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**THE TRANSPORT AND FATE OF DETONATION RESIDUES
ORIGINATING FROM CRACKED UNEXPLODED ORDNANCE
IN THE VADOSE ZONE**

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Ce travail porte sur le transport des matériaux énergétiques (ME) dissous en transit dans la zone vadose. Contrairement à la plupart des études publiées dans ce champ d'expertise, notre travail présente une approche d'ingénierie. Pour cette recherche, les conditions climatiques et les sources d'explosifs ont été reproduites en laboratoire dans l'objectif de produire de l'information applicable aux champs de tirs des secteurs d'entraînement.

De grandes colonnes de sol non saturé ont été construites et placées dans un laboratoire à conditions climatiques contrôlées. Les précipitations et la température ont été ajustées pour reproduire les conditions réelles observées au champ de tir Arnhem, sur la base des forces Canadiennes (BFC) de Valcartier. La BFC de Valcartier est localisée à 25 km au nord de la ville de Québec. Le champ de tir repose sur un dépôt de sable moyen d'origine glaciaire et deltaïque. Le sable d'origine glaciaire d'Arnhem a été mis dans les colonnes.

Les sources d'explosifs ont été générées avec des mortiers de 81 mm à l'explosif brisant remplis avec de la composition B. La composition B est une combinaison de 60% de 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), de 39% de trinitrotoluène (TNT) et de 1% de cire. La composition B et ses composantes explosives RDX et TNT sont souvent utilisées dans les munitions militaires. Il était donc nécessaire de produire artificiellement des sources de contaminants à partir de ces munitions, dans des conditions contrôlées. Il est extrêmement difficile et dangereux de trouver et de récupérer des munitions non explosées (UXO – de l'expression anglaise *unexploded ordnance*) sur les champs de tirs. Il y a plusieurs façons de créer des UXO's. Cela peut être fait par des détonateurs défectifs, par l'impact de la munition sur les sols mous, par déflexion, par des vides créés lors du remplissage en explosif de la munition, ou encore par les détonateurs qui sont mal ajustés ou mal installés. Toutes les différentes sortes de munitions explosives peuvent générer des UXO. Le taux de production de UXO se chiffre entre 3-5%, selon le type de munition. La façon aléatoire dont les UXO's sont produits, l'accès difficile au terrain et le fait que la plupart des UXO's sont enterrés rend la tâche de trouver deux UXO identiques impossible. La similarité entre les sources d'explosifs disposées sur les colonnes expérimentales est très importante pour comparer les résultats. Pour ces raisons, il était nécessaire de produire des UXO's de façon contrôlée.

La génération expérimentale des sources d'explosifs a permis de démontrer expérimentalement pour la première fois le phénomène des munitions fendues. Les munitions fendent quand un UXO qui est déjà en place sur le terrain est frappé par un fragment d'une autre munition qui explose à proximité. Les fragments pénètrent l'extérieur de l'UXO et projettent les particules du remplissage d'explosif aux alentours du UXO. De plus, l'extérieur fendu de l'UXO laisse l'explosif qui reste à l'intérieur disponible pour la dissolution par l'eau qui entre en contact par les fissures. L'UXO qui est frappé par le fragment ne détonne pas. Il a été démontré que les munitions fendues produisent de grandes quantités d'explosifs qui sont disponibles pour être transportées dans la zone vadose. Jusqu'à 165.9 grammes de particules de composition B ont été mesurés autour d'une munition fendue, suite à l'impact de fragments. Puisque ces quantités d'explosifs peuvent être projetées dans l'environnement, les munitions fendues pourraient être des sources importantes de matériaux énergétiques sur les champs de tir, même si elles ne sont pas produites souvent. Il a été démontré que la distance idéale entre les deux munitions pour produire des munitions fendues varie entre 15 et 200 cm. Si les munitions sont plus près de 15 cm l'une de l'autre, l'UXO détonne au lieu de se fendre. Si elles sont plus éloignées que 200 cm l'une de l'autre, très peu de fragments pénètrent l'acier du UXO.

Ces sources d'explosifs ont été mises à la surface des colonnes de sols de 60 cm de diamètre et qui contiennent une épaisseur de sable de 60 cm. Ces colonnes ont été exposées à une année d'infiltration qui reproduisait les cycles de précipitation, d'évaporation et de transpiration pour la région de la BFC de Valcartier. Le cycle annuel de précipitation dans cette région est caractérisé par deux événements majeurs, soit la fonte de la neige au printemps et les fortes pluies en automne. Il n'y a presque aucune infiltration pendant l'hiver et l'été.

L'eau qui s'écoulait à travers les colonnes était recueillie et analysée pour son contenu en explosifs par chromatographie liquide de haute performance (HPLC), selon la méthode EPA 8330. Les concentrations en matériaux énergétiques dans l'eau sortant des colonnes étaient près des valeurs de saturation, après deux semaines d'infiltration. La première période d'infiltration a reproduit la fonte de la neige. L'hypothèse qui explique pourquoi ces valeurs sont aussi élevées est que les particules très fines du résidu de détonation provenant des munitions fendues sont dissoutes très rapidement. Les particules fines ont un ratio surface spécifique élevé, ce qui accélère les cinétiques de dissolution, malgré les valeurs de solubilité qui sont très faibles pour les explosifs. Vers la fin de la première période d'infiltration, les concentrations d'explosifs dans

l'eau ont commencé à diminuer. Ceci est une indication que les fractions très fines des résidus de détonation ont été complètement dissoutes.

Une des colonnes de sol était utilisée pour une expérience avec un traceur inerte et ne contenait aucun explosif. Dix grammes de KBr ont été mis sur la surface au début de l'expérience et les concentrations en bromure étaient mesurées dans l'effluent de la colonne. Le bromure est un traceur inerte et sa concentration dans l'effluent était utilisée pour la caractérisation de l'écoulement non saturé dans les colonnes. La courbe des concentrations « bromure vs. temps » était aussi utilisée pour la calibration du modèle numérique d'écoulement dans les colonnes. Le facteur de retard pour les trois explosifs TNT, RDX et HMX a été de 1.56 ± 0.5 , ce qui indique que le temps nécessaire pour que ces trois composés sortent de la colonne est de 1.56 fois plus long que pour le bromure. Ceci est une indication d'adsorption minimale des matériaux énergétiques sur le sol sableux dans les colonnes. Les coefficients d'adsorption mesurés étaient de 0.123 L/kg pour le TNT, de 0.091 L/kg pour le RDX et de 0.18 L/kg pour le HMX. Ces valeurs sont en accord avec les valeurs de la littérature. Ces faibles valeurs sont une autre indication qu'il y a très peu d'adsorption de ces trois composés sur le sol, dans les colonnes provenant de la zone vadose du champ de tir Arnhem.

La période d'infiltration du printemps était suivie par quatre mois de sécheresse. Pendant les mois d'été au Québec, les pertes d'humidité par évaporation et transpiration sont équivalentes aux précipitations. Il n'y a donc pas d'écoulement vers la zone vadose.

Pendant la période d'infiltration d'automne qui a suivi les quatre mois de sécheresse, les concentrations initiales en composantes explosives dans l'effluent des colonnes ont augmenté très brièvement jusqu'aux valeurs de saturation. Ceci s'explique par une dissolution des résidus de détonation dans les eaux interstitielles qui étaient immobiles pendant la période de sécheresse. Cette masse dissoute très mobile a été immédiatement transportée dans la zone vadose lorsque l'infiltration d'automne a débuté.

Pendant les infiltrations du printemps et de l'automne, les concentrations en produits de dégradation du TNT dans l'eau de l'effluent étaient en général de plus d'un ordre de grandeurs plus faibles que les concentrations en TNT. Ceci est une indication de la vitesse à laquelle ces composantes sont transportées dans la zone vadose : il n'y a pas eu assez de temps pour que la transformation du TNT commence.

Les expériences de dissolution ont démontré que la fraction la plus fine des résidus de détonation a produit les concentrations les plus fortes dans l'eau, par rapport à la masse initiale. Les cinétiques de dissolution sont quant à elles linéaires et proportionnelles à la dimension des grains de résidus de détonation. De plus, les résultats préliminaires de dissolution supportent l'hypothèse que la fraction la plus fine des résidus de détonation est dissoute rapidement. Par contre, une fois que ces grains fins sont complètement dissous, les concentrations en matériaux énergétiques dans l'eau commencent à diminuer. Les tests de dissolution ont aussi fourni la fonction d'entrée pour les concentrations en matériaux énergétiques au sommet des colonnes qui ont servi au modèle numérique.

Le sol a été caractérisé afin que les résultats de ce travail puissent être comparés avec les autres données de la littérature concernant l'adsorption des matériaux énergétiques. Les caractéristiques physiques et chimiques des sols ont un impact important sur l'adsorption et le transport des matériaux énergétiques dans la zone vadose. La densité, la granulométrie, la courbe caractéristique sol-eau, le carbone organique total, la capacité d'échange cationique, la porosité et la fonction de conductivité hydraulique non saturée ont tous été définis par différents tests. Le sol était un sable moyen, relativement uniforme. Il y avait très peu de matière organique et presque aucune fraction argileuse. Tous les autres paramètres étaient en accord avec les valeurs de la littérature basée sur ces données.

Un modèle d'écoulement et de transport dans la zone vadose a été conçu avec le logiciel de modélisation numérique FEFLOW. Un modèle d'écoulement reproduisant chaque orifice au fond de la colonne était impossible à réaliser à cause des variations de tension produites par les mèches en fibre de verre qui étaient mises dans chacun des orifices. De plus, il a été démontré que les chemins d'écoulement non saturés étaient trop courts pour appliquer la loi de Fick, ce qui indique que l'équation de convection-dispersion n'était pas valide. Ce fait a limité la capacité du modèle numérique à reproduire parfaitement l'écoulement observé.

Le travail de cette thèse a démontré que les munitions fendues sont faciles à produire si les conditions sont favorables. Il est raisonnable d'assumer que ces conditions s'observent dans les champs de tir. Il a été démontré que les munitions fendues produisent de grandes quantités de matériaux énergétiques si une comparaison est faite avec les UXO's qui ne sont pas endommagés. Les contaminants libérés sont également très mobiles dans la zone vadose composée de sable

moyen. Il a aussi été démontré qu'il y a une augmentation temporaire de la concentration en matériaux énergétiques dissous dans l'eau d'écoulement, suite à une période de sécheresse. Jusqu'à 4.9 g de matériaux énergétiques provenant d'une munition fendue sont dissous et transportés dans la zone vadose pendant la première année où la munition est ouverte à l'environnement.

De plus, il a été démontré que le volume d'infiltration est la variable la plus importante permettant de prévoir la masse nette de matériaux énergétiques qui est transportée dans la zone vadose. Par contre, il y a aussi des corrélations positives entre la masse nette en matériaux énergétiques transportée et la source de ces matériaux. Les matériaux énergétiques provenant de munitions fendues sont plus disponibles au transport que les matériaux provenant d'explosifs purs. Ceci est probablement un effet dû aux différences physiques entre les grains des deux sources.

En parallèle avec les travaux complétés dans cette thèse, il y a eu beaucoup d'échantillonnage et de forage de puits d'observation faits sur différentes bases des forces Canadiennes. Ce travail avait pour but de caractériser l'eau souterraine des champs de tirs pour les traces en matériaux énergétiques. L'auteur a participé ou supervisé plusieurs de ces campagnes entre 2001 et 2004. Ces programmes d'observation d'eau souterraine avaient fourni des résultats avec lesquels l'effluent des colonnes expérimentales pouvait être comparé. Pendant les campagnes d'échantillonnage entre 1995 et 2004, seulement 1.4% des puits avaient des traces détectables de matériaux énergétiques. En raison des grandes quantités des matériaux énergétiques dissous observées dans l'effluent des colonnes expérimentales, il faut que l'effet de dilution créé par les aquifères sous plusieurs des bases des forces canadiennes ait un rôle clé pour atténuer les concentrations en matériaux énergétiques. Donc, le volume d'eau dans l'aquifère est une condition primordiale dans l'évaluation des risques reliés aux activités militaires sur l'environnement. Les grandes quantités d'eau diluent les matériaux énergétiques rapidement et il a été calculé que 14 800 munitions fendues par kilomètre carré seraient nécessaires pour produire des concentrations en RDX dissous dans l'eau souterraine qui soient supérieures aux limites mandatées par le US EPA de 2 ppb.

ABSTRACT

This work is an investigation of the transport of dissolved explosive contaminants as they pass through the vadose zone. Contrary to most research in this field, it is an applied science study. Field conditions and source terms were reproduced as closely as possible, in order to produce data that was applicable and relevant to actual ranges.

The work was performed in large unsaturated soil columns that were constructed in a climate-controlled laboratory capable of reproducing both the temperature and precipitation conditions at a given field site. These soil columns reproduced the vadose zone of the Arnhem range at Canadian Forces Base (CFB) Valcartier, located 25 km north of Quebec City. This range is located on an glacial and deltaique deposit of sand. This sand was used in the construction of the soil columns.

The explosive source terms were manufactured experimentally from 81 mm high explosive (HE) mortars filled with Composition B. Composition B is a combination of 60% 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), 39% trinitrotoluene (TNT) and 1% wax as a binder. Composition B, as well as its component explosives RDX and TNT are extensively used in military munitions. It was necessary to produce the source terms experimentally because of the difficulty and extreme danger involved in recovering unexploded ordnance (UXO) in the field. There are limitless ways that UXO's may be caused, including defective fuzes, impact on soft ground, deflection, voids in the explosive filler and improperly installed or set fuzes to name a few. Any type of explosive munition may fail to detonate and become a UXO. Typical failure rates with artillery rounds and mortars is in the range of 3-5%. Due to the random nature of UXO generation, the rugged and remote terrain onto which rounds are generally fired and the fact that many rounds are buried at significant depths, finding multiple UXO's that are physically similar is virtually impossible. Physical similarity of the source terms used on the experimental columns was important in order to allow a meaningful comparison of results between columns in subsequent leaching experiments. For this reason, it was necessary to generate the UXO source terms experimentally under controlled conditions.

The experimental generation of these source terms resulted in the first demonstration of the phenomenon of "cracked shell" unexploded ordnance. Cracked shells are generated when

unexploded ordnance, which is already lying on the ground, is hit by shrapnel from other munitions that explode nearby. The shrapnel fragments penetrate the exterior steel casing of the unexploded ordnance and spray fine particles of the explosive filler into the surrounding area. In addition, the cracked outer casing exposes the explosive filler which remains inside the shell. The cracked round that is hit by the shrapnel does not detonate. It was demonstrated that cracked shell UXO's generate large amounts of environmentally available energetic materials. Up to 165.9 grams of composition B fragments and particles may be projected from the cracked shell into the environment. They therefore may be important sources of energetic material contamination even if they are infrequently produced. It was found that the ideal proximity between the two munitions necessary to produce cracked shells was between 15 cm and 200 cm. If the munitions were held closer than 15 cm, both munitions would explode. If they were held further apart than 157 cm, only a slight amount of damage was produced.

These source terms were placed on the surface of 60 cm diameter and 60 cm deep cylindrical soil columns. The columns were subjected to one year of water infiltration that matched predicted precipitation, evaporation and transpiration for the region around CFB Valcartier. The annual infiltration cycle in this region is characterized by two major annual events, the spring snowmelt and the autumn rainstorms, with minimal infiltration during the winter or summer periods.

The water that flowed through the soil columns was collected and analyzed for energetic materials by high performance liquid chromatography (HPLC), using EPA method 8330 for low levels of explosives. It was found that the concentrations of energetic materials in the outflow water approached saturation levels less than two weeks into the first infiltration period. The first infiltration period mimicked the springtime snowmelt. It was hypothesized that these very high values were caused by the rapid dissolution of extremely fine particles of detonation residue. These fine particles, having a very high specific surface area, dissolve very quickly despite the low solubility of explosives. Towards the end of the springtime infiltration period (lasting one month), the concentration of explosives in the outflow water began to decline. This indicated the exhaustion of the easily dissolved fine fraction of detonation residue.

One soil column was used for an inert tracer experiment and did not contain any explosives. 10 g of KBr was introduced onto the column surface at the beginning of the experiment, and

concentrations of bromide were monitored in the outflow. The bromide ion is an inert tracer and monitoring its concentration in the outflow allowed better characterization of the flow characteristics of the soil column. The breakthrough curve of this inert tracer, as it appeared in the effluent, was used to calculate the retardation factor of the explosives and was also useful in the calibration of the numerical modelling of the unsaturated columns. The retardation factor for the three explosives TNT, RDX and HMX were found to be 1.56 ± 0.5 , meaning the time to breakthrough of all three explosives was approximately 1.56 longer than the breakthrough of the inert tracer. This is an indication of minimal adsorption of the energetic materials onto the sandy soil. The adsorption coefficients were measured to be 0.123 L/kg for TNT, 0.091 L/kg for RDX and 0.18 L/kg for HMX. These values agreed with literature values, and are very low. There is therefore very little adsorption of these three energetic materials onto the sandy soil found in the vadose zone of the Arnhem range.

The springtime infiltration period was followed by a four-month dry period. During the summer months in Quebec, evaporation and transpiration losses of soil moisture are equivalent to the moisture gained by precipitation, meaning there is no net flow of water through the vadose zone.

In the subsequent autumn infiltration period, which reproduced the rainy period of October and November, it was found that the concentrations of explosives in the effluent briefly spiked upwards at the beginning of infiltration. It was hypothesized that during the dry period, the detonation residue continued to dissolve into the immobile interstitial pore water at the surface of the vadose zone which was in continuous contact with the solid detonation residue. This created a highly mobile and concentrated solution of energetic material near saturation that was immediately flushed through the unsaturated zone once the autumn infiltration began.

During both the springtime and autumn infiltrations, the concentrations of TNT breakdown products in the effluent from the columns was typically over an order of magnitude below the concentrations of TNT. This was due to the very rapid transport of contaminants through the soil columns, allowing minimal time for transformation.

Dissolution tests showed that the finest fraction of detonation residue produces the highest concentration of dissolved explosives per unit mass, and that the kinetics of dissolution are both linear and proportional to the grain size of the residue. In addition, preliminary dissolution results

supported the hypothesis that the fine fraction of detonation residue dissolves rapidly, but once this fraction is exhausted, effluent concentrations of energetic materials begins to decline. The dissolution test also provided the input function of the dissolved energetic materials for the purposes of numerical modeling.

The soil in the columns was fully characterized in order to link this work to other investigations of adsorption that exist in the literature. The physical and chemical characteristics of a soil have a direct and significant influence on the adsorption and transport behaviour of energetic materials through the vadose zone. The solid density, grain size curves, soil-water characterization curve, total organic carbon, cation exchange capacity, porosity and the unsaturated hydraulic conductivity function of the soil in the columns were all defined through various tests. It was demonstrated that the soil was a medium, well-sorted sand with a narrow grain size distribution. There was very little organic material, and almost no clay fraction. Based on this, the other soil parameters fell comfortably within the expected ranges based on predictions from literature values.

The flow and transport through the unsaturated columns was modeled numerically using FEFLOW software. Modeling the outflow from each of the seven individual nozzles on each column proved impossible because the head created by the fibreglass wicks could not be properly characterized. As well, it was proposed that the unsaturated flow paths were not long enough to allow the application of Fick's Law, meaning the convection-dispersion equation could not be applied.

The work in this thesis demonstrated that cracked shell unexploded ordnance are easily produced under the right conditions, and that it is reasonable to assume that these conditions do occur in the field. It was shown that cracked shell munitions produce large amounts of available energetic materials when compared to undamaged unexploded ordnance and that this contamination will travel very rapidly through a vadose zone composed of sandy soil. It was also demonstrated that there is a temporary increase in the concentration of energetic materials at when infiltration begins following an extended dry period. Over the course of one full year, it was shown that up to 4.9 g of energetic material produced by a single cracked shell ordnance may be dissolved and transported through the vadose zone.

In addition, it was demonstrated that the volume of infiltration is the variable that has by far the largest impact on the total mass of energetic materials transported through the vadose zone. However, small positive correlations were also observed between the quantity of energetic materials transported through the vadose zone and the type of source term. Energetic materials originating from detonation residue appear to be slightly more available for transport than those originating from pure explosives. This may be due to the physical differences between detonation residue grains and the grains from crushed, pure composition B.

Concurrent to the work in this thesis, a great deal of field sampling and monitoring well construction was performed at various Canadian Forces bases across Canada. The purpose of this was to monitor the energetic material concentrations in the groundwater below military training areas. The author participated in or supervised seven different drilling or sampling campaigns between 2001 and 2004. The results of these diverse groundwater monitoring programs furnished field results against which the lab results of the leaching experiments could be compared. Given the very infrequent detection of energetic materials in the groundwater of these bases (only 1.4% of wells were found to have measurable levels of EM) when compared with the significant concentrations measured during the column experiments, it was proposed that the dilution effect of the enormous aquifers underlying the majority of these bases played a key role in attenuating the concentrations of energetic materials. Therefore, the volume of water present in the underlying aquifer is a very significant factor in the risk assessment of a base for contamination by energetic material. Large volumes of groundwater will quickly dilute the dissolved energetic material produced by cracked shell munitions and upwards of 14 800 cracked shells per square kilometre were calculated to be required on a sandy aquifer in order to produce groundwater concentrations in excess of the US EPA standards for lifetime exposure.

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1. INTRODUCTION

Cette thèse a été effectuée dans le but d'améliorer la compréhension de la façon dont les obus non explosés ou fissurés pourraient avoir un impact sur l'environnement. Récemment, la caractérisation environnementale des bases militaires canadiennes et américaines a permis de découvrir que des explosifs et des produits de dégradation des explosifs se retrouvaient dans les eaux souterraines. Ces découvertes ont suscité des craintes pour l'avenir de l'eau potable provenant de l'eau souterraine dans ces régions et des craintes quant à l'entraînement militaire.

Cette thèse devrait fournir l'information concernant la façon dont les résidus explosifs provenant des munitions fissurés sont transportés à travers la zone vadose. L'approche retenue est de type ingénierie, c'est-à-dire que les travaux étaient planifiés pour répondre aux besoins des gestionnaires des champs de tir militaires. Des recommandations utiles sont faites quant à la planification à long terme des entraînements qui nécessitent l'utilisation de munitions explosives et aussi pour les efforts déployés pour le nettoyage des champs de tir.

Les essais ont été effectués sur des colonnes de sols non saturés provenant d'un champ de tir militaire localisé sur la base des forces canadiennes de Valcartier, situé à trente-cinq km au nord de la Ville de Québec.

1.1. Structure du document

Les expériences qui ont été effectuées mais qui ne sont pas primordiales pour cette thèse sont **annexées** à la fin du présent document. Les autres informations sont incluses dans les **appendices**. Les documents publiés sont ajoutés à la fin de la thèse. Cette organisation est nécessaire pour garder l'attention sur le travail principal : les essais sur les colonnes de sols non saturés.

1.2. Contexte militaire

Les Forces canadiennes sont composées de trois branches indépendantes : l'armée, la marine et la force aérienne. Chaque branche possède ses propres bases et est responsable pour son propre entraînement. Le caractère d'entraînement est très différent pour chaque branche et les munitions utilisées également. On peut dire que l'armée a plus d'influence sur l'environnement

parce qu'elle a le plus haut cycle opérationnel, elle utilise le plus grand nombre de munitions explosives et des terrains énormes nécessaires pour l'entraînement. Malgré le fait que la force aérienne possède deux bases gigantesques (BFC Cold Lake dans le nord de l'Alberta et BFC Goose Bay au Labrador), leurs munitions sont utilisées seulement sur des petits champs de tirs de quelques kilomètres carrés. Le reste de leur terrain est utilisé seulement pour les manœuvres aériennes et le ciblage avec les lasers. Ni l'une ni l'autre de ces activités n'ont un impact sur l'environnement terrestre du point de vue des résidus de munitions.

La branche de la marine a des bases sur l'océan Atlantique (BFC Halifax) et l'océan Pacifique (BFC Esquimaux), mais presque tout leur entraînement est effectué par les bateaux déployés en mer et de manière générale en utilisant des munitions inertes, sans charge explosive. Les effets des munitions utilisées par la marine sont dispersés par le volume d'eau dans l'océan et par conséquent leur impact environnemental est minime.

Quatre des bases d'armée qui existent aujourd'hui datent de la première guerre mondiale. Ces quatre bases sont : BFC Valcartier à Québec, BFC Petawawa en Ontario, BFC Borden en Ontario et BFC Shilo au Manitoba. Toutes étaient utilisées comme des terrains de regroupement ou encore pour l'entraînement des unités de la Force Expéditionnaire Canadienne. Toutes ont été établies entre les années 1914 et 1918. En plus, Borden et Shilo étaient utilisées avant la guerre pour des manœuvres de la milice. Une autre série de bases a été mise sur pied en raison de la deuxième guerre mondiale, entre 1941 et 1945. Ces bases sont : BFC Wainwright, Calgary et Suffield en Alberta, BFC Meaford en Ontario et BFC Chilliwack en Colombie Britannique. Finalement, en 1952 le gouvernement Canadien a exproprié des propriétés de 1129 km² de terrain entre Fredericton et Saint John au Nouveau Brunswick, pour l'établissement de la BFC Gagetown. Cette acquisition était la dernière pour les besoins d'entraînement de l'armée. Depuis 1952, une série de fermetures a diminué le nombre de bases disponibles pour l'entraînement militaire. Pendant les années 1970, les plus petites stations des Forces canadiennes (SFC) ont été fermées, mais dans les années 1980, les restrictions budgétaires ont forcé la fermeture de 13% des terrains des Forces canadiennes, la plupart appartenant à l'armée. Le tableau 1 montre les bases et les aires d'entraînements fermées depuis 1989. En kilomètres carrés, l'aire disponible pour l'entraînement militaire au Canada a atteint un sommet à la fin des années 1950. Les restrictions budgétaires et l'attitude sociale au Canada minimisent les chances pour l'ouverture de futures bases militaires.

Dans ce contexte, le concept d'entraînement durable commence à influencer l'usage stratégique des bases militaires au Canada. Pour garder les troupes à un niveau acceptable de préparation, les forces doivent être capables de planifier un entraînement réaliste. L'entraînement réaliste nécessite un terrain. Si ce terrain n'est pas gardé dans un état de propreté régi selon les normes environnementales canadiennes, éventuellement le public va souhaiter limiter ou enlever complètement le droit d'usage de ces terrains d'entraînement. Il faut éviter qu'une telle situation arrive, parce que l'effet qui pourrait en résulter sur les troupes serait dramatique. Pour assurer que les forces auront accès aux terrains d'entraînement dans l'avenir, il faut qu'elles acceptent le concept d'entraînement durable et il faut également enrayer ou nettoyer la contamination provenant des 100 dernières années d'entraînement.

Avant qu'un effort de nettoyage ne commence, il faut définir l'ampleur du problème. Dans les années 1990, RDDC-Valcartier a débuté un programme de caractérisation environnementale dans le but d'améliorer notre compréhension de la façon dont les bases militaires canadiennes ont été contaminées par l'entraînement (Ampleman et al, 1998, 2003, 2004, Thiboutot et al, 1998, 2000, 2001, 2002, 2003, Ballard et al, 2004, Martel et al, 1998, 1999, 2004a, 2004b, Lewis et al, 2005). Le travail est réparti sur deux axes : 1) la contamination du sol sur la surface et 2) la contamination de l'eau de surface et souterraine.

Cette thèse était supportée par le Directeur d'environnement terrestre (DLE), et par la Strategic Environmental Research and Development Program (SERDP, provenant des États-Unis). Ce travail était intégré dans un programme de développement et recherche dédié à la compréhension des impacts environnementaux des munitions pendant tout leur cycle de vie. Les travaux effectués sur les eaux souterraines sur les bases militaires sont reliés au travail accompli dans cette thèse.

Lors de mes travaux de doctorat, j'ai organisé plusieurs campagnes d'échantillonnage et de forage des eaux souterraines et des sols de surface sur plusieurs bases des forces canadiennes. J'y ai aussi participé. Ces travaux m'ont donné une excellente compréhension de la problématique créée par 100 ans d'activités militaires ou presque. Il n'existe aucune archive pour indiquer l'usage historique de nos bases. Les prochains paragraphes servent à décrire ces travaux.

Tableau 1. Fermetures des bases Canadiennes depuis 1989

Base	Date Fermé	Endroit
CFB SUMMERSIDE	1989	Prince Edward Island
CFS BARRINGTON	1989	Nova Scotia
CFS MONT APICA	1990	Québec
CFS SYDNEY	1990	Nova Scotia
CFS HOLBERG	1990	British Columbia
CFB PORTAGE LA PRAIRIE	1992	Manitoba
CFB LONDON	1992	Ontario
CFB BADEN-SOLLINGEN	1994	Germany
CFB PENHOLD	1995	Alberta
CFB CORNWALLIS	1995	Nova Scotia
CFB OTTAWA	1995	Ontario
CFB ST-JEAN	1995	Québec
CFS CARP	1995	Ottawa
CFS SHELBURNE	1995	Nova Scotia
Regional Medical Equipment Depot Valcartier	1995	Québec
Regional Medical Equipment Depot Chilliwack	1995	British Columbia
CF Ammunition Depot Angus	1995	Ontario
Land Engineering Test Establishment	1995	Ontario
Camp Ipperwash	1995	Ontario
Defence Research Establishment Pacific	1995	British Columbia
CMR St. Jean	1995	Québec
Royal Roads Military College	1995	British Columbia
CFS ALDERGROVE	1996	British Columbia
CFS MILL COVE/NEWPORT CORNER	1996	Nova Scotia
CFB TORONTO	1996	Ontario
CFB SHEARWATER	1996	Nova Scotia
CFB CHATHAM	1996	New Brunswick
CFB LAHR	1996	Germany
CFB MONCTON	1996	New Brunswick
CFS DEBERT	1997	Nova Scotia
CFS MASSET	1997	British Columbia
CF Detachment Jericho Beach	1997	British Columbia
CFB CHILLIWACK	1998	British Columbia
CFB CALGARY	1999	Alberta

1.2.1. Travaux d'échantillonnage et de forage effectués

Les détails qui suivent ont été publiés dans les rapports techniques de RDDC-Valcartier ou de l'INRS-ETE. Le travail décrit dans ces rapports a été effectué entre les années 1995 et 2004, et les rapports ont été publiés entre 1998 et 2005. J'ai été impliqué dans tous les travaux effectués entre 2001 et 2004.

1.2.1.1. Cold Lake Air Weapons Range (CLAWR)

CLAWR couvre un territoire de 11 000 km² dans le nord des provinces de l'Alberta et de la Saskatchewan. C'est une des deux bases principales de la Force aérienne destinée aux manœuvres des avions de chasse.

Les deux zones d'impact où les munitions explosives ont été (et sont toujours) utilisées sont toutes les deux de moins de 10 km². La majorité des munitions sont utilisées sur le champ de tir Shaver River. Les munitions aériennes qui sont souvent utilisées sont la Mk82, bombe de 500 livres et le Mk83, bombe de 1000 livres.

Il y a 21 puits qui ont été forés aux alentours des champs de tir à CLAWR. En mars 2004, 14 échantillons d'eau souterraine ont été récoltés et parmi eux 5 étaient contaminés avec des résidus explosifs. Dans un des échantillons, de faibles concentrations de RDX (3.2 ppb) ont été détectées. Dans les quatre autres échantillons contaminés, la nitroglycérine a été détectée à des concentrations entre 0.8 à 5.1 ppb.

En août 2004, une autre campagne d'échantillonnage a permis de récolter dix-neuf échantillons d'eau souterraine et seulement un était contaminé avec des résidus d'explosifs. Dans le même puits où en mars nous avons détecté 3.2 ppb du RDX, nous avons alors trouvé 7.0 ppb du RDX. Ce puits est localisé à 200 m de la cible la plus bombardée du champ de tir Shaver River. La nitroglycérine trouvée pendant la première campagne était probablement due à une erreur de laboratoire, vu qu'aucune nitroglycérine n'a été trouvée pendant la deuxième campagne d'échantillonnage et vu qu'aucune des munitions des Forces aériennes ne comporte de la nitroglycérine comme composante.

1.2.1.2. Western Area Training Center (WATC) Wainwright

WATC est localisé à 300 km au sud-est d'Edmonton, dans la province de l'Alberta. Cette base appartient à l'armée et au cours des dernières années elle est devenue une

des bases canadiennes les plus utilisées, grâce à ses terrains ouverts et variés qui sont adéquats pour les manœuvres des troupes se préparant pour l'Afghanistan.

L'INRS-ETE et RDDC-Valcartier ont installé trente puits à WATC, en 2003. En octobre 2003, vingt-huit échantillons d'eau souterraine ont été récoltés et analysés. Aucun échantillon n'était contaminé avec des résidus d'explosifs.

1.2.1.3. BFC Gagetown

Une autre des grandes bases de l'armée, la BFC Gagetown, est localisée dans la province du Nouveau Brunswick, entre les villes de Fredericton et de Saint John. Gagetown est la base où la plupart des écoles des armes de combat sont localisées, incluant les écoles de génie militaire, de fantassins et de blindés. Cette base comporte les plus hauts cycles d'entraînement pendant l'été, quand les centaines de cours de la force régulière et de la milice sont donnés.

Il y a quarante-trois puits localisés à la BFC Gagetown et deux études y ont été conduites. La première, en août 2001, a démontré qu'il y avait quinze échantillons sur quarante-deux contaminés avec de très faibles quantités de RDX, TNT ou HMX. Douze des quinze échantillons contaminés l'étaient avec du RDX et les concentrations étaient toutes de 1.6 ppb.

La deuxième étude, en octobre 2002, n'a démontré aucune présence d'explosifs dans l'eau souterraine. Il est probable que les échantillons contaminés en août 2001 l'étaient à cause d'une contamination au laboratoire.

1.2.1.4. BFC Shilo

La BFC Shilo est située à 200 km à l'ouest de Winnipeg, dans la province du Manitoba. C'est la base où l'école d'artillerie est localisée et pour cette raison, c'est la base où une grande partie de l'entraînement d'artillerie au Canada se passe. La BFC Shilo est aussi localisée directement au-dessus de l'aquifère Assiniboine, qui fournit beaucoup d'eau pour l'agriculture dans la région centrale de la province du Manitoba.

Il y a soixante-dix-huit puits d'observation à BFC Shilo. Pendant trois campagnes d'échantillonnage en octobre 2000, septembre 2001 et septembre 2002, plus de 200 échantillons d'eau souterraine ont été prélevés et aucun n'a testé positif pour les explosifs.

1.2.1.5. BFC Valcartier

À trente-cinq km au nord de la ville de Québec, la BFC Valcartier est la seule base de l'armée dans la province de Québec qui a des terrains pour l'entraînement. L'INRS-ETE et RDDC Valcartier ont installé cinquante-cinq puits sur les terrains d'entraînement de Valcartier. Presque la moitié (vingt-cinq), ont été installés sur un champ de tir anti-char (champs de tir Arnhem). Entre 1998 et 1999, 325 échantillons ont été prélevés à Arnhem et cinquante-cinq ont testé positif pour le HMX.

Ailleurs qu'à Arnhem, vingt-quatre échantillons d'eau souterraine ont été prélevés en 2001. Les dix-sept échantillons qui ont testé positif pour les explosifs étaient probablement contaminés dans le laboratoire, vu qu'ils ont tous eu une concentration d'exactly 25 ppb, ce qui est suspect. En 2002, vingt-neuf échantillons ont été récoltés et aucun n'a eu de concentration d'un quelconque explosif.

1.3. Devenir et transport des matériaux énergétiques

Aux États-Unis, la contamination de l'eau souterraine au Massachusetts Military Reservation (MMR) par l'explosif Royal Demolition Explosive (RDX) a forcé la fermeture de la base par l'Environmental Protection Agency (EPA). Le RDX est classé comme un cancérigène potentiel par l'EPA. Au MMR, il y a quelques possibilités pour l'origine du RDX. Ces possibilités incluent les détonations incomplètes (« low order »), les munitions non explosées qui sont fissurées ou les résidus provenant de la destruction intentionnelle des munitions de surplus. La contamination et les résidus créés par les munitions qui explosent complètement et les munitions non explosées qui sont détruites intentionnellement par les experts ont été investigués par différents chercheurs, mais aucun travail n'a été fait à date en ce qui a trait au transport des résidus provenant de ces sources.

Pour le travail courant, la munition choisie comme source d'explosifs était le mortier C70A1 avec un diamètre de 81 mm. Ce choix a offert plusieurs avantages : premièrement, cette munition est utilisée par la plupart des pays de l'OTAN, incluant les États-Unis et le Canada. Deuxièmement, l'explosif dans le mortier est la composition B qui est utilisée dans plusieurs autres munitions, et c'est aussi celle qui est utilisée dans plusieurs pays. Troisièmement, cette

munition avait une largeur parfaite pour être placée dans les colonnes de sols non saturés qui sont primordiaux dans cet essai.

Le mortier est rempli avec 0.9 kg de composition B. Cette composition est un mélange de 59.5% du RDX, 39.5% trinitrotoluene (TNT), et de 1% de cire. En plus, le High Melting Explosive (HMX) est toujours présent comme contaminant dans le RDX. La composition B est un explosif qui peut être fondu avec l'application de chaleur, et se fabrique quand le TNT est fondu et que le RDX est dispersé dans le fluide. Le détonateur n'était pas en place pendant les essais pour des raisons de sécurité. Aussi, les charges de propulsif n'étaient pas incluses dans les essais parce qu'elles sont brûlées quand la munition est tirée.

La compréhension des processus fondamentaux du transport est critique pour comprendre le travail effectué dans cette thèse. Les prochaines sections vont décrire les variables qui sont reliées aux trois explosifs militaires TNT, RDX et HMX et les produits de dégradation de chacun. Il manque de mesures pour plusieurs variables, surtout pour les produits de dégradation du RDX et du HMX. Depuis la fin des années 1980, il y a des compilations de variables de transport et du devenir des explosifs qui ont été publiées (Rosenblatt *et al.* 1989, McGrath, 1995, Brannon and Myers 1997, Talmage *et al.* 1999, Brannon *et al.* 1999, Brannon and Pennington 2002). Ceci est un indicateur des progrès rapides de la science pendant les quinze dernières années. L'information est aussi disponible sur l'internet avec le Hazardous Substance Data Base (HSDB) sur le réseau de toxicologie (<http://toxnet.nlm.nih.gov/>).

1.3.1. Dissolution et solubilité

La dissolution est la première étape nécessaire pour le transport des matériaux énergétiques à travers la zone vadose. Tous les explosifs utilisés par les militaires sont des munitions conventionnelles solides aux températures environnementales (-30° C à +30° C). Avant que ces explosifs puissent devenir mobiles, il faut qu'ils soient solubilisés dans l'eau. Il y a deux valeurs qui sont intéressantes pour nous : la concentration maximale dans l'eau (solubilité) et la vitesse à laquelle un produit va se solubiliser (taux de dissolution). Ces deux valeurs vont limiter le potentiel de transport des explosifs dans l'environnement pendant les événements de précipitation. Le tableau 2 montre les valeurs disponibles dans la littérature pour ces caractéristiques.

Taylor *et al.* (1923) sont les premiers qui ont indiqué dans la littérature la solubilité du TNT. Depuis ce temps, les valeurs dans la littérature pour la solubilité du TNT, RDX et HMX sont souvent contradictoires (Spangford *et al.* 1983; Ro *et al.* 1996; Phelan *et al.* 2001; Banerjee *et al.* 1980). Il existe maintenant plus d'une douzaine de sources publiant les variables de solubilité des explosifs et il existe encore des contradictions. Lynch *et al.* (2001, 2002a, 2002b) sont parmi les articles les plus rigoureux sur ce sujet. Ils ont examinés le pH, la température, la solubilité et les taux de dissolution des explosifs. La recherche suggère que le pH a très peu d'influence sur la solubilité et le taux de dissolution des matériaux énergétiques. Par contre, la température a un effet considérable. Entre +3° C et +30° C, les solubilités et les taux de dissolution du TNT, RDX et HMX vont augmenter d'un facteur de 3 à 5. Les variations dans les valeurs publiées sont probablement reliées avec la pureté et la forme cristalline des explosifs qui étaient utilisés.

Les caractéristiques de solubilité et de taux de dissolution peuvent être influencées par la présence de plus d'un produit chimique dans la solution. Tel que mentionné précédemment, la composition B est un mélange du TNT, RDX et HMX. Donc, il est improbable que les valeurs de dissolution pour chaque explosif soient les mêmes que pour le mélange au complet. Lever *et al.* (2005), Lynch *et al.* (2002) et Phelan *et al.* (2002) ont tous fait les recherches concernant les caractéristiques de dissolution des particules de composition B. Lever *et al.* ont obtenu une bonne corrélation entre les mesures de dissolution et leurs deux modèles. Un de leurs modèles, « drip impingement », est pertinent pour le travail de cette thèse. L'idée de ce modèle est que la percolation d'eau dans le sol est assez rapide pour que l'eau ne reste pas sur la surface dans les flaques. Donc, quand une goutte de pluie frappe une particule de composition B, une couche très mince d'eau va se former autour de la particule et le reste de la goutte sera absorbé dans le sol. Si la couche d'eau est assez mince, elle va devenir saturée avec la composition B dissoute, avant que la prochaine goutte d'eau frappe la particule. Un graphique de la masse non dimensionnelle M_{lossj} vs. le temps non dimensionnel t/t_0 a fourni une bonne corrélation quand les variables étaient définies comme ci-dessous :

$$M_{lossj} = 1 - \left(\frac{a}{a_o} \right)^3 \quad \text{Équation 1}$$

et

$$t_o = t_d \frac{\rho_j}{S_j} \left[x_o + \frac{1}{\sqrt{3}} \arctan(\sqrt{3}(1+2x_o)) - \frac{1}{2} \ln(1+3x_o+3x_o^2) - \frac{1}{\sqrt{3}} \arctan\sqrt{3} \right] \quad \text{Équation 2}$$

a = rayon d'une particule sphérique de composition B

a₀ = rayon initial d'une particule sphérique de composition B

t_d = intervalle de temps entre les gouttes de pluie

ρ_j = densité de la composante j dans la composition B (fraction de masse)

S_j = limite de solubilité de la composante j dans l'eau

x_o = a/h ou h est l'épaisseur d'eau sur la particule de composition B

Les bonnes corrélations ont été atteintes quand h était entre 0.1 à 0.2 mm, mais le modèle prédit que la dissolution du TNT sera plus rapide que ce qui est observé.

Il y a un conflit entre les données de Lynch *et al.* (2002b) et celles de Lever *et al.* (2005). Lynch *et al.* (2002b) démontrent que les solubilités et les taux de dissolution du TNT, RDX et du HMX ne sont pas influencées par la présence de plus d'un de ces explosifs dans la même solution. Par contre, Lever *et al.* (2005) ont clairement démontré que le RDX cristallin contrôle le taux de dissolution dans la composition B. Les expériences de Lynch *et al.* (2002b) ont seulement mesuré le taux initial de dissolution. Elles n'ont pas mesuré les différences de dissolution avec le temps, ce qui pourrait expliquer la différence.

Les mesures des taux de dissolution du TNT, RDX et HMX ne sont pas faciles à trouver. Lynch *et al.* (2001) ont mesuré les taux de dissolution comme une fonction du pH et de la température. Jenkins et Miyares ont fait les mesures qui apparaissent dans Brannon et Pennington (2002). Ces mesures sont présentées dans le Tableau 2.

1.3.2. Adsorption et désorption

L'adsorption est le processus d'adhésion physique des molécules, ions ou atomes sur une surface solide. C'est un processus qui n'implique pas une réaction chimique; il est donc réversible. La sorption des matériaux énergétiques va avoir un impact sur leur mobilité souterraine, qui va par extension avoir un impact sur leur devenir environnemental. Des caractéristiques d'adsorption différentes sont observées pour les nitroaromatiques et pour les

nitramines. Il va donc falloir observer chacun d'une façon indépendante. Brannon et Pennington (2002) ont rassemblé plusieurs tableaux de coefficients publiés pour le TNT, le RDX et le HMX. Ces tableaux ont été utilisés comme point de départ pour les tableaux dans ce texte, mais plusieurs ont été mis à jour avec les données qui furent publiées subséquemment. La Figure 1-4 montre les données des tableaux 3 et 4 avec les graphiques. Ces quatre graphiques démontrent qu'il y a toujours beaucoup d'incertitudes reliée aux constantes d'adsorption pour le TNT et le RDX.

1.3.2.1. L'adsorption du TNT

Les valeurs du coefficient d'adsorption du TNT dans les sols naturels varient entre 0.4 et 11 L/kg (Brannon et Pennington, 2002) (figure 1, tableau 2). Dans des sols homoioniques argileux artificiels, des coefficients d'adsorption ont été mesurés jusqu'à 21 500 L/kg.

La mesure d'adsorption réversible du TNT sur les sols est souvent compliquée par les réactions qui enlèvent le TNT d'une façon permanente. Le TNT est susceptible à la transformation par plusieurs processus incluant la photolyse et l'activité microbienne.

Le lien irréversible chimique du TNT et des produits de dégradation du TNT peut limiter l'adsorption. En plus, la transformation du TNT dans les sols va enlever plus de TNT que l'adsorption. Vu que la transformation est un processus continu les concentrations en TNT dans le sol et celles dissoutes dans l'eau des pores vont rarement se stabiliser (Price *et al.* 1995; Myers *et al.* 1998). Les études qui ont supprimé les effets de transformation par l'empoisonnement des microbes ou des temps d'équilibre très courts ou une combinaison de ces deux méthodes ont indiqué des coefficients d'adsorption dont les isothermes suivent les formes typique de Langmuir, Freundlich ou linéaire (Leggett, 1985; Pennington et Patrick, 1990; Haderlein *et al.*, 1996).

Tableau 2. Valeurs dans la littérature pour la solubilité et dissolution pour TNT, RDX et HMX

Explosive	Solubilité (mg/L)	Référence	Dissolution ($\mu\text{g cm}^{-2} \text{s}^{-1}$)	Référence
TNT	51.3 (6 °C, pH 6.9) 64.0 (12 °C, pH 6.9) 88.5 (20 °C, pH 7.3) 100.5 (25 °C, pH 6.8) 204.5 (42 °C, pH 6.8) 55.9 (2.7 °C, pH 6.2) 56.7 (4.7 °C, pH 6.2) 100.2 (20 °C, pH 6.2) 234.4 (37.8°C, pH 6.2)	Ro et al (1996) Ibid Ibid Ibid ibid Lynch et al (2001) Ibid Ibid ibid	0.69 ($R^2= 0.984$) 1.15 ($R^2= 0.986$)	LYNCH ET AL 2001 JENKINS AND MIYARES 1997 (UNPUBLISHED) ¹
RDX	28.9 (10 °C) 42.3 (20 °C) 38.4 (20 °C) 59.9 (25 °C) 59.9 (26.5 °C) 75.7 (30 °C) 18.1 (2.1 °C, pH 6.2) 14.1 (3.9° C, pH 6.2) 37.5 (20°, pH 6.2) 85.2 (34.1° C, pH 6.2)	Sikka et al. (1980) Sikka et al. (1980) Spanggord et al. (1983b) Banerjee, Yalkowsky, & Valvani (1980) Sikka et al. (1980) Sikka et al. (1980) Lynch et al (2001) Ibid Ibid Ibid	0.096 0.100	LYNCH ET AL (2001) JENKINS AND MIYARES 1997 (UNPUBLISHED)
Comp B	<u>TNT:</u> 127.02 (26.3° C) <u>RDX</u> 52.52 (26.6° C) <u>HMX</u> 4.46 (26.6° C)	LYNCH ET AL (2002)	<u>TNT</u> .016 (10° C) <u>RDX</u> 0.0024 (10° C) <u>HMX</u> 9.1 (10° C)	LYNCH ET AL (2002)
1. T. F. JENKINS AND P. H. MIYARES, COLD REGIONS RESEARCH AND ENGINEERING LABORATORY, U.S. ARMY ENGINEER RESEARCH AND DEVELOPMENT CENTER, HANOVER, NH, 3 DECEMBER 1997, DATA NON PUBLIÉ, EN BRANNON ET PENNINGTON (2002)				

Pour les polluants organiques, il est souvent présumé que le chemin principal d'adsorption se trouve sur les composantes organiques dans les sols. L'adsorption des composantes hydrophobes qui ont une faible solubilité ($< 10^{-3}$ M) et qui ne sont pas susceptibles à la transformation ni à la formation de complexes est généralement contrôlée par la fraction de carbone organique dans les sols (Karickhoff, 1981). Les contributions des minéraux à l'adsorption sont généralement masquées quand le ratio des minéraux inorganiques sur le carbone organique est de moins de 30 (Karickhoff, 1984). Ceci est souvent le cas dans les sols de surface.

Par contre, d'autres chercheurs ont démontré que le contenu en carbone organique a moins d'influence sur l'adsorption du TNT que les autres paramètres du sol comme la capacité d'échange cationique (CEC) et la fraction d'argile dans le sol (Pennington et Patrick, 1990; Haderlein *et al.*, 1996) (figure 2).

Le TNT et les autres nitroaromatiques s'adsorbent de façon réversible sur la surface siloxane des minéraux argileux comme la kaolinite, l'illite et la montmorillonite, mais pas sur les autres minéraux comme les oxydes d'aluminium et de fer, les carbonates et la quartz (Haderlein *et al.*, 1993, 1994). L'affinité du TNT avec les autres nitroaromatiques est fortement liée avec le type de cations échangeables qui se trouvent sur la surface siloxane de la kaolinite. Les cations faiblement hydratés comme K^+ et NH^+ encouragent l'adsorption, et les cations qui sont fortement hydratés comme H^+ et Na^+ réduisent l'adsorption sur les argiles. La concentration ionique n'a aucun effet sur l'adsorption du TNT sur les argiles, dans les concentrations qui sont normalement retrouvées dans les environnements d'eaux souterraines, c'est-à-dire entre 10^{-4} M et 10^{-1} M. Par contre, pour les concentrations de l'ordre de 10^{-1} M et 10^0 M, il existe une relation directe entre la concentration et le coefficient d'adsorption K_d . En plus, les effets de « salting out » peuvent contribuer à l'augmentation de l'adsorption des composantes organiques neutres si les plus hautes concentrations sont atteintes (Schwarzenbach *et al.* 1993). Les coefficients d'adsorption des nitroaromatiques sur l'argile ne sont pas influencés par le pH entre les valeurs de pH 3 – pH 9 (Haderlein *et al.*, 1996). Les cinétiques de ces réactions sont rapides et l'équilibre est atteint en quelques minutes. Il arrive donc que les composantes nitroaromatiques comme le TNT soient adsorbées principalement sur les sites facilement accessibles, à la surface des argiles.

L'adsorption compétitive entre le TNT et ses composantes de transformation ou les autres explosifs peut avoir un effet sur l'adsorption et le transport (Ainsworth *et al.*, 1993). La compétition entre les composantes adsorbées est négligeable seulement à des concentrations très faibles. Sur les argiles, Haderlein *et al.* (1996) ont démontré que les composantes explosives avec les plus hauts coefficients de distribution ont déplacé les composantes explosives avec les moins hauts coefficients. Les coefficients de distribution ont été attribués dans l'ordre suivant : TNT > 2 ADNT > 4 ADNT > 2,6 DANT > 2,4 DANT.

1.3.2.2. L'adsorption du RDX

L'adsorption du RDX peut être décrite avec des isothermes linéaires (Ainsworth *et al.*, 1993; Haderlein *et al.*, 1996; Myers *et al.*, 1998). Les coefficients d'adsorption sont en général faibles : entre 0 et 8.4 L/kg (figures 3 et 4, tableau 4). Ceci est une indication que l'adsorption n'est pas un facteur important dans les aquifères.

1.3.2.3. L'adsorption du HMX.

Il y a très peu d'études qui ont mesuré l'adsorption du HMX. Myers *et al.* (1998) ont démontré que l'isotherme d'adsorption du HMX est linéaire et que dans les aquifères, le coefficient d'adsorption est de moins de 1 L/kg (figure 5 et 6, tableau 5). Dans les sols de surface, les coefficients d'adsorption varient entre 1 L/kg et 18 L/kg. Ces résultats sont une indication que le HMX est plus mobile dans les sols que le TNT.

1.3.3. Transformation

La transformation peut signifier plusieurs choses. Elle peut décrire n'importe quelle modification d'une composante chimique dans l'environnement par les moyens biotiques ou abiotiques. Sur le terrain, les deux phénomènes sont normalement possibles. La biodégradation est une autre expression pour la transformation biotique. La minéralisation est une expression pour la biodégradation complète d'un composé organique en des composés inorganiques comme le CO₂ et l'H₂O. Une autre forme de transformation est la photolyse ou la photodégradation. Ce mécanisme a besoin d'énergie provenant des rayons ultraviolets pour briser les liens chimiques d'une molécule.

