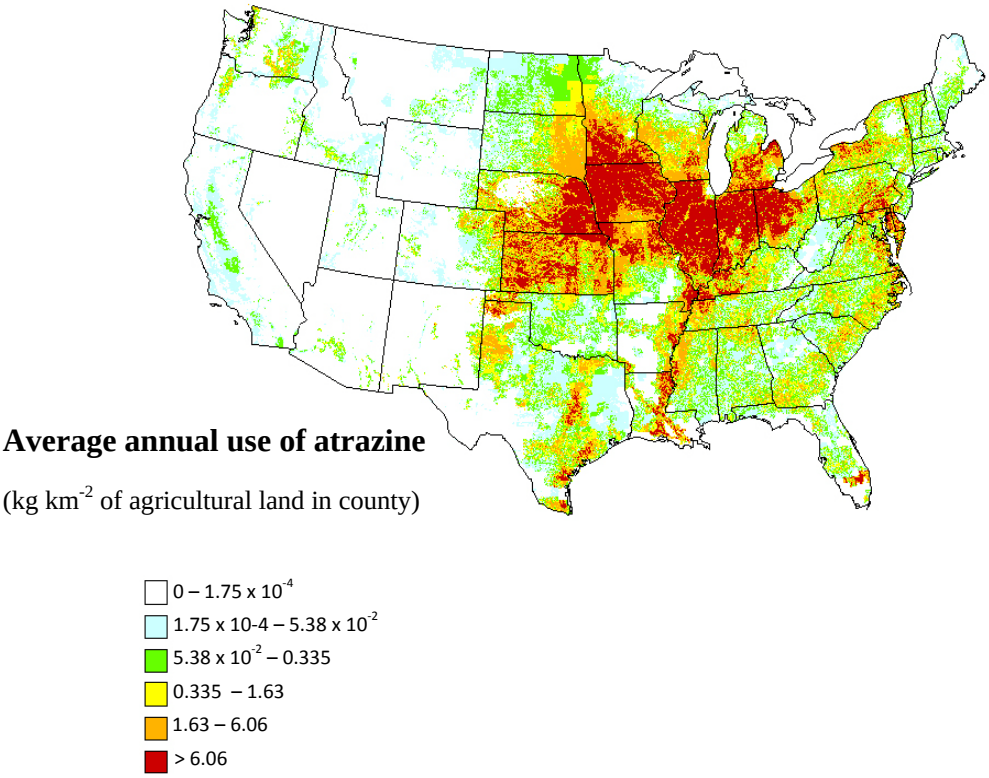

Figure 2. Estimated annual agricultural use of atrazine in 2002.[2]

The World Health Organization has set an atrazine concentration limit of 2 µg L^{-1} for drinking water (World Health Organization, 2006), and in 2003 the European Union banned the use of atrazine (Sass and Colangelo, 2006).

The health concerns associated with atrazine affect both humans and wildlife. Among human populations there is evidence of a possible link between atrazine exposure

[2] From the United States Geological Survey's National Water Quality Assessment (NAWQA) Program Pesticide National Synthesis Project - 2002 Pesticide Use Maps at http://water.usgs.gov/nawqa/pnsp/usage/maps/show_map.php?year=02&map=m1980, accessed 30 April 2009.

and cancers such as bladder, lung, non-Hodgkin's lymphoma, and multiple myeloma (DeRoos et al., 2003; Rusiecki et al., 2004). There is also support of a correlation between atrazine exposure and reduced semen levels in humans (Swan et al., 2003a; Swan et al., 2003b) and rodents (Kniewald et al., 2000).

Among wildlife the foremost concern is for amphibians. Amphibians are particularly at risk due to their permeable skin and their habitation within the aquatic environment during developmental stages (Hayes, 2006). For frogs, at exposures to low concentrations of atrazine (less than 0.1 µg L^{-1}), there is evidence for limb deformities, hermaphroditism, endocrine disruption and impaired immune system function (Hayes, 2006; Hayes, 2003; Kiesecker, 2002; Hayes, 2002). The adverse health effects of atrazine could also be intensified by simultaneous exposure to multiple pesticides which has been suggested to compound the effects for humans and wildlife (DeRoos et al., 2003; Hayes et al., 2006). But because laboratory experiments often isolate atrazine and fail to replicate the natural environment where atrazine is frequently found in water systems together with other pesticides (Gilliom et al., 2006), the effects are not well understood.

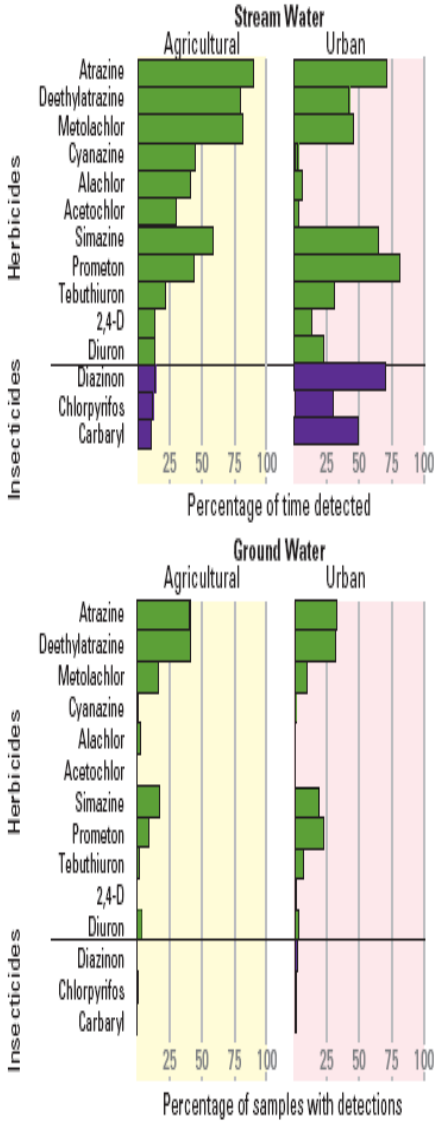

Figure 3. Frequently detected pesticide compounds from (Gilliom et al., 2006).

Once in the environment, the half-life of atrazine can vary between days to years depending on conditions. The average field half-life is about 60 days (Vencill, 2002) while the half-life in the saturated zone has been estimated to be as high as 3470 days (Levy and Chesters, 1995). The degradation of atrazine (Figure 4) is typically by way of dehalogenation or dealkylation and is controlled by a variety of environmental conditions such as soil type, organic matter content, pH, amount of light, water content, and biologic activity. Although both degradation pathways are possible by biotic and abiotic means, dehalogenation is commonly thought to be associated with abiotic processes and dealkylation to biotic processes. The further degradation of atrazine, including ring cleavage, is also possible by way of microbial action (Mandelbaum et al., 1995).

The dehalogenation of atrazine proceeds by removal of the chlorine by hydrolysis to produce the degradation product hydroxyatrazine (HA). The rate of atrazine hydrolysis is increased at high and low pH conditions and is catalyzed by the adsorption to soil or organic matter (Armstrong et al., 1967). The production of hydroxyatrazine can also be accomplished biologically (Mandelbaum et al., 1993; Radosevich et al., 1995) or by photolysis (Prosen and Zupancic-Kralj, 2005).

The dealkylation of atrazine is controlled by the microbial removal of the alkyl side chains by oxidation to produce deethylatrazine (DEA) or deisopropylatrazine (DIA). Conditions favorable for this degradation pathway include an oxidizing environment, increased moisture and increased temperature. Within the saturated zone microbial activity is diminished and the rate of atrazine degradation decreases (Blume et al., 2004). Further degradation products, to compounds such as didealkylhydroxyatrazine (DDHA)

and beyond, will not be considered in this study due to limitations of the laboratory procedure.

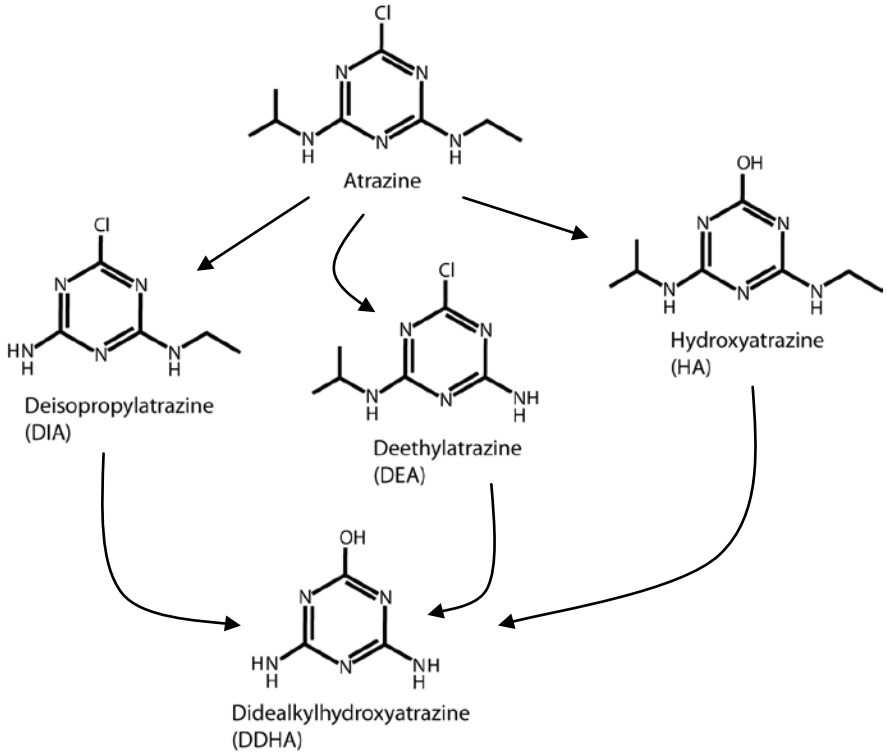

Figure 4. Degradation pathways for atrazine. Further degradation of DDHA is possible but not considered for this study.

Deethylatrazine to atrazine ratio

The degradation products of atrazine possess characteristics different from their parent compound, which may affect their mobility in the environment. HA is the least mobile due to its affinity for adsorption to clay minerals and organic matter; consequently, it is not regularly found in groundwater and was not included in this study.

DIA is less common than DEA or atrazine, and its lack of mobility could be attributed to several factors, including slower reaction rates for deisopropylation than deethylation, DIA's higher partitioning coefficient to organic matter (suggesting that it is bound), or microbial preference to produce less DIA or degrade it faster than DEA (Adams and Thurman, 1991; Blanchard and Donald, 1997; Kruger et al., 1996; Widmer and Spalding, 1995). DEA has the lowest sorption coefficients and highest solubility, so it is expected to have the highest mobility of the compounds considered. Therefore the hierarchy of mobility in groundwater is accepted to be DEA > Atrazine > DIA > HA (Kruger et al., 1996; Blanchard and Donald, 1997; Widmer and Spalding, 1995). Based on this mobility difference, the DEA to atrazine ratio (DAR) could be indicative of the pathway of atrazine contamination as being diffuse flow through the soil or discrete transport by preferential flow paths (Adams and Thurman, 1991). The DAR as defined by Adams and Thurman (1991) is

$$DAR = \frac{[DEA]}{[Atrazine]}$$, where the brackets represent concentration in mol L^{-1}.

A high DAR would suggest that the atrazine has been in the soil environment for ample time to produce a large amount of DEA. As the atrazine travels through the soil column and vadose zone it should have its maximum exposure to proper degradation conditions, such as high microbial activity, which would contribute to DEA production. Once in the saturated zone degradation to DEA essentially stops, so a low DAR would suggest that the atrazine was transported directly to the phreatic zone before degradation to DEA could proceed (Adams and Thurman, 1991). Presumably by preferential flow that by-passes surface soil and precludes degradation of atrazine.

Field site

The location chosen for this project includes portions of the Goodwater Creek and Young's Creek watersheds located in central Missouri. More specifically, the project at a field scale examines an individual 0.36 km^2 (36 ha) field (ARS Field 1) located just northeast of Centralia, Missouri. The field crop rotation alternates between production of corn and soybeans with corn production in even years and soybeans in odd years. The selected field has been operated by the United States Department of Agriculture – Agricultural Research Services (USDA-ARS) as part of the Midwest Management Systems Evaluation Area (MSEA). The MSEA project is a long term study designed to observe runoff and infiltration characteristics of pesticides. The ARS Field 1 has been closely monitored for pesticides since 1991 with less accurate pesticide usage information dating back several more decades. The surface hydrology of the field has been monitored by the USDA-ARS since 1991. The field has also been equipped since 1991 with five groundwater observation well nests. Each well nest consists of five observation wells varying in depth from 3m to the surface of the bedrock at about 15m.

The field site is typical of the Central Claypan Region of Missouri and Illinois. From the surface to about 3 m depth are Wisconsin and Illinoian aged loess and soils derived from the loess containing, at about 0.33 m of depth, an argillic horizon from the Wisconsin stage of glaciation (70 – 10 ka). Below this loess lies about 12 m-15 m of Pleistocene glacial drift that is pre-Illinoian (1.8 Ma – 300 ka) and is likely the McCredie or Moberly formation as described by Rovey and Kean (1996) and discussed further in

the methods section. The till is mostly gray, silty clay with layers and lenses of coarser material of sand and gravel. The bedrock below the field site, as described from drill core analysis from the observation wells within the field site, is gray clay and weathered shale likely of the lower Pennsylvanian aged Cheltenham Formation. The exact thickness of the Pennsylvanian section is unknown but has been estimated to be between 6 and 7.6 m (Unklesbay, 1952). Below the Pennsylvanian section is the Burlington Formation, a limestone of Mississippian age.

The freshwater aquifer of interest consists of the glacial drift and lower portions of the loess. The aquifer is semi-confined with the claypan above and the low permeability clay, shale and limestone bedrock below. Glacial till generally has poor permeability; however, slug tests of the location have shown greater hydraulic conductivity than lab scale tests suggesting the till is well fractured (Blanchard and Donald, 1997). Both the claypan and till show seasonal variation in hydraulic conductivity with a substantial increase during the dryer seasons caused by increased fracturing and fracture size. Although conditions favor runoff, previous investigations have shown atrazine concentrations in the deep observation wells adequate for this study.

Groundwater modeling

The theoretical portion of the study is a series of computer based groundwater flow models of the study area. The purpose of the model was to determine the direction

and magnitude of groundwater flow for the region, and to make predictions of the extent of atrazine transport within the aquifer. The models only consider the saturated zone. The first model is a general groundwater flow model of the area of interest at a regional scale of about 65 km^2 using the software package Groundwater Modeling System 6.0 using the MODFLOW package. Using the hydraulic head values generated by the regional model, a field scale groundwater flow model was produced focusing on a 0.36 km^2 field. The resulting model was repeated, including atrazine as a solute, to represent the transport of atrazine controlled by advection and dispersion.

Purpose

The purpose of this study is to investigate the subsurface transport of atrazine through a freshwater glacial till aquifer using a coupled field and theoretical approach. Previous studies have indicated the presence of atrazine in this aquifer despite the historical belief that the claypan protects the groundwater from atrazine contamination by inducing runoff. This study investigated not only the presence and quantity of atrazine in the subsurface but also used numerical groundwater modeling techniques to predict atrazine distribution. The main focus of the project was to construct a series of groundwater models to predict the direction and magnitude of groundwater flow and to simulate the transport of atrazine through the aquifer in order to understand observed concentrations of atrazine in the field study area. The initial groundwater flow model

was created at a regional scale using the hydrogeolgic boundaries present in the area. The regional model was necessary to determine the characteristics of the aquifer at a large scale. From the hydraulic head values generated by the regional model, the boundary conditions for a field scale flow model were developed. The smaller scale groundwater flow model ultimately incorporated solute transport equations to predict the distribution of atrazine throughout the aquifer. These model results were then verified by comparison to the actual atrazine distribution within the aquifer as determined by analyzing groundwater samples of the aquifer in the lab for the presence and quantity of atrazine and select atrazine degradation products using gas chromatography-mass spectrometry (GC-MS). The transport model allows for prediction of the spatial and temporal changes of atrazine concentrations within the aquifer. They also were used to estimate atrazine accumulations in the field study area in the future.

Chapter 2 - Methods

Field work

The field area chosen for this study is located in central Missouri north of the town of Centralia in northeastern Boone County and western Audrain County (Figure 5; Figure 6). Positioned at Sec 2 T51N R11W, the area of the ARS Field 1 is 0.36 km^2 (36 ha) and is representative of the Central Claypan Region of Missouri and Illinois. The field is currently operated by the United States Department of Agriculture – Agricultural Research Services (USDA-ARS) as part of the Midwest Management Systems Evaluation Area (MSEA) and has been since 1991. The field has been used for corn and soybean production, which are rotated annually (Table 1). Atrazine is applied only for the corn rotation with a distribution of 224 kg km^{-2} (2.24 kg ha^{-1}) (Table 1) (Lerch et al., 2005). Since 2004 the field has been operated using a precision management system; by dividing the field into several zones of variable crop

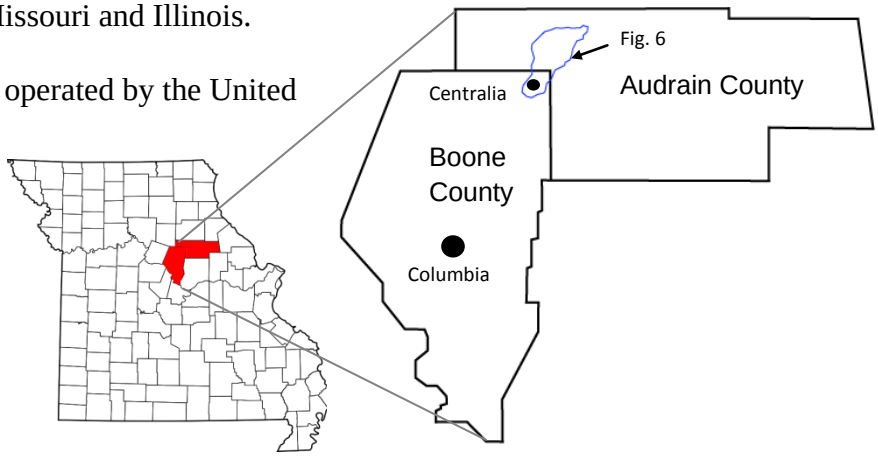

Figure 5. Location of the study area.

production, productivity is increased while protecting soil and water resources (Figure 7). The northern portion of the field, zone 1, is no longer planted with corn so that area does not receive atrazine (Table 1) (Kitchen et al., 2005). The western boundary of the field area is a small, intermittent stream flowing north to Goodwater Creek. The eastern edge of the field is approximately a topographic high separating the Goodwater Creek watershed to the west and the Young's Creek watershed to the east. The northern boundary is the property line and the southern boundary is Mockabee Road. The topography of the field is minimal with an elevation of about 265 m in the southeast corner of the field and sloping northwest to an elevation of about 259 m near the stream on the western boundary. Through the middle of the field there is also a slight topographic low from a small drainage trending north and exiting the field in the northeast corner along the northern boundary (Figure 7).

ARS Field 1 is equipped with five groundwater observation well nests constructed in 1991 and 1992 (Figure 7; Table 2). Each well nest consists of five observation wells within about a 25 m^2 area (Blanchard and Donald, 1997). The wells are constructed from 5.08 cm inner diameter polyvinylchloride (PVC) pipe with a sand pack backfill to 30 cm above the well screen and backfilled with bentonite and cement to the surface (Blanchard and Donald, 1997). The wells range from about 3.20 to 16.37 m depth with the deepest well of each nest drilled to bedrock and the other wells screened at shallower intervals representing zones of observed changes in lithology, color, or fractures during drilling (Blanchard and Donald, 1997; Lerch et al., 2005). Deep wells are fitted with 1.2 m long slotted PVC screens and the shallowest well of each nest has a 0.6 m long slotted PVC screen.

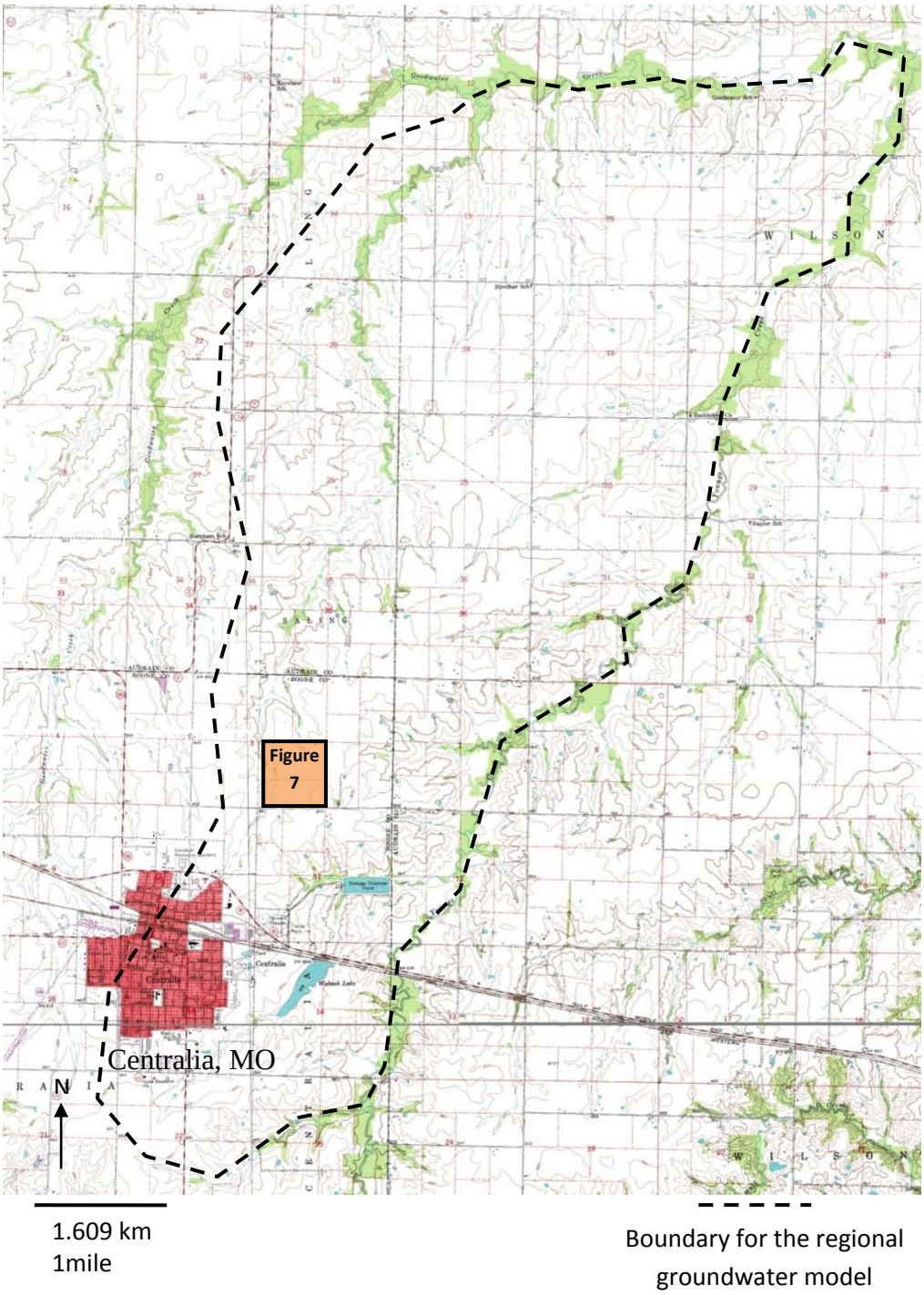

Figure 6. Map of the study area adapted from the 7.5' USGS topographic maps for Centralia, Centralia NE, Rowena, and Tulip, MO. The location of the study field is represented by the box called "Figure 7."

