

**DETERMINING FATE AND TRANSPORT PARAMETERS FOR  
NITROGLYCERINE, 2,4-DINITROTOLUENE, 2,6-DINITROTOLUENE  
AND NITROGUANIDINE IN SOILS**

By

Damian Gosch

---

A Thesis Submitted to the Faculty of the

DEPARTMENT OF HYDROLOGY AND WATER RESOURCES

In Partial Fulfillment of the Requirements  
For the Degree of

MASTER OF SCIENCE  
WITH A MAJOR IN HYDROLOGY

In the Graduate College

THE UNIVERSITY OF ARIZONA

2012

## STATEMENT BY AUTHOR

This thesis has been submitted in partial fulfillment of requirements for an advanced degree at The University of Arizona and is deposited into the University Library to be made available to borrower under rules of the Library.

Brief quotations from this thesis are allowed without special permission, provided the accurate acknowledgement of source is made. Request for permission for extend quotation from or reproduction of this manuscript in whole or in part may be granted by the head of the major department of the Dean of the Graduate College when in his or her judgment the proposed use of the material is in the interest of scholarship. In all other instances, however, permission must be obtained from the author.

SIGNED: Damian L. Gosch

## APPROVAL BY THE THESIS DIRECTOR

This thesis has been approved on the date shown below:

\_\_\_\_\_  
Dr. P.A Ferre  
Professor of Hydrology and Water Resources

May 11, 2012  
Date

## ACKNOWLEDGEMENTS

This thesis was funded by the United States Army Cold Regions Research and Engineering Laboratory (CRREL) and the United States Army Corp of Engineers (USACE). I thank my advisory committee: Dr. P.A Ferre, Dr. Katerina Dontsova, Dr. Jon Chorover, and Dr. Tom Meixner. I appreciate Dr. Dontsova for choosing me for the project and helping me to reach my goals. Dr. Chorover who was invaluable in helping to manage the work associated with this project. Dr. Meixner for having an open door to any questions I may have. Special thanks to Angelica Vazquez-Ortega, Selene Hernandez Ruiz, and Ed Hunt for your help in the Water Research Lab. Thanks to students in HWR, Seshadri Rajagopal, Andrew Hartz, Andrew Hinnell, Scott Simpson, Jeff Gawad, Tim Bayley and Grey Nearing for their time and help. Lastly, I would like to send my gratitude to Dr. P.A “Ty” Ferre. Your ability to simplify and explain the most complex issues helped me finish this thesis project. The dedication to your numerous students shows me you enjoy your profession and really care about the well-being of us prospective hydrologists. I am forever grateful for your mentoring.

## DEDICATION

This is to my beautiful and loving wife and daughter, Kathryn and Anahla, to whom I owe this work. You are the world to me and I give you much of the credit for what I have been able to achieve over these past years. Through hard times we were able to find the strength and adversity to overcome such tribulations. Without your patience, as Anahla was learning in the halls outside the laboratory, and strong support, I would not be where I am today. Kathryn's hard work and continued motivation to finish school, gave me the intestinal fortitude needed to get through such a difficult degree program. I look forward to the many years of happiness that come with great success.

## TABLE OF CONTENTS

LIST OF FIGURES.....	6
LIST OF TABLES.....	9
ABSTRACT.....	10
INTRODUCTION.....	12
MATERIALS AND METHODS.....	22
RESULTS.....	31
DISCUSSION.....	59
REFERENCES.....	65

## LIST OF FIGURES

Figure 1: Textural classification of Plymouth, Catlin, and Sassafras soil used in kinetic batch studies.....	24
Figure 2: Nitroglycerin concentration as a function of time for studied soils.....	31
Figure 3: Nitroguanidine concentration as a function of time for studied soils.....	32
Figure 4: 2,4-dinitrotoluene concentration as a function of time for studied soils.....	33
Figure 5: 2,6-dinitrotoluene concentration as a function of time for studied soils.....	34
Figure 6: Concentration changes of constituents as a function of time in Catlin soil.....	35
Figure 7: Concentration changes of constituents as a function of time in Plymouth (MMR) soil.....	36
Figure 8: Concentration changes of constituents as a function of time in Sassafras soil.....	37
Figure 9: Linear sorption coefficients as a function of organic carbon content at 1hr.....	38
Figure 10: Linear sorption coefficients as a function of organic carbon content at 120hr.....	39

## LIST OF FIGURES – Continued

Figure 11: Simulated breakthrough curve of 2,4-DNT in soils at column experimental depth of 17cm.....	42
Figure 12: Simulated breakthrough curve of 2,4-DNT in soils at a depth of 34cm.....	43
Figure 13: Simulated breakthrough curve of 2,4-DNT in soils at a depth of 51cm.....	44
Figure 14: Simulated breakthrough curve of 2,4-DNT in soils at a depth of 100cm.....	45
Figure 15: Simulated breakthrough curve of 2,6-DNT in soils at column experimental depth of 17cm.....	46
Figure 16: Simulated breakthrough curve of 2,6-DNT in soils at a depth of 34cm.....	47
Figure 17: Simulated breakthrough curve of 2,6-DNT in soils at a depth of 51cm.....	48
Figure 18: Simulated breakthrough curve of 2,6-DNT in soils at a depth of 100cm.....	49
Figure 19: Simulated breakthrough curve of NG in soils at column experimental depth of 17cm.....	50
Figure 20: Simulated breakthrough curve of NG in soils at a depth of 34cm.....	51

## LIST OF FIGURES – Continued

Figure 21: Simulated breakthrough curve of NG in soils at a depth of 51cm.....	52
Figure 22: Simulated breakthrough curve of NG in soils at a depth of 100cm.....	53
Figure 23: Simulated breakthrough curve of NQ in soils at column experimental depth of 17cm.....	54
Figure 24: Simulated breakthrough curve of NQ in soils at a depth of 34cm. ....	55
Figure 25: Simulated breakthrough curve of NQ in soils at a depth of 51cm.....	56
Figure 26: Simulated breakthrough curve of NQ in soils at a depth of 100cm.....	57

## LIST OF TABLES

Table 1: Results of soil textural analysis and particle distribution using Laser Diffraction Particle Size Analyzer and Pipette Methods.....	23
Table 2: Properties of propellant constituents used in kinetic batch studies.....	25
Table 3: Organic carbon content of soils, calculated dispersion coefficients, logKoc, degradation constants, and half-life of constituents within studied soils.....	40
Table 4: Cation Exchange Capacity measured using Sodium Acetate Method, pH, and Electrical Conductivity.....	41

## ABSTRACT

During military operations, a small fraction of propellant mass is not consumed during firing and is deposited onto the ground surface. Soluble propellant constituents can be released from particulate residues into the environment. The release of uncombusted propellant residues and transformation products results in soil, surface water, and ultimately groundwater contamination. It is important to study the potential for off-site migration of munitions and to provide qualitative data that helps better understand transit of these propellant constituents. Propellant constituents of interest for this study were nitroglycerine (NG), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), and nitroguanidine (NQ). The goal of this work is to determine fate and transport parameters, partition/distribution coefficients and transformation rates for these compounds in three soils that represent a range of geographic locations and soil properties. This supports a companion study that looks at dissolution of constituents from fired and unfired solid propellant formulations and

their transport in soil.

## INTRODUCTION

Propellants are energetic materials that react at a controlled rate to produce pressure (Kirchner, D. B., J. C. Gaydos, and M. C. Battigelli 1993). They are used for propelling projectiles from guns, mortars, rockets, and other firearms. Propellants are composed of low explosive materials and high explosive chemical ingredients that are diluted and burned at a controlled rate called deflagration. Propellants can be found in either a solid or liquid form. Solid propellants are complex composite materials that consist of energetic compound mixtures infused in an insoluble nitrocellulose matrix. This study focuses on the energetic compounds within these matrices. Additional compounds in this mixture serve to bind and stabilize the propellant during storage (Kirchner, D. B., J. C. Gaydos, and M. C. Battigelli, 1993). When exposed to air, water, and sunlight, energetic compounds will leach from propellant pellets and flakes as the nitrocellulose matrix loses its integrity. Propellant mixtures consist of five components that includes an oxidizer, or main propellant grain; a stabilizer, which reacts with

nitrogen oxides to stabilize the propellant during storage (Bergens, A 1985); a burning-rate modifier to slow the rate of deflagration; and binders and plasticizers, which enable loading and packing of propellant into the shell (Mirecki, June E. 2006). Solid propellants are classified into four different composition types: single-based, double-based, triple-based, and composites. A single-base propellant consists primarily of nitrocellulose. Double-base propellants consist of nitrocellulose infused with nitroglycerin. Triple-base propellants consist of nitrocellulose, nitroglycerin, and nitroguanidine. This study does not consider single-based propellants or composites.

Energetic plasticizers and binder compounds react in sunlight to produce a variety of transformation products within an aqueous solution. Nitroguanidine biotransformation in soil occurs under both aerobic and anaerobic conditions and the biotransformation rate is highly affected by the presence of organic carbon. The biotransformation process is significant due to the potential of nitrosoguanidine formation, a known carcinogen. However, generally, nitroguanidine is fairly stable in soils. Nitroguanidine dissolved

solution reacts to form nitrosoguanidine, hydroxyguanidine, and/or cyanoguanidine intermediates, and end products of guanidine, nitrite, nitrate, and ammonia (Kaplan,D.L. 1982),(Burrows,W.D. 1988), (Haag,W.R. 1990). Nitrosoguanidine transforms readily to cyanamide under UV light (Kaplan,D.L. 1982). These products of nitroguanidine photochemical transformations are more toxic than nitroguanidine (Vander Schalie, W. H. 1985),(Burrows,W.D. 1988). These transformation products give reason for concern when nitroguanidine is being deposited into the environment where water resources are present.

2,4-dinitrotoluene and 2,6-dinitrotoluene are suspected human carcinogens and can react resulting in new nitro aromatic compound products that are also known to be carcinogenic. Aerobic transformation of 2,4-dinitrotoluene to carbon dioxide and nitrite has been documented in soil slurries and munitions plant wastewater inoculated with known DNT-degrading microbes (Spain JC 1995),(Nishino,S.F. 1999),(Nishino SF 2000),(Christopher,H.J. 2000),(Zhang,C. 2000),(Snellinx,Z. 2003) and by

native microbes in DNT contaminated soil and aquifer material (Bradley,P.M. 1994),(Bradley,P.M. 1997). However, the persistence of 2,4-dinitrotoluene in soils colonized by DNT degrading microbes suggests slow rates of mineralization, possibly due to inhibition by 2,6-DNT (Nishino SF 2000)or nitrite (Smets BF 2001),(Fortner JD 2003).

Microbe-mediated transformation of nitroglycerine has been documented under aerobic ( Bhaumik,S. 1997),(Accashian,J.V. 1998),(Accashian,J.V. 2000),(White,G.F. 1996),(Marshall,S.J. 2001) and anaerobic (Wendt TM 1978),(Christodoulatos,C. 1997),(Bhaumik,S. 1997) conditions, by pure and mixed microbe cultures and cell extracts (Ducrocq C 1989),(Meng M 1995),(Blehert,D.S. 1997),(Accashian,J.V. 1998), and fungal cell cultures and extracts (Zhang,C. 2000). Both aerobic and anaerobic transformation pathways are described as successive denitrification reactions, from glycerol trinitrate, to dinitrate, then to mononitrate isomer intermediates, ultimately to form glycerol.

Chemical constituents undergo sorption processes that involve the association of a solute with a solid at the solid-solution interface at the pore scale. The specific reaction and the rate at which it occurs,

depends on the nature of the molecule in solution. The molecule may be hydrophobic where it prefers not to be in water or hydrophilic where the molecule prefers to interact with water. Charge of the molecule plays a major role in the sorption processes as well. Ionic or charged molecules will interact with soil particles and neutral molecules prefer to follow flow paths. The nature of the soil surface has an influence on sorption as well. Organic matter within soils influences fate and transport of compounds through interactions of carbon atoms with the compound. This study considers only linear descriptors of sorption behavior of contaminants within soil and utilizes linear sorption isotherms to describe phase changes of the contaminants. A direct, linear relationship between the amount of a solute sorbed onto the solid and the concentration of the solute, a sorption isotherm will plot as a straight line. The linear sorption descriptor used for analysis is the distribution coefficient,  $K_d$  ( $\text{cm}^3\text{g}^{-1}$ ), and is calculated by finding the slope of the linear isotherm. The distribution coefficient is a measure of a solute's tendency to partition to the solid phase. Larger distribution coefficient values indicate a high tendency for partitioning out of

solution and into solid phase ( $C_{\text{sorbed}}/C_{\text{solution}}$ ). Experimental data was used for this calculation and data was not extrapolated outside the limits of data, so as to eliminate assumption errors associated with linearity. Soils of this study showed that organic carbon content was greater than 1% from a soil weight basis. Under these circumstances a normalized partition coefficient for soil organic carbon,  $K_{\text{oc}}$  ( $K_{\text{d}}/f_{\text{oc}}$ ), with respect to the organic fraction of the soil can be determined. Larger values for soil organic carbon partition coefficients indicate the tendency for a hydrophobic organic solute to partition into the non-polar soil organic carbon fraction. Another descriptor used to measure how hydrophobic a compound within soils is the octanol-water partition coefficient,  $K_{\text{ow}}$ . The octanol-water partition coefficient is experimentally determined and is the ratio of a solute concentration in octanol to the solute concentration in water. Soils with low organic carbon content would retain organic compounds with high octanol-water partition coefficient values but might not retain those with low octanol-water partition coefficient values. Two other characteristics of soils that can have a large influence on the ability for solute transport

throughout a soil matrix are the cation exchange capacity, CEC and pH. Within the soil matrix there exists electrostatic attractions that govern solute interactions between ions. This is influenced by the gradient in surface charge densities. The soil property of cation exchange capacity is defined as the capacity for ion exchange of cations between the soil and the soil solution. The solution parameter of pH is the negative log of the H<sup>+</sup> ion concentration, which means a lower pH value has higher H<sup>+</sup> concentration. Soil pH can affect the capacity of a soil to exchange ions because the concentration of hydrogen atoms affects surface charge of soil surfaces and protonation of species in solution.

In order to better understand the interactions between soils and constituents during transport, analytical model simulations were conducted utilizing observed and calculated parameter values. By utilizing the experimental data from the transport column studies of contaminant constituents, model simulations can be developed with a high confidence about parameter estimation. The model simulations provide the ability to analyze fate and transport of constituents and extend the findings beyond the experimental column depths. This

provides a benefit to those interested in conducting remediation projects that require better insight to constituent fate and transport at depths that are more representative of field conditions.