Tableau 3. Constantes d'adsorption du tnt dans la littérature

Sol	Origine	Kd (L/kg)	CEC (mmol/g)	COT%	Argile%	Reference
LAAP ML	Aquifer	0.04	3.5	0.015	5	Pennington et al, 1999
LAAP SP-SM	Aquifer	0.09	3.6	0.015	5	
LAAP CL	Aquifer	0.27	8.1	0.162	15	
LAAP SM	Aquifer	0.17	5.5	0.02	7.5	
Norborne C	Surface	1.24	9.14	0.23	13	Ainsworth et al, 1993
Cloudland C	Surface	0.81	5.6	0.05	30	
Westmoreland B1	Surface	0.58	6.9	0.98	13.6	
Ocala C4	Surface	4.3	33.5	0.08	33	
Burbank AP	Surface	1.04	5.5	0.5	4	
Sand	Surface	0.47	1.73	0.36	2.5	Brannon et al, 1992
Silt	Surface	2.23	73	0.96	6.3	
Kolin	Surface	2.66	16.3	0.18	10.6	
Norwood	Surface	3.64	4.1	0.32	3	Xue, Iskandar and Selim, 199
Cornhuskers	Surface	4.1	35.3	0.83	20	
Crane	Surface	3.7	31.2	2.8	20.6	Pennington and Patrick, 1990
Holston A	Surface	4.4	28.8	2.7	18.1	
Holston B	Surface	3	35.2	1.2	43.8	
Iowa	Surface	5.2	44.7	1.4	20	
Joliet	Surface	6.8	102	3.6	23.8	
Kansas	Surface	5.7	130.4	2.6	26.3	
Lonestar	Surface	2.5	15.5	0.56	10	
Longhorn	Surface	3.7	20.9	0.56	15	
Louisiana	Surface	2.5	16.3	0.37	10.6	
Newport	Surface	2.3	13.4	3.5	5.6	
Radford	Surface	3.2	21.5	1.1	25	
Savanna	Surface	2.5	13.2	1.3	5	
Volunteer	Surface	4.05	46.4	1.7	5	
Clay	Surface	11	124.9	2.4	54.4	
Silt	Surface	2.8	17.2	0.57	17.5	
Sharkey clay	Surface	10	38.9	2.4	48.7	Townsend, Myers and Adrien, 1995
WES-silt	Surface	4.5	12.4	0.57	7.5	
Ottawa sand	Surface	1.5	NM	NM	0	
Crane sifter	Surface	6.16	15	1.3	23	Pennington et al, 1995
Agricultural topsoil	Surface	6.38	14.6	4.9	4	Sheremata and Hawari (2000)
Agricultural topsoils	Surface	6.38 - 11.96	14.6	8.4	4	Sheremata et al. (2001)
Various		0-10	NA	NA	NA	Townsend and Myers (1996)
LAAP A	Surface	1.09	2.5	0.31	6	Price et al.(2000)
LAAP C	Surface	1.06	6.6	0.08	12	
LAAP D	Surface	1.67	15.5	0.2	32	
Montmorillonite	argile	413	27.7	NM	NM	
Sand (Borden)	sable	0.4	NM	0.02	2	
Sand (4% clay)	Surface	1.3	NM	NM	4	Cattaneo et al.(2000)
Loam	Surface	1.6	NM	NM	NM	
Kaoliniteclay	argile	1	NM	NM	NM	
Montmorillonite	argile	156	NM	NM	NM	

* NM = non mesuré

Tableau 4. Constantes d'adsorption du RDX dans la littérature

Sol	Kd (L/kg)	CEC (mmol/g)	COT %	Argile %	Reference
LAAP ML	0.21	3.5	0.015	5	Pennington et al.(1999)
LAAP SP-SM	0.33	3.6	0.015	5	
LAAP CL	0.33	8.1	0.162	15	
LAAP SM	0.33	5.5	0.02	7.5	
Elk-B1	0.27	6.92	0.45	16.5	Ainsworth et al (1993)
Cloudland C	0.12	5.6	0.05	30	
Cecil AP	0.43	4.88	0.59	62	
Cecil BT	0.31	2.92	0.32	53	
Burbank Ap	0.16	5.5	0.5	4	
Kenoma BC	0.93	31.4	0.5	44	
Kenoma Bt1	1.21	26	1.43	44	
Ocala C4	2.37	33.5	0.08	33	
Watson Bxg	1.45	10.3	0.4	47	
Westmoreland A1	1.65	6.91	2.03	14.4	Tucker et al.(1985)
	2.39	73.4	6.04	38.2	
	0.81	39.3	0.54	30.3	
	0.5	27.7	0.32	10.3	
	2.42	41.8	6.32	0.8	
	7.3	14.5	3.1	3.8	
	0.07	0.7	0.18	0.2	
	0.74	8.7	1.22	10.7	
	0.57	2.9	0.1	4.8	
	0.06	22	0.23	30.1	
	0.7	19	0.4	37.8	
	0.57	44.7	0.98	22.2	
	0.87	41.5	0.66	20.3	
Sable	0.29	1.73	0.36	2.5	Brannon et al. (1992)
Silt	1.2	73	0.96	6.3	
Rathbun (extracted)	8.4	114	0.92	16.5	
Kolin soil	1.59	16.3	0.18	10.6	Xue Iskandar and Selim (1995)
Norwood soil	1.57	4.1	0.32	3	
Yokena clay	3.5	38.9	2.4	48.7	Brannon, unpublished data
West end	2.2	45.7	0.18	7.5	
Yuma	1.07	5.4	0.04	5	
D Street	0.82	1.8	0.17	0	
Yokena clay	0.95	38.9	2.4	34	Myers et al.(1998)
WES silt	0.77	12.4	0.57	7.5	
Sable d'ottawa	0	NM	NM	0	
Sharpsburg A horizon	0.97	18.3	1.7	36	Singh et al (1998)
Sharpsburg C horizon	0.95	19	0.4	32	
Agricultural topsoil	6.382	14.6	4.9	4	Sheremata et al (2001)
Various	0.2-7.8	NA	NA	NA	Townsend and Myers (1996)
LAAP D	0.29	15.5	0.2	32	Price et al (2000)

- NM = non mesuré

Tableau 5. Constantes d'adsorption du HMX dans la littérature

Soil	Source	Kd (L/kg)	CEC (mmol/g)	COT %	Argile %	Reference
LAAP ML	Aquifère	0.086	3.5	0.015	5	Pennington et al. (1999)
LAAP SP-SM	Aquifère	0.2	3.6	0.015	5	
LAAP CL	Aquifère	0.37	8.1	0.162	15	
LAAP SM	Aquifère	0.2	5.5	0.02	7.5	
LAAP D	Aquifère	2.39	15.5	0.2	32	Price et al. (2000)
Browns Lake	Surface	7.42	15.3	0.38	10	Brannon et al. (1999)
Sharkey clay	Surface	12.1	38.9	2.4	48.8	
St. Mary Parish,	Surface	17.7	14.2	0.19	20	
Picatinny B	Surface	4.25	9.8	0.634	5	
Socorro S	Surface	3.25	34	0.08	35	
Socorro P	Surface	1.17	27.3	0.12	27.5	
Grange Hall silt	Surface	0.12	16.7	0.29	10	
Yuma 1B	Surface	5.02	8.6	0.03	5	
China Lake	Surface	1.65	3.5	0.02	5	
Sharkey clay	Surface	1.6	38.9	2.4	48.7	Myers et al. (1998) ¹
WES-silt	Surface	1.17	12.4	0.57	7.5	
Sable d'Ottawa	Surface	0	NM	NM	0	
Holston River	Sediment	8.7	NM	1.3	NM	McGrath (1995)
² Montmorillonite	Pure clay	4.99	13.2	0.19	30	Brannon et al. (1999)

*NM = non mesuré

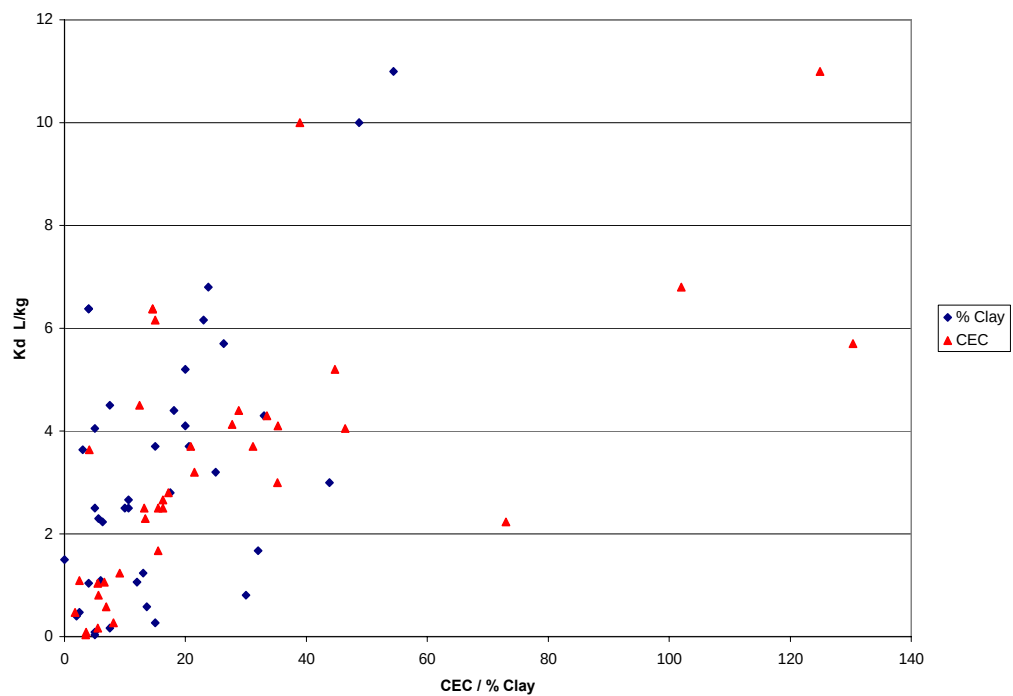


Figure 1. Valeurs publiées de K_d pour TNT vs. % argile et Capacité d'échange cationique (CEC)

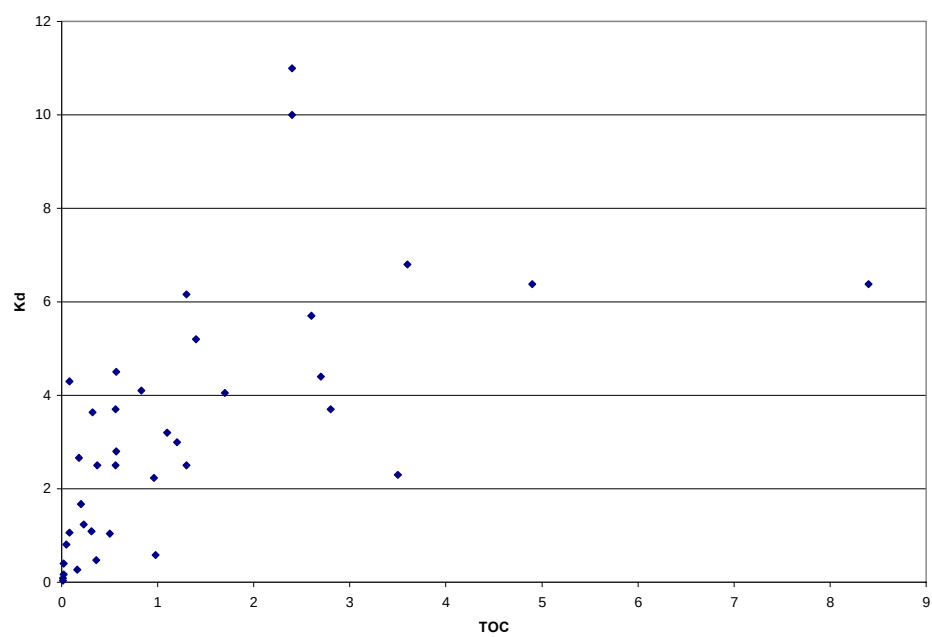


Figure 2. Valeurs publiées de K_d pour TNT vs. Carbone organique totale (COT)

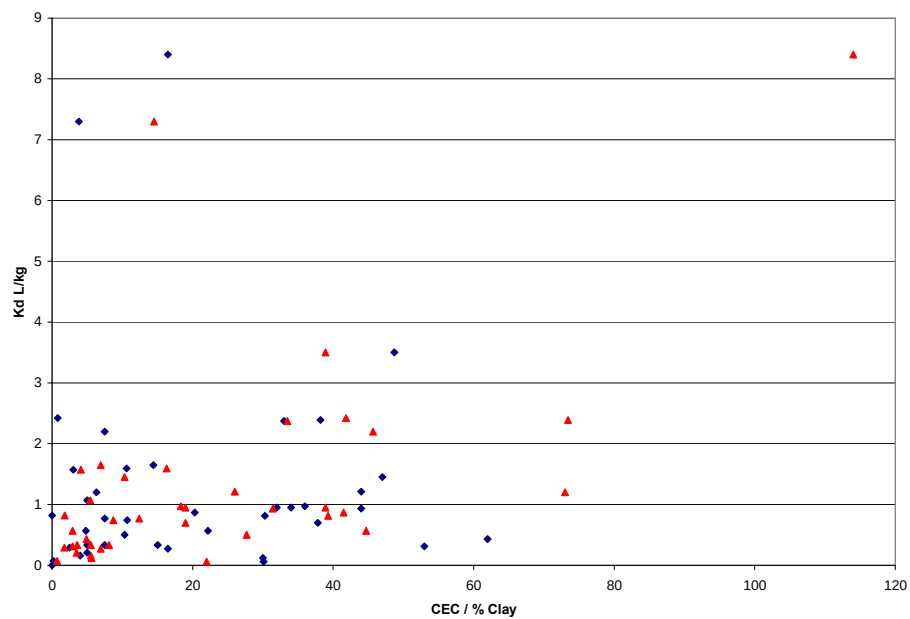


Figure 3. Valeurs publiées de K_d pour RDX vs. % argile et CEC

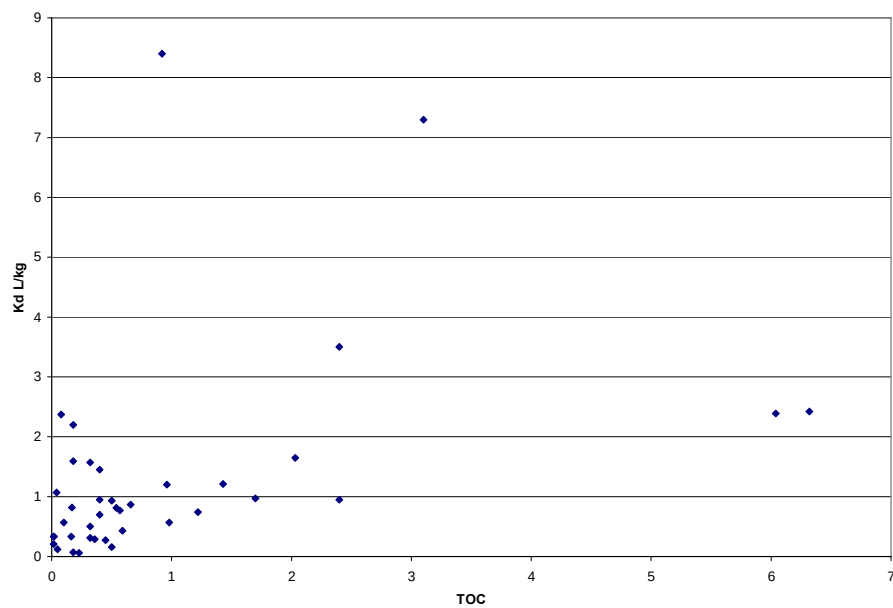


Figure 4. Valeurs publiées de K_d pour RDX vs. COT

1.3.3.1. Transformation du TNT

La transformation du TNT est très rapide (Pennington & Patrick, 1990). Dans des conditions normales, la transformation commence après quelques secondes. Les trois groupes nitro de la molécule TNT sont susceptibles d'être réduits en amines. La formation des monoamines 2-ADNT et 4-ADNT est énergétiquement favorisée (Reifler et Smets, 2000). Ces deux produits sont souvent rencontrés sur les sites contaminés au TNT. Les produits de diamines ont une plus haute énergie de formation et ils sont donc trouvés dans des concentrations beaucoup plus faibles. La triamine 2,4,6 triaminotoluene (TAT) n'est pas rencontrée souvent à cause de sa haute énergie de formation.

Plusieurs facteurs environnementaux contribuent à la transformation du TNT. Des conditions anaérobiques et réductrices (E_h -150 mV) accélèrent la transformation du TNT (Price, Brannon et Hayes, 1997). Des conditions très réductrices ($E_h < -150$ mV) accélèrent tant la transformation que le TNT disparaît complètement d'une solution en moins d'une journée. Dans des conditions oxydantes ($E_h > 500$ mV), quatre jours sont nécessaires pour la disparition du TNT d'une solution (ibid.). De plus, le pH, la CEC, les agents réducteurs et le carbone organique total peuvent avoir un effet sur la transformation du TNT.

Hawari *et al.* (2000) suggèrent que, malgré le fait que le TNT est susceptible à la transformation biotique et abiotique, la minéralisation complète du TNT en CO_2 et en H_2O est inconnue et n'a jamais été rapportée.

Le TNT est susceptible à la transformation photolytique. Dissous dans l'eau et exposés au soleil, les produits de photolyse donnent à la solution une teinte rose ou rouge. Cet effet est plus prononcé dans l'eau naturelle que dans l'eau distillée. Spangford *et al* (1980) ont postulé que les substances naturelles dans l'eau augmentent l'absorption de la lumière, ce qui sensibilise le TNT et encourage la transformation photolytique.

1.3.3.2. Transformation du RDX

Très peu d'information est disponible concernant la transformation du RDX. Price *et al.* (2001) ont observé la transformation du RDX dans les sols sous des conditions anaérobiques. Les conditions réductrices créent les conditions nécessaires pour la déstabilisation, le bris du cycle et éventuellement la minéralisation du RDX (Kaplan, 1996). Les intermédiaires nitro du

RDX n'ont presque jamais été trouvés pendant les essais sur le terrain (*ibid.*). Le manque d'information est grandement attribuable au fait que le standard pour l'analyse des explosifs, EPA Méthode 8330 (Appendix 6), n'inclut pas ces composantes.

1.3.3.3. Transformation du HMX

Si peu d'information est disponible concernant la transformation du RDX, une quantité encore moindre est disponible pour le HMX. Price *et al.* (1998) ont démontré que le HMX est stable sous une grande variété de conditions d'oxydoréduction et de pH. De plus, les produits de transformation n'ont presque jamais été détectés. Il est probable que le HMX soit moins susceptible à la transformation que le RDX.

1.4. Caractéristiques de la zone vadose

La zone vadose se retrouve entre la surface du sol et la surface de la nappe phréatique. Elle pourrait être non existante dans les marécages, ou encore d'une centaine de mètres d'épaisseur dans les zones les plus sèches de la planète. Même si elle se retrouve par-dessus la zone saturée, la zone vadose inclut la frange capillaire. Cette frange est la portion de la zone vadose qui est en contact avec la nappe et qui peut être moins de 1 cm d'épaisseur pour les sables et les graviers et de plus de quelques mètres d'épaisseur dans les argiles (Charbenneau, 2000, p. 7)

Dans la plupart des sols, les particules solides occupent entre 40% et 70% de l'espace total. Le reste de l'espace est occupé par les pores qui peuvent être remplis d'eau ou d'air. Si les pores sont remplis d'eau, le sol est saturé. Si les pores contiennent de l'eau et de l'air, le sol est non saturé. Les caractéristiques de la phase aqueuse changent avec la teneur en eau. Dans les sols relativement secs, l'eau sera non continue, avec de petites poches qui occupent seulement les plus petits pores. Parce que les pores ne sont pas connectés, l'écoulement d'eau n'est pas possible, donc la conductivité hydraulique est très faible. Par contre, dans cette situation, l'air peut circuler librement. Quand le contenu en eau augmente, les petites poches vont s'agrandir jusqu'à devenir toutes connectées. Une fois que ceci est atteint, l'écoulement d'eau et d'air devient possible en même temps. Si le contenu en eau continue d'augmenter, éventuellement les pores qui sont remplis d'air deviennent discontinus et l'air devient immobile et forme des bulles d'air dans les pores.

La complexité de l'étude de la zone vadose provient de la corrélation entre la teneur en eau (θ), la conductivité hydraulique (K) et la pression (ψ). Une augmentation de la teneur en eau (volume d'eau dans le sol) force l'eau à occuper les pores qui sont de plus en plus gros. Une des conséquences est que le rayon du ménisque à l'interface de l'eau et de l'air doit aussi devenir plus grand. Un grand rayon est lié directement à une faible tension de surface, qui implique une plus grande pression. Autrement dit, une augmentation de la teneur en eau entraîne une augmentation dans la conductivité hydraulique et de la pression. La relation entre la teneur en eau d'un sol non saturé et la pression d'eau est connue comme la courbe caractéristique d'eau dans les pores. Cette courbe sera discutée plus en détail dans la section suivante.

Pour décrire la zone vadose, deux termes sont communs : la capacité au champ et le point de flétrissement. La capacité au champ indique le volume d'eau dans un sol qui peut être retenu contre la force de gravité. Si un sol saturé se draine pendant plusieurs jours, la teneur en eau à l'équilibre est définie comme la capacité au champ. Cette définition est l'originale, mais n'est pas très rigoureuse. Une autre définition serait que la capacité au champ est la teneur en eau du sol à une pression de -0.1 atm. Le point de flétrissement est la teneur en eau du sol quand une plante de référence ne peut plus extraire d'eau par ses racines pour atteindre un équilibre avec la transpiration. Comme la capacité au champ, ce terme ne peut pas être rigoureusement défini et est souvent défini comme la teneur en eau d'un sol à une pression de -15 atm.

1.4.1. Écoulement dans un sol à saturation variable

L'écoulement dans la sous-surface peut être examiné de façon microscopique ou macroscopique. L'écoulement microscopique concerne l'écoulement dans les pores individuels et l'écoulement macroscopique concerne l'écoulement dans tout le volume du sol. Presque toutes les études en hydrogéologie sont en lien avec l'écoulement macroscopique. La loi de Darcy, qui est à la base de toutes les études en hydrogéologie, concerne l'écoulement d'eau en vrac à travers un milieu poreux. On le voit à l'équation 3 :

$$q = -K(\theta) \frac{\partial h}{\partial z} \quad \text{Équation 3}$$

q = flux Darcy ($\text{cm}^3/\text{cm}^2/\text{jour}$)

$K(\theta)$ = conductivité hydraulique (cm/jour)

h = pression hydraulique

z = distance verticale

La loi de Darcy est le point de départ pour toutes les autres équations d'écoulement en milieu poreux. Dans des conditions saturées dans les sols homogènes et avec l'écoulement constant, K est une constante. Le phénomène se complique lorsque l'on observe la zone vadose, parce que la conductivité hydraulique est une fonction de la teneur en eau dans le sol. Si l'écoulement est constant, le profil de teneur en eau du sol ne change pas et la conductivité hydraulique change avec la profondeur z . La loi de Darcy est valide dans des conditions d'écoulement en régime permanent, même dans la zone vadose. Si on dévie de l'écoulement en régime permanent, nous avons besoin d'autres équations pour décrire l'écoulement transitoire.

L'écoulement transitoire se produit quand l'écoulement dans le milieu poreux varie en fonction du temps. Dans la zone vadose, ceci est normalement le cas car le sol près de la surface est ouvert aux événements d'écoulement et de recharge qui sont reliés à la météorologie. Les exemples de recharge sont les pluies d'automne et la fonte de neige au printemps. L'écoulement sous ces conditions est décrit par l'équation de Richard, qui est une combinaison de la loi de Darcy et de l'équation de continuité (Équation 4). L'équation de Richard est la norme en modélisation et est la façon de décrire l'écoulement dans les sols à saturation variable en eau (Miller *et al* 2005). C'est une équation différentielle non linéaire qui peut prendre plusieurs formes, selon le choix des variables.

$$\frac{\partial \theta}{\partial t} = -\frac{\partial q}{\partial z} \quad \text{Équation 4}$$

La loi de Darcy peut être écrite dans la forme suivante, étant donnée la relation entre la pression totale h , la pression hydraulique ψ et la pression d'élévation z : $h = \psi + z$.

$$q = -k \frac{\partial h}{\partial z} = -k \frac{\partial (\psi + z)}{\partial z} = -k \left(\frac{\partial \psi}{\partial z} + 1 \right) \quad \text{Équation 5}$$

Si on substitue l'équation 5 dans l'équation 4, nous avons la formulation mixte d'équation de Richard :

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[k \left(\frac{\partial \psi}{\partial z} + 1 \right) \right] \quad \text{Équation 6}$$

Le désavantage de l'équation 6 est qu'il y a deux variables interdépendantes : la teneur en eau θ et la pression hydraulique ψ . On peut la simplifier avec l'insertion de la dérivée de la courbe caractéristique de l'eau dans le sol (section 1.4.3). Cette dérivée est définie comme suit (Koorevaar *et al.*, 1983) :

$$c(\psi) = \frac{d\theta}{d\psi} \quad \text{Équation 7}$$

Dans cette équation, c = le différentiel de la teneur en eau en fonction de la pression c'est à dire la capacité différentielle en eau. La combinaison des équations 6 et 7 donne la formulation de l'équation de Richard basée sur la pression :

$$c(\psi) \frac{\partial \psi}{\partial t} = \frac{\partial}{\partial z} \left(k \frac{\partial \psi}{\partial z} \right) + \frac{\partial k}{\partial z} \quad \text{Équation 8}$$

Si D (diffusivité) est définie comme le ratio entre la conductivité hydraulique k et la capacité différentielle en eau c , nous avons la relation suivante :

$$D = \frac{k}{c} = \frac{k}{d\theta/d\psi} = k \frac{dh}{d\theta} \quad \text{Équation 9}$$

La combinaison de l'équation 9 avec l'équation 6 donne la forme de l'équation de Richard basé sur θ .

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left(D \frac{\partial \theta}{\partial z} \right) + \frac{\partial k}{\partial z} \quad \text{Équation 10}$$

Il existe plusieurs méthodes pour résoudre les solutions pour l'équation de Richard : les méthodes analytiques, les méthodes semi-analytiques, et les méthodes numériques. Voici ce qui a trait à chacune de ces méthodes.

Analytiques

Cette méthode inclut les techniques de transformation de Laplace, Fourier, Kirchoff et Boltzmann. Ces méthodes produisent des solutions analytiques qui sont des expressions mathématiques qui peuvent être écrites. L'avantage de ces solutions est qu'elles sont intuitives et elles présentent le problème d'une façon qui est facile à comprendre. Par contre, leur simplicité demande une solution différente pour chaque limite. Elles sont aussi limitées aux géométries simples et aux écoulements simples. Puisque l'équation de Richard est non-linéaire, il est presque impossible de la résoudre de façon analytique, mis à part pour quelques cas faciles (Kung, 1997, Kavetski *et al.*, 2001).

Semi-Analytiques

Ces méthodes utilisent les moyennes analytiques pour résoudre une partie d'un problème et les méthodes numériques pour résoudre le reste. Elles sont plus flexibles que les méthodes analytiques, mais elles sont encore limitées aux problèmes relativement simples.

Numériques

Avec les méthodes numériques, l'aire d'écoulement est divisée en plusieurs cellules. L'équation différentielle, les conditions aux limites et les conditions initiales sont évaluées avec les équations discrètes. L'utilisation d'un ordinateur pour la résolution de ces équations discrètes fournit la teneur en eau ou la pression dans chaque cellule ou à chaque noeud aux différents pas de temps. Les deux méthodes qui sont souvent utilisées sont : différences finies et éléments finis. Les méthodes numériques ont le plus large rayon d'application et plusieurs problèmes complexes peuvent seulement être résolus de façon numérique. La forme de l'équation de Richard qui utilise la pression (ψ) au lieu de la teneur en eau (θ) comme variable est souvent utilisée parce qu'elle est applicable dans les zones saturées et non saturées. Par contre, les approximations numériques pour la pression (ψ) ont les mauvaises caractéristiques d'équilibre de masse (Kavetski *et al* 2001). Les approximations numériques qui utilisent la teneur en eau (θ) comme variable donnent de meilleurs résultats pour l'équilibre de masse, mais ces approximations sont seulement valides dans des conditions non saturées et homogènes. A l'interface de deux couches de sols différents, la teneur en eau est souvent discontinue, ce qui limite l'applicabilité de cette forme de l'équation de Richard. La forme mixte 'pression et teneur en eau' est considérée

meilleure (Celia *et al.* 1990, Mansell *et al.* 2002), mais le fait que l'équilibre de masse soit plus fiable n'est pas une garantie que le modèle donne des résultats qui sont adéquats. Le bon choix de la géométrie du maillage et le choix judicieux du pas de temps entre chaque itération sont critiques pour produire des résultats qui reflètent la réalité.

FEFLOW, le logiciel de modélisation utilisé pour cette thèse, utilise la méthode des éléments finis avec la formulation de pression (ψ) de l'équation de Richard. FEFLOW utilise une méthode de deuxième ordre pour augmenter la précision du modèle. Cette méthode calcule l'erreur de chaque étape et ajuste la durée d'étape en conséquence. Une étude publiée dans le manuel de référence FEFLOW indique qu'avec cette méthode de deuxième ordre, les résultats produits par FEFLOW sont comparable aux les résultats produits par les logiciels qui utilisent la forme de l'équation de Richard (ψ - θ), mais avec beaucoup moins de calculs.

Le maillage choisi est primordial pour arriver aux bons résultats dans la zone non saturée. La même étude dans le manuel de référence FEFLOW démontre que les résultats fiables sont fortement influencés par la discrétisation temporelle et spatiale. La partie temporelle est contrôlée par la méthode de deuxième ordre, mais la partie spatiale est une fonction du maillage et doit être définie par l'utilisateur. La modélisation de la zone non saturée demande des maillages très raffinés et des intervalles de temps très courts entre les itérations.

1.4.2. Transport des solutés dans le sol

Les explosifs comme le TNT, le RDX, le HMX, ou encore les mélanges comme la composition B et l'octol, deviennent mobiles dans l'environnement seulement après la dissolution. Aussi longtemps qu'ils restent solides, ils ne peuvent pas être transportés vers l'eau souterraine. La dissolution des matériaux énergétiques a déjà été discutée dans la section 1.3.1. Il s'agit de la première étape pour le transport des matériaux énergétiques à travers la zone vadose. Le reste de cette section comporte des informations sur le transport à travers les milieux poreux. Ce transport est caractérisé par trois processus simultanés.

1) Transport convectif : Il s'agit du transport passif d'un soluté avec l'eau souterraine. Dans une dimension, le transport convectif est contrôlé par l'équation

$$J_m = qC \quad \text{Équation 11}$$

où q est le flux de Darcy (volume d'eau qui coule à travers une unité d'aire de surface par unité de temps, $\text{cm}^3/(\text{cm}^2 \times \text{temps})$) et où C est la concentration de la solution.

2) Transport diffusif : Il s'agit du résultat du mouvement des concentrations de solutés d'une zone de forte concentration à une zone de faible concentration. Dans les sols, le mouvement des solutés est restreint à cause des espaces étroits créés par les pores. Un des résultats est que la diffusion est toujours plus lente dans les sols que dans les bassins d'eau à même équivalence. Le transport diffusif suit la relation suivante :

$$J_D = -\theta D_m \frac{\partial C}{\partial z} \quad \text{Équation 12}$$

J_D est le transport diffusif, D_m est le coefficient de diffusion dans un bassin d'eau, θ est la teneur en eau, C est la concentration et z est la distance verticale. Cette équation est connue comme la première Loi de Fick.

3) Dispersion Mécanique : Cette dispersion des solutés est créée par les variations microscopiques des vitesses quand l'eau coule dans un milieu poreux. La largeur des pores est hétérogène, donc la vitesse d'écoulement dans ces pores sera aussi hétérogène. De plus, à un niveau microscopique, la friction avec les surfaces des pores va créer des gradients de vitesse à l'intérieur des pores. Cette situation est aussi décrite avec la première loi de Fick, dans le format suivant :

$$J_h = -\theta D_h \frac{\partial C}{\partial z} \quad \text{Équation 13}$$

La seule différence avec l'Équation 12 est que J_h est le transport dispersif et que D_h est le coefficient de dispersion mécanique.

Les contributions de la diffusion et de la dispersion sont montrées dans la figure 5. Cette figure présente l'injection de solutés dans une colonne de matériaux poreux avec une fonction instantanée, c'est-à-dire que la concentration relative monte de 0 à 1 d'une façon instantanée et elle est ensuite tenue à 1 pour la durée d'expérience.

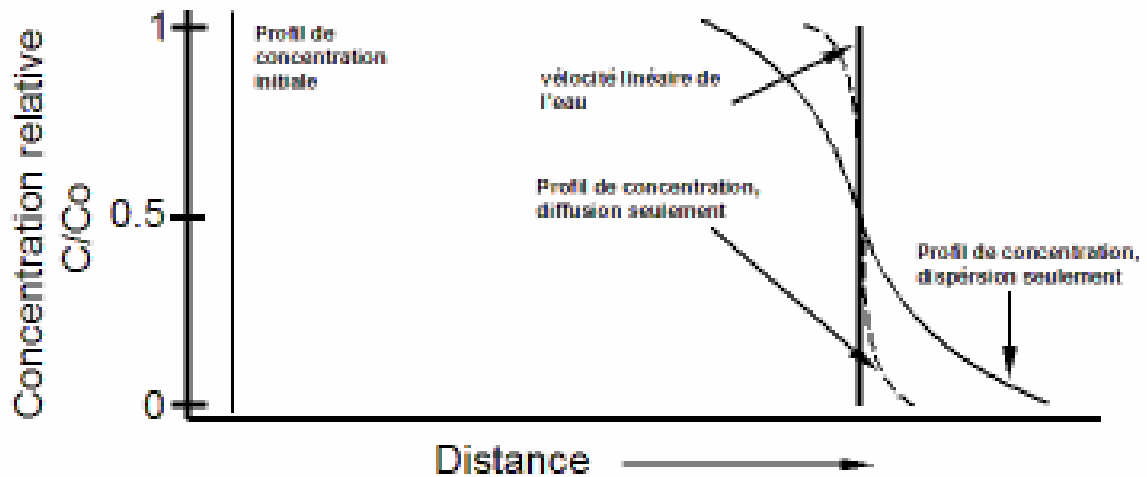


Figure 5. Contributions de dispersion et diffusion à la concentration de soluté

À l'échelle macroscopique, il est impossible de faire une distinction entre la diffusion et la dispersion, donc les deux sont normalement ajoutées ensemble pour donner le *coefficient longitudinal hydrodynamique de dispersion* D , qui est aussi connu tout simplement comme la dispersivité (Bear, 1972).

$$D = D_m + D_h \quad \text{Équation 14}$$

L'effet de dispersivité est illustré encore une fois à la figure 6 et pour une fonction instantanée. Le traceur, pendant son transport dans un milieu poreux, est assujéti à la dispersion. Quand la première concentration sort la colonne, elle est très diluée. Avec le temps, plus il y a de liquide injecté dans la colonne, plus la concentration augmente. Dans des conditions saturées, quand un volume de traceur équivalent à un volume des pores est injecté dans la colonne, la concentration à l'effluent atteint la moitié de la concentration initiale.

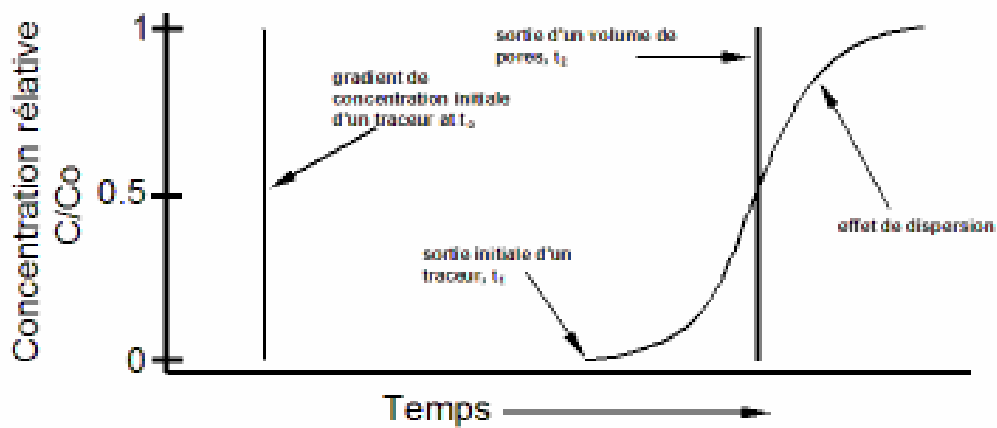


Figure 6. Effet de dispersivité

Les figures 5 et 6 montrent l'effet de dispersivité pour une fonction instantanée. Pour une fonction en mode pulsation où la concentration relative change de 0 à 1 à 0, d'une façon rapide, le comportement est un peu différent, comme l'indique la figure 7. Au moment où un traceur est introduit dans la colonne, il est indiqué comme t_0 . Après un certain temps, le profil change et la concentration prend la forme d'une courbe Gaussienne.

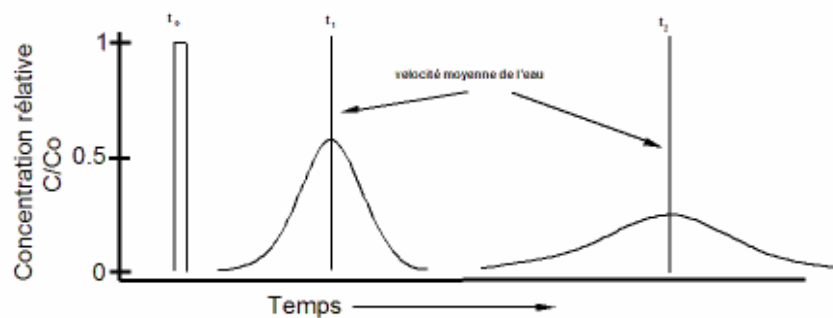


Figure 7. Effet de dispersion sur une fonction de pulsation

À la figure 7, les courbes à t_1 et t_2 démontrent que même avec un accroissement de la dispersion avec le temps, l'aire sous la courbe reste la même. Ceci indique qu'aucune masse de soluté n'est perdue pendant le transport puisque l'aire sous la courbe représente la masse totale de soluté.

La relation entre la concentration d'un soluté et la masse cumulative de soluté recueillie à la sortie d'une colonne est présentée à la figure 8. Dans cette figure, une pulsation instantanée de masse totale de 25 mg est introduite sur le dessus d'une colonne. Le profil de concentration relative est surimposé à la courbe de masse cumulative. Le maximum sur la courbe de concentration relative arrive à un volume de pores. Ce point est également présent quand la moitié de la masse totale du soluté est sortie de la colonne.

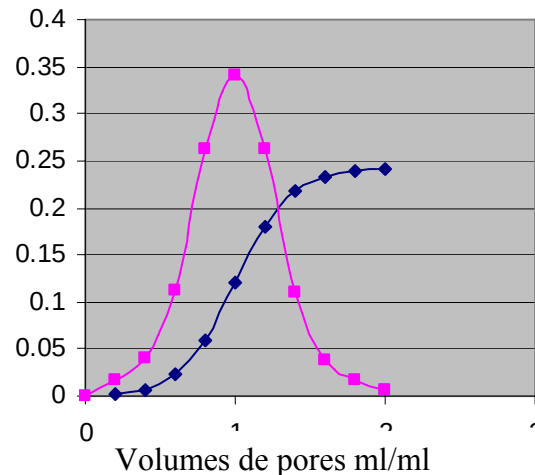


Figure 8. Courbe de masse cumulative et de concentration relative pour une injection en mode de pulsation

La diffusion moléculaire et la dispersion mécanique peuvent toutes les deux créer le mélange des solutés dans un fluide qui s'écoule dans le milieu poreux. Ces valeurs peuvent être définies comme suit :

$$D_m = D_w \tau \quad \text{Équation 15}$$

$$D_h = \alpha v^n \quad \text{Équation 16}$$

Où,

D_w est le coefficient de diffusion dans l'eau ;

τ est la tortuosité;

α est la dispersivité

v est la vitesse moyenne de l'eau dans les pores;

n est une valeur empirique (dans les matériaux granulaires, autour de 1)

L'importance de la diffusion moléculaire par rapport à la dispersion mécanique peut être évaluée par le nombre de Peclet P_e

$$P_e = \frac{vd}{D_m} \quad \text{Équation 17}$$

où d est la largeur moyenne des particules du sol.

La diffusion moléculaire présentée à l'équation 15 est du même ordre de grandeur que la dispersion mécanique quand $0.3 < P_e < 5$. Quand le nombre de Peclet est supérieur à 5, la dispersion mécanique est dominante.

Par contre, la dispersion hydrodynamique dans les sols non saturés est beaucoup plus complexe que dans les sols saturés. Quand la teneur en eau dans un sol baisse, plusieurs choses se produisent et elles ont toutes un impact sur la dispersivité. Les pores les plus larges se vident immédiatement, ce qui diminue l'aire effective pour l'écoulement de l'eau qui reste. La conductivité hydraulique diminue et la tortuosité augmente, parce que pour couler, l'eau restante doit passer à travers les plus petits pores. La vitesse de l'eau diminue et il y a moins d'opportunités pour l'eau restante de se mélanger. Puisque la dispersivité est une fonction de la teneur en eau et de la vitesse, l'équation 14 (combinée à l'équation 16) peut être écrite de cette façon :

$$D(\theta, v) = D_m(\theta) + \alpha(\theta)v \quad \text{Équation 18}$$

Si nous combinons les équations 11, 12, 13 et 14, nous arrivons à la relation pour le flux de soluté J_s

$$J_s = -\theta D \frac{\partial C}{\partial z} + qC \quad \text{Equation 19}$$

L'équation de continuité pour les solutions dans les sols est:

$$\frac{\partial \theta C}{\partial t} = \frac{-J_s}{\partial z} \quad \text{Équation 20}$$

Une combinaison des équations 19 et 20 donne l'équation générale du transport pour les composés chimiques qui ne sorbent pas, dans la direction verticale (z).

$$\frac{\partial \theta C}{\partial t} = \frac{\partial}{\partial z} \left[\theta D \frac{\partial C}{\partial z} - qC \right] \quad \text{Équation 21}$$

La plupart des composés chimiques se sorbent a un certain degré, donc l'équation 21 est théorique. La relation entre la concentration qui sorbe et la concentration en solution (si nous utilisons l'isotherme de Freundlich) est :

$$S = K_d C^n \quad \text{Équation 22}$$

Où,

S = concentration sorbée

K_d = coefficient de sorption à l'équilibre

C = concentration en solution

n = paramètre non dimensionnel près de 1

L'équation 21 pour les composés chimiques qui se sorbent devient :

$$\frac{\partial}{\partial t} (\theta C + \rho S) = \frac{-\partial J_s}{\partial z} \quad \text{Équation 23}$$

où ρ est la densité totale du sol. Si nous combinons les équations 19 et 23, nous avons

$$\frac{\partial}{\partial t} (\theta C + \rho S) = \frac{\partial}{\partial z} \left(\theta D \frac{\partial C}{\partial z} - qC \right) \quad \text{Équation 24}$$

La différentiation de l'équation 22 (avec l'hypothèse que $n=1$) et sa substitution dans l'équation 24 donnent l'équation convective dispersive (ECD) pour un élément qui sorbe:

$$R \frac{\partial \theta C}{\partial t} = \frac{\partial}{\partial z} \left(\theta D \frac{\partial C}{\partial z} - qC \right) \quad \text{Équation 25}$$

Si nous divisons par θ , nous avons

$$R \frac{\partial C}{\partial t} = \frac{\partial}{\partial z} \left(D \frac{\partial C}{\partial z} - \frac{q}{\theta} C \right) \quad \text{Équation 26}$$

Et finalement, si nous appliquons la relation que la vitesse de l'eau dans les pores v est égale à q/θ , nous pouvons mettre l'EDC dans son format plus commun:

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} \quad \text{Équation 27}$$

Où R est la *facteur de retard* égal à

$$R = 1 + \frac{\rho K_d}{\theta} \quad \text{Équation 28}$$

L'EDC est applicable pour le transport unidimensionnel des solutés dans un milieu poreux homogène ayant un écoulement, une teneur en eau et une vitesse constante. L'EDC est l'équation fondamentale pour la description du transport de soluté dans un milieu poreux (Bear, 1972). Par contre, cette équation est seulement valide quand le transport d'un soluté obéit à la loi de Fick (Fischer *et al*, 1979). Les effets de la loi de Fick sont créés à une échelle microscopique dans les pores, mais ils sont observés à une échelle macroscopique. Donc, la loi de Fick devient valide seulement quand le soluté a traversé suffisamment d'hétérogénéités pour que ça devienne représentatif du sol global. Dans un sol saturé, cette distance est de l'ordre de quelques milliers de grains de sol (Yeh, 1998). Puisque cette distance est beaucoup moindre que la plupart des colonnes expérimentales, normalement cette condition est facilement atteinte. Par contre, dans les sols non saturés, le nombre de chenaux d'écoulement diminue quand la teneur en eau diminue parce que les pores commencent à se désaturer. Le résultat est que la variation de la vitesse de l'eau dans les pores augmente et qu'un soluté doit traverser une plus grande distance pour devenir entièrement mélangé. Souvent, cette distance est plus grande que celle de la longueur de la colonne expérimentale (Yeh, 1998). Par conséquent, la concentration de soluté qui sort de la colonne est souvent caractérisée par des pics multiples, une arrivée de soluté et de faibles concentrations de soluté qui sortent de la colonne sur des périodes de temps étendues, une fois que la concentration maximale ait été détectée. Ces comportements ne peuvent pas être expliqués par l'équation 27, l'équation convective dispersive (*ibid.*).

Il existe un manque d'information pour décrire la dispersion non saturée. Une des raisons de ce manque est que c'est extrêmement difficile de mesurer les paramètres. Il est nécessaire d'établir les conditions d'écoulement uniformes avec la teneur en eau où la vitesse d'écoulement est constante partout dans la colonne expérimentale. Ces conditions sont très difficiles à

reproduire et n'existent pas dans les conditions naturelles. La recherche à propos de la diffusivité non saturée est encore à un stade peu avancée, avec peu d'études disponibles.

1.4.3. Courbe caractéristique d'eau dans le sol

L'information donnée par cette courbe est fondamentale pour la compréhension de l'écoulement de l'eau dans un sol non saturé, parce qu'elle fournit la relation entre la teneur en eau et la pression d'eau dans les pores.

Cette relation est non linéaire et chaque sol est unique. Un exemple d'une courbe est donné à la figure 9. Une des caractéristiques de cette courbe est qu'elle est différente si le sol s'assèche ou s'humidifie. Ce phénomène est appelé hystérèse.

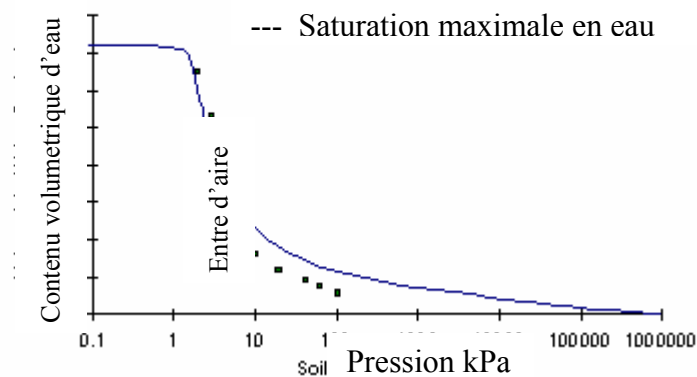


Figure 9. Courbe caractéristique d'eau dans un sol

Même à des pressions très basses, le sol ne perd jamais toute son eau. Cette limite est la saturation résiduelle en eau. La saturation maximale en eau est tout simplement la porosité du sol et elle est atteinte quand la pression d'eau dans le sol est égale ou supérieure à la pression atmosphérique. Le point d'entrée d'air est la pression où le sol commence à se drainer.

Plusieurs modèles mathématiques peuvent reproduire la courbe caractéristique de l'eau dans le sol, si l'information expérimentale est disponible. Par contre, chacun a des limites et aucun n'est capable de reproduire la courbe pour toutes les valeurs possibles de pression. Les trois des modèles les plus connus sont Brooks et Corey (1964), Van Genuchten (1980) et Fredlund et Xing (1994).

Brooks et Corey ont défini une des premières équations qui simule la courbe caractéristique de l'eau dans le sol. Pour les valeurs plus élevées que le point d'entrée d'air, l'équation est valide. Pour les valeurs près de la saturation résiduelle en eau, l'erreur est considérable.

$$\Theta = \left[\frac{\psi_b}{\psi} \right]^\lambda$$

Équation 29

Θ = contenu d'eau normalisé

(i.e., $\Theta = (\theta - \theta_r)/(\theta_s - \theta_r)$, où θ_s et θ_r sont les contenus volumétrique saturé et volumétrique résiduelle,

ψ = succion,

ψ_b = point d'entrée d'air, et

λ = distribution des largeurs des pores

L'équation de Van Genuchten est peut-être une des formules les plus utilisées pour définir la courbe caractéristique de l'eau dans le sol. Cette équation utilise trois différents paramètres (n, m et p) qui doivent être déterminés avec la régression non linéaire. Ces trois paramètres ne sont pas reliés aux caractéristiques physiques du sol.

$$\Theta = \left[\frac{1}{(1 + p\psi)^n} \right]^m$$

Équation 30

Θ = contenu d'eau normalisé

ψ = succion

n, m, p = paramètres non physiques

Fredlund et Xing ont proposé une équation qui donne des résultats supérieurs pour la reproduction de la courbe caractéristique entre les valeurs de pression de 0 kPa à -1000 MPa, où le sol est considéré comme sec (Fredlund et Rahardjo, 1993). Le premier terme dans l'équation est une fonction pour forcer la courbe à une valeur de 0 à -1000 MPa. Le deuxième donne la relation entre le contenu d'eau volumétrique et la pression.

$$\theta = \left[\frac{-\ln(1 + \psi / \psi_r)}{\ln[1 + (1000000 / \psi_r)]} + 1 \right] \left[\frac{\theta_s}{\{ \ln(e + (\psi/a)^n) \}^m} \right] \quad \text{Équation 31}$$

θ_s = contenu d'eau saturé volumétrique

ψ = succion

ψ_r = succion au contenu d'eau résiduel volumétrique θ_r

a, n, m = paramètres non physiques

1.4.3.1. Les fonctions de transfert pédologique

Dans le domaine des sciences du sol, les fonctions qui tentent d'établir des relations entre les propriétés physiques d'un sol comme la granulométrie, la porosité ou la densité et les propriétés hydrauliques comme la conductivité et la courbe caractéristique de l'eau dans le sol sont connues comme les fonctions de transfert pédologique. Compte tenu de la difficulté à mesurer la courbe caractéristique, il y a eu plusieurs efforts dédiés à trouver une telle relation.

Les deux grandes difficultés avec la plupart de ces fonctions sont leur complexité et le fait que ces fonctions ne s'appliquent pas nécessairement à la plupart des sols. Toutes les différentes fonctions de transfert pédologique utilisent une des trois approches suivantes. La méthode de régression d'un point essaie d'établir une corrélation entre la granulométrie et la teneur en eau et la pression interstitielle. La méthode d'estimation des paramètres fonctionnels fait une relation entre une propriété fondamentale du sol comme le point d'entrée d'air avec un paramètre comme le pourcentage de sable ou la porosité. Finalement, la méthode physico-empirique essaie de déterminer la teneur en eau connaissant le rayon des pores. Cette information est par la suite convertie en pression, par la théorie capillaire. Une difficulté de la méthode physico-empirique est le fait qu'il n'existe pas de relation simple entre la granulométrie d'un sol et la dimension des pores. Arya et Paris (1981) ont trouvé une équation physico-empirique valide, en assumant que toutes les particules de sol sont sphériques. La granulométrie est divisée en M fractions, et la masse de la fraction dans la i^{iem} fraction est corrélée avec la masse de N_i particules de rayon R_i . Le volume est donc:

$$V_{ri} = \frac{4}{3} N_i \pi R_i^3 \quad \text{Équation 32}$$

Le volume des pores est représenté par un simple tube capillaire avec un rayon r_i

$$V_{ri} = \pi r_i^2 h_i \quad \text{Équation 33}$$

où h_i est la longueur du tube capillaire. Arya et Paris ont défini la longueur du tube capillaire pour la fraction D_i comme :

$$h_i = 2D_i N_i^\alpha \quad \text{Équation 34}$$

Où α est une constante empirique entre 1 and 2.

La fonction de transfert pédologique de Fredlund et Wilson (1997) est l'une des plus avancées et elle est fondée sur trois points de vue :

- 1) Un sol composé par des particules de dimensions uniformes et homogènes donne une courbe caractéristique de l'eau dans le sol unique.
- 2) Le modèle capillaire est mieux utilisé pour l'estimation de la valeur d'entrée d'air pour un sol avec des particules uniformes et homogènes.
- 3) La courbe caractéristique de l'eau dans le sol pour un sol qui est composé par plus d'une dimension de particules sera la somme des courbes pour chaque dimension de particules.

L'équation 35 (Fredlund et Xing, 1994) est utilisée dans la fonction de transfert pédologique Fredlund et Wilson pour décrire la courbe pour chaque dimension unique de particules.

$$w(\psi) = w_s \left[1 - \frac{\ln\left(1 + \frac{\psi}{h_r}\right)}{\ln\left(1 + \frac{10^6}{h_r}\right)} \right] \left[\frac{1}{\left[\ln \left[\exp(1) + \left(\frac{\psi}{a_f} \right)^{n_f} \right] \right]^{m_f}} \right] \quad \text{Équation 35}$$

a_f est un paramètre qui est relié à la valeur d'entrée d'air. La relation entre le rayon des particules et la valeur associée d'entrée d'air peut être définie par l'équation capillaire :

$$a_f = 2\gamma \frac{\cos \Theta}{\rho_w g r} \quad \text{Equation 36}$$

où γ = tension de surface pour l'eau
 Θ = angle de contact
 ρ_w = densité de l'eau
 g = accélération gravitationnelle
 r = rayon des pores
 a_f = paramètre Fredlund and Xing (1994)

Comme point de départ, les courbes caractéristiques pour un sable uniforme et une argile uniforme sont mesurées. Ces deux courbes sont les limites pour tous les autres types de sols. Pour un sol expérimental, la granulométrie est utilisée pour fractionner les sols en plusieurs dimensions. Par la suite, la dimension effective des grains est déterminée par l'équation 37 :

$$\frac{1}{d_e} = \frac{3}{2} \frac{\Delta g_i}{d_i} + \sum_{i=2}^{i=n} \frac{\Delta g_i}{d_i} \quad \text{Équation 37}$$

où d_i = plus large diamètre de la dernière fraction de sol
 Δg_i = masse normalisée de la fraction la plus fine
 d_e = diamètre effectif

Le diamètre effectif est par la suite utilisé pour trouver les valeurs de n et de m dans l'équation 36, en faisant une comparaison avec une base de données. Une courbe pour chaque fraction est produite et les courbes sont combinées en commençant par la plus petite fraction. Les plus larges fractions sont ajoutées l'une après l'autre juste qu'à ce que le volume des espaces théoriques des pores soit équivalent à la valeur mesurée. À ce point, le résultat final est la courbe caractéristique de l'eau dans le sol pour le sol expérimental.

1.4.4. L'écoulement préférentiel

L'écoulement préférentiel peut prendre plusieurs formes. Il existe quand il y a de grandes différences entre les vitesses d'écoulement dans les sols homogènes.

L'écoulement préférentiel peut se produire quand des chenaux sont créés dans le sol par des racines qui sont ensuite décomposées, l'activité des animaux comme les vers de terre et les rongeurs, par les fractures créées par les tremblements de terre ou par l'assèchement des sols argileux.

Un autre exemple qui est plus difficile à visualiser est la digitation, qui se produit quand l'eau coule dans les sols secs et texturés comme le sable. Sous ces conditions, l'eau a tendance à s'infiltrer dans les régions isolées. La Figure 10 montre la relation qui existe entre le diamètre des particules et le diamètre des « doigts ». Le flux d'eau n'a pas un grand impact sur la largeur des « doigts » s'il reste inférieur à la conductivité des sols saturés. Dans les conditions naturelles, la conductivité des sols non saturés est de un ou deux ordres de grandeur plus faible que la conductivité saturée. Quand le flux approche la conductivité saturée, le nombre de « doigts » et leur diamètre augmentent jusqu'au moment où ils forment un front uniforme.

Lui *et al.* (1993) démontrent que le sol qui est à la capacité aux champs va développer des « doigts » qui sont d'un ordre de grandeur plus large que ceux qui se développent dans des conditions sèches. Donc, dans un sable moyennement humide, il faut prévoir un diamètre de « doigts » entre 20-50 cm.

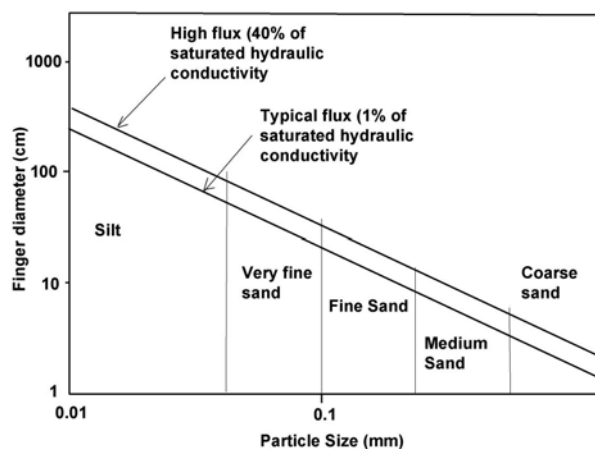


Figure 10. Les diamètres des « doigts » en fonction de la granulométrie (Selker *et al.*, 1999)

1.4.5. Les fluctuations dans la zone vadose

Le cycle naturel des températures tièdes pendant la journée et fraîches le soir pénètre dans le sol à une profondeur de 10-30 cm. Par contre, les variations saisonnières peuvent pénétrer plusieurs mètres (Stephens, 1996). Cette fluctuation suit une courbe sinusoïdale qui est étouffée de plus en plus avec la profondeur. Cependant, en fonction des caractéristiques thermiques du sol, de la magnitude de la variation en température et de la période du cycle, la fluctuation est éventuellement étouffée complètement pour atteindre une température constante.