Table 1. Historical use of ARS Field 1 from Lerch et al., 2005 and Kitchen et al. 2005.

Management of the Missouri claypan soil study field	
Time Period	Management Practices
1991-2003	• Uniform management (i.e., no variable-rate management). • Mulch tillage, typically 1 disc and 1 or 2 field cultivation passes in spring prior to planting. • Corn - odd years Soybean - even years - (grain sorghum replaced corn in 1995 because persistent spring rains delayed planting) • Atrazine application 2.24 kg ha^{-1} - Odd years only
2004 - Present	• Precision agriculture system • No tillage • Management zone 1 (Figure 6) - Winterwheat – odd years - Soybean – even years • Management zone 2 (Figure 6) - Corn – odd years - Soybean – even years • Atrazine application 2.24 kg ha^{-1} - Zone 2 - Odd years only

Figure 7. Satellite image, shot 17 August 2003 (image by Digital Globe accessed 30 April 2009 through the software Google Earth), of the study field with the locations of well nests A-E and crop management zones 1

Each well is equipped with a manual pump for sampling consisting of a narrow plastic tube, fitted with a ball check valve and extending to the depth of the well. A groundwater sample was collected from each well in the fall of 2007 and 2008 and spring of 2008. The sampling dates were 30 October through 2 November 2007, 15 April

Table 2. The groundwater observation wells of ARS Field 1.

Well Nest	Well	Depth (m)	Screened Interval (m)
A	1A	15.09	13.89 - 15.09
	2A	10.85	9.65 - 10.85
	3A	7.77	6.57 - 7.77
	4A	6.22	5.018 - 6.22
	5A	3.26	2.66 - 3.26
B	1B	16.15	14.95 - 16.15
	2B	11.46	10.26 - 11.46
	3B	7.77	6.57 - 7.77
	4B	6.31	5.11 - 6.31
	5B	3.23	2.63 - 3.23
C	1C	16.37	15.17 - 16.37
	2C	12.50	11.30 - 12.50
	3C	10.36	9.16 - 10.36
	4C	8.32	7.12 - 8.32
	5C	4.15	3.55 - 4.15
D	1D	12.47	11.27 - 12.47
	2D	10.88	9.68 - 10.88
	3D	9.45	8.25 - 9.45
	4D	6.98	5.78 - 6.98
	5D	3.20	2.60 - 3.20
E	1E	11.58	10.38 - 11.58
	2E	10.42	9.22 - 10.42
	3E	8.90	7.70 - 8.90
	4E	7.38	6.18 - 7.38
	5E	4.07	3.47 - 4.07

through 17 April 2008, and 21 October through 24 October 2008. Before a sample was taken, the well was purged of three times the initial volume of water within the well to ensure an uncontaminated sample from the aquifer and not from within the well bore or immediately surrounding the well. Low permeability often necessitated several days of pumping from some of the wells to produce three volumes of water before a sample could be taken.

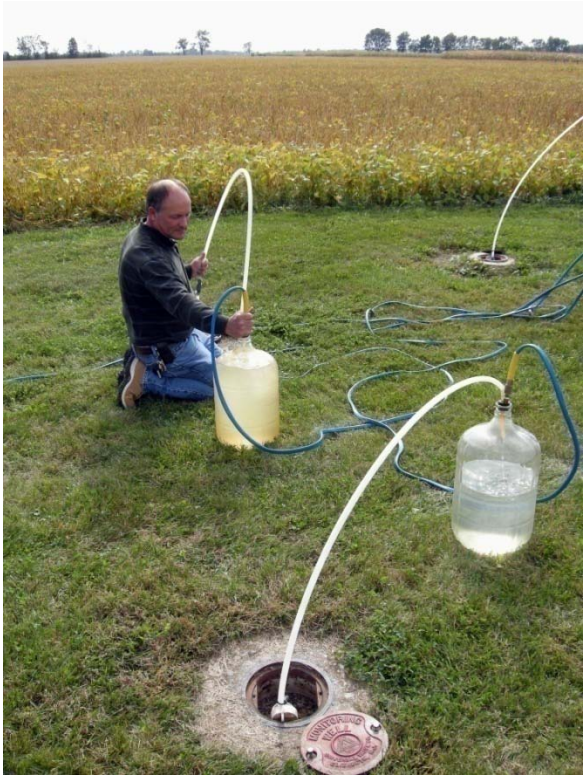

Figure 8. Mark Olson, a USDA-ARS hydrologic technician, purging a well at D nest.

Initial pumping was expedited by means of a truck-mounted vacuum system and final pumping was performed by manual bailing of the well (Figure 8). After removing 3 volumes of water, the samples were taken from the bottom of each well. The samples were pumped directly into opaque 500 ml Nalgene jars until full and logged. A field spike, field blank and a duplicate sample were also taken to aid in the laboratory analysis. The field spike was a sample of water with a herbicide standard (50 µg liter $^{-1}$) added. The field blank was a sample jar of water opened while samples were taken to collect any ambient contaminant. A duplicate sample was taken to assure reproducibility. After returning from the field site, the water samples were kept chilled until analysis.

Laboratory analysis

Laboratory analysis was performed at the USDA-ARS Cropping Systems and Water Quality Research Unit **(**CSWQRU) - Water Quality Laboratory located in the University of Missouri Agricultural Engineering building. The groundwater samples were analyzed for atrazine and atrazine metabolites using gas chromatography-mass spectrometry (GC/MS). Before a sample could be analyzed by GC/MS, the herbicides were separated from other substances in the water that may interfere with the analysis. The herbicides were removed from the sample water using C_{18} solid phase extraction (SPE) for the atrazine, DEA, DIA, metolachlor, and simazine. SPE is accomplished by passing the sample through a cartridge in which $C_{18}H_{37}$ hydrocarbon chains are bound to a silica backbone (Figure 9). SPE cartridges are essentially crude liquid chromatography columns to which non-polar molecules will preferentially bind while allowing polar contaminants to pass through it. Thus, atrazine and its metabolites will bind to the SPE column while polar organic and inorganic constituents will remain in the aqueous phase. The concentrated herbicide can then be eluted with ethyl acetate from the SPE cartridge

Figure 9. Varian Inc. Bond Elut C18 SPE cartridge.

for GC/MS analysis. The SPE cartridges used were 500 mg C_{18} Bond Elut LRC from Varian, Inc. (Figure 9). The cartridge consists of a plastic tube containing a non-polar medium of silica bonded to C_{18} alkyl chains. Each cartridge is used only once and then discarded. The SPE process begins by conditioning the SPE cartridges using a series of solvents allowing the C_{18} to separate from the silica. The cartridges were loaded onto the SPE vacuum manifold (Figure 10). While pulling a vacuum (7.62 cm Hg), 8 ml of ethyl acetate was passed through each cartridge. The medium cannot be allowed to dry between solvents, so the valve to each cartridge was shut with a small amount of solvent visible just above the media bed. Next, 8 ml of methanol was passed through the cartridge, followed by 8 ml of distilled, deionized H_2O. After these steps the cartridges are conditioned and ready for use. Following setup of the SPE apparatus (Figure 10), the groundwater samples were prepared for extraction. Each sample was initially filtered to remove any large particles using a 0.45 μm nylon filter. Subsequently, 200 ml of each groundwater sample was measured into clean containers and 1 ml of 100 μg L^{-1} tertbutylazine was added to each sample as a reference for recovery

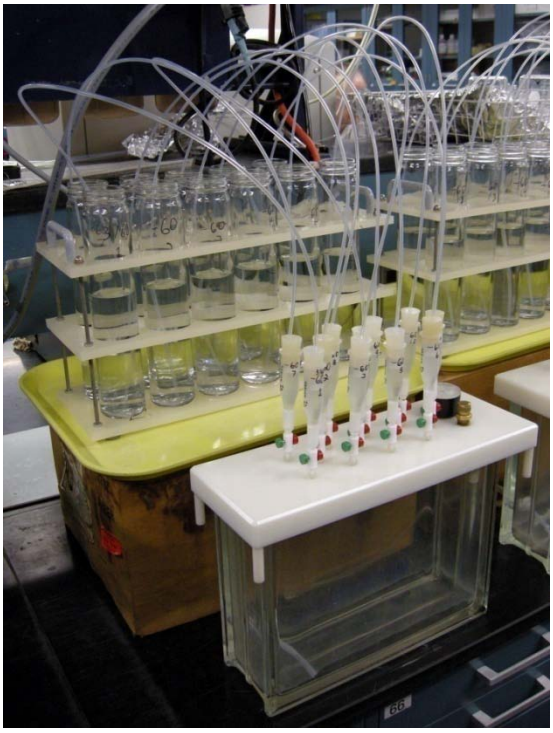

Figure 10. SPE system setup including the vacuum chamber and manifold, with SPE cartridges, in the foreground and samples in the background.

assessment. Tertbutylazine was used because of its similar structure to atrazine and it is not used as a pesticide in the United States. The sample containers were then connected to the SPE cartridges using Teflon tubing with plastic adaptors. The vacuum was increased to 20.32 cm Hg, the valves were opened, and the samples were passed through the cartridges. Just before the entire sample was through, the sides of the sample container were rinsed by adding 10ml of deionized water while rotating the sample container to allow the water to rinse the sides of the container. After all the liquids had passed through the container, the tubing and adapters were removed and the cartridges were allowed to dry for 2 hours under vacuum.

The final preparation step before the GC/MS analysis was to elute the herbicides from the cartridges. To do this, a rack of 5 ml test tubes was arranged inside the vacuum chamber with a test tube below each cartridge. With the valves closed, 2.2 ml of ethyl acetate was added to each cartridge and allowed to thoroughly penetrate the C_{18} silica phase for about 15 seconds. The vacuum was set to 5.08 cm Hg and the valves were opened, allowing the absorbed material to be released from the sorbent, as the ethyl acetate passed through, and deposited in the test tube. The test tubes were then removed from the SPE apparatus and the samples were then concentrated to ~0.20 mL under a stream of nitrogen at room temperature. Next, 0.10 ml of phenanthrene-d_{10} was added to each sample as a known mass to calculate the volume of the final solution. Finally an aliquot of each sample was transferred to a GC vial. The vials were stored in the freezer until analysis.

Gas Chromatography-Mass Spectrometry

The groundwater samples were analyzed for atrazine and atrazine degradates using gas chromatography-mass spectrometry (GC/MS) by Joe Absheer at the USDA-ARS Cropping Systems and Water Quality Research Unit (CSWQRU) - Water Quality Laboratory located in the University of Missouri Agricultural Engineering building. The gas chromatograph used was a Varian, Inc. model Star 3400 CX equipped with a Varian 8200 autosampler (Figure 11). The capillary column was from J & W Scientific, model DB-1MS. The column used was 12 m in length with an inside diameter of 0.2 mm, 0.33µm film and 100% dimethylopolysiloxane phase. A sample size of 1 µL was loaded into the GC with an injector temperature of 250ºC. The temperature program began with an initial column temperature of 70ºC which increased to 123ºC at 50ºC min^{-1}, then increased to 179ºC at 4.0ºC min^{-1}, and finally up to 250ºC at 50ºC min^{-1}. The mass spectrometer used was a Varian, Inc. model Saturn 2000. This instrument uses an ion trap detector with electron ionization and was set for selective ion storage of 120 – 250 m/z. The GC/MS analysis used phenanthrene-d_{10} as an internal standard and tertbutylazine as the surrogate ion used for recovery calculations. The detection limits are atrazine = 0.0025 µg L^{-1}, DEA = 0.0037 µg L^{-1} and DIA = 0.019 µg L^{-1}.

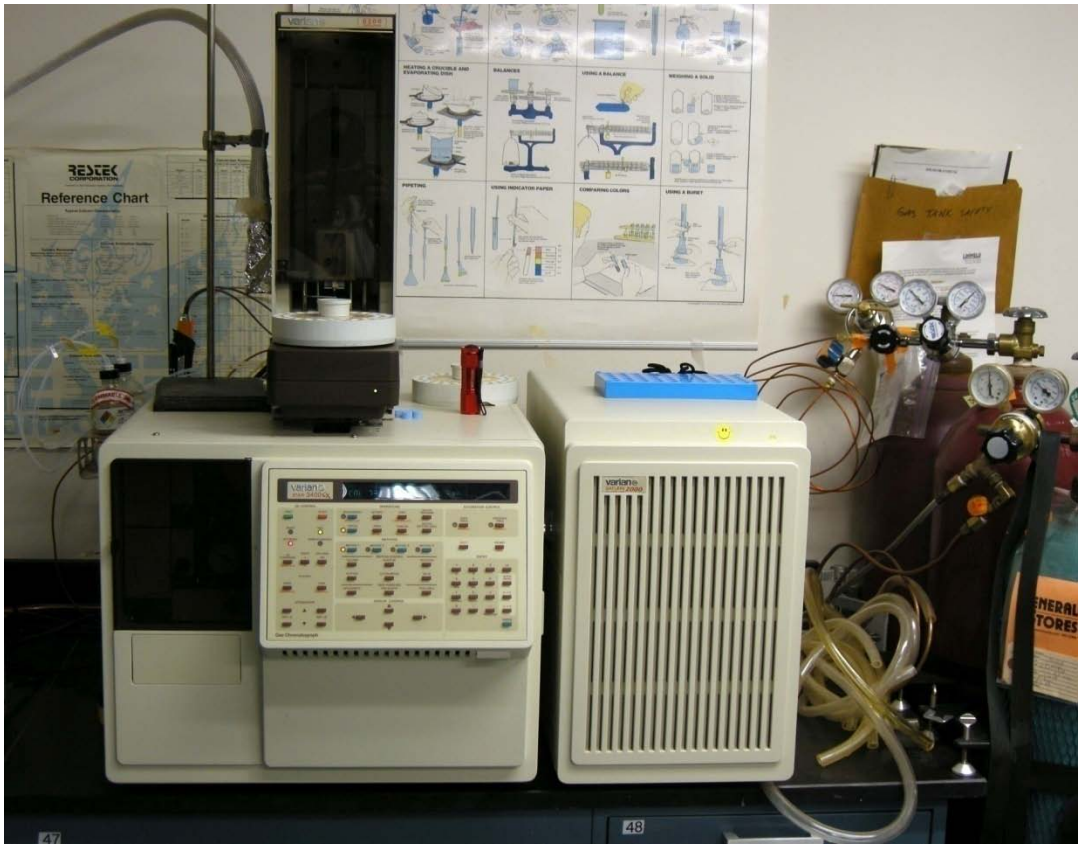

Figure 11. The Varian, Inc. GC/MS instrument used for this study.

Groundwater modeling

The computer based groundwater modeling portion of the project consisted of three parts. Initially a regional scale model, about 65 km^2 (6500 ha), in area was created to determine estimated hydraulic head values and three dimensional groundwater flow direction. The values generated with the regional model were then applied to a more focused study at a field scale of about 0.36 km^2 (36 ha). The final model added a solute

transport component to the field scale model in an attempt to estimate the spatial and temporal distribution of atrazine in the aquifer below the study field.

The software used in this study was the United States Geological Survey's MODFLOW-2000 operated with the graphical user interface Groundwater Modeling System 6.0 (GMS 6.0). MODFLOW is a three dimensional numerical modeling program, which operates by approximating the governing groundwater flow equation by finite difference method using a block centered grid as described by Harbaugh et al. (2000).

The model construction method used for this study was a "conceptual model approach," which consisted of defining the boundary area and geologic parameters before fitting the three dimensional numerical grid to the area. This method employs the Map Module of GMS 6.0 to orient the components using a topographic map as a base. The base map was created by suturing the USGS 7.5' topographic quadrangle maps Centralia, Centralia NE, Rowena, and Tulip, MO to accommodate the large study area.

Regional model

The area included in the regional groundwater flow model is defined by hydrogeologic boundaries with Young's Creek to the east, Goodwater Creek to the north, and to the south and west by a topographic high within the Goodwater Creek groundwater basin (Figure 12). Ideally for this type of model, the entire study area

should lie within a single basin; however, the head values generated from this regional model were to be used in a smaller scale model, of ARS Field 1, whose eastern boundary is the divide between Young's Creek and Goodwater Creek. By using an area straddling the two watersheds, the area to be used for the ARS Field 1 model could be oriented in the interior portion of the grid where the results would be most accurate because the area would be isolated from boundary effects. The boundaries represented by Young's Creek and Goodwater Creek were assigned Dirichlet conditions (for which the head is specified and held constant). The specified head along these boundaries was defined by assigning a value at the point where a perennial stream representing the boundary crosses an elevation contour line. For the boundaries represented by a topographic high, a no-flow boundary was needed; therefore, Neumann conditions were assigned to these boundaries by specifying the flux to be zero.

The grid used for the regional model was created based on a rectangular frame fit to the coverage area defined by the boundaries (Figure 13). Before interpolating the grid to the boundary polygon, the grid dimensions were 75 cells along the x axis, 100 cells along the y axis, and 3 cells along the z axis. This grid spacing proved to be adequately coarse to allow large hydraulic conductivity values and yet maintain fine model resolution. The three vertical cells were scaled to represent three stratigraphic layers. Only the uppermost layer (Layer 1) representing the loess, glacial till and the extent of the aquifer was desired, but the model proved to be numerically unstable when only this layer was considered because the layer at a thickness of 16.8 m was too thin to be represented over such a large area. To correct for this, two additional layers were included in the model.

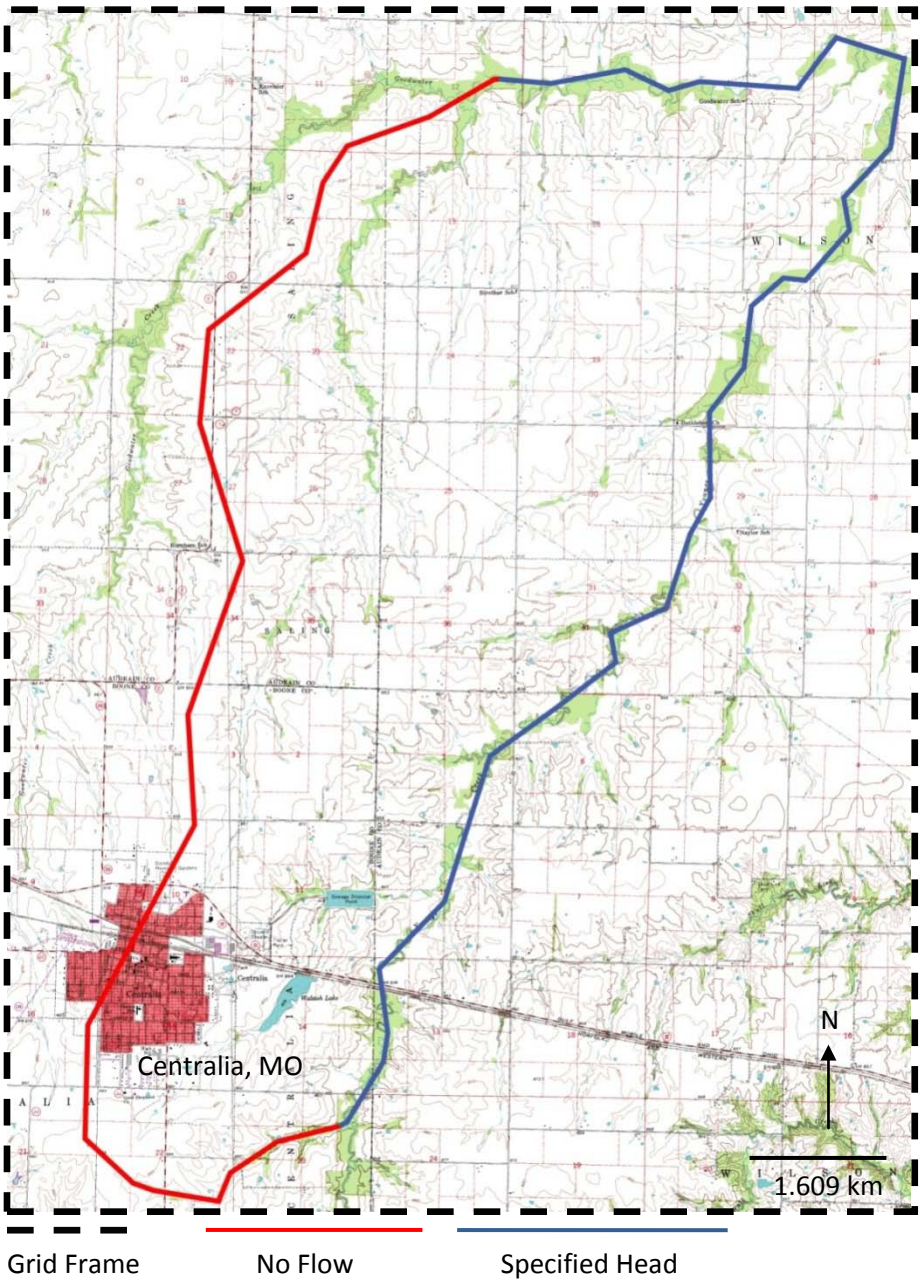

Figure 12. A map of the boundaries used for the regional groundwater model.