Model simulations replicate a one-dimensional vertical transport condition and do not consider the lateral component of solute transport called horizontal dispersion. The analytical solution used for the solute transport model simulations includes multiple transport characteristics such as simultaneous adsorption and first-order decay of constituents (Van Genuchten, 1981). This model integrates both soil and contaminant parameters to measure changes in concentration over time within a vertical one-dimensional flow regime. Experimental data that includes sorption isotherms, dispersivity, and constituent degradation are utilized in the Van Genuchten model to estimate transport of constituents in the different homogenous soil types. Constituent interactions occurring between the different soils are captured within model simulations through the integration of a calculated retardation factor. Retardation is determined from the bulk density of soils, porosity of soils, and the distribution coefficient attained in batch

experimentation and laboratory analysis. To determine fate and transport of contaminants within the homogeneous media it is important to quantify dispersion of constituents. Dispersion is the result of local fluid velocities inside individual pores and between pores of different shapes, sizes, and directions that deviate from the average pore-water velocity. These velocity variations cause the solute to be transported down-gradient at different rates, thus leading to a mixing process similar to that of molecular diffusion. Dispersion is a passive process that occurs only during water movement and is a function of fluid velocity and dispersivity, a soil specific parameter. Soil type values for dispersivity are determined within the laboratory column experiments. The assumption made during the column studies is that the soil used for experiments is homogeneous and that throughout the duration of the column study, homogeneous integrity remains constant. Dispersivity is a soil parameter and the numerical value remains constant throughout the column depth, as long as compaction or preferential flow paths do not compromise soil homogeneity. The results of these models provide essential information to the fate and

transport of organic constituents within the different soil types. Coupling both models and experimental data provides insight to estimates of contaminant migrations and will help in implementation of environmental controls of contaminants for regulatory procedures.

The objective of this study is to quantify kinetic transport parameters through the use of batch experimentation. This work will help in determining the potential for several propellant constituents to be transported through different soils. Results of this work will provide critical information regarding fate in the soils for propellant constituents to support environmental management decisions in areas subjected to high munitions expenditure. The hypothesis is that soil organic carbon content will have a large influence on fate and transport of constituents. The propellant constituent parameter of aqueous solubility will have an implicit effect on the interactions of ions within the soil matrix and will be a governing factor in determining distribution.

## MATERIALS AND METHODS

### MATERIALS:

There were three soil types selected for the study of adsorption kinetics, which includes Catlin silt loam (fine-silty, mixed, mesic, superactive Oxyaquic Argiudoll), Plymouth (MMR) sandy loam (mesic, coated Typic Quartzipsamment), and Sassafras loam (fine-loamy, siliceous, mesic Typic Hapudult). Two of these soils, Plymouth sandy loam and Sassafras loam, were collected on military installations. Soils were air dried on a tarp and then sieved to a maximum particle size of 2mm and stored in 5gal buckets. Soils underwent particle size analysis using laser diffraction (Beckman Coulter LS 13 320) at the Center for Environmental Physics and Mineralogy and then classified. Soils were also analyzed using the pipette method at the Environmental Pedology Laboratory, University of Arizona.

Table 1: Results of soil textural analysis and particle distribution using laser diffraction and pipette methods.

	 Catlin	 Plymouth	 Sassafras
	Laser diffraction		
Clay (%)	15.73	14.04	16.37
Silt (%)	71.53	22.15	42.27
Sand (%)	12.75	63.46	41.37
Avg. diameter	27.67	302.02	86.00
Textural class	Silt loam	Sandy loam	Loam
	Pipette Method		
Clay (%)	20.93	12.66	16.38
Silt (%)	66.66	11.27	33.39
Sand (%)	12.41	76.06	50.23
Textural class	Silt loam	Sandy loam	Loam

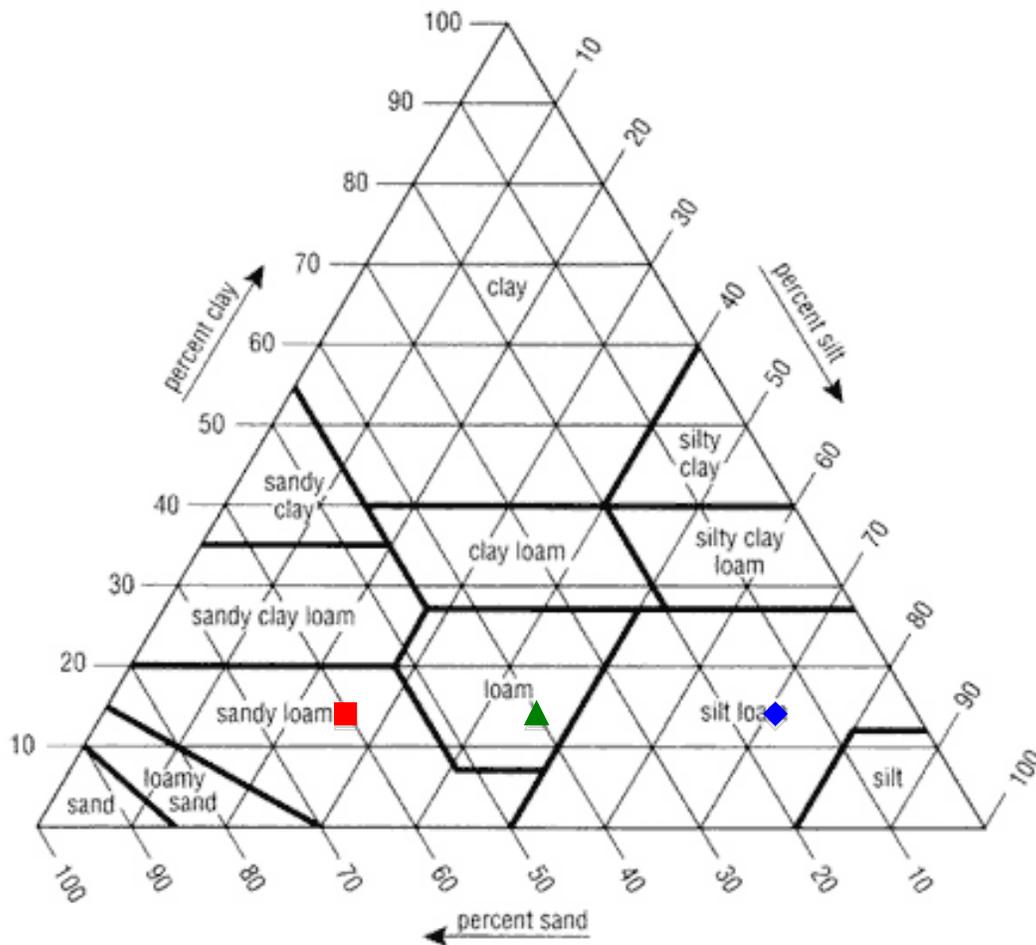
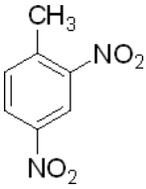
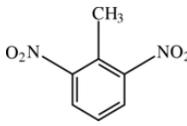
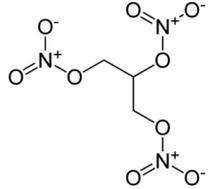
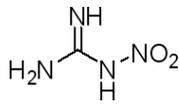


Figure1: Textural classification of Plymouth, Catlin, and Sassafras soil used in kinetic batch studies using laser diffraction measurements.

Propellants of interest for this study include 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), nitroglycerin (NG), and nitroguanidine (NQ). Propellant stock solution with a concentration of 1000 mg L<sup>-1</sup> from Restek were used to prepare input solutions for the batch experiments. NG and NQ stock solutions were preserved with

methanol, while 2,4-DNT and 2,6-DNT with acetonitrile and stored in a refrigerator at 4 °C.

Table 2: Properties of propellant constituents used in kinetic batch studies.

	2,4-DNT	2,6-DNT	NG	NQ
Molecular formula	$C_7H_6N_2O_4$	$C_7H_6N_2O_4$	$C_3H_5N_3O_9$	$CH_4N_4O_2$
Molecular structure				
$K_d$	2.34-15.30	0.27-2.49	0.26-1.41	0.14-0.61
$\log K_{ow}$	1.98-2.01	2.05-2.28	1.62-2.81	-0.89-0.156
$\log K_{oc}$	2.26-2.61	1.20-2.09	1.31-1.91	0.58-1.67
Solubility	0.166-0.280	0.182-0.208	1.25-1.95	2.60-5.00
$t_{1/2}$	0.9-2.6	1.2-1.7	0.7-2.0	21.7-41.5

(Mabey, W.R. 1982)

## METHODS:

When conducting kinetic adsorption batch studies, input solutions were prepared with stock solutions of 2,4-dinitrotoluene, 2,6-dinitrotoluene, nitroglycerin, and nitroguanidine. Triplicate samples of the four propellant constituents were individually mixed with the three soil types. Input solutions were made by mixing 0.5mL of 1000mg L<sup>-1</sup> liquid stock solution into a 250mL amber glass bottle containing 249.5mL of a 0.05 M CaCl<sub>2</sub> solution. Batch experiments were conducted by mixing 10mL of a 2mg L<sup>-1</sup> input solution with 2.5g of soil in 25mL glass centrifuge vials. Triplicate batch experiments maintained a 4:1 solution/soil mass ratio. Samples were placed on a reciprocating shaker at 180 excursions per minute and equilibrated for 0, 1, 2, 6, 12, 24, 48, and 120hr. Samples were centrifuged for 30 min. at 2980RCF at a temperature of 21°C immediately after removal from the reciprocating shaker. 3ml of supernatant solution was sampled into a 3mL BD syringe with a Millex 0.45µm Hydrophobic fluoropore (PTFE) filter and put into a 4ml. amber bottle with 1mL of acetonitrile. Nitroguanidine solutions were filtered without the addition of acetonitrile. Samples were analyzed for target compounds by high performance liquid

chromatography (HPLC) using U.S. EPA Method 8330b for nitroglycerin, 2,4-dinitrotoluene, and 2,6-dinitrotoluene, and Walsh (1989) method for nitroguanidine. Equipment used for HPLC analysis included Waters 600 controller, 717 plus autosampler, and 996 Photodiode Array Detector (Waters Inc.). The two column types used for HPLC analysis included a Waters 150x3.9mm Nova-Pak C8 4 $\mu$ m and Grace 250x4.6mm RP-C18 100A 5 $\mu$ m. The C-8 column was used for nitroglycerin, 2,4-dinitrotoluene, and 2,6-dinitrotoluene. Their mobile phase for the column was an 85 percent 45 $\mu$ m filtered water and 15 percent isopropanol solution. The C-18 column was used for the nitroguanidine using 100 percent 45 $\mu$ m filtered water as a mobile phase. All mobile phase solutions were sparged for a 4hr minimum time with helium to remove dissolved air. The 600 Waters controller was used in isocratic mode with a flow rate of 1.5 ml min<sup>-1</sup> during the analysis. Experiment standard concentrations of 2500  $\mu$ g L<sup>-1</sup>, 1000  $\mu$ g L<sup>-1</sup>, 500  $\mu$ g L<sup>-1</sup>, 100  $\mu$ g L<sup>-1</sup>, and 50  $\mu$ g L<sup>-1</sup> were prepared by diluting 1000 mg L<sup>-1</sup> stock propellant solution. Standards for 2,4-dinitrotoluene, 2,6-dinitrotoluene, and nitroglycerin were diluted from the 2500ppb standard with 1:4 acetonitrile and 0.45 $\mu$ m filtered ultrapure water. Nitroguanidine

standards are only diluted with the mobile phase 0.45 $\mu$ m filtered ultrapure water.

The analytical model developed to better understand and present ideal predictions of the fate and transport of chemical constituents utilizes many transport parameters for concentration estimates. Several processes act simultaneously on a chemical constituent while being transported through soils which is why the analytical solution chosen for this research includes as many of these processes as possible. The solution presented for simulating movement of the solute within the porous medium is influenced by linear equilibrium adsorption and first-order decay. The model is a one dimensional simulation and is limited to vertical fluxes and ignores horizontal flow and transport of constituent concentrations over time. The upper boundary condition is a type-one or concentration-type which includes a 24 hour pulse input of constituents with a relative concentration of 1. The lower boundary condition is a third-type or flux-type boundary. These boundary conditions replicate boundary conditions of laboratory column studies. The model simulations were developed and programmed utilizing the MathWorks MATLAB R2011b software.

Multi-parameter analytical solution to chemical transport in a porous medium (Van Genuchten, 1981)

$$c(x, 0) = C_0$$

$$-D \frac{\partial c}{\partial x} + vc \Big|_{x=0} = \begin{cases} vC_0 & 0 < t < t_0 \\ 0 & t > t_0 \end{cases}$$

$$\frac{\partial c}{\partial x}(\infty, t) = 0$$

$$\text{equation parameters} \left\{ \begin{array}{l} C_0 = \text{initial concentration} \\ v = \text{groundwater velocity} \\ t = \text{time (hrs)} \\ x = \text{depth (cm)} \\ \mu = \text{contaminant production} \\ \gamma = \text{contaminant degradation} \\ D = \text{dispersion} \\ R = \text{retardation} \end{array} \right.$$

$$C(x, t) = \begin{cases} C_0 - \frac{\mu}{\gamma} * A(x, t) + B(x, t), & 0 < t \leq t_0 \\ C_0 - \frac{\mu}{\gamma} * A(x, t) + B(x, t) - C_0 A(x, t - t_0), & t > t_0 \end{cases}$$

$$\begin{aligned} A(x, t) &= \frac{v}{v+u} \exp \left[ \frac{(v-u)x}{2D} \operatorname{erfc} \left[ \frac{Rx-ut}{2(DRt)^{0.5}} \right] + \frac{v}{(v-u)} \exp \left[ \frac{(v+u)x}{2D} \right] \operatorname{erfc} \left[ \frac{Rx-ut}{2(DRt)^{0.5}} \right] \right. \\ &\quad \left. + \frac{v^2}{2\gamma D} \exp \left[ \frac{vx}{D} - \frac{\gamma t}{R} \right] \operatorname{erfc} \left[ \frac{Rx-vt}{2(DRt)^{0.5}} \right] \right] \end{aligned}$$

$$\begin{aligned}
& B(x, t) \\
&= \left( \frac{\mu}{\gamma} - C_0 \right) \exp \left[ -\frac{ut}{R} \right] \left\{ \frac{1}{2} \operatorname{erfc} \left[ \frac{Rx - vt}{2(DRt)^{0.5}} \right] + \left( \frac{v^2 t}{\pi R D} \right)^{1/2} \exp \left[ -\frac{(Rx - vt)^2}{4DRt} \right] \right. \\
&\quad \left. - \frac{1}{2} \left( 1 + \frac{vx}{D} + \frac{v^2 t}{DR} \right) \exp \left[ \frac{vx}{D} \right] \operatorname{erfc} \left[ \frac{Rx + vt}{2(DRt)^{0.5}} \right] \right\} + \frac{\mu}{\gamma} + \left( C_0 - \frac{\mu}{\gamma} \right) \exp \left[ -\frac{\gamma t}{R} \right]
\end{aligned}$$

$$u = v \left( 1 + \frac{4\gamma D}{v^2} \right)^{1/2}$$

## RESULTS

LABORATORY:

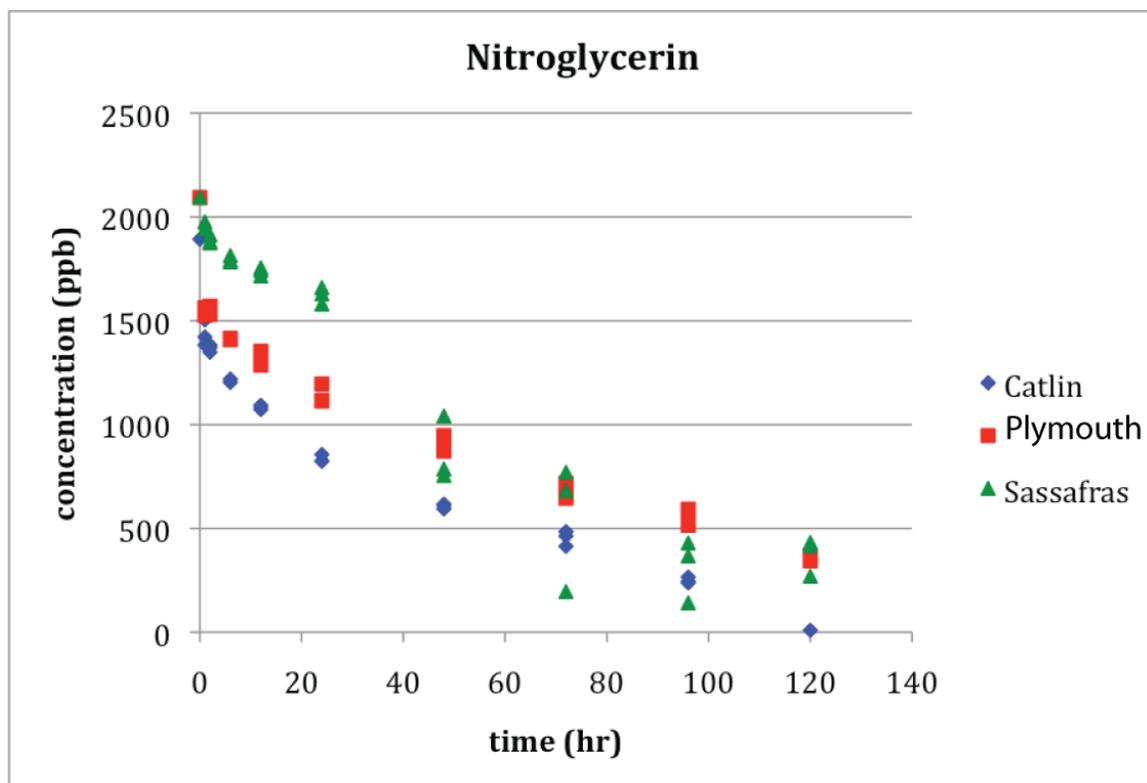


Figure 2: Nitroglycerin concentration as a function of time for studied soils.

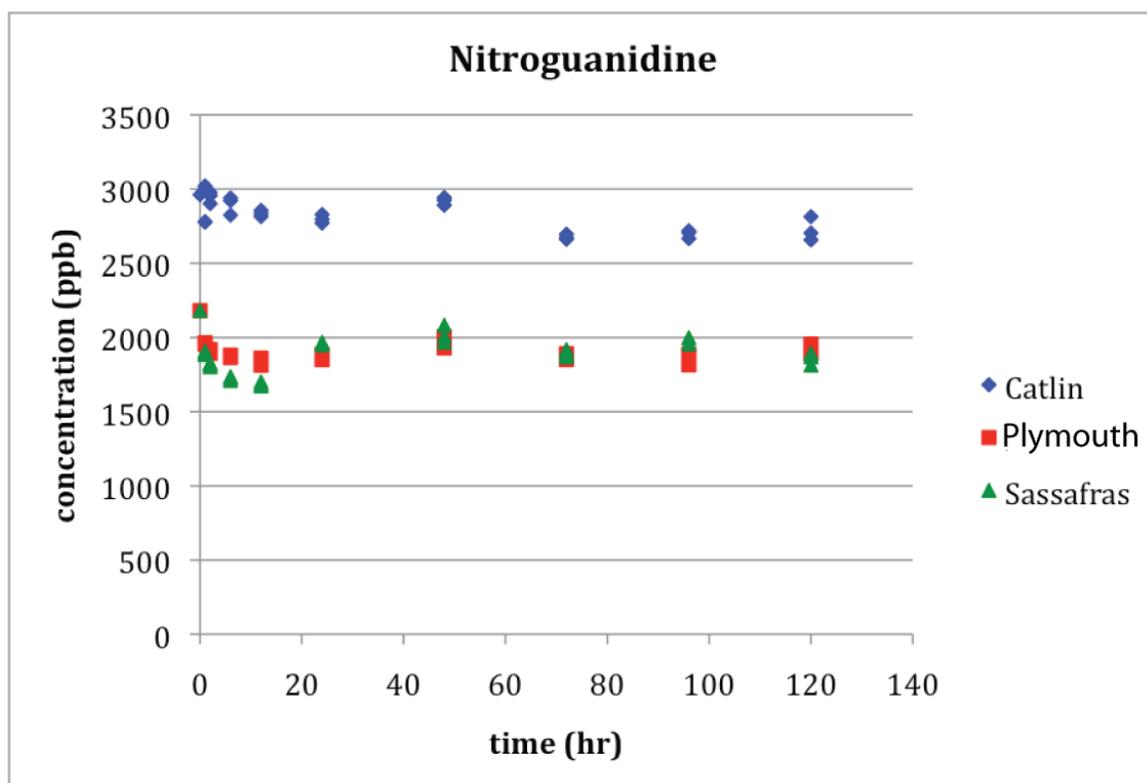


Figure 3: Nitroguanidine concentration as a function of time for studied soils.

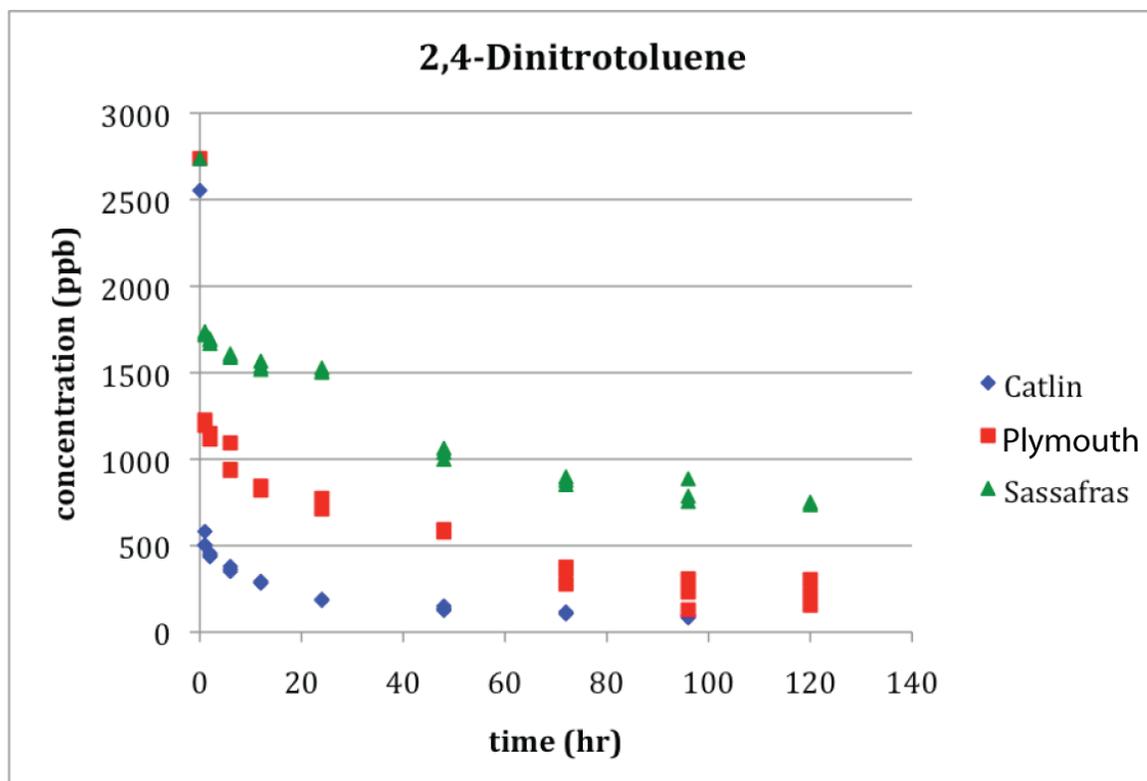


Figure 4: 2,4-dinitrotoluene concentration as a function of time for studied soils.

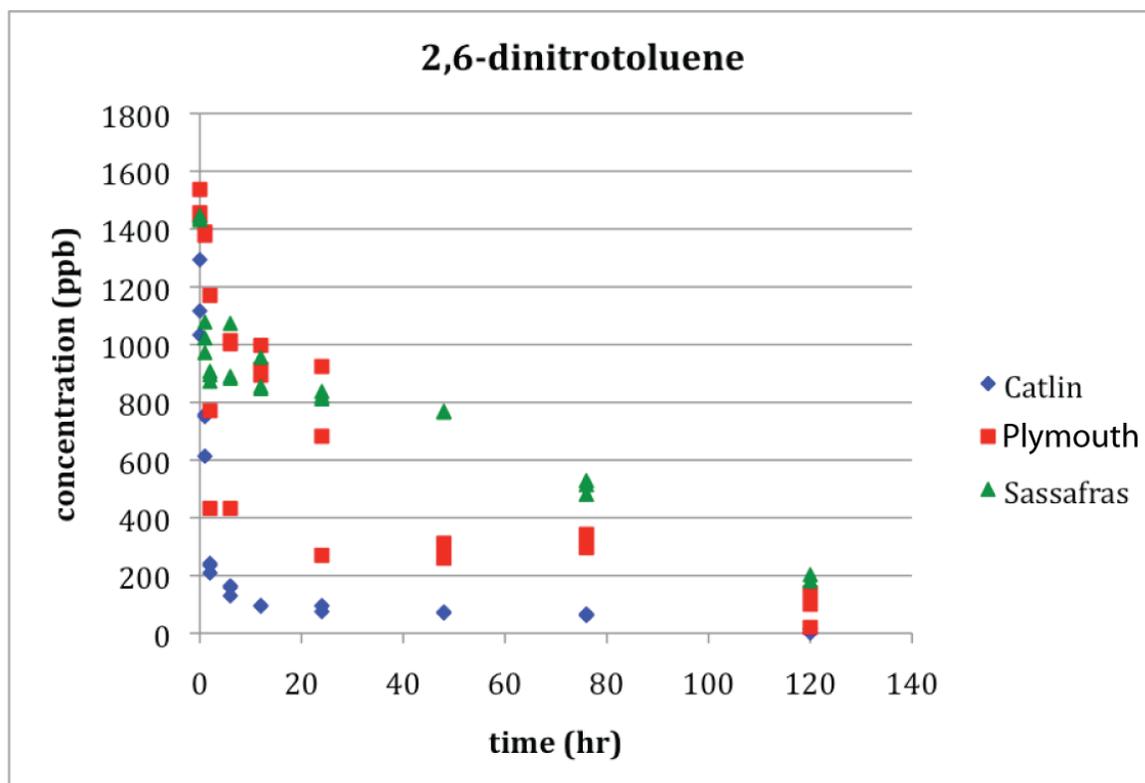


Figure 5: 2,6-dinitrotoluene concentration as a function of time for studied soils.

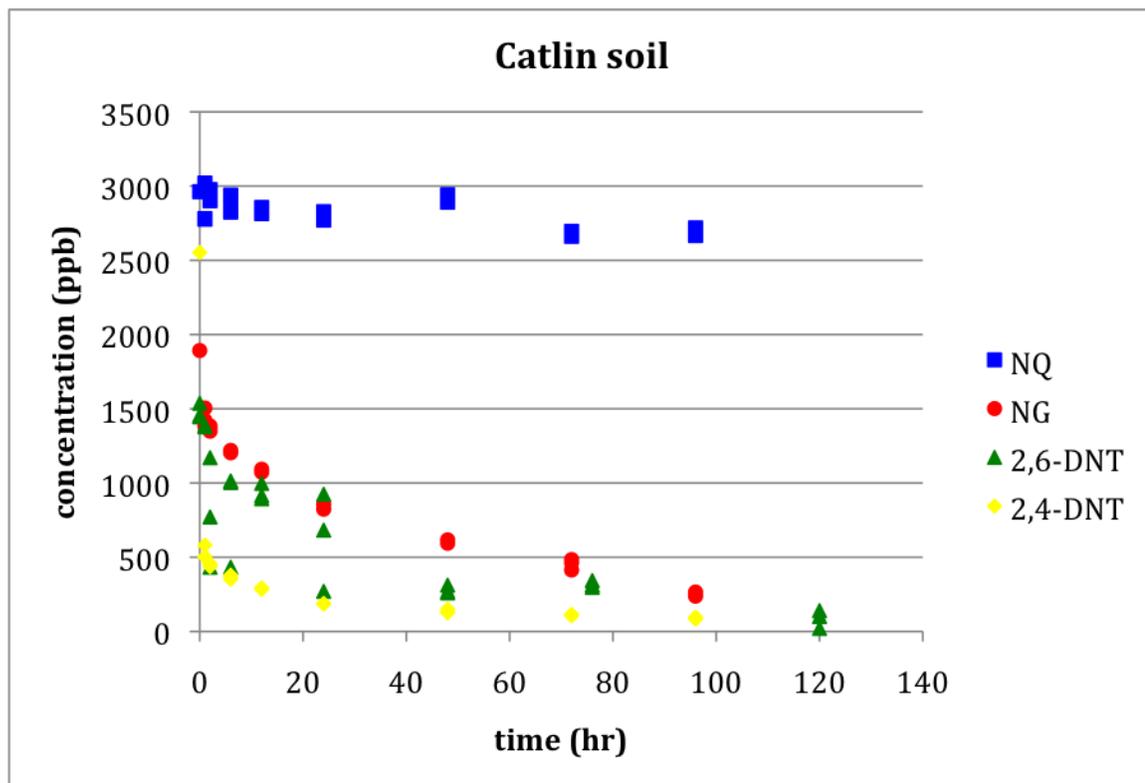


Figure 6: Concentration changes of constituents as a function of time in Catlin soil.