1.4.6. Réflectométrie

La réflectométrie est connue par l'acronyme TDR, *Time Domain Reflectometry*. Elle était utilisée originalement pour la détection des bris dans les filages de communications. Dans les années 1970, elle a été modifiée pour la mesure d'humidité dans les sols (Topp *et al.*, 1985). Elle est basée sur la propriété physique appelée « constante diélectrique », qui détermine l'habileté d'un matériel à résister à une charge électrique. Le Tableau 6 présente les constantes diélectriques de quelques matériaux communs et il est évident que l'eau a une constante beaucoup plus haute que la plupart des matériaux.

Tableau 6. Constants dielectric

Matériaux	Constant dielectrique K_a
L'eau	80
Aire	1
Minéraux	3-7
Matière Org.	2-5
Glace	3

Il y a deux étapes pour la mesure de la constante diélectrique. Premièrement, il faut mesurer la constante diélectrique (K_a) du sol. Deuxièmement, il faut faire une corrélation entre le K_a et l'eau dans le sol (θ).

La première étape est faite avec la transmission d'une pulsation de voltage dans une sonde TDR qui est enterrée. La pulsation est réfléchi au bout de la sonde et retourne pour être enregistrée par un oscilloscope. Un exemple typique d'un graphique d'une pulsation réfléchi est

donné à la Figure 11. La forme de la courbe est une indication du temps requis à la pulsation pour traverser la sonde. Cette vitesse est reliée avec le K_a de façon linéaire.

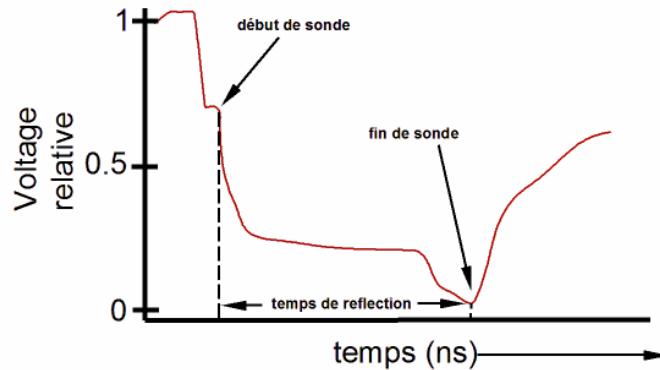


Figure 11. Réflexion de voltage avec sonde TDR

La deuxième étape est accomplie avec l'équation Topp (Topp *et al.* 1980), (équation 38). Cette équation donne la relation entre K_a et θ :

$$\theta = -0.053 + .0292K_a - 5.5 \times 10^{-4} K_a^2 + 4.3 \times 10^{-6} K_a^3 \quad \text{Équation 38}$$

1.5. Cycle d'infiltration annuel d'eau pour la ville de Québec

Le cycle annuel d'infiltration de l'eau pour la ville de Québec est caractérisé par deux événements de recharge. Le premier (qui est plus important) est la fonte de la neige au printemps. Pendant à peu près trente jours au mois de mars et d'avril, toute la précipitation accumulée pendant l'hiver sous forme de neige fond. Cet événement représente presque 70% de la recharge annuelle de la nappe phréatique, avec en moyenne 253 mm d'infiltration (Mailloux, 2002).

La deuxième période d'infiltration est pendant les mois d'octobre et novembre, lors des pluies d'automne. Cet événement représente le reste de l'infiltration annuelle avec en moyenne 116.1 mm d'eau.

La pluie qui tombe pendant l'été n'arrive pas à recharger la nappe phréatique. La totalité de l'eau qui tombe en été à Québec est retournée à l'atmosphère par évaporation ou transpiration de la végétation. En hiver, le sol est gelé et la précipitation est sous forme solide (neige). En hiver, il n'y a aucune recharge d'aquifère.

La recharge au printemps arrive surtout pendant le jour, quand les températures sont supérieures à 0° C. En automne, les précipitations peuvent avoir lieu 24 heures sur 24, jour et nuit.

1.6. Profondeur des munitions non explosées dans la zone vadose

La profondeur des munitions non explosées (UXO's) qui peuvent pénétrer dans le sol est reliée au type de sol et à l'énergie cinétique des munitions quand elles atterrissent. L'artillerie peut avoir des vitesses entre 500 m/s et 800 m/s, ce qui donne à la munition beaucoup d'énergie cinétique. Les mortiers sont beaucoup moins rapides et donc leur capacité à pénétrer le sol est aussi moins grande, comparativement à l'artillerie. Les UXO's sont normalement générés quand le détonateur ne fonctionne pas. Le pourcentage des munitions qui deviennent des UXO's varie selon la sorte de munition. Les munitions anti-char peuvent avoir des taux de ratés jusqu'à 30%. Les munitions d'artillerie et de mortier ont normalement des taux de ratés entre 3% et 8%.

En temps de paix, l'information sur la capacité de pénétration des munitions est limitée. La raison est qu'il est difficile de faire de telles expériences de façon sécuritaire. Les munitions sont lancées à de très grandes distances et il est difficile de trouver le point précis d'impact. Par contre, il existe des récits de temps de guerres qui fournissent des informations subjectives. Les deux passages qui suivent viennent de *The Guns of Normandy*, par George Blackburn (1995). Ce livre raconte l'histoire d'un officier d'artillerie pendant l'invasion de Normandie, lors de la deuxième guerre mondiale en 1944. Ce livre a été écrit en anglais ; les passages ont donc été laissés dans leur langue originale.

“To excavate a dud 88-mm for examination is a major operation, since their extremely high muzzle velocity imbeds them several feet down in the soft earth. One hole, drilled no more than six inches from the sleeping head of Gunner James Beatty, in the end of a slit trench he'd

excavated in the side of a gun pit, is so deep that even when measured with a pole nine feet long the bottom can't be reached.”(p. 145).

“Some large calibre duds thud into the position, which would have caused damage to men and guns had they gone off. One, landing on Baker Troop, drills a hole so deep that the bottom can't be reached with a 15 foot pole” (p. 319).

La Figure 12 est une photo d'une munition de 155 mm d'artillerie non explosée qui a été trouvée à une profondeur de 7 mètres dans un tunnel sur les champs de bataille de Vimy, dans le nord de la France. Cette munition a été lancée en 1917.

Ces observations sont circonstanciées, mais elles sont suffisantes pour affirmer qu'il est possible de trouver des munitions non explosées jusqu'à une profondeur de 7 mètres. Dans plusieurs régions aux aquifères peu profonds, l'implication est que les UXO's peuvent être trouvés partout dans la zone vadose, et même dans la nappe phréatique.



**Figure 12. Munition d'artillerie 155 mm
dans le tunnel Grange, Vimy Ridge, France**

Des UXO's peuvent également être déposés en surface lorsqu'ils proviennent de tir quasi horizontaux ou lorsque les sols sont durs ou gelés et que la munition n'a pas une énergie cinétique suffisante pour pénétrer le sol. Au Canada, lorsque ces UXO's de surface sont trouvés, ils sont détruits par détonation afin d'éliminer le risque associé à leur présence. Cependant, il est

extrêmement difficile de localiser tous ces UXO's et leur présence permet la libération potentielle du contaminant s'ils sont frappés par des fragments de munition, tel qu'il sera démontré dans cette thèse.

2. OBJECTIVES

Explosive residues have been detected in the groundwater of several U.S. and Canadian bases. The presence of this contamination has led to the closure of at least one U.S. base, the Massachusetts Military Reserve (MMR). Very little is known about the potential sources of this contamination, which may originate from direct fire unexploded ordnance, indirect fire unexploded ordnance, munitions dumps or any one of a host of other sources. Very little is also known about the transport of such contamination through the vadose zone. Understanding this transport is important, because as long as the contamination is limited to the vadose zone it can only travel vertically. Once it reaches the saturated zone, however, it becomes horizontally mobile and may contaminate regions outside the base boundaries. A better understanding of this problem is vital to the interests of the Canadian Forces. An international precedent has been set with the MMR with respect to the closure of a military installation for environmental reasons. If this were to happen in Canada, it would have serious and long-reaching impacts on the operational readiness of our troops.

In this context, the two main objectives of this thesis are the following:

- 1) Test the hypothesis that cracked shell UXO's are a significant source of explosive contamination which is easily mobilized.
- 2) To improve our understanding of how dissolved explosive residues are carried through the vadose zone.

3. EXPERIMENTAL METHOD

3.1. Production of cracked shell munitions

Parts of this section were published as Chapter 7 in the 2004 SERDP Annual report which is available as Attachment 1 of this thesis. The following experimental section summarizes the 2004 SERDP chapter.

3.1.1. Materials & methods

The Canadian 81-mm C70A1 high explosive (HE) mortar, filled with composition B explosive (39% TNT, 60% RDX, 1% wax), was used for all trials. This munition is fully described in Canadian Forces Technical Order (CFTO) C-74-315-D00/TA-000. It is a fragmentary attack high explosive munition which contains 900 g of composition B in a steel casing up to 1 cm in thickness.

The fuze was removed for safety purposes. The fuze was not replaced with an inert fuse for most tests, to increase the likelihood of obtaining cracked shells. An inert plug was used for one test only. The trials were performed on snow, with the detonation residue collected by removing a 2-5 cm thick layer of snow and storing it in large plastic bags. The cracked shell itself was also collected.

PCB 113B52 pressure gauges were placed at 10 meters from the detonation point to measure the overpressure generated by the events. The overpressure data suggest whether the round detonated completely, or a low-order detonation was produced. The gauges were triggered by an ionization pin placed in the C4. When electrical continuity in the pins was broken (by the detonating charge), the pressure gauges began taking readings, which were stored digitally.

Two methods of producing the cracked shells were attempted. The first was by straight C4 attack using either linear shaped charges or simple charges of varying mass. The second method was by attack from a second round which detonated nearby at varying ranges. These methods will be described below.

3.1.1.1. Method 1: C4 charge

Blocks or linear shaped charges fabricated from C4 explosive, the standard RDX-base demolition plastic explosive used by the Canadian Forces, were applied to the outside of the 81 mm shell to simulate the blow-in-place of unexploded ordnance. This method was intended to reproduce what would happen in the case of an unsuccessful range clearance event. During range clearance, unexploded ordnance are destroyed by placing a C4 kicker charge on or near the munition. If the charge is insufficiently powerful or the contact between the C4 and the munition is inadequate, the UXO may be broken open rather than detonated. During this trial, C4 was applied in various amounts and at various positions on the outside of the mortar round. Various sizes of shaped charges were used, with different stand-off distances.

Twenty-three trials of Method 1 were performed in January 2004 at the DRDC Valcartier trial site on the Canadian Force Base Valcartier (Table 7). The early trials were done on a thick metal plate until the right conditions were found to crack the shells. The successful ones were then repeated on snow to ensure a maximum recovery of the explosives and a minimum contamination by soil. This approach was taken to minimize the number of trials on snow, as preparation of the snow-pack was very time consuming. Several experimental configurations are shown in figure 13.

3.1.1.2. Method 2: Fragment impact

The second method consisted in detonating a mortar shell next to another similar round, in order to simulate the impact on a UXO by another incoming round that explodes properly. Two 81-mm mortar projectiles (A and B) were used for each trial. Projectile A was the intentionally detonated projectile, which simulated a round that functions normally. A booster charge of 40-g of C4 was employed in all trials in the fuze well of projectile A. Projectile B reproduced a UXO lying on the ground in the vicinity of the point of impact of an incoming round (projectile A).

The two 81-mm mortars were placed one over the other, one was laid on a metal plate and the other was suspended by chains (figure 14). Two necessary steps in Method 2 were to determine the distance at which the reaction would change from a detonation of Projectile B to the production of a cracked shell and to determine the distance at which Projectile B would remain entirely intact. A final objective of these trials was to determine the effects of placing Projectile B on the ground, on snow and underwater. The purpose of this was to identify how or

if there was any protection offered by a layer of soil or a depth of water should the unexploded munition be found buried or underwater. Since mortars do not have the kinetic energy of artillery, mortar UXO's will not become buried to the great depths that artillery UXO's may (Section 1.6). The trials reflected this reality, with the mortars either being partially exposed at the surface, or being buried to a depth of no more than 10 cm. The one underwater trial was designed to reproduce the situation of a UXO being found in the many shallow bodies of water found on or near many impact areas.

Table 7. Experimental parameters for method 1

Trial #	Type of attack	Position	Amount of C-4 used (g)
1	Mk 7 Mod 1 shaped charge	Longitudinal, 0 stand-off	15.1
2	Mk 7 Mod 1 shaped charge + C4 ball	Longitudinal, 0 stand-off	16.3 + 5.7*
3	Mk 7 Mod 2 shaped charge + C4 ball	Longitudinal, 0.5-cm stand-off	15.4 + 7.7*
4	Mk 7 Mod 3 shaped charge + C4 ball	Longitudinal, 0 stand-off	24.7 + 5.0*
5	Mk 7 Mod 2 shaped charge + C4 ball	Perpendicular, 2.9-cm stand-off	16.0 + 7.0*
6	Mk 7 Mod 4 shaped charge cut in half	Perpendicular, 1.5-cm stand-off	27.1 + 6.0*
7	Mk 7 Mod 8 shaped charge cut in half	Perpendicular, 9.5-cm stand-off	71.0
8	C4 ball	In fuze well	20.0
9	C4 ball	In fuze well, 2.5 cm stand-off	10.0
10	C4 block	Outside, at the nose	72.3
11	C4 block	Outside, at the nose	72.0
12	C4 block	Outside, at the nose	72.0
13	C4 block	Outside, at the nose + plug fuze	70.2
14	C4 block	Outside, at the nose	72.1
15	C4 block	Outside, at the nose	90.0
16	C4 block	Outside, at the nose	80.0
17	C4 hemisphere	Outside, at the nose	80.0
18	C4 hemisphere	Outside, at the nose	80.0
19	C4 hemisphere on cracked shell	Outside, at the nose	80.0
20	C4 hemisphere	Outside, at the nose	80.0
21	C4 hemisphere on cracked shell	Outside, at the nose	80.0
22	C4 hemisphere on cracked shell	Outside, at the nose	63.2
23	C4 hemisphere on cracked shell	Outside, at the nose	64.0

Seventeen different trials were conducted for Method 2. The experimental parameters for each are shown in Table 8.



Figure 13. Configurations used in method 1.

Top left: small shaped charge longitudinal, minimal stand-off.

Top right: larger shaped charge, large stand-off. Bottom left: Small block of C4 at the nose.

Bottom right: Hemispherical configuration of C4 at the nose.

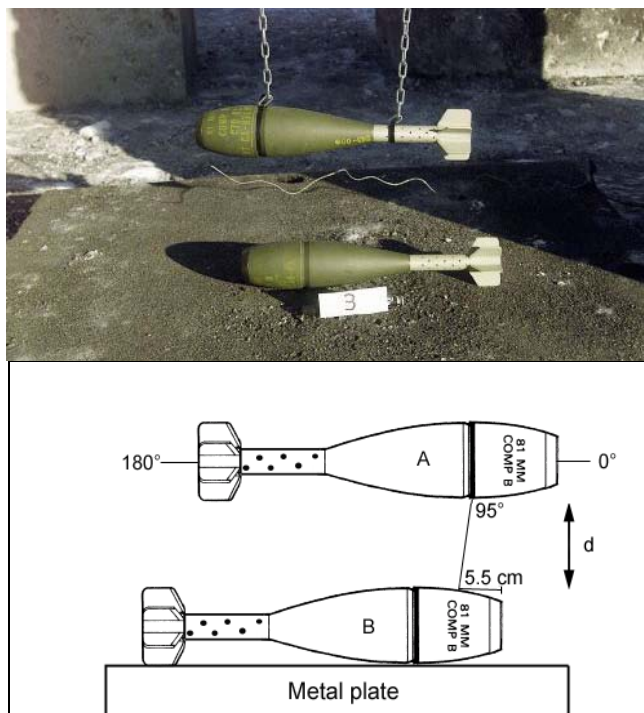


Figure 14. Photo and schematic for experimental set-up of method 2

3.1.2. Detonation residue collection

For both Methods 1 and 2, once the condition necessary to produce cracked shells were identified, the desired conditions were reproduced on a large area of clean snow. The detonation residue was largely composed of composition B filling and/or soot particles. The munitions were photographed after the test, after which an area 2m x 2m was delineated in the snow around the cracked munition. All of the detonation residue and Composition B filling in the top 10 cm of snow in the delineated area was collected. The munition was then removed and further photographed. Typically 3-4 garbage bags of snow were collected for each sample. These garbage bags were then brought back to the lab and stored in industrial freezers until the residue could be extracted from the snow.

Table 8. Experimental parameters for fragment impact

Trial #	Distance between projectiles (cm)	Material underneath Projectile B	Material above Projectile B
1	0	Metal plate	-
2	20	Metal plate	-
3	15	Metal plate	-
4	10	Metal plate	-
5	13	Metal plate	-
6	15	Metal plate	-
7	15	Metal plate	-
8	25	Metal plate	-
9	45	Metal plate	-
10	100	Metal plate	-
11	157	Metal plate	-
12	15	Snow	-
13	15	Snow	Sand 2.5 cm
14	15	Sand	Sand flush with top
15	15	Sand	Sand 10 cm
16	15	Sand	Sand (proj. planted at 45°)
17	15	Sand	Water 5 cm

3.1.3. Detonation residue extraction from snow

Because the goal of the column studies was to measure the leaching characteristics of cracked shells and their detonation associated residue, the residue had to be extracted from the snow in such a way as to minimally interfere with its physical structure. Contact with liquid water would cause some dissolution, so melting the snow and filtering out the residue was not an option. The option which was chosen was to freeze dry all of the snow samples. Freeze-drying the samples caused minimal disruption to the detonation residue. The snow samples were placed in glass flasks and exposed to a vacuum of 5 $\mu\text{m Hg}$ ($6.6\text{E-}6$ atm) and a temperature of -50 degrees Centigrade. Under these conditions, which fall below the triple point of water (0.006 atm, 0.01°C) water sublimates from a solid directly to a gas, with no liquid water intermediary.

3.2. Leaching experiment source terms

The explosive source terms were obtained from detonation trials performed on 81 mm mortars. A schematic for this munition is found in Figure 15. It is a very common munition used by all NATO armies, and it is frequently used on Canadian Forces training bases. This, combined with its compact size compared to many artillery rounds, made it an ideal choice for use during these experiments.

Each cracked shell trial produced a limited quantity of detonation residue (8.7 g to 165.8 g, see Table 9). To achieve reproducibility during the leaching trials, a uniform detonation residue source term was required, in sufficient quantity to be used on all the soil columns. The only way to achieve this was to produce a composite detonation residue sample. The residue from trials 14, 21 and 23 of Method 1 and trial 12 from Method 2 was used for the composite, as these trials produced the most detonation residue and were successfully extracted from the snow by freeze drying without any exposure to liquid water. In all trials, the coarse fraction was significantly larger than the fine fraction, although this is due more to the fracture mechanics of amorphous, non crystalline solids such as composition B than it does with the type of trial performed. Amorphous solids tend to break into larger pieces or chunks preferentially because of the free energy required to fracture their surfaces at smaller and smaller size fractions. In other words, a larger mass-percentage of material will be found in larger, rather than smaller size fractions.

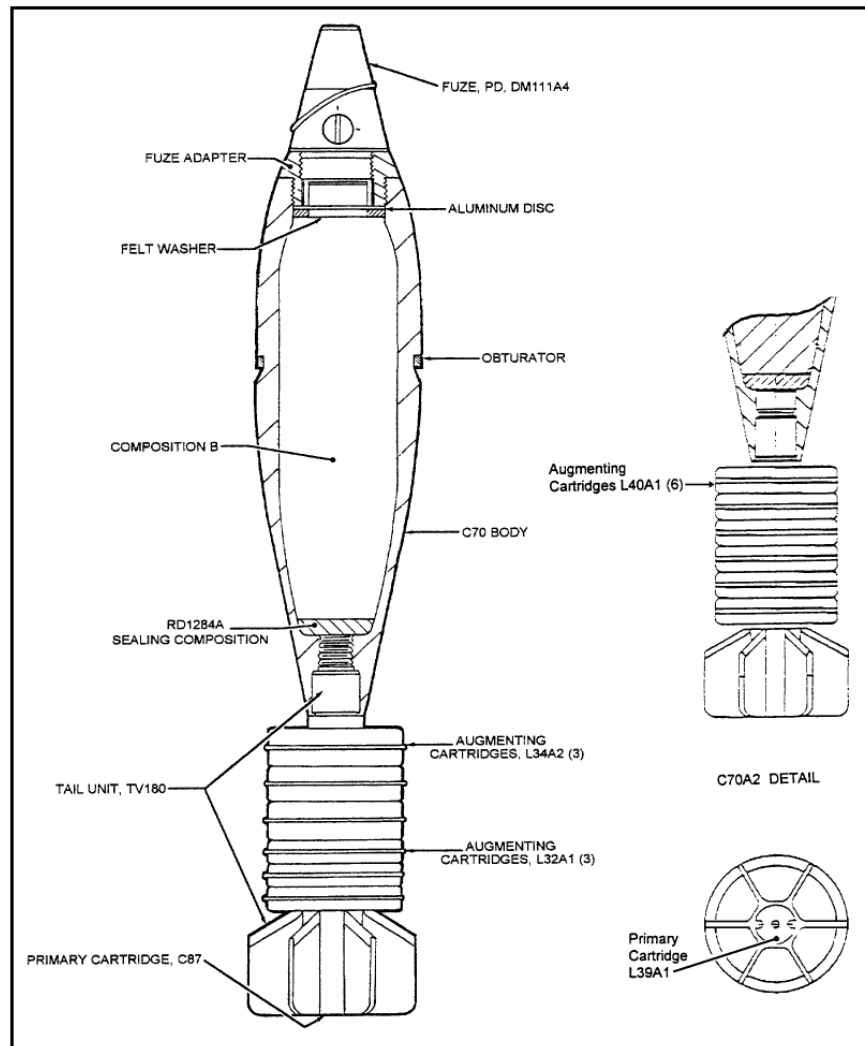


Figure 15. 81 mm high explosive mortar schematic

The samples were separated into a fine fraction (<0.7 mm) and a coarse fraction (>0.7 mm). These were then combined into a fine composite sample and a coarse composite sample. The exact source of the composite sample is given in Table 9.

Columns D and F included the actual cracked mortar as part of the source term. These two cracked mortars, obtained from trials 12 and 3 of Method 2, both had a significant amount of powdered and crushed loose composition B inside the metal casing. All loose composition B was removed from the mortars prior to the mortars being installed on the soil columns. The mortar from trial 12 had an initial mass of 2895.0 g. The mortar from trial 3 had an initial mass of 3370.0 g.

Table 9. Source of composite sample

	Total Sample Mass (g)	Mass (g) of fine Fraction (>0.7 mm)	Mass (g) of coarse Fraction (<0.7mm)
Sample 12, Method 2	165.8	38.9	126.9
Sample 14, Method 1	8.7	1.3	7.4
Sample 21, Method 1	129.8	30.7	99.1
Sample 23, Method 1	163.2	38.3	124.9
Composite Sample Fine fraction (<0.7 mm)	109.2	109.2 (sum of above four masses)	
Composite Sample Coarse fraction (>0.7 mm)	358.3		358.3 (sum of above four masses)

Pure, crushed composition B was produced from laboratory grade composition B flakes. This source terms acted as a control to determine if the transport behaviour of the detonation residue was significantly different from just pure composition B. Detonation residue which has been exposed to the high heat and pressure of an explosion may be expected to have glazed or rounded grains, which may have an impact on dissolution. However, if the transport behaviour of the detonation residue is shown to be the same as the pure composition B, future leaching experiments will be much easier to conduct, as no preliminary detonation trials will need to be performed to obtain an explosive source term.

The composite sample fine fraction was uniformly distributed on the surface of the columns with a saltshaker. Similarly, the composite sample coarse fraction was uniformly distributed by shaking the pieces from a glass bottle onto the column surface. The mortars were placed centrally on the surface of columns D and F. The inert KBr brine tracer was uniformly sprayed onto the surface of column A with a spray bottle. Details of the source terms placed on the surface of each column are given in Table 10. The choice of source terms was intended to strike a balance between maximizing the number of source terms and ensuring there were a meaningful number of replicates. There are therefore four source terms being investigated: an inert tracer, detonation residue alone, crushed, pure composition B and detonation residue with the mortar shell. Columns B and C are replicates for the detonation residue alone and columns D and F are replicates for the detonation residue with the mortar shell. Column E contains the pure composition B and it acts as a control, allowing a comparison of leaching characteristics between

the detonation residue of composition B with pure composition B. The idea is that the detonation residue may undergo physical melting and granularization, as well as carbonization which could have an impact on the leaching behaviour.

Since this experiment involved the use of kilogram quantities of high explosive, it was necessary to obtain a 1.1 high explosive license from the Department of National Defence. In the safety study performed prior to the start of the experiment, it was demonstrated that given the safety radius of a detonating mortar and the physical constraints of the steel column and poured concrete building it was housed in, there was no danger to the general public. The license was granted in 2002.

Table 10. Source term distribution on columns

Column	Composite Sample fine fraction (<0.7 mm dia.)	Composite Sample coarse fraction (>0.7 mm dia.)	Cracked Mortar	Crushed Composition B control	Inert Tracer (KBr)
A	0	0	No	0	10 g KBr
B	20.00 g	25.00 g	No	0	0
C	20.00 g	25.00 g	No	0	0
D	20.00 g	25.00 g	Yes	0	0
E	0	0	No	20.00	0
F	20.00 g	25.00 g	Yes	0	0

3.2.1. Source term grain size curves

Grain size curves were obtained for the detonation residue and the composite source terms by passing the material under investigation through a series of calibrated screens as described in table 11. Each sieve was individually weighed on a Mettler electronic scale accurate to 0.01 g.

The sieves were then stacked from largest aperture (2.00 mm) on top to smallest aperture (0.125 mm) on the bottom. A solid pan was stacked beneath the smallest aperture sieve. The entire stack was placed on a vibrating table and the sample to be sieved placed on the top of the stack. The vibrating table was turned on for 5 minutes. Each sieve was then re-weighed with the sample fraction still on it, and the sample weight was obtained by subtraction. With the finer sieve sizes, particles tend to get caught in the mesh, so the empty sieves were re-weighed prior to

each sample run. Safe handling of the detonation residues required that the sieving be performed remotely, with the vibrating table located in a strong room.

Following sieving, the finest grain sizes collected (those which passed through the 125 micron sieve) were analyzed on a Malvern Mastersizer 2000 using a 50% water 50% methanol dispersant. This instrument is capable of determining the grain sizes for fractions which are smaller than any physical screen. The complete grain size curve was obtained by adding the sieving results and the Malvern Mastersizer results and is shown in Figure 16. In some cases, the largest grain sizes detected by the Malvern were larger than the smallest sieve. In these cases, the mass from the Malvern measurements was added to the corresponding sieve size.

3.2.2. Controls

Both an inert tracer and pure composition B were used as controls. The inert tracer was a brine of 10.00g potassium bromide dissolved in 200 mL of distilled water. This gave an initial concentration of 50 000 mg/kg KBr. As is shown in Figure 17, this is still an order of magnitude below the solubility limit for KBr in water at environmental temperatures.

The pure composition B was laboratory grade, and was crushed to a powder on a milling machine. The grain size distribution of the composition B was heterogeneous, and varied from 10 microns to 2 mm, as shown in Figure 17. The pure composition B allowed a point of comparison for the leaching behaviour of the detonation residue. It was hypothesized that the detonation residue grains, having been exposed to the high heat and pressure of an explosion, may contain impurities or may be partially melted, which would have an effect on the transport and dissolution when compared to pure composition B. Table 10 describes the source terms that were used on each column, including the controls. Figures 19-24 show the surfaces of the columns including the source terms, prior to the start of the experiment.

Table 11. Sieves used to obtain grain size curves

Sieve order in stack*	Sieve size	Mesh No. (U.S. Tyler)	Mesh No. (U.S. ASTM-E11)	Microns	Mesh No. (UK BS-410)
	mm	#	#	μm	#
1	2.00	9	10	2000	9
2	1.40	12	14	1400	12
3	0.850	20	20	850	20
4	0.600	28	30	600	28
5	0.500	32	35	500	32
6	0.425	35	40	425	35
7	0.355	42	45	355	42
8	0.300	48	50	300	48
9	0.212	65	70	212	65
10	0.180	80	80	180	80
11	0.150	100	100	150	100
12	0.125	120	120	125	115

* sieves manufactured by W.S. Tyler Co. of Canada, St. Catharines, ON

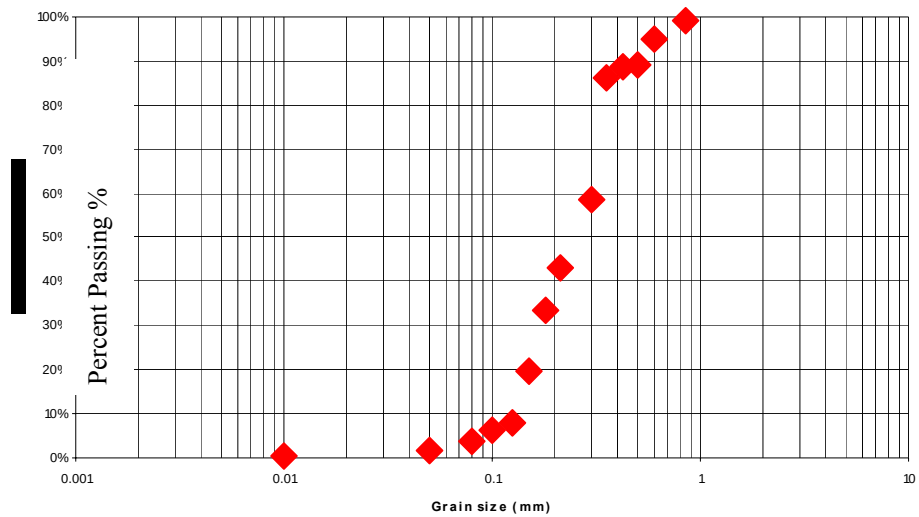


Figure 16. Initial grain size distribution of composite detonation residue fine fraction

3.2.3. Flotation Separation

At the end of the experiment, I re-characterized the detonation residue in order to compare it to its original state. This required separating the detonation residue from the soil. This was accomplished with a zinc bromide brine having a density of 2.25 g/mL. The density of composition B is 1.64 g/mL and the soil solid density is 2.69 g/mL. Any liquid with a density between these values will allow separation by flotation. Further details are provided in Annex 1. The separation process was shown to be capable of recovering approximately 80% of the detonation residue.

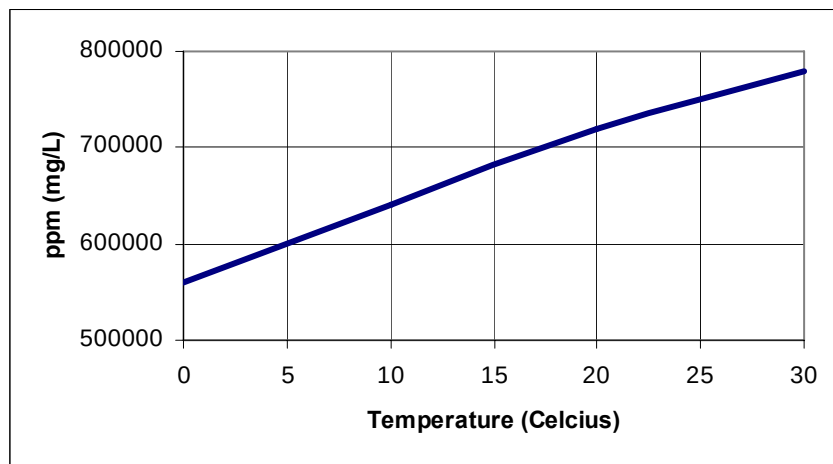


Figure 17. KBr solubility curve in water (CRC handbook)

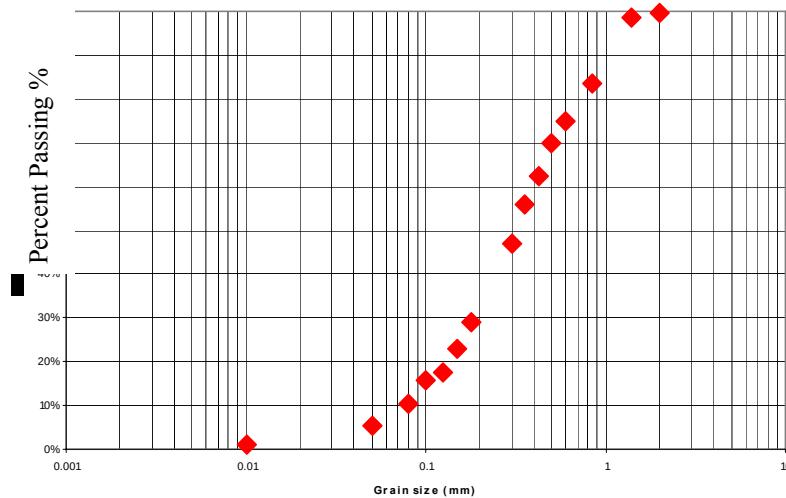


Figure 18. Initial grain size distribution of crushed composition B control



**Figure 19. Column A surface prior start of experiment
Br tracer**



**Figure 20. Column B surface prior to start of experiment
Detonation residue**



**Figure 21. Column C surface prior to start of experiment
Detonation residue**



**Figure 22. Column D surface prior of experiment
Mortar with detonation residue**



**Figure 23. Column E surface prior to start of experiment
Composition B control**



**Figure 24. Column F surface prior to start of experiment
Mortar with detonation residue**

3.3. Unsaturated soil columns

3.3.1. Soil column construction

Figure 25 shows the physical dimensions of the soil columns. The soil columns were constructed of $\frac{1}{4}$ inch stainless steel and the interiors were coated with TeflonTM. The base of each column was a $\frac{1}{2}$ inch TeflonTM plate supported by a 1 inch thick mild steel plate. These two plates were bolted to the bottom of the stainless steel containers.

The Teflon baseplates were machined with seven holes for the outflow nozzles, spaced and numbered according to the diagram in Figure 25. Each of these seven holes was in the middle of a very shallow cone 20 cm in diameter that was also machined into the Teflon. A fibreglass wick was threaded through each of the seven holes (see section 2.3.2).

Once the fibreglass wicks were all in place, soil was loaded into the columns. This was done in 7.6 kg lifts which produced a 1.5 cm thick layer of soil in the column. This layer of soil was compacted using a jack drill with a ram attachment. The ram was a flat circular steel plate, 25 cm in diameter. Following compaction, the surface of compacted soil was scarified to a depth of 1-2 mm in order to provide a good hydraulic link between soil layers. The next lift of soil was then added to the column, and the process repeated. The total mass of soil added to each column is shown in Table 12. Both the actual mass of humid sand used, and the equivalent mass of dry sand are shown in Table 12.

Table 12. Mass of sand used in soil columns

Column	Mass dry Sand (kg)	Mass humid Sand (kg)
A	285,6	292,3
B	287,1	297,2
C	280,7	289,2
D	286,9	300,1
E	292,0	299,3
F	286,8	294.0

Once the columns were filled with sand, they were moved and manipulated as little as possible. This was to avoid any flexing of the steel containers which could cause fractures to develop in the compacted sand, which would lead to preferential flow pathways.

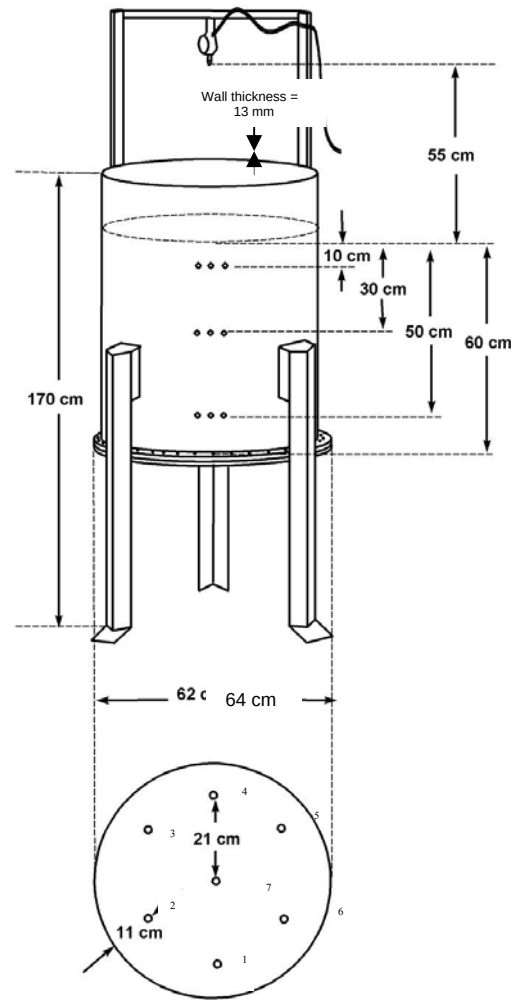


Figure 25. Physical measurements of soil column

3.3.2. Wick measurements

Fibreglass wicks were used in each of the seven outflow nozzle at the base of the soil column in order to provide a capillary head to the unsaturated soil to allow pore water to flow out of the columns. These wicks were fabricated by hand out of fiberglass. Since the capillary pressure produced by the wick is theoretically related to wick length, table 13 indicates the length of the wick used for each nozzle. All measurements in table 13 are measured from the top of the

Teflon plate to the lowest fibre of fibreglass. The wick was connected to a ball of fibreglass placed in a shallow cone which was machined in the Teflon. This fibreglass ball was approximately 20 cm in diameter, filling the cone.

Table 13. Fiberglass wick lengths

Wick	Total wick	Wick	Total wick	Wick	Total wick
	length (cm)		length (cm)		length (cm)
A1	8.2	C1	8.6	E1	7
A2	8.8	C2	9.9	E2	8.9
A3	8.8	C3	10.6	E3	8.9
A4	9.3	C4	7.8	E4	9.3
A5	8.3	C5	9.2	E5	8.5
A6	7.9	C6	8.2	E6	9.5
A7	9.7	C7	9.5	E7	9.1
B1	9.1	D1	6.6	F1	8.4
B2	8.5	D2	7.4	F2	8.9
B3	8.8	D3	11.8	F3	8.4
B4	8.9	D4	9.6	F4	8.9
B5	8.9	D5	10.7	F5	8.7
B6	9.1	D6	7.3	F6	8.1
B7	8.7	D7	8	F7	7.8

3.3.3. Soil characterization

The soil used in the columns was sieved prior to use to remove all stones larger than 0.8 cm. The soil was uncontaminated quartz sand obtained near an active range on Canadian Forces Base Valcartier. This sand comes from an alluvial formation around the Jacques Cartier River. The sand was well mixed and screened manually prior to use to ensure homogeneity and to remove any stones larger than 0.7 cm diameter. This soil was characterized for hydraulic conductivity, grain size distribution, solid soil density, porosity, clay content, cation exchange capacity (CEC) and total organic carbon (TOC).

3.3.3.1. Hydraulic conductivity testing

The hydraulic conductivity (K) of the soil was measured using a disc tension infiltrometer. The method of multiple tensions (Wilson, Everett & Cullen, 1995, p. 197) was used to determine the permeability of the soil after it had been loaded and compacted in the columns. A complete description of the hydraulic conductivity tests that were conducted may be found in Annex 2.

3.3.3.2. Grain size distribution curves

Grain size curves were measured using sieves manufactured by W.S. Tyler Co. of Canada, St. Catharines, ON, using the screen sizes shown previously in Table 11. A model FT-7-200 vibrating table manufactured by the Cleveland Vibrator Co. was used during the sieving process, and a Malvern Mastersizer 2000 was used to measure grain sizes of the particles which passed through the finest (0.125 mm) sieve. The Malvern is an optical grain size measurement system which is capable of measuring grain size distributions down to 0.020 μm . This instrument used a 50% water 50% methanol by volume dispersant during the measurements.

3.3.3.3. Clay content

The clay content of the soil is an important parameter in adsorption processes because of its extremely high surface area. The USDA identifies clay as having a maximum grain size of 0.002 mm (2 microns) in diameter. The clay content was therefore obtained directly from the grain size distribution curve as the percent mass passing at 0.002 mm as measured by the Malvern Multisizer grain size instrument.

3.3.3.4. Cation Exchange Capacity

This parameter measures the negative charge of the soil surface per unit weight. As a result, high CEC values are normally associated with fine grained materials that have very high surface areas in relation to their mass. The CEC is obtained by saturating the negative charge sites with a positively charged ion such as ammonium cations, then chemically stripping these ions from the soil and measuring their concentration. The result will give the cation exchange capacity. This measurement is relevant to leaching experiments which involve cations. CEC is a good indicator of soil fertility, as essential nutrients in the root zone bind more strongly as the

CEC increases, which prevents the nutrients from leaching beyond the roots. CEC was measured in the lab using soil samples obtained from the same source as that of the columns.

3.3.3.5. Porosity

The porosity of the soil in the columns was determined two ways, which are described in detail in Annex 3. The first method measured the porosity by completely saturating the pore spaces with water, and measuring the mass of water required to achieve saturation. The density of water being 1 g/mL, the volume of water and hence the porosity was determined.

The second method relies on measured values of the moisture content of the soil as it was being loaded into the columns to determine the exact dry mass of soil in each column. The solid density of the soil grains as determined in the soil solid density experiment above is then used to determine the volume of the column occupied by solid soil grains. The difference between the volume of sand grains and the total column volume is the porosity.

3.3.3.6. Solid soil density

This measurement was used to determine the exact density of the individual soil grains. This is not the same as the soil bulk density, which also takes into account the porosity. The soil solid density is needed to accurately determine the porosity. A complete description of this experiment is in Annex 4. Fundamentally, this experiment was very similar as that performed by Archimedes in 200 BC to determine density and therefore the composition of a gold crown. By pouring a known mass of sand into a known volume of water and measuring the displacement, we can calculate the density of the sand particles.

3.3.4. Automated infiltration system

3.3.4.1. Infiltration rates

The springtime infiltration rate for the Quebec City area is 253 mm over a roughly 30 day period in March –April as a result of the snow melt (section 1.5). Given the surface area of the soil column of 0.322 m², this gives a volume of infiltration of 81.5 L. Assuming that the temperature drops to below freezing at night, the infiltration will take place daily between approximately 8:00 am and 4:00 pm, or 8 hours. Therefore, the 81.5 L must flow at a rate of $(81.5 \text{ L} / (8 \text{ hrs} * 30)) = 0.34 \text{ L/hr}$. This is the target spray rate for springtime infiltration.

The summer infiltration period in Quebec City, lasting from the end of April to the beginning of October is characterized by little to no infiltration. In these months there is some rainfall, but the water introduced through precipitation is immediately returned to the atmosphere through evaporation or transpiration, meaning almost none reaches the water table.

The autumn infiltration rate for Quebec City is 116 mm spread over two months (61 days). This reproduces the rainfall which occurs in the months of October-November. Again, given the surface area of 0.322 m², this gives a volume of infiltration of 37.3 L. Given that rain can and does occur at any time of the day or night, the 37.3 L must flow at a rate of $(37.3 / (24 \text{ hrs} * 61)) = 0.025 \text{ L/hr}$. This is the target spray rate for autumn infiltration.

The automated infiltration system was built to allow exact monitoring of the volume of water being introduced into each separate column. Each column was fed by a separate water reservoir which held up to 30 litres of simulated rainwater. The simulated rainwater was distilled water that was pH adjusted to 4.7, which is the mean annual pH of rainwater in the Quebec City area (Mailloux, 2002). The reservoirs were connected in parallel with pressurised air to ensure equal pressure (30 psi) and therefore equal spray rates throughout the system.

Each reservoir was constructed of 80 gauge PVC pipe, with an outside diameter of 8 inches (20.32 cm). The reservoirs were 2 meters high and were connected to a clear PVC pipe which showed the level of water inside the tank. This pipe allowed daily measurement of the water level in each reservoir, to a precision of 1 mm. 1.0 litre of water added to the reservoir raised the water level by 6.0 cm.

The spray apparatus needed to be capable of evenly spraying water in a circular pattern at extremely low fluxes. Hourly infiltration rates are as low as 0.025 L/hr during the autumn infiltration event, so the spray system had to be capable of operating at this flux.

Since no commercial spray nozzles were capable of even spray coverage at such an extremely low flow rate, we used a UniJet full cone small capacity spray nozzle model ¼ T SS TG 22 0.3 which was turned on at intervals of 22 seconds every 15 minutes during the springtime infiltration and up to 6.3 seconds every hour for the autumn infiltration.

The electric valves which controlled the flow of water were connected directly to the spray. The electric valves used were Orbit WaterMaster Model 91103 ¾" automatic in-line valves and these were directly controlled by a CR-10 which was programmed to follow the set

spray intervals (see Appendix 1 for CR-10 programs). Later in the experiment, the Orbit valves were exchanged for ASCO Valve Canada electronic valves, catalog no. 8262G22.

3.3.5. Leachate collection

Since the pore water in unsaturated soil by definition has a head less than 1 atm, a method of applying suction is required to remove it from the soil. In the unsaturated columns of soil used in this experiment, this suction was applied passively using the wicking properties of fibreglass batt. The very fine capillaries created by the space between individual fibreglass fibers generate sufficient tension to overcome the negative head in the pore spaces of the unsaturated soil. Seven wicks on the bottom of the columns channelled pore water out of the soil column and into 2000 mL graduated cylinders. The volumes of leachate in the graduated cylinders were measured daily. Leachate was collected for chemical analyses from the graduated cylinders. Samples were analyzed on a weekly basis until breakthrough of the contaminants was observed. Following breakthrough samples were analyzed daily, or when there was a minimum of 500 mL of leachate collected in the graduated cylinder, whichever came first. Since the outflow from the wicks was highly variable, a different volume of outflow was analyzed for each wick.

3.3.6. Time domain reflectometry

Time domain reflectometry (TDR) allows very accurate measurement of soil pore water without disturbing the soil. Three TDR probes were installed in each soil column, at depths of 10, 30 and 50 cm below the surface. TDR readings were taken automatically every 15 minutes and saved on the CR-10 datalogger. The data was then downloaded weekly and saved as an excel spreadsheet file. See Annex 5 for further details on the TDR setup and calibration.

4. RESULTS

4.1. Cracked shell & detonation residue results

The generation of the cracked shells was very successful, and demonstrated that surface unexploded munitions are easily cracked open by shrapnel of shells which explode nearby.

4.1.1. Results from method 1: C4

Linear shaped charges did not generate satisfactory cracked shells (Table 14). The shaped charges were not powerful enough to penetrate the metal casing of the shell, and failed to significantly expose the Comp. B filler. An example of such an event is shown in Figure 26. Only the largest shaped charge (trial # 7) pierced the mortar round significantly.

C4 placed on the nose of the projectile, however, produced satisfactory results. The C4 broke open the metal in the fuse cavity and exposed the Composition B contained inside of the mortar rounds (Figure 27). This was considered acceptable, and some of the trials were repeated on clean snow. These projectiles and the detonation residue surrounding them were kept for the leaching study. The threshold of the amount of C4 that would cause a round to detonate was achieved in trial #15 when the projectile detonated with 90 g of C4 was placed on the 81 mm casing. During the trials involving C4, only 2 rounds detonated, all other rounds were physically damaged or broken when the C4 exploded, but the round itself did not detonate. No low-orders were produced, and only small amounts of explosives were scattered around the site. Creating cracked shells was not difficult, an indication that this may also occur in the field during firings or range clearances. Many UXO's in the field are partially buried or awkwardly located, making effective charge placement of the C4 difficult. Improper or ineffective charge placement can undoubtedly lead to partial detonations or cracked shells.

4.1.2. Method 2: fragment impact

The attack by fragments proved to be a very efficient way of obtaining cracked shells and exposing explosives, and was even more effective than Method 1. When the distance between the projectiles was smaller than 15 cm, a sympathetic detonation occurred and both rounds were destroyed (Table 15). At distances up to 157 cm the projectiles were damaged and the explosives were exposed. At the maximum distance of 157 cm, only one fragment hit Projectile B resulting

in a small, 3 cm hole in the casing. This is an indication that, in an impact area with many UXOs, the likelihood of a UXO being hit by a fragment is substantial given that incoming rounds potentially generate thousands of fragments. Examples of the cracked projectiles produced at short and long distances between the rounds are shown in Figures 27 and 28. It should be pointed out that in Figure 29, the composition B explosive can be clearly seen through the damaged casing. For purposes of comparison, Figure 30 shows a munition found in the impact area of Ft Carson, Colorado which shows very similar damage patterns to the munition in Figure 29.

Table 14. Results for C4

Trial	C4 application	Resulting Condition of Projectile B
1	Mk 7 Mod 1 shaped charge	No effect
2	Mk 7 Mod 1 shaped charge + C4 ball	Groove blasted into projectile casing, casing intact
3	Mk 7 Mod 2 shaped charge + C4 ball	Thick groove blasted into projectile casing, casing intact
4	Mk 7 Mod 3 shaped charge + C4 ball	Long thick groove blasted into projectile casing, casing intact
5	Mk 7 Mod 2 shaped charge + C4 ball	Thin groove blasted into projectile casing, casing intact
6	Mk 7 Mod 4 shaped charge cut in half	Thick longitudinal groove, casing intact
7	Mk 7 Mod 8 shaped charge cut in half	Thick longitudinal groove, casing opened, Comp. B exposed
8	C4 ball	Detonation
9	C4 ball	Exposed Comp. B in the fuze well
10	C4 block	Cracked, exposed Comp. B
11	C4 block	Cracked, exposed Comp. B
12	C4 block	Cracked, exposed Comp. B
13	C4 block	Partial Crack at the nose & plug fuze
14	C4 block	Nose cracked, exposed Comp. B
15	C4 block	Detonation
16	C4 block	Approx. 5 cm of nose cracked off, exposed Comp. B
17	C4 hemisphere	Approx. 5 cm of nose cracked off, exposed Comp. B
18	C4 hemisphere	Approx. 5 cm of nose cracked off, exposed Comp. B
19	C4 hemisphere on cracked shell	Approx. 5 cm of nose cracked off, exposed Comp. B
20	C4 hemisphere	Approx. 5 cm of nose cracked off, exposed Comp. B
21	C4 hemisphere on cracked shell	Approx. 5 cm of nose cracked off, exposed Comp. B
22	C4 hemisphere on cracked shell	Approx. 5 cm of nose cracked off, exposed Comp. B
23	C4 hemisphere on cracked shell	Approx. 5 cm of nose cracked off, exposed Comp. B



Figure 26. Effect of a 16.3 g C4 shaped charge with 5.7 g initiating C4 ball on projectile casing (trial #2)



Figure 27. Cracked shell produced by 63.2 g C4 placed on the nose (trial # 22)

Table 15. Results for fragment attack

Trial	Distance between projectiles (cm)	Resulting Condition of Projectile B
1, on metal plate	0	Detonation
2, on metal plate	20	Cracked and explosives scattered
3, on metal plate	15	Cracked and explosives scattered
4, on metal plate	10	Detonation
5, on metal plate	13	Detonation
6, on metal plate	15	Cracked and explosives scattered
7, on metal plate	15	Cracked and explosives scattered
8, on metal plate	25	Cracked and explosives scattered
9, on metal plate	45	Cracked and explosives scattered
10, on metal plate	100	Pierced and bare explosives exposed
11, on metal plate	157	Small 3 cm hole pierced and bare explosives exposed
12, on snow	15	Cracked and explosives scattered
13, on snow	15, UXO under 5 cm of sand	Lost its shape but not pierced
14, on sand	15, UXO flush with sand surface	Low order detonation and explosives scattered
15, on sand	15, UXO half buried in sand	Cracked and explosives scattered
16, on sand	15, UXO projecting out of sand at 45 degree angle	Cracked and explosives scattered (Only the exposed part and 3 cm of the buried part)
17, in water	15, UXO under 5 cm water	Low order detonation and explosives scattered

Results of the trial done on snow (# 12) did not produce significantly different results. However, it was found that sand at a thickness of 2.5 cm, protected the projectile (# 14) from the fragments and apparently acted as confinement in the case of trial # 14, when a low-order detonation was observed. Water did not protect the projectile from the fragments, and also acted as confinement to cause a low-order detonation. In both cases of low-order detonations, the likelihood of getting this result in the impact area seems quite high.



Figure 28. Projectile impacted by fragments from a mortar detonation 15 cm away (trial #6)



Figure 29. Projectile impacted by fragments from a mortar detonation 157 cm away (trial # 11)



Figure 30. UXO found in impact area of Ft. Carson, CO showing similar damage pattern as in Fig. 28 (Photo courtesy of Alan Hewitt, CRREL)

4.1.3. Sample recovery

I recovered the detonation residue from a matrix of snow, which I then extracted by freeze-drying. Freeze drying proved to be a reliable and effective way of sample collection. The advantages of collecting detonation sample residues on snow have been discussed by Jenkins *et al* (2000). Jenkins *et al* used this method extensively to study the spread of detonation residue around artillery shells. Attempting to collect detonation residue on solid surfaces such as soil, metal witness plates or tarpaulins is difficult because immediately after a detonation, the detonation residue particles are semi-liquid due to the heat of detonation partially melting the TNT. These semi-liquid particles will stick to any solids that they land on, making separation of the detonation residues from the solid particles difficult. In contrast, liquid detonation particles that land on snow quickly solidify, although they may melt through the uppermost several centimetres of snow. However, there are no solids for the particles to adhere to. By collecting the top 10 cm of snow around a detonation, the majority of detonation residue is collected.

When only chemical analyses of the detonation residue are required, it is acceptable to separate the detonation residue from the snow by melting the snow and passing it through a filter funnel. The energetic materials may then be extracted by passing acetonitrile or acetone through the filter to completely dissolve the solid particles, and by passing the meltwater through a solid phase extraction (SPE) device such as a Waters Sep Pak TM cartridge to recover any dissolved

explosives. However, if the experimental setup requires that the detonation residue remains physically intact, then exposing the detonation residue to meltwater is not acceptable. I determined (Figure 31) this by measuring the grain size distribution of three samples of crushed Composition B (detonation residue surrogate). The three data sets shown in this figure are 1) the original grain size distribution prior to any manipulations, 2) the grain size distribution after the Comp B is extracted from snow by freeze drying, and 3) the grain size distribution of the composition B after extraction by melting the snow sample overnight, then passing the sample through filter paper to recover the residue. The curves show clearly that while freeze drying has little effect on the grain size distribution, melting the samples overnight and allowing them to sit in contact with the melt water leads to measurable differences in grain size distributions below 0.2 mm.