Layer 2 represents the first unit of bedrock, the lower Pennsylvanian aged formations. The upper contact of the bedrock was estimated from bedrock structure contour maps (Hesemann, 1979) but was adjusted to accommodate the 16.8 m thickness of Layer 1 at the smaller scale field site. Neither the thickness of the Pennsylvanian bedrock nor the exact elevation of the top of the Burlington Formation, represented by Layer 3, were known in this area. The top of the Pennsylvanian bedrock is difficult to distinguish from the lower till since both consist of weathered shales, sands and gravel. Layer 2 was given a thickness of 7.6 m from estimates of the thickness of this formation in Northern Boone County (Unklesbay, 1952). Layer 3, the Burlington Limestone, was given a maximum thickness of 52 m by setting the bottom elevation to 197 m. The extent of the Burlington, estimated from drill logs from nearby wells (Unklesbay 1952), could be variable but a flat bottom was chosen for numerical stability.

The surface topography was interpolated to the grid from a scatter point set constructed from the topographic base map. The scatter point set representing the top elevations of Layer 2 was created from a portion of a bedrock map available for this area (Hesemann, 1979). The top elevations of Layer 3 were estimated by creating a scatter point set offset 7.6 m below the top elevations of Layer 2. The thicknesses of Layers 1 and 2 were maintained by using the check simulation option of GMS 6.0 with the minimum cell thickness set to 16.8 m for Layer 1 and 7.6 m for Layer 2.

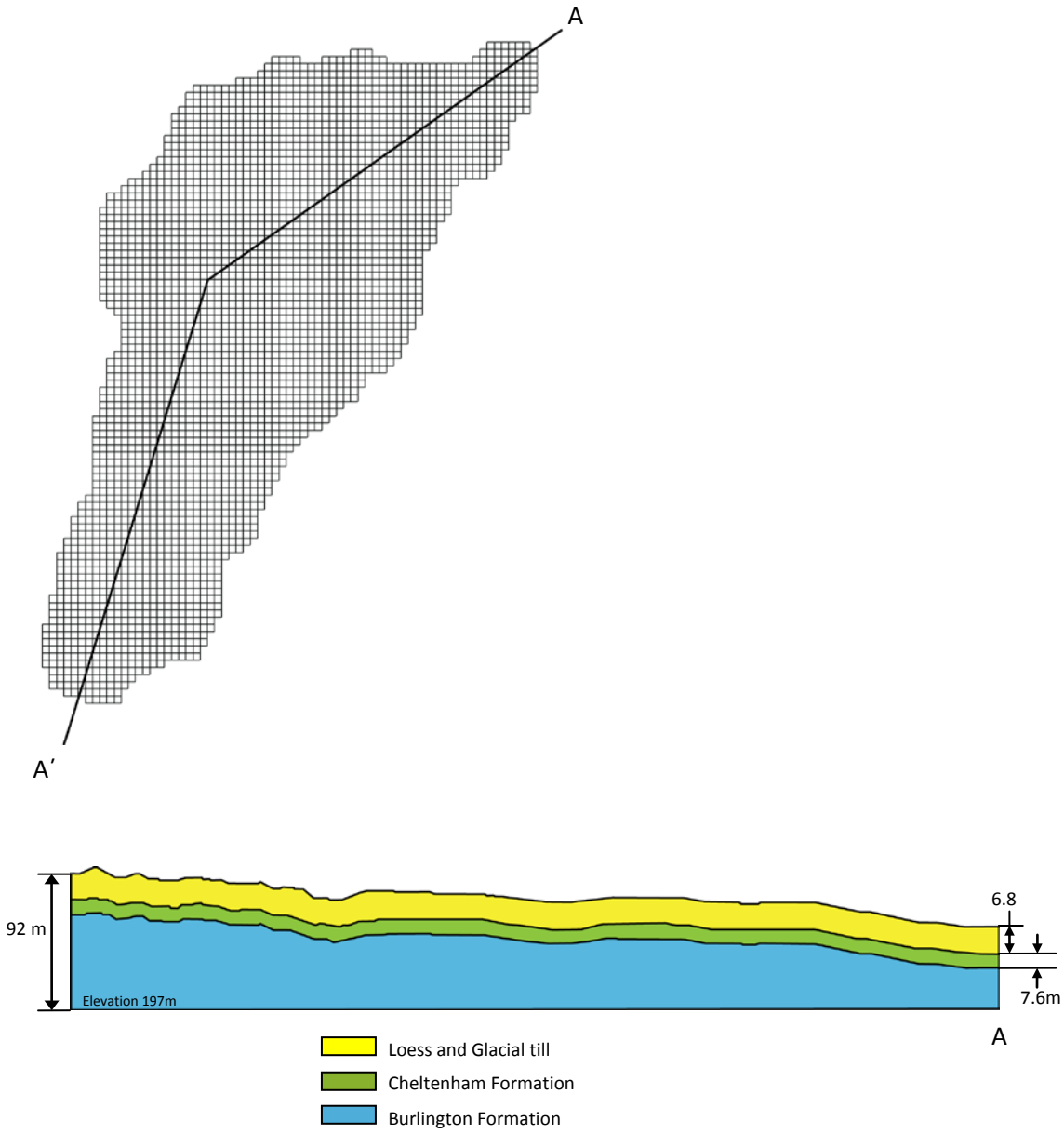

Figure 13. The grid used for the regional flow model with cross section A - A′ showing the layers used in the model.

The regional model was set to be steady-state and used the layer property flow (LPF) package with the pre-conditioned conjugate gradient (PCG2) solver. Other parameters applied to the model include values of hydraulic conductivity and recharge (Table 3). The hydraulic conductivity (K) values used were isotropic. For Layer 1 a value of 4.5×10^{-6} m s^{-1} was used. This value is the median value for glacial till, measured by slug tests, reported by Blanchard and Donald (1997). The K value used for Layer 2 was 2×10^{-9} m s^{-1}, a representative K value for clay and shale (SCHWARTZ and ZHANG, 2003). Layer 3 was given anisotropic values because they were available. Horizontal hydraulic conductivity (K_h) assigned for the Burlington Limestone was 3.2×10^{-9} m s^{-1} and vertical hydraulic conductivity (K_v) was assigned 2.0×10^{-9} m s^{-1} (Hoag, 1957). Groundwater recharge for the regional model was assigned a value of 0.3 cm $year^{-1}$, which is at least one order of magnitude less than the realistic value for the area, but a higher value creates flooding or numerical instability.

Table 3. The parameters used for the Regional groundwater model.

Regional Model Parameters		
Layer 1	Thickness = 16.8 m	
	K = 4.5×10^{-6} m s^{-1}	(Blanchard and Donald, 1997)
	Recharge = 0.3 cm yr^{-1}	
Layer 2	Thickness = 7.6 m	
	K = 2×10^{-9} m s^{-1}	(Schwartz and Zhang, 2003)
Layer 3	Thickness = 52 m	
	K_h = 3.2×10^{-9} m s^{-1}	(Hoag, 1957)
	K_y = 2.0×10^{-9} m s^{-1}	(Hoag, 1957)

Field Scale Model

Following construction of a regional groundwater flow model a steady-state field scale groundwater flow model was produced using the head values obtained from the regional simulation as boundary conditions. The boundaries of the model defined a slightly larger area than the field of interest to keep the result associated with the well nests in a more numerically stable portion of the grid (Figure 14). The three dimensional grid was given the dimensions of x = 40 cells, y = 60 cells and z =2 cells. All four boundaries were given Dirichlet boundary conditions with the values of head obtained from the regional model. The east boundary is approximately the divide separating the two watersheds used in the regional model. By using both watersheds, the regional groundwater flow is to the northeast, directed towards the confluence of the two streams. The divide between the two watersheds, as determined by a topographic high, is approximately located along the eastern boundary of ARS Field 1. To account for the divide a line parallel to the eastern boundary was created and was assigned specified head values 0.3048 m greater than those of the eastern boundary. This increase in head along the divide was chosen because it is larger than the head values of the eastern boundary and less than that of the western boundary as to not dramatically alter the head gradient obtained from the regional model. The influence of the simulated divide directed the groundwater flow in a slightly more northern direction, which is reasonable given the northern trending drainage at the surface within the ARS Field 1. The field has very little topography and thus topography was omitted from the model.

The groundwater flow model of ARS Field 1 consisted of two layers correlated to the stratigraphy, with the loess unit being Layer 1, the glacial drift being Layer 2 and the top of the bedrock assumed to be a no flow boundary at the base of Layer 2. Layer 1 was assigned a thickness of 3 m as determined by review of drill core analysis of the deepest well in each observation well nest. The thickness of the loess unit is consistent at all five well nests so no topography is needed for the contact between Layers 1 and 2.

Figure 14. Satellite image showing the boundary area of the model and the ARS Field 1. See Figure 6 for location.

The glacial drift unit was assigned a thickness of 12.19 m as determined by review of drill core analysis. The K values assigned to Layer 1 and Layer 2 were 5.0×10^{-7} m s^{-1} and 4.5×10^{-6} m s^{-1}, respectively (Blanchard and Donald, 1997). A groundwater recharge of 0.02 m yr^{-1} which represents an average value at the location was assigned (Table 4).

Table 4. The parameters used for the ARS Field 1 groundwater model.

ARS Field 1 Model Parameters		
Layer 1	Thickness = 3 m	
	K = 5.0×10^{-7} m s^{-1}	(Blanchard and Donald, 1997)
	Recharge = 0.02 m yr^{-1}	
Layer 2	Thickness = 12.19 m	
	K = 4.5×10^{-6} m s^{-1}	(Blanchard and Donald, 1997)

The heterogeneity of the glacial till could present difficulties for hydrologic modeling. The till contains many small layers and lenses of sand along with erratic cobbles and gravel. In addition the contact between the lower till and the weathered Pennsylvanian shales and clay is indistinct. The difficulties of characterizing the till are substantiated by a stratigraphic and hydrological discrepancy within the literature. Blanchard and Donald (1997) suggested there to be a paleosol in the lower portion of the drift with a K value two orders of magnitude less than the till. A detailed description of

the paleosol, or any differences in the two till units it separates, was not given. However, Hesemann (1979) also separated the till using a layer of similar depth to Blanchard and Donald's (1997) paleosol, although he described the layer as being sandy with a K value an order of magnitude greater than the till. A review of the drill core analysis logs of the observation wells revealed a layer of increased sand and gravel at about 10 m depth from the surface that could possibly be correlated across the field (Figure 15). The till below this layer has a greater sand content than the till above. The stratigraphy described in the drill logs was compared to the work of Rovey and Kean (1996) who attempted to correlate divisions within the till of this region (Figure 16). Based on their test sites nearest to this field location, the till units at this location could be a pairing of the Macon and Columbia members of the McCredie formation, Columbia and Fulton members of the McCredie formation, or the Fulton member of the McCredie formation and the Moberly formation. The descriptions of the till given by Rovey and Kean (1996) indicate that the Columbia member of the McCredie formation and the Moberly formation have a much coarser texture than the Macon and Fulton members of the McCredie formation. Rovey and Kean's (1996) nearest test site revealed the till to be the Macon and Columbia members determined by a textural change with no indication of

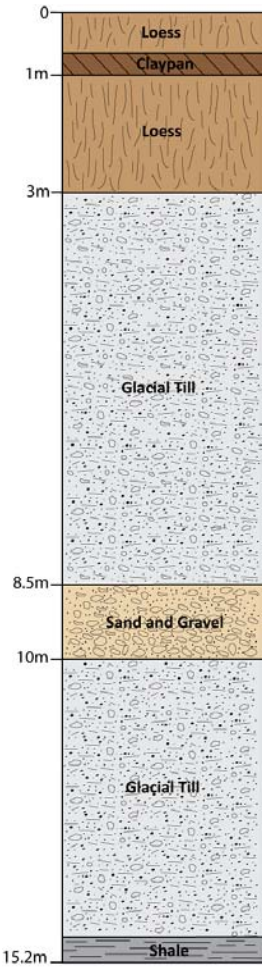

Figure 15. Typical stratigraphy of the field from the drill core log of well A1.

an intermediate layer such as a paleosol. Another nearby location shows no Macon member, and correlation of the drill logs by depth would suggest a Columbia and Fulton stratigraphy separated by a paleosol. The problem with this correlation is that the Columbia has a coarser texture than the Fulton member, an opposite arrangement of the core descriptions from the study field. A third option would be the Fulton member of the McCredie formation above the Moberly formation. The Moberly formation is also described as being coarser in texture than the Fulton member, and the two layers are separated by a paleosol. However, at two test sites further north the contact is described as being a layer of sand and gravel and not a paleosol. Rovey and Kean (1996) do not give a description of the paleosol beyond being a surface exposed to weathering by means other than an icesheet. The stratigraphic interpretations of Blanchard and Donald (1997) and Hesemann (1979) are likely both correct given the variability within the till over such a vast area. Even within ARS Field 1 the correlation of the sand and gravel layers is not complete. At well nest B the sand and gravel layer is absent. It is possible that the till is too irregular in composition for regional correlations and that the till is best described locally. One scenario is that the intermediate layer was produced by outwash or subglacial flow, which could produce areas of increased gravel and sand deposition with deposition of finer material between channels that could develop into a paleosol. Regardless, the areal extent of these

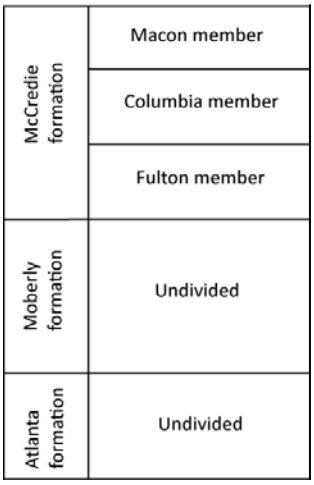

Figure 16. Pre-Illinoian till stratigraphy, north - central Missouri (Rovey and Kean, 1996).

variations within the till are unknown so for this study the till is represented by single layer and lithology.

Transport modeling

A transient mass transport model of atrazine and DEA was created using the program Modular 3-Dimensional Transport Multi-Species (MT3DMS) software. The program MT3DMS works in conjunction with MODFLOW, so the solutions generated from groundwater flow model were the base for the transport model. The program's governing partial differential equation is described by Zheng and Wang (1999). The model parameters are shown in Table 5.

Within the MT3DMS program the advection, dispersion, source/sink mixing, transport observation, and chemical reaction packages were activated. The primary mechanism for transport is advection and the solver used was the third order total-variation-diminishing (TVD) solution scheme implementing the Universal Limiter for Transient Interpolation Modeling of the Transport Equations (ULTIMATE) algorithm. The generalized conjugate gradient (GCG) solver package was set to Jacobi preconditioner. The dispersion package was assigned a longitudinal dispersivity of 0.06 m for the glacial till and 0.192 m for the loess (Mascioli et al., 2005; Schulze-Makuch, 2005).

Most of the transport models were set up to be transient to account for seasonal variations. The stress periods used grouped October through May and June through September to represent seasonal variations in groundwater recharge. The length of a stress period was total days within that period with time steps set to months. A small stress period was created for the first week of May of odd years to represent the application of atrazine. The maximum transport steps were set to 1000, the maximum allowed based on numerical stability criteria.

The concentrations of the solute were assigned using the source/sink package. The recharge of atrazine was set up to be a transient coverage on layer 1 to represent the fact that atrazine is not applied every year and only once per year when it is. Two atrazine recharge boundaries were established to represent the 2003 change in area of atrazine application. The first application coverage within the model represented the application of atrazine to the whole field from 1991 – 2001. The second application coverage represented zone 2, the southern portion of the field and the only area that has received atrazine since 2001. By switching to applying atrazine only to the southern portion of the field, the prediction can be made that the atrazine distribution would change from being an area wide distribution to being a plume emanating from zone 2. The concentration of the atrazine slug must be similar to values found at the surface of the saturated zone. A previous study by Ghidey et al. (1997), measured atrazine concentrations at the surface to be 1608 μg kg^{-1} three days after application; however, the atrazine still must be transported to the subsurface and through the vadose zone where it is most vulnerable to degradation. The concentration that reaches the saturated zone will be much less and potentially variable within the areal extent being considered. Several

simulations of varying initial concentration were run but the value of atrazine concentration measured at this location by Tindall and Vencill (1995)

(400 µg kg^{-1} at a 1 m depth, 30 days after application) produced reasonable results. This value could be conservative in that atrazine for their study was applied at a rate of only 1.4 kg ha^{-1}, is less than the 2.24 kg ha^{-1} normally applied to ARS Field 1. However, 400 µg kg^{-1} was measured above the saturated zone so there is the potential that the atrazine concentration in contact with the aquifer is lower.

Recharge for the aquifer was also set to be a transient coverage with recharge only occurring from October through May when evapotranspiration is diminished (Blevins et al., 1996). Recharge at this location has been estimated to be 32% of the precipitation (Blevins et al., 1996). Rainfall data[3] were compiled and 32% of the per day average was applied during each October through May stress period.

After completing the steady state transport model, the chemical reaction package was enabled. The two chemical reactions implemented were sorption and degradation. The sorption reaction used a linear Freundlich isotherm with distribution coefficients (K_d) of 1.98 ml g^{-1} for the loess and 2.58 ml g^{-1} for the till (Montgomery, 1997). The bulk densities, 1.57 g cm^{-3} for the loess and 1.85 g cm^{-3} for the till, were selected from

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[3] Rainfall data for 2008 are from the National Oceanic and Atmospheric Administration (NOAA) Record of Climatological Observations - Mexico and Columbia, MO stations, http://www.ncdc.noaa.gov/oa/mpp/freedata.html accessed 30 April 2009.
Rainfall data for 1991-2007 are from Teri Oster (personal communication) of the USDA-ARS.

measurements taken by Cammy Drost (personal communication), a graduate student at the University of Missouri's Agricultural Engineering Department, from a nearby location. The half life was assigned as the dissolved rate constant (λ_1) within the transport equation. Values of 12 days for the loess (Ghidey et al., 1997) and 1000 days for the till were first tested. The value of 1000 days for the half life was chosen as a conservative length compared to estimates > 3400 days within the saturated zone (Levy and Chesters, 1995). Some other variables required by the chemical reaction package include porosity, specific storage (Ss) and specific yield (Sy). The effective porosity of the loess is 9% (Blevins et al., 1996) and the effective porosity of the till has been estimated at 1% (Blanchard and Donald, 1997). Site specific values for Ss and Sy were not available so values for similar materials were used. Specific storage was determined from storativity (Hesemann, 1979) and set to 5.6×10^{-4} m^{-1} for the loess and 1×10^{-3} m^{-1} for the till (McKay et al., 1993). Specific yield was set to 18% for the loess and 6% for the till (Johnson et al., 1967).

Table 5. The parameters used for the atrazine transport model.

Atrazine Transport Model Parameters		
Layer 1	Thickness = 3 m	
	K = 5.0 x 10^{-7} m s^{-1}	(Blanchard and Donald, 1997)
	Recharge = 32% of monthly precipitation - Rainfall data are from the NOAA website http://www.ncdc.noaa.gov/oa/mpp/freedata.html, accessed 30 April, 2009 and Teri Oster (Personal Communication)	(Blevins et al., 1996;
	Half life = 12 days *Changed to 300 days for the final models	(Ghidey et al., 1997)
	Initial atrazine concentration = 400 µg kg^{-1}	(Tindall and Vencill 1995)
	Effective porosity = 9%	(Blevins et al., 1996)
	S_s = 5.6 x 10^{-4} m^{-1}	(Hesemann, 1979)
	S_y = 18%	(Johnson et al., 1967)
	K_d = 1.98 ml g^{-1}	(Montgomery 1997)
	Bulk density = 1.57 g cm^{-3}	(Cammy Drost, personal communication)
	Logitudinal dispersivity = 0.192 m	(Schulze – Makuch 2005)
Layer 2	Thickness = 12.19 m	
	K = 4.5 x 10^{-6} m s^{-1}	(Blanchard and Donald, 1997)
	Half life = 1000 days	
	Effective porosity = 1%	(Blanchard and Donald, 1997)
	S_s = 1 x 10^{-3} m^{-1}	(McKay et al., 1993)
	S_y = 1%	(Johnson et al., 1967)
	K_d = 2.58 ml g^{-1}	(Montgomery 1997)
	Bulk density = 1.85 g cm^{-3}	(Cammy Drost, personal communication)
	Logitudinal dispersivity = 0.06 m	(Mascioli et al., 2005)

Chapter 3 – Results and Discussion

Atrazine and metabolites in groundwater

The results of the groundwater sampling and laboratory analysis are shown in Tables 6, 7 and 8. Figures 17-19 and Appendix A show the atrazine, DEA and DIA concentration as a function of the depth of the wells. The atrazine, DEA and DIA concentrations are given in $\mu g\ L^{-1}$ and only values above the detection limits are shown. The depth to water is measured from the top of the well head before pumping the well. The wells that had slow recharge while purging the well, which may indicate a change in lithology, are also indicated. Wells C2 and E2 recharged too slowly in Spring 2008 to purge the well adequately to take a sample.

Atrazine is distributed throughout the aquifer with no concentrations found greater than the EPA's 3 $\mu g\ L^{-1}$ maximum concentration limit. The Fall 2007 data have the highest concentration, which is expected since it was a year with atrazine application. The Spring 2008 samples have the lowest concentrations possibly driven by recharge to the aquifer which diluted concentrations. The Fall 2008 samples have slightly higher concentrations, which could be from an increase in preferential flow paths from soil cracking during the summer. The higher concentrations are at the shallower depths but atrazine was also detected in the deepest wells. Some of the intermediate depths showed

unusually high concentrations, which could be representative of heterogeneity within the till capable of trapping atrazine. Evidence for this is the correlation between slow recharging wells and high concentrations. Any well with slow recharge during purging is shown in Tables 6, 7, and 8. Well nests A and B in particular, excluding the shallowest well, tend to have high solute concentration in wells with slow recharge. If a lens of finer grained material was present at that location, the conditions could be favorable to retain atrazine and the permeability would be reduced as indicated by slow recharge. Also of interest is the relatively high concentration of atrazine in the northern wells since no atrazine has been applied near these wells in several years. The atrazine is either residual, transported from the south, or a combination of these.