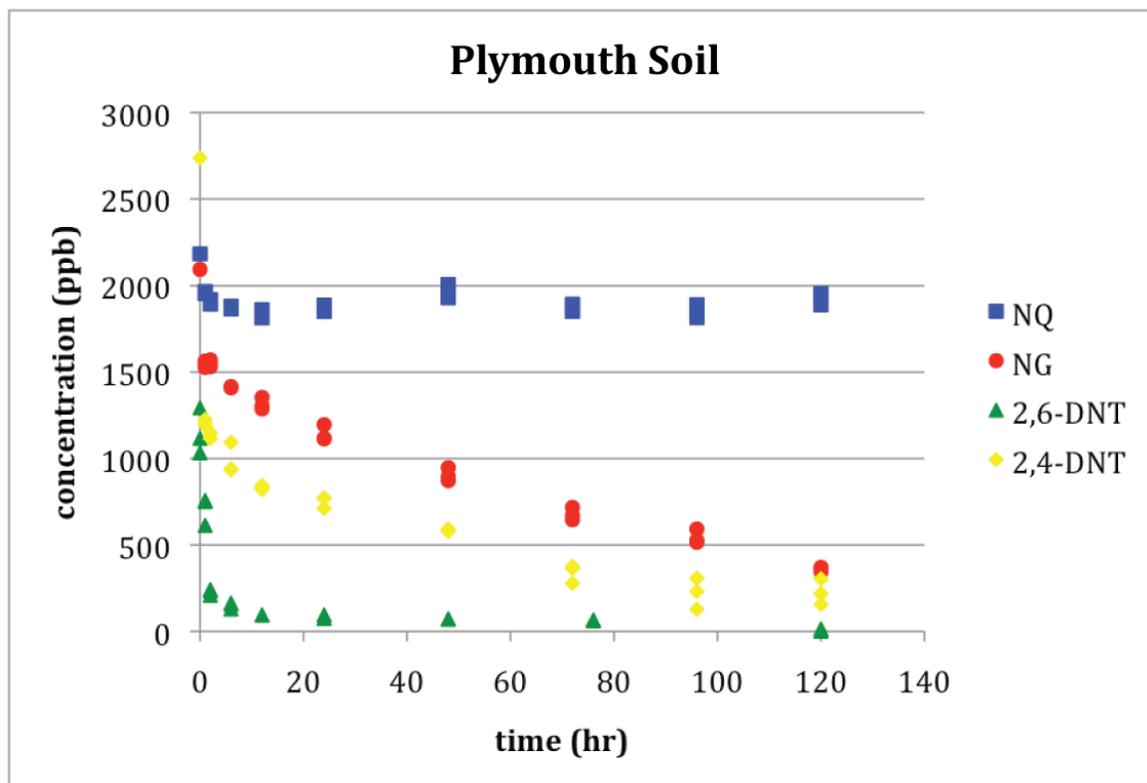


Figure 7: Concentration changes of constituents as a function of time in Plymouth (MMR) soil.

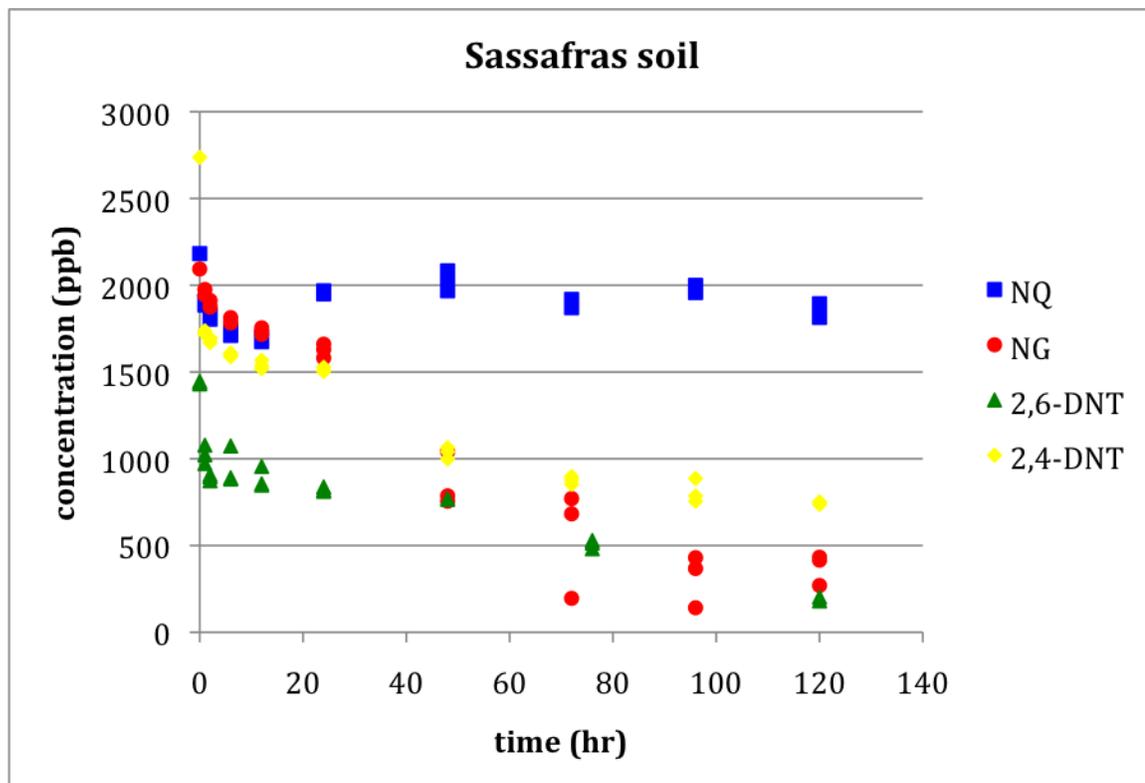


Figure 8: Concentration changes of constituents as a function of time in Sassafras soil.

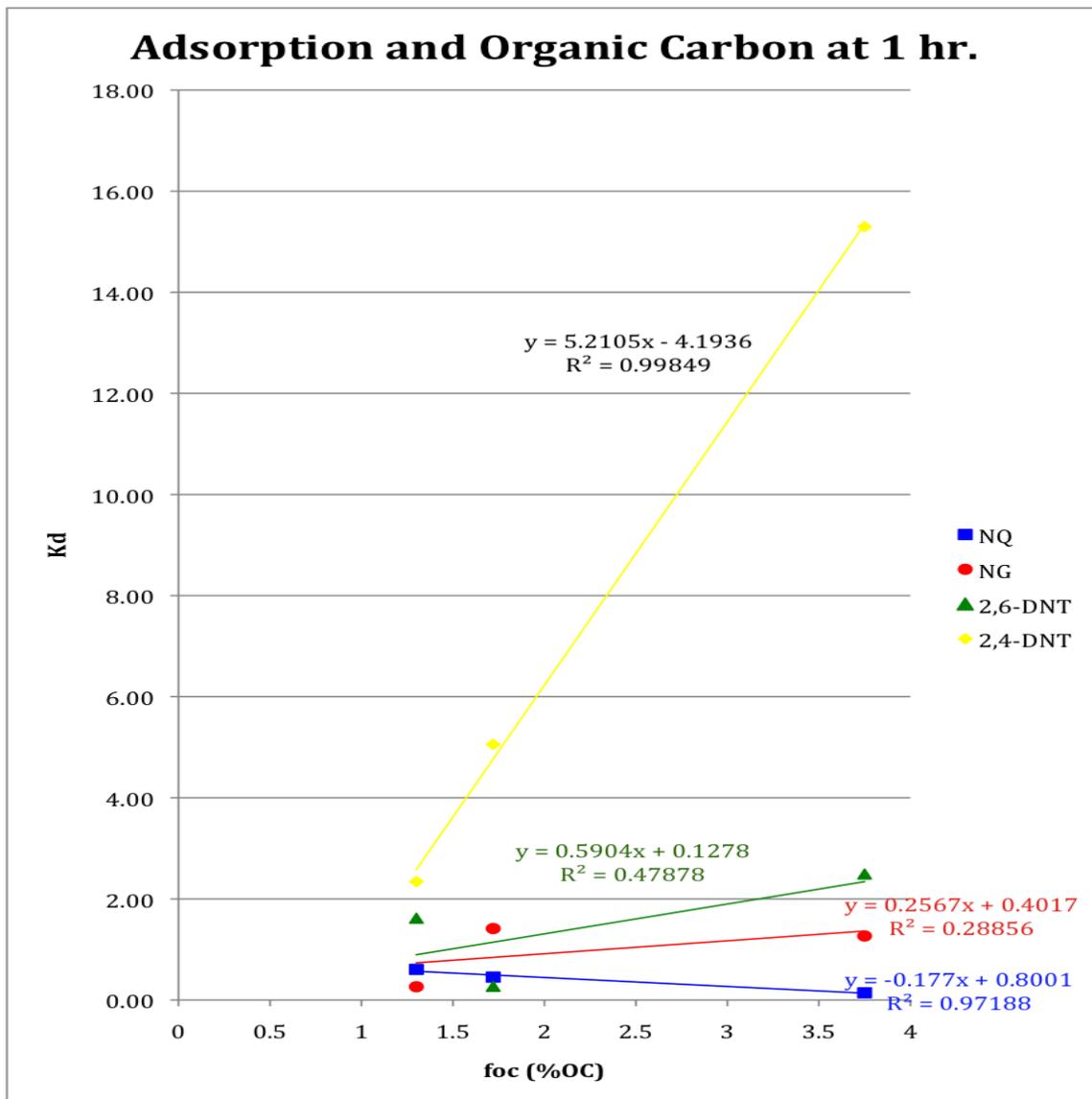


Figure 9: Linear sorption coefficients as a function of organic carbon content at 1hr.

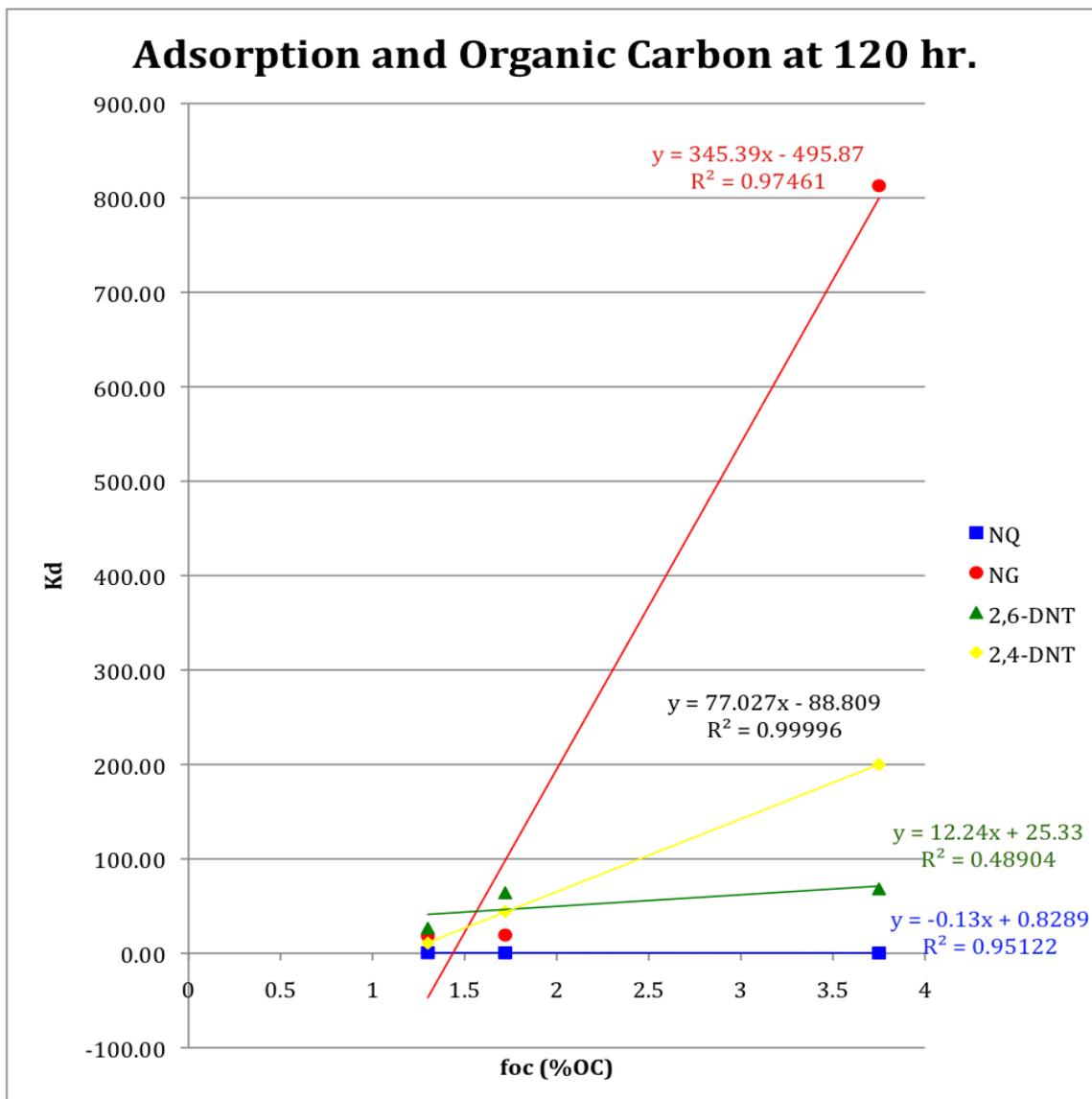


Figure 10: Linear sorption coefficients as a function of organic carbon content at 120hr.

Table 3: Calculated organic carbon content of soils, distribution coefficients, logKoc, degradation constants, and half-life of constituents within studied soils.

Compound	Soil	OC	K <sub>d</sub>	K <sub>oc</sub>	logK <sub>oc</sub>	k	R <sup>2</sup>	t <sup>1/2</sup>
		%	cm <sup>3</sup> g <sup>-1</sup>			h <sup>-1</sup>		days
NG	Sassafras	1.3	0.26	20	1.31	0.014	0.95	2.0
NG	Plymouth	1.72	1.41	82	1.91	0.015	0.99	2.0
NG	Catlin	3.75	1.27	34	1.53	0.044	0.78	0.7
NQ	Sassafras	1.3	0.61	47	1.67	0.001	0.19	21.7
NQ	Plymouth	1.72	0.45	26	1.42	0.001	0.01	26.3
NQ	Catlin	3.75	0.14	4	0.58	0.001	0.6	41.5
2,4-DNT	Sassafras	1.3	2.34	180	2.26	0.011	0.96	2.6
2,4-DNT	Plymouth	1.72	5.06	294	2.47	0.021	0.97	1.4
2,4-DNT	Catlin	3.75	15.30	408	2.61	0.033	0.94	0.9
2,6-DNT	Sassafras	1.3	1.62	124	2.09	0.017	0.91	1.7
2,6-DNT	Plymouth	1.72	0.27	16	1.20	0.024	0.92	1.2
2,6-DNT	Catlin	3.75	2.49	66	1.82	0.024	0.79	1.2

Table 4: Cation Exchange Capacity measured using Sodium Acetate Method, pH, and Electrical Conductivity.