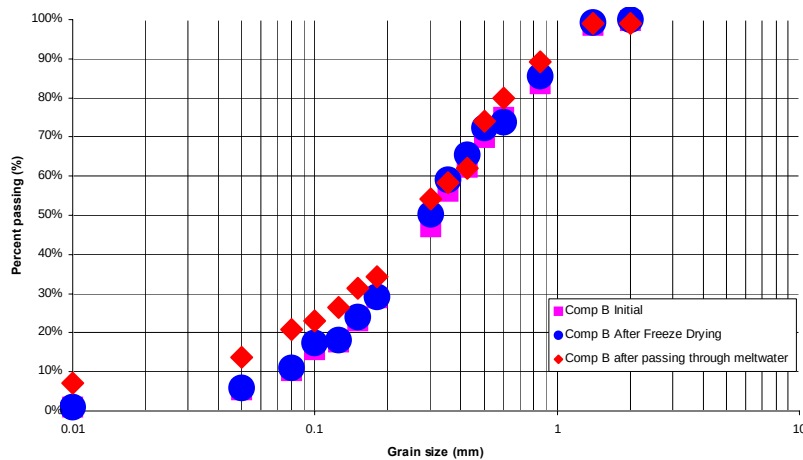


**Figure 31. Comparison of grain size distributions
For composition B exposed to melt water, freeze drying and no manipulation**

4.2. Hydrogeologic characterization of unsaturated columns

4.2.1. Physical characteristics of the soil

The measured physical characteristics of the soil used in the soil column are listed in Table 16. The soil used is a loamy sand with effectively no clay fraction. As a result, we would expect the CEC to be quite low, which it is. There is also very little organic matter, which is

logical because the soil was not obtained from surface deposits, but rather from the mineral soil in a quarry near the impact area at CFB Valcartier. The soil solid density is in agreement with literature values for quartz sand, as are the measured values for porosity.

4.2.2. Soil grain size distribution

The measured grain size distribution with a fitted curve is shown in Figure. 31. Overlaid on this figure are the maximum USDA size limits for silt (75 μm) and for sand (4.5 mm). This grain size distribution classifies this soil sample as being a loamy sand. It has a uniform distribution, which allows for a unimodal Fredlund & Xing (1994) model to be used in curve fitting.

Table 16. Soil parameters

Parameter	Value
Cation exchange capacity (CEC)	3.6 mmol/g
Total organic carbon (TOC)	0.31%
% clay (USDA)	<1%
% silt (USDA)	6%
% sand (USDA)	78%
% coarse (USDA)	16%
Soil Classification (USDA)	Loamy sand
Soil solid density	2.69 kg/l
Porosity	0.374-0.385

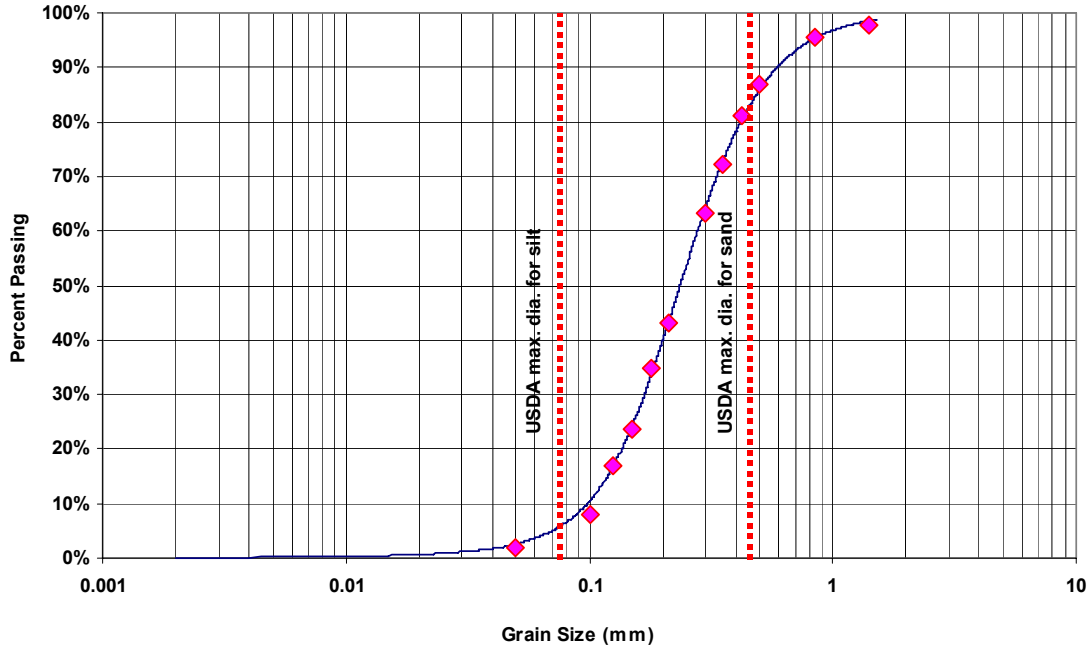


Figure 32. Soil grain size distribution of soil used in these tests, including overlaid Fredlund (2000) distribution curve

Figure 32 shows the curve fitted to the data using the Fredlund three parameter unimodal equation (Fredlund, 2000) for grain size distribution (Equation 39). Non linear curve fitting was performed using NLREG non linear regression software. The fitting parameters were calculated to be $g_a = 0.216$, $g_n = 2.29$ and $g_m = 2.96$.

$$P_p(d) = \frac{1}{\ln \left[\exp(1) + \left(\frac{g_a}{d} \right)^{g_n} \right]^{g_m}} \left[1 - \frac{\left[\ln \left(1 + \frac{d_r}{d} \right) \right]^7}{\left[\ln \left(1 + \frac{d_r}{d_m} \right) \right]^7} \right]$$

Equation 39

$P_p(d)$	=	percent passing a particular grain-size, d
g_a	=	fitting parameter corresponding to the initial break in the grain-size curve,
g_n	=	fitting parameter corresponding to the maximum slope of grain-size curve,
g_m	=	fitting parameter corresponding to the curvature of the grain-size curve,
d	=	particle diameter (mm),
d_r	=	residual particle diameter (mm),
d_m	=	minimum particle diameter (mm)

4.2.3. Soil-Water Characteristic Curve (SWCC)

The soil water characteristic curve is an important measurement when studying the vadose zone. It gives the relationship between the unsaturated soil suction and the volumetric water content of the soil. This relationship has a direct bearing on the unsaturated hydraulic conductivity and by extension, the ability of the soil to transmit fluids and dissolved contaminants.

The soil water characteristic curve was determined two ways – through indirect measurement of the soil water tension at varying moisture contents using the filter paper method (see Annex 6) and by using SoilVision software to interpolate the soil water characteristic curve based on the grain size distribution. From the grain size distribution, SoilVision determines either the Fredlund (2000) unimodal (Equation 38) or the Fredlund (1999) bimodal distribution equation parameters which describe the cumulative grain size curve. These parameters are compared against a proprietary database of fully characterized soils to provide an estimate of the soil water characteristic curve using the Fredlund and Wilson pedo-transfer function. The software then furnishes the variables for the Burdine, Gardner, Brooks and Corey, Gitirana and Fredlund, Fredlund and Xing, Fredlund bimodal, Van Genuchten or Mualem equations which match the curve predicted by the pedo-transfer function.

The experimental method and results for the filter paper method of measuring soil water suction are outlined in Annex 6. The SWCC as determined by both the experimental method and by SoilVision software (only the Fredlund and Xing output is graphed) is shown in Figure 33. It must be stressed that the experimental data and the Fredlund & Xing data were obtained from two completely different sources. The exceptional agreement between the data sets provides a great deal of confidence in these results.

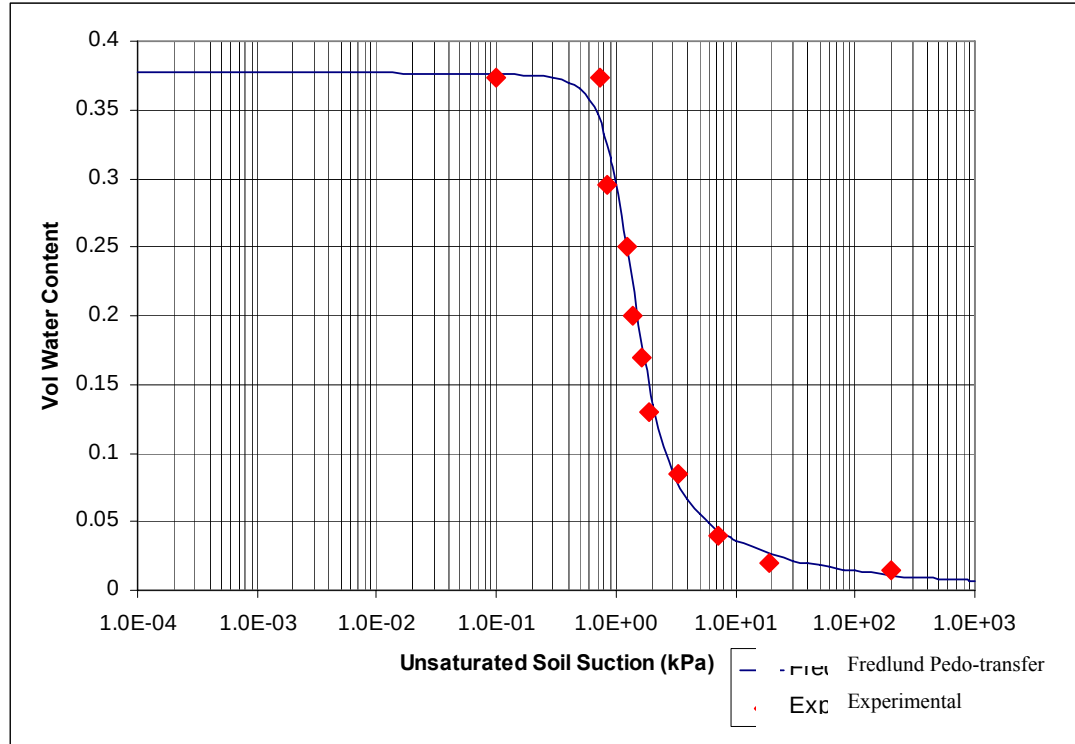


Figure 33. Soil water characteristic curve for column soil

4.2.4. Measurement of K_{SAT} Using Guelph Permeameter

The saturated hydraulic conductivity of the soil as measured using the Guelph permeameter varied between 0.0006 cm/s and 0.032 cm/s, with the average being 0.017 cm/s (Annex 2). These values compare favourably with published values for clean sand of between 1.0 cm/s and 0.0001 cm/s (Freeze & Cherry, 1979, p. 29). Given that hydraulic conductivity is one of the physical parameters with the largest range, (thirteen orders of magnitude: from 10^2 cm/s for gravel to 10^{-11} cm/s for shale and unfractured igneous rock), the consistency of our results for K_{sat} , is very satisfactory. As well, the results are reproducible from one column to another. Full details concerning hydraulic conductivity measurements are found in Annex 1.

4.2.5. Calculation of K_{UNSAT} using Guelph Permeameter

Hydraulic conductivity is dependent on the degree of saturation of the soil. The unsaturated hydraulic conductivity is therefore a function of the moisture content and the saturated hydraulic conductivity. Figure 34 displays the data for the unsaturated hydraulic

conductivity and the volumetric water content graphed against the unsaturated soil suction. This shows very clearly the relationship that exists between the volumetric water content and the conductivity. Figure 35 shows this relationship in another way, graphing the conductivity directly against the water content. Figure 36 and 36 graph these properties with respect to depth in the column, which shows how water flows through the experimental columns. Full details of the unsaturated hydraulic conductivity measurements and calculations are given in Annex 2.

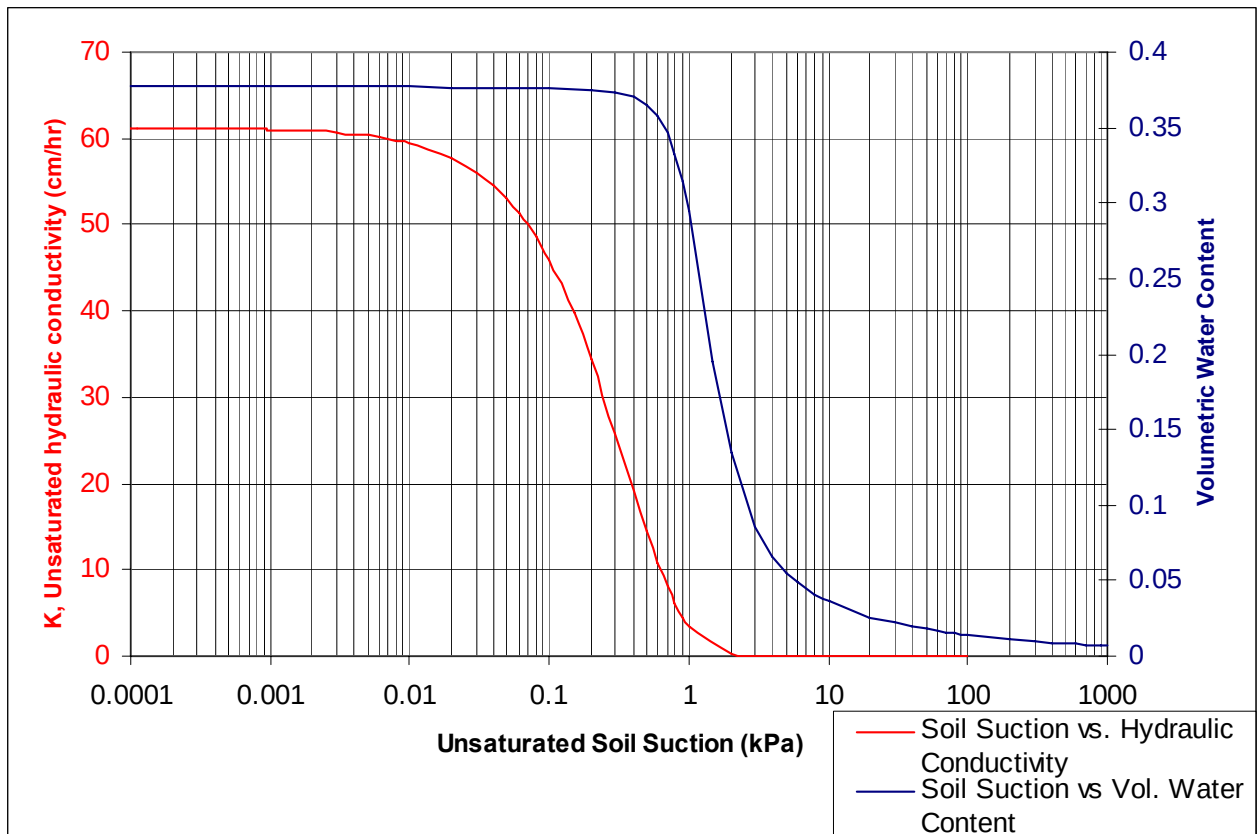


Figure 34. K_{unsat} and vol. water content vs. tension for column A

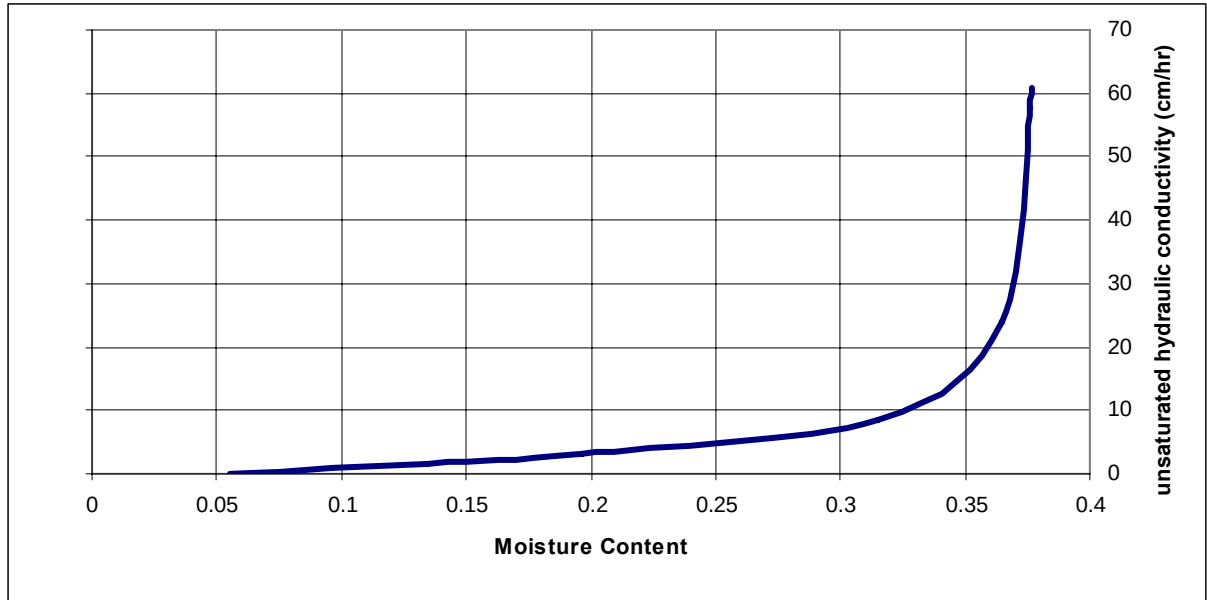


Figure 35. K_{unsat} vs.moisture content for column A

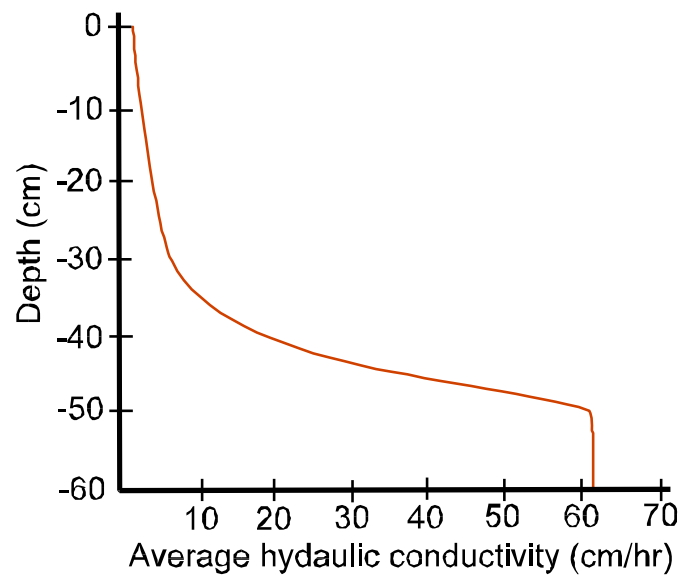


Figure 36. Measured hydraulic conductivity vs depth in soil columns (average of all columns)

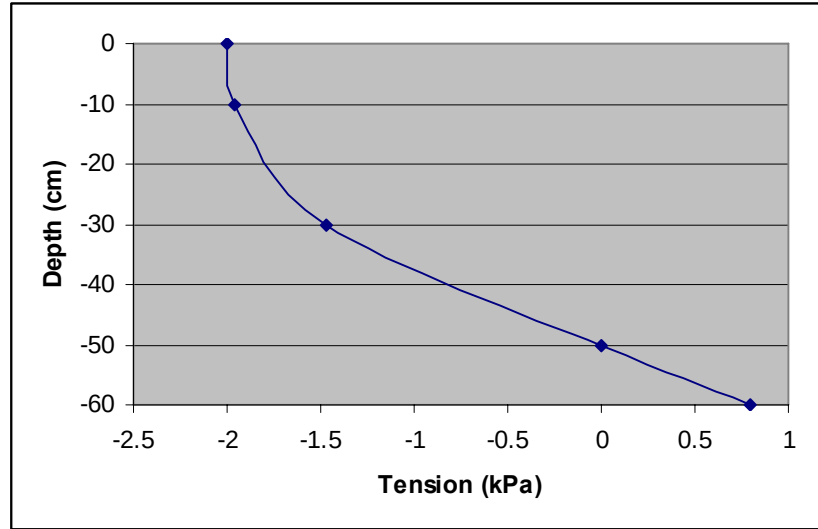


Figure 37. Measured hydraulic head vs. depth in soil columns (average of all columns)

4.3. Characterization of the explosive residue

4.3.1. Initial explosive residue grain size curves

Prior to adding the explosive residues to the surface of the columns, their grain size distribution was measured. The following curve (Figure 38) represents the grain size distribution for the fine fraction of detonation residue (<0.8 mm). The grain size at 50% passing was 0.25 mm.

The grain size curve for the Composition B control is shown in Figure 39. It is reasonably close to the detonation residue grain size curve, with a slightly larger coarse grain fraction. The grain size at 50% passing was 0.65 mm.

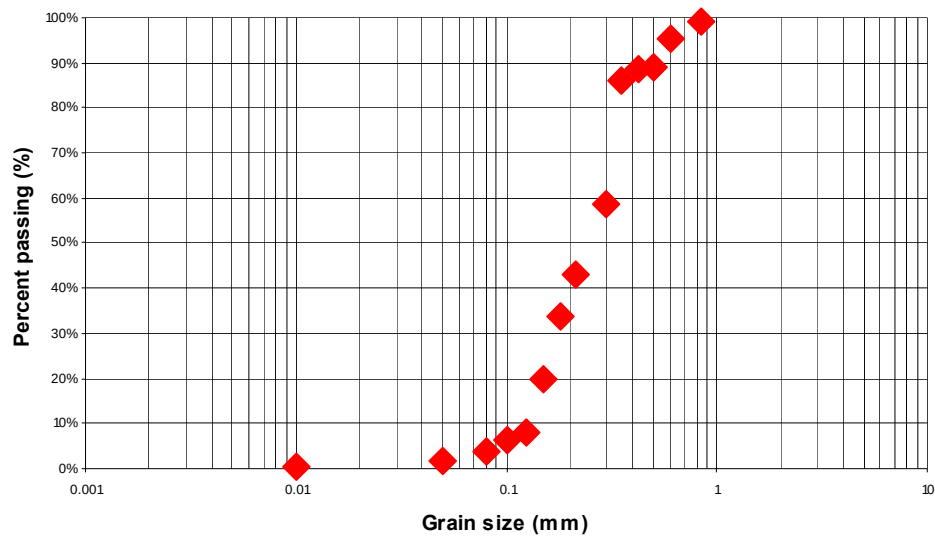


Figure 38. Grain size distribution of fine fraction of detonation residue prior to start of experiment

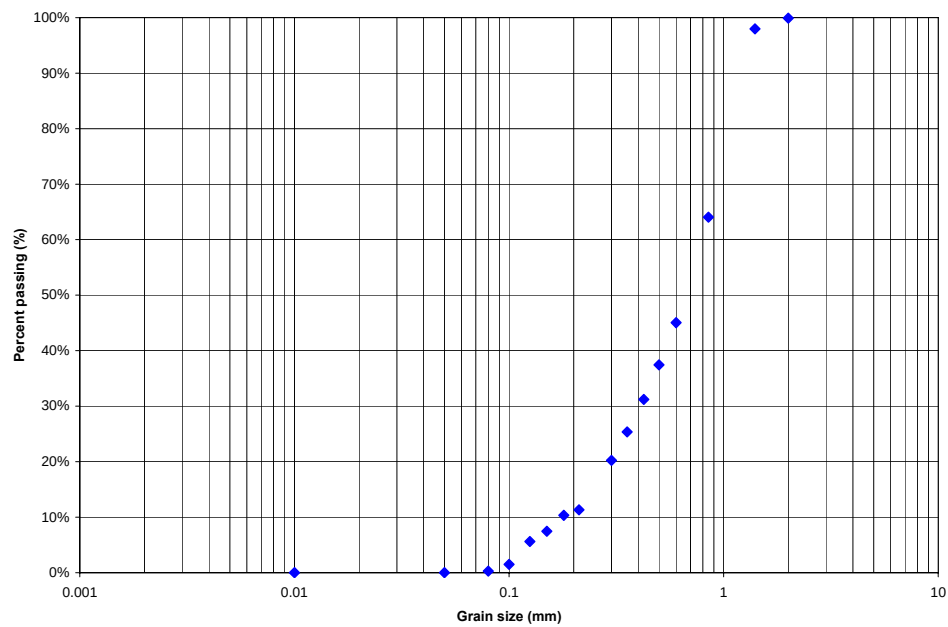


Figure 39. Grain size distribution of composition B control prior to start of experiment

4.3.2. Explosive residue grain size after leaching experiment

Following the springtime and autumn infiltrations, the detonation residue was separated from the soil of the column by flotation in a ZnBr brine (Annex 1). The grain size distribution of the following this process was determined for Column B, C, D E and F – those columns with explosives as a source term. The flotation process recovered 80% of the energetic materials (Annex 1). The curves show a trend to finer grain sizes. This is consistent with the dissolution of a range of grain sizes: The finer grain sizes, having a higher surface area to volume ratio, will lose relatively more mass during dissolution than the larger grain sizes. The slope of the detonation residue grain size curves following infiltration are shallower at 50% passing than they were prior to infiltration. This indicates that the grain sizes fall over a wider spectrum of sizes following infiltration. However, the grain size curves as a whole do not shift significantly – the percent passing of the larger grain sizes (0.8 mm) does not change significantly. Again, this indicates that the smaller grain sizes are dissolving relatively more quickly than the larger grains sizes. The grain size of the detonation residue at 50% passing for all columns is shown in Table 17.

Table 17. 50% Passing diameter for end state grain size detonation residue (not including the munition)

Sample	Grain size at 50% passing
Initial (all columns)	0.25 mm
B	0.21 mm
C	0.11 mm
D	0.12 mm
F	0.1 mm

4.3.3.Initial mass

Recall that the initial source term masses were listed in Table 10. 25 g of the fine fraction (>0.8 mm diameter) of detonation residue was placed on columns B,C,D and F, as well as 20 g of the coarse fraction (<0.8 mm diameter).

4.3.4. End-state mass

End state masses of the detonation residue are listed in Table 18. As for the grain size curves (figures 39-43), it must be stressed that the masses as listed are those recovered following the detonation residue by flotation in the ZnBr brine, a process which was measured to have up to 20% losses (Annex 1). However, a comparison with the initial grain size curves (figures 37, 38) indicates a that the end state grains sizes have moved towards the left, suggesting that the detonation residues have gotten smaller following the infiltration.

End state photos of the column surfaces are shown in figures 44-46.

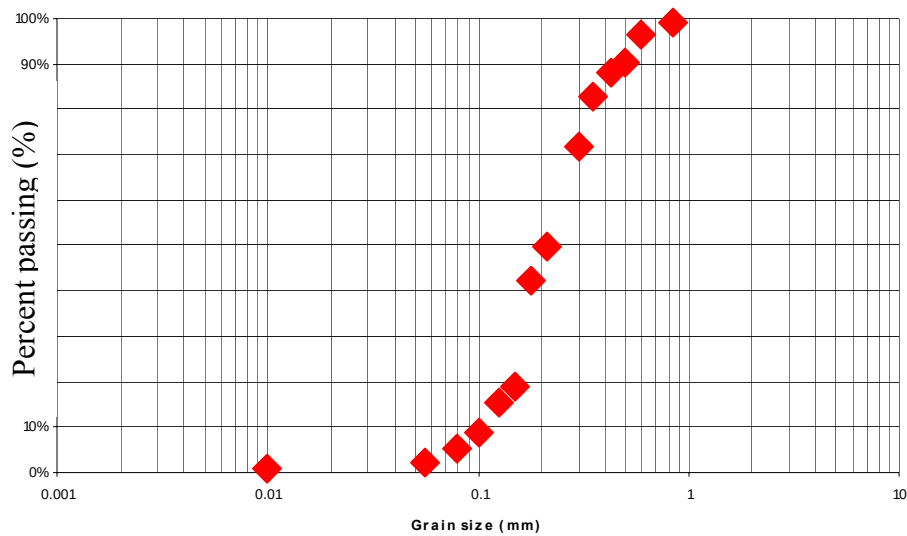


Figure 40. End state grain size curve of detonation residue in Column B

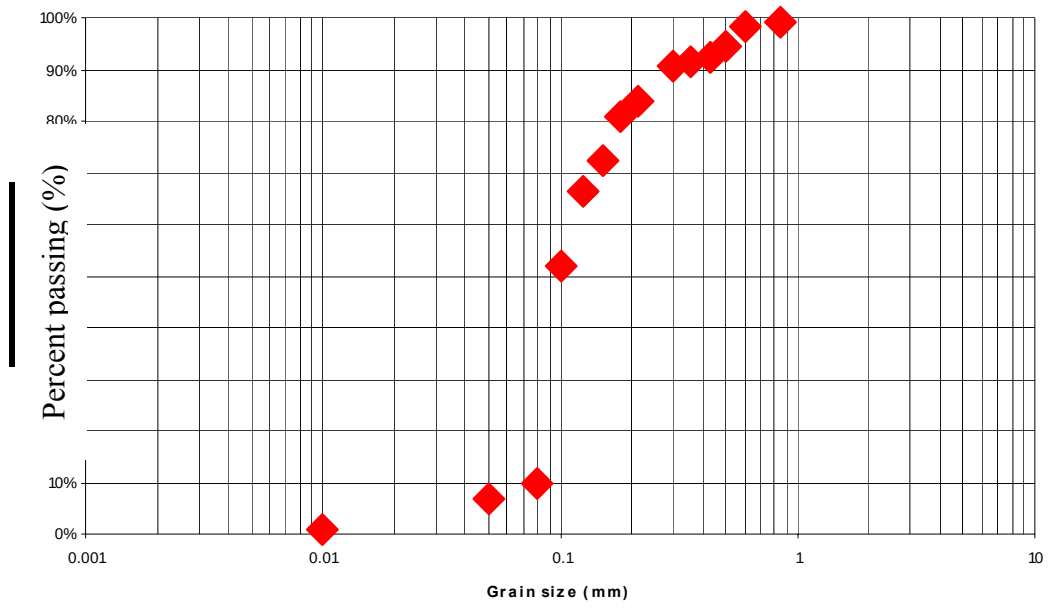


Figure 41. End state grain size curve of detonation residue in Column C

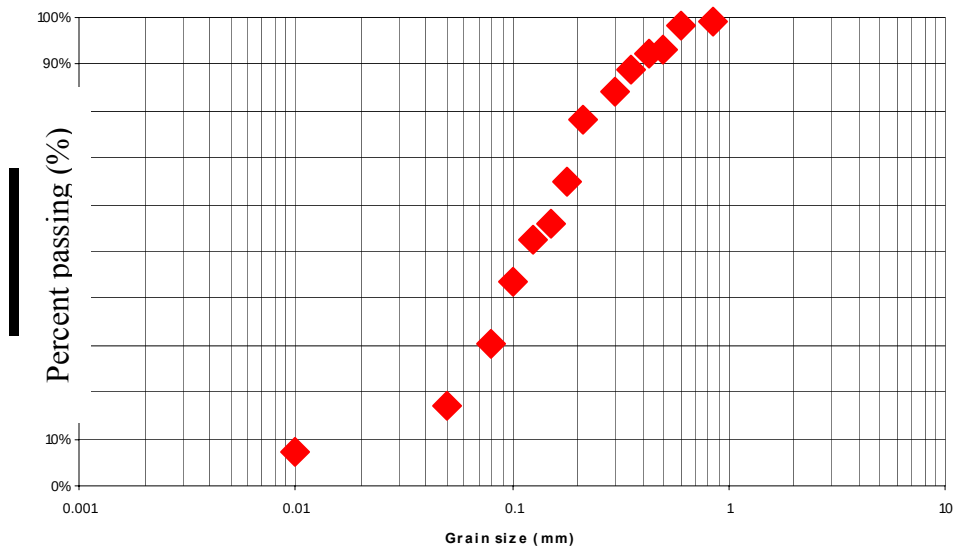


Figure 42. End state grain size curve of detonation residue in column D

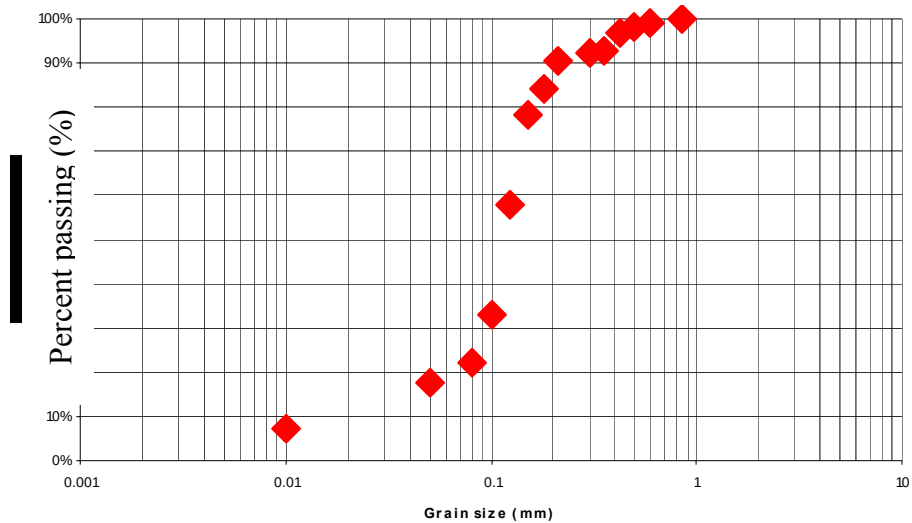


Figure 43. End state grain size curve of detonation residue in column F

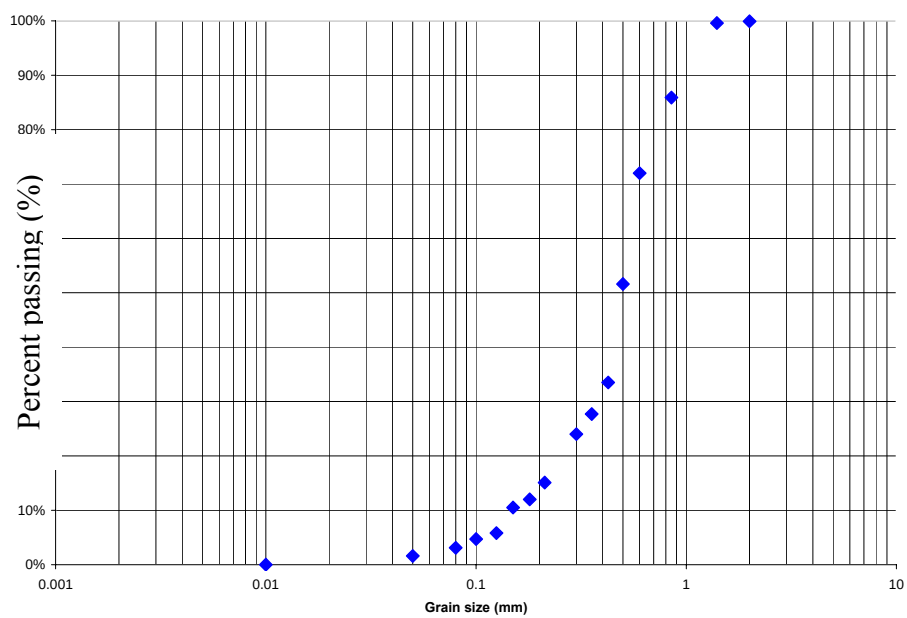


Figure 44. End state grains size curve of composition B control on column E

Table 18. End state mass of residue on columns

	End state mass (g)	Intial Mass (g)	Percent recovery
Column B	30.7 g	45 g	68%
Column C	30.4 g	45 g	67%
Column D	32.3 g	45 g	72%
Column E	33.4 g	45 g	74%
Column F	32.1 g	45 g	71%

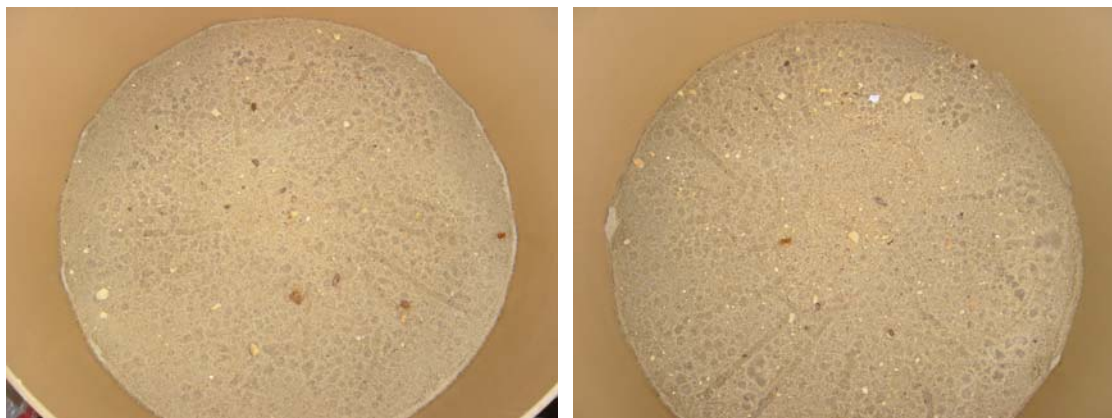


Figure 45. Surface of Column B (L) and Column C (R) at end of experiment

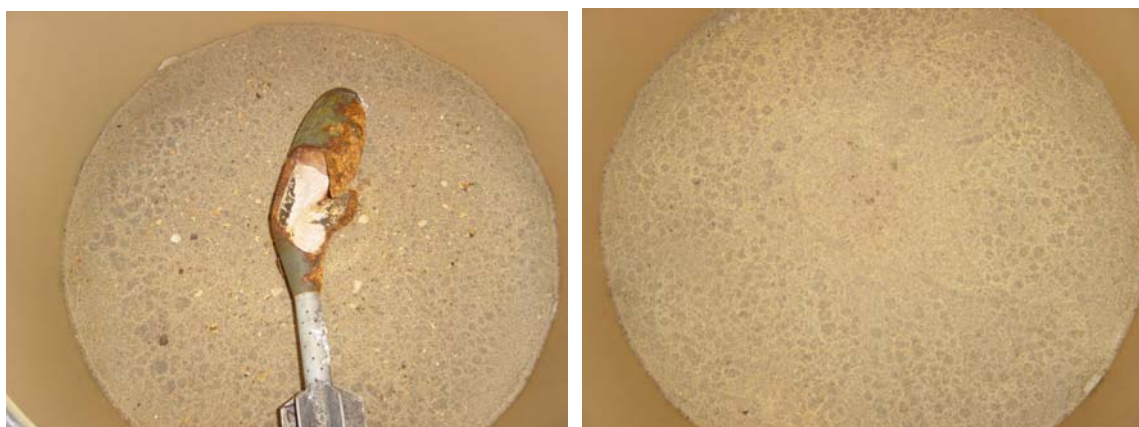


Figure 46. Surface of Column D (L) and Column E (R) at end of experiment



Figure 47. Surface of Column F at end of experiment

4.4. Observed infiltration flow

4.4.1. Infiltration

The infiltration at the top of the column was achieved with a single spray nozzle per column, connected in series with an electric valve that was controlled by the CR-10. The electric valves that were initially installed (Orbit WaterMaster Model 91103) proved unreliable and they jammed open on several occasions, flooding the soil column with. Because of the possible impact that this flooding had on the results, we will look at the mechanical performance of the equipment during the springtime and autumn infiltration periods, followed by observations concerning the flow characteristics of the soil itself.

4.4.1.1. Springtime infiltration period – mechanical performance

The springtime infiltration period had two significant deviations for the inflow rate. The electric valve on column E jammed closed on day 17 of the infiltration, and was replaced on day 25. During this 7 day period, there was no inflow of water into column E. Column D became partially blocked on day 14, slightly reducing the spray volume. This was detected and corrected on day 25. However, this valve then failed during the evening of day 25, and the subsequent flooding was only stopped the morning of day 26. This valve was again replaced, and the infiltration was restored on day 30. In order to reach the required 81.5 L of infiltration in columns A,B,C and F (those which functioned normally throughout the experiment without valve difficulties), the test was extended to 33 days. Since the springtime infiltration volume estimate

of 253 mm water (81.5 L total for the columns having an area of 0.322 m²) occurs during the spring snowmelt, and snowmelt can take place over 25-40 days, this slight change in protocol was appropriate.

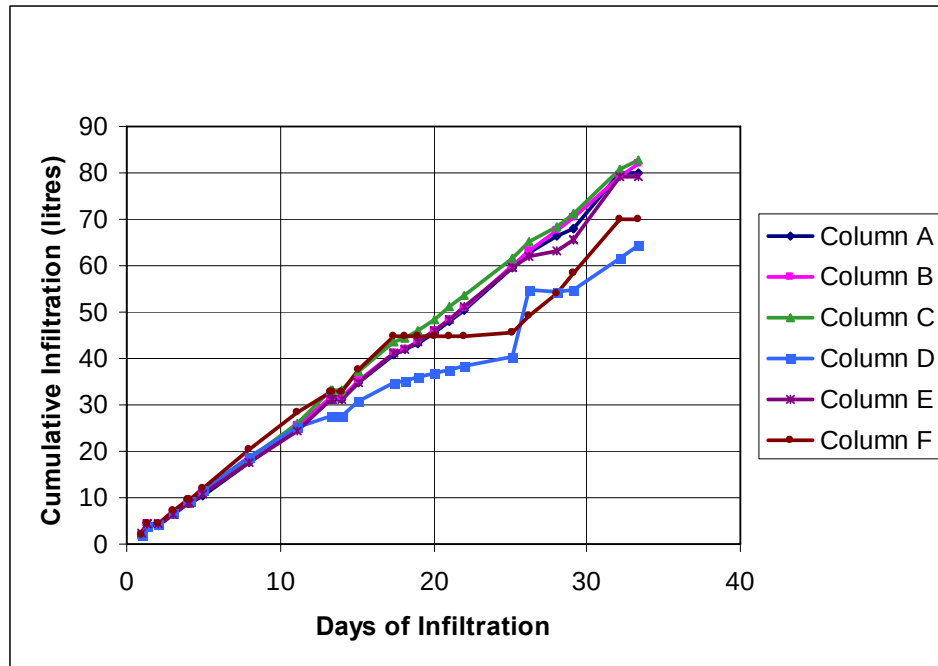


Figure 48. Cumulative measured springtime infiltration

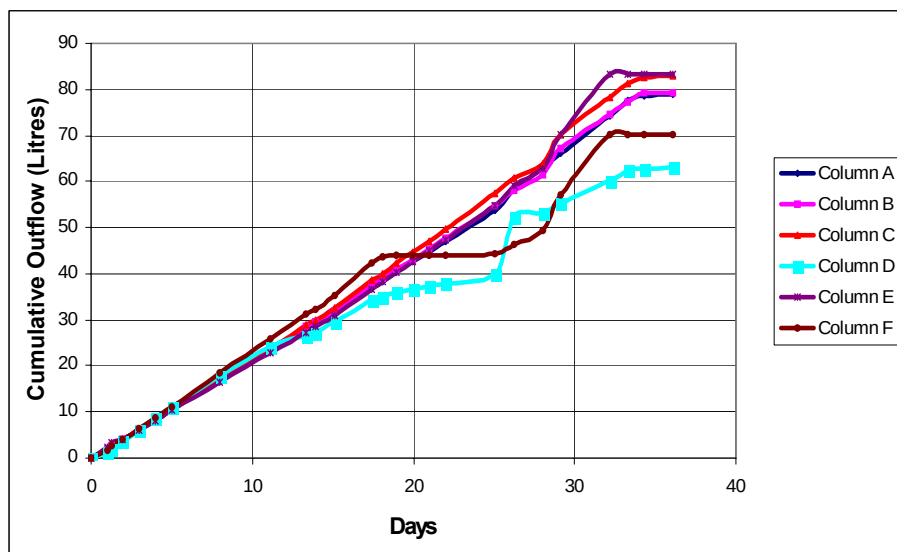


Figure 49. Cumulative measured springtime outflow

The infiltration in columns D and E was stopped at the same time as the other 4 columns, although these two columns only received 63 and 70 L respectively. It is clear that the volume of infiltration is a more important factor in comparing results from different columns than the time of exposure, so in hindsight the test should have been extended.

The columns were brought to a steady state of flow prior to the experiment. The inflow and outflow were therefore theoretically the same, and the data in figures 47 and 48 support this. The columns showed virtually identical inflow and outflow.

4.4.1.2. Autumn infiltration period –mechanical performance

The autumn infiltration was mechanically more challenging than the springtime infiltration because of the much lower flow rate: 116mm of infiltration in 61 days, or 1.9 mm per day. Our columns, having a surface area of 0.322 m², required a total volume of 37.4 litres over the 61 day period, which equalled an average spray flux of 0.025 L/hr. This infiltration period was designed to reproduce the autumn rainy period in the Quebec City region, so infiltration continued 24 hours a day, as rainfall can occur at any time. The initial calculated infiltration cycle of 1.5 seconds of spray per 30 minutes was based on the spray characteristics obtained from the springtime infiltration period. However, this flux rate proved to be inadequate, probably because the electric valves were unable to efficiently cycle through an open-close sequence so rapidly. For this reason, after 28 days of infiltration the spray cycle was increased to 6 seconds/ 30 minutes. Again, this spray cycle was inadequate to achieve the 37.4 L of total volume and on day 44 the rate was increased to 14 seconds/ 30 minutes. The spray cycle was continued for 65 days rather than 61 days to allow sufficient infiltration. The changes in spray rates can be seen in Figure 50 as changes in the slope of the curves.

The autumn infiltration period in Quebec City is characterized by several periods of rain in the months of October and November. The 24 hour infiltration cycle which was used during the experiment was chosen for reproducibility. In reality, the total flux would occur over a period of several days interspersed with dry periods. For the purposes of this experiment, the flux rates were kept constant, primarily for logistical and control reasons.

The only major irregularities during the autumn infiltration period occurred with column E. The Orbit Watermaster electric valve on column E jammed open the first night of operation, and in one 12 hour period, 14 litres flowed through this column. The valve on column E was

again replaced. On day 40, when the cumulative flow in the other columns reached 14 litres, column E was again activated. It again jammed open during the night. Another 17 litres flowed through column E in one 12 hour period. The flow results from column E for the autumn infiltration period is not comparable with the results from the other columns.

The autumn infiltration flow measurements are shown in Figure 50 and the autumn outflow measurements are shown in Figure 51.

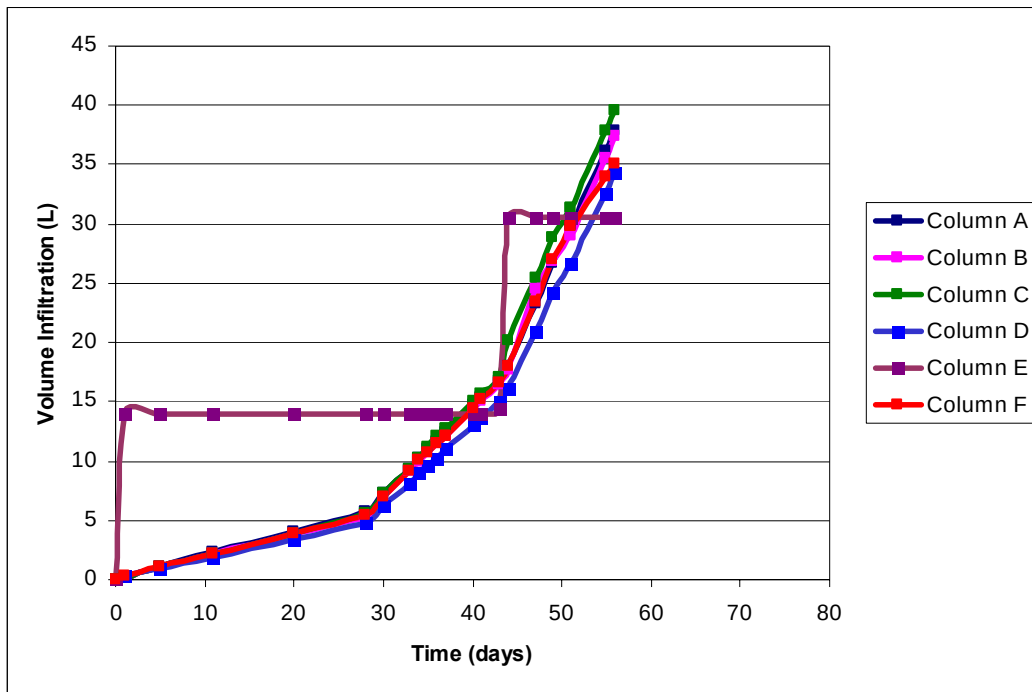


Figure 50. Cumulative measured autumn infiltration

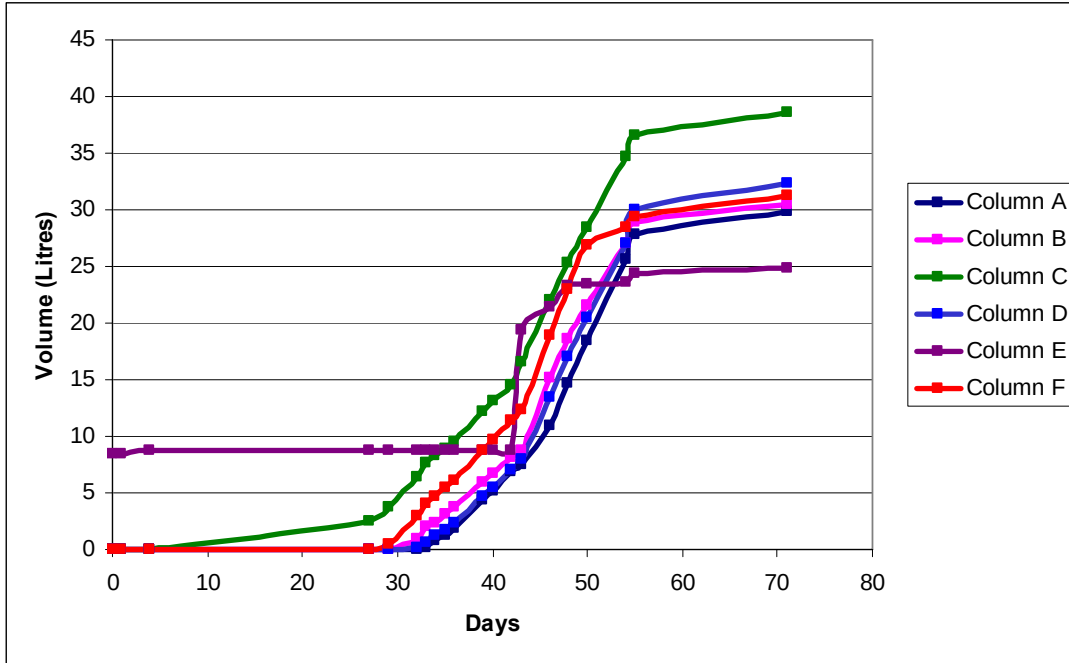


Figure 51. Cumulative measured autumn outflow

However, since the natural infiltration cycle is of heavy rainfall followed by a dry period, the flow which occurred through Column E was possibly more representative of actual conditions than the flow rate in the other columns. An unexpected benefit of the irregular infiltration of column E was that it offered the opportunity to observe the reaction of the soil columns under very different flux conditions. This was helpful during the numerical modeling of the soil columns.

4.4.2. Fluid flow characterization

This section addresses the hydraulic characteristics of the soil columns, and does not deal at all with energetic transport results. Complete outflow charts for the duration of the entire experiment are shown in Figures 51 and 52. The data is shown with respect to pore volumes in Figure 53 to simplify comparison with data to be presented later.

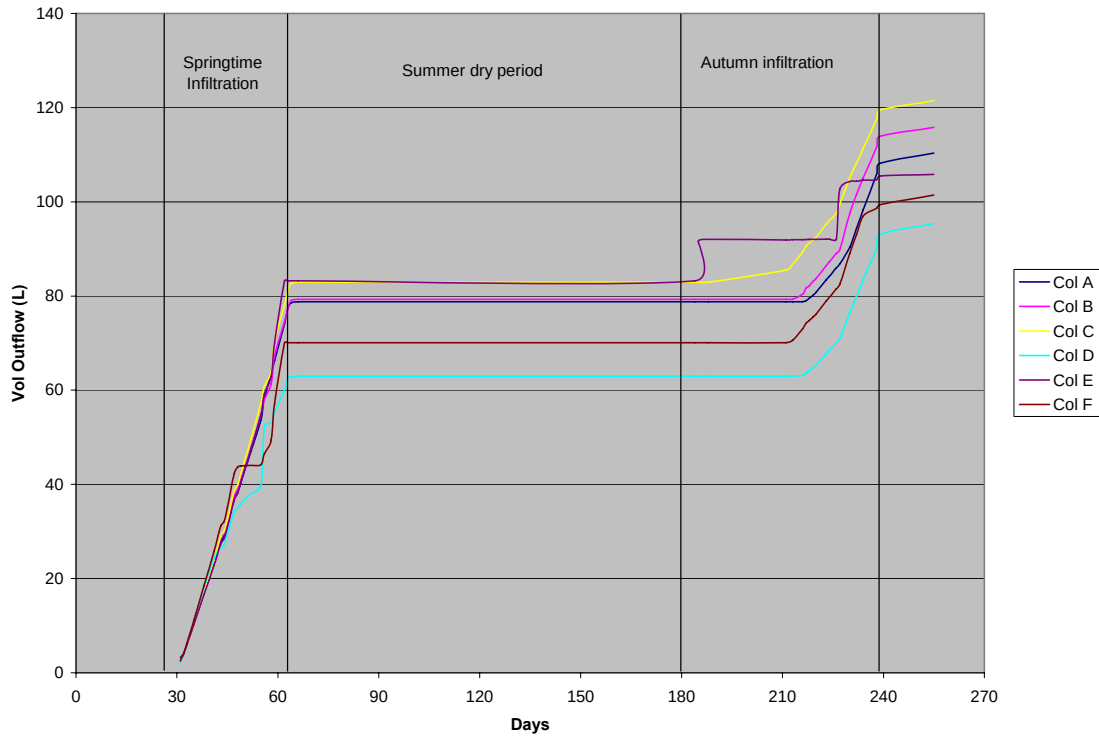


Figure 52. Total outflow from columns during experiment

The overall outflow from one column to another was comparable and the inflow was a strong predictor of outflow (figs. 51 and 53). Since hydraulic conductivity is a function of the moisture content, and the moisture content of the soil columns at a given depth is a function of time due to the cyclic nature of the infiltration, a rigorous analytical calculation of the time of passage of water from the time of infiltration to the time of outflow is impossible. Such a problem can only be approached numerically (Piver, 1991). However, the TDR measurements of the soil water content during the cyclical springtime infiltration (infiltration only occurred between 8:00 am and 4:00 pm) provides us with insight into the unsaturated hydraulic characteristics of the soil columns.