Deethylatrazine to atrazine ratio

From the concentration data shown in tables 3-5, the DEA to atrazine ratio (DAR) was calculated. The DAR could be indicative of the pathway of atrazine contamination as being preferential or diffuse recharge (Adams and Thurman, 1991). A high DAR would suggest that the atrazine has been in the soil environment for ample time to produce a large amount of DEA. As the atrazine travels through the soil column and vadose zone it should have its maximum exposure to proper degradation conditions, such as high microbial activity, which would contribute to DEA production. Once in the saturated zone degradation to DEA essentially stops, so a low DAR would suggest that

the atrazine was transported directly to the phreatic zone before degradation to DEA could proceed (Adams and Thurman, 1991) presumably by preferential flow that

Table 6. Results of the Fall 2007 groundwater samples. The wells marked "Slow" had slower recharge while purging the well.

Fall 2007 Well Sampling Results					
Well	Well Depth (m)	Depth to water (m)	Atrazine ($\mu g\ L^{-1}$)	DEA ($\mu g\ L^{-1}$)	DIA ($\mu g\ L^{-1}$)
A1	15.1	2.17	0.0250	BDL	BDL
A2	10.9	2.15	0.0596	0.0091	BDL
A3	7.8	2.15	0.0101	0.0042	BDL
A4	Slow 6.2	2.07	0.0586	BDL	BDL
A5	3.3	3.51	0.0692	0.0982	0.0855
B1	16.2	3.36	0.2040	0.0089	0.0967
B2	Slow 11.5	3.28	0.0155	0.0070	BDL
B3	Slow 7.8	1.79	0.5159	0.0079	BDL
B4	Slow 6.3	1.36	0.1315	0.0285	BDL
B5	3.2	1.71	1.6503	0.6007	0.2726
C1	16.4	3.74	0.3181	0.0070	0.0892
C2	Slow 12.5	3.33	0.1220	0.0879	BDL
C3	10.4	3.54	0.0257	0.0074	0.0985
C4	8.3	3.48	0.0131	0.0048	0.0666
C5	4.1	4.46	0.0912	0.1248	0.1237
D1	12.5	2.54	0.0723	0.0221	BDL
D2	Slow 10.9	2.35	0.0111	0.0099	BDL
D3	9.4	2.51	0.0113	0.0061	BDL
D4	7.0	2.43	0.8277	BDL	0.1302
D5	3.2	3.44	0.1357	0.0777	0.1127
E1	Slow 11.6	2.46	0.0264	0.0218	0.1231
E2	Slow 10.4	2.33	0.1882	0.0143	BDL
E3	8.9	2.62	0.0305	0.0118	BDL
E4	7.4	2.67	0.0665	0.0059	0.0762
E5	4.1	4.38	0.2283	0.2136	BDL

BDL = Below Detection Limit

Table 7. Results of the Spring 2008 groundwater samples. The wells marked with "Slow" had slower recharge while purging the well.

Spring 2008 Well Sampling Results					
Well	Well Depth (m)	Depth to water (m)	Atrazine ($\mu g\ L^{-1}$)	DEA ($\mu g\ L^{-1}$)	DIA ($\mu g\ L^{-1}$)
A1	15.1	0.61	0.0315	BDL	BDL
A2	10.9	0.59	0.0205	BDL	BDL
A3	7.8	0.56	0.0084	BDL	BDL
A4	Slow 6.2	0.61	0.0142	BDL	BDL
A5	3.3	0.08	0.0220	0.0072	BDL
B1	16.2	2.01	0.0111	BDL	BDL
B2	11.5	1.97	0.0228	BDL	BDL
B3	7.8	0.61	0.0292	0.0072	BDL
B4	Slow 6.3	0.94	0.0792	0.0066	BDL
B5	3.2	0.27	0.6434	0.1639	BDL
C1	16.4	1.97	0.0106	BDL	BDL
C2	Slow 12.5	1.84			
C3	10.4	1.55	0.0565	BDL	BDL
C4	8.3	1.48	0.0262	BDL	BDL
C5	4.1	1.58	0.0687	0.0616	BDL
D1	12.5	0.84	0.2070	0.0072	BDL
D2	Slow 10.9	0.78	0.0241	BDL	BDL
D3	9.4	0.52	0.0382	0.0068	BDL
D4	7.0	0.52	0.0130	BDL	BDL
D5	3.2	0.44	0.1236	0.0126	BDL
E1	Slow 11.6	0.87	0.0260	0.0099	BDL
E2	Slow 10.4	1.48			
E3	8.9	0.99	0.0276	0.0143	BDL
E4	7.4	1.08	0.0389	0.0062	BDL
E5	4.1	1.08	0.1349	0.0666	BDL

BDL = Below Detection Limit

Table 8. Results of the Fall 2008 groundwater samples. The wells marked with a "Slow" had slower recharge while purging the well.

Fall 2008 Well Sampling Results					
Well	Well Depth (m)	Depth to water (m)	Atrazine ($\mu g\ L^{-1}$)	DEA ($\mu g\ L^{-1}$)	DIA ($\mu g\ L^{-1}$)
A1	15.1	0.82	0.0153	BDL	BDL
A2	10.9	0.78	0.0096	BDL	BDL
A3	7.8	0.76	0.0123	BDL	BDL
A4	Slow 6.2	0.82	0.0457	BDL	BDL
A5	3.3	0.43	0.0621	BDL	BDL
B1	16.2	2.36	0.0138	BDL	BDL
B2	11.5	2.26	0.0182	BDL	BDL
B3	Slow 7.8	1.05	0.0133	BDL	BDL
B4	Slow 6.3	0.75	0.0830	0.0174	BDL
B5	3.2	0.64	0.5890	0.1338	0.0833
C1	16.4	2.55	0.0853	BDL	BDL
C2	Slow 12.5	1.55	0.0723	0.0792	0.0437
C3	10.4	2.47	0.0920	BDL	BDL
C4	8.3	2.39	0.0151	BDL	BDL
C5	4.1	2.50	0.0608	0.0648	BDL
D1	12.5	1.31	0.0548	0.0073	BDL
D2	Slow 10.9	1.23	0.0174	0.0064	BDL
D3	9.4	1.39	0.0260	BDL	BDL
D4	7.0	1.34	0.1147	BDL	BDL
D5	3.2	1.28	0.1124	0.0149	BDL
E1	Slow 11.6	1.30	0.0158	0.0095	0.0296
E2	Slow 10.4	1.39	0.0261	0.0074	BDL
E3	8.9	1.42	0.0419	BDL	BDL
E4	7.4	1.46	0.0741	BDL	BDL
E5	4.1	1.43	0.1810	0.0478	BDL

BDL = Below Detection Limit

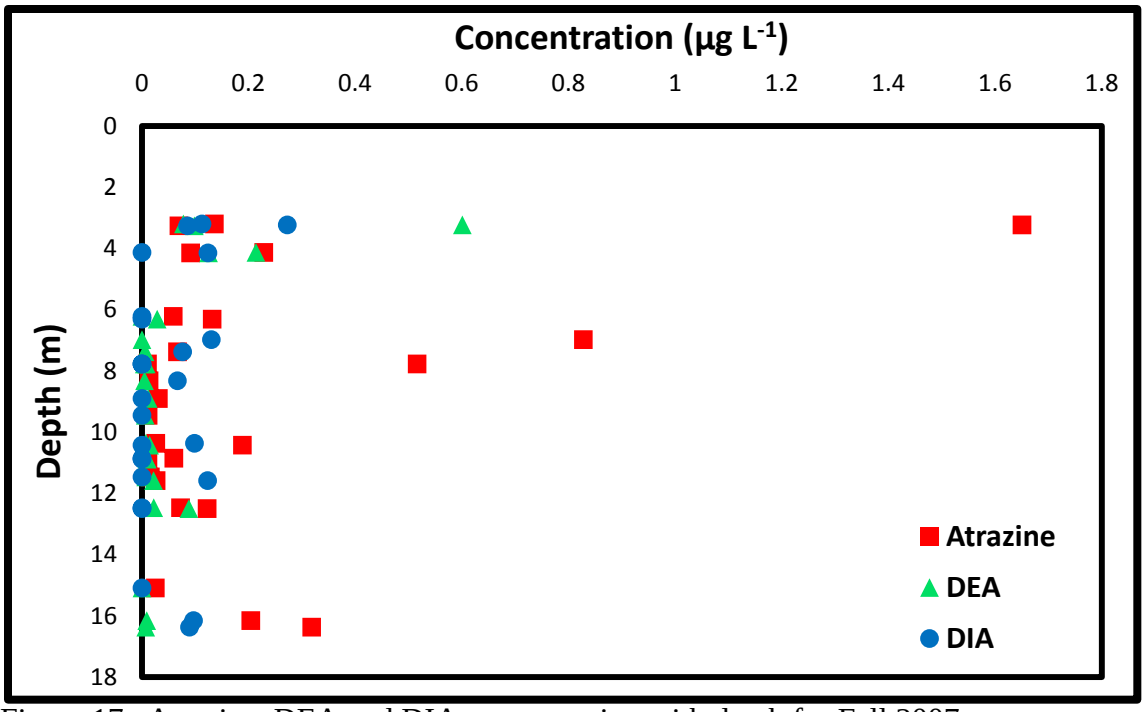


Figure 17. Atrazine, DEA and DIA concentration with depth for Fall 2007.

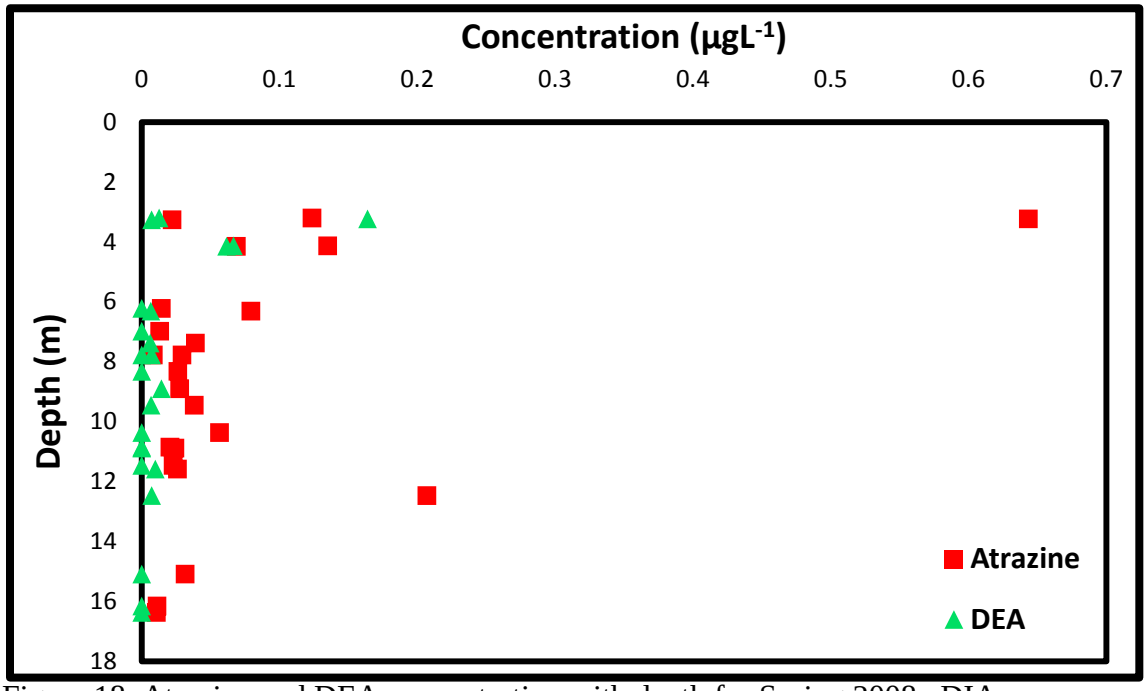


Figure 18. Atrazine and DEA concentration with depth for Spring 2008. DIA concentrations were below the detection limits.

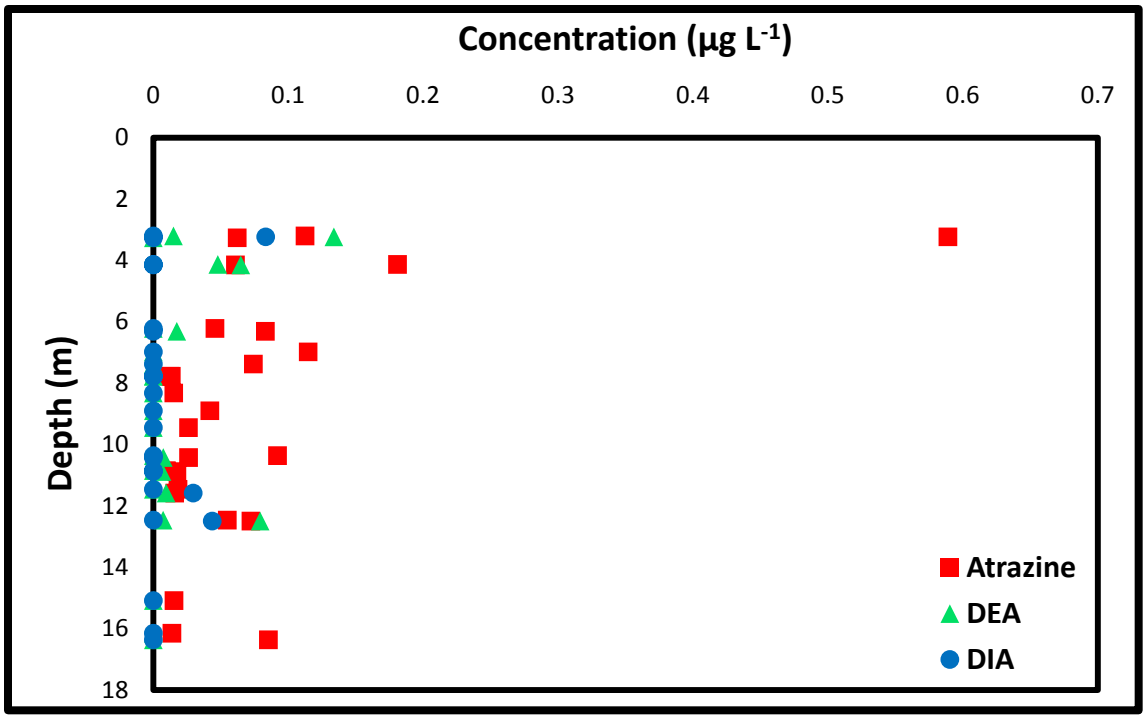


Figure 19. Atrazine, DIA, and DEA concentration with depth for Fall 2008.

by-passes surface soil and precludes degradation of atrazine. The DAR as defined by Adams and Thurman (1991) is

$$DAR = \frac{[DEA]}{[Atrazine]}$$, where the brackets represent concentration in mol L^{-1}.

To calculate the DAR, the field concentrations were converted to molarity using the molar mass (187.6319 g mol^{-1} for DEA and 215.6857 g mol^{-1} for atrazine). The DAR results are given in Tables 9, 10 and 11, and shown in relation to depth in Figures 20, 21 and 22. Most of the DAR values are much less than equality suggesting a discrete source of contamination. If the contaminant was allowed to percolate through the soil where degradation rates are highest the production of DEA would be increased and the DAR should be closer to one. With most of the DAR values being much lower than one, the

atrazine must have had a shorter residence time in the unsaturated zone where it is most vulnerable to degradation. The claypan is believed to have low permeability, increasing runoff and protecting the aquifer from contamination; however, studies have shown preferential flow paths exist within the claypan that could allow for direct transport of atrazine to the saturated zone (Blanco-Canqui et al., 2002; Tindall and Vencill, 1995). It is possible that these preferential flow paths could extend to depths near enough to the saturated zone to be flushed into the aquifer with a seasonal rise of the watertable.

Regional model

The regional groundwater flow model was created using the extents and values described in the methods section. In the initial attempt, only a single layer 16.8 m deep representing both the loess and the till was treated. The result was that the model was never able to converge numerically. Even after numerous adjustments to various parameters, computed hydraulic head values continued to oscillate spatially over the model domain. The likely cause was that at only 16.8 m, the layer was too thin relative to the areal extent of 65 km^2 (6500 ha). The solution was to increase dramatically the thickness of the model by adding a bedrock unit. The actual extent of the first layer of bedrock, the Pennsylvanian shales and clay, is variable across this area and is often grouped with the overlying till. The layer was set to 7.6 m, a high estimate of the thickness of the Cheltenham Formation in Northern Boone County (Unklesbay, 1952).

Table 9. The DAR from the Fall 2007 samples.

Fall 2007 DAR				
Well	Well Depth (m)	Atrazine (mol L^{-1})	DEA (mol L^{-1})	DAR
A1	15.1	1.16×10^{-10}	BDL	-
A2	10.9	2.77×10^{-10}	4.86×10^{-11}	0.18
A3	7.8	4.67×10^{-11}	2.26×10^{-11}	0.48
A4	6.2	2.72×10^{-10}	BDL	-
A5	3.3	3.21×10^{-10}	5.24×10^{-10}	1.63
B1	16.2	9.46×10^{-10}	4.75×10^{-11}	0.05
B2	11.5	7.18×10^{-11}	3.71×10^{-11}	0.52
B3	7.8	2.39×10^{-9}	4.23×10^{-11}	0.02
B4	6.3	6.10×10^{-10}	1.52×10^{-10}	0.25
B5	3.2	7.65×10^{-9}	3.20×10^{-9}	0.42
C1	16.4	1.47×10^{-9}	3.75×10^{-11}	0.03
C2	12.5	5.66×10^{-10}	4.69×10^{-10}	0.83
C3	10.4	1.19×10^{-10}	3.92×10^{-11}	0.33
C4	8.3	6.06×10^{-11}	2.55×10^{-11}	0.42
C5	4.1	4.23×10^{-10}	6.65×10^{-10}	1.57
D1	12.5	3.35×10^{-10}	1.18×10^{-10}	0.35
D2	10.9	5.17×10^{-11}	5.26×10^{-11}	1.02
D3	9.4	5.26×10^{-11}	3.24×10^{-11}	0.62
D4	7.0	3.84×10^{-9}	BDL	-
D5	3.2	6.29×10^{-10}	4.14×10^{-10}	0.66
E1	11.6	1.23×10^{-10}	1.16×10^{-10}	0.95
E2	10.4	8.73×10^{-10}	7.62×10^{-11}	0.09
E3	8.9	1.41×10^{-10}	6.27×10^{-11}	0.44
E4	7.4	3.08×10^{-10}	3.14×10^{-11}	0.10
E5	4.1	1.06×10^{-10}	1.14×10^{-9}	1.08

BDL = Below Detection Limit

Table 10. The DAR from the Spring 2008 samples.

Spring 2008 DAR				
Well	Well Depth (m)	Atrazine (mol L^{-1})	DEA (mol L^{-1})	DAR
A1	15.09	1.46×10^{-10}	BDL	-
A2	10.85	9.49×10^{-11}	BDL	-
A3	7.77	3.89×10^{-11}	BDL	-
A4	6.22	6.60×10^{-11}	BDL	-
A5	3.26	1.02×10^{-10}	3.81×10^{-11}	0.37
B1	16.15	5.17×10^{-11}	BDL	-
B2	11.46	1.06×10^{-10}	BDL	-
B3	7.77	1.36×10^{-10}	3.83×10^{-11}	0.28
B4	6.31	3.67×10^{-10}	3.52×10^{-11}	0.10
B5	3.23	2.98×10^{-9}	8.74×10^{-10}	0.29
C1	16.37	4.92×10^{-11}	BDL	-
C2	12.50			
C3	10.36	2.62×10^{-10}	BDL	-
C4	8.32	1.22×10^{-10}	BDL	-
C5	4.15	3.18×10^{-10}	3.28×10^{-10}	1.03
D1	12.47	9.60×10^{-10}	3.84×10^{-11}	0.04
D2	10.88	1.12×10^{-10}	BDL	-
D3	9.45	1.77×10^{-10}	3.61×10^{-11}	0.20
D4	6.98	6.04×10^{-11}	BDL	-
D5	3.20	5.73×10^{-10}	6.73×10^{-11}	0.12
E1	11.58	1.20×10^{-10}	5.25×10^{-11}	0.44
E2	10.42			
E3	8.90	1.28×10^{-10}	7.62×10^{-11}	0.60
E4	7.38	1.81×10^{-10}	3.30×10^{-11}	0.18
E5	4.13	6.26×10^{-10}	3.55×10^{-10}	0.57

BDL = Below Detection Limit

Table 11. The DAR from the Fall 2008 samples.