Soil	Sassafras		Plymouth		Catlin	
Property	avg.	standard deviation (+/-)	avg.	standard deviation (+/-)	avg.	standard deviation (+/-)
pH	4.40	0.01	6.87	0.01	6.87	0.01
EC (uS cm <sup>-1</sup> )	212	27	130	6	538	20
CEC (cmolc kg <sup>-1</sup> )	16.58	1.32	18.78	2.87	23.59	0.98

## MODEL SIMULATIONS:

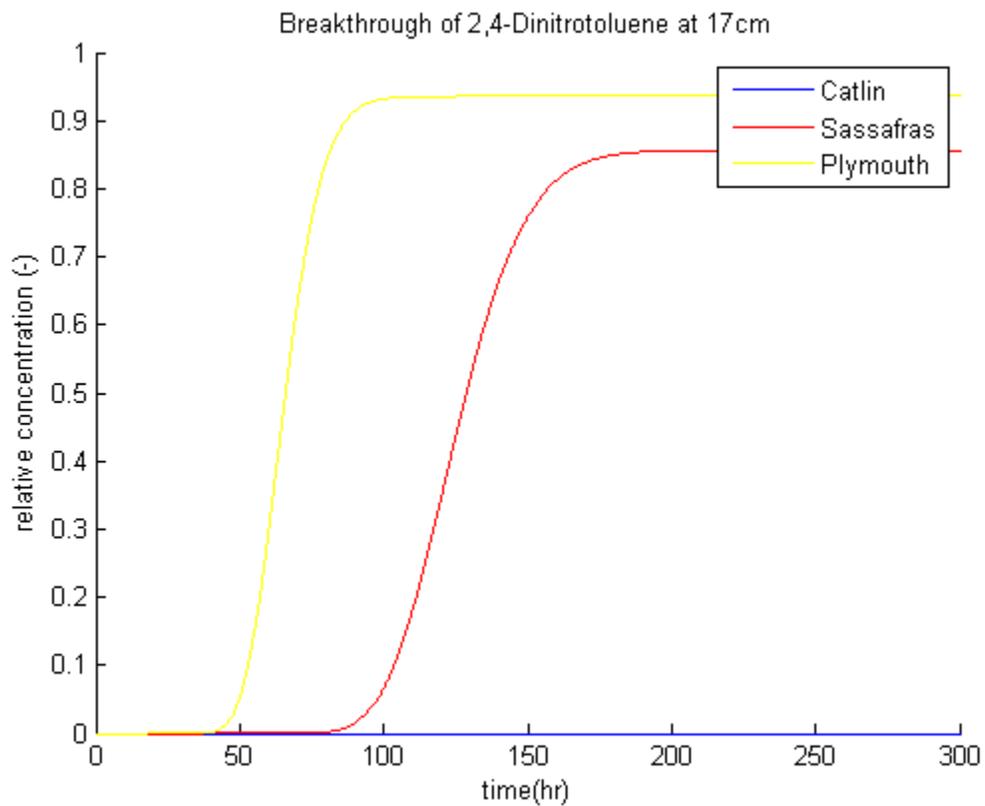


Figure 11: Simulated breakthrough curve of 2,4-DNT in soils at column experimental depth of 17cm.

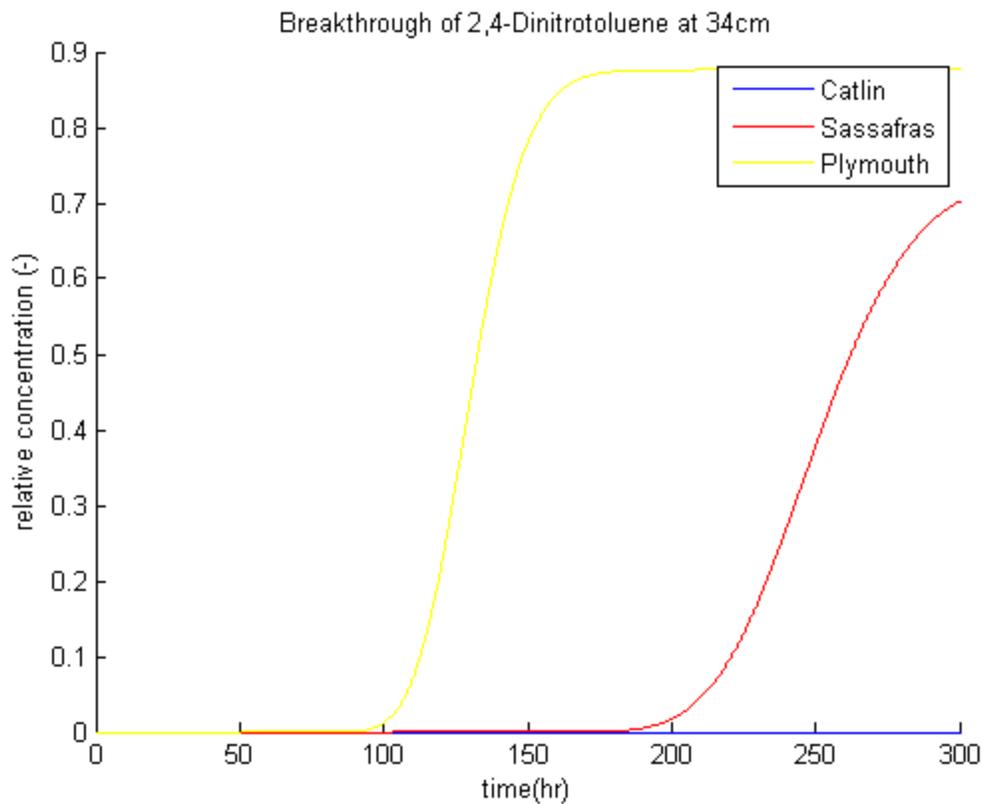


Figure 12: Simulated breakthrough curve of 2,4-DNT in soils at a depth of 34cm.

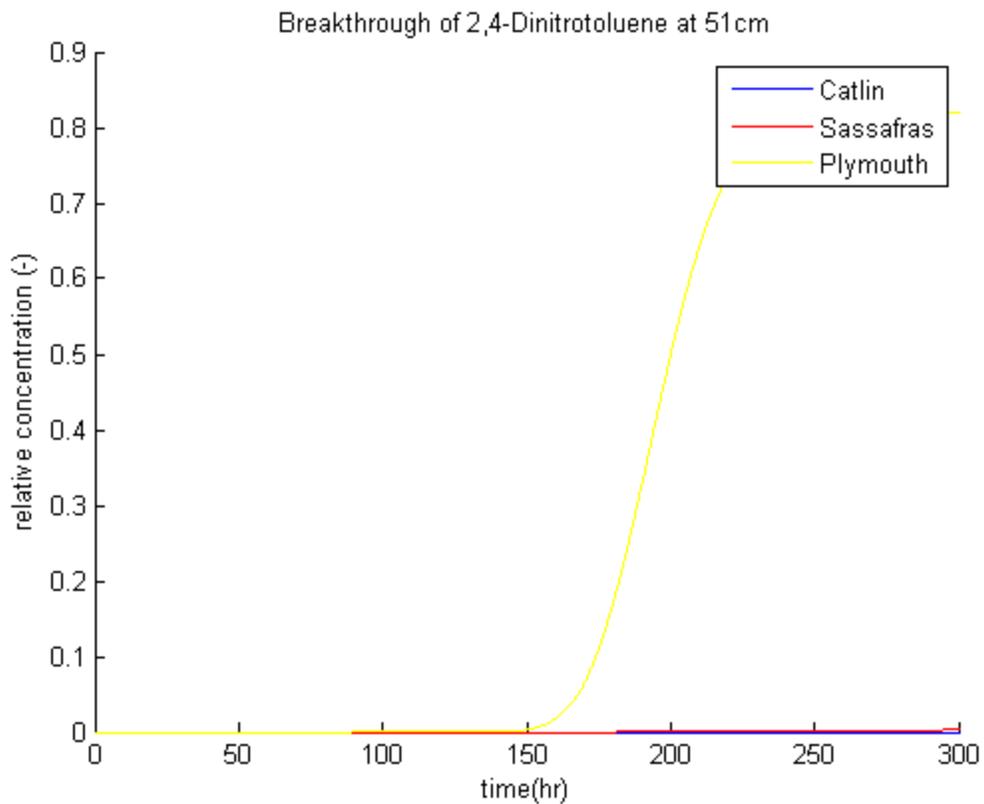


Figure 13: Simulated breakthrough curve of 2,4-DNT in soils at a depth of 51cm.

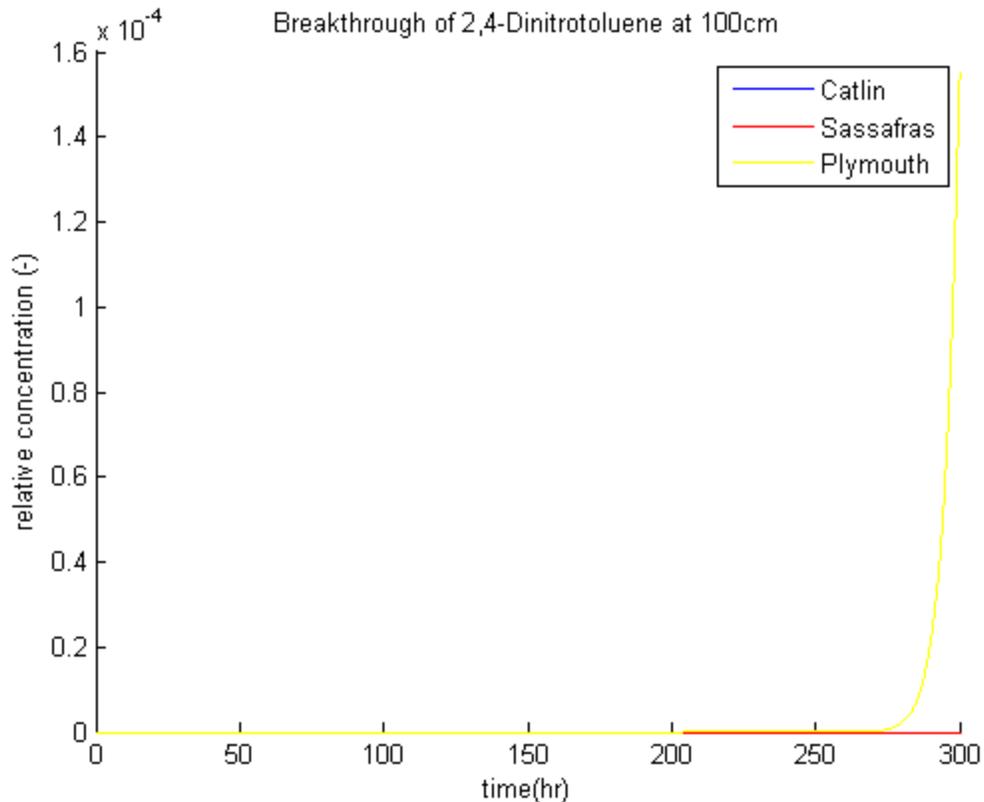


Figure 14: Simulated breakthrough curve of 2,4-DNT in soils at a depth of 100cm.

Model results for 2,4-DNT indicate constituent interactions within the soil is high and that soils high in organic carbon content have a heavy influence on the fate and transport of 2,4-DNT. Its interactions with soils containing lower organic carbon content contribute little to constituent transport. At depths greater than 34cm, the constituent transport is extremely delayed and the breakthrough in two soils is not captured in the time designated for the model simulation (figure 12).

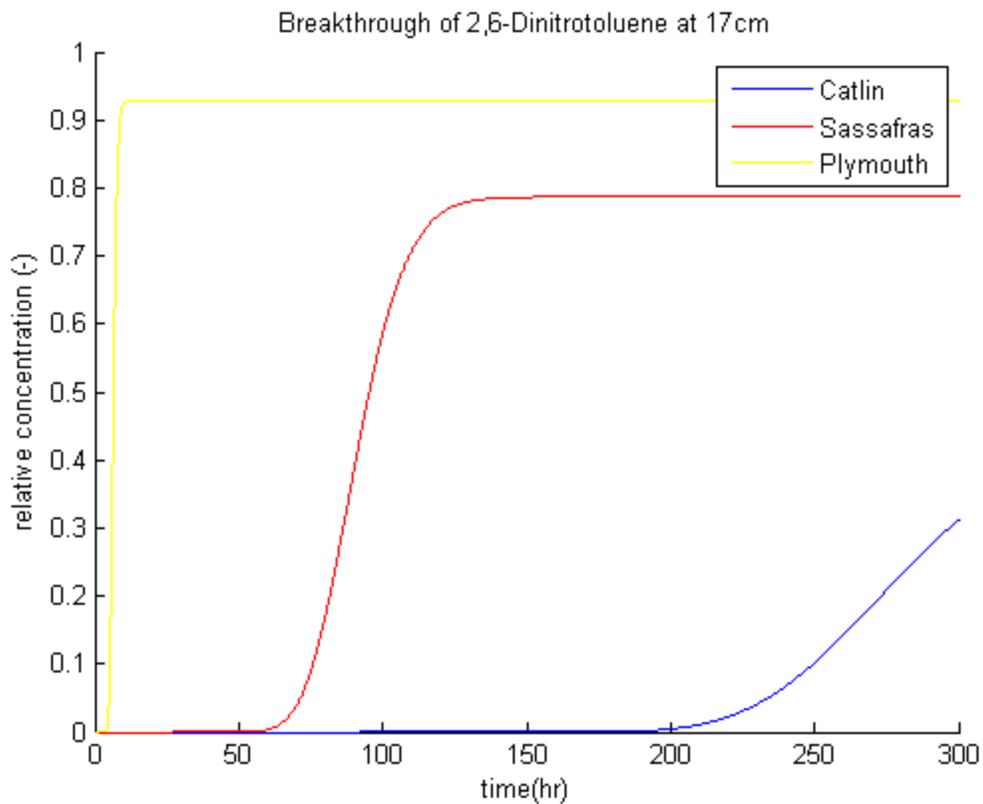


Figure 15: Simulated breakthrough curve of 2,6-DNT in soils at column experimental depth of 17cm.