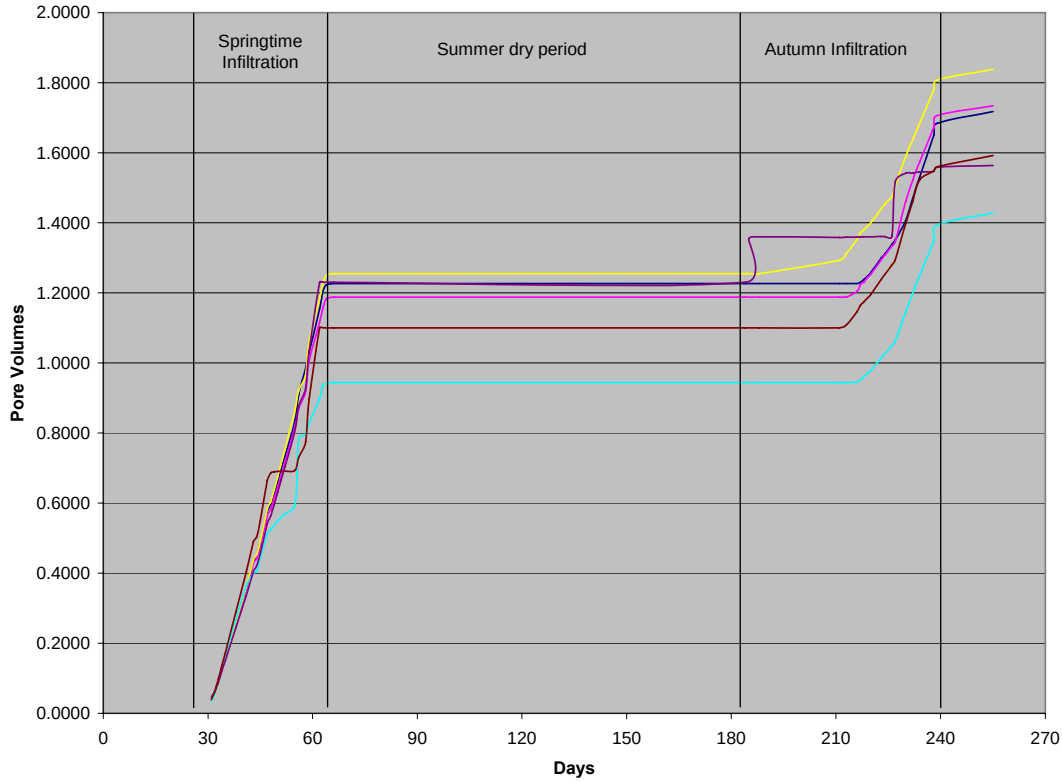


Figure 53. Total outflow from columns for entire experiment, shown as pore volumes

The full TDR graph in Figure 55 shows that daily equilibrium conditions were achieved during the 4th day of infiltration. Figure 57 indicates very similar flow characteristics in all six columns. The TDR data from the probes located at depths of 10 cm and 30 cm are of particular interest, since the change in moisture content caused by the transient fluid flux is clearly visible. The TDR data at a depth of 50 cm does not show a cyclical response, which is likely due to the attenuation caused by depth as well as saturated conditions at this depth. In all columns, the moisture content at a depth of 10 cm begins to rise at 9:30 am (± 5 minutes). At a depth of 30 cm, the moisture content begins to increase at 11:30 am (± 5 minutes). While the moisture content at various depths between the columns differs, the time of reaction to the infiltration cycle is extremely consistent. Infiltration always began at 8:00 am. This means it takes $1:30 \pm 0:05$ for the infiltration response to reach a depth of 10 cm (average linear velocity $\bar{v} = 10 \text{ cm}/1.5 \text{ hrs}$, or 0.0019 cm/s), and a further $2:00 \pm 0:05$ hours (3:30 total) to reach a depth of 30 cm. For this

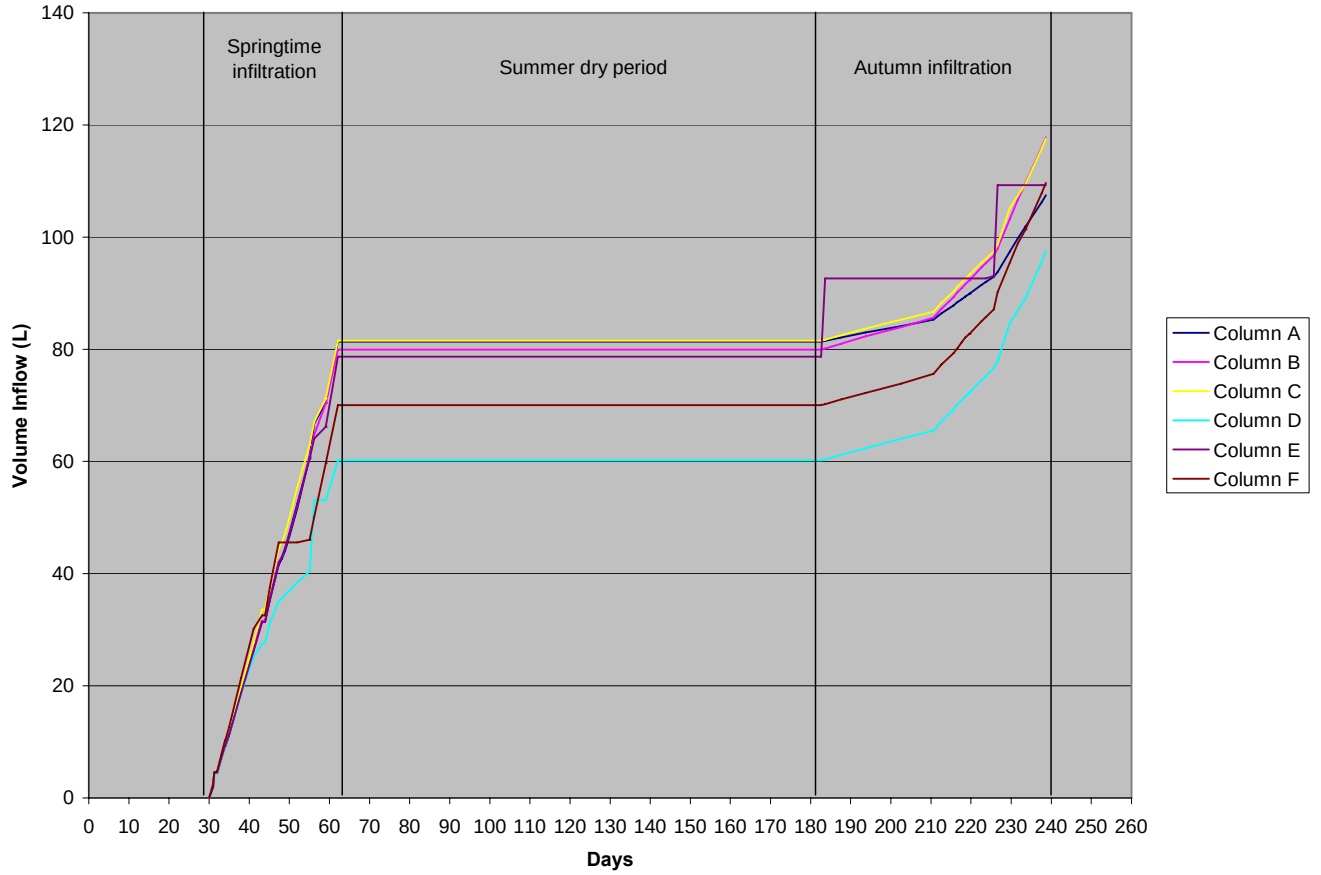


Figure 54. Total water volume applied to columns over the course of the experiment

20 cm slice, then, the overall average linear velocity is $\bar{v} = 20\text{cm}/2.0 \text{ hrs}$ or 0.0028 cm/s . As we would expect, the velocity increases with greater depth as the soil moisture content increases. The corresponding average hydraulic conductivities may be calculated using equation 40 (Freeze and Cherry, p. 71), a variation of Darcy's Law (equation 3).

$$\bar{v} = -\frac{K}{n} \frac{\partial h}{\partial z} \quad \text{Equation 40}$$

Using this equation, and the values for h obtained from Figure 37 at different heights in the soil column, we obtain the following data:

$n = 0.38$ (average porosity for all columns – see Annex 3)

$$\bar{v}_{10} = 0.0019 \text{ cm/s} = 0.000019 \text{ m/s}$$

$$\bar{v}_{30} = 0.0028 \text{ cm/s} = 0.000028 \text{ m/s}$$

$$z_0 = 0 \text{ (surface of column)}$$

$$z_{10} = -10 \text{ cm} = -0.1 \text{ m}$$

$$z_{30} = -30 \text{ cm} = -0.3 \text{ m}$$

$$h_0 = -2 \text{ kPa}$$

$$h_{10} = -1.9 \text{ kPa}$$

$$h_{30} = -1.5 \text{ kPa}$$

Inserting these values into Equation 40 gives $K_{10} = 0.0007 \text{ cm/s} = 2.52 \text{ cm/hr}$ and $K_{30} = 0.002 \text{ cm/s} = 7.2 \text{ cm/hr}$. These values match the data in Figure 36 very well, which shows hydraulic conductivity data obtained with the Guelph permeameter (Annex 2) as a function of depth. It is important to note that these calculated K values are average K values for the intervals of 0 to -10 cm and -10 to -30. Unfortunately, the data concerning the precise time that each column began to flow following the start of daily infiltration was not taken. With such data, the average hydraulic conductivity could have been determined for the soil columns.

The equilibrium water content profiles of the columns are shown in Figure 58. This data was taken once the columns achieved steady state flow conditions, one day prior to the beginning of the experiment. The data was obtained from the TDR charts in Appendix 2. Table 19 compares the moisture content as measured by the deepest TDR probe (50 cm depth) with the calculated porosity (Annex 3). It is very likely that the bottom of the columns was saturated. The greatest difference between the moisture content and the porosity is in Column C, where the measured water content and porosity differ by 15%. There was enough opportunity for error in the porosity measurements and TDR calibration to explain even this 15% difference. The fact that the moisture content at the lowest TDR showed absolutely no cyclical variation as did the two higher probes provides convincing evidence that the soil was saturated at the lowest TDR probe.

Saturation at the bottom of the soil columns does not have a serious impact on the validity of the chemical analyses of this study. The capillary fringe above the water table in a coarse sand

is on the order of magnitude of 10 centimetres (Charbeneau, 2000), which reflects the conditions in the soil columns. It may therefore be argued that even with saturated conditions at the bottom of the columns, they still reflected conditions in the vadose zone. Saturation had the side-benefit of negating any preferential flow which may have occurred in the unsaturated areas of the columns.

The form of preferential flow most likely to occur in the soil columns is fingering, since there were no floral pathways such as roots, no animal pathways such as worm or mouse tunnels, and no fractures in the soil which could have created preferential flow pathways. Fingering typically occurs in dry sandy homogeneous soils, exactly the soil type found in the columns. It is caused by wetting front instability that may occur when there is continuous slow infiltration. Under these conditions, flow will occur preferentially along narrow fingers in the soil. However, Liu et al (1993) demonstrated that in soils which are already at field capacity, finger diameters are approximately 10 times the diameter of dry soils. Figure 10 showed the relationship between soil grain size and finger width. Correlating this data with the measured grain size curve of the soil used in this experiment (Figure 32), suggests that we would expect finger diameters of approximately 2.5-5.0 cm diameter in dry soil, or 25-50 cm in soil which is at field capacity. Given the soil column diameter was 60 cm, and the soil was at or near field capacity upon being loaded into the columns, fingering should not play a significant role in fluid transport in this experiment.

Another possible form of preferential flow is due to subtle variations in soil density and grain size. In unsaturated regimes, very subtle differences in grain size distribution or bulk soil density can have a major impact on flow patterns (Gardner, 1956). Such changes can have a significant influence on the capillarity of the soil since a subtle increase in porosity or pore volume will have an impact on the suction head that the soil can exert. Although every effort was made to achieve homogenous compaction and to create hydraulic links between soil layers by scarifying the soil surface between lifts, it is possible that subtle differences could exist throughout the column. This concept will be further explored during the discussion on autumn leachate.

While the flux of the infiltration cycle through the soil columns is on average comparable from one column to another, outflow from the seven nozzles at the base of each column displayed

significantly preferential flow. Indeed, fluid flow rates varied by up to an order of magnitude between the seven outflow nozzles in the same soil column. However, this variation was consistent: there was a strong trend for the same nozzles to maintain either the highest or lowest rates of flow (Figs.58-60) throughout the experiment. The remainder of these charts can be found in Appendix 3. Columns A, C, D, and E had the same nozzle producing the heaviest flow in both springtime and autumn infiltration periods. Likewise, in columns A,C,D and F, the nozzle with the lowest flow remained the same during both infiltration events. Unfortunately, these results do not appear to have any relationship to the measured wick lengths as listed in table 13. A fibreglass wick should produce suction or head which is proportional to its length. This is due to the hanging column of water which creates a negative head. While the length of the fibreglass wick is related to the suction it exerts, the cross sectional area will have an influence on the total flux, in much the same way that at a given water pressure, more water will flow through a large diameter pipe than through a narrow diameter pipe. However, fibreglass wicks are extremely difficult to characterize and their dimensions are almost impossible to quantify with any precision. More consistent flow results will be dependent upon achieving a more constant and reproducible head in the outflow nozzles. The advantage of wicks – they operate passively – makes them very attractive for many field applications. However, for a lab study such as this one, a system using peristaltic pumps to create the required negative head would produce more consistent results.

In addition, the fact that the rate of flow between the various nozzles did change somewhat between the springtime infiltration event and the autumn infiltration event suggests that some subtle physical change had an impact on the capillary pressure exerted by the wicks. One possibility is that mineral deposits could have blocked some of the capillaries of the wicks between the infiltration events. Preferential flow due to fingering was unlikely because the soil was at or near field capacity prior to the start of infiltrations, as discussed above.

4.4.2.1. Time domain reflectometry results

The moisture content in the columns was monitored using time domain reflectometers at 10 cm, 30 cm and 50 cm depths (see sections 2.3.6 and Annex 5). The complete data from the TDRs of column A (KBr tracer) is shown in Figure 55. Figure 56 shows the TDR moisture readings from the 35 days of springtime infiltration in Column A. Further detail is shown in

Figure 57, which shows the TDR moisture readings taken in each column during the fourth day of the springtime infiltration. Figures 54-56 therefore show the same data, at increasing resolutions. The complete TDR graphs for all the other columns are shown in Appendix 2.

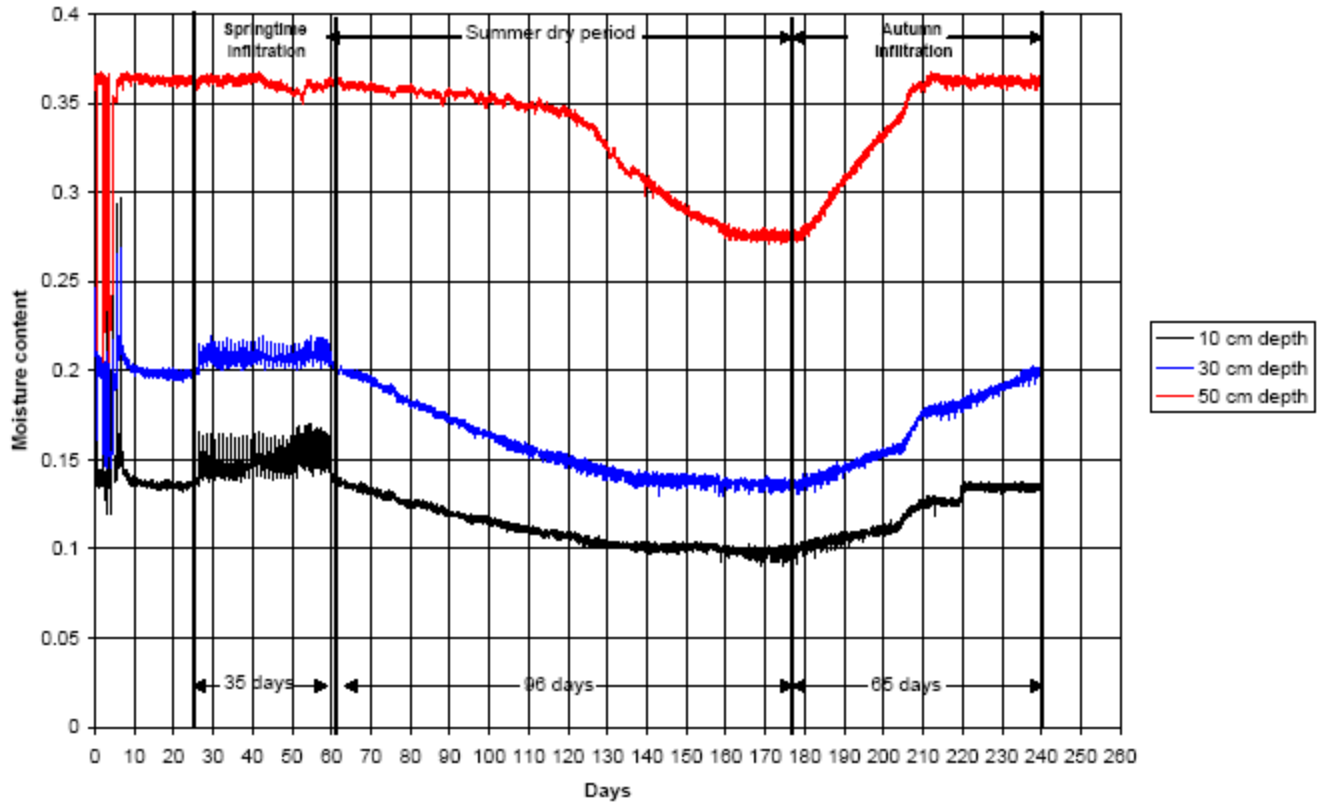


Figure 55. Complete TDR moisture data for Column A (KBr tracer)

Figure 55 shows how the columns were brought to steady state flow prior to the beginning of the springtime infiltration. The poor quality of the data during this period reflects adjustments that were being made with the equipment prior to the start of the tests. The beginning of the springtime infiltration took place on day 25 of the recorded TDR data. It ended on day 60. The transient daily fluctuations in moisture content are clearly visible during this period. The flow, although transient, is at equilibrium. This means that from one day to the next, the overall moisture content does not increase or decrease during the springtime flow. In other words, the daily fluctuations do not show long-term trends up or down during the springtime infiltration period.

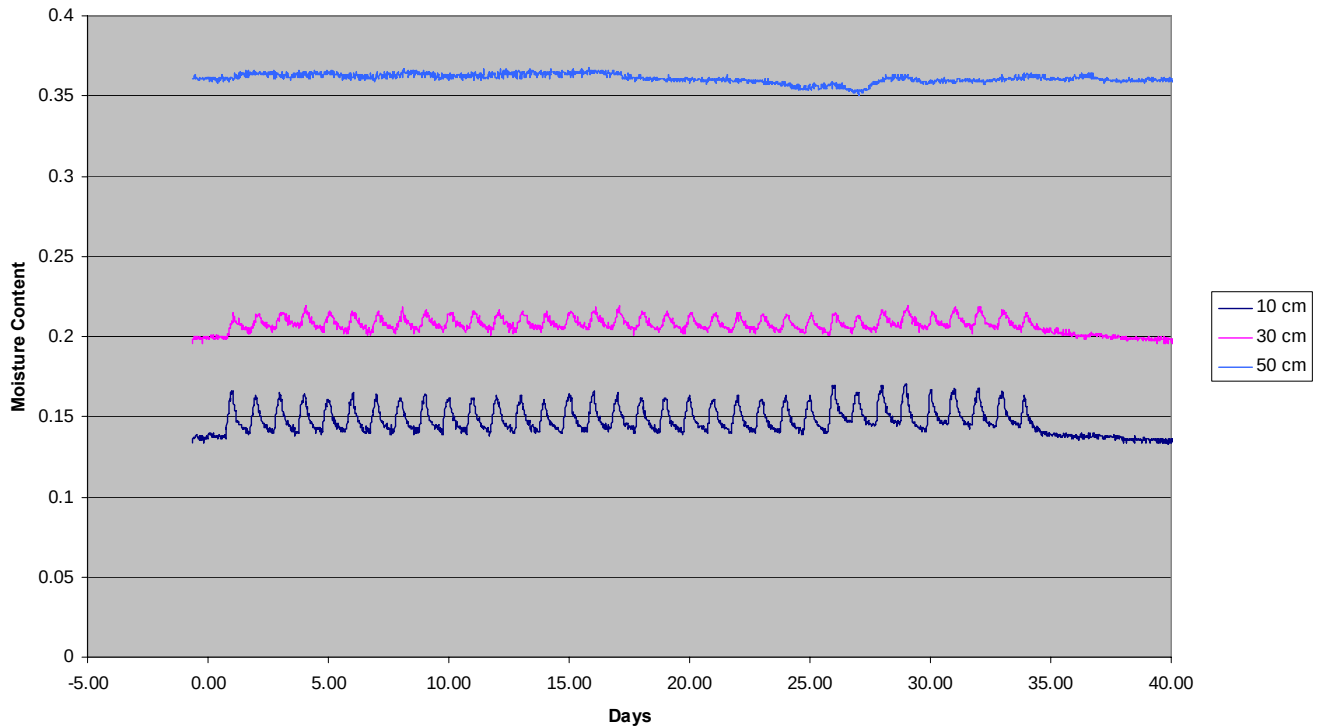


Figure 56. TDR data from springtime infiltration of Column A (KBr tracer)

All outflow from the columns ceased within two days of the end of the springtime infiltration period. The top of the columns were sealed to prevent evaporative losses, and the columns left to sit without inflow for 96 days. This period represented the summer months, when there is little or no infiltration due to low rainfall and evapo-transpiration losses. However, as is clear in Figure 55 from the drop in moisture content at all soil depths, there were indeed substantial moisture losses from the column during this dry period. Although there was no liquid outflow, it is hypothesized that the losses resulted from evaporation off the fibreglass wicks in the outflow nozzles at the base of the soil columns. These wicks remained saturated and open to the atmosphere during the dry period when temperatures rose up to 27° Centigrade. Column A showed the greatest moisture losses during this period. All three measured depths (10 cm, 30 cm and 50 cm) showed a drop of approximately 30% in the moisture content during the 96 days between the end of the springtime infiltration and the beginning of the autumn infiltration. The exact volume of water loss that this represents can only be indirectly calculated. The only information available is the behaviour of the columns during the subsequent autumn infiltration. From the autumn outflow results, (Figure 51), we can see that the first outflow from the columns

occurred between 25-30 days of autumn inflow. The volume of water sprayed between days 178-208 was between 5-7 L depending on the column (Figure 54). Table 20 shows the difference

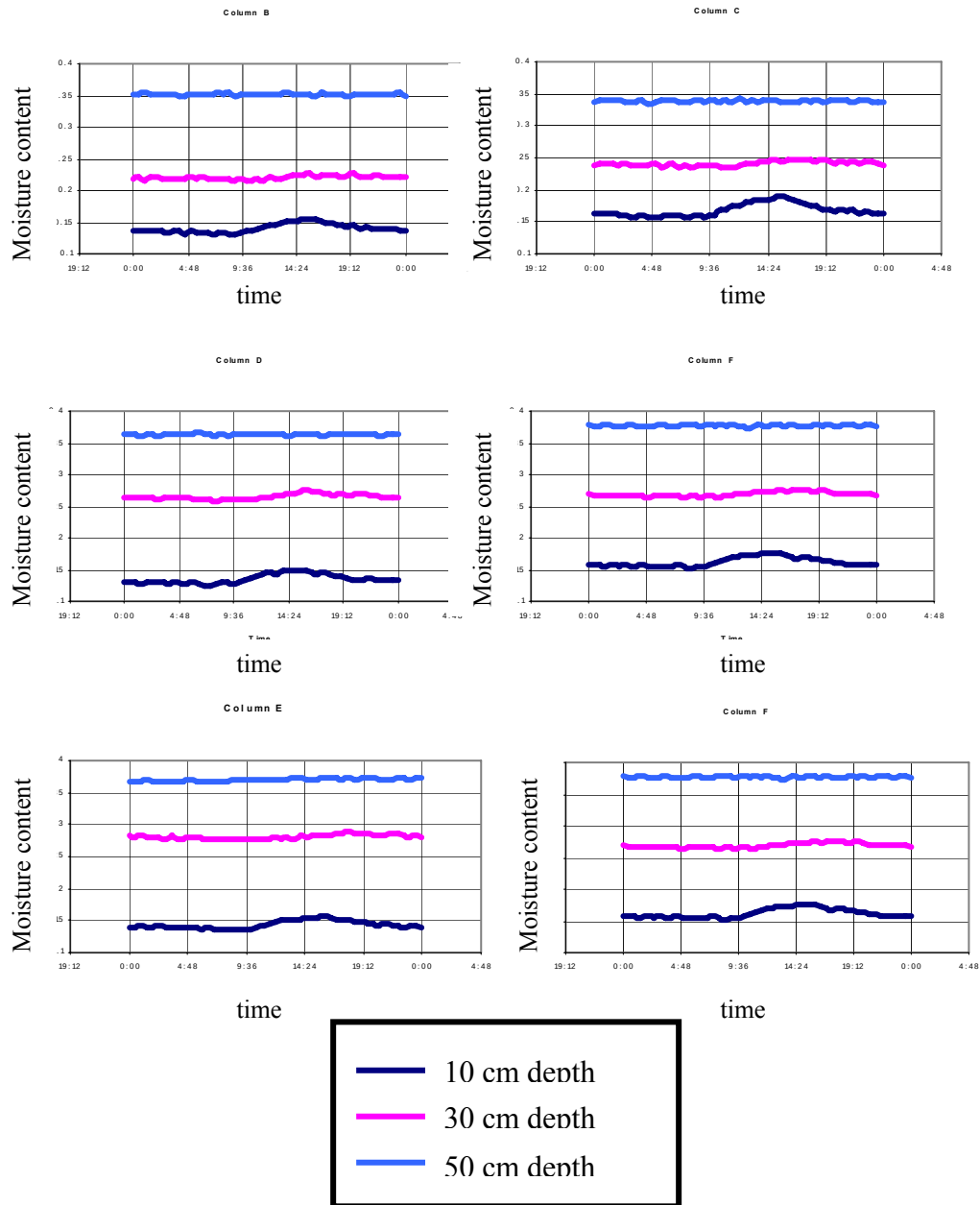


Figure 57. Moisture contents of all columns during 4th day of springtime infiltration showing increase in moisture around 09h 26 at a depth of 10 cm following the start of infiltration at 08h00.

between the autumn inflow and outflow over the entire autumn infiltration period. This difference should be representative of the volume of water required to bring the columns back to equilibrium and therefore the volume of loss during the summer dry period.

Therefore the rate of loss during the summer months was on the order of 5 litres over a 96 day period or 52 mL/day. Given that there are 7 nozzles, this gives an evaporative loss of approximately 7.4 mL per nozzle per day. A loss of 7.4 mL per day per nozzle to evaporative losses would appear possible. All columns appear to have lost between 1-8 L of water during the summer dry period based on the data in Table 20. As well, all columns began flowing within a 5 day period during the autumn infiltration.

In columns C, D, E and F the summer dry period produced a decrease in the moisture content at the top (10 cm) and middle (30 cm) probes, but the moisture levels at the bottom probe (50 cm) remained relatively constant. This provides a clue about the amount of saturation at the bottom of the columns. It is likely that in columns A and B, the bottom TDR probes were at or near the top of the saturated zone, so a small drop in moisture content would be able to drop the level of the water table enough to be picked up by the TDR. In the rest of the columns, presumably the water table was high enough that moisture losses were incapable of dropping it below the TDR probe.

Figure 56 was useful for the purposes of numerical modeling. This graph clearly shows the water transport behaviour of the unsaturated soil columns when exposed to transient flux. The amplitude of the daily peaks in moisture content at the 10 cm and 30 cm depths, as well as the absolute value of the moisture content at all three depths provided an excellent data set to train the flow conditions in a numerical model.

Figure 57 provides an opportunity to compare both the amplitude of the change in moisture content and the absolute moisture contents at three different depths of the six macroscopically identical soil columns when they are subjected to transient flux conditions. At the bottom of the columns, the moisture content is quite similar in all of the columns. At a depth of 50 cm, once the columns reached equilibrium just prior to the beginning of the experiment, moisture contents vary between 0.34 (Column C) and 0.365 (Column F), a difference of 7 %. However, at the top, moisture content varies between 0.13 (Column D) and 0.16 (Column F), a difference of 19%. Similarly, the moisture content measured at the middle of the columns varies

from 0.21 (Column A) to 0.27 (Column F), a difference of 23%. While the columns were macroscopically identical, there were clearly heterogeneities present which allowed for these differences. Small differences in compaction could have had an effect on the capillarity and therefore the hydraulic properties of the columns. The compaction of the columns, which was performed with a jack drill, was impossible to quantify while the columns were being filled and could have led to density variations at different points in the soil columns.

The field capacity of the soil is the water content below which hydraulic conductivity is sufficiently small that redistribution of moisture in the soil profile due to a hydraulic head gradient may be disregarded. In other words, it is the water content at which the soil does not drain any further. It is highly dependent on the microstructure of the soil, but in sandy soils it is around 4%. (Domenico & Schwartz, 1990) However, given that the bottom of the soil columns ended up being saturated, the fibreglass wicks exerted a smaller potential on the soil column than the soil matrix itself would have exerted had it continued down indefinitely instead of ending at the bottom of the columns. We therefore find that the moisture profile of the soil changes rapidly over the 60 cm depth (Figure 58). Such a profile would be found in areas where the water table is reasonably close to the surface.

Table 19. Moisture Content of columns at 50 cm depth

Column	Moisture Content at depth of 50 cm at equilibrium	Measured Porosity (Annex 2)
A	0.357 ± 0.01	0.377
B	0.35 ± 0.01	0.385
C	0.34 ± 0.01	0.388
D	0.36 ± 0.01	0.385
E	0.36 ± 0.01	0.384
F	0.365 ± 0.01	0.374

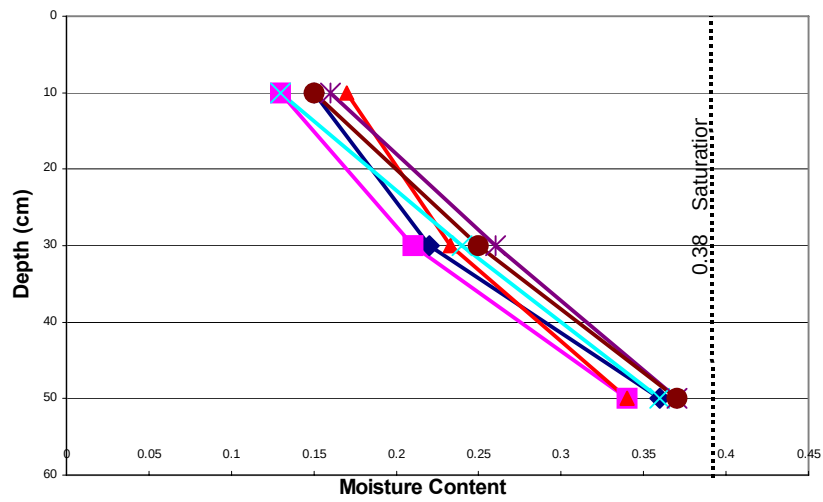


Figure 58. Water content profiles of soil columns.

Table 20. Infiltration and outflow difference

	Difference between autumn infiltration and outflow (L)
Column A	+8.1
Column B	+6.9
Column C	+1.1
Column D	+1.9
Column E	+5.9
Column F	+3.8

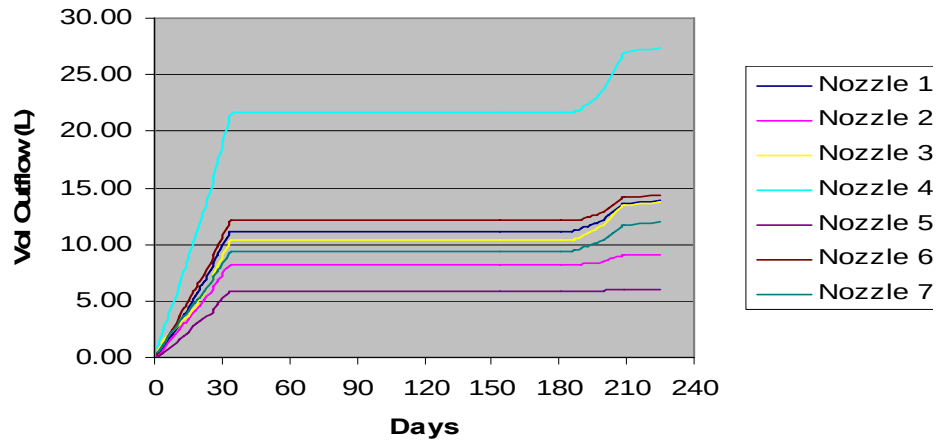


Figure 59. Outflow from column A by nozzle

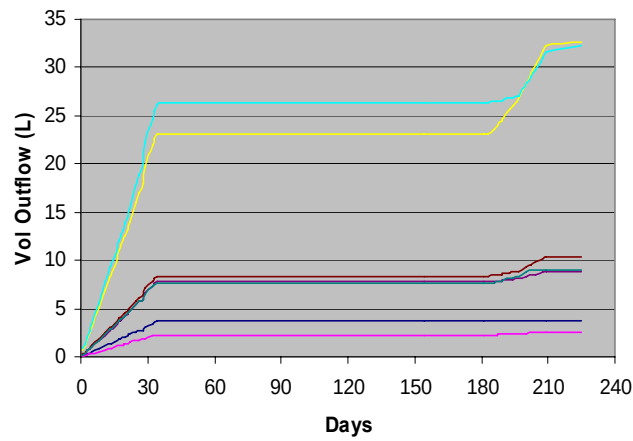


Figure 60. Outflow from column B by nozzle

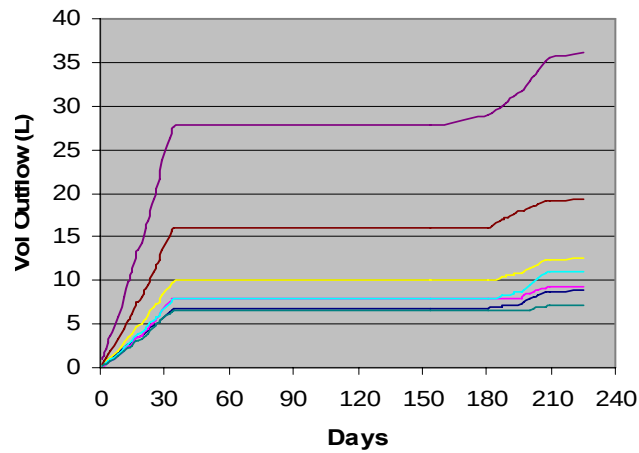


Figure 61. Outflow from column C by nozzle

4.5. Solute transport results

The graphical data in figures 61-69 is presented with respect to pore volumes eluted. In the saturated regime, one pore volume is the quantity of water required to completely fill the pore spaces of a given quantity of soil. Most contaminant transport studies are performed in saturated conditions, and the concept of the pore volume is commonly used in the literature to describe the quantity of fluid which has passed through a saturated soil column. To make a connection with another concept discussed earlier, the breakthrough of fluid travelling at the average linear velocity is achieved when one pore volume has passed through a column of soil. Of course, in the unsaturated regime, the pore spaces are filled with a mixture of both water and air, so one pore volume will not represent the point at which all the water in a column has been (theoretically) replaced. However, it is interesting to present the data in this fashion in order to compare transport behaviour with saturated conditions. It also allows a somewhat more standardized presentation of the data, since each column has slightly different pore volumes (Annex 3).

Prior to examining the energetic material outflow data, we must first look at the KBr inert tracer data (figures 61-63). This data will provide insight into the behaviour of a solute as it passes through the unsaturated soil columns, without any adsorption or transformation losses.

4.5.1. KBr inert tracer transport (Column A)

Recall from section 2.2 that 10 g of KBr was sprayed on the surface of Column A prior to the start of the springtime infiltration. This KBr solution was an instantaneous pulse type input, and as such, its outflow behaviour should mimic the curves presented as figures 7 and 8. Figure 62 shows the cumulative mass of KBr which was recovered with respect to pore volumes eluted. Two points of interest are the total mass recovered, which was 9.1 g, and the location of the curve when the recovered mass = 4.5 g (total recovered mass/2). KBr, being an inert tracer, should have no losses, especially not 9% losses, as we found here. The explanation lies in the difference between the effective water content (θ_e) and the volumetric water content (θ). In unsaturated soil, there exist isolated pockets of soil water which are not connected to any other pore water. This water is in effect trapped in the pores, and it does not move or contribute to the transport of solutes. In medium sand, the volumetric water content is commonly around 0.39, while the effective water content is around 0.3 (Charbeneau, 2000). The missing KBr is to be found in these pockets of isolated fluid. As long as the water content does not rise significantly

and flood these isolated pockets, the KBr will remain trapped and immobile. In the saturated regime, there is much less of a difference between the effective water content and the volumetric water content (in porous materials, they are limited to occluded voids inside the soil grains themselves) so such losses are usually negligible.

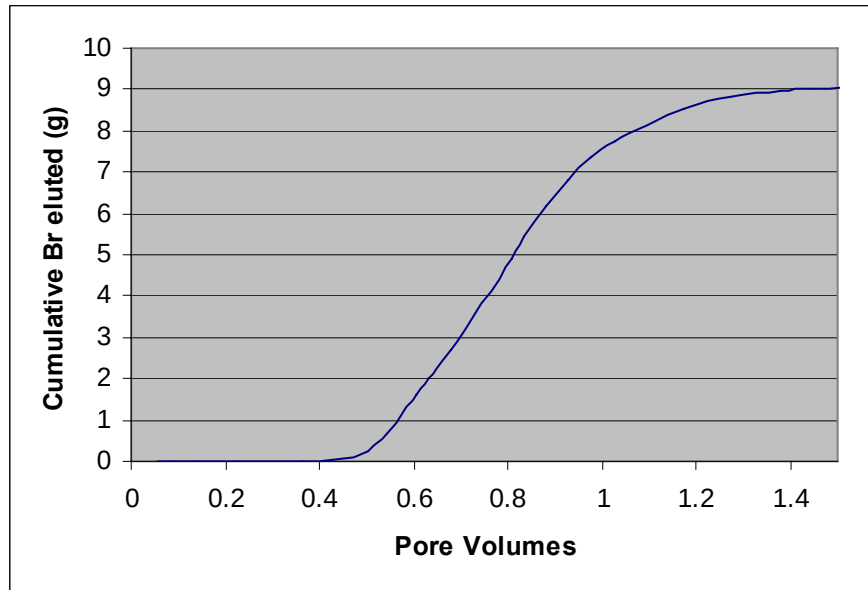


Figure 62. KBr leachate cumulative mass vs. pore volumes from column A

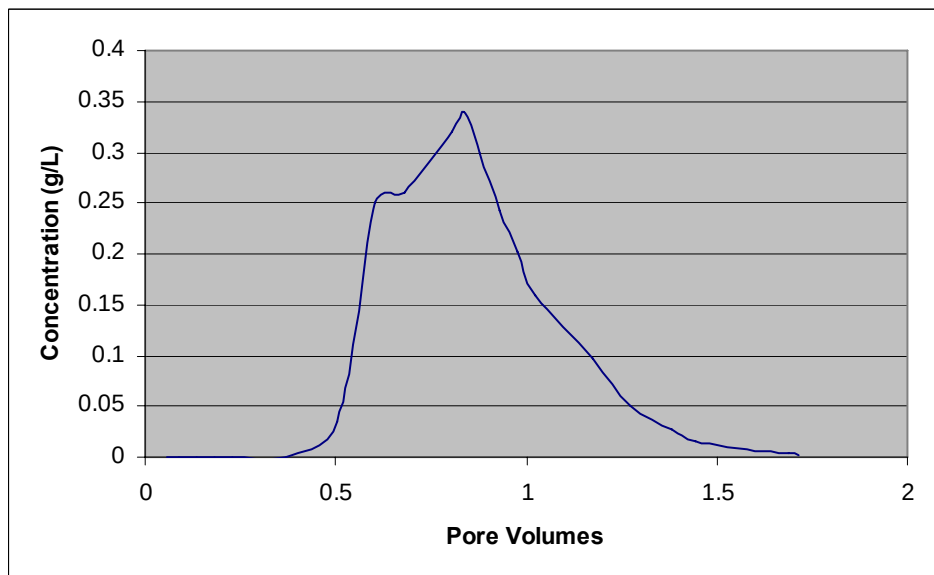


Figure 63. KBr leachate concentrations vs. pore volumes from column A

The displacement of the KBr breakthrough curve is also explained by the difference between the effective water content and the volumetric water content. As was discussed in section 1.4.2, after one pore volume of solute has passed through a porous material, the total recovered mass should ideally be $M_0/2$. However, in some porous materials the initial breakthrough occurs after fewer pore volumes of water have passed through. This is attributable to fact that the effective water content is lower than the volumetric water content. As a result of the reduced cross sectional area of the water-filled pores as compared to saturated conditions, the fluid velocity of the effective water content is greater than that of the volumetric water content, so solutes arrive earlier (Stephen, p 34). In other words, the volume of fluid that conducts the solute is less than the calculated porosity, leading to a faster than anticipated breakthrough.

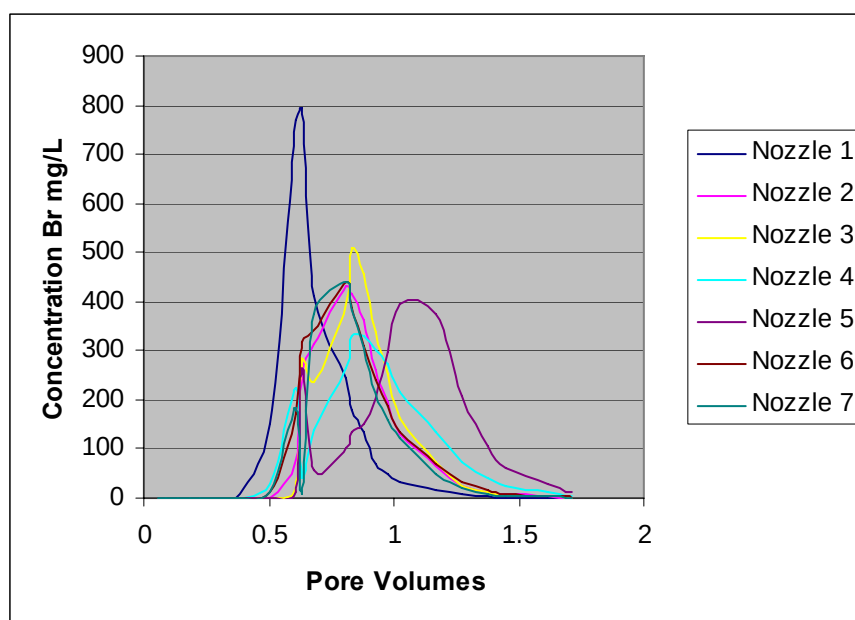


Figure 64. Springtime KBr leachate concentrations by nozzle vs. time

Figure 64 shows the concentration of KBr in the outflow of each of the 7 outflow wicks, again with respect to pore volumes. It is clear from the variations in solute breakthrough that either the KBr has not travelled far enough to achieve the Fickian regime where the convection-dispersion equation (Equation 27) applies, or there is macro-scale preferential flow occurring. Let us look at each possibility separately.

The velocity of solutes travelling through the vadose zone is generally defined as the average velocity over all flow paths in a representative volume – in this case, the soil columns. This average velocity therefore does not describe differences in flow velocities caused by heterogeneities which occur at scales less than the representative volume. These deviations are of course real, and they are described using the concept of hydrodynamic dispersion (section 1.4.2 provides further details). In other words, deviations in concentration fluxes that result from velocity fluxes are described as being analogous to the classical description of molecular diffusion processes called Fick's Law. For the purposes of hydrogeology, Fick's Law is used to relate the flux with the change in solute concentration with respect to distance. This concept is embedded in the convection-dispersion equation (equation 27, shown again below) through the variable D , the hydrodynamic dispersion coefficient.

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} \quad \text{Convection-dispersion equation (Eqn 27)}$$

Recall that the convection dispersion equation (CDE) is the fundamental equation for describing solute flow through porous materials (Bear, 1972). One big assumption that is made when applying the CDE, however, is that the solute has travelled far enough to have been influenced by the entire possible spectrum of velocity deviations. In other words, the flow must have gone far enough to have encountered sufficient small scale heterogeneities in order for the CDE to be valid. It has been calculated by Yeh (1998), that in fully saturated, packed sand columns this distance is on the order of several thousand sand grains, which is much smaller than most experimental soil columns. However, as the soil drains and enters the unsaturated regime, the number of flow paths decrease while velocity differences increase. As a result, a solute travelling through unsaturated soil must travel much greater distances in order to achieve complete mixing than a solute travelling through saturated soil. Incomplete mixing will result in early initial arrival of the solute breakthrough, multiple concentration peaks, and long effluent tailings which cannot be described by the CDE (Padilla *et al.*, 1999).

This would appear to describe well the behaviour observed for KBr transport in Column A. The concentration gradients shown in Figure 64 vary both in time and space and multiple peaks are observed, particularly in the case of nozzle 5. It is acknowledged that the bottom of the

column was almost certainly saturated. However, while Fickian mixing may have occurred in this saturated layer, it was not sufficiently deep to fully homogenize the concentration variations which were created in the unsaturated zone.

Of course, this effect of multiple peaks and early arrivals of solute breakthrough should also be observed in the energetic material solute curves.

Preferential flow, while a possibility, is considered unlikely. As has been noted previously, the soil is a homogeneous, screened sand which has no roots or animal burrows which could lead to macro scale preferential flow. Cracks in the sand monolith are possible but unlikely since the columns were moved as little as possible after being filled. Incomplete hydraulic contact between the layers of soil could lead to preferential flow in the horizontal direction. However, given that each sand layer was roughly 1.7 cm thick after compaction and that the layers were scarified, the combined effect of preferential flow in the horizontal plane at several depths should increase vertical mixing, not decrease it. Therefore, macro scale preferential flow which could lead to the concentration variations observed in the outflow are impossible to rule out entirely, but are considered very unlikely.

4.5.2. Energetic materials solute transport

346 samples of outflow were collected and analyzed for energetic materials during the course of this experiment, 24 during the springtime infiltration and 322 during the fall infiltration. With the exception of some overflow from the flooding that occurred in column E during the autumn, all autumn outflow was sampled and analyzed. This represented 205 litres of outflow. If over 500 mL of outflow was present in a graduated cylinder, a 500 mL sample was drawn and the analytical mass multiplied by the total volume. However, in the springtime, only 10 litres were analyzed. The reason for the large difference in number and volume of samples between the springtime and autumn infiltrations was due to two different factors. In the autumn infiltration, outflow wicks were sampled individually, which meant that 7 samples were taken from each column every time sampling was performed. During the springtime infiltration, a composite sample was taken from all seven wicks of each column. The second reason was the speed that breakthrough occurred. The experimental plan called for weekly sampling until the dissolved contaminants were detected in the outflow. The purpose of this was to eliminate hundreds of blank samples at the beginning of the experiment, when no dissolved contaminants were in the

outflow. However, breakthrough occurred within 2 weeks, and the 2 month turn around for energetic material analysis meant that the springtime infiltration period was finished before this fact was known.

Figures 64-69 show the transport processes observed in the soil columns. The remainder of the figures can be found in Appendix 4, which shows the cumulative mass and concentration outflows for the columns during the springtime and autumn infiltrations, and in Appendix 5 which shows the energetic material outflow from individual nozzles in the columns during the autumn infiltrations. As discussed above, during the autumn infiltration, leachate concentrations were tracked for each nozzle. The springtime leachate concentrations were only tracked as average concentrations from the column as a whole. Measurement of the cumulative outflow masses for the springtime leachate, was done by calculating the area under the concentration/volume graphs for each species. It was impossible to simply add up the analyzed values for energetic materials because during the springtime not all of the outflow was analyzed, and the majority of mass transport occurred during the springtime.

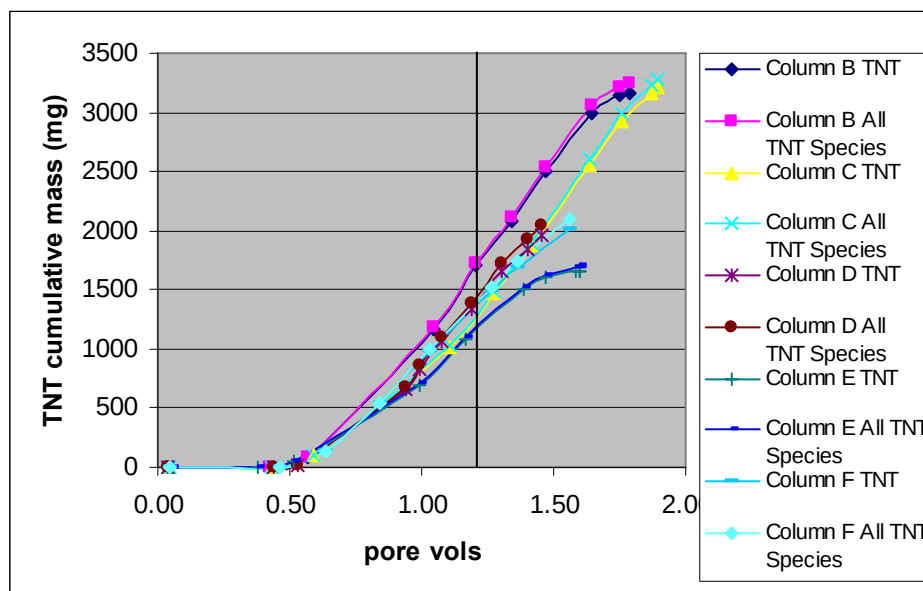


Figure 65. Cumulative TNT and ADNT breakdown products vs. pore volumes outflow. Black vertical line separates springtime from autumn infiltrations

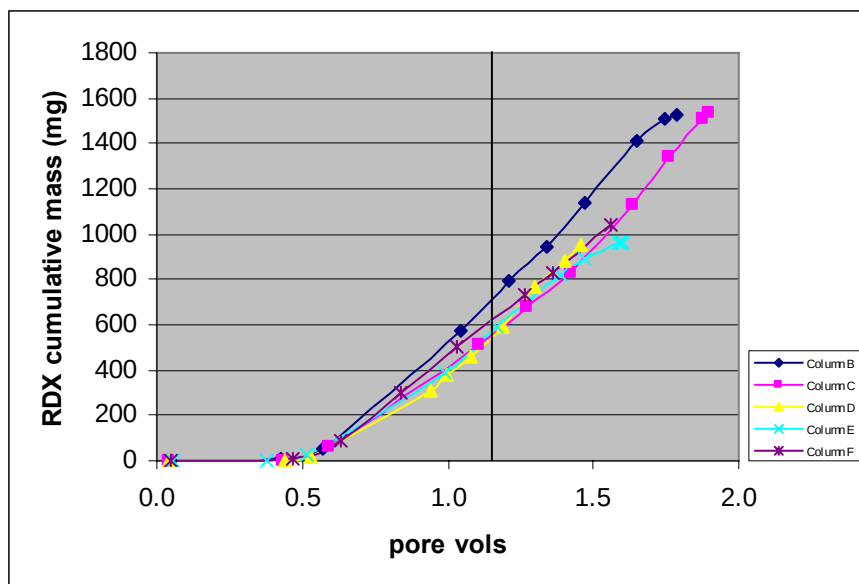


**Figure 66. Cumulative RDX mass in leachate vs pore volumes outflow.
Black vertical line separates springtime from autumn infiltrations**

Figures 64-66 graph the cumulative mass of energetic materials which were recovered in the outflow with respect to pore volumes. Figure 65 shows the cumulative mass of both the TNT alone and for TNT combined with the TNT breakdown products, 2-ADNT and 4-ADNT. This diagram makes it immediately clear that transformation of TNT in the unsaturated columns was extremely limited. The concentrations of TNT breakdown products are at least an order of magnitude lower than the concentration of TNT in the outflow of all five soil columns. This suggests that very little TNT transformation takes place in the near-surface vadose zone. The contact time of the pore water with the column soil was nearly a month at the start of the autumn infiltration period, which is ample time for transformation reactions to occur. This suggests that transformation in the field likely occurs largely due to processes which were absent during this experiment: photolysis and biodegradation in organic as opposed to mineral soils. However, another clear trend was the dominance of 2-ADNT and 4-ADNT as principal breakdown species. As well, the amino species showed accelerating rates of concentration as the experiment progressed.

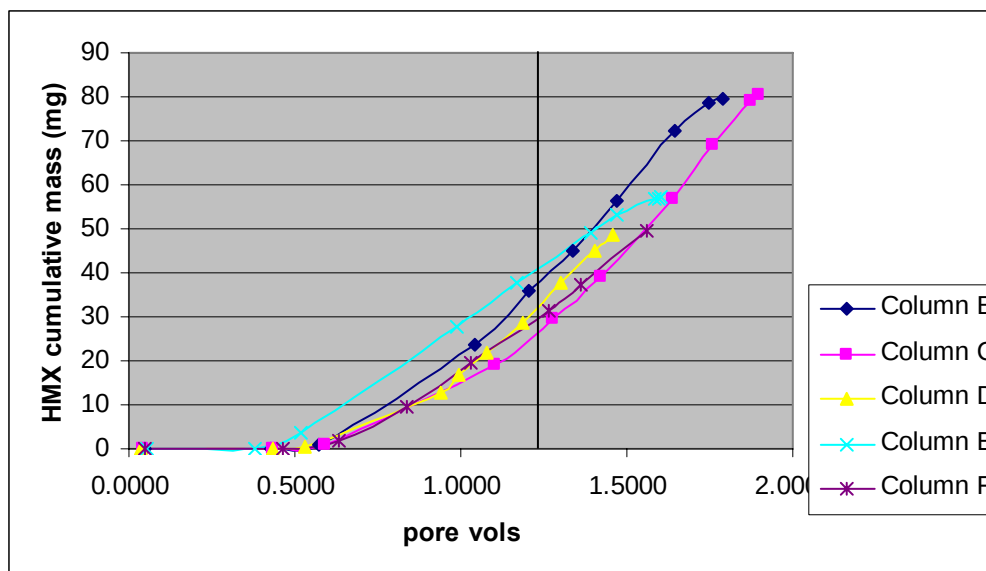


**Figure 67. Cumulative HMX in leachate vs. pore volumes outflow.
Black vertical line separates springtime from autumn infiltrations**

The cumulative mass of RDX in the outflow is shown in Figure 66. The ratio of the cumulative masses of TNT to RDX found in the outflow of the columns with detonation residue as source terms are all in very close agreement of 2.1: 1. Although the ratio of TNT to RDX in composition B is 2:3, the ratio of solubilities of TNT to RDX at 6-10° C is 1.8:1 (Brannon and Pennington, 2002), which fits the data perfectly. Indeed, Lynch et al (2002) found that component interactions had no effect on the solubility of RDX, TNT and HMX originating from composition B. This finding also agrees with the experimental data of Phelan et al (2002) who conducted dissolution experiments using composition B. The ratio they found between the aqueous concentrations of TNT and RDX was at 7.6°C was 2.93:1.

The cumulative mass of the HMX found in the outflow is shown in Figure 67. The ratio of RDX to HMX as aqueous species is in all cases very close to 20:1, which once again fits the ratio of solubilities of RDX to HMX at 10°C of 23.8:1 (Brannon and Pennington, 2002).

Figure 68-69 show the concentration of TNT and RDX respectively in the outflow of column B. The black vertical line indicates the summer dry period when no infiltration took place. The curves all have a distinctive double peak, which occurs immediately before and after the summer dry period. Other curves for columns C, D, E, and F are all in Appendix 4, and all

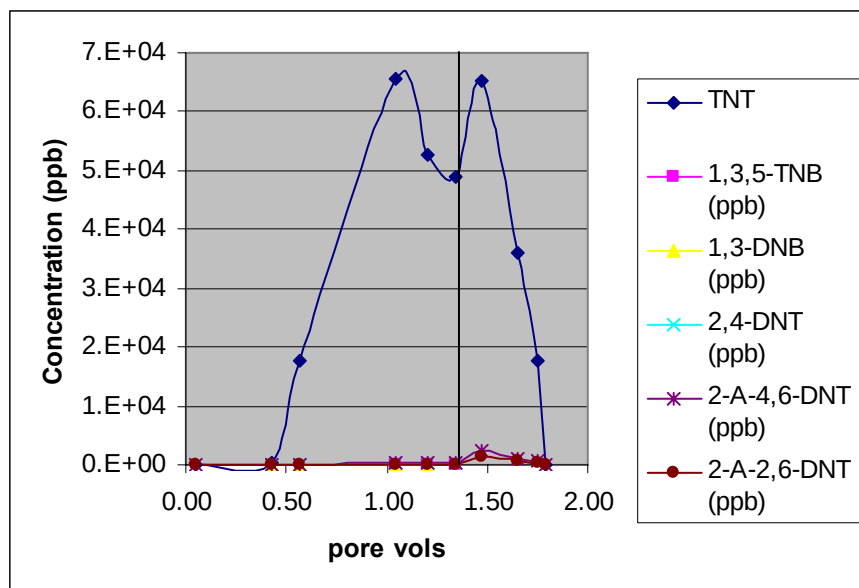


Figure 68. TNT leachate concentrations vs. Pore volume infiltration for Column B. Black vertical line separates springtime from autumn infiltrations

columns display this double peak, although it not always as distinct as that shown by column B. This can be explained by assuming that the rate controlling step in the transport through the columns is dissolution. Concentrations of all energetic materials go up very quickly during the first infiltration period as the finest fraction of detonation residue quickly enters solution due to its very high surface area to mass ratio. This fine fraction becomes exhausted within 2-3 weeks, and concentrations peak and then begin to decline. Once infiltration stops during the summer dry period, the detonation residue which remains in solid form is still in contact with the residual pore water at the surface of the columns. This detonation residue is coarser than the fine fraction which dissolved so quickly at the beginning of the trial. However, this residue is in contact with stagnant pore water for several months and given this amount of time, the pore water which is in contact with the residue eventually reaches saturation. When the next infiltration event occurs in the autumn, this stagnant water which is saturated with energetic material, is immediately flushed through the soil column and collected in the first outflow. The coarse solid detonation residue which remains on the surface now has a much lower surface/mass ratio so the kinetics of dissolution slow down, and concentrations in the outflow water drop off very quickly. It is very likely that this cycle will continue with decreasing amplitude until the detonation residue is completely exhausted. The beginning of each infiltration period will bring a sudden influx of

energetic material, followed by a very rapid drop off in concentrations. This observation should be considered when planning groundwater sampling campaigns in shallow wells.