Fall 2008 DAR				
Well	Well Depth (m)	Atrazine (mol L^{-1})	DEA (mol L^{-1})	DAR
A1	15.09	7.1×10^{-11}	BDL	-
A2	10.85	4.44×10^{-11}	BDL	-
A3	7.77	5.68×10^{-11}	BDL	-
A4	6.22	2.12×10^{-10}	BDL	-
A5	3.26	2.88×10^{-10}	BDL	-
B1	16.15	6.39×10^{-11}	BDL	-
B2	11.46	8.46×10^{-11}	BDL	-
B3	7.77	6.16×10^{-11}	BDL	-
B4	6.31	3.85×10^{-10}	9.27×10^{-11}	0.24
B5	3.23	2.73×10^{-9}	7.13×10^{-10}	0.26
C1	16.37	3.95×10^{-10}	BDL	-
C2	12.50	3.35×10^{-10}	4.22×10^{-10}	1.26
C3	10.36	4.27×10^{-10}	BDL	-
C4	8.32	7.02×10^{-11}	BDL	-
C5	4.15	2.82×10^{-10}	3.46×10^{-10}	1.23
D1	12.47	2.54×10^{-10}	3.87×10^{-11}	0.15
D2	10.88	8.08×10^{-11}	3.43×10^{-11}	0.42
D3	9.45	1.21×10^{-10}	BDL	-
D4	6.98	5.32×10^{-10}	BDL	-
D5	3.20	5.21×10^{-10}	7.96×10^{-11}	0.15
E1	11.58	7.34×10^{-11}	5.05×10^{-11}	0.69
E2	10.42	1.21×10^{-10}	3.94×10^{-11}	0.33
E3	8.90	1.94×10^{-10}	BDL	-
E4	7.38	3.44×10^{-10}	BDL	-
E5	4.13	8.39×10^{-10}	2.55×10^{-10}	0.30

BDL = Below Detection Limit

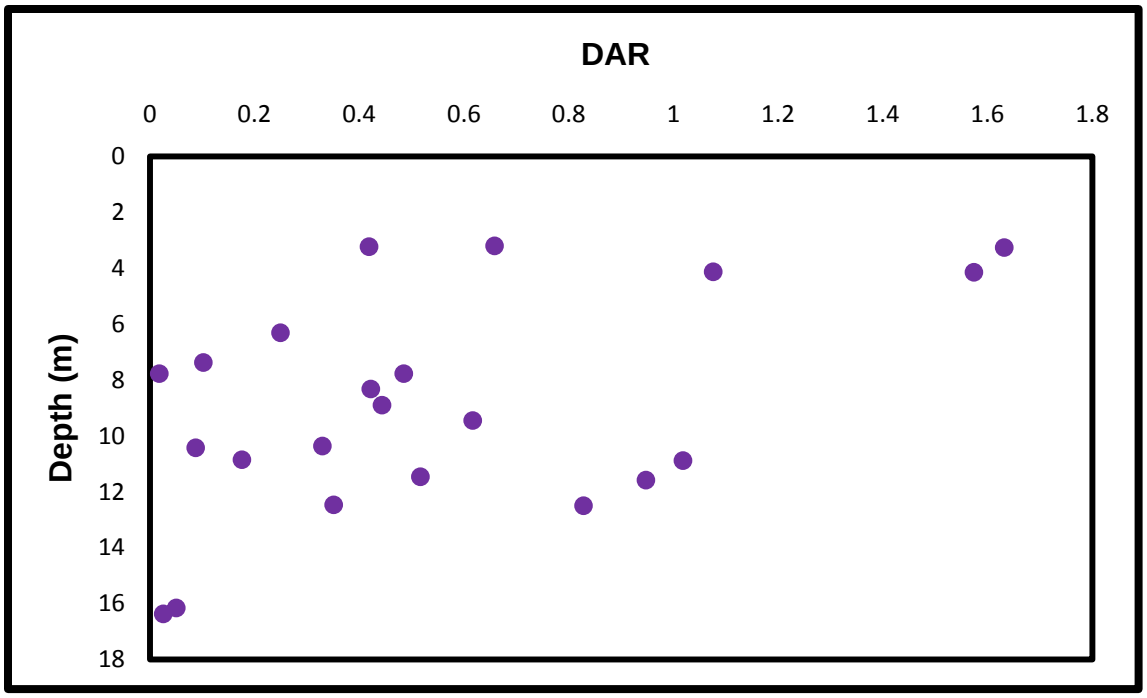


Figure 20. The DAR with depth for the Fall 2007 samples. Three samples contained measureable concentrations of atrazine but DEA was below the detection limit.

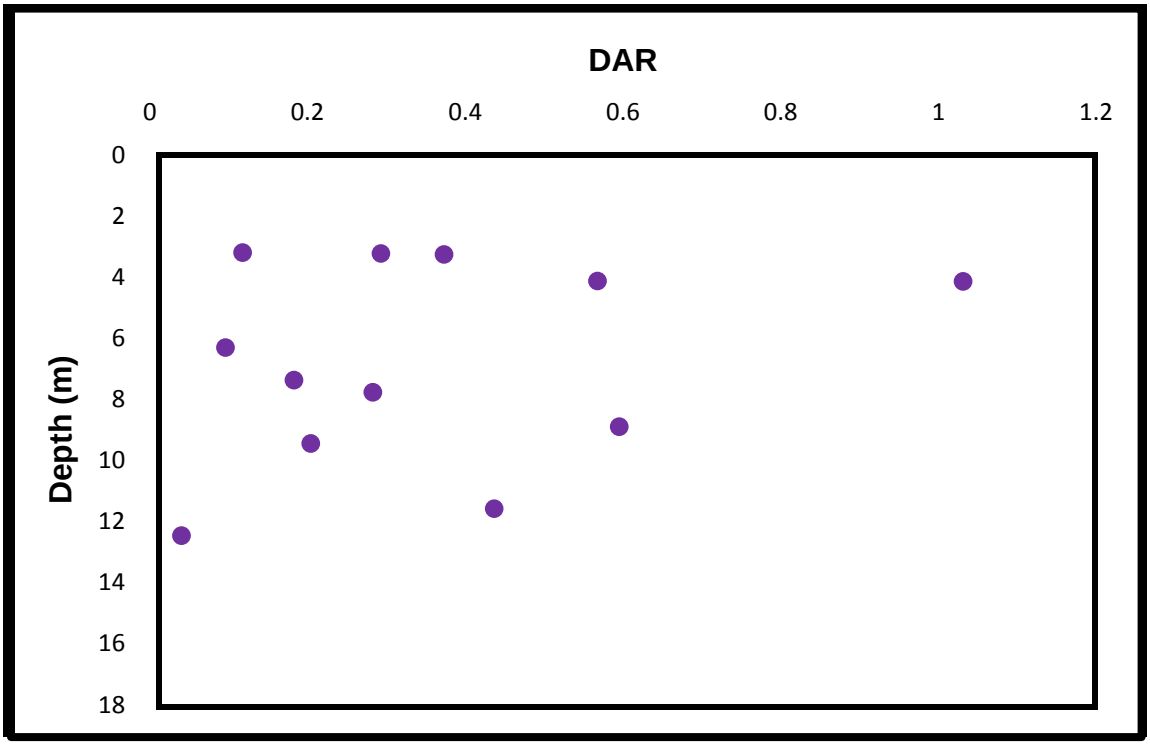


Figure 21. The DAR with depth for the Spring 2008 samples. Seven samples contained measurable concentrations of atrazine but DEA was below the detection limit.

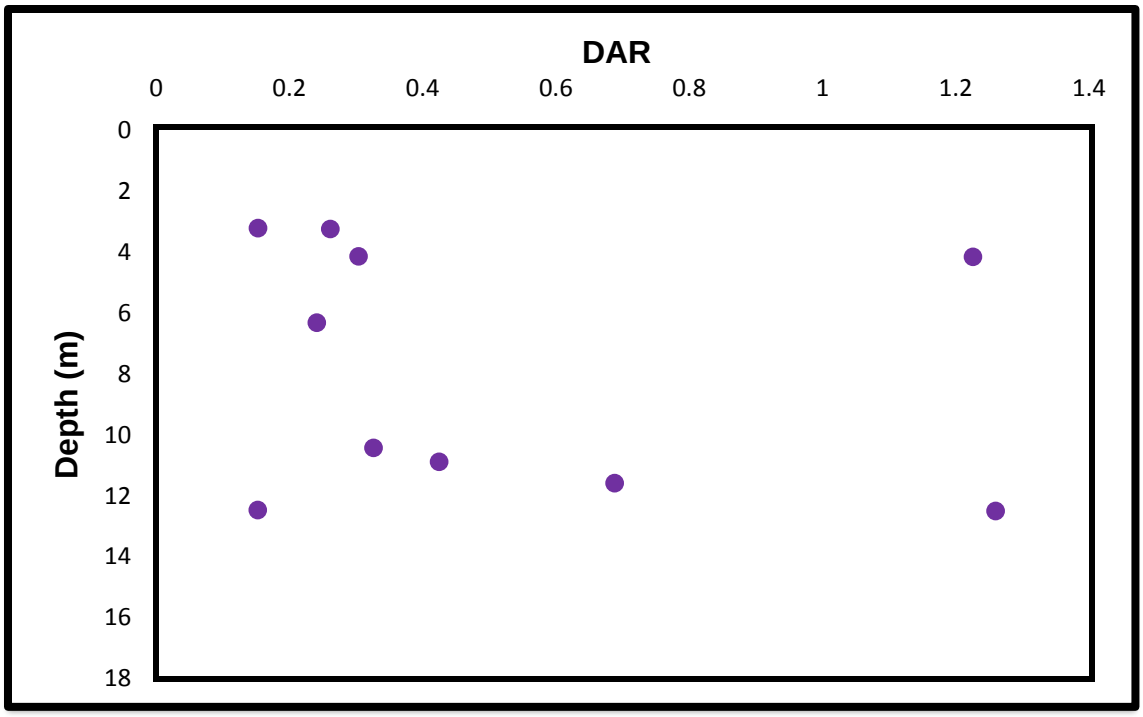


Figure 22. The DAR with depth for the Fall 2008 samples.

The Burlington Formation (a Mississippian limestone unit) was also added. The actual lower elevation of the Burlington was not known, so a flat base at 197 m was chosen based on data from nearby well logs (Unklesbay, 1952). A hydraulic conductivity (K) value of 2×10^{-9} m s^{-1} was assigned for Layer 2. The K for this formation has not been measured so an average value representative of clay and shale was chosen (Schwartz and Zhang, 2003). Layer 3 (Burlington Limestone) was given a horizontal hydraulic conductivity (K_h) value of 3.2×10^{-9} m s^{-1} and a vertical hydraulic conductivity (K_v) value of 2.0×10^{-9} m s^{-1} (Hoag, 1957). The hydraulic conductivities of Layers 2 and 3 are well below the 4.5×10^{-6} m s^{-1} assigned to Layer 1, so the boundary between Layer 1 and the bedrock effectively acted as a no flow boundary.

By increasing the vertical thickness, the model became numerically stable and produced reasonable results (Figure 23). The predicted direction of flow is towards the northeast where Goodwater Creek and Young's Creek intersect with localized deviations controlled by drainage channels. This result is reasonable because the model was set up with the highest values of hydraulic head in the southwest and the lowest values in the northeast at the confluence of the two creeks. The hydraulic head values, generated by the simulation, decrease from the southwest to the northeast as expected. Because the size of the velocity vectors increases as the magnitude of the velocity increases, the lack of vectors visually present in layer 2 would confirm that the top of layer 2 is a no flow boundary.

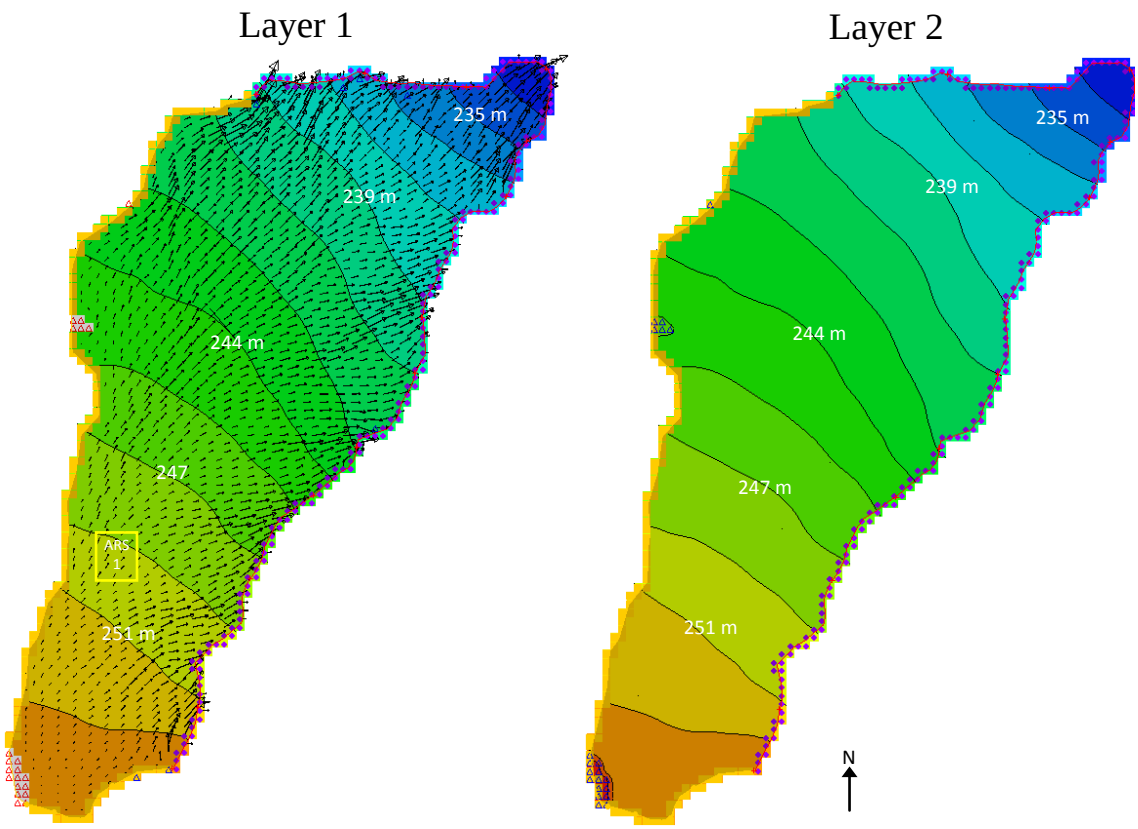


Figure 23. Map view of the regional model with contoured hydraulic head and flow vectors. The contours represent hydraulic head with higher values shown in orange and lower values in blue. The arrows represent velocity vectors whose size is a function of the magnitude of velocity. Layer 1 is shown on the left and layer 2 on the right. The yellow rectangle represents the location of ARS Field 1.

Field scale model

The purpose of the regional model was to generate hydraulic head values which could be used to telescope the area of study to a smaller scale that better represents ARS Field 1. The hydraulic head values generated from the regional scale model were used

for boundary conditions for a steady-state groundwater flow model at a field scale. ARS Field 1 (Figure 6) is represented as a 6 cell by 8 cell area of the regional model grid and the hydraulic head values of these cells (Table 12) were assigned to points along the corresponding boundaries of the models of ARS Field 1. Since the regional model combined the loess and glacial till into one layer, the resulting water table was below the base of the loess when the two lithologies were separated into two individual layers. Realistically the water table is within the lower loess, so the hydraulic heads used for boundary conditions were uniformly increased to an elevation within the lower loess while maintaining the hydraulic head gradient produced by the regional model. If head values were not increased, layer 1 of the ARS Field 1 models would start with dry conditions along the boundaries of the model and the model would be unrealistic as the difference in the starting head within the center of the grid and those of the boundaries would be too drastic. The groundwater flow conditions demonstrated by the regional model were carried to the field scale model by maintaining the hydraulic head gradient produced by the regional model at ARS Field 1. Also, the specified head values representing the divide between Young's Creek and Goodwater Creek were increased by 0.3048 m greater than those of the eastern boundary. This increase in head along the divide was chosen because it is larger than the head values of the eastern boundary and less than that of the western boundary so that the head gradient for ARS Field 1 obtained from the regional model was not dramatically altered. The head gradient along the eastern boundary of ARS Field 1 is about 0.001 which is consistent with the land surface, which has a gradient of 0.002.

The results of the steady-state model (Figure 24) indicate that the flow is mostly to the north with a slight eastward component. The flow vectors in layer 1 are not visible as the flow is not only low in magnitude but also vertical because the horizontal K of layer 2 is greater than that of layer 1. An area larger than ARS Field 1 was modeled so that ARS Field 1 could be isolated from boundary effects by locating the field towards the center of the grid for the most accurate results.

Expanding upon the steady-state model, a transient flow model was created by introducing variable recharge values as described in the methods section. The transient model indicates that during periods of recharge the hydraulic head values within the center of the grid are slightly increased.

Table 12. The corrected hydraulic head values (m) generated by the regional model used for defining the boundaries of the field scale model. Each value represents a cell of the regional model used as a value of a node along the specified head boundaries of the field scale model.

262.8019	262.746	262.6667	262.598	262.5426	262.4639
262.9687					262.5903
263.1316					262.7141
263.2937			**ARS Field 1**		262.838
263.4656			**Boundary**		262.9865
263.651					263.1976
263.8388					263.4418
264.0227					263.5407
264.2135	264.1591	264.093	264.0297	263.9765	263.9158

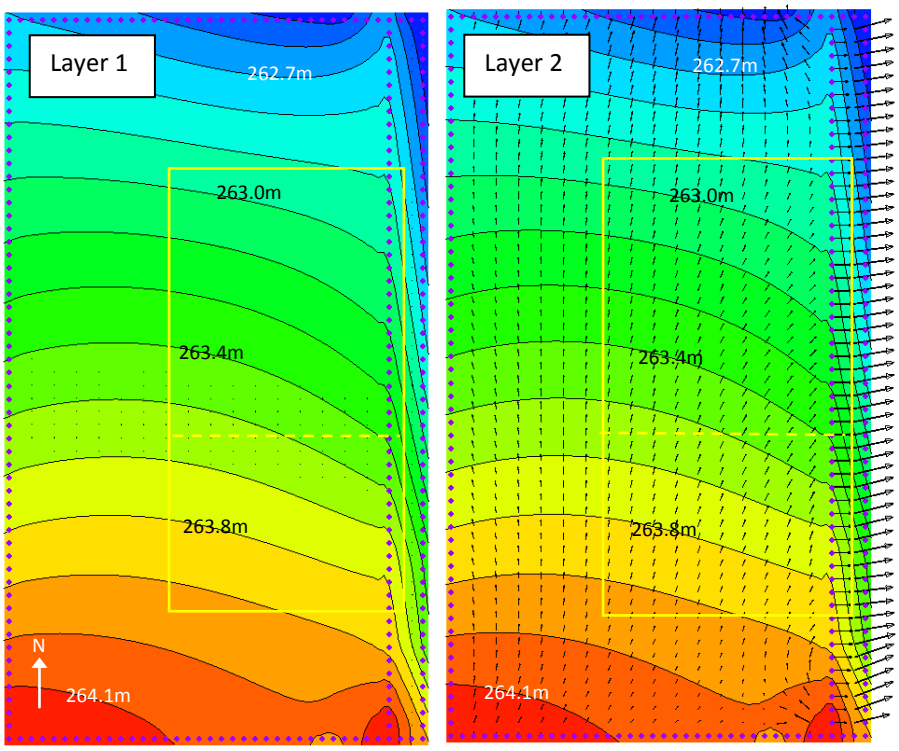


Figure 24. A steady-state simulation of the field scale groundwater flow model. The contours represent hydraulic head with red being high values and blue being low. The vectors represents groundwater flow direction. The yellow rectangle represents the boundary of ARS Field 1 with the dashed line separating zones 1 and 2.

Transport modeling

The final necessary set of models was for transport of atrazine through the glacial till. The MT3DMS package was activated and parameters were set up as described in the methods section. The first transport simulation was done for steady state with no degradation or retardation factors. This model represented a worst case scenario in that the atrazine was continuously applied with only groundwater flow as a means of leaving

the aquifer. A continual application of atrazine at a concentration of 400 µg L^{-1}, which is the site specific measured value below the claypan following atrazine application (Tindall and Vencill, 1995), was used. Two simulations were run with a model representing atrazine application to the entire ARS Field 1 and a second representing application only to zone 2 of ARS Field 1. Both versions were run from 1991 – 2008 and included groundwater recharge of 0.02 m yr^{-1}, which represents an average value at the location. The model with atrazine applied over the entire field showed very high atrazine concentrations throughout both layers with atrazine distributed across the entire field. The model with atrazine applied only to the southern field (Figure 25) resulted in a plume of atrazine moving from zone 2 towards the north.

The switching of atrazine introduction in 2003 to just being over zone 2 can help identify the relative age of the atrazine identified in the northern well nests. The atrazine present in the northern part of the field could be remaining from earlier applications when atrazine was applied in that area, or the atrazine is more recent and was transported from the south. A model in which atrazine lingers near the northern wells would require parameters that encourage the atrazine to have a long residence time and slow transport within the aquifer. However the development of a plume would require increased solute transport that would flush the old atrazine from the aquifer. By using one set of parameters for both the entire field application and the application limited to zone 2, the model system is protected from influence by the operator from choosing conditions that would bias atrazine concentration in zone 1 as being a result from either loading within the aquifer or a progressing plume.

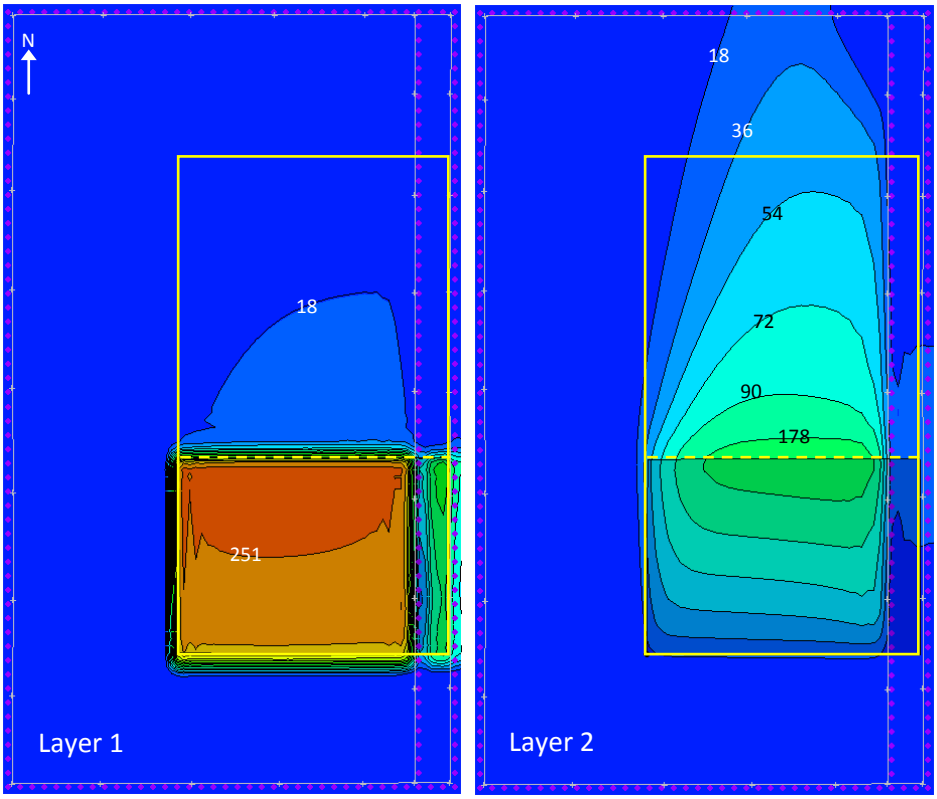


Figure 25. Simulated steady state atrazine transport with no degradation. The contours represent atrazine concentration in µg L^{-1} with red and orange representing higher values and blues representing lower values. This example is when atrazine is only applied to the southern part of the field. The yellow rectangle represents the boundary of ARS Field 1 with the dashed line separating zones 1 and 2.