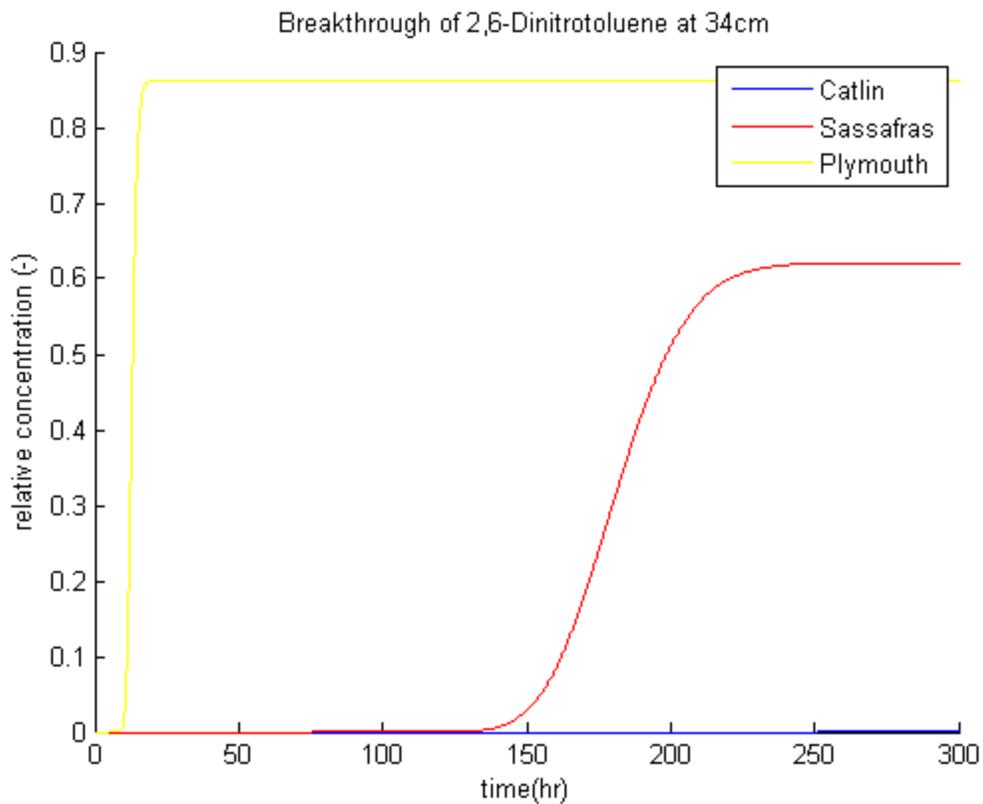


Figure 16: Simulated breakthrough curve of 2,6-DNT in soils at a depth of 34cm.

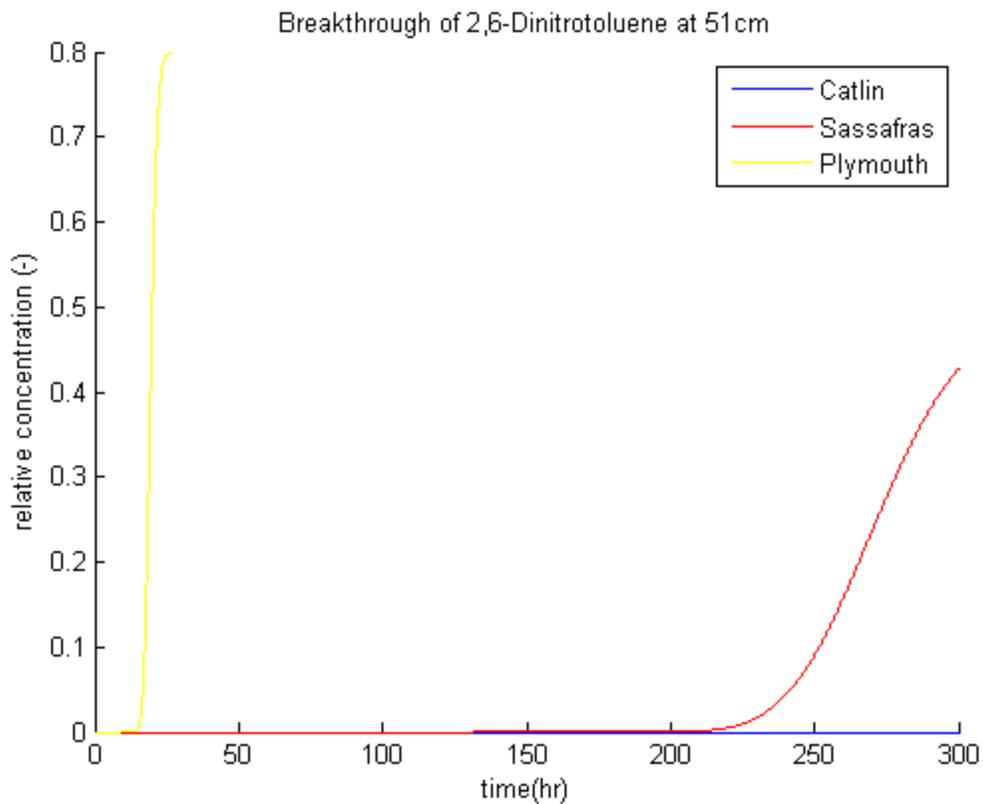


Figure 17: Simulated breakthrough curve of 2,6-DNT in soils at a depth of 51cm.

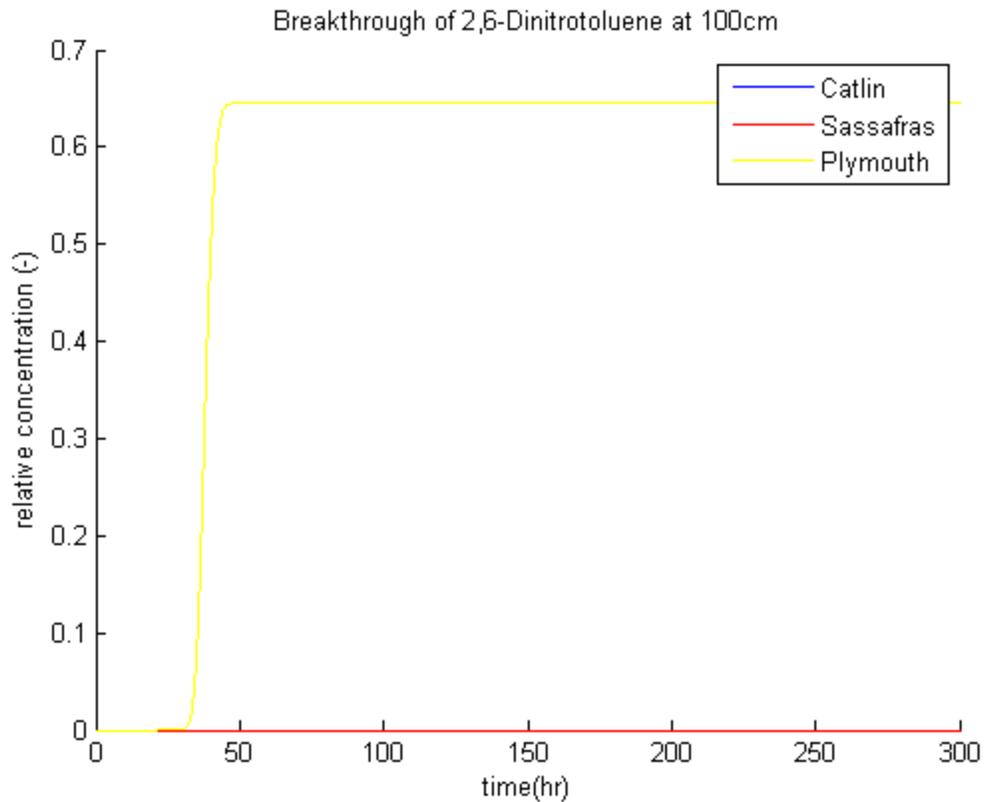


Figure 18: Simulated breakthrough curve of 2,6-DNT in soils at a depth of 100cm.

Breakthrough curves of 2,6-DNT show similar trends to that of 2,4-DNT except that breakthroughs are observed in Plymouth and Sassafras soils at depths of 51cm (figure 17). The high organic content of Catlin soils is a major factor to why constituent concentrations are not observed in the breakthrough curves of this simulation time duration.

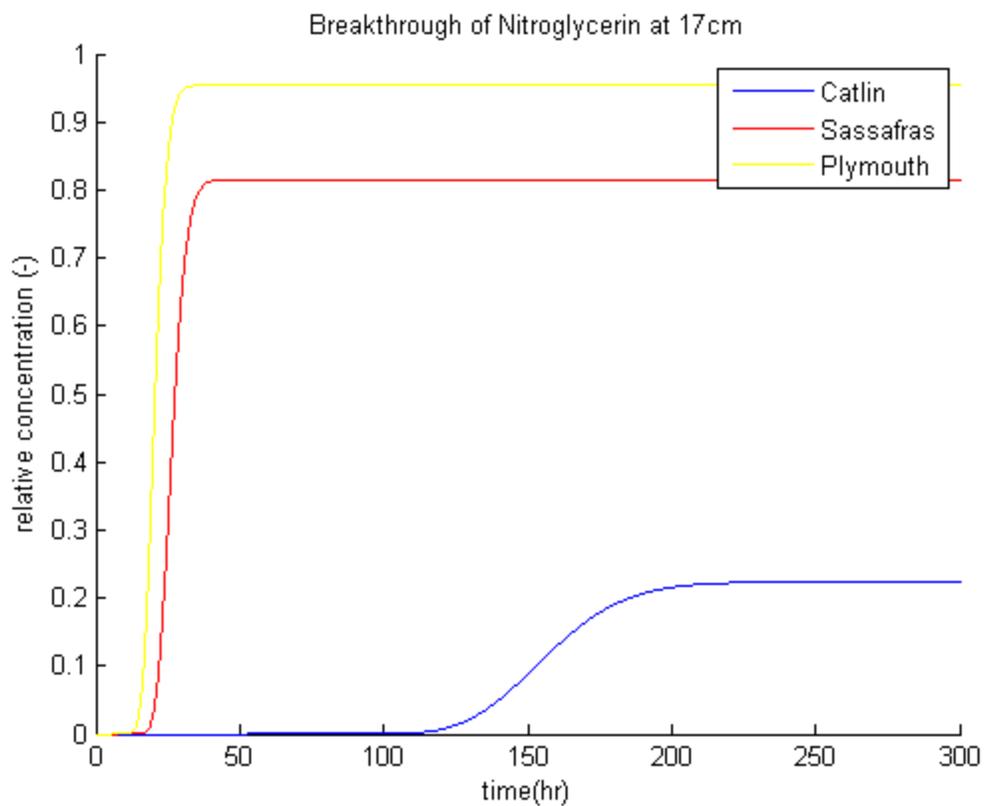


Figure 19: Simulated breakthrough curve of NG in soils at column experimental depth of 17cm.

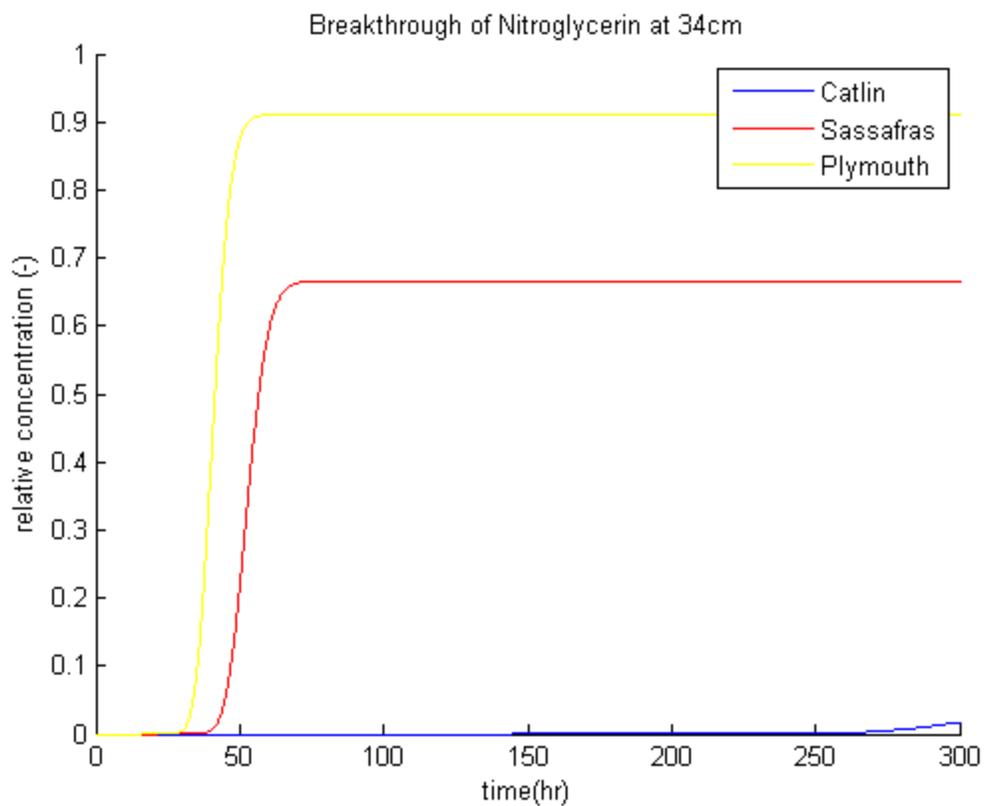


Figure 20: Simulated breakthrough curve of NG in soils at a depth of 34cm.