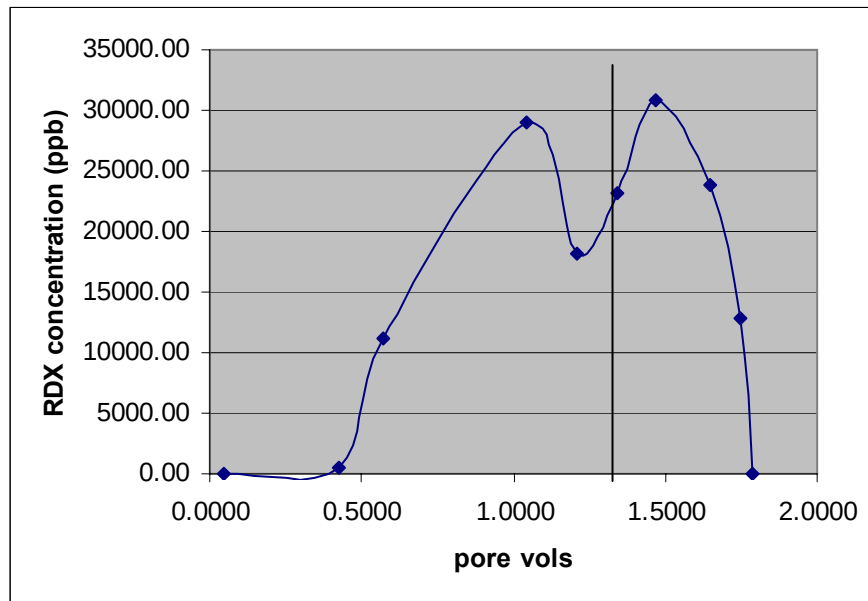


Figure 69. Springtime RDX leachate concentrations vs. Pore Volumes for Column B. Black vertical line separates springtime from autumn infiltrations

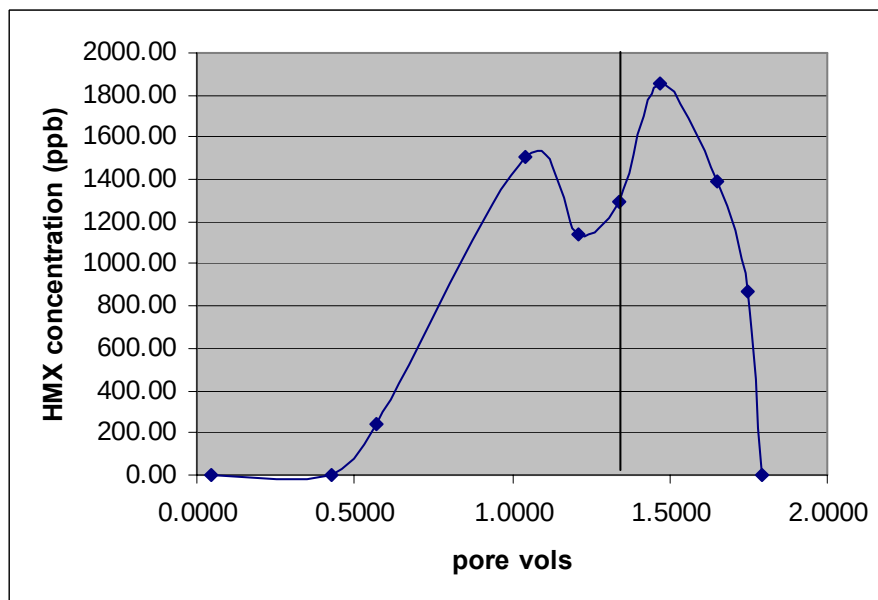


Figure 70. Springtime HMX leachate concentrations vs. Volume infiltration for Column B.

Figures 70 & 71 show the concentrations of RDX detected from each of the seven outflow wicks of Column B during the autumn infiltration. The complete graphs for all columns and all energetic compounds are available in Appendix 5. It is immediately evident that the concentrations of RDX are not homogenous with respect to either time or volume of flow. That is, the concentrations varied by up to a factor of two between wicks in the same column, on the same day. The differences in concentrations were persistent with respect to time, and less so with respect to volume of flow. The ranking of the nozzles from highest to lowest concentrations in the outflow at the beginning of the autumn infiltration period tended to predict the ranking at the end of the infiltration period. In addition, there was no relationship between the rate of flow and concentration. The nozzles which showed the highest flow rates were not those with the highest measured concentrations. Nor were they the lowest – there does not appear to be any relationship whatsoever. There was also no obvious relationship between the volume of flow and the concentration: outflow from the nozzles did not have the same concentration when 2 litres had flowed through each of them, for example. The dissimilar, nearly random concentrations flowing from the nozzles during the autumn infiltration (and during the springtime infiltration of Column A) reinforces the argument made in section 3.6.1 that the unsaturated conditions in the column greatly increased the variation in microscopic flow rates through the pores, which led to non-Fickian mixing conditions. In other words, the columns were not long enough to allow complete mixing and homogeneous outflow at the level of the individual nozzles.

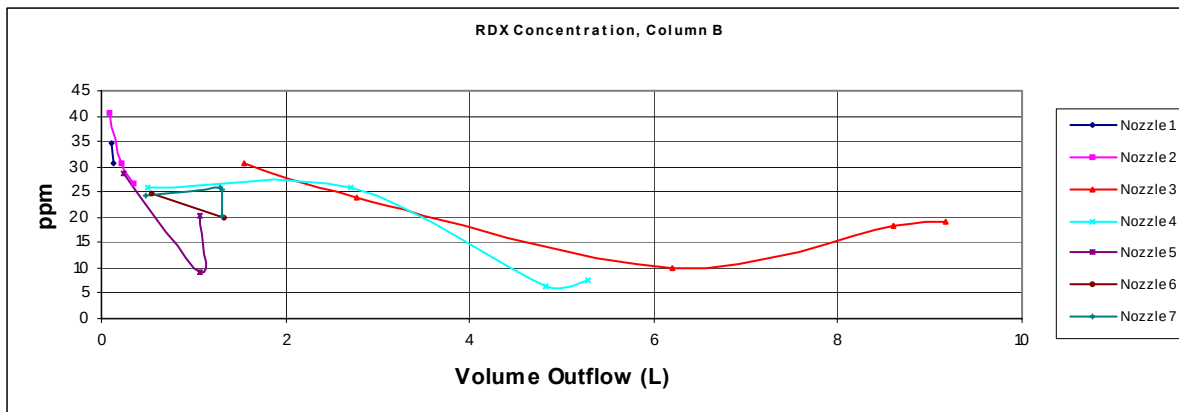


**Figure 71. RDX concentration in autumn outflow
From column B with respect to volume**

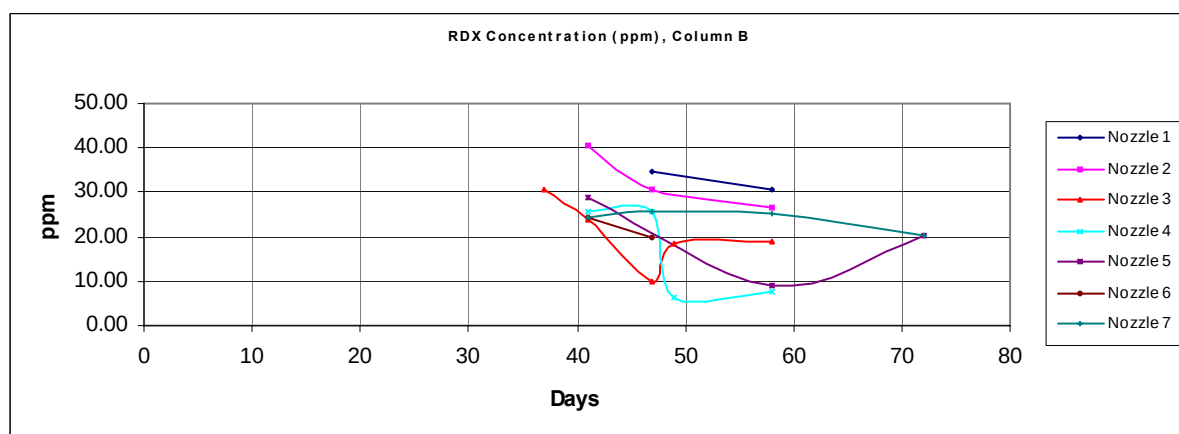


**Figure 72. RDX concentration in autumn outflow
from column B with respect to time**

4.5.3. Comparison of leachate produced by different source terms

Although all energetic material source terms were derived from composition B, there were differences between the source terms used, as was discussed in section 2.2. Columns B and C were identical, with a source term consisting of 45 g. of detonation residue. Columns D and F were also identical with a source term consisting of 45 g of detonation residue *and* an 81 mm mortar with a cracked casing. The energetic material source term of column E was crushed composition B.

The leachate collected from these columns show good reproducibility between columns with identical source terms. Care must be taken when interpreting these results, however, as they

are strongly influenced by the total volume of water which flowed through the columns during the experiment. Figures 64, 65 and 66 showed the cumulative energetic material outflow from all columns. Table 21 summarizes this data. Recall that the total mass of the detonation residue placed on each column was 45 g. Table 21 indicates that the total mass transported through column B during one year of infiltration was 4.9 g, or nearly 11%. However, the total outflow from these columns was different, and in order to compare the cumulative masses in a meaningful way, we need to normalize the data to the volume of outflow. This normalized data is shown in Table 22.

Table 21. Cumulative masses of energetic materials detected in outflow

	Column B	Column C	Column D	Column E	Column F
TNT mg	3220	3215	2136	2054	1735
RDX mg	1555	1579	954	957	1132
HMX mg	80	81	48	57	50
Total mass mg	4855	4875	3138	3068	2917

The TNT breakdown products detected in the outflow were so low as to make meaningful comparisons difficult. Table 23 shows the normalized cumulative masses of TNT breakdown products found in the outflow from the columns. As for Table 22, the normalized cumulative masses were obtained by dividing the total cumulative mass by the number of pore volumes eluted by each column.

Table 22. Normalized cumulative mass of energetic materials in outflow

	Column B	Column C	Column D	Column E	Column F
TNT mg	1777	1684	1428	1062	1250
RDX mg	861.1	815.8	633.3	593.8	656.3
HMX mg	44.44	42.11	32.10	34.55	33.35

The data in Tables 22 and 23 show two trends. The first trend is that the normalized cumulative mass of energetic materials was lowest in column E in almost all cases. Only the value for HMX was comparable to that of other columns. Column E had pure composition B as a source term. This would appear to indicate that energetic material from the detonation residue was more readily available for transport than pure composition B. This could be due to a greater quantity of fine particles in the detonation residue (the grain size curve for composition B was slightly coarser than that of the detonation residue – see figures 37 & 38), or it could be due to a physical change caused by detonation.

The second trend is that the normalized masses in the outflow from columns D and F of TNT, RDX and HMX are lower than in column B and C. However, the normalized cumulative breakdown products of TNT in column D and F are higher than in columns B and C. This would suggest that the energetic materials in columns D and F are undergoing more rapid transformation than in columns B and C. Columns D and F contained the cracked mortar rounds. It has been shown (Hundal et al, 1997) that as little as 1% weight per volume of zero valent iron is highly effective in removing both TNT and RDX from aqueous solution. It is therefore proposed that the presence of the steel cracked shell contributed to the transformation of the energetic species as they entered solution and were transported through the soil columns.

Table 23. Normalized cumulative masses of TNT breakdown products

	Column B	Column C	Column D	Column E	Column F
4 ADNT mg	22.2	17.4	23.0	14.9	18,75
2 ADNT mg	9.44	12.1	13.33	9.33	11.3
2,4-DNT	5.72	3.89	12.0	1.25	11.3
1,3 DNB	1.72	1.32	4.67	0.781	5.63
1,3,5-TNB	0.611	0.632	3.13	0	1.25

4.5.4. Solute transport: retardation factor

The retardation factor of a dissolved contaminant as it travels through the soil is the difference in the rate of flow of the contaminant when compared to an inert tracer. The retardation factor R_f may be calculated one of two ways, either from a known partitioning coefficient, or from solute breakthrough curves. The retardation factor describes how many times faster a nonsorbing tracer is moving relative to the contaminant being sorbed. Since all columns have the same physical dimensions and the same infiltration rate, the outflow rate (L/hr) is a direct function of the average variably saturated hydraulic conductivity (m/hr). The inert tracer will travel through the column faster than a species that is being sorbed, so breakthrough for the inert tracer will occur at a lower volume of cumulative outflow. Therefore, the ratio between the outflow volumes at which breakthrough occurs will be the inverse of the ratio of transport velocities. This ratio, R_f , is called the retardation factor. Referring to figures 62, 67, 68 and 69, we see that the crest of the concentration curve for KBr arrives at a pore volume of 0.8 while the crest of the concentrations for TNT, RDX and HMX arrive at approximately the same time, at 1.05 pore volumes. R_f is therefore 1.05/0.8, or **1.31** (non-dimensional).

4.5.5. Calculation of Adsorption Coefficient

R_f may be defined according to the retardation equation (Domenico & Schwartz, 1990). This equation allows us to calculate K_d if we know the porosity (n) and the bulk density (ρ_s).

$$R_f = 1 + \left(\frac{1-n}{n} \right) \rho_s K_d \quad \text{Equation 40}$$

For the soil used in the column study, it had a measured porosity of 0.377 and a bulk density of 1.662 g/cm³. This gives us a calculated K_d of 0.11 L/kg for all energetics, TNT, RDX and HMX. This value is the same order of magnitude as the experimentally determined K_d (Annex 5) of 0.123 for TNT, 0.22 for RDX and 0.18 for HMX.

These values compare to the literature values for K_d in sand for TNT of 1.5 L/kg (Townsend *et al.*, 1996), 0.47 L/kg (Brannon *et al.*, 1992) and 1.3 L/Kg (Cattaneo *et al.*, 2000). Fewer literature values are available for the K_d of RDX and HMX in sand, but available values are also on the order of magnitude of 0 L/kg to 1 L/kg (Brannon and Pennington 2002). As was shown in figure 2, 3 and 4, measured K_d values appearing in the literature vary widely.

4.6. Observed laboratory temperature

The experiment was housed in a climate controlled laboratory in order to reproduce sub-surface conditions. Seasonal fluctuations in temperature will impact the vadose zone to a depth of approximately 10 m. As was discussed previously, most unexploded ordnance are found between ground surface and a depth of 10 m (section 1.6).

The experimental plan called for refrigerating the laboratory to 8 degrees Centigrade during the springtime infiltration. Following the infiltration period, the lab would be warmed to 15 degrees C to reproduce sub surface conditions at soil depths of 1 to 2 meters during the summer dry period. The temperature would then be reduced back to 8 degrees Centigrade for the autumn infiltration period. The offset of the seasonal temperature found a depth of 1 to 2 meters is on the order of weeks, so such a temperature cycle in the lab would closely mimic actual conditions in the field. However, a major mechanical failure of the refrigeration unit which cooled the laboratory caused temperatures to begin to rise on day 15 of the springtime infiltration. They continued to rise until day 27 when they reached 23 degrees. A temporary fix of the refrigeration unit brought lab temperatures down to 10-13 degrees C. until the end of the springtime infiltration (Figure 73).

While the refrigeration unit was unserviceable, laboratory temperatures were between 15°-20° C for the duration of the summer period, briefly spiking above 25° C on day 110.

The refrigeration unit was repaired on day 134, and the autumn infiltration began on day 140 to allow the soil columns to cool sufficiently. Temperatures for the autumn infiltration stayed between 6° and 9° Centigrade with the exception of day 182, when the refrigeration system was accidentally turned off, and temperatures rose to 12 degrees.

While the mechanical breakdown of the refrigeration unit had an impact upon the temperature cycle in the laboratory, temperatures during the summer dry period were not unreasonable. The only period during which warm temperatures may have had an impact on the analytical results were at the end of the springtime infiltration.

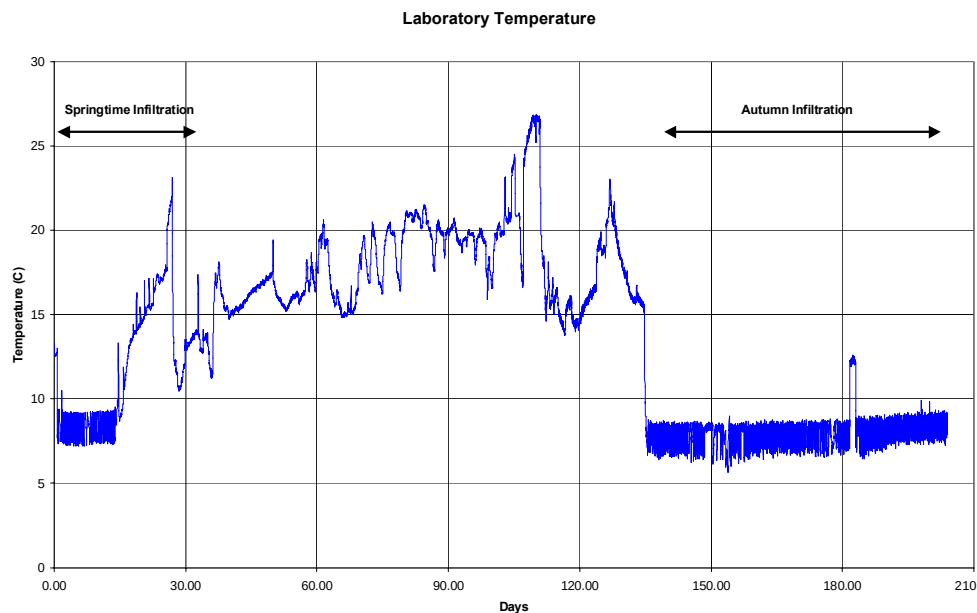


Figure 73. Laboratory temperatures

4.7. Rationalization of observed results with field data

It is interesting to observe how these column trial results fit with observed field data. The following section presents a very brief summary of the published data concerning EM

contamination of groundwater and surface water on Canadian Forces bases. This summary only discusses results that have been published as either DRDC Valcartier or INRS-ETE technical reports. The work included in these reports covers the time period 1995-2004, and the reports have been published between 1998 and 2005. It does not include results from reports that are pending, and it only discusses analytical results for energetic materials in ground and surface water.

The purpose of presenting this summary of data is to allow a meaningful rationalization of the results obtained from the column experiments with the data obtained in the field.

Sampling campaigns in both Cold Lake, Wainwright and Petawawa have recently tested groundwater and surface water for energetic materials, but these results have yet to be published and are not included in this summary. For details on the wells or surface water locations where energetic materials were detected, the reader is encouraged to refer to the source documents which are identified in the text.

Unless otherwise specified, all energetic material analyses reported in these studies were conducted using the US EPA Method 8330 (Analytical method shown in Appendix 6). Using this method, the following analytes were evaluated: nitrobenzene, 2-nitrotoluene, 3-nitrotoluene, nitroglycerine, 1,3-dinitrobenzene, 2,6-dinitrotoluene, 2,4-dinitrotoluene, 2,4,6-trinitrotoluene, trinitrobenzene, 4-A-2,6-dinitrotoluene, 2-A-4,6-dinitrotoluene, tetryl, RDX and HMX.

It is important to mention that range standard operating procedures vary from one base to another, and common practices for clearing unexploded ordnance also vary. There are three levels of unexploded ordnance clearance. Level 1 means that a surface sweep has been conducted and that there are no visible munitions or munition components lying on the ground surface. Such a sweep is commonly conducted on a yearly or semi-yearly basis, although when range personnel or resources are limited, this may not be done for a long period of time. Level 2 clearance is performed with a standard issue mine detector and indicates that there are no unexploded munitions within 60 cm of the surface. Level 3 clearance means that the site is completely clear of all ordnance, and that there is no unexploded munitions at all down to a depth of 3 meters.

4.7.1. Cold Lake Air Weapons Range (CLAWR)

Cold Lake Air Weapons Range covers over 11 000 square kilometers in northern Alberta. However, the impact areas where live munitions are dropped are limited to two relatively small ranges: the Alpha/Bravo range complex and the Jimmy Lake/Shaver River Range complex, each being under 10 square kilometers in area. The vast majority of live munitions are dropped on the Shaver River Range. Munitions that are commonly dropped on the Shaver River Range include the Mk82 500 lb general-purpose bomb and the Mk83 1000 lb general-purpose bomb.

Table 24. Cold Lake energetic materials (EM) sampling summary

Total Number of Monitoring Wells	Sampling Campaign	No. of groundwater (GW) Samples Taken	No. GW Samples Contaminated with E.M.	E.M. Species detected in GW	GW E.M. conc'n (ppb)
21	Aug. 2003	0	0	N/A	N/A
	Mar. 2004	14	5	RDX	3.2
	Aug. 2004	19	1	NG	5.1, 3.0, 2.6, 0.8
	Aug. 2004	19	1	RDX	7.02
	Aug. 2003	6	1	E.M. Species detected in SW	SW E.M. conc'n (ppb)
				NG	0.002
				1,3-DNB	0.595
				2,6-DNT	0.377
				2,4-DNT	6.486
				TNT	13.1
				RDX	2.046
	Mar. 2004	5	1	NG	0.5
	Aug. 2004	7	0	N/A	N/A

Two government reports are currently available which discuss surface and groundwater contamination by energetic materials at the Cold Lake Air Weapons Range.

The first report (Ampleman *et al.*, 2003) sampled six surface water locations for energetic materials. These included two locations in Primrose Lake and three locations in Jimmy Lake. None of these samples contained any energetic materials. However, surface water collected from a bomb crater on Shaver River Range did show significant amounts of explosives: 0.002 ppb NG, 0.595 ppb 1,3-DNB, 0.377 ppb 2,6-DNT, 6.486 ppb 2,4-DNT, 13.1 ppb TNT and 2.046 ppb RDX.

The second report (Martel *et al.*, 2004) discusses work conducted in both March and August 2004. In March 2004 a total of 21 wells were drilled and installed at the Jimmy Lake/Shaver River range complex and the Alpha/Bravo range complex. Fourteen of the wells were sampled. Of the 14 groundwater samples, there was one hit for RDX in well GW-SR-11 on

Shaver River Range. This sample showed a concentration of 3.2 ppb of RDX. In addition, nitroglycerine (NG) was detected in four samples: GW-SR-1-A (5.1 ppb), GW-JL-9 (3.0 ppb), GW-JL-4 (2.6 ppb), and GW-SR-6 (0.8 ppb). These wells are widely spaced over the Shaver River/Jimmy Lake range complex. Sample GW-SR-1-B, a duplicate of GW-SR-1-A, showed no NG. In addition to the groundwater samples, 5 surface water samples were taken in March from under the frozen surfaces of the lakes and rivers. One of these, SW-SHAVER-UP, showed a concentration of 0.5 ppb NG.

In August 2004, a second sampling campaign was executed. No new wells were installed, but 19 of the wells that were drilled in March were tested including 14 sampled in the earlier campaign. No NG was detected in any samples, but groundwater obtained from well GW-SR-11 showed a concentration of 7.02 ppb RDX. Seven surface water samples were taken, including the same sites tested in March, and no energetic materials were detected.

The RDX detected in well GW-SR-11 in two separate sampling campaigns provides substantial confidence that persistent concentrations of dissolved RDX are present in the groundwater at this location. This well is located about 200m down gradient from the primary target on Shaver River Range, a derelict tank where the majority of live munitions are dropped. The nitroglycerine detected in the first sampling campaign may be due to laboratory error, as no NG was detected in the August sampling campaign, and no Air Force bombs contain NG.

4.7.2. Western Area Training Center (WATC) Wainwright

One report on the groundwater and surface water conditions of WATC Wainwright has been written (Martel et al, 2004b). This campaign was conducted in October 2003.

Table 25. Wainwright energetic materials (EM) sampling summary

Total Number of Monitoring Wells	Sampling Campaign	No. of groundwater (GW) Samples Taken	No. GW Samples Contaminated with E.M.	E.M. Species detected in GW	GW E.M. conc'n (ppb)
30	Oct. 2003	28	0	N/A	N/A
	Sampling Campaign	No. Surface water (SW) Samples Taken	No. SW Samples Contaminated with E.M.	E.M. Species detected in SW	SW E.M. conc'n (ppb)
	Oct. 2003	20	1	TNT	0.2

Thirty monitoring wells were installed during this study, and 28 wells were tested for energetic materials. No energetic materials were detected in any samples. As well, 20 surface

water samples were taken from lakes, streams and ponds across the training area. One sample taken from the Battle River, the major river running along the western border of the training area, showed a concentration of 0.2 ppb TNT. However, no TNT degradation products were detected in this sample. Three other samples taken from the same river at different locations showed no energetic materials.

4.7.3. Canadian Forces Base (CFB) Gagetown

Two published reports discuss energetic materials in the groundwater and surface water at CFB Gagetown. The first report (Thiboutot *et al.*, 2003) presents results from the first hydrogeological campaign by INRS-ETE performed at CFB Gagetown in 2001. During this campaign, 35 monitoring wells were installed. 42 groundwater samples were collected, by obtaining seven samples from previously existing supply wells in addition to the installed monitoring wells. As well, 8 surface water samples were collected.

Table 26. Gagetown energetic materials (EM) sampling summary

Total Number of Monitoring Wells	Sampling Campaign	No. of groundwater (GW) Samples Taken	No. GW Samples Contaminated with E.M.	E.M. Species detected in GW	GW E.M. conc'n (ppb)
43	Aug. 2001	42	15	RDX	1.6,1.6,1.6,1.6
					1.6,1.6,1.6,1.6
					1.6,1.6,1.6,1.7
				TNT	1.0, 1.1
				HMX	2.1
	Oct. 2002	87	0	N/A	N/A
	Sampling Campaign	No. Surface water (SW) Samples Taken	No. SW Samples Contaminated with E.M.	E.M. Species detected in SW	SW E.M. conc'n (ppb)
	Aug. 2001	8	2	Tetryl	2.2, 2.2
	Oct. 2002	22	0	N/A	N/A

Of these samples, 15 groundwater samples tested positive for energetic materials. Two surface water samples tested positive for tetryl. The results are summarized in Table 26.

The second report (Lewis et al, 2005) outlines the results from the October 2002 drilling and sampling campaign. During this campaign, 18 further wells were drilled, and 87 groundwater samples were taken. All of the wells sampled during the August 2001 campaign were re-sampled. Twenty-two surface water samples were taken and analyzed. No energetic

materials were detected during this campaign in any samples, either groundwater or surface water.

The unusual uniformity of the concentrations detected during the first hydrogeological campaign, combined with the fact that no energetic materials were detected in the second campaign one year later suggests that either contamination occurred in the laboratory during analysis or vertical contamination occurred during the drilling of the wells in the first campaign, with contaminated surface soils falling into the boreholes during well installation.

4.7.4. Canadian Forces Base Shilo

There are two reports published which discuss sampling campaigns that looked at energetic materials in ground and surface water. Thiboutot et al (2001) includes results from the first hydrogeological sampling campaign conducted at CFB Shilo in October 2000. Forty-two monitoring wells were installed during this campaign, and 38 wells were tested for explosives. No energetic materials were found. Nine surface water sites were tested during this campaign. No energetics were detected in these samples either.

The second report (Ampleman *et al.*, 2003) discusses results from the September 2001 and September 2002 sampling campaigns. In 2001, a further 36 monitoring wells were installed for a total of 78 monitoring wells at CFB Shilo.

Table 27. Shilo energetic materials (EM) sampling summary

Total Number of Monitoring Wells	Sampling Campaign	No. of groundwater Samples Taken	No. Of Wells Contaminated with E.M.	No. Of Surface water Samples Taken	No. Of Surface Water Samples Contaminated with E.M.
78	Oct. 2000	38	0	9	0
	Sept. 2001	101	0	17	0
	Sept. 2002	75	0	20	0

In September 2001, 92 groundwater sampling locations were tested for energetics. These included 70 of the 78 installed wells, 14 previously existing wells, 2 drinking water supply wells, 2 wells in neighboring Spruce Woods Provincial Park, and 1 private well. In addition, 13 duplicates were taken. No energetic materials were detected over the quantification limit of 0.01 ppb. 17 surface water samples were also tested, and no energetic materials were detected.

In September 2002, 67 groundwater sampling locations were tested. These included 52 of the 78 monitoring wells, 6 previously existing wells, three drinking water supply wells, one well

in Spruce Woods Provincial Park, and 5 private wells. Eight duplicates were also taken. Twenty surface water sampling locations were tested, including all sites previously sampled in the 2000 and 2001 sampling campaigns. No energetic materials were detected in any samples, either ground water or surface water.

4.7.5. Canadian Forces Base Valcartier

Two reports have been published which cover groundwater and surface water contamination by energetic materials at CFB Valcartier. The first deals specifically with a single range, the Arnhem anti-tank range (Martel *et al.*, 1999). This range is used for M-72 Short Range Anti-Armour Weapon (SRAAW). The warhead on the M-72 is a shaped charge composed of Octol, a 70% HMX / 30% TNT explosive compound. This report discusses work performed between June 1998 and June 1999.

A total of 25 wells were installed on, or downgradient to, Arnhem range in June 1998. Beginning in July 1998, groundwater samples were collected in two-week intervals, 13 times altogether. No surface water samples were taken during this campaign. Of all studies published to date, the results from the 1998-1999 Arnhem study show the most conclusive evidence of the presence of energetic compounds dissolved in the groundwater on a Canadian Forces base. This data was the basis for the work published by Michel Mailloux as his Master's thesis (2000). In his thesis, Mr. Mailloux discusses the fact that only 7 of the 325 ground water samples showed traces of TNT, while 55 of the samples showed traces of HMX. He postulated that a thin layer of subsurface clay or organic material was causing irreversible adsorption of the TNT.

The second report (Ballard *et al.*, 2004) was published in French by INRS-ETE. The English translation of the title is "Research on the environmental conditions of groundwater and surface water at three sites at CFB Valcartier, Québec." This study covered the work done in 2001 and 2002, where 19 monitoring wells were installed around the DRDC-RDDC Valcartier explosive test range, and a further 11 wells were installed around the Vaucelles hand grenade range. Both of these sites are quite small. The DRDC-RDDC Valcartier range is approximately 1 square kilometer, and the grenade range is approximately 100 meters square. On the third site, the Liri Impact area, three surface water samples and one ground water sample were taken and analyzed.

In the 2001 study, 17 of the 24 groundwater samples taken and all four surface water samples showed very uniform, low levels of both RDX and TNT, at concentrations of 25 ppb.

In 2002, none of the 29 wells or 5 surface water samples tested showed any energetic materials, although these samples were taken from the same wells as the 2001 campaign. As in the case of the 2001 Gagetown campaign, the 2001 Valcartier analytical results are uncertain, and the uniformity of the 2001 Valcartier results (all concentrations for both TNT and RDX were 25 ppb in all 17 hits), suggest that the energetic materials that were detected were likely due to laboratory contamination.

Table 28. CFB Valcartier energetic materials (EM) sampling summary

Total Number of Monitoring Wells	Sampling Campaign	No. of groundwater (GW) Samples Taken	No. GW Samples Contaminated with E.M.	E.M. Species detected in GW	GW E.M. conc'n (ppb)
55	1998-1999	325	55	HMX (55 hits)	2.4-230
				TNT (7 hits)	0.25-6.35
				RDX (8 hits)	1-5.8
	2001	24	17	RDX, TNT	25 ppb (all)
	2002	29	0	N/A	N/A
	Sampling Campaign	No. Surface water (SW) Samples Taken	No. SW Samples Contaminated with E.M.	E.M. Species detected in SW	SW E.M. conc'n (ppb)
	2001	4	4	RDX, TNT	25 ppb (all)
	2002	5	0	N/A	N/A

4.7.6. Canadian Forces Ammunition Depot (CFAD) Dundurn

The work done at CFAD Dundurn began in 1995. The report entitled “Study of the impacts of OB/OD activity on soils and groundwater at the destruction area in CFAD Dundurn” (Ampleman et al, 1998) includes groundwater sampling work performed in 1995 and 1996. Another report (Martel et al, 1998) discusses the December 1996 analytical results and provides more details concerning the hydrogeological situation at CFAD Dundurn, including borehole logs, water table elevations, and groundwater flow.

In November 1995, 16 observation wells were installed at CFAD Dundurn. In December 1996, a further 14 monitoring wells were installed. Four sampling campaigns were conducted during this time frame, in November 1995, April 1996, September 1996 and December 1996. The samples from the first three campaigns were analyzed using US EPA method 8330, but only HMX, RDX and TNT were analyzed: no TNT breakdown products were analyzed. The December 1996 results were analyzed using the D-Tech method rather than the U.S. EPA 8330

method, and only RDX and TNT were analyzed for (HMX was not analyzed). Of the 16 samples taken in November 1995, 12 showed detectable levels of RDX, HMX or TNT. In April 1996, 8 of the 16 groundwater samples showed detectable levels of energetic materials. In both November 1995 and April 1996, reported concentrations of up to 5.7 ppb HMX, 159.0 ppb TNT, and 2.4 ppb RDX. HMX was detected 4 times in November, and 3 times in April. TNT was detected 12 times in November and 8 times in April. RDX was detected 4 times in November and once in April.

TABLE 29. CFAD DUNDURN EM SAMPLING SUMMARY

Total Number of Monitoring Wells	Sampling Campaign	No. of groundwater (GW) Samples Taken	No. of GW Samples Contaminated with E.M.	E.M. Species detected in GW	GW E.M. conc'n (ppb)
30	Nov.. 1995	16	12	HMX (4 hits)	2.2, 5.7, 0.9, 1.1
				RDX (12 hits)	1.3 to 159.0
				TNT (4 hits)	2.0, 1.6, 2.7, 2.4
	Apr. 1996	16	8	HMX (3 hits)	2.9, 0.9, 1.1
				RDX (8 hits)	0.9 to 120.8
				TNT (1 hit)	1.9
	Sept. 1996	16	2	RDX (2 hits)	6.6, 79.2
	Dec. 1996	35	3	RDX (3 hits)	40, 159, 3.4

In contrast, energetic materials were only detected in 2 wells out of 16 in September 1996, and in 3 wells of 30 in December 1996. This was attributed to vertical cross contamination of the soil during installation of the wells. It was hypothesized that soil from the contaminated surface dropped into the open borehole, carrying a quantity of energetic materials with it that would slowly dissolve in the well and dissipate with time.

Surface water was not studied during any sampling campaigns to CFAD Dundurn.

Groundwater contamination by RDX was found to be limited to shallow depths (the top 1.5 m of the aquifer) around the open burning/open detonation (OB/OD) site. As well, all contamination was found to be down gradient of the OB/OD site.

4.7.7. Summary of Field Data

Very little energetic material has been found to date in the ground water on Canadian Forces bases. Only 62 out of 814 groundwater samples have had detectible levels of EM observed. These numbers do not include those samples which tested positive but which were subsequently attributed to sampling error, laboratory error or vertical contamination during well

construction. However, 55 of those 62 samples came from a single range – Arnhem range in Valcartier. This anti tank range is less than 1 square kilometre in area, but was sampled intensively by Michel Mailloux for his INRS_ETE Master’s thesis (2000). Leaving out the 325 Arnhem samples which skew the results substantially, only 7 out of 489 groundwater samples have been reliably determined to contain dissolved energetic materials. This is an overall rate of 1.4%. It must be recalled that the wells have all been installed in locations which were judged likely to be contaminated, either due to detected EM in the surface soil, or due to their proximity to intensively used training locations such as anti tank ranges and artillery impact zones. The concentrations of EM in these groundwater samples were in the low ppb range.

Based on the published data, very little EM is found in groundwater on Canadian Forces bases despite the concerted effort to locate wells in the regions most likely to be contaminated.

4.7.8. Comparison of field data with column trial results

The unsaturated column leaching experiments demonstrated that cracked shell munitions – which we can expect to occur in the field – produce up to 4.9 g of dissolved energetic material contamination in the first year they are exposed to the environment. This dissolved contamination has been shown to be highly mobile in sandy unsaturated soil. Many of the Canadian Forces bases which were the subject of published studies are situated at least partially on sandy soils (CFB Wainwright, CFB Shilo, CFB Valcartier, CFB Dundurn, CFB Cold Lake). However, very little energetic materials are found in the groundwater of these bases. This apparent contradiction needs to be explained.

The 4.9 g of mobile energetic material is assumed to be a worst case scenario, and it includes 1.5 g of dissolved RDX. We will work with RDX because it has the lowest acceptable lifetime limit (2 ppb) according to U.S. EPA guidelines. The effluent from the unsaturated columns showed concentrations of 25 to 30 ppm RDX, which is 5 orders of magnitude higher than the EPA guidelines. This would appear to be of some concern. However, the real question is not how much RDX one munition releases, but rather how many of these cracked shells would be required to produce an aquifer concentration above the EPA limit.

To calculate this we need to determine the volume of water held in an porous soil aquifer below an impact area. For the purposes of calculation, we will assume a training range which is 1 km². This is a reasonable size for an anti tank range or an artillery impact zone. Further, we

will assume that the underlying aquifer is 30 m deep. In other words, the saturated zone of soil under the 1 km² range is 30 m in thickness. Further, the porosity of the sandy soil is 0.37 in keeping with the values measured in the leaching columns.

From this data we can determine:

$$V_{\text{bulk, aquifer}} = 1000 \text{ m}^2 \times 30 \text{ m} = 30\,000 \text{ m}^3.$$

If the porosity is 0.37 as was measured in the columns, the volume of water held in this underlying aquifer is

$$V_{\text{water, aquifer}} = 30\,000 \text{ m}^3 \times 0.37 = 11\,100 \text{ m}^3 = 11\,100\,000 \text{ litres}.$$

The US EPA limit of 2 ppb = 2 µg/L.

This indicates that if this aquifer were uniformly contaminated up to the limit determined by the EPA, the total mass of RDX in the entire aquifer would be:

$$M_{\text{RDX}} = 2 \text{ µg/L} \times 11\,100\,000 \text{ litres} = 22\,200\,000 \text{ µg} = 22.2 \text{ kg}.$$

Returning to the results of the column leaching experiment, 1.5 g of RDX leached from the cracked shell in the first year of exposure. Assuming that subsequent years would release less RDX given that the finest fraction of residue was already dissolved, the number of cracked shell munitions that would be needed to contaminate the aquifer to the limit determined by the US EPA would be

$$22\,200 \text{ g} / 1.5 \text{ g} = 14\,800 \text{ cracked shells}.$$

This number, in practical terms, would mean that cracked shells would need to be found at a density of:

$$14\,800 / 1 \text{ km}^2 = 0.015 \text{ cracked shells per square meter}.$$

In other words, one cracked shell every 68 m².

While intact (uncracked) UXO's may be found at this kind of density, the likelihood of cracked shells being found at this kind of density is extremely slim. As was pointed out during the cracked shell trials, while it was reasonably easy to produce such cracked shells, very specific conditions must be in place, and these conditions are not likely to occur 14 800 times in one square kilometer.

The number of contaminant source terms diminishes rapidly when the volume of water held by the aquifer decreases. Therefore, it is expected that in very small areas of high density UXO's, such as anti tank ranges have the highest probability of producing measurable concentrations of energetic material in the underlying groundwater. Similarly, a decrease in the porosity of the underlying aquifer, as would be the case in fractured aquifers, would also be expected to yield higher concentrations of dissolved energetic materials for a given density of cracked shell munitions.

5. NUMERICAL MODELING OF UNSATURATED COLUMNS

5.1. Introduction

FEFLOW, a finite element groundwater simulation package, was chosen for the numerical modeling of the unsaturated columns. This software package offers all of the features which were required to produce a reliable model: 3 dimensional modeling; variably saturated flow; transient or steady state flow conditions; transient or steady state transport conditions, adsorption effects; and the integration of chemical reactions or degradation mechanisms.

There are two distinct steps to producing a reliable transport model. The first step requires the creation of a model which reliably reproduces the unsaturated flow characteristics of the columns. This step represented 95% of the work. Once a reliable flow model was established, the second step – establishing the transport characteristics – was fairly straightforward. The two steps are described below.

5.2. Flow modeling

5.2.1. Dimension

1-dimensional, 2-dimensional and 3-dimensional models can all be used for various applications in hydrogeology. Frequently, modeling in the vadose zone is performed in 1 dimension, because virtually all flow is vertical. A much greater computing power is required for 2 dimensional and 3 dimensional models, which consequently slows down model development. In the present case, although the columns were largely unsaturated, the bottom layers were found to be in the saturated regime. This, combined with the nozzle placement meant that fluid flow near the bottom of the columns would need to be partially horizontal. For this reason, a three dimensional model was used.

5.2.2. Background map

The first step in creating a model is importing an appropriate map, which serves as a framework. Since no maps exist for the unsaturated columns, one had to be built. It is important to use the correct scale for the map, because this scale will be transposed onto the model itself. FEFLOW does not offer tools for manipulating maps once they have been imported, so scaling

had to be performed prior to the map being imported. Various graphic formats were tried, such as .jpg and .bmp, but these were inadequate because FEFLOW assumed their scale to be orders of magnitude larger than was desired. AutoCAD files of the format .dwg were found to be suitable. The map was a horizontal cross section of the column (a circle 0.64 m diameter) with the locations of the outflow nozzles indicated as points. The correct geometry of the location of the nozzles and the proper scale were the most important points for the background map.

5.2.3. Superelement mesh

The mesh geometry across the horizontal plane was a standard triangular mesh. The mesh was refined around the nozzles, where the majority of horizontal flow would be taking place (Figure 74). The triangular elements were identical in each horizontal slice of the model, and each node on the mesh was connected to the node immediately above and below it. This created a 3 dimensional grid of triangular prisms. By stacking horizontal slices on top of each other, a 3 dimensional volume in the shape of a cylinder was created (Figure 75). This formed the basis of the remainder of the model. The number of nodes in a single slice in the final model was established at 1415, giving a total of 106125 nodes for the 75 slices, and 200836 elements.

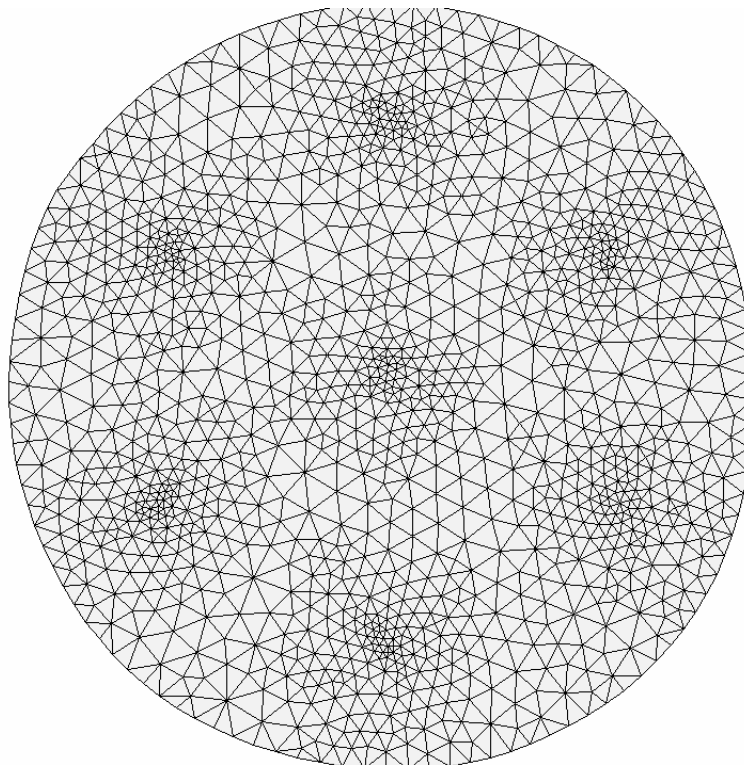


Figure 74. Superelement mesh of a single slice of column model.

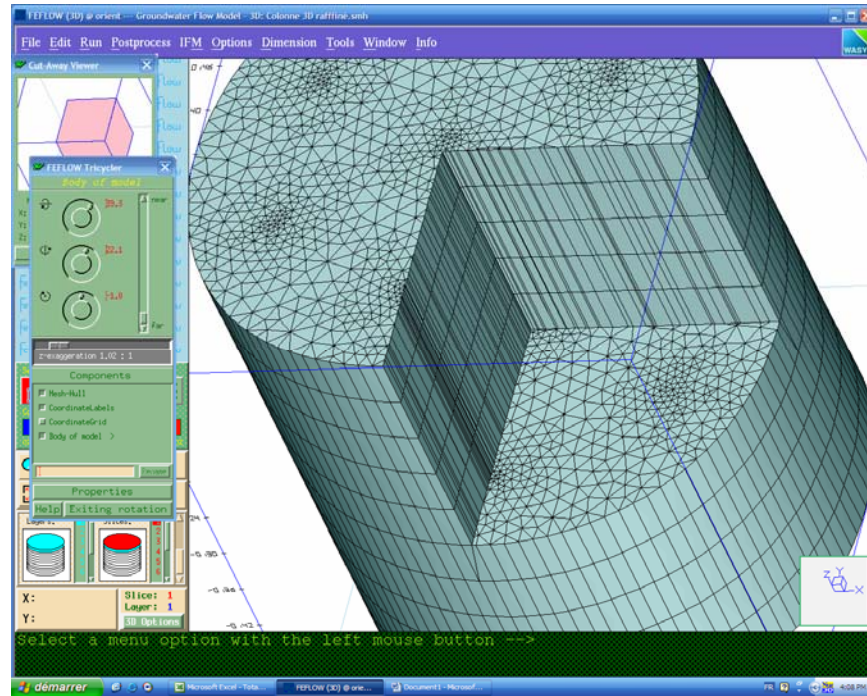


Figure 75. Column mesh cutaway showing prism structure

5.2.4. Flow materials

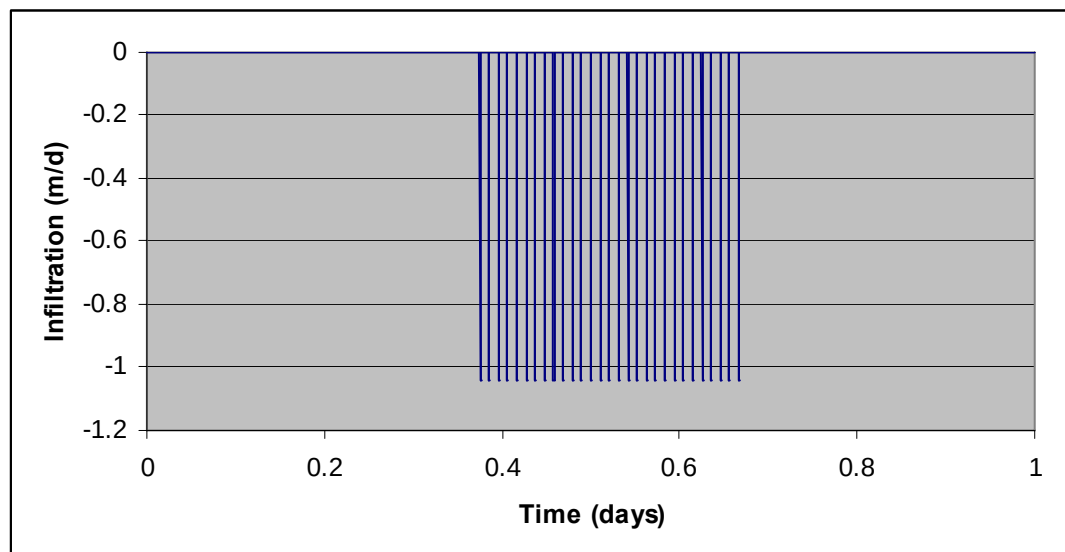
This pull-down menu in FEFLOW allows the user to input the physical characteristics of the soil being modeled. There are two options, saturated flow and unsaturated flow. The unsaturated flow menu allows the user to choose which unsaturated flow equation he wishes to use. The options are the Van Genuchten (Equation 30), Brooks and Corey (Equation 29), the modified Van Genuchten, Havercamp, exponential and linear. The Van Genuchten model was selected. The initial values for the Van Genuchten variables (Table 24) were obtained from the estimates provided by the SoilVision software using the Fredlund & Wilson (1997) pedo-transfer function based on the grain size distribution of the column soil. These initial values are summarized below. The value for m is related to that of n and does not need to be specified.

Table 30. Van Genuchten unsaturated parameters used in FEFLOW

Van Genuchten Parameter	Initial Value (determined with SoilVision software)	Final Value (provided best fit)
α	7.43 1/m	8 1/m
n	3	1.65
S_s	1.00	1.00
S_r	0.0025	0.0025

5.2.5. Flow boundaries

The flow boundaries refers to the head or flow parameters which define the exterior boundaries conditions of the model. For the purposes of the column model, three boundary conditions were defined. The walls and base of the column were defined as no-flow boundaries across which no flux could take place. The surface of the column was defined as having an infiltration function equivalent to that which was programmed for the real columns. The springtime infiltration function is shown in figure 76. The imposed influx occurred for 22.5 seconds every 15 minutes between 8:00 am and 4:00 pm daily at a flux of -1.05 m/d. This reproduced the sprayed inflow at the top of the columns.

**Figure 76. Springtime influx function**

The final boundary condition was the head imposed by the fibreglass wicks at the base of the column. The nozzles were modeled as both point heads, to reproduce the nozzle itself, and area heads to reproduce the draw caused by the 10 cm² pad of fibreglass inside the columns which was connected to the wicks. It was found both types of head produced identical results. The point head was chosen, with an imposed head of -0.62 m (1 cm lower than the base of the column).

5.2.6. Flow results

The flow characteristics of the column were modeled on the springtime response, as the results from the springtime inflow provided very clear periodic moisture content curves at depths of -10 cm and -30 cm. In order to achieve the correct magnitude of fluctuations, at the correct depths in the soil columns, the Van Genuchten parameters, porosity and outflow head had to be adjusted independently. The porosity was the most stable of the parameters, and it remained at 0.38. The outflow head, as mentioned above, had an imposed head of -0.62 m. The Van Genuchten parameters proved finicky, and final values of $\alpha = 8.0 \text{ m}^{-1}$ and $n = 1.65$ were selected as the most representative. The maximal saturation S_s and residual saturation S_r were kept at 1.0 and 0.0025 throughout the simulations.

The saturation profile at steady state of the column with these imposed parameters is shown in figure 77. The horizontal dimension in this figure is exaggerated in order to fit the entire column into the printable area. The cyclical fluctuations produced by the model at depths of -10 cm and -30 cm are shown in figure 78, along with a blow-up of the actual springtime moisture fluctuations of Column A. The results are very satisfactory and the model reproduces the actual column behaviour very reliably.

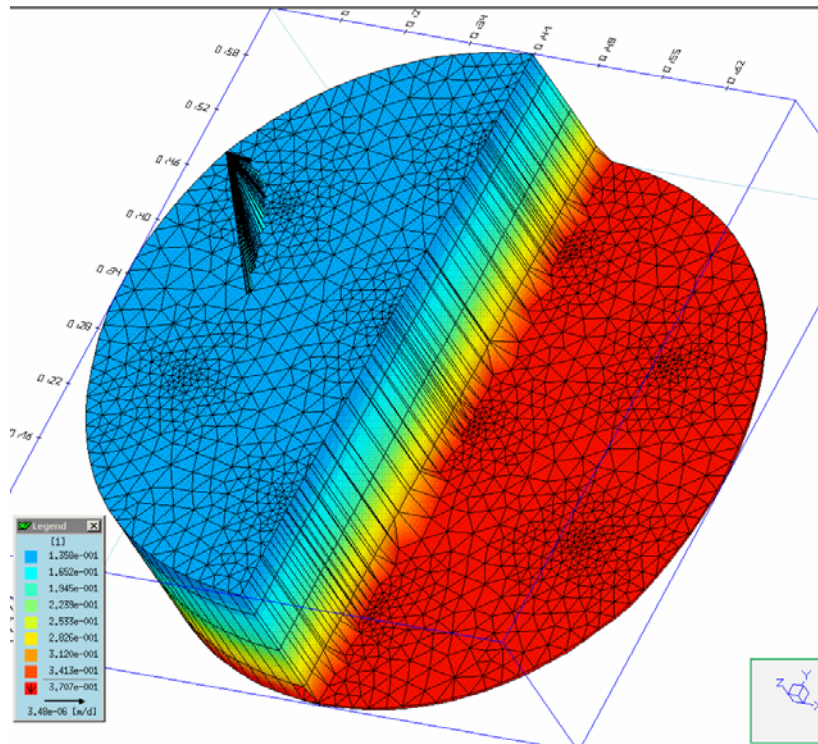


Figure 77. Moisture content profile of column

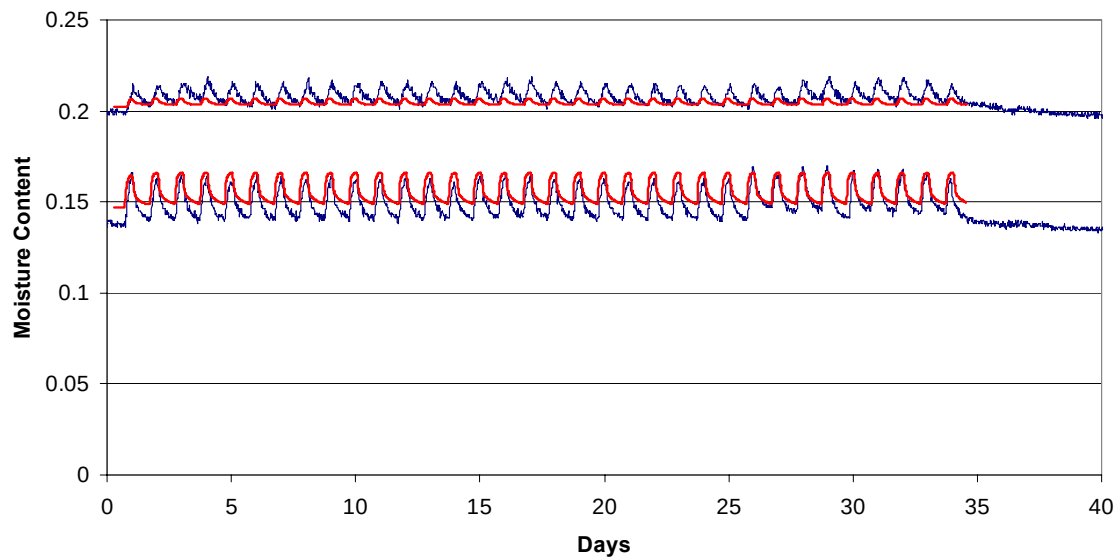


Figure 78. Moisture content fluctuations of model (red) and actual columns (blue) at depths of -10 cm (bottom curve) and -30 cm (top curve)

5.3. Transport modeling

Transport modeling was less challenging than flow modeling, although the definition of a variable input function which reproduced the dynamic dissolution of detonation particles was not successful. For the KBr, the input function was initially defined as a slug input of 50 g/L KBr during the first 200 mL of water sprayed during day 1 of the simulation. This reproduces as closely as possible the actual application of 10 g of KBr dissolved in 200mL of water applied just prior to the start of the experiment. However, with such an abrupt and large change in concentrations (from 0 to 50000 ppm instantaneously), convergence was impossible. A compromise of ramping up the concentration gradually from 0 to 42000 ppm over 15 minutes, then maintaining a concentration of 42 000 ppm for 15 minutes and then ramping down the concentration from 42000 ppm to 0 over a further 15 minutes was attempted and convergence was achieved. The total mass deposited on the surface remained 10 g KBr. The adsorption of the KBr was set to 0.