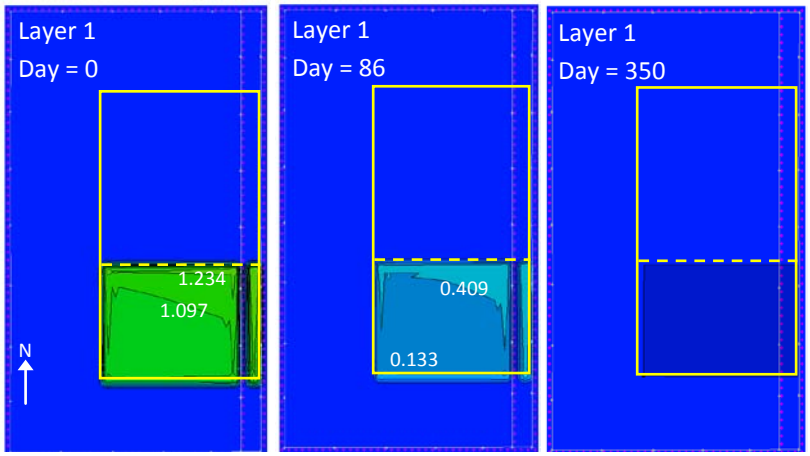
The transient transport model varied both the groundwater recharge according to seasonal variation and limited the introduction of atrazine. The stress periods used grouped October through May and June through September to represent seasonal variations in groundwater recharge. The length of a stress period was total days within that period and with time steps set to months. A small stress period was created for the first week of May of odd years to represent the application of atrazine. For simulations occurring from 1991 -2003, the application of atrazine was defined as a coverage of the

entire ARS Field 1. After 2003 the coverage area activated during the first week of May for atrazine recharge was limited to the zone 2 portion of ARS Field 1. A difficulty encountered with the transient model was that the program failed when attempting long simulations, such as from 1991- 2008. This problem was addressed by running the model as separate 5 year time intervals, with the results of each model being used as the starting concentration for the next time set. The results of the initial transient model were similar to those for the steady state because the mechanism for atrazine to leave the system was limited to flow and discharge since no factors for retardation were activated. The loading of atrazine was inevitable.

The final model includes applying retardation factors for atrazine sorption and destruction. For the simulations with a dissolution rate, a first-order kinetic irreversible reaction was applied with a half life value originally set to 12 days for the loess (Ghidey et al., 1997) and 1000 days for the till (the half life value for the till is not site specific and is estimated from other atrazine studies within the saturated zone). The reported half life values can include several mechanisms for atrazine degradation. The half life could potentially include microbial action as well as sorption. For the purpose of this study, the rate of atrazine loss is more important than the method. The initial value considered for atrazine half life within the loess was 12 days (Ghidey et al., 1997), which represents the site measured half life within the loess, followed by a half life of 60 days (Vencill, 2002) representing the average field half life. The findings (Figures 26 and 27) for these real world settings were that the atrazine was lost before the next slug was introduced or the atrazine could move into layer 2. The half life value for layer 2 was less sensitive. Changing layer 2 from 1000 to 3000 days did not have much of an effect. The

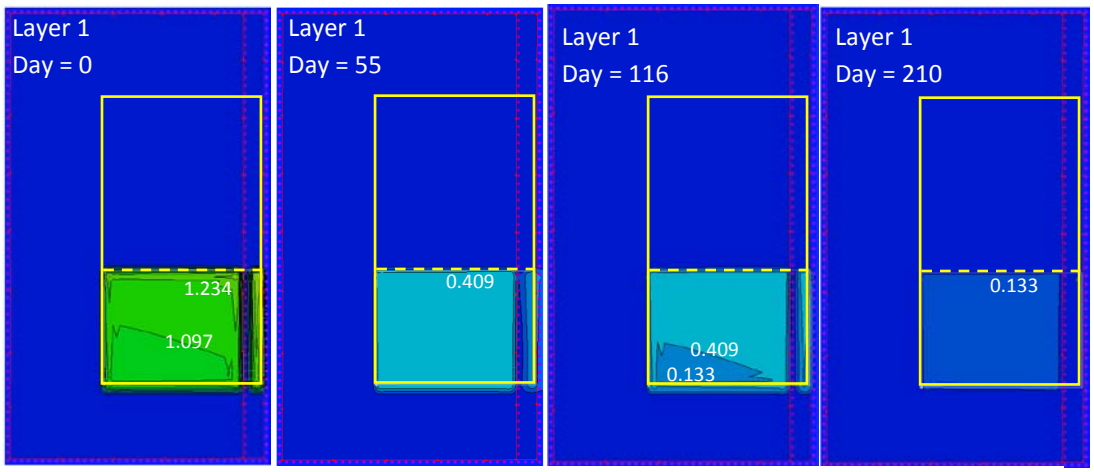
combination that produced the most realistic representation of the field data was for half lives of 300 days for the loess and 1000 days for the till (Figures 26 and 27). The 300 day half life within the loess is possible given that this model only includes the lowest portion of the loess. The water table is typically within the lower loess so this region is either saturated or at least has a high moisture content. This region includes conditions of both the saturated and unsaturated zones, so a half life value of 300 days is representative of a transitional degradation zone between the unsaturated zone, where there are many mechanisms for atrazine degradation and the saturated zone, where there are very few.

Initial simulations used an adsorption reaction. A linear Freundlich isotherm (an equation modeling sorption derived by fitting experimentally obtained values at individual temperatures to a theoretical equation) was used along with a distribution coefficient (K_d), not measured at this location, of 1.98 ml g^{-1} for the loess and 2.58 ml g^{-1} for the till (Montgomery, 1997). The reaction for the sorbed atrazine was very effective at removing the atrazine from the system. With this condition there would be no atrazine detected in the wells, so either the sorption values are much lower or sorption of atrazine is not important in this system. Furthermore, with depth the sorption of atrazine is reduced as the potential binding sites are lost by the decrease in organic and clay content (Koskinen and Clay, 1997). The grain size of the till at this location increases with depth as was previously discussed. Measurements of organic carbon content were not made but if the concentration of organic matter decreases with depth sorption to organic carbon would become negligible within the saturated zone being modeled.



Loess half life = 12 days
Till half life = 3000 days

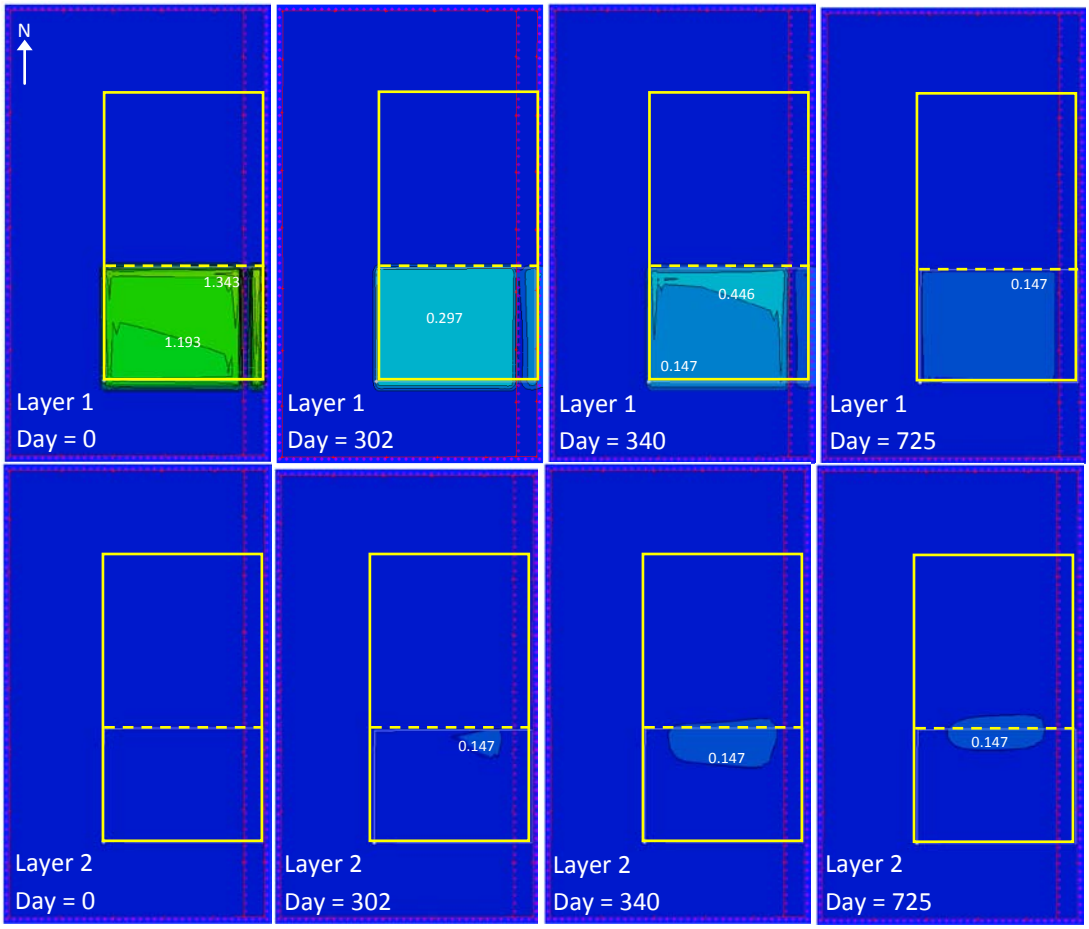
No atrazine was transported to layer 2
Atrazine concentration applied = 400 µg L^{-1}



Loess half life = 60 days
Till half life = 3000 days

No atrazine was transported to layer 2
Atrazine concentration applied = 400 µg L^{-1}

Figure 26. Examples of trials with different half lives. The contours represent atrazine concentration with greens representing higher concentrations and blues being low concentrations. The yellow rectangle represents the boundary of ARS Field 1 with the dashed yellow line separating zones 1 and 2.



Loess half life = 300 days
Till half life = 3000 days Atrazine concentration applied = 400 µg L^{-1}

Figure 27. Examples of trials with different half lives. The contours represent atrazine concentration with greens representing higher concentrations and blues being low concentrations. The yellow rectangle represents the boundary of ARS Field 1 with the dashed yellow line separating zones 1 and 2.

After testing many different values within the model, the combination of model variables that produced the results most similar to the field data were not too dissimilar to the values from the literature initially considered. The only variable that is not similar is the half life of atrazine within the loess. A simulation was achieved that generated concentrations of atrazine comparable to those detected in the field, including the high

concentrations located near well nest B. The concentrations of atrazine at shallow depths before atrazine application are well below the 2.0 μg kg^{-1} concentration that has been observed before atrazine application (Ghidey et al., 1997). The parameters used were half lives of 300 and 1000 days for layers 1 and 2 respectively, no sorption, and an applied atrazine concentration of 400 μg kg^{-1}. All other values, such as porosity and permeability, were left as the values obtained from the literature supporting their accuracy as representative values at this location.

Final model

The ultimate transport model of ARS Field 1 used boundary conditions derived from regional groundwater flow modeling and a set of parameters obtained from the literature. The simulation began with the first of May 1991. Atrazine was applied to the entire field during the first week of May during odd years with the model indicating a concentration of atrazine within the aquifer remaining resident between applications. Atrazine did not appear in layer 2 until December of 1992. In May 2003, the field management was switched to applying atrazine only to the southern section, zone 2, of ARS Field 1. In layer 1 a higher atrazine concentration is present within zone 2 but atrazine is also still present in the northern portion of layer 1. From 2003 on, transport has a point source (plume) character where the atrazine concentration in layer 2 moves north from the application area. The plume's highest concentration is near the

topographic divide. This simulation also shows an area of high atrazine concentration near well nests B, D and E. The lowest concentrations are near well nests A and C, which are near the boundary of the application area. These results are similar to the distribution observed in the field (Tables 13). What the model is not able to capture is the observed variation in concentration with depth. Some of the field observations detected horizons within some wells of high atrazine concentration. These areas of high concentration could be caused by lithologic changes, such as lenses of sand or clay, which could act as a trap for atrazine. This model uses a homogeneous till layer so atrazine concentration is a gradation of high concentrations near the surface and concentrations decrease with depth (Figures 28 and 29).

Once the model results provided a reasonable representation of the field observations through Fall 2008, a simulation of future atrazine concentrations within the aquifer (Figure 30) was created. The model was an extension of the simulation shown in Figure 27 using the same parameters and an average of the previous seasonal recharge rates. This model also assumes that atrazine application and crop management remain the same. This simulation runs through 2014 and predicts that atrazine contamination of the aquifer is sustained at current loads. The concentration of atrazine is predicted to slightly decrease to the west of the application area and is transported as a plume flowing northward from the southern field along the groundwater divide towards the confluence of Goodwater Creek and Young's Creek.

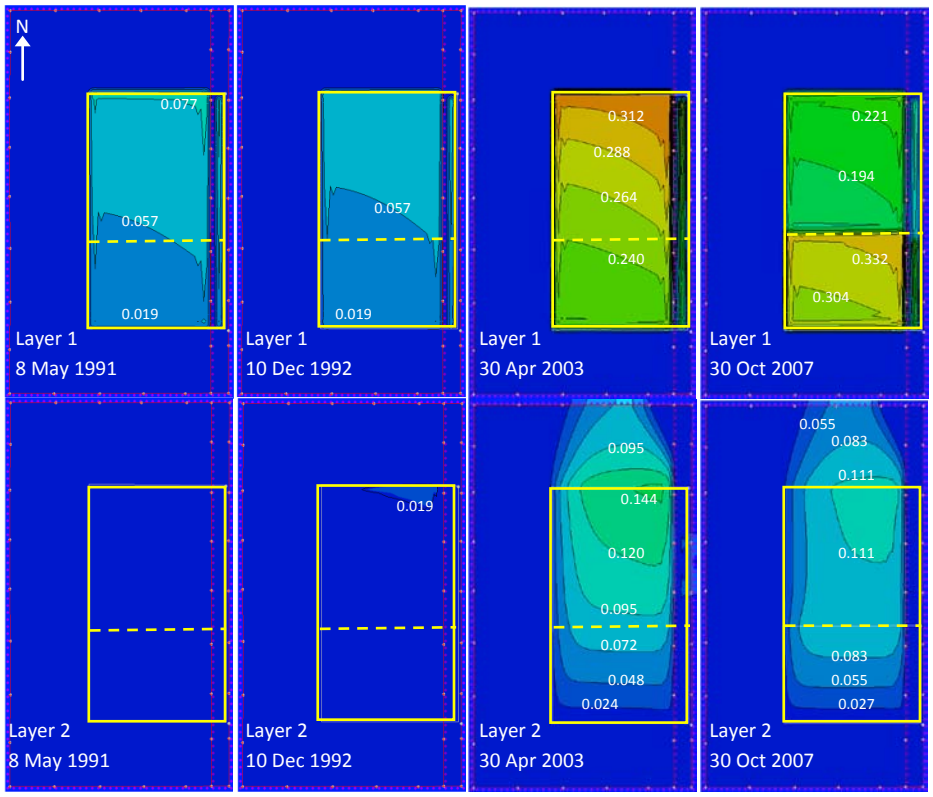


Figure 28. The transport model from May 1991 – October 2007. The yellow rectangle represents the ARS Field 1 boundary with the dashed yellow line separating zones 1 and 2.

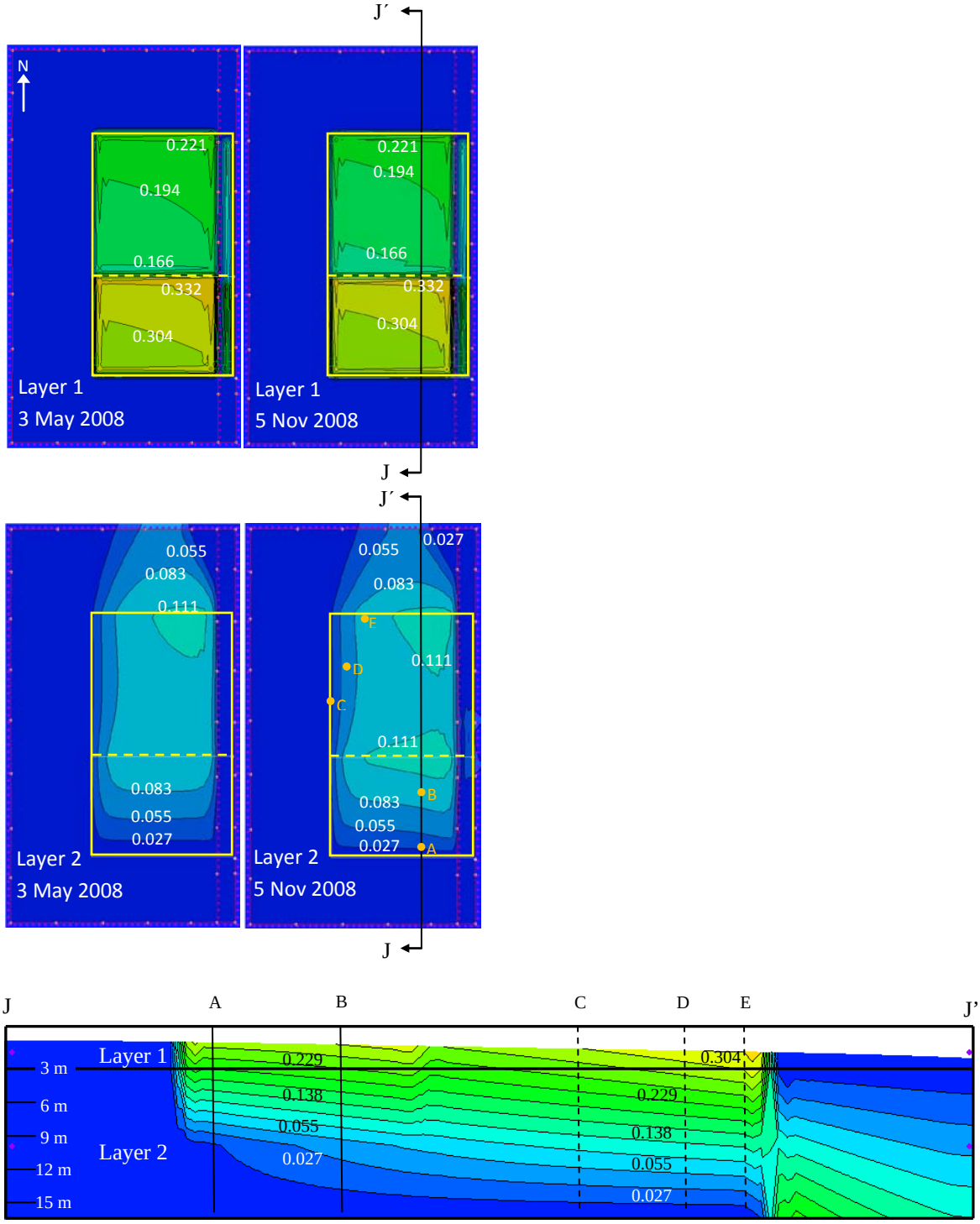


Figure 29. The transport model from May 2008 – November 2008 with well nests A-E and cross section J – J'. The cross section is shown with 10x vertical exaggeration. The yellow rectangle represents the ARS Field 1 boundary with the dashed line separating zones 1 and 2.

Table 13. The concentration of atrazine detected within the aquifer and estimated by the transport model. Both results were from Fall 2008.

		Field Sampling Results	Model Results
Well	Well Depth (m)	Atrazine ($\mu g\ L^{-1}$)	Atrazine ($\mu g\ L^{-1}$)
A5	3.3	0.0621	0.21
A4	6.2	0.0457	0.11
A3	7.8	0.0123	0.06
A2	10.9	0.0096	BDL
A1	15.1	0.0153	BDL
B5	3.2	0.5890	0.23
B4	6.3	0.0830	0.14
B3	7.8	0.0133	0.10
B2	11.5	0.0182	0.03
B1	16.2	0.0138	BDL
C5	4.1	0.0608	0.21
C4	8.3	0.0151	0.09
C3	10.4	0.0920	0.06
C2	12.5	0.0723	0.03
C1	16.4	0.0853	BDL
D5	3.2	0.1124	0.26
D4	7.0	0.1147	0.16
D3	9.4	0.0260	0.11
D2	10.9	0.0174	0.07
D1	12.5	0.0548	0.04
E5	4.1	0.1810	0.26
E4	7.4	0.0741	0.17
E3	8.9	0.0419	0.12
E2	10.4	0.0261	0.10
E1	11.6	0.0158	0.07

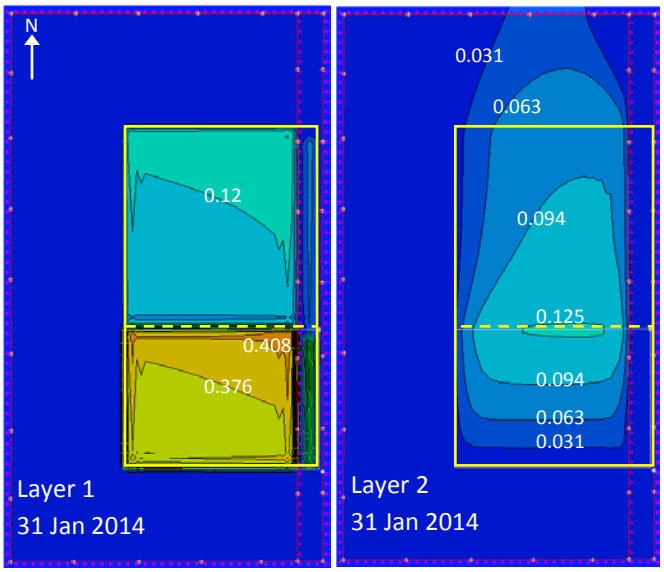


Figure 30. The prediction model extended through January 2014.

Chapter 4 – Conclusions

Atrazine was detected in measurable quantities at all five well nests and at all depths in the field study area. Well Nest A contains the lowest concentration of atrazine, which was expected by its location along the southern edge of the application area, and at a location where groundwater flow is moving away from this nest. Well Nest B has the highest concentration of atrazine caused by its central location within the field capable of receiving atrazine throughout the time periods of study. Well Nest C has a lower atrazine concentration caused by its location along the edge of the application area and not within the direction of groundwater flow. Well Nests D and E also had high concentrations due to their location within the central part of the field. The presence of atrazine in the wells in zone 2, Well Nests C, D and E, suggests that atrazine has a long residence time within the saturated zone since no atrazine has been applied to this portion of the field since 2001. The degradation product DEA (deethylatrazine) was detected in many wells while DIA (deisopropylatrazine) was not. The concentrations of DEA and DIA were considerably less than atrazine concentration in the same well. Either the conditions are not favorable for degradation of atrazine to DIA and DEA, atrazine is transported to the saturated zone more efficiently than DEA or DIA, or atrazine is being transported by preferential flow, with limited opportunity for degradation.