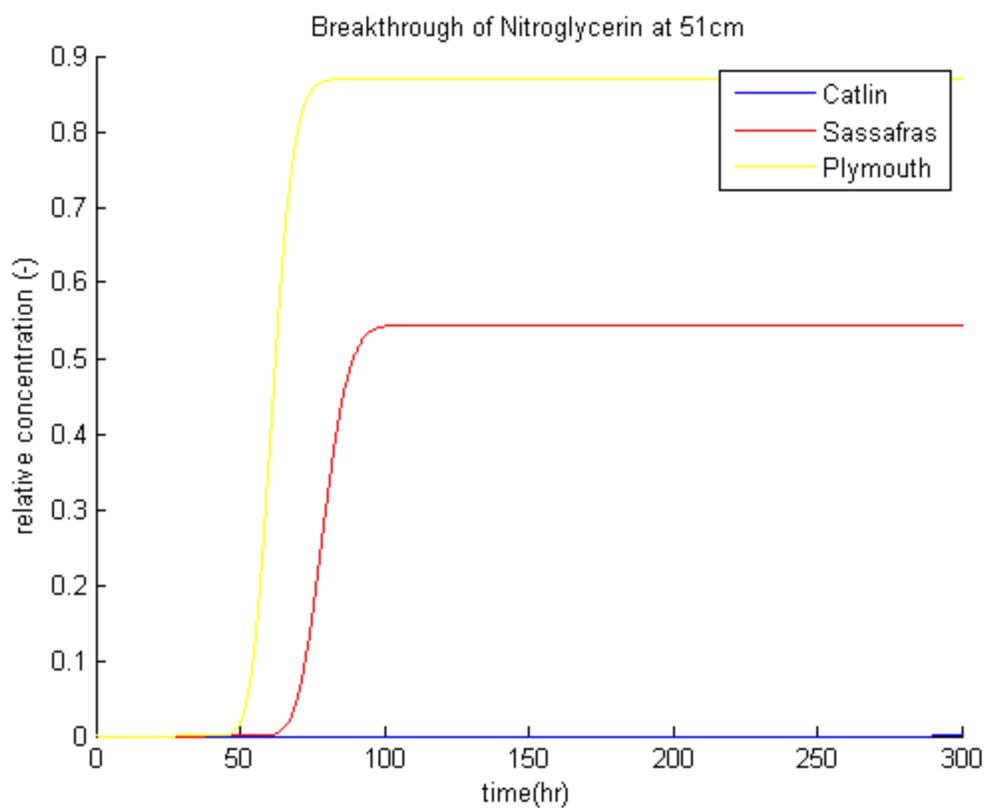


Figure 21: Simulated breakthrough curve of NG in soils at a depth of 51cm.

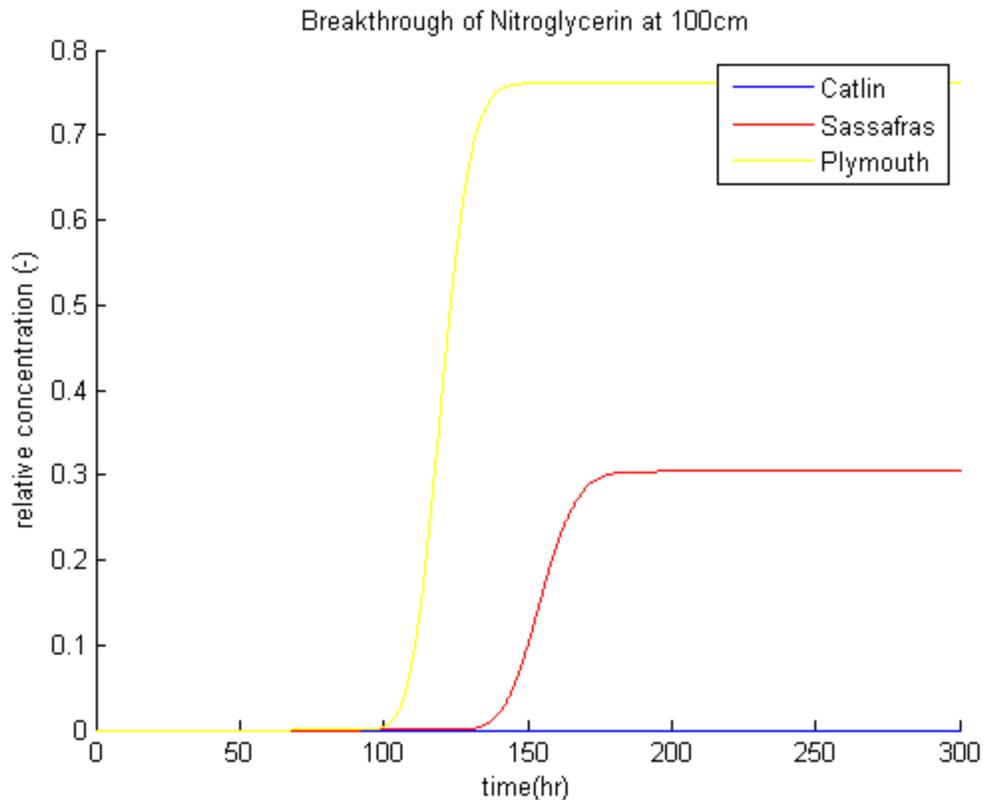


Figure 22: Simulated breakthrough curve of NG in soils at a depth of 100cm.

Breakthrough curves of NG within both Plymouth and Sassafras soils show relatively rapid transport rates at every depth. Even at 100cm depth Sassafras soil breakthrough curves show a relative concentration greater than 30% (figure 22). At depths of 34cm breakthrough of NG in Catlin soil only begins to start at later times in the simulation, approximately 250hrs (figure 20).

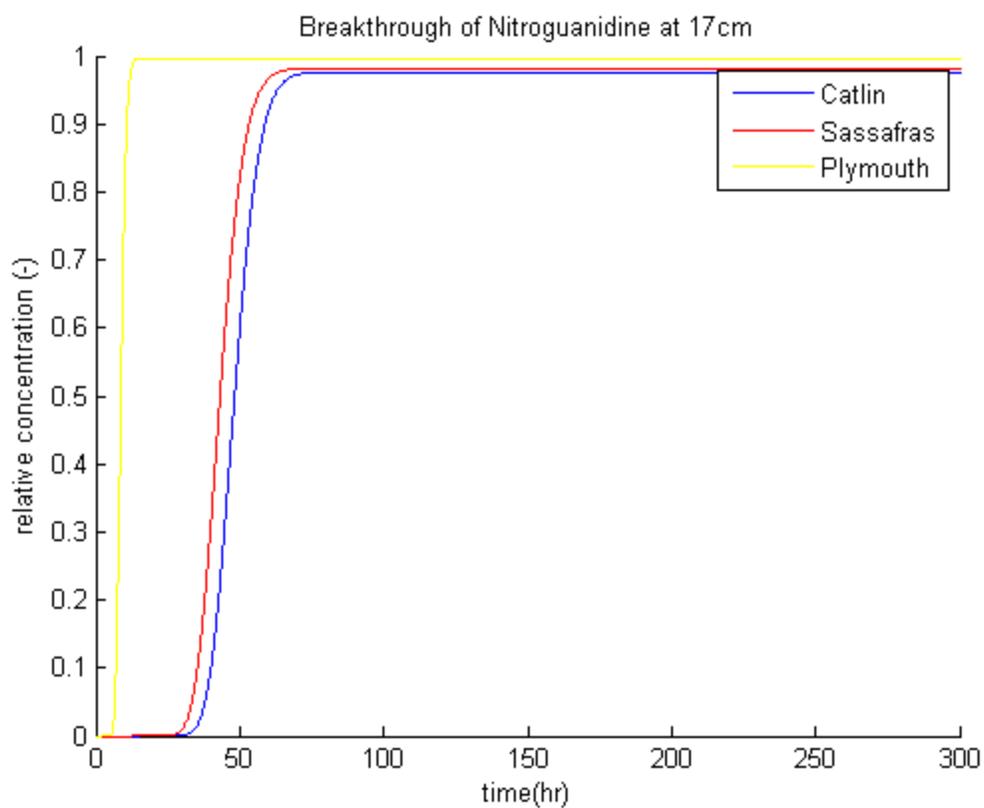


Figure 23: Simulated breakthrough curve of NQ in soils at column experimental depth of 17cm.

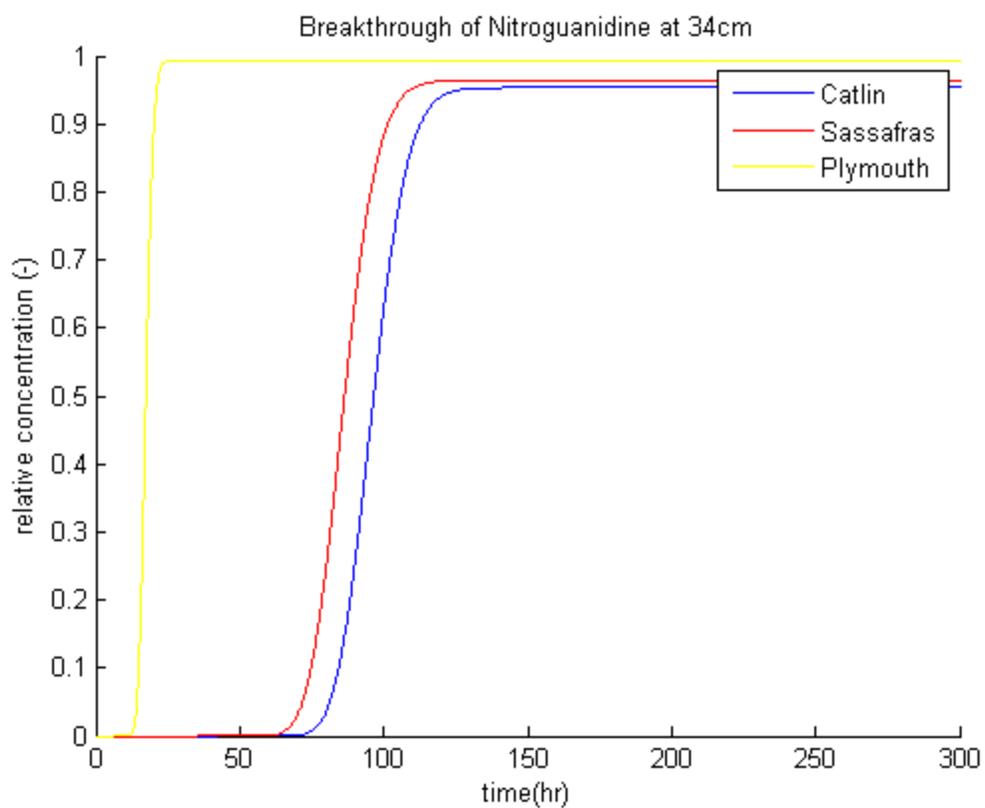


Figure 24: Simulated breakthrough curve of NQ in soils at a depth of 34cm.

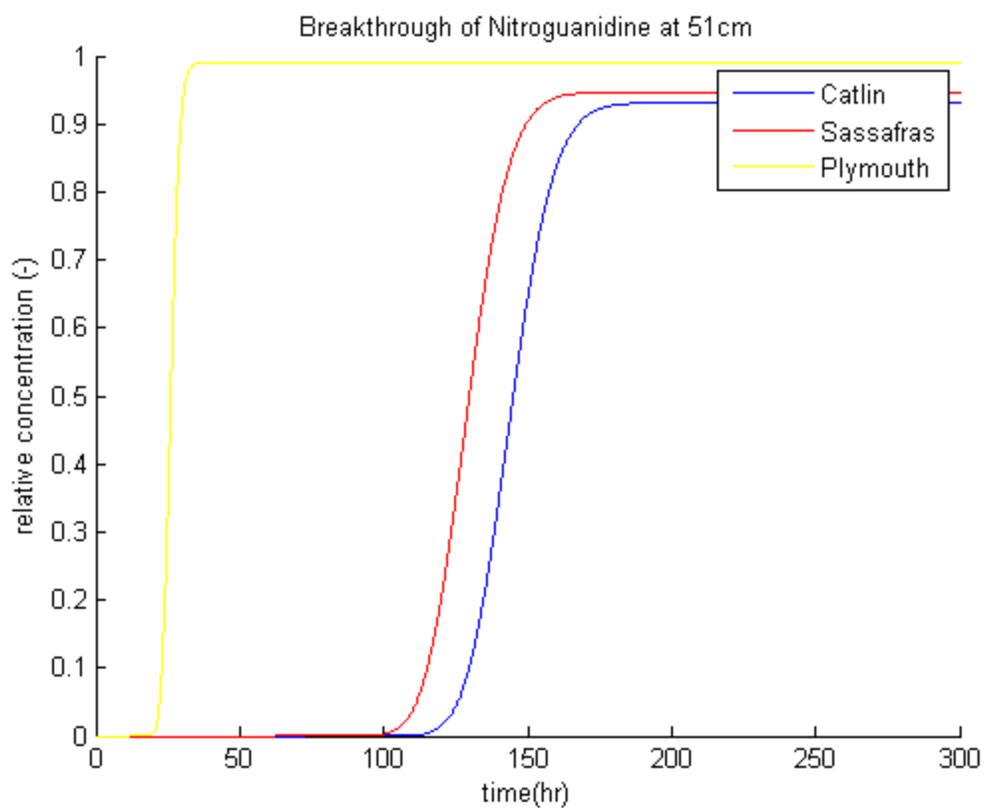


Figure 25: Simulated breakthrough curve of NQ in soils at a depth of 51cm.

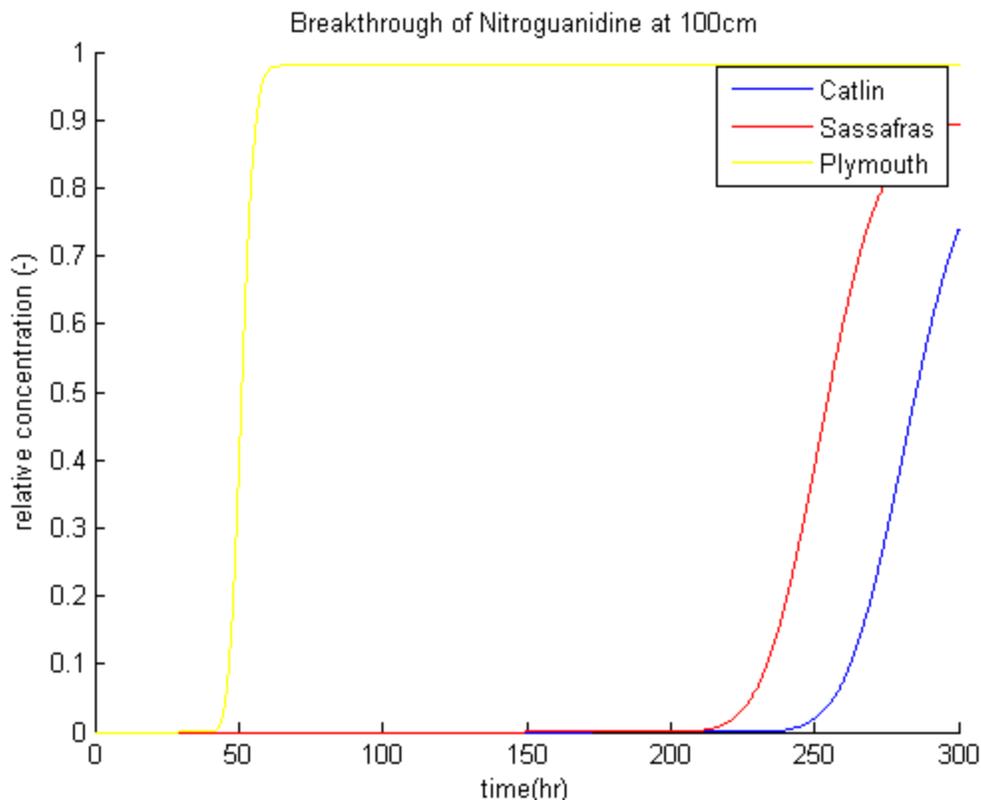


Figure 26: Simulated breakthrough curve of NQ in soils at a depth of 100cm.