The input function of the TNT, RDX and HMX were set to saturation values, and were defined as slug type inputs, using the same ramping up/ramping down approach used with the KBr in order to facilitate convergence. The input lengths were modified to achieve outflow concentrations which approximated the actual values observed. For the TNT, this length was found to be 0.8 days, for the RDX it was found to be 0.6 days and for the HMX it was found to be 0.9 days. While this approach was effective in reproducing the observed concentration curves, it does not necessarily represent the reality of the rate controlling step being dissolution. Such a dissolution function for the input flux is not integral to FEFLOW. Reproduction of the dissolution rate by using an automatically variable input function was attempted, with limited success. The dynamics of particle dissolution proved very challenging to encode.

The partitioning coefficients were defined according to the results obtained in Annex 7: 0.123 L/Kg for TNT, 0.091 L/kg for RDX and 0.18 L/kg for HMX, all using linear isotherms. In FEFLOW, output is saved to a .csv file which, depending on the number of nodes in the mesh and the length of time which the model runs, may be many thousands of lines long. Unfortunately, the data is not saved in columns, and must be extracted using a macro before it can be plotted on a graph. The solute breakthrough curves (figures 78-80) shown below do not contain all of the data points. Only a limited number were extracted and imported into Excel to

be plotted. Therefore, the curves shown below are a little bit more angular than the actual output curves. However, they are representative of the actual data.

The KBr curve is almost perfectly symmetrical about its vertical axis (fig. 78). This is to be expected for an inert tracer having no adsorption. However, the TNT and RDX (Figs 79 & 80) curves are skewed, and show long effluent tailings. These are thought to be effects of the adsorption function. The location of the peaks relative to the pore volumes eluted is representative of what was observed in the effluent, which increases confidence in the validity of the K_d values obtained experimentally.

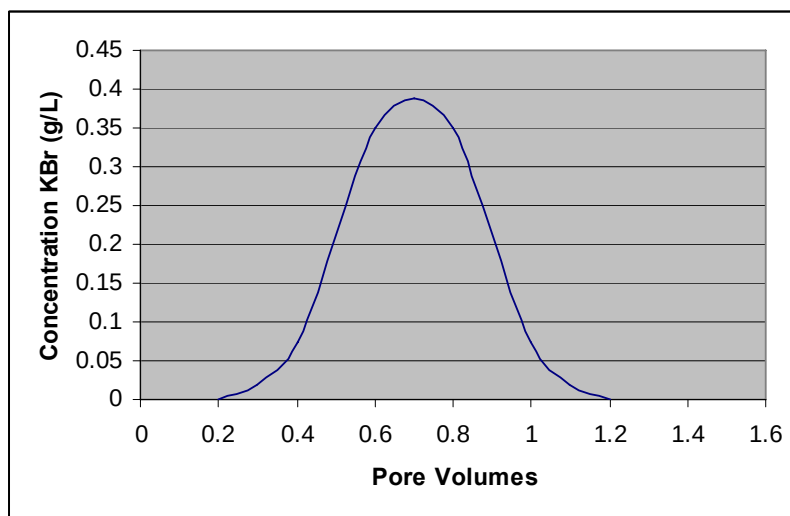


Figure 79. Modeled KBr solute breakthrough curve

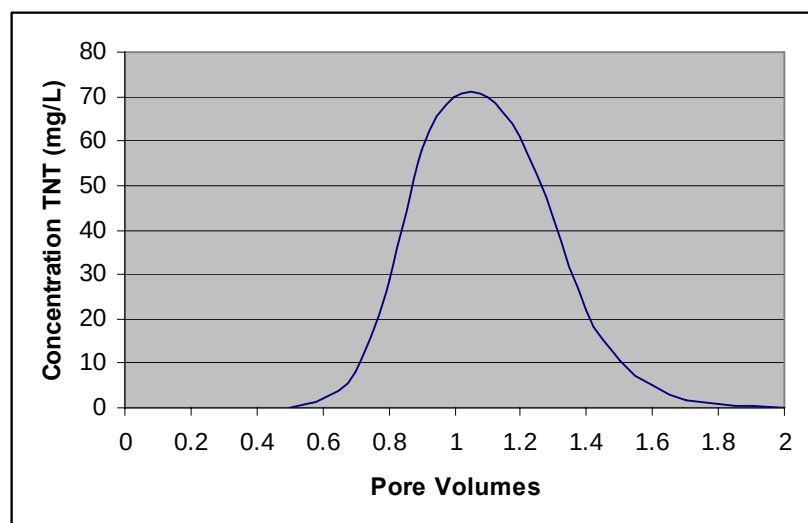


Figure 80. Modeled TNT solute breakthrough curve

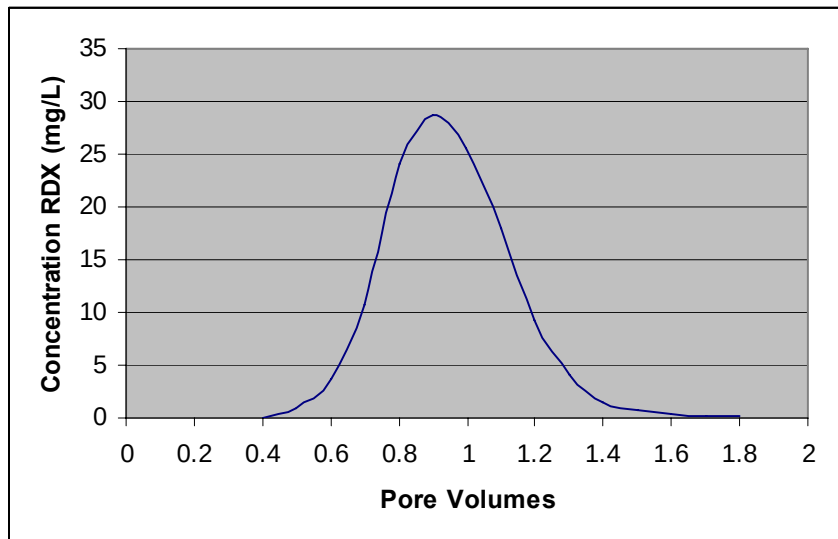


Figure 81. Modeled RDX solute breakthrough curve

The numerical model proved effective in reproducing the moisture content fluctuations and the solute transport curves of the inert tracer and the energetic materials. No attempt was made to reproduce the variations in both flow and concentration observed coming from the 7 outflow nozzles. As has been discussed above, it is felt that these variations are largely due to the columns operating in the pre-Fickian regime. The observed results for flow and concentration were nearly random. These data were difficult, if not impossible, to predict. Modeling such data would have proven extremely challenging, as numerical models assume the applicability of the convection-dispersion equation, which may not apply.

6. CONCLUSIONS AND CONTRIBUTIONS TO THE STATE OF THE ART

This work demonstrated that energetic materials originating from cracked shell munitions are easily transported through unsaturated, sandy soil. It was shown that a single cracked shell and its resulting detonation residue can cause up to 4.9 g of energetic materials to be mobilized through the vadose zone during the first year of exposure. This mobilization happens very quickly when the detonation residue is exposed to significant water infiltration. Pore water concentrations of energetic materials approached saturation levels within two weeks of the start of the experiment. This finding should be considered by range managers when they establish their range standing orders. At present range cleanup occurs at such long intervals that the majority of available energetic contaminants will have already entered solution and become mobile. Ideally, UXO's and detonation residue needs to be removed from ranges prior to being exposed to a single infiltration event. This should take the form of not only conducting a routine level 1 clearance more frequently than the current once per year, but by conducting a level 2 clearance in highly impacted and sensitive areas.

This thesis demonstrated beyond doubt that cracked shell UXO's on the surface, near surface and under water are significant sources of short term energetic materials.

It was hypothesized that the very fine fraction of detonation residue is responsible for this rapid increase in concentration. This hypothesis was subsequently supported by dissolution experiments on different grain size fractions of detonation residue. The very high surface to mass ratio of the finest fraction of detonation residue (<0.125 mm) allows rapid dissolution despite the low solubility of energetic materials. It was also demonstrated that at the beginning of an infiltration event that follows a dry period, the concentration of energetic materials in the pore water temporarily increases. It was proposed that this effect was due to the continued dissolution of energetic materials into the immobile pore water of the unsaturated soil during the dry period. This mass of dissolved energetic material became highly mobile at the beginning of the next infiltration event and was quickly transported through the soil as a slug.

The origin of the energetic materials had a small influence on the cumulative mass that was transported through the soil column, although the biggest influence on the total mass transported was the volume of infiltration. It was shown that energetic materials originating from

detonation residue appeared slightly more mobile than energetic materials originating from pure explosives. This effect was likely caused by the different grain size distribution of the source terms. It was also shown that the solid bulk explosives present in the cracked 81 mm mortar shell had little impact on the total mass of explosive which was mobilized through the unsaturated soil. The primary source of the dissolved energetic species was the fine fractions of the detonation residue scattered around the shells.

The detonation trials that generated the source terms for this thesis demonstrated experimentally the phenomenon of cracked shell unexploded ordnance. It was shown that under the right conditions, unexploded ordnance may be broken open from the shrapnel of other munitions which detonate nearby. For 81 mm mortars, the distance between the unexploded ordnance and the detonating round had to be held between 15 cm and 157 cm to obtain cracked shells. These cracked shell munitions scattered a large amount of pulverized energetic material to the surrounding area. Since many artillery and mortar targets on Canadian Forces bases have been in use for decades, it is highly likely that the conditions necessary to produce cracked shells do occur. Further, it was demonstrated that the primary mechanism of UXO perforation and damage was the fragmentary impact of rounds which detonate nearby, and not the sympathetic low order detonation of UXO's as was previously believed.

In addition, it was shown that neither sand nor water protects a UXO from the fragments of a detonating round. This means that all UXO's that are on the soil surface, which are buried in the near surface or which are resting in shallow water are subject to potential hits from fragments if they are in current live fire impact areas. Any UXO's which are found in these conditions are therefore potential explosive source terms.

The leaching trials performed in this thesis were innovative for several reasons. Most experiments in the literature were performed on bench scale soil columns with a single outflow nozzle. On this type of apparatus, dispersivities are often measured to be on the order of 1 cm. Actual dispersivities in the field have been estimated at up to 100 m, which indicates that there is a need for larger scale unsaturated leaching apparatus such as the one used in this thesis. This research was also the first to use actual cracked shells and detonation residue as source terms, and as such the results obtained during the course of this work are by far the most relevant and applicable to actual field conditions.

Freeze drying of snow samples that contain detonation or energetic materials residue was shown to be highly effective at recovering energetic material residues and detonation residues, with fewer losses than other methods. By freeze drying the samples rather than melting the snow and physically filtering it, contact with liquid water and the consequent dissolution losses were completely eliminated. The recovered residue is representative of the particles released upon detonation not only chemically, but in their physical structure as well.

Another significant finding during the course of this thesis was that the adsorption isotherm for RDX in a solution of Composition B is highly non-linear, and neither Freundlich nor Langmuir isotherms will adequately describe its shape. It was proposed that this behaviour is caused by competitive adsorption between TNT and RDX onto soils with a limited number of adsorption sites such as sand.

7. RECOMMENDATIONS

While cracked munitions produce large quantities of mobile energetic material residue in relation to their total mass, what is unknown is how frequently these cracked shells occur in the field. A study needs to be done relating the dud rates, UXO densities and training practices to determine the statistical likelihood for cracked shells to occur in a given location. Similarly, risk assessment for environmental impact and danger templates on ranges requires reliable historical information about range use to be effective. This information does not currently exist, as detailed range logs do not extend back beyond 1980. It is recommended that historical studies of UXO densities be commissioned on all active and decommissioned ranges. These studies should draw their information from historical data, known dud rates, unit training records and interviews with former commanding officers (CO's), operations officers (OpsO's), officers commanding (OC's) and regimental or company level sergeant majors. The goal is to estimate the number of unexploded ordnance on a given range without having to perform extremely costly remote sensing studies.

Since clean-up of UXO's and cracked shell munitions in impact areas is an extremely costly endeavour, future work should be aimed at attenuating transport of contaminants and preventing further contamination. To this end, a research program must be established to reduce the dud rate of our munitions to 0%. It may be more cost effective for the Forces to establish permanent groundwater monitoring programs on all active bases with a view to conducting pump and treat or in-situ remediation programs similar to the Valcartier TCE initiative, than to clean up all training areas of all possible sources of explosive contaminants. Given the current contamination rate of only 1.4% of all wells, this strategy may be acceptable. Placement of impact areas over large, fast flowing aquifers would also attenuate the concentrations of explosives and prevent those concentrations from reaching levels of concern. In addition, it is recommended that impact areas be rotated on a yearly basis to allow sufficient time to clean up previous impact areas, preferably by conducting a level 2 clearance. To reduce the concentration of UXO'st areas need to be a minimum of 1 square kilometre and the target areas need to be moved for every exercise within that impact area.

Further studies need to be conducted on dissolution rates for various grain sizes of energetic materials. Dissolution appears to be the controlling step in transport through sandy aquifers, so any further data would be welcome.

As well, further leaching studies need to be performed with different types of soil and different explosive source terms, including propellants which are frequently dispersed on ranges during live fire activities. It is recommended that future studies use crushed, pure explosives rather than detonation residue. The pure explosives are easier to obtain in sufficient quantities to have reproducibility between three or more soil columns. Results were close enough in the present study to allow that the pure explosives were an acceptable substitute for the detonation residue. Different military explosives need to be studied, in particular Octol. Octol is the explosive most commonly used in direct fire weapons such as anti-tank rounds. Anti-tank ranges have been among the most heavily contaminated among those ranges which have been characterized.

Since the total volume of infiltration was the primary predictor of total mass of explosives mobilized and transported, it is important that future studies take into account the precipitation and infiltration rates at specific sites. Although the soil on various bases may be similar, weather patterns can be extremely different. This will have a direct impact on the transport results.

8. GLOSSARY

CFB	Canadian Forces Base
Comp B	Composition B, 60% RDX 39% TNT explosive compound
EPA	Environmental Protection Agency (U.S.)
Erfc	Error function
HMX:	High Melting Explosive
HPLC:	High performance liquid chromatography
K_d :	Adsorption coefficient
K_a :	Dielectric constant
K_{sat} :	Saturated hydraulic conductivity
K_{unsat} (or K_{wet})	Unsaturated hydraulic conductivity
KBr	Potassium Bromide
n:	Porosity
NAPL	Non Aqueous Phase Liquid
R_f	Retardation factor
RDX:	Royal Demolition Explosive
SPE:	Solid phase extraction
TDR:	Time domain reflectometry
TNT:	Trinitrotoluene
UXO:	Unexploded ordnance
h	soil water pressure or tension
θ :	Soil water content
ψ	Pressure head
λ	dispersivity
λ_c	capillary length
ρ_s	bulk soil density
ρ_{solid}	soil solid density
2-ADNT	2 amino dinitro toluene, TNT decomposition product
4-ADNT	4 amino dinitro toluene, TNT decomposition product

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ANNEX 1. FLOTATION SEPARATION OF DETONATION RESIDUE FROM SOIL

INTRODUCTION

The detonation residue that was placed on the surface of the columns was characterized prior to the test, including the generation of grain size curves. Generating the grain size curves of the same detonation residue at the end of the tests was desirable in order to determine the percentage dissolution that occurred for each grain size fraction. However, the detonation residue was mixed with loose sand on the column surface, and separating the sand from the detonation residue was problematic. This trial was performed to determine the feasibility of separating the sand from the detonation residue by means of flotation in a dense liquid, by using a known control of 10.00 g crushed composition B in a clean soil matrix.

This method is modified from a flotation process being performed by participants in STANAG 4022 to determine the density difference between reduced sensitivity (RS) RDX and normal RDX.

THEORY

The density of pure composition B is 1.64 g/ml. The solid density of the soil used in the columns is 2.69 g/ml. By using a liquid with a density between these two figures, the Composition B will separate from the soil through flotation. Given the large difference in densities between the composition B and the soil, this method is quite forgiving in terms of the preparation of the standard density solution. Any solution with a density between 1.64 and 2.69 g/mL will work, although solutions with densities falling close to the mid-point (around 2.2 g/mL) will separate the composition B from the soil more quickly. Fluids which having the correct range of densities include several perfluorocarbons, several aqueous salt solutions including cesium chloride (up to 1.9 g/mL), and zinc bromide (up to 2.25 g/mL), and sulphuric acid (up to 1.83 g/mL).

An aqueous solution of ZnBr_2 was selected, because this solution is being used in the STANAG 4022 round robin on RS RDX (reduced-sensitivity RDX) to determine the density of individual grains of RS RDX.

APPARATUS

1. 4L Erlenmeyer flask with vacuum port
2. 15 kg anhydrous ZnBr
3. 500 mL uncontaminated soil
4. 10.00 g ground composition B
5. Ultrasonic bath
6. Large filter funnel with filter paper and rubber gasket
7. 2 L Erlenmeyer flask with vacuum port
8. Vacuum pump

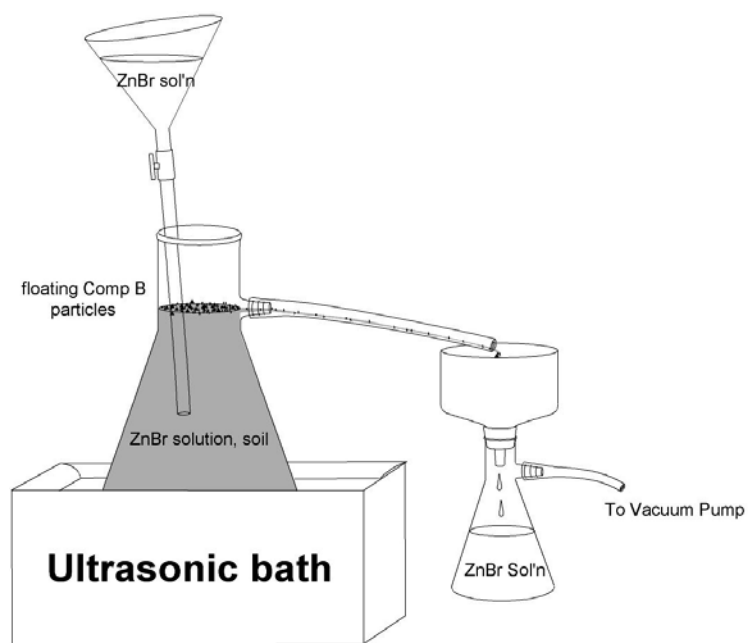


Figure 1. Experimental Setup

METHOD

1. Mix 11 kg. of the ZnBr_2 in 5 L of tapwater. Allow time to fully dissolve.
2. Thoroughly mix 10.00g composition B with 500 mL uncontaminated soil.
3. Assemble vacuum filter apparatus: filter funnel, filter paper, 2L Erlenmeyer with rubber gasket, and vacuum pump
4. Place 2 L of ZnBr_2 solution in the 4 L Erlenmeyer
5. Place 4L Erlenmeyer in ultrasonic bath, turn on bath
6. begin stirring ZnBr_2 solution, slowly add contaminated soil. Soil must stay in suspension.
7. When all soil is added, stop stirring. Allow the soil to settle to the bottom and detonation residue to rise to surface (approx. 30 minutes).
8. Remove 4L Erlenmeyer from ultrasonic bath, place vacuum port over the filter funnel of the vacuum filter apparatus
9. Slowly add more Zn Br_2 solution to 4 L Erlenmeyer until fluid level reaches vacuum port
10. Allow solution to re-stabilize (1-2 min).
11. Add 1 mL ZnBr_2 solution at a time, allow fluid to overflow through vacuum port onto filter paper. Floating detonation residue and composition B will be recovered on surface of filter paper.

RESULTS AND DISCUSSION

Recovery of the crushed composition B was 80%. 7.90 g of composition B was recovered in the first trial, and 8.11 g composition B was recovered in the second trial. For comparison, reported losses during the RS-RDX trials were 96%-99%.

The higher losses during the soil-Comp B separation as compared to the RS-RDX separation may be due to one of three different mechanisms. The first is greater losses due to dissolution. However, this appears unlikely. The procedure used during the RS RDX trials required the RDX to remain in the ZnBr_2 solution for 24 hours at 25° C. The analytical recoveries indicate that dissolution of RDX is not a serious problem in the ZnBr_s solution. TNT, which like RDX is a ring shaped organic molecule with low polarity should have similar solubility characteristics.

The second possible source of losses is incomplete separation of the Comp B in the ZnBr_2 solution. The RS-RDX procedure had the RDX separate out for a full 24 hours. In the soil-Composition B trials, that time was reduced to 30-60 minutes in order to minimize losses due to solubility. However, this may have had the effect of preventing the fine Comp B particles from reaching the surface of the solution. The ZnBr_2 solution has the viscosity of cooking oil. The force of friction due to viscosity on a particle is related to its surface area, while the force of buoyancy is related to its volume. Smaller particles have a higher surface area to volume ratio, and therefore the force of buoyancy would be partially counteracted by the force of fluid friction, to a greater degree than larger particles. This would increase the time required for the finer fractions of detonation residue to float to the surface.

The third source of potential losses was during filtration. The RS-RDX flotation trials calculated recoveries based on the net gain in mass of the fritted glass separating funnels. However, the entire purpose of the soil-Comp B separation was to determine the final grain size distribution of the Comp B. In other words, the Comp B had to be removed from the separating funnel and graded. The Comp B showed a tendency to cling to the separating funnel once it was dried in the oven. There is no question that finer particles were lost preferentially during this step. The final recovered mass of the Comp B was only measured after the Comp B had been removed from the separating funnels.

While exact figures are not available, it seems likely that the greatest source of loss was during the flotation, with the finer fractions of Comp B unable to overcome the fluid friction caused by viscosity. Recovery could be improved by increasing the time for equilibrium from 30 min to 24 hours as in the RS-RDX separation. Use of a centrifuge to speed separation is also possible.

Part of the recovered mass was organic contaminants. Performing this experiment in soil with a high fraction of organic matter would cause significant difficulties, as the organic contaminants are of approximately the same density as the composition B. These organic species are mixed in with the composition B, which could cause some skewing of the results.

The initial grain size curve of the Composition B is shown in Figure 1. The grain size curves of the recovered Composition B are shown in Figure 2 and 3. Although the curves are similar, indicating that the grain size distribution is not significantly changed during flotation extraction, it does appear that any losses that do occur tend towards the finer grain sizes. This may be caused by either losses during flotation itself, or during the filtration of the Comp B suspended in the ZnBr_2 solution as discussed above.

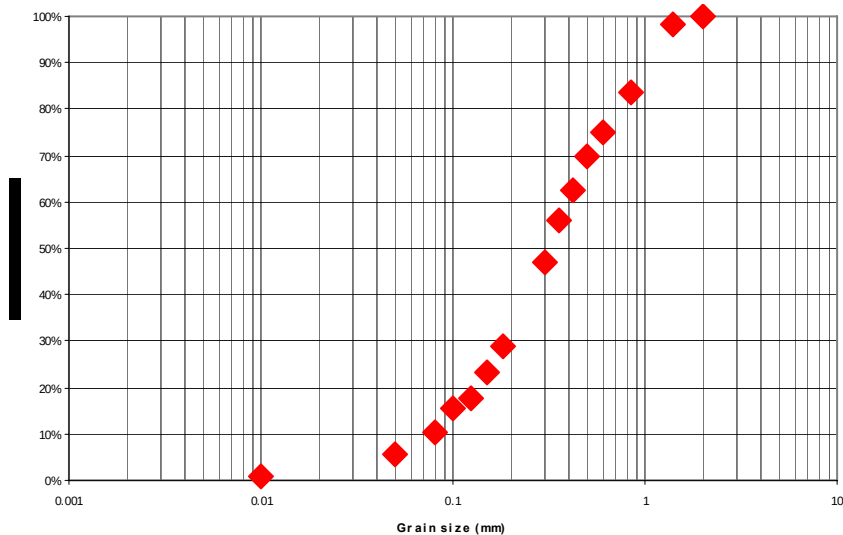


Figure 1. Initial Comp B grain size distribution

The volume of material which must be separated was a major difference between the RS-RDX separation procedure and the Comp B-soil separation procedure. 5 g of RS-RDX was separated at a time, whereas up to 5 kg of each soil/Comp B mixture had to be separated. While the lab procedure for the RS-RDX could in theory be followed by separating the soil/Comp B mixture into 1000 separate samples and applying the flotation method to each individually, this would require a great deal of either manpower or of time. While the use of the 4 L Erlenmeyer flask was acceptable, a very large separating funnel would be preferable.

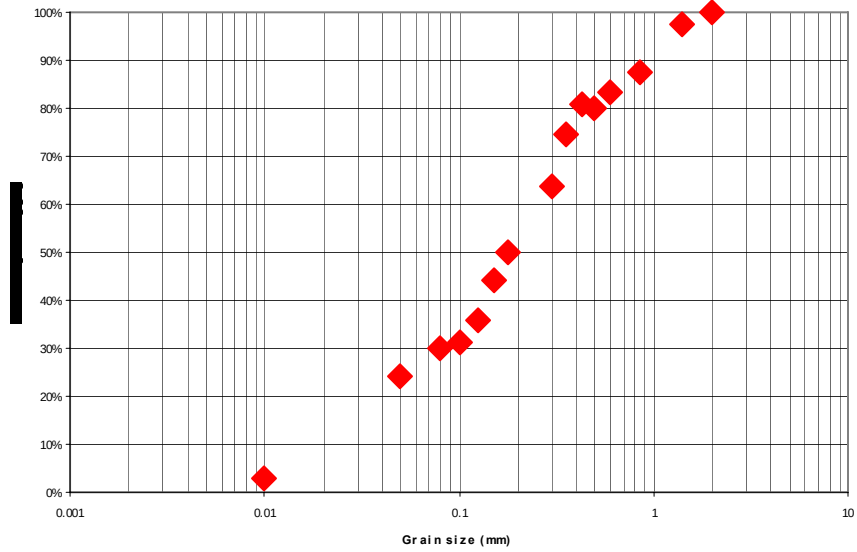


Figure 2. Sample A grain size distribution following flotation separation

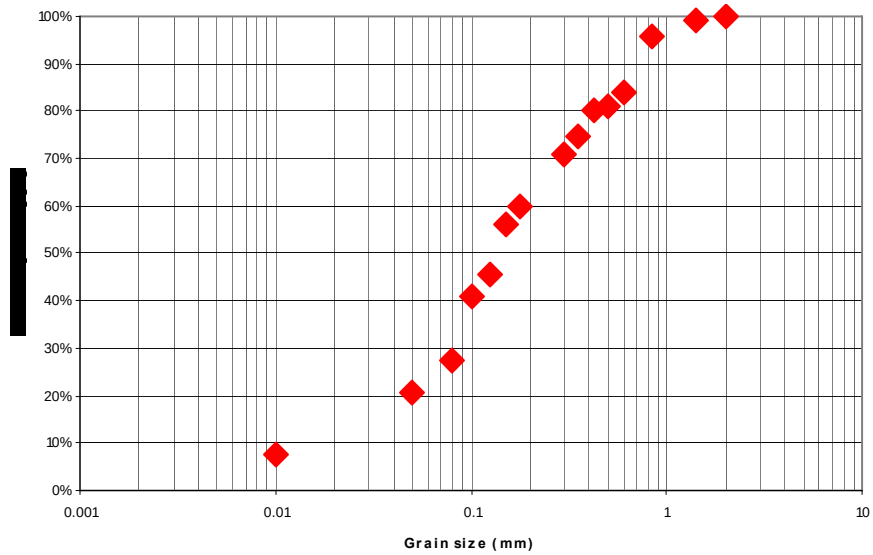


Figure 3. Sample B grain size distribution following flotation separation

CONCLUSION

The flotation separation of Composition B from soil by using an aqueous solution of ZnBr_2 resulted in recoveries of 79.0 % to 81.1% of the initial mass of Composition B. Losses were determined to be largely due to two factors: insufficient time to equilibrium and losses due to the cohesion of particles to the filtration funnel. Data from similar trials performed on pure RDX crystals indicates that losses due to dissolution are very small – no more than 4%.

Improvements to the method for future trials include the use of a large separation funnel instead of an Erlenmeyer flask, and increasing the time of separation.

ANNEX 2. HYDRAULIC CONDUCTIVITY MEASUREMENTS

ABSTRACT

Hydraulic conductivity measurements were taken with a Guelph permeameter fitted with a disc tension infiltrometer. The multiple tension method (Wilson, Everett & Cullen, 1995 p. 197) was used to characterize the soil in all six columns. Steady state conditions were achieved in eleven trials over four columns. Columns E and F did not produce sufficient steady-state data to calculate saturated hydraulic conductivity. The average value of the saturated hydraulic conductivity was 0.017 ± 0.015 cm/s, which is in agreement with published values of saturated hydraulic conductivity for sands.

APPARATUS

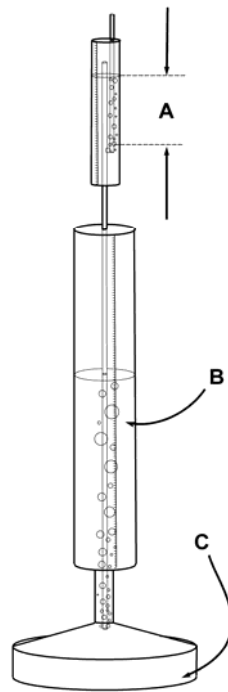


**Figure 1. Guelph permeameter. A: Tension measurement B: water reservoir
C: porous plate**

THEORY

The design and use of the disc tension infiltrometer has been described by Perroux and White (1988). The goal when using a tension infiltrometer is to measure the rate of flow of water (Q) from the instrument into the soil at a given matric potential or tension (h). Several hours of continuous infiltration may be required before steady state conditions are achieved. Steady state conditions are achieved when the flow per unit area Q does not change.

Steady state Q is measured at several different tensions. Once this data is collected, there are two calculations required to calculate the saturated hydraulic conductivity K_{sat} . Once K_{sat} is known, the unsaturated hydraulic conductivities K_{unsat} may be calculated for different moisture contents.

- 1) Calculate the macropore capillary length (λ_c) (units of length)

$$\lambda_c = \frac{|h_2 - h_1|}{|\ln(Q_2 / Q_1)|} \quad (\text{Eq.1})$$

where h_1 & h_2 (units of length) are the two tensions at which the rates of flow Q_1 & Q_2 (units of length/time) were measured

- 2) Calculate the saturated hydraulic conductivity K_{sat}

$$K_{sat} = \frac{Q}{\left(\exp \left[\frac{h}{\lambda_c} \right] \right) \left(1 + \frac{4\lambda_c}{\pi r_o} \right)} \quad (\text{Eq.2})$$

where Q is the flow rate at a given h (either of the values used in step 1 may be used)
and r_o is the disc radius of the infiltrometer

3) Calculate unsaturated hydraulic conductivities K_{wet}

$$K_{wet} = K_{sat} \exp\left(\frac{h}{\lambda_c}\right) \quad (\text{Eq.3})$$

where h is the tension at which the hydraulic conductivity is to be calculated

RESULTS AND DISCUSSION

Steady state flow conditions were not achieved for all tensiometer tests. Graphs of those tests which did reach steady state conditions are shown below. In the case of Column F, only one test achieved steady state conditions, which is insufficient to calculate K_{sat} using the multiple tensions method.

The usable data collected from the six columns is shown in Table 1. From this data, the K_{sat} values were calculated – these results are provided in Table 2.

Column	Tensions Tested (h) cm	Steady State Achieved	Steady State Flow Rate (Q), cm/s
A	-1.3 cm	No	-
	-4.8 cm	No	-
	-5.6	No	-
	-8.3	No	-
	-10 cm	No	-
	-12.0	No	-
	-12.6 cm	Yes	0.002 cm/s
	-18.2 cm	Yes	0.000187 cm/s
B	-1 cm	No	-
	-4.7 cm	No	-
	-10 cm	Yes	0.0058 cm/s
	-15 cm	No	-
	-20 cm	Yes	0.0011 cm/s
	-23.7 cm	Yes	0.00056 cm/s
C	-2.5 cm	No	-
	-5 cm	No	-
	-7.7 cm	Yes	0.0031 cm/s
	-9.5 cm	No	-
	-12.8 cm	Yes	0.0013 cm/s
	-18.3	Yes	0.00023 cm/s
D	-2 cm	Yes	0.016 cm/s
	-5 cm	No	-
	-10 cm	No	-
	-15.1 cm	No	-
	-20.2 cm	Yes	0.000304 cm/s
	-24.8 cm	Yes	0.000136 cm/s
E	-5.0 cm	No	-
	9.7 cm	No	-
	-14.4 cm	No	-
	-17.8 cm	No	-
F	-2.0 cm	No	-
	-5.0 cm	No	-
	-10.0 cm	No	-
	-15.0 cm	No	-
	-20.0 cm	No	-
	-25.0 cm	Yes	0.000234 cm/s

Table 1. Tension infiltrometer source data

Column A

Steady state flow was achieved at two different flow rates.

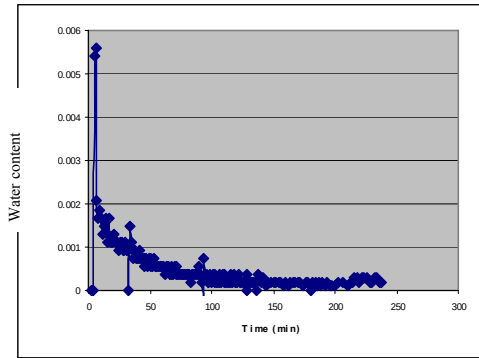


Fig.1 $h = -18.2$ cm

$Q = 0.000187$ cm/s

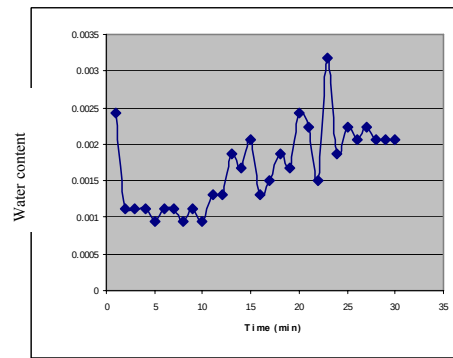


Fig. 2. $h = -12.6$ cm

$Q = 0.0020$ cm/s

Column B

Steady state flow was achieved at three different tensions:

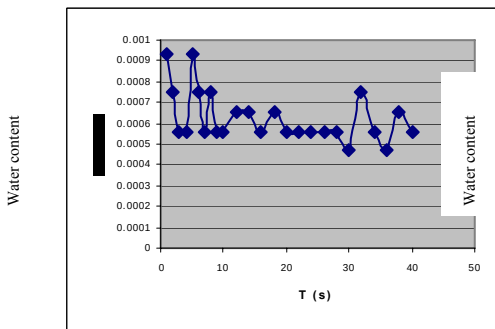


Fig. 3. $h_1 = -23.7$ cm

$Q_1 = 0.00056$ cm/s

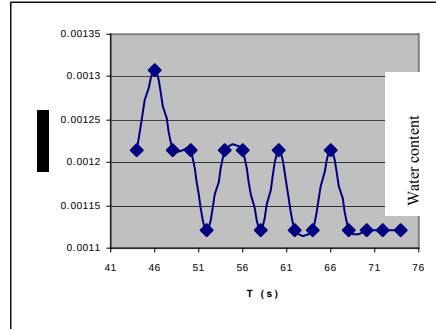


Fig. 4. $h_2 = -20.0$ cm

$Q_2 = 0.0011$ cm/s

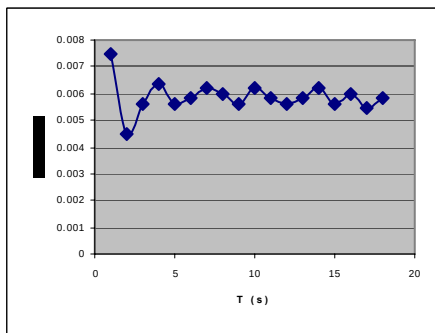


Fig.5 $h_3 = -10.0$ cm

$Q_3 = 0.0058$ cm/s

Column C

Steady state flow was achieved at three different tensions:

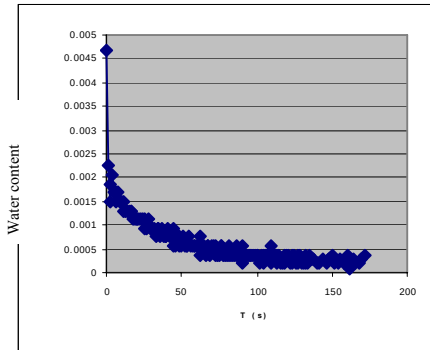


Fig. 6. $h = -18.3$ cm

$Q = 0.00023$ cm/s

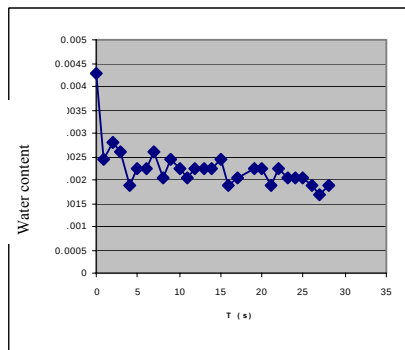


Fig. 7. $h = -12.8$ cm

$Q = 0.0013$ cm/s

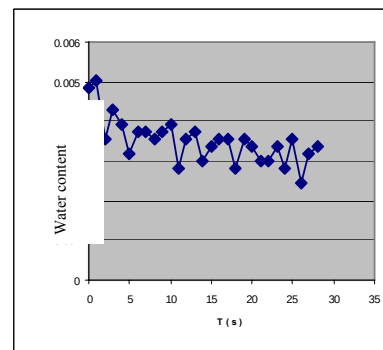


Fig. 8. $h = -7.7$ cm

$Q = 0.0031$ cm/s

Column D

Steady state flow was achieved at three different tensions:

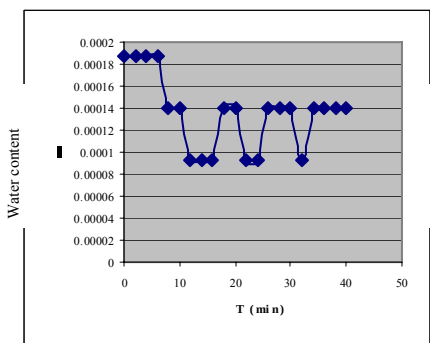


Fig. 9. $h = -24.8$ cm

$Q = 0.000136$ cm/s

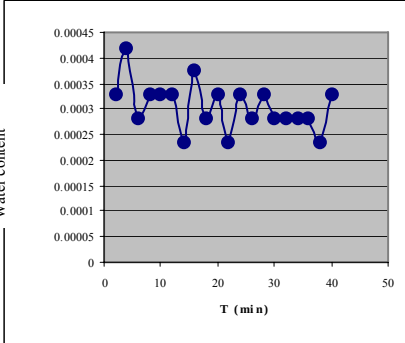


Fig. 10 $h = -20.2$ cm

$Q = 0.000304$ cm/s

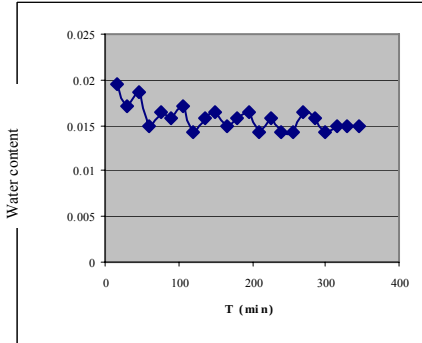


Fig. 11. $h = -2.0$ cm

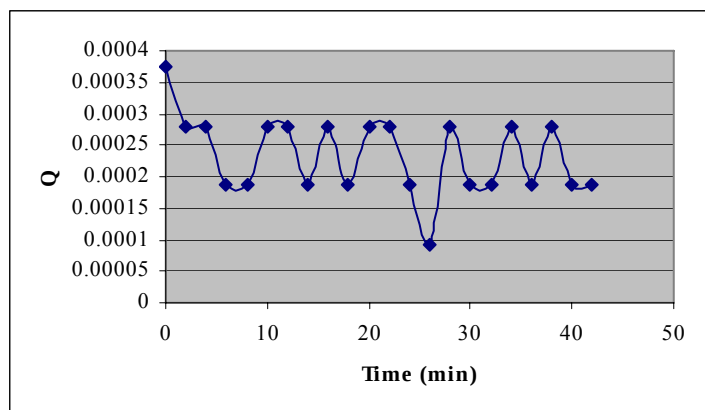
$Q = 0.016$ cm/s

Column E

No steady state flow values were achieved in column E

Column F

Only one steady state flow was achieved in Column F, which is insufficient to calculate K_{sat}



$$h = -0.000234 \text{ cm}$$

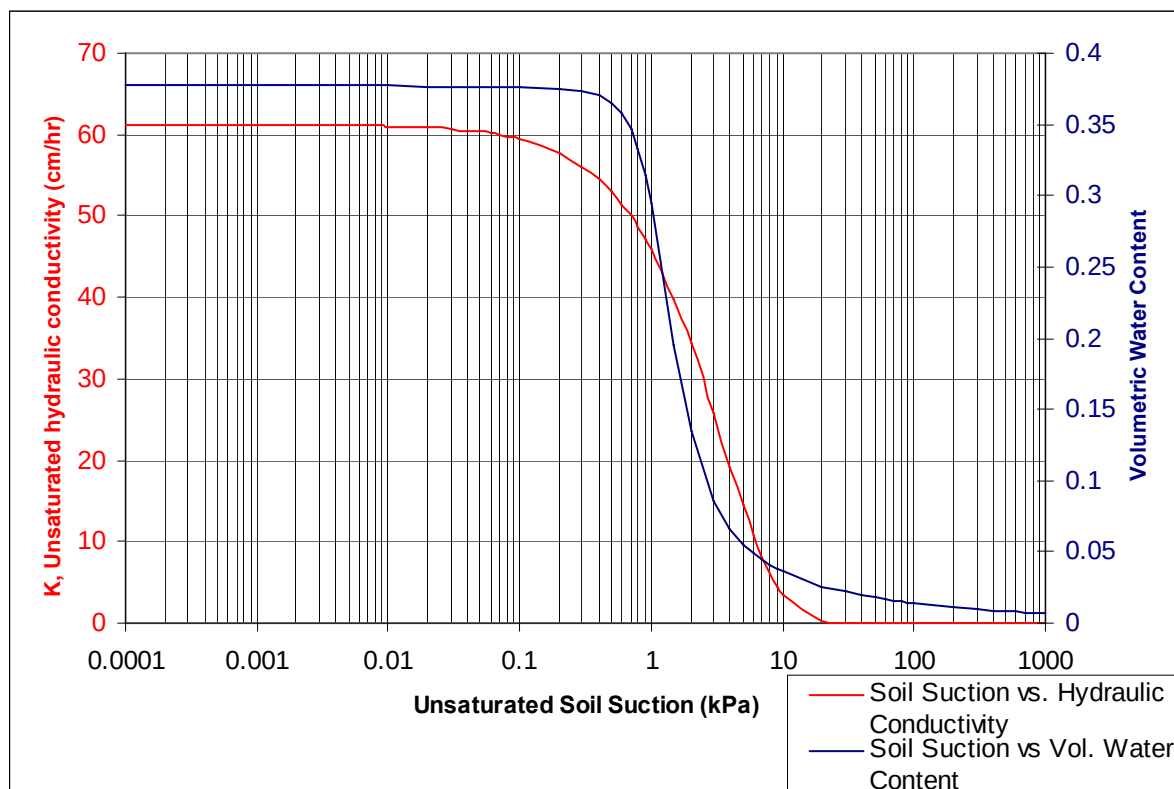
Column	Tensions Used in calculations (cm)	K_{sat} Saturated Hydraulic Conductivity (cm/s)
A	-18.2, -12.6	0.025
B	-23.7, -20.0	0.025
B	-23.7, -10.0	0.018
B	-20.0, -10.0	0.017
C	-18.3, -12.8	0.032
C	-12.8, -7.7	0.0066
C	-18.3, -7.7	0.011
D	-24.8, -20.2	0.006
D	-20.2, -2.0	0.015
D	-24.8, -2.0	0.015

Table 2. Calculated saturated hydraulic conductivities

The average K_{sat} value from Table 2 is 0.017 cm/s (85 cm/hr), which falls in the middle of the range given by Freeze and Cherry (1979, p.29), 1.0 cm/s to 0.0001 cm/s for clean sand. Given that hydraulic conductivity is one of the physical parameters with the largest ranges (thirteen orders of magnitude, from 10^2 cm/s for gravel to 10^{-11} cm/s for shale and unfractured igneous rock), the

consistency of our results for K_{sat} , which ranged from a low of 0.006 cm/s to 0.032 cm/s is very satisfactory. As well, the results are reproducible from one column to another, which provides confidence that similar results would be found in the two columns – E and F – which did not achieve sufficient steady-state flow results to calculate the hydraulic conductivities.

Once K_{sat} has been calculated, the unsaturated hydraulic conductivity of the soil K_{unsat} (or K_{wet}) may be calculated in turn, using Equation 3. This value varies according to the saturation of the soil, increasing with increasing wetness until eventually it equals K_{sat} when the soil reaches saturation. Table 3 provides several calculated values for K_{unsat} , using the values for $K_{sat} = 0.017$ cm/s and the average calculated macropore capillary length (λ_c) of 4.77 cm. The corresponding vol. water contents shown in the figure below were obtained from the soil-water characteristic curve (SWCC), discussed in section 4.2.2.



CONCLUSION

Using the method of multiple tensions and data obtained from a Guelph permeameter, the saturated hydraulic conductivity of the sand used for the soil columns was found to be 0.017 ± 0.015 cm/s. This value is in agreement with literature values for the hydraulic conductivity of sand, and the error associated with this value is very low considering the very large range of values which hydraulic conductivities can have. Corresponding unsaturated conductivities were calculated for all values of matric potential.

ANNEX 3. POROSITY MEASUREMENTS

ABSTRACT

Two methods were used to determine the porosity of the unsaturated columns. Method 1, a lab-based saturation test, is less representative of the column as a whole since it is only performed on a small soil sample. Method 2 is more detailed and is the more reliable of the two methods. There was excellent agreement between the tests, with porosities for all columns using both methods found in the range of 0.370 – 0.388.

METHOD 1

Theory, Method 1

The porosity of the soil can be measured directly by obtaining a small, undisturbed quantity of soil of known volume, and saturating it fully with water. Weighing the saturated sample, then drying the soil completely in an oven and re-weighing the dry soil sample will give the mass of water which occupied the pores at saturation. This will then allow calculation of the volume of the water sample and thus the pore volume given the density of water is 1 g/mL.

The total porosity (n) does not necessarily equal the effective porosity (n_{eff}), which can skew the results in a test such as this one. In some soils, there may be pore spaces or voids which are not in communication with the rest of the pores. In other words, they are isolated and cannot be filled with water. In these cases, the technique of saturating the soil will underestimate the pore volume because the isolated pores will not fill with water. However, in sandy soils such as are being used in the columns, this rarely occurs unless voids exist in the sand grains themselves. In sand, total porosity can be assumed to be equal to the effective porosity.

The equations used in the porosity calculations are:

$$V_{\text{total}} = 100 \text{ mL}$$

$$\rho_{\text{water}} = 1 \text{ mg/mL}$$

$$m_{\text{saturated sample}} - m_{\text{dry sample}} = m_{\text{water}}$$

$$m_{\text{water}} / \rho_{\text{water}} = V_{\text{water}}$$

$$V_{\text{water}} = V_{\text{void}}$$

$$n = V_{\text{void}} / V_{\text{total}}$$

Apparatus, Method 1

1. straightedge
2. flexible lab tubing (1 m approximately)
3. hollow brass nipple with same thread as the pressure valve on the espresso maker
4. straightedge
5. Lab oven
6. Espresso maker (stovetop)

The espresso maker must be modified by removing the pressure valve and replacing it with a brass nipple which will accept any type of flexible tubing. This tubing must then in turn be attached to a source of running water under pressure. A common faucet will do.

Experimental procedure, Method 1

- 1) Remove a sample of undisturbed soil from the column (V_{total}) by turning the coffee filter funnel from the espresso maker upside down and pressing it into the surface of the soil.
- 2) Remove funnel from soil (with sand sample inside it).
 - 1) Smooth surface of the soil sample down to the top edge of coffee filter with straightedge.
 - 2) Place coffee filter with soil sample in espresso maker, screw espresso maker tightly closed.
- 3) Attach flexible tubing to water faucet, turn on water very slowly.
- 4) Watch the outflow of the espresso maker. When the water runs out smoothly without any entrained air bubbles, the soil sample is saturated.
- 5) Remove soil sample from espresso maker, weigh sample.

- 6) Place sample in a heat-resistant container, place in oven at 60 degrees Centigrade for 24 hours.
- 7) Re-weigh dry soil sample.
- 8) Calculate mass of evaporated water.
- 9) Calculate volume of evaporated water = pore volume.

Results, method 1

Six samples were taken, one from each column. Measured results are provided in Table 1.

Table 1. Measured values from method 1.

Column	m_{saturated sample} (g)	m_{dry sample} (g)	m_{water} (g)
A	223.25	186.29	36.96
B	224.57	185.79	38.78
C	225.91	187.32	38.59
D	224.12	186.62	37.50
E	223.89	185.21	38.68
F	225.43	186.65	38.78

METHOD 2

Theory, method 2

If the total mass of the sand loaded into the columns is known exactly, and the moisture content of the soil was recorded as it was being loaded into the column, then the dry weight of the sand in the columns may be calculated. The total volume of the soil columns is known. If the solid density of the sand grains is known, then the volume occupied by the sand grains may also be calculated. The pore volume will be the solid volume of the sand grains subtracted from the total volume of the soil columns.

Experimental procedure, method 2

1. Load sand into columns in 7.600 kg lifts.
2. Record exact mass of each lift, and the number of lifts.

3. Take small soil samples periodically and store them in sealed Mason jars.
4. Determine moisture content of soil by method of lost mass. Weigh soil samples, dry them, the re-weigh them to determine moisture content.
5. Calculate total water content of each column in kg.
6. Calculate dry soil mass in each column.
7. Calculate dry soil solid volume.
8. Calculate total volume of soil column.
9. Subtract soil solid volume from total column volume.

Results, method 2

This method for calculating the porosity is more rigorous than Method 1 because it looks at the entire soil column, rather than one small representative sample. The measured parameters are given in Table 2. Tables 3 and 4 provide successive calculations which lead to the porosities given in Table 5.

Table 2. Physical measurements of soil columns

Column	H Column (cm)	D Column (cm)	Vol Column (L)	M colonne acier (+0.6 kg TDRs)	M au 3e TDR	M sable 3e TDR	M totale (kg)	M sable totale
A	61,1	59,6	170,3740262	189,3			481,6	292,3
B	62,2	59,6	173,4413163	202,6	465,1	262,5	499,8	297,2
C	61,1	59,6	170,3740262	203,2	447,6	244,4	492,4	289,2
D	62,2	59,6	173,4413163	196,3	450,8	254,5	496,4	300,1
E	63,2	59,6	176,2297619	200			499,3	299,3
F	61,1	59,6	170,3740262	197,8	419,6	221,8	491,8	294

Table 3. Water content of samples (method 2)

Column	Echantillon	Mass initiale (g)	Mass sec (g)	Mass eau (g)	Mass pot (g)
		sable, eau, pot	sable, pot		
A	Baril 10	790,9	789,6	1,3	235,99
A	Baril 11	653,6	645,8	7,8	235,26
A	Baril 12	730,5	710,7	19,8	235,12
A	Baril 13	738,3	728,6	9,7	235,32
A	Baril 14	436	432,88	3,12	164,92
B	Baril 1	411,14	405,98	5,16	163,56
B	Baril 2	453,18	433,25	19,93	164,93
B	Baril 3	414,92	403,9	11,02	165,25
B	Baril 15	434,91	432,86	2,05	164,92
C	Baril 3	414,92	403,9	11,02	165,25
C	Baril 4	769,7	754,2	15,5	236,75
C	Baril 5	782,7	767,5	15,2	233,93
C	Baril 14	436	432,88	3,12	164,92
D	Baril 8	728,7	704,2	24,5	236,89
D	Baril 9	668,2	645,8	22,4	237,5
D	Baril 14	436	432,88	3,12	164,92
E	Baril 9	668,2	645,8	22,4	237,5
E	Baril 10	790,9	789,6	1,3	235,99
E	Baril 14	436	432,88	3,12	164,92
F	Baril 6	668,8	656,8	12	236,7
F	Baril 7	700,5	690,6	9,9	236,51
F	Baril 14	436	432,88	3,12	164,92

Table 4. Calculation of dry sand mass in soil columns (method 2)

	Mass sec (g)	Mass initiale	% eau	Number of	% of column	M of column	M of column
Column	sable	sable eau	Meau / Meau sable	layers sand		(kg)	dry sand (kg)
A	553,61	554,91	0,0023	38,5	0,0769	22,4846	22,4319
A	410,54	418,34	0,0186	38,5	0,2564	74,9487	73,5513
A	475,58	495,38	0,0400	38,5	0,3077	89,9385	86,3437
A	493,28	502,98	0,0193	38,5	0,1795	52,4641	51,4523
A	267,96	271,08	0,0115	38,5	0,1795	52,4641	51,8603
B	242,42	247,58	0,0208	46	0,4130	122,7565	120,1981
B	268,32	288,25	0,0691	46	0,1739	51,6870	48,1132
B	238,65	249,67	0,0441	46	0,2826	83,9913	80,2841
B	267,94	269,99	0,0076	46	0,1304	38,7652	38,4709
C	238,65	249,67	0,0441	42,4	0,1887	54,5660	52,1576
C	517,45	532,95	0,0291	42,4	0,5189	150,0566	145,6924
C	533,57	548,77	0,0277	42,4	0,1651	47,7453	46,4228
C	267,96	271,08	0,0115	42,4	0,1274	36,8321	36,4082
D	467,31	491,81	0,0498	39	0,7436	223,1513	212,0348
D	408,3	430,7	0,0520	39	0,1026	30,7795	29,1787
D	267,96	271,08	0,0115	39	0,1538	46,1692	45,6378
E	408,3	430,7	0,0520	39	0,4103	122,7897	116,4037
E	553,61	554,91	0,0023	39	0,4103	122,7897	122,5021
E	267,96	271,08	0,0115	39	0,1795	53,7205	53,1022
F	420,1	432,1	0,0278	40	0,6512	191,4419	186,1253
F	454,09	463,99	0,0213	40	0,2326	68,3721	66,9133
F	267,96	271,08	0,0115	40	0,1163	34,1860	33,7926

Table 5 Calculated porosities of columns (method 2)

Column	Total mass	Solid density	Solid volume	Bulk Volume	Porosity
	dry sand (kg)	of sand (kg /L)	of sand (L)	of sand (L)	
A	285,6395	2,6900	106,1857	170,3740	0,377
B	287,0663	2,6900	106,7161	173,4413	0,385
C	280,6810	2,6900	104,3424	170,3740	0,388
D	286,8513	2,6900	106,6362	173,4413	0,385
E	292,0079	2,6900	108,5531	176,2298	0,384
F	286,8311	2,6900	106,6287	170,3740	0,374

DISCUSSION

The porosities measured using Methods 1 and 2 showed excellent agreement. Table 6 summarizes the results from the two methods. The porosities were found to vary overall between 0.370 and 0.388, which is a reasonable result for sandy soil. The largest discrepancy between the porosities measured by methods 1 and 2 were found in Column F, with Method 1 showing a porosity of 0.388 and Method 2 showing a porosity of 0.374. This difference of 0.014 represents an error of $\pm 3.7\%$, which is very satisfactory. Only one other column, Column A, had an error above 1%. These results provide significant confidence in their accuracy. However, as was previously pointed out Method 2 provides more reliable results, since it takes into account the properties of the entire soil column rather than a

small representative sample. Therefore, the results of Method 2 will be preferred over those of Method 1. The variation between columns using only Method 2 was between 0.374 and 0.388.