Examination of the ratios of the concentration of DEA to atrazine (DAR) in the wells from the field area, which range from X to Y, supports the hypothesis that atrazine is transported to the subsurface by way of preferential flow paths. Low DAR values

would suggest that the atrazine did not spend sufficient time within the unsaturated zone to allow degradation and significant DEA production.

The groundwater flow models of the field indicate flow is to the north-northeast driven by regional hydrogeologic features. The magnitude of groundwater flow within the aquifer was more than sufficient for the transport of atrazine. Historical atrazine application amounts were used to constrain the initial amounts of atrazine introduced into the system, and application amounts were varied in time as a model parameter. The transport model reproduced the concentrations of atrazine measured in the field reasonably well. The result was that with a set of appropriate parameters, with most being site specific values, the atrazine within the aquifer exists as a combination of the older atrazine persisting throughout the aquifer and a plume of recent atrazine emanating from zone 2 and traveling north. The model sensitivity indicated that the only deviation from model parameter values reported in the literature was a half life of atrazine in the system. The half life of atrazine in the loess may be higher than the reported values for the unsaturated zone. The model performed best with a half life of atrazine within the loess of about 300 days because with lower values the atrazine is destroyed before it can be transported to the till or maintain residence between atrazine applications. The half life within the saturated zone could be 1000 days or more, so the 300 day half life required within the loess may represent a transition between the saturated and unsaturated zone. The initial atrazine concentration of 400 $\mu g\ L^{-1}$ below the claypan (Tindall and Vencill, 1995) proved to be a reasonable starting concentration for the saturated zone. The model was also used to predict the concentration of atrazine in the aquifer through

2014 assuming no change in cropping practices. This simulation did not indicate a major increase in the concentration of atrazine to levels of human health concern.

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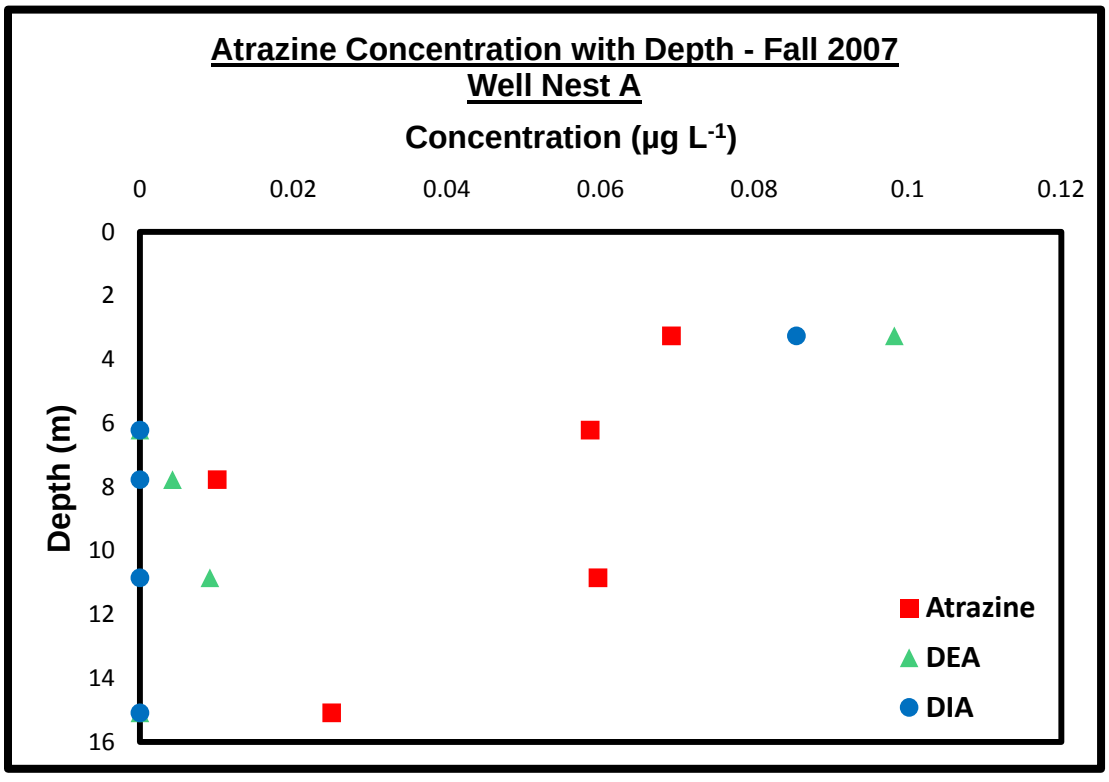
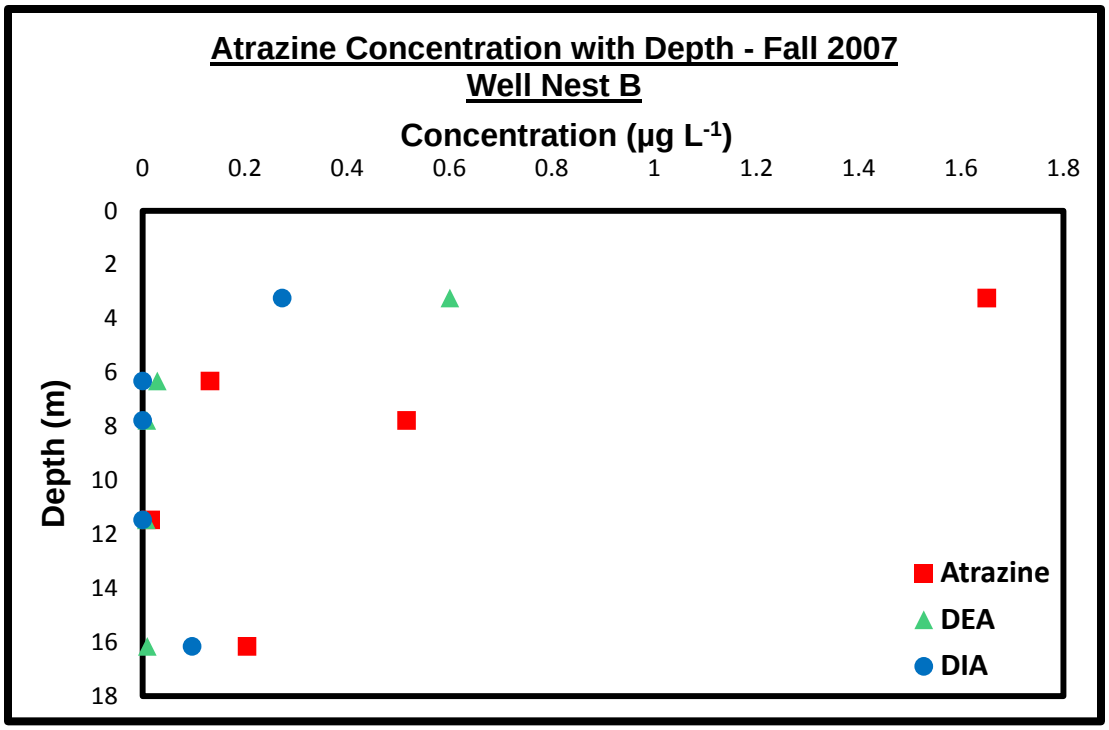
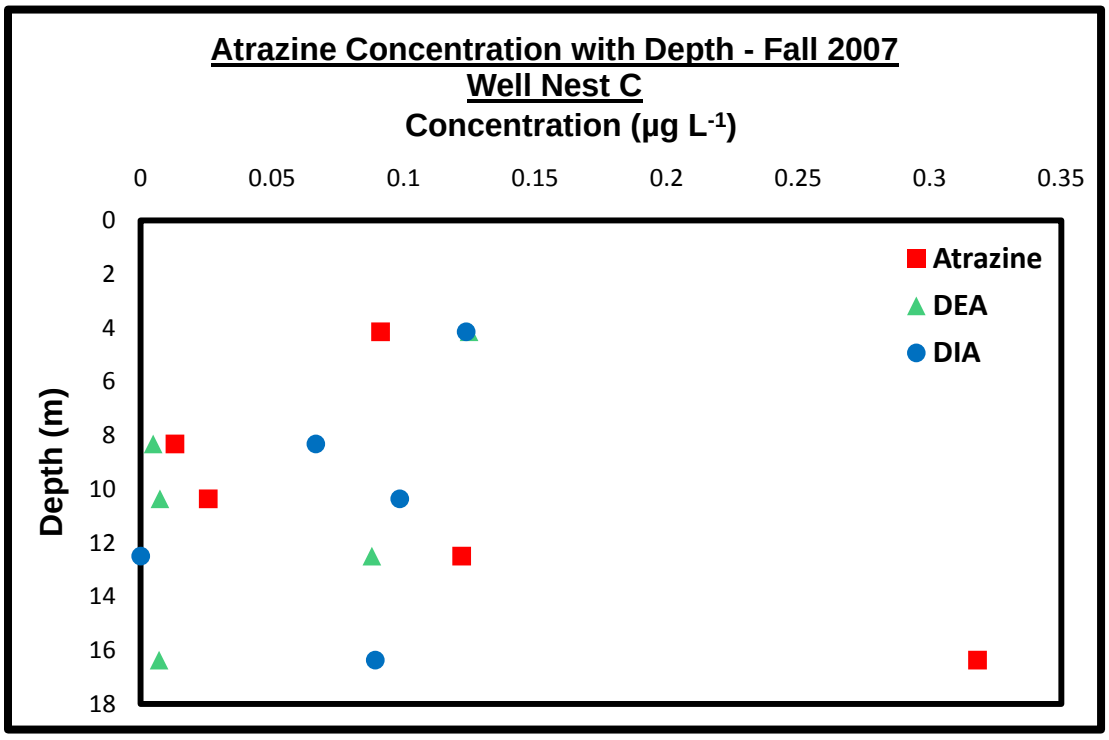
Appendix A

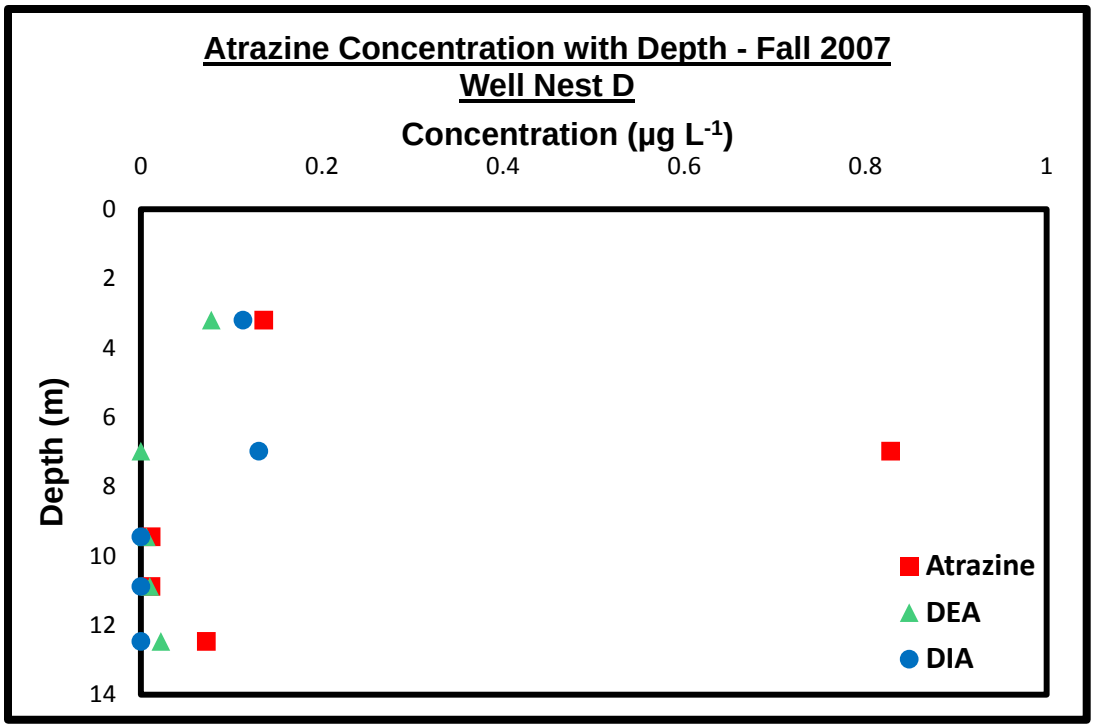
Groundwater sampling results for each well nest

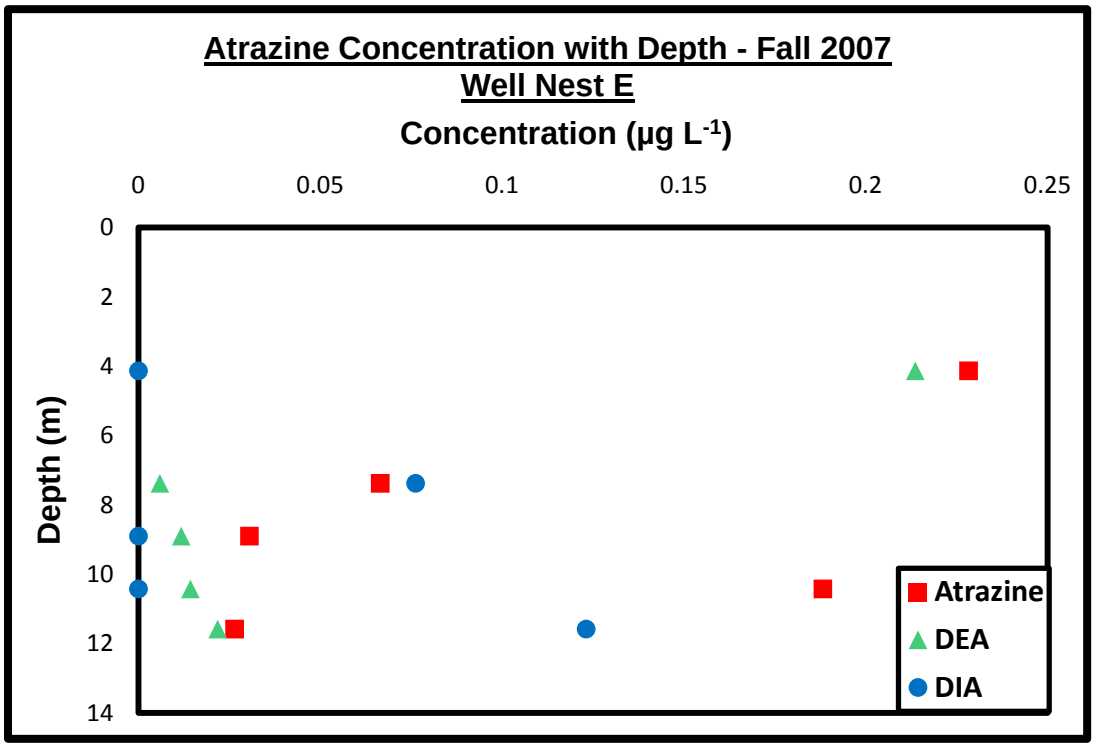
These plots represent the results of measured atrazine, DEA and DIA concentrations at each well nest for each sampling event. The concentrations are plotted along the x axis with the units, µg L^{-1}. The concentrations shown as 0 µg L^{-1} represent measurements below the detection limit. The y axis represents depth in meters. The well nest and sampling event are shown in the heading of each plot.

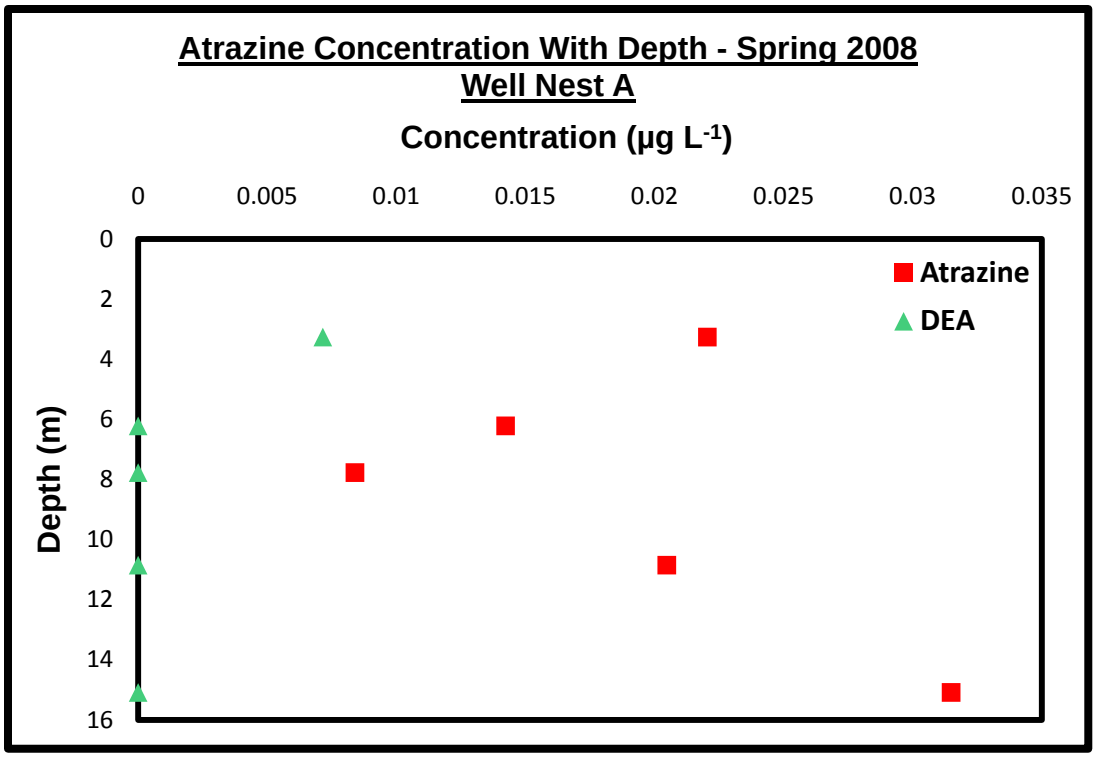


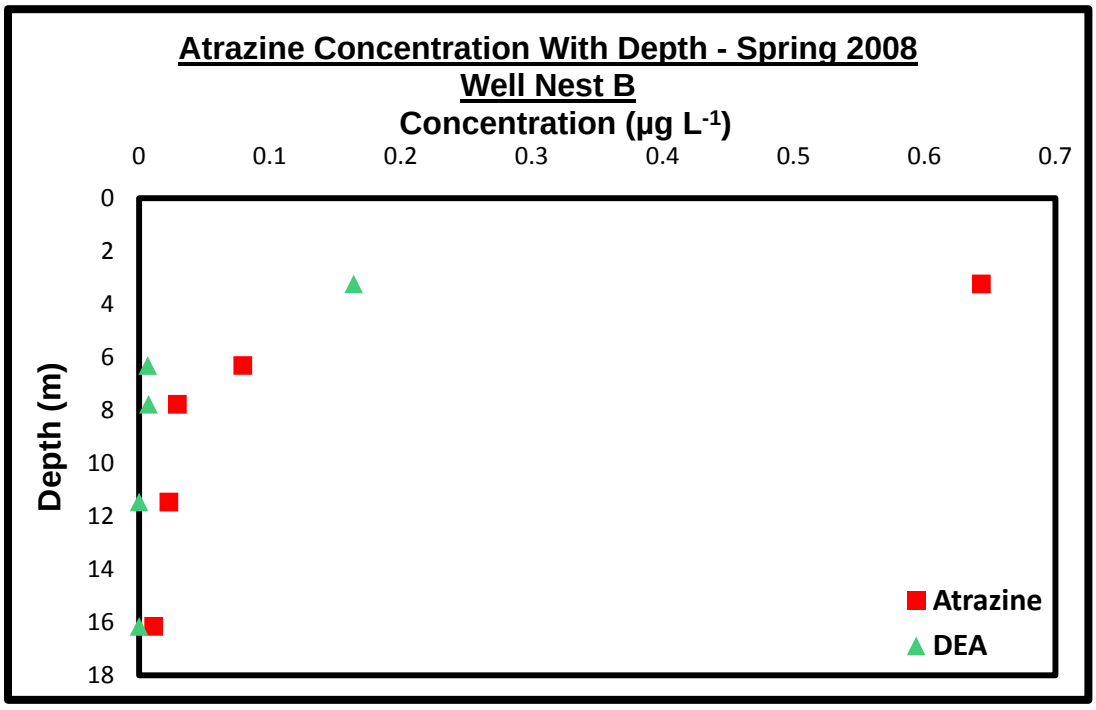

Atrazine Concentration with Depth - Fall 2007
Well Nest B
Concentration (µg L-1)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
Depth (m)
0
2
4
6
8
10
12
14
16
18
Atrazine
DEA
DIA