Breakthrough curves of NQ through soils are very consistent with projected trends. Due to its structure, the constituent is highly soluble with a very low distribution coefficient which means very limited interactions with the soil surfaces during transport. Even at depths of 100 cm the simulation captures nearly 80% of the initial concentration (figure 26). The results of the model simulations show that depth and soil type have little effect on fate and transport of NQ within the subsurface. Analysis of the simulations reveals that constituent

contaminants are likely to be mobile in the environment at great depths and concentrations will remain high.

## DISCUSSION

Kinetic batch experiments were conducted to help determine the fate and transport parameters of propellant constituents within soils. Contaminants, such as these propellant constituents, are a growing problem because there is limited knowledge of their interactions within the environment. The batch study evaluated kinetic adsorption of propellant constituents to better understand distribution within the environment. These batch kinetic studies show trends in adsorption and degradation/transformation of propellant constituents as influenced by different soil types. HPLC analysis of the triplicate batch samples was able to capture the changes in concentration within a soil through time. Equilibrium time was determined from kinetic adsorption curves from experimental results of constituents within different soils representing multiple soil conditions. Distribution coefficients were calculated from the kinetic batch experiment results and a single-point linear sorption isotherm was utilized to calculate distribution coefficients of the contaminant constituents. Linear

adsorption isotherms are calculated from the initial solution concentrations and the partition of sediment concentrations. Mobility of propellant constituents is also indicated by high aqueous solubility and low distribution coefficient values. Where there is a low partition coefficient for soil organic carbon values it is an indicator that sorption is limited due to a low affinity to soil organic carbon. Catlin soil contained the largest amount of organic carbon. The distribution coefficient values of constituents and soil organic carbon content in Sassafras, Plymouth, and Catlin soils were calculated (Table 3). To make comparisons between propellant constituents and degradation within soils, a linear regression was fitted through all data comprised within the time of kinetic adsorption equilibrium. Propellant concentrations were calculated at the log scale for linear regression. Plymouth and Sassafras soil cation exchange capacities are relatively low compared to organic rich soils and clays. Likewise, the pH for both soils is low and thus hydrogen ion presence is high and there are less interactions of contaminants with the soils than if there were lower amounts of hydrogen ions, or a higher pH (table 4).

Results of this study show nitroguanidine (NQ) is highly mobile in soil environments. In recent studies, NQ has been found to have low log octanol-water partition coefficient values that suggest hydrophilic behavior. We found NQ to have a low log partition coefficient for soil organic carbon values that indicate limited sorption. NQ has high aqueous solubility, ranging between 2.60-5.00 gL<sup>-1</sup> and once in aqueous solution, NQ concentrations remain relatively constant with half-lives ranging from 41.5 to 21.7 days.

Few experimental data are available to interpret sorption behavior of both 2,4-dinitrotoluene (2,4-DNT) and 2,6-dinitrotoluene (2,6-DNT) so the results of these batch experiments will help in understanding its behavior in soil environments. Contaminant 2,6-dinitrotoluene (2,6-DNT), an isomer of 2,4-DNT, shares many similar chemical properties to that of its isomer. Larger log octanol-water partition coefficients and log distribution coefficients for soil organic carbon suggest moderately hydrophilic behavior and sorption that is fairly limited. Batch sorption experiments yielded high distribution coefficient values for 2,4-DNT, suggesting significant partitioning into

sediment. 2,6-DNT distribution coefficient values were an order of magnitude lower, which suggests partitioning into sediments not as significant.

Based on measured adsorption and transformation behavior it can be expected that NG would be mobile in the environment. It has a larger log octanol-water partition coefficient value which suggests moderately hydrophilic behavior, and low log soil organic carbon partition coefficient values that indicate limited sorption behavior. NG has a high aqueous solubility, ranging between 1.25-1.95 gL<sup>-1</sup>, which suggests an ability of the constituent to stay in solution NG half-lives were estimated to be in the range of 0.7-2.0 days.

Nitroguanidine exhibited minimal interaction with soils and exhibited little degradation/transformation over the experimental time period (Figure 3). Nitroglycerin, 2,4-DNT, and 2,6-DNT results show that there was a steady decrease in solution concentration indicating adsorption and degradation within all three soils (Figure 2, Figure 4, and Figure 5). All four compounds (NG, NQ, 2,4-DNT, and 2,6-DNT) exhibited dependence of adsorption on organic carbon (OC) content in

the soil (Figure 9). 2,4-DNT showed to have the strongest relationship of adsorption on organic carbon.

One-dimensional solute transport models were able to simulate predictions of the transport of constituent relative concentrations over distance and time. Nitroguanidine concentrations show sharp breakthrough curves within soils at great depths. This is expected when considering the experimental parameters indicate low interactions within the soil matrix between contaminant and soil surfaces (table 1). NQ has the longest half-life of any of the other contaminant constituents but its transformation products are highly carcinogenic. When soils are found to be rich in organic carbon content then the rest of the contaminants show little to no breakthrough at depths greater than 51cm (figures 11 through 26). The resulting data outputs are reason for careful planning of remediation considerations. Depth and time issues associated with the constituent contaminants are critical in choosing which contaminant should be prioritized during the cleanup process. The amount of time that it takes for constituents to breakthrough at least 10% of relative concentrations is greater than that of contaminant

half-lives. As a consideration for real world applications of these findings, they only hold true for absolutely homogenous soils throughout the entire depths being considered for remediation. When subsurface heterogeneity begins to play a role in the fate and transport of contaminant constituents, then the findings of the column experiments and model simulations are not very good predictors. Preferential flow paths in heterogeneous medium tend to increase in size and there is less exposure to solid surfaces within the soil and therefore, lowers the amount of interactions between contaminants and soil particles. Further investigations can be made that introduce heterogeneity into soil columns and the model simulations.

## REFERENCES

- Accashian, J. V., B. F. Smets, and B. J. Kim. "Aerobic Biodegradation of Nitroglycerin in a Sequencing Batch Reactor." *Water Environment Research* 72.4 (2000): 499-506. Print.
- Accashian, J. V., et al. "Aerobic Growth on Nitroglycerin as the Sole Carbon, Nitrogen, and Energy Source by a Mixed Bacterial Culture." *Applied and Environmental Microbiology* 64.9 (1998): 3300-4. Print.
- Bergens A, Lundström K, and Asplund J. "Voltammetric Determination of the Stabilizing Additives Acardite II, Centralite I and Diphenylamine in Propellants." *Talanta* 32.9 (1985): 893-9. Print.
- Bhaumik, S., et al. "Aerobic and Anaerobic Biodegradation of Nitroglycerin in Batch and Packed Bed Bioreactors." *Water science and technology : a journal of the International Association on Water Pollution Research*. 36.2/3 (1997): 139. Print.

Blehert, D. S., et al. "Regioselectivity of Nitroglycerin Denitration by Flavoprotein Nitroester Reductases Purified from Two *Pseudomonas* Species." *Journal of Bacteriology* 179.22 (1997): 6912-20. Print.

Bradley, P. M., et al. "Microbial Transformation of Nitroaromatics in Surface Soils and Aquifer Materials." *Applied and Environmental Microbiology* 60.6 (1994): 2170-5. Print.

---. "Potential for Intrinsic Bioremediation of a DNT-Contaminated Aquifer." *Ground Water* 35.1 (1997): pp. 12-17. Print.

Burrows, W. D., et al. "Photochemistry of Aqueous Nitroguanidine." 1988.Web.

Christodoulatos, C., S. Bhaumik, and B. W. Brodman. "Anaerobic Biodegradation of Nitroglycerin." *Water research* 31.6 (1997): 1462-70. Print.

Christopher, H. J., G. D. Boardman, and D. L. Freedman. "Aerobic Biological Treatment of 2,4-Dinitrotoluene in Munitions Plant Wastewater." *Water research* 34.5 (2000): 1595-603. Print.

Dontsova KM, et al. "Dissolution and Transport of TNT, RDX, and Composition B in Saturated Soil Columns." *Journal of environmental quality* 35.6 (2006)Print.

---. "Dissolution and Transport of TNT, RDX, and Composition B in Saturated Soil Columns." *Journal of environmental quality* 35.6 (2006)Print.

Dontsova, Katerina M., et al. "Sorption of High Explosives to Water-Dispersible Clay: Influence of Organic Carbon, Aluminosilicate Clay, and Extractable Iron." *Journal of environmental quality*. 38.4 (2009): 1458. Print.

---. "Sorption of High Explosives to Water-Dispersible Clay: Influence of Organic Carbon, Aluminosilicate Clay, and Extractable Iron." *Journal of environmental quality*. 38.4 (2009): 1458. Print.

- Dontsova, Katerina M., et al. "Dissolution and Transport of 2,4-DNT and 2,6-DNT from M1 Propellant in Soil." *Chemosphere* 77.4 (2009): 597-603. Print.
- Ducrocq C, Servy C, and Lenfant M. "Bioconversion of Glyceryl Trinitrate into Mononitrates by Geotrichum Candidum." *FEMS microbiology letters* 53.1-2 (1989): 1-2. Print.
- Fortner JD, et al. "Soil Column Evaluation of Factors Controlling Biodegradation of DNT in the Vadose Zone." *Environmental science & technology* 37.15 (2003): 3382-91. Print.
- Haag, W. R., et al. "Aquatic Environmental Fate of Nitroguanidine." *Environmental Toxicology and Chemistry* 9.11 (1990): 1359-67. Print.
- Kaplan, D. L., J. H. Cornell, and A. M. Kaplan. "Decomposition of Nitroguanidine." *Environmental science & technology* 16.8 (1982): 488-92. Print.

Kirchner, D. B., J. C. Gaydos, and M. C. Battigelli, ed. *Combustion Products of Propellants and Ammunition*. . Office of the Surgeon General: Walter Reed Medical Center, 1993. Web.

Mabey, W. R. *Aquatic Fate Process Data for Organic Priority Pollutants : Final Report*. Washington, DC: Monitoring and Data Support Division, Office of Water Regulations and Standards, 1982. Print.

Marshall, S. J., and G. F. White. "Complete Denitration of Nitroglycerin by Bacteria Isolated from a Washwater Soakaway." *Applied and Environmental Microbiology* 67.6 (2001): 2622-6. Print.

Meng M, et al. "Denitration of Glycerol Trinitrate by Resting Cells and Cell Extracts of *Bacillus thuringiensis/cereus* and *Enterobacter Agglomerans*." *Applied and Environmental Microbiology* 61.7 (1995): 2548-53. Print.

Mirecki, June E., et al. "Environmental transport and fate process descriptors for propellant compounds." 2006.Web.

---. "Environmental transport and fate process descriptors for propellant compounds." 2006.Web.

Nishino SF, Paoli GC, and Spain JC. "Aerobic Degradation of Dinitrotoluenes and Pathway for Bacterial Degradation of 2,6-Dinitrotoluene." *Applied and Environmental Microbiology* 66.5 (2000): 2139-47. Print.

Nishino, S. F., et al. "Mineralization of 2,4- and 2,6-Dinitrotoluene in Soil Slurries." *Environmental Science and Technology* 33.7 (1999): pp. 1060-1064. Print.

Pennington, Judith C., et al. "Distribution and fate of energetics on DoD test and training ranges interim report 5." 2005.Web.

---. "Distribution and fate of energetics on DoD test and training ranges interim report 5." 2005.Web.

Pennington, Judith C., et al. "Distribution and fate of energetics on DoD test and training ranges interim report 3." 2003.Web.

---. "Distribution and fate of energetics on DoD test and training ranges interim report 3." 2003.Web.

Pennington, Judith C., et al. "Distribution and fate of energetics on DoD test and training ranges interim report 2." 2002.Web.

---. "Distribution and fate of energetics on DoD test and training ranges interim report 2." 2002.Web.

Pennington, Judith C., et al. "Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 2." 2002.Web.

---. "Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 2." 2002.Web.

---. "Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 3." 2003.Web.

---. "Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 3." 2003.Web.

Pennington, Judith C., et al. "Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 5." 2005.Web.

---. "Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 5." 2005.Web.

- Pennington, Judith, et al. "Explosive Residues from Low-Order Detonations of Heavy Artillery and Mortar Rounds." *Soil and Sediment Contamination* 17.5 (2008): 533-46. Print.
- . "Explosive Residues from Low-Order Detonations of Heavy Artillery and Mortar Rounds." *Soil and Sediment Contamination* 17.5 (2008): 533-46. Print.
- Smets BF, and Mueller RJ. "Metabolism of 2,4-Dinitrotoluene (2,4-DNT) by *Alcaligenes* Sp. JS867 Under Oxygen Limited Conditions." *Biodegradation* 12.4 (2001): 209-17. Print.
- Snellinx, Z., et al. "Microbial Consortia that Degrade 2,4-DNT by Interspecies Metabolism: Isolation and Characterisation." *Biodegradation* 14.1 (2003): 19-29. Print.
- Spain JC. "Biodegradation of Nitroaromatic Compounds." *Annual Review of Microbiology* 49 (1995): 523-55. Print.
- Van der Schalie, W. H. *The Toxicity of Nitroguanidine and Photolyzed Nitroguanidine to Freshwater Aquatic Organisms*. 8404 (ADA153-

045) Vol. Fort Detrick, MD: U.S. Army Medical Bioengineering Research and Development Laboratory, 1985. Print.

Wendt TM, Cornell JH, and Kaplan AM. "Microbial Degradation of Glycerol Nitrates." *Applied and Environmental Microbiology* 36.5 (1978): 693-9. Print.

Wendt, T. M., J. H. Cornell, and A. M. Kaplan. "Microbial-Degradation of Glycerol Nitrates." *Applied and Environmental Microbiology* 36.5 (1978): 693-9. Print.

White, G. F., J. R. Snape, and S. Nicklin. "Biodegradation of Glycerol Trinitrate and Pentaerythritol Tetranitrate by *Agrobacterium Radiobacter*." *Applied and Environmental Microbiology* 62.2 (1996): 637-42. Print.

Zhang, C., et al. "Slurry-Phase Biological Treatment of 2,4-Dinitrotoluene and 2,6-Dinitrotoluene: Role of Bioaugmentation and Effects of High Dinitrotoluene Concentrations." *ENVIRONMENTAL SCIENCE AND TECHNOLOGY -WASHINGTON DC-* 34 (2000): 2810-6. Print.

Zhang, Y. Z., et al. "Biodegradation of Glyceryl Trinitrate by *Penicillium Corylophilum* Dierckx." *Applied and Environmental Microbiology* 63.5 (1997): 1712-4. Print.