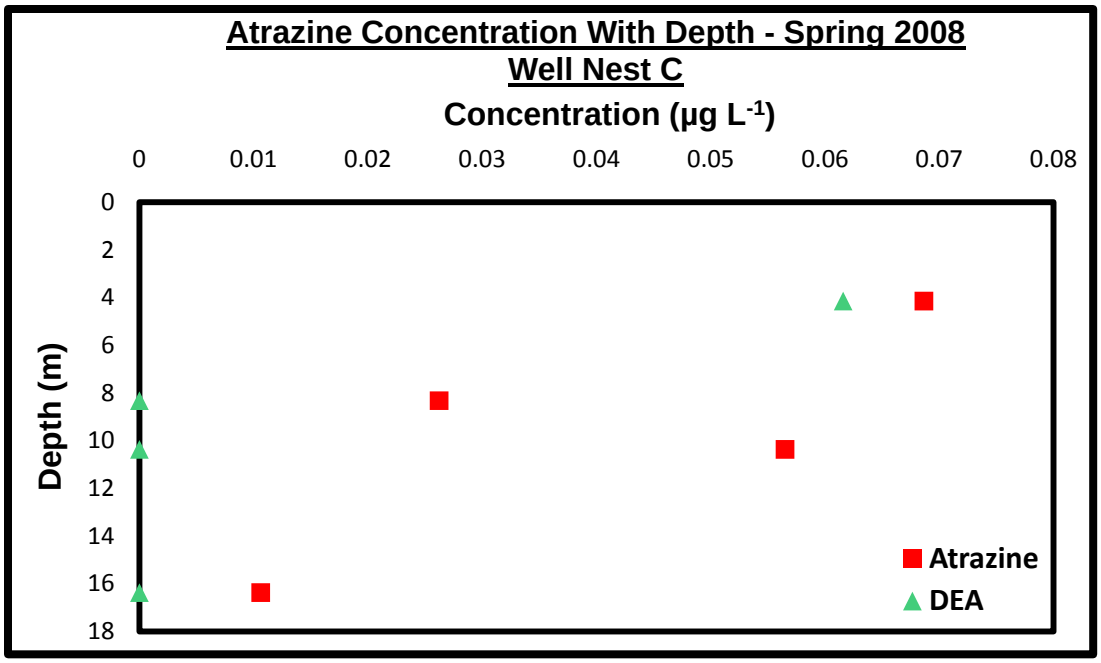

Atrazine Concentration with Depth - Fall 2007
Well Nest C
Concentration (µg L-1)
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
Depth (m)
0
2
4
6
8
10
12
14
16
18
Atrazine
DEA
DIA

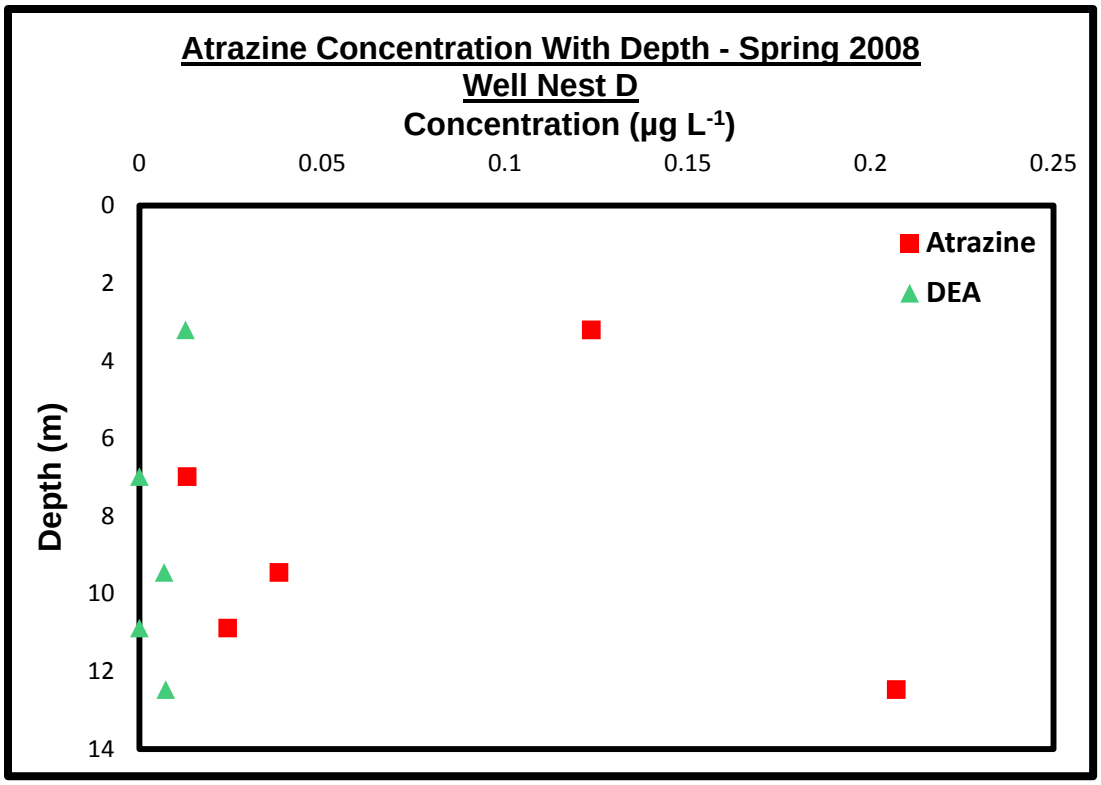

Atrazine Concentration with Depth - Fall 2007
Well Nest D
Concentration (µg L-1)
0
0.2
0.4
0.6
0.8
1
Depth (m)
0
2
4
6
8
10
12
14
Atrazine
DEA
DIA

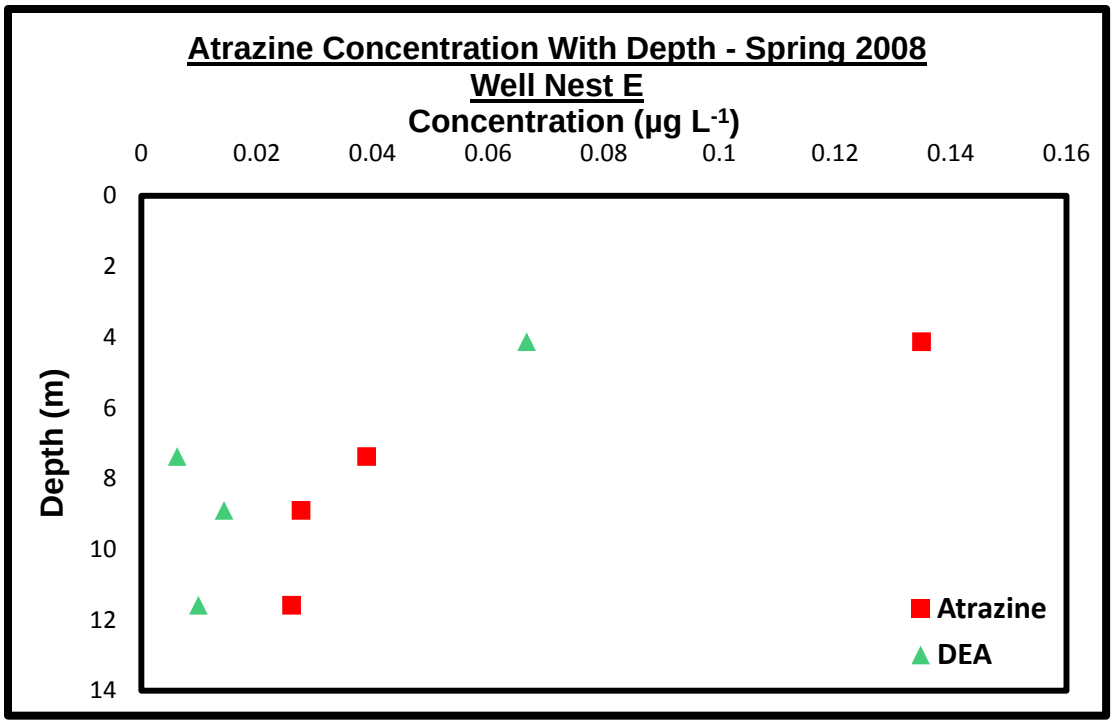

Atrazine Concentration with Depth - Fall 2007
Well Nest E
Concentration (µg L-1)
0
0.05
0.1
0.15
0.2
0.25
Depth (m)
0
2
4
6
8
10
12
14
Atrazine
DEA
DIA

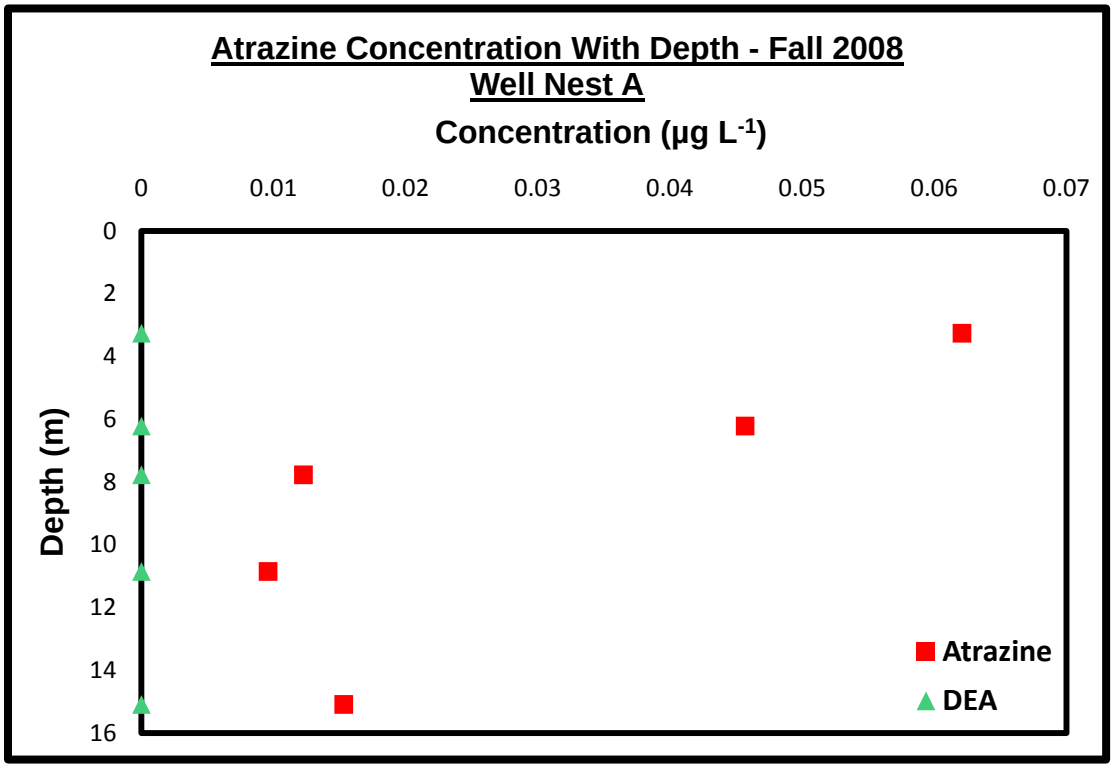

Atrazine Concentration With Depth - Spring 2008
Well Nest A
Concentration (µg L-1)
0
0.005
0.01
0.015
0.02
0.025
0.03
0.035
Depth (m)
0
2
4
6
8
10
12
14
16
Atrazine
DEA

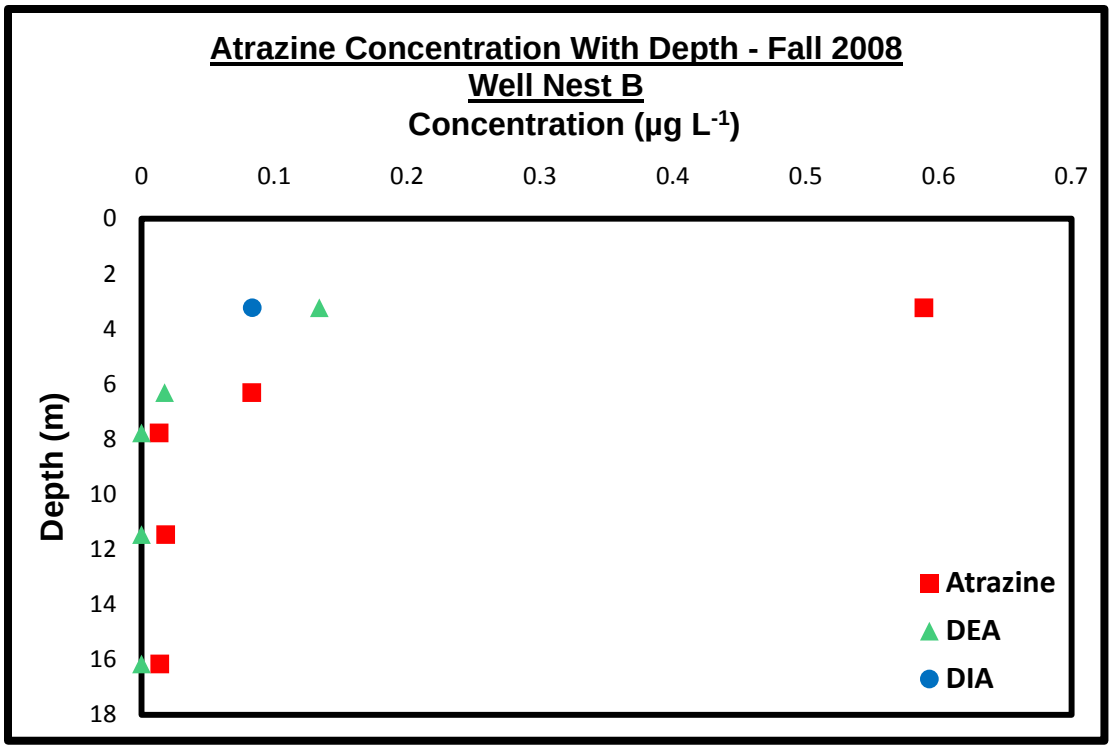

Atrazine Concentration With Depth - Spring 2008
Well Nest B
Concentration (µg L-1)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Depth (m)
0
2
4
6
8
10
12
14
16
18
Atrazine
DEA

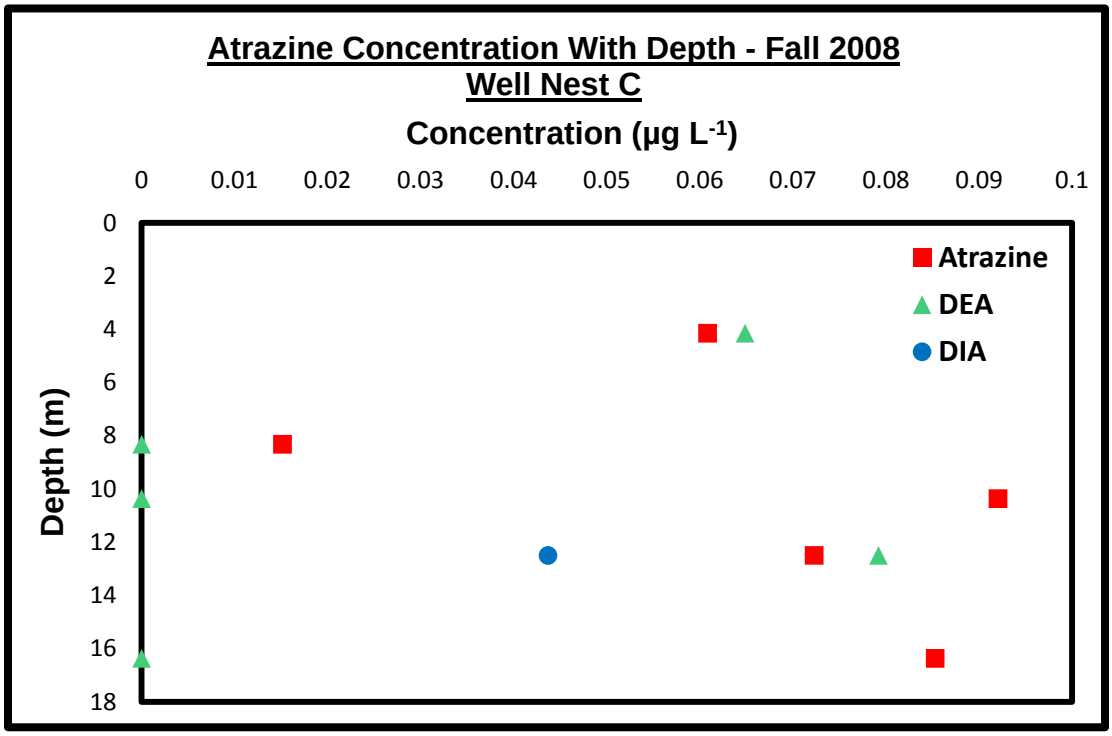

Atrazine Concentration With Depth - Spring 2008
Well Nest C
Concentration (µg L-1)
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
Depth (m)
0
2
4
6
8
10
12
14
16
18
Atrazine
DEA

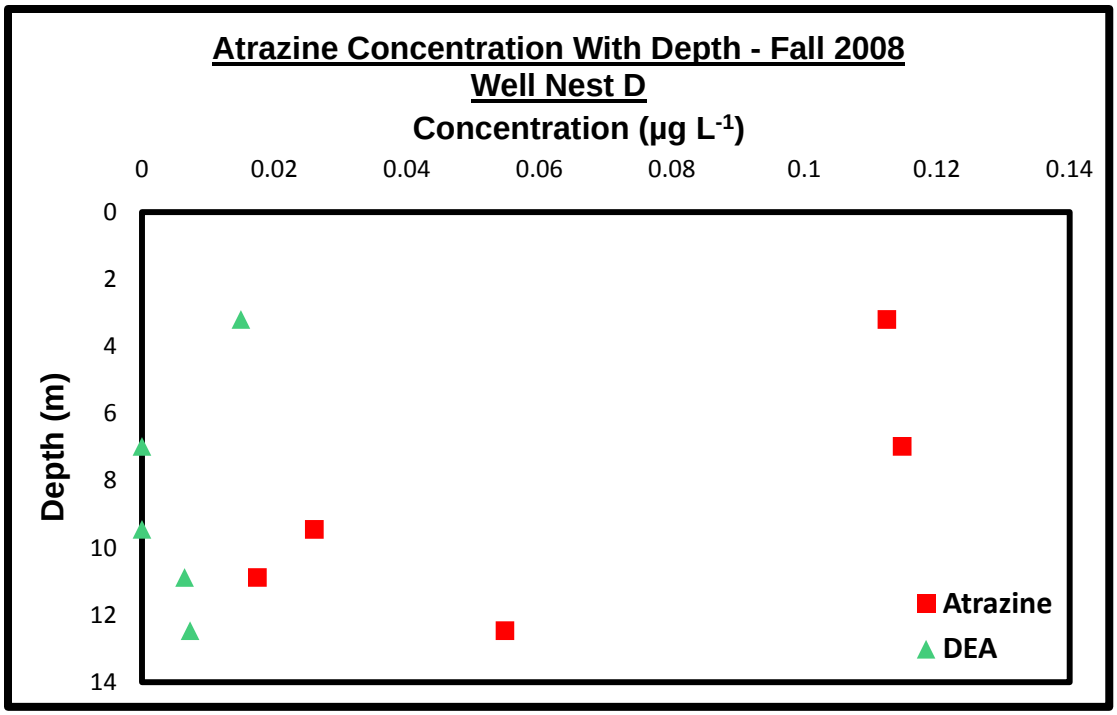

Atrazine Concentration With Depth - Spring 2008
Well Nest D
Concentration (µg L-1)
0
0.05
0.1
0.15
0.2
0.25
Depth (m)
0
2
4
6
8
10
12
14
Atrazine
DEA

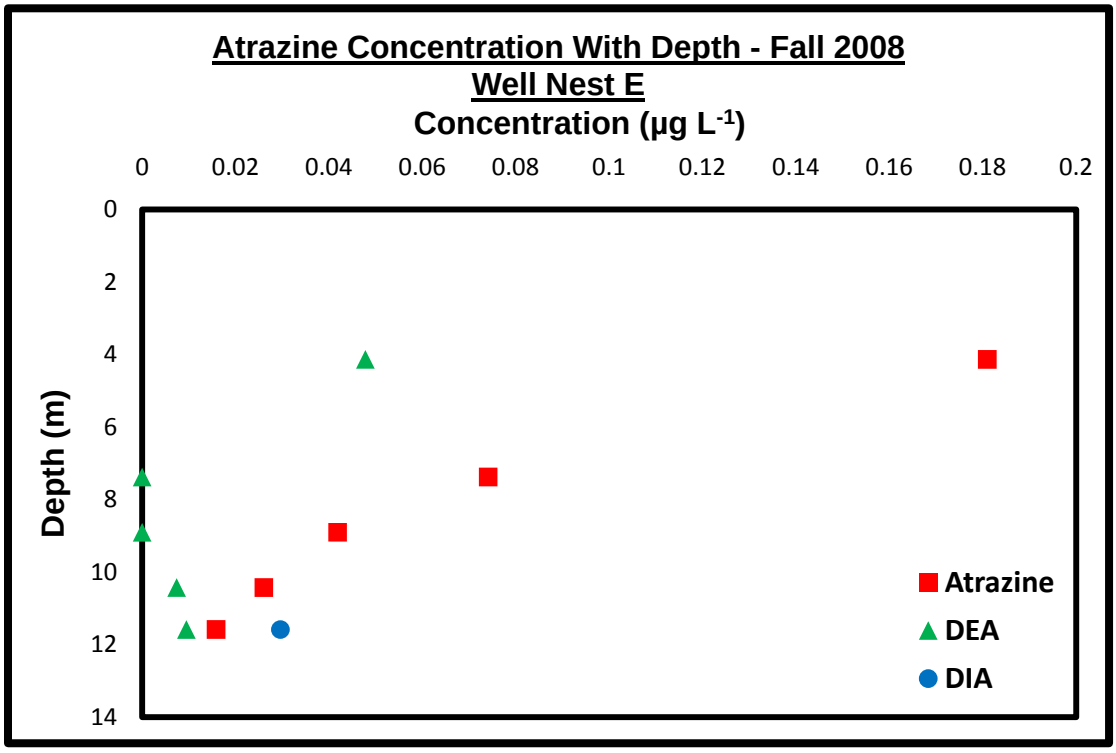

Atrazine Concentration With Depth - Spring 2008
Well Nest E
Concentration (µg L-1)
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
Depth (m)
0
2
4
6
8
10
12
14
Atrazine
DEA


Atrazine Concentration With Depth - Fall 2008
Well Nest A
Concentration (µg L-1)
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
Depth (m)
0
2
4
6
8
10
12
14
16
Atrazine
DEA


Atrazine Concentration With Depth - Fall 2008
Well Nest B
Concentration (µg L-1)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Depth (m)
0
2
4
6
8
10
12
14
16
18
Atrazine
DEA
DIA


Atrazine Concentration With Depth - Fall 2008
Well Nest C
Concentration (µg L-1)
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
Depth (m)
0
2
4
6
8
10
12
14
16
18
Atrazine
DEA
DIA


Atrazine Concentration With Depth - Fall 2008
Well Nest D
Concentration (µg L-1)
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
Depth (m)
0
2
4
6
8
10
12
14
Atrazine
DEA


Atrazine Concentration With Depth - Fall 2008
Well Nest E
Concentration (µg L-1)
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
0.2
Depth (m)
0
2
4
6
8
10
12
14
Atrazine
DEA
DIA