Table 6. Porosity results comparison

Column	Porosity Method 1	Porosity Method 2	Pore Volume (L)
A	0.370	0.377	64.23
B	0.388	0.385	66.77
C	0.386	0.388	66.10
D	0.375	0.385	66.77
E	0.387	0.384	67.67
F	0.388	0.374	63.71

CONCLUSION

The porosities in the columns were found to be between 0.374 and 0.388. There was very good agreement between the porosities found with two different methods of measurement, providing considerable confidence in the results. Error between the two methods was found to be a maximum of 3.7%

ANNEX 4. SOIL SOLID DENSITY MEASUREMENT:

ARCHIMEDES PRINCIPLE

INTRODUCTION

Measuring soil solid density is necessary to accurately measure and calculate the soil porosity. This value is the density the soil minerals would have if all pores were removed and only the solid mineral remained. Solid density can be measured using Archimedes' principle. Given its pertinence to soil science, this famous story is worth repeating.

Legend has it that around 200 BC, King Heiro of Syracuse suspected that a pure gold crown he had purchased was actually alloyed with silver. However, he had no way of determining if this was true. He asked his friend Archimedes to consider the matter. Archimedes happened to go to the bath, and on getting into a tub observed that the more his body sank into it the more water ran out over the tub. As this pointed out the way to explain the case in question, without a moments delay and transported with joy, he jumped out of the tub and rushed home naked, crying in a loud voice that he had found what he was seeking; for as he ran he shouted repeatedly in Greek, "Eureka, Eureka."

Taking this as the beginning of his discovery, it is said that he made two masses of the same weight as the crown, one of gold and the other of silver. After making them, he filled a large vessel with water to the very brim and dropped the mass of silver into it. As much water ran out as was equal in bulk to that of the silver sunk in the vessel. Then, taking out the mass, he poured back the lost quantity of water, using a pint measure, until it was level with the brim as it had been before. Thus he found the weight of silver corresponding to a definite quantity of water.

After this experiment, he likewise dropped the mass of gold into the full vessel and, on taking it out and measuring as before, found that not so much water was lost, but a smaller quantity: namely, as much less as a mass of gold lacks in bulk compared to a mass of silver of the same weight. Finally, filling the vessel again and dropping the crown itself into the same quantity of water, he found that more water ran over for the crown than for the mass of gold of the same weight. Hence, reasoning from the fact that more water was lost in the case of the crown than in that of the mass, he detected the mixing of silver with the gold and made the theft of the contractor perfectly clear.

In exactly the same way, the solid density of a soil can be measured by weighing a quantity of dry soil, saturating it with water and weighing it again to determine the mass of water added. The

density of water being 1 kg/L, the volume of this water is easily calculated, and this represents the volume of pore space. Once the volume of the saturated soil is measured, the solid density is easily calculated.

While this process is easy in theory, in practice there are two technical challenges that are fairly difficult to overcome. The first is that any soil which starts out dry will have entrapped pockets of air in the pores when it is saturated. These very small trapped air bubbles will prevent the water from fully saturating the soil, and will therefore underestimate the porosity and the density. The second challenge is determining exactly when the soil is at the point of saturation. To overcome these two challenges, the following methodology was used.

APPARATUS

1. Electronic scale capable of measuring 0.01 g.
2. 4 L Erlenmeyer Flask with vacuum port
3. Vacuum pump
4. Ultrasonic bath
5. Drying oven
6. Kimwipes
7. 1 L graduated cylinder

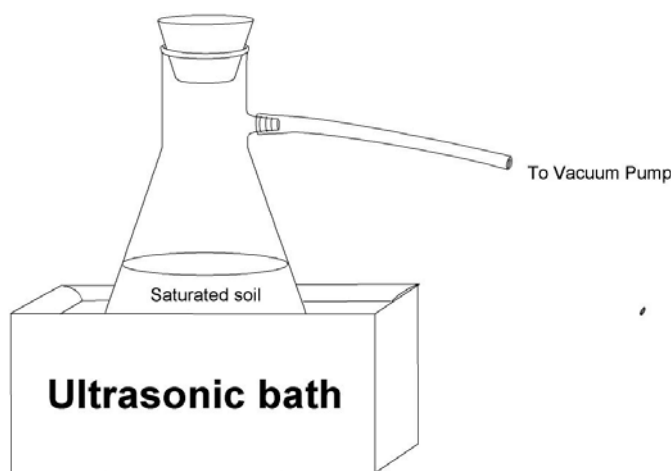


Figure 1. Density measurement apparatus

SOLID DENSITY MEASUREMENT METHODOLOGY

1. Use uncontaminated soil which is identical to that used in the columns.
2. Spread soil thinly on a metal sheet.
3. Dry soil in oven at 60° C for 24 hours.
4. Weigh empty 4 L Erlenmeyer flask to +/- 0.01 g.
5. Pour 300.00 mL. dry soil into 4 L Erlenmeyer flask.
6. Add distilled water until approximately 0.5 cm of free water is above the surface of the soil.
7. Stopper Erlenmeyer flask, attach to vacuum pump and place in ultrasonic bath.
8. Reduce pressure in Erlenmeyer flask to 600 mm mercury vacuum. Turn on ultrasonic bath.
9. Allow to sit for 8 hours.
10. Remove Erlenmeyer flask from ultrasonic bath, turn off vacuum.
11. Use Kimwipes to absorb remaining free water above surface of the sand.
12. Pour saturated soil into graduated cylinder, measure total volume (V_{total}).

Calculations

$$M_{\text{water}} (\text{g}) = V_{\text{water}} (\text{mL}) \quad (\text{Eq. 1})$$

$$V_{\text{water}} (\text{mL}) = V_{\text{pores}} (\text{mL}) \quad (\text{Eq. 2})$$

$$V_{\text{total}} (\text{mL}) = V_{\text{solid}} (\text{mL}) + V_{\text{pores}} (\text{mL}) \quad (\text{Eq. 3})$$

$$\rightarrow V_{\text{solid}} (\text{mL}) = V_{\text{total}} (\text{mL}) - V_{\text{pores}} (\text{mL}) \quad (\text{Eq. 3a})$$

$$\rho_{\text{solid}} (\text{g/mL}) = M_{\text{solid}} / V_{\text{solid}} \quad (\text{Eq. 4})$$

RESULTS

This experiment was repeated four times with different initial volumes of sand. The results are summarized in Table 1.

Table 1. Experimental results of density tests

V_{total}	M_{solid}	V_{pores}	V_{solid}	ρ_{solid}
300 mL	512.3 g	109.7 mL	190.3 mL	2.69 g/mL
400 mL	683.4 g	146.4 mL	253.6 mL	2.69 g/mL
500 mL	854.1 g	183.4 mL	316.6 mL	2.70 g/mL
750 mL	1276.3	275.3 mL	475.7 mL	2.68 g/mL

The results are in excellent agreement with each other, and with the literature value for the solid density of mineral soils: 2.65 g/mL (Freeze and Cherry, 1979, p. 337).

ANNEX 5. TIME DOMAIN REFLECTOMETRY CALIBRATION

INTRODUCTION

Time Domain Reflectometry (TDR) is an extremely accurate method of measuring soil pore moisture non destructively. It works by measuring the dielectric constant (which is unitless) of the soil with electric pulses produced by a wave generator. The theory of time domain reflectometry is given in section 1.5.2.

Because water has a dielectric constant (80) much higher than any mineral (3-7), TDR analysis of soil moisture is reliable in virtually any soil without changing the calibration. However, when coatings are used on the TDR probes to prevent chemical interactions, it is necessary to calibrate the coated probes against uncoated probes, as the coating may have an influence on the overall dielectric constant. This annex will explain the calibration which was performed on the Teflon-coated TDR probes which were used in this experiment.

THEORY

Measuring the dielectric

The dielectric (also called relative dielectric, dielectric constant, relative dielectric permittivity, and a few others) is a (dimensionless) measure of the ability of a material to oppose charges, to compensate internally for charges. In water, this compensation is accomplished by the polar water molecules rotating to align themselves with the gradient. If we used direct current (DC), the molecules would stay aligned, but if we use alternating current (AC), the molecules will keep changing orientation as the direction changes. If the current alternated too fast, the molecules would not be able to reorient themselves quickly enough, and the dielectric would go to zero: it is therefore not a constant, but a function of frequency. As long as the frequency isn't too high, we can obtain a good measure of the dielectric (Figure 1).

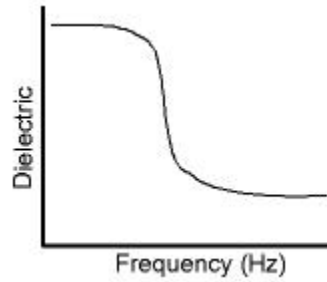


Figure 1. Dielectric variation with frequency

The dielectric is measured using a TDR probe (a waveguide with 2 prongs) and a “cable tester”, a sort of wave-generator plus oscilloscope. We send a voltage step pulse down a wire into the TDR probe. The signal travels down the waveguide, bounces off the end, and returns to the wave generator/oscilloscope. The information that comes with the bounced pulse is in the form of a reflection versus time plot (Figure 2).

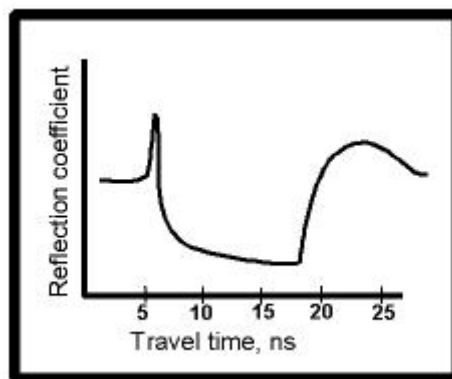


Figure 2. General TDR reflection vs. time plot

The pulse time between the start of the valley after the peak around 6 ns, and the bottom corner of the valley (around 18 ns), is the travel time we’re interested in. This section corresponds to the time spent in the waveguides (i.e., affected by the soil), and the dielectric ϵ is related to the travel time of this section of the plot by $\epsilon = (ct / 2L)^2$ (c = speed of light, and L = length of the waveguide).

The clay content of the soil may impact the dielectric, and therefore the wetness because of the influence it has on the water molecule absorbed on the clay surface. These molecules are somewhat constrained in their movement, and since the dielectric measures how quickly the water molecules will

move, it will influence the dielectric. Salt will also have an influence on the dielectric because of the effect it has on conductivity. Temperature can also influence the dielectric.

Obtaining soil wetness from the dielectric

The volume wetness can be related to the dielectric by using Topp's famous equation:

$$\theta = -5.3 \times 10^{-2} + 2.92 \times 10^{-2} \epsilon - 5.5 \times 10^{-4} \epsilon^2 + 4.3 \times 10^{-6} \epsilon^3 \quad (\text{Eq. 1})$$

This equation is a polynomial which was chosen to fit the data. It has no physical meaning.

CALIBRATION: APPARATUS

1. Cable tester
2. Teflon-coated and uncoated TDR probes, which are otherwise identical
3. Small container of soil
4. Jack drill with compaction attachment
5. Coaxial cable

CALIBRATION: METHOD

1. Measure probe length and offset (in meters)
2. Install uncoated TDR probe in container of soil, compact soil with jack drill
3. Set probe length and offset to 1 and 0, respectively
4. Measure apparent length L_a of uncoated TDR probes
5. Repeat steps 2-4 for coated TDR probes
6. Add water to container of soil, mix well
7. Repeat steps 2-5
8. Add more water to container of soil, mix well

9. Repeat steps 2-5
10. Repeat 8-9 until at least 5 different soil moistures have been measured
11. Plot L_a uncoated vs. L_a coated
12. Perform linear regression, obtain best fit line and equation
13. Use the linear equation to transform all coated L_a 's obtained during experiment

RESULTS & DISCUSSION

Figure 3 shows the graph comparing the apparent lengths of Teflon coated and uncoated TDR probes, along with the linear regression giving the equation of the best-fit line. This transformation was used for all subsequent wetness calculations.

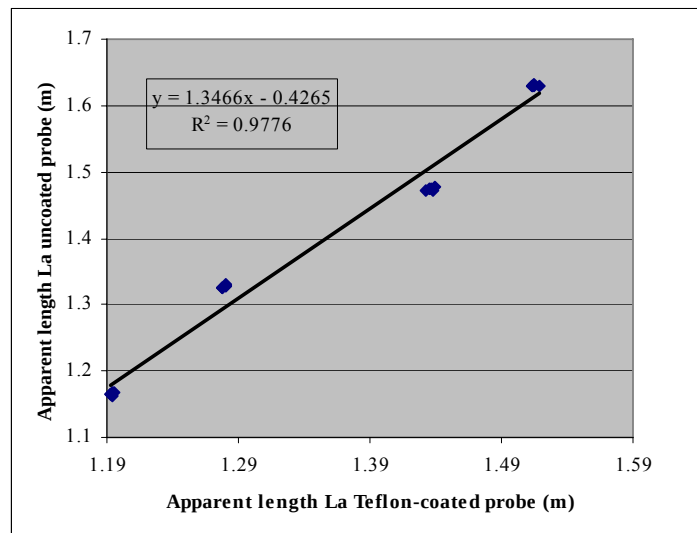


Figure 3. Teflon coated apparent lengths vs uncoated apparent lengths

Figures 4 and 5 show screen captures of the Teflon coated TDR reflection vs apparent length plot and an uncoated TDR reflection vs apparent length plot. The two curves, while very similar, have very slight differences in observed values of apparent length: the dotted vertical line represents the end of the pulse “valley”, which is slightly longer for the uncoated TDR probe. This small difference in apparent length (L_a) of the TDR probes produces the results in Figure 3.

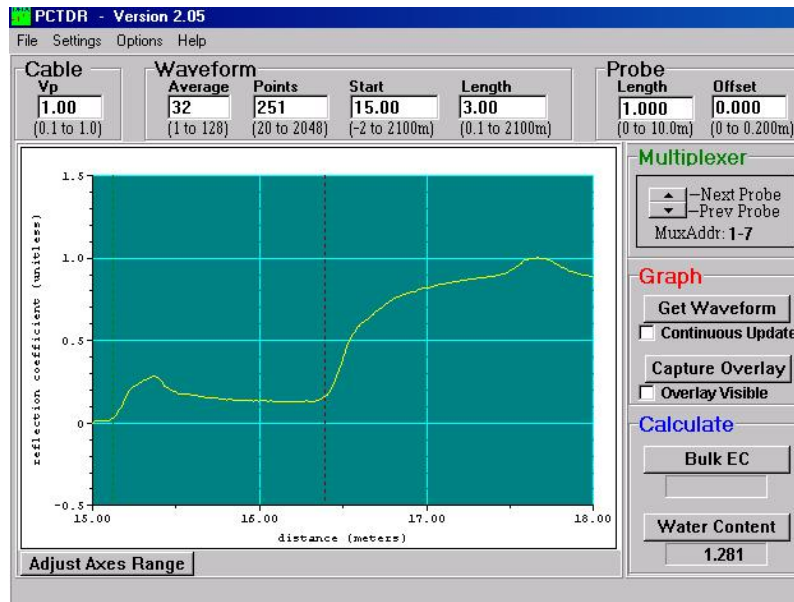


Figure 4. Teflon coated TDR reflection vs time plot

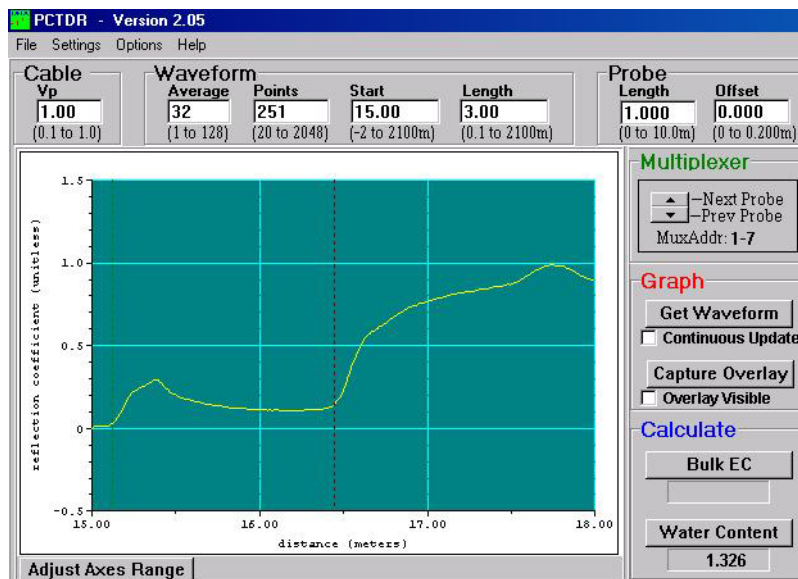


Figure 5. Uncoated TDR reflection vs. time plot

CONCLUSION

The Teflon coating of the TDR probes had a small but measurable effect on the measured dielectric and therefore the apparent length of the probes. This effect was successfully measured and accounted for with a linear relationship function.

ANNEX 6. MEASUREMENT OF SOIL SUCTION USING FILTER PAPER

INTRODUCTION

One of the key descriptors of variably saturated soil is the soil-water characteristic curve (SWCC). This relationship provides the link between matric suction and moisture content – in other words, the relationship between the amount of water held in soil and its energy status. The filter paper method is a soil suction measurement technique. It is an inexpensive and relatively simple laboratory test method, from which both the total and matric suction measurements are possible. The work of this thesis deals with transport phenomena in the vadose zone, and as such the measurement of the total suction is somewhat less relevant. Matric suction comes from the capillarity, texture, and surface adsorptive forces of the soil. Osmotic suction arises from the dissolved salts contained in the soil water. Osmotic suction is the stronger force, but its range of influence is limited to about 100 Å. As such, it mostly acts to immobilize water near the surface of soil grains. Matric suction on the other hand, is due to the effects of surface tension, which is a weaker force but has a range of influence up to about 1mm. In terms of controlling flow through variably saturated media, matric suction is more influential. The total suction of a system is the summary of the matric and osmotic suctions or tensions.

THEORY AND BACKGROUND

The filter paper method evolved in Europe in the 1920's and was first used in the United States by Gardner (1937). It is a reasonably simple method which has some advantages over other suction measurement devices. Many of these devices have limitations with regard to range of measurement, equilibration times, and cost. The filter paper method has the advantages of covering the practical suction range, of being simple, and of being inexpensive.

The method consists of allowing the filter paper to come to equilibrium with the soil either through vapor (total suction measurement) or liquid (matric suction measurement) flow. At equilibrium, the suction value for the filter paper and the soil will be equal. Once equilibrium is established, the water content of the filter paper is measured by weighing and the suction value found by correlating the water content value with the suction value on a calibration curve. This method has been adopted and

standardized in ASTM D 5298, Standard Test Method for Measurement of Soil Potential (Suction) Using Filter Paper.

The calibration curve for Schleicher & Schuell No. 589-WH Filter Paper is shown in Figure 1.

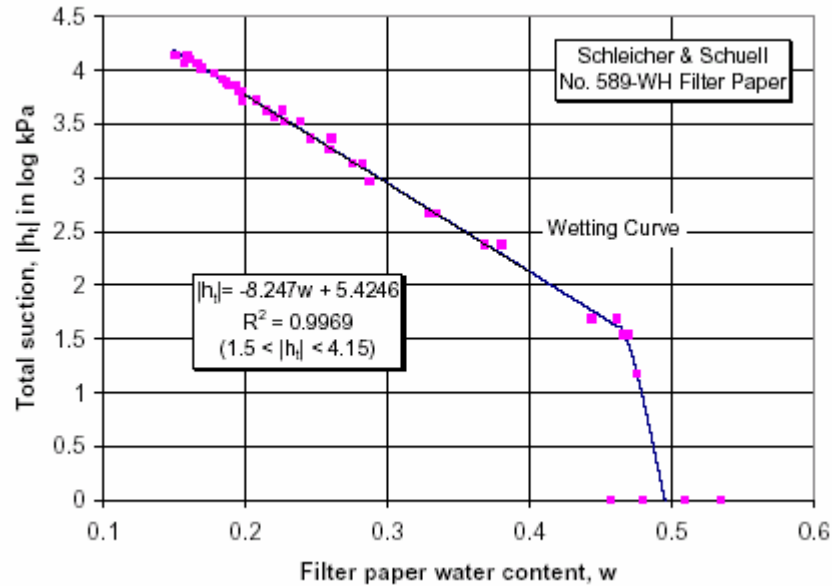


Figure 1. Calibration curve for Schleicher & Schuell No. 589 WH Filter Paper

APPARATUS

- 1) Filter Papers
- 2) Sensitive Balance
- 3) Constant temperature container
- 4) Oven
- 5) Moisture Tins
- 6) Glass jars
- 7) Tweezers
- 8) Gloves
- 9) Electrical Tape
- 10) Pestle

METHODOLOGY

- 1) Prepare 10 samples of soil with known water contents varying from 0 (dry) to 0.35 (near saturation).
- 2) For each soil sample, half-fill jar with layers of sand 1 cm thick (approximately), compacting each layer with a pestle. Ensure last layer (at the half-full point of the jar) is well-smoothed.
- 3) Remove a Schleicher & Schuell No. 589-WH filter paper from the box using tweezers.
- 4) Place Schleicher & Schuell filter paper between two protective filter papers. Any high permeability filter papers of larger diameter will do.
- 5) Using tweezers, place sandwiched filter paper on top of soil sample in half-filled jar.
- 6) Continue to fill jar with successive 1 cm layers of soil, compacting each with pestle.
- 7) When jar is full, put lid on and seal tightly with electrical tape.
- 8) Place jar in well-insulated container.
- 9) Allow filter paper to come to equilibrium with soil for one week.
- 10) At the end of the 1 week equilibration period, weigh moisture tins, record masses to accuracy of 0.0001 g.
- 11) Remove jar from temperature controlled container.
- 12) Open jar, remove filter paper, discard protective filter paper and place Schleicher & Schuell paper in moisture tin as quickly as possible (< 5 sec).
- 13) Immediately close tin and weigh.
- 14) Half-open tin lid, place inside oven for 24 hours.
- 15) Before removing tins from oven, close lid and leave in oven 5 min. to come to equilibrium
- 16) Weigh hot tin with filter paper inside.
- 17) Remove filter paper, discard.
- 18) Re-weigh hot empty tin.
- 19) Calculate moisture content of each filter paper.
- 20) Obtain suction value from calibration curve.
- 21) Plot all suction values against known soil moisture content to obtain the soil water characteristic curve (SWCC).

RESULTS

The experimental results are shown in Figure 2 as red data points. The data was modeled successfully using the Fredlund and Xing (1994) unimodal equation, shown as the blue line in Figure 2.

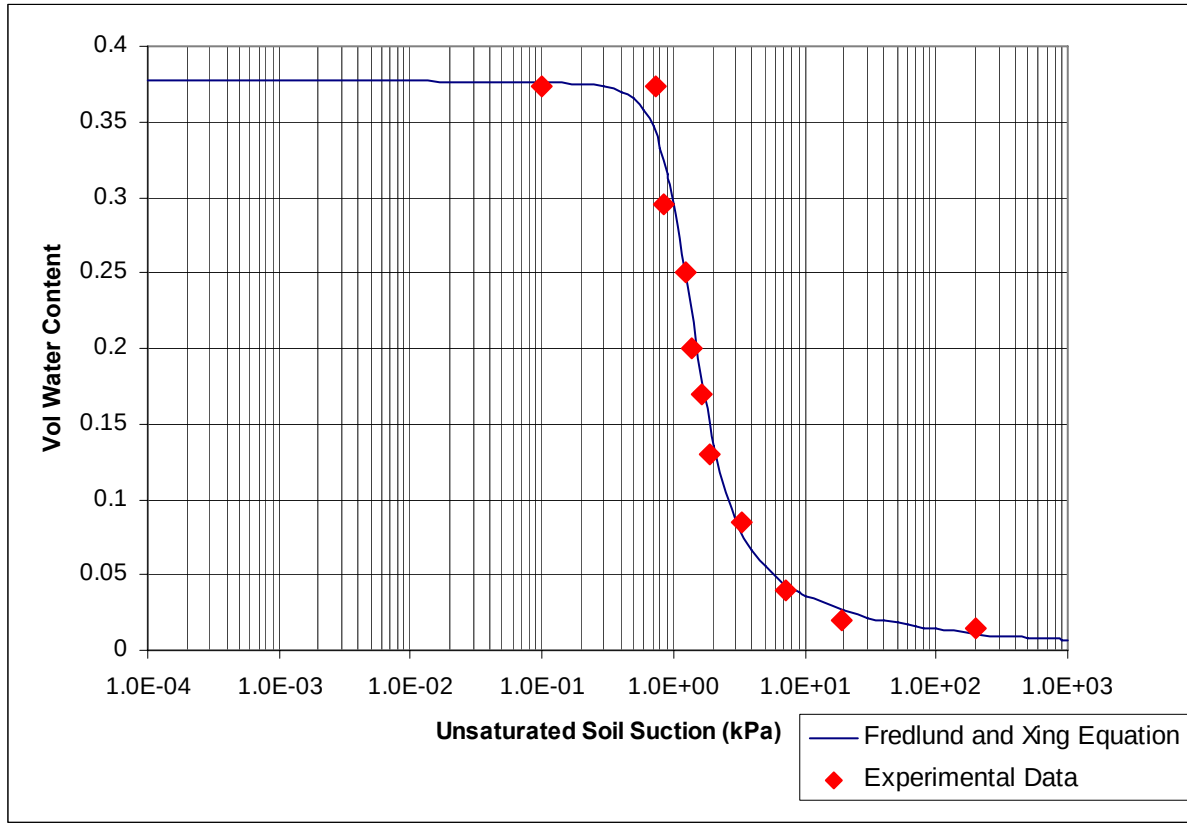


Figure 2. Experimental Data overlaid with Fredlund Pedo-transfer function, expressed by the Fredlund & Xing (1994) equation.

The Fredlund and Xing (1994) equation is shown below

$$w(\psi) = w_s \left[1 - \frac{\ln\left(1 + \frac{\psi}{h_r}\right)}{\ln\left(1 + \frac{10^6}{h_r}\right)} \right] \left[\frac{1}{\ln\left[\exp(1) + \left(\frac{\psi}{a_f}\right)^{n_f} \right] \right]} \right]^{m_f}$$

The parameters required to model the experimental data were:

$$\alpha_f = 1.08496$$

$$n_f = 3.838531$$

$$m_f = 1.0364$$

$$h_r = 2.87$$

The Fredlund model was satisfactory in modeling the experimental results at both high and low pressures, although the sharp break in the curve at the air entry value is rounded off somewhat.

The data was also modeled using the Van Genuchten (1980) equation. The results are shown in Figure 3. The Van Genuchten model, which satisfactorily modeled the data at lower pressures, was not satisfactory at modeling the data at higher pressures. Above 10 kPa, the Van Genuchten equation overestimates the soil water content.

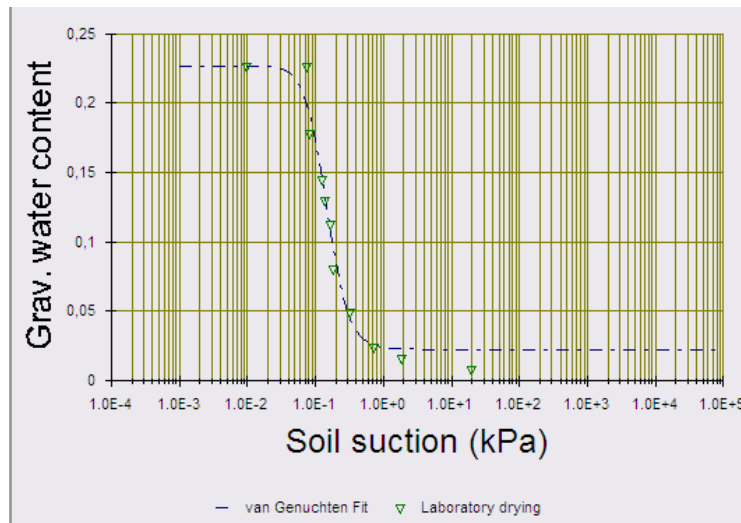


Figure 3. Experimental data overlaid with Van Genuchten model

The Brooks and Corey (1964) model was also used and is shown in Figure 4. It too satisfactorily modeled the experimental data.

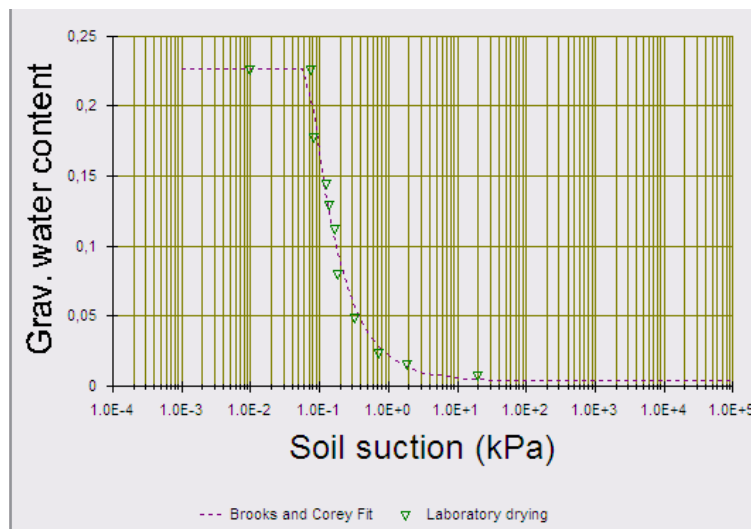


Figure 4. Experimental data overlaid with Brooks and Corey model

The air entry value value ψ_a is the pressure head at which the soil begins to drain. The experimental data indicates that this occurs at 0.73 kPa.

By convention, the wilting point is defined to occur at a pressure of -1500 kPa. For this soil, this equates to a volumetric water content of 0.015. Similarly, by convention the field capacity is defined in the laboratory as being achieved at a pressure of approximately -10 to -30 kPa. At these pressures, the volumetric water content is approximately 0.1 to 0.05.

CONCLUSION

The soil water characteristic curve was successfully measured using the filter paper method. The experimental data was modeled satisfactorily using both the Brooks and Corey model and the Fredlund and Xing model.

ANNEX 7. SOIL ADSORPTION TESTS

INTRODUCTION

It was desirable to rigorously define the adsorption of Composition B (TNT and RDX) onto the surface of the soil used in the columns. Although a comparison of the breakthrough curves of the inert tracer KBr in column A and the energetic materials in columns B through F allowed the calculation of the retardation factor, confirmation of these results was necessary to fully understand the behaviour of the energetic residues as they travelled through the unsaturated columns. The goal of this experiment was to define the adsorption coefficient K_d of the TNT and RDX originating from the composition B detonation residue.

APPARATUS

1. Table shaker with space for 32 bottles
2. 20 x 250 mL amber glass bottles
3. 2 mm diameter screen
4. 100 x 10 mL syringes with 45 μ m filters
5. 1 L acetonitrile

EXPERIMENTAL

1. Heat 2 kg uncontaminated soil in oven at 60° Centigrade for 48 hours to kill all microbes.
2. Grade uncontaminated soil by passing it through 2 mm diameter seive
3. Produce energetic material (EM) solution
 - a. Two methods for producing EM solution
 - b. Method 1: production of solution from contaminated soil
 - i. Add 1.5 kg of soil from columns B, C, D, E, or F to 3 L distilled water
 - ii. Agitate for 72 hours , ensuring soil stays in suspension (no settling)

- iii. Filter soil from solution
- iv. Analyse for energetic materials using HPLC
- v. Repeat steps i to iv
- vi. Concentration of TNT must be between 25 mg/L and 70 mg/L
- c. Method 2: production of solution from Composition B
 - i. Add 100 mg of crushed composition B to 4 L distilled water
 - ii. Agitate for 72 hours
 - iii. Analyse for energetic materials using HPLC
 - iv. Repeat steps I to iii
 - v. Concentration of TNT must be between 25 mg/L and 70 mg/L
- 4. Determine time to equilibrium
 - a. Mix 27 x 50 mL of EM solution with 12.5 g uncontaminated soil in 250 mL amber glass bottles sealed with Teflon septums
 - b. Place the 27 bottles on shaker table
 - c. Sample three bottles at each time period of 0, 1, 6, 12, 18, 24, 32, 48, 72 and 96 hours
 - i. Bottles to be sampled by drawing off 30 mL of solution with syringe then filtering the sample with a 45 µm filter into 4x30 mL centrifuge test tubes.
 - ii. Centrifuge sample for 30 minutes at 1200 rpm
 - iii. Analyse the 1 mL acetonitrile by HPLC
 - iv. Graph results, determine time required to achieve equilibrium
- 5. Use EM solution to produce dilutions of 1:4, 1:10, 1:20, 1:40, 1:60, 1:100, 1:200, 1:500. Each dilution to be produced by mixing distilled water with EM solution in ratios indicated.
- 6. Mix each dilution with uncontaminated soil in ratios given in Table 1 to produce 1:4 ratio of soil/solution.
- 7. Place all bottles on shaker table
- 8. Agitate bottles for equilibrium time determined in step 4

9. Bottles to be sampled by drawing off 120 mL of solution with syringe through the Teflon septum, then filtering the sample with a 45 μ m filter into 4x30 mL centrifuge test tubes.
10. Extract sample through Sep-Pak solid phase extraction cartridge
11. Analyse the 1 mL acetonitrile extract by HPLC
12. Determine adsorption constant K_d according to calculations given below

Table 1 Masses required to produce 1:4 ratio of soil/solution

Ratio	Mass of soil	Vol. EM sol'n	Vol. Distilled water
1:1	12.5 g	25 mL	25 mL
1:4	12.5 g	10 mL	40 mL
1:10	13.75 g	5 mL	50 mL
1:20	10.5 g	2 mL	40 mL
1:40	20.5 g	2 mL	80 mL
1:60	30.5 g	2 mL	120 mL
1:100	25.25 g	1 mL	100 mL

CALCULATIONS

Once the concentration in free solution (C_w) vs concentration sorbed (C_s) data obtained from the HPLC results has been plotted, the adsorption constant K_d is determined assuming a linear isotherm. If non-linear behaviour is observed, the data may be fitted using the Freundlich or Langmuir isotherms, finding for K_d . as the Freundlich adsorption coefficient, N is the Freundlich characteristic constant and b as the Langmuir characteristic constant. All isotherms for this test were at 8° Centigrade.

Linear

$$C_s = K_d \times C_w$$

Freundlich

$$C_s = K_d' \times C_w^N$$

Langmuir

$$C_s = \frac{q_{\max} \times b \times C_w}{1 + b \times C_w}$$

RESULTS AND DISCUSSION

The plots of C_s vs. C_w is shown in Figures 1, and 3. The best fit data is shown in Table 1

Table 1. Best fit adsorption coefficients

	K_d (linear)	R^2	K_d (Freundlich)	N (Freundlich)	R^2
TNT	0.123 L/kg	0.99	NA	NA	NA
RDX	0.091 L/kg	0.96	0.22	0.4	0.87
HMX	0.18 L/kg	0.97	NA	NA	NA

The TNT adsorption data had combined experimental and analytical error less than 3%, and shows linear adsorption behaviour. The calculated K_d was 0.123 L/kg, and had an excellent R^2 value of 0.99 for the data fit. This is in keeping with the findings of Yamamoto et al (2004) who determined a linear isotherm for TNT in batch tests on sandy soil, with K_d values of 0.34 L/kg. These results are also broadly in line with other published adsorption coefficients for TNT, which range from 0.04 L/kg to 11 L/kg (Brannon and Pennington, 2002).

The complete RDX adsorption data was distinctly non-linear, with a very distinct reduction in relative adsorption occurring at higher concentrations. The data could not be fit satisfactorily with either the Langmuir or Freundlich isotherms, as the decrease in adsorption at higher concentrations was too pronounced. Complete data with the best fit Freundlich isotherm are shown in figure 2. The complete

data had a linear K_d of 0.036 L/kg with an R^2 value for the data fit of 0.74, which is still better than some data appearing in the literature (Yamamoto et al, 2005). With a Freundlich isotherm having values of $K_d = 0.25$ and an N value of 0.33, the R^2 value increased to 0.87. However, the N value of 0.33 is somewhat questionable, since N tends to be near 1 in most cases.

The non-linear adsorption behaviour of the RDX is not described in the literature. Most literature values for the partitioning coefficient of RDX modeled their data with very little error using a linear isotherm (Yamamoto et al, 2005, Singh et al, 1998, Xue et al, 1995). However, either these studies used soil with a high clay content (Singh et al, 1998) or they used RDX solutions which were less concentrated than that which we used (Yamamoto et al, 2005, Xue et al 1995). The distinctly non-linear shape of the RDX isotherm in our data is either due to competitive adsorption with TNT or with a limited number of sites to which the RDX can sorb. The laboratory error associated with the manipulations and analysis were on the order of 5%, and each data point represents the average of 6 individual measurements. Laboratory error cannot explain the non-linearity of the data point found at a solution concentration of 15 mg/l. Physically, what this indicates is that when RDX can be expected to be found at high concentrations, such as in pore water near detonation residue, relatively little of the RDX will sorb to the soil. Solute transport of RDX under these conditions will be facilitated.

If we remove the data point found at a solution concentration of 15 mg/L, the data may be modeled using a linear isotherm ($R^2 = 0.98$). The calculated partitioning coefficient in this case becomes 0.091 L/kg, which is in agreement with Yamamoto (2005) who found a K_d for RDX in sandy soil of 0.072 L/kg, as well as Myers et al (1998) and Tucker et al (1985) who found that in sandy soils having low clay contents, the adsorption coefficient for RDX was 0 and 0.07 L/kg respectively. It should be pointed out that the experimental K_d values are in general approximately one order of magnitude below the majority of published adsorption coefficients for RDX (Brannon and Pennington, 2002).

The HMX data was fit linearly with the partitioning coefficient $K_d = 0.18$ L/kg. The R^2 value of this data fit was 0.97. However, only two data points for HMX were retained, as the dilutions 1:20, 1:40, 1:60 and 1:100 all produced results below detection limits. The proximity of the two remaining points to the detection limit increases the error associated with the results to the order of 10%. The data agrees well with published adsorption coefficients, which range from 0.086 L/kg to 17.7 L/kg (Brannon and Pennington, 2002). For comparable sandy soils, the published K_d values are on the order of 0.2 L/kg (Pennington, 1999) to 5.02 L/kg (Brannon et al., 1999)

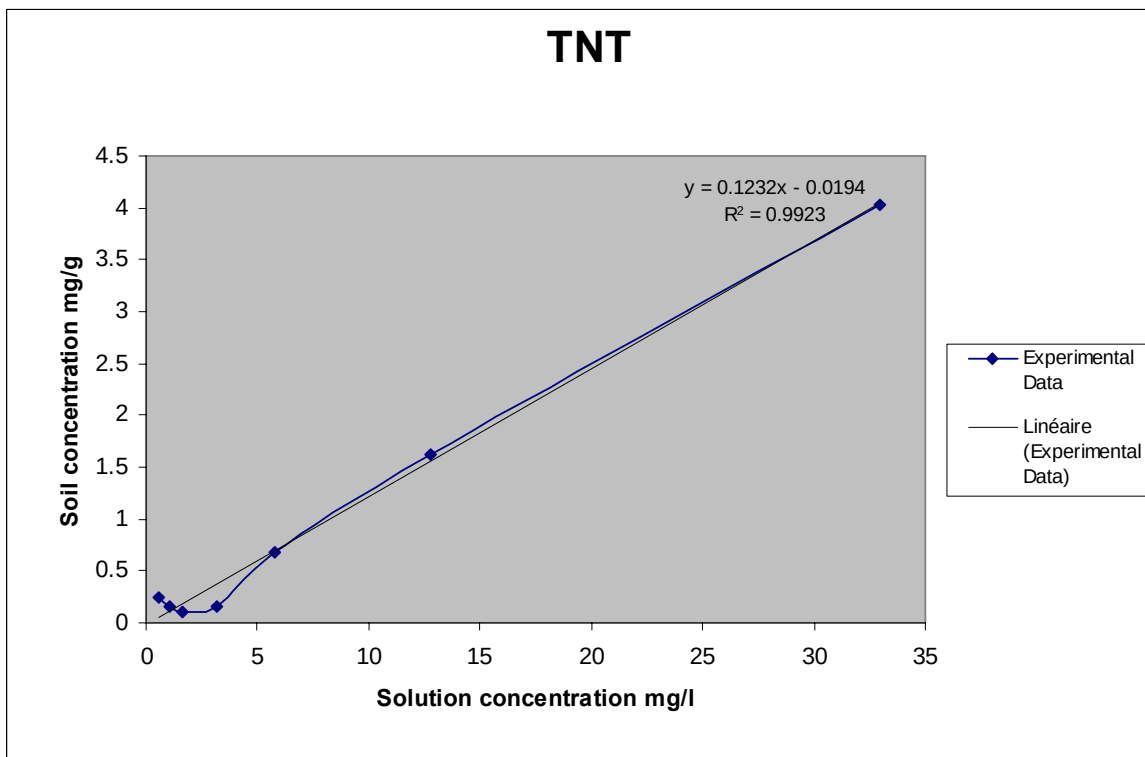


Figure 1 TNT Adsorption diagram

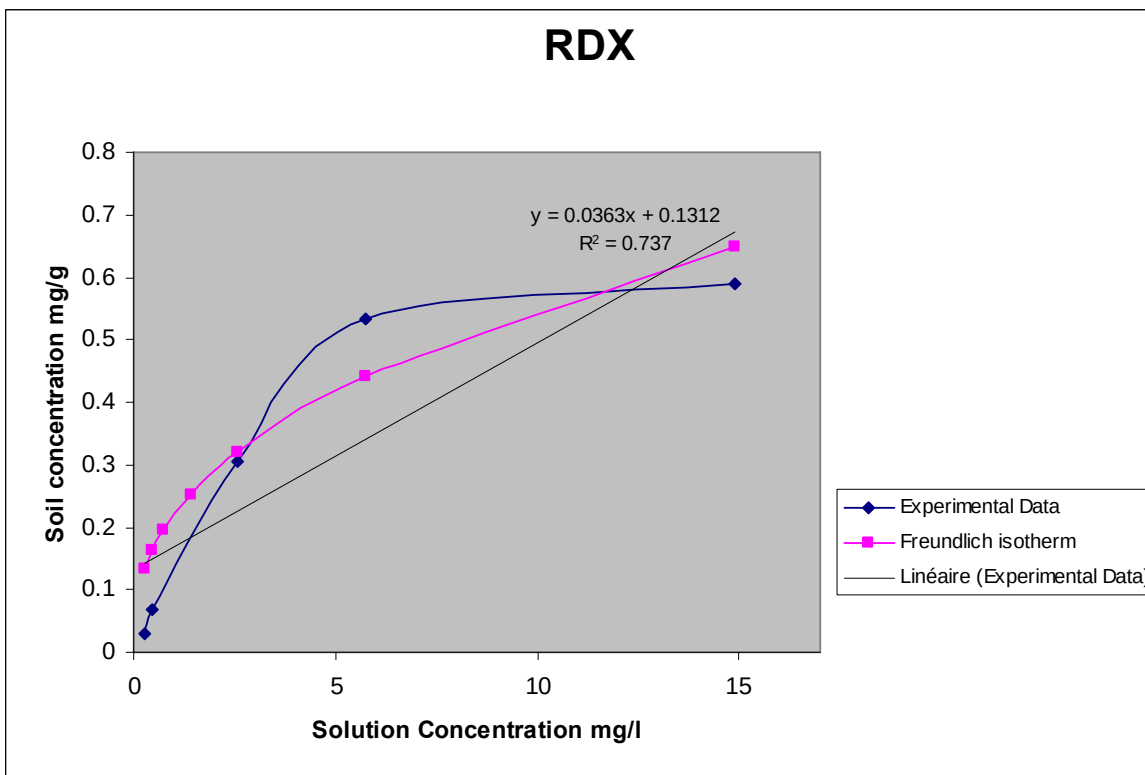


Figure 2 RDX adsorption diagram

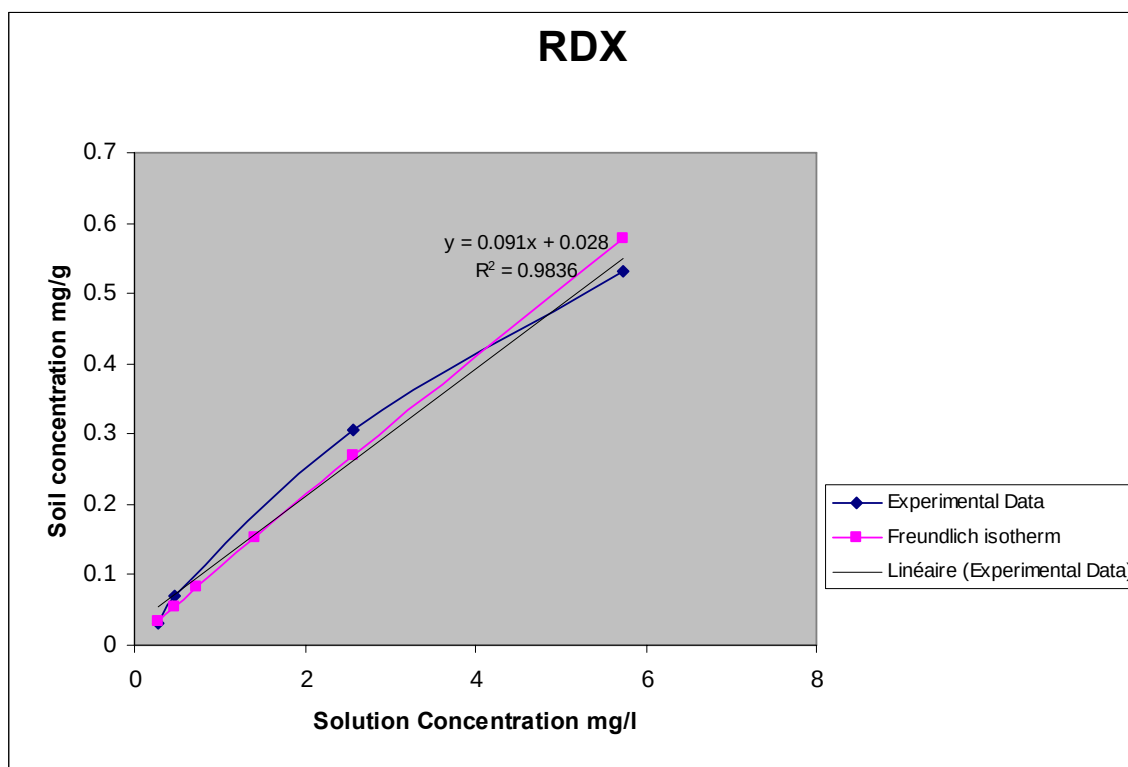


Figure 3. RDX adsorption diagram, without highest concentration datapoint

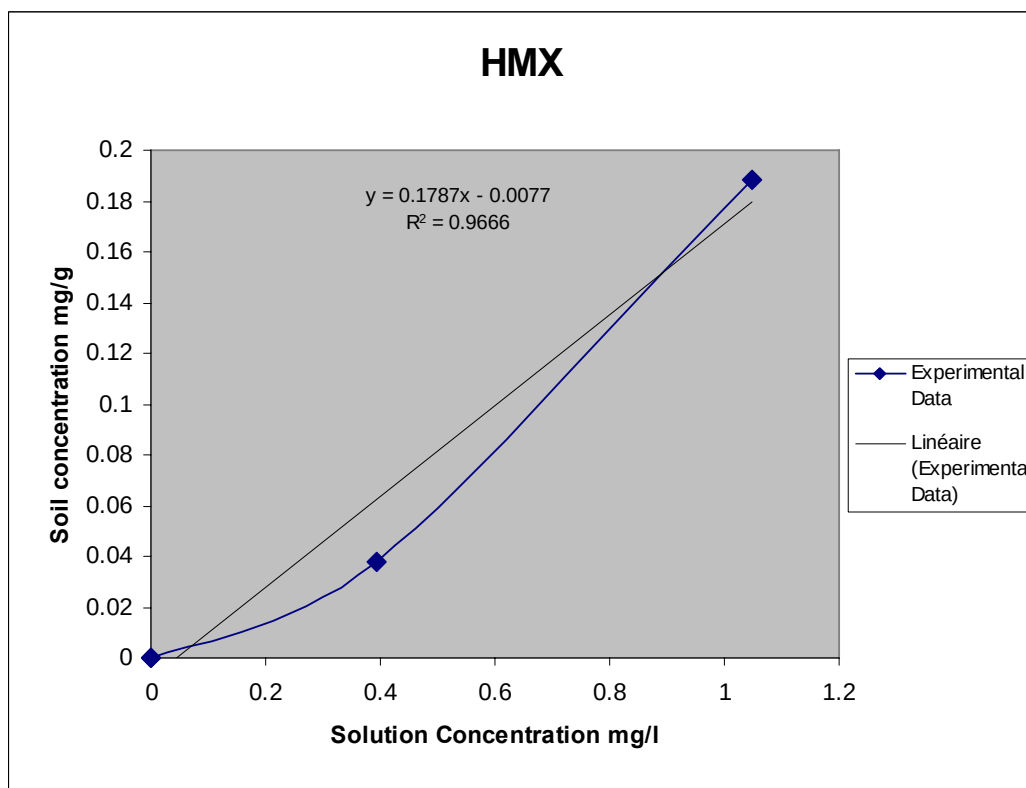


Figure 4. HMX Adsorption diagram

CONCLUSION

The adsorption coefficient for TNT in a Composition B solution allowed to adsorb to a sandy soil was satisfactorily modeled with a linear isotherm having an adsorption coefficient K_d of 0.123 L/kg. This fit was extremely reliable, having an R^2 value of 0.99. The linear portion of the RDX adsorption isotherm was found to have a K_d of 0.091 L/kg. However, the overall curve was best fit with a Freundlich isotherm having values of 0.22 L/kg for the partition coefficient K_d , and 0.4 for the Freundlich adsorption coefficient N . For HMX, a linear fit was established with a K_d of 0.18 L/kg and an R^2 value of 0.97. These values are all in agreement with literature values.

ANNEX 8. DETONATION RESIDUE DISSOLUTION TEST

INTRODUCTION

The column leaching experiments, which form the backbone of this thesis, were designed to reproduce field conditions as closely as possible. Unexploded ordnance and detonation residue were placed on soil columns obtained from near an impact area. While such an experimental setup provides results that are highly applicable to field conditions, it is not conducive to determining the input function of the explosive contaminants as they enter the soil, since the detonation residue is mixed with the soil. Since the detonation residue must dissolve prior to becoming mobile, full characterization and modeling of the soil columns requires knowledge of the dissolution kinetics of the detonation residue.

This test was designed to measure the dissolution kinetics of the detonation residue.

APPARATUS

- Harvard Apparatus Model 22 Syringe Pump
- 25 mL syringe
- 2.2 cm diameter filter funnel with sintered glass filter

CHEMICALS

- Distilled water
- Detonation residue

CALCULATIONS

- 1) Determine amount of detonation residue to be used in dissolution test

The amount of detonation residue placed on the 2.2 cm diameter glass filter must be proportional to the amount of detonation residue placed on the 30 cm diameter soil column.

Known:

- 20 g fine fraction (>0.75 mm diameter) detonation residue placed on soil column
- 25 g coarse fraction (< 0.75 mm diameter) detonation residue placed on soil column
- soil column diameter = 31 cm
- filtration funnel diameter = 2.2 cm
- Springtime infiltration = 253 mm water /30 days (between 0800 hrs and 1600 hrs)
- Autumn infiltration = 116 mm water /61 days (24 hrs)

$$\text{Soil column area} = \pi (32 \text{ cm})^2 = 3.14 (1024 \text{ cm}^2) = \mathbf{3220 \text{ cm}^2}$$

$$\text{Filtration funnel area} = \pi (0.35 \text{ cm})^2 = 3.14 (0.1225 \text{ cm}^2) = \mathbf{0.385 \text{ cm}^2}$$

$$\text{Detonation residue fine fraction density} = 20 \text{ g} / 3220 \text{ cm}^2 = \mathbf{0.00708 \text{ g/cm}^2}$$

$$\text{Mass of fine fraction used on filtration funnel} = (0.00708 \text{ g/cm}^2)(3.8 \text{ cm}^2) = \mathbf{0.027 \text{ g}}$$

$$\text{Detonation residue coarse fraction density} = 25 \text{ g} / 3220 \text{ cm}^2 = \mathbf{0.00885 \text{ g/cm}^2}$$

$$\text{Mass of coarse fraction used on filtration funnel} = (0.00885 \text{ g/cm}^2)(3.8 \text{ cm}^2) = \mathbf{0.034 \text{ g}}$$

Rate of water infiltration (See section 2.3.5.1 for details on flow rate)

Springtime

Flow rate: 0.34 L/hr (see sect. 2.3.5.1) over 0.322 m^2 or $0.00034 \text{ m}^3/\text{hr}$ over 0.322 m^2 . = 0.0011 m/hr

$$= 0.0011 \text{ m/hr over } 0.385 \text{ cm}^2 = 0.0011 \text{ m/hr over } 0.0000385 \text{ m}^2$$

$$= 0.0000000423 \text{ m}^3/\text{hr} = 0.000046 \text{ L/hr} = \mathbf{0.046 \text{ mL/hr}}$$

Autumn

$$\begin{aligned}\text{Flow rate: } & 0.025 \text{ L/hr (see sect 2.3.5.1) over } 0.322 \text{ m}^2 \text{ or } 0.000025 \text{ m}^3/\text{hr over } 0.322 \text{ m}^2 \\ & = 7.76 \text{ E-5 m/hr over } 3.8 \text{ cm}^2 = 7.76 \text{ E-5 m/hr over } 0.00038 \text{ m}^2 \\ & = 3.4 \text{ E-8 m}^3/\text{hr} = 3.4 \text{ E-5 L/hr} = \boxed{0.034 \text{ mL/hr}}\end{aligned}$$

METHOD

- Evenly distribute 0.108 g of fine fraction detonation residue residue on 2.2 cm diameter glass filter.

- Samples tested :
- 1) Complete fine fraction detonation residue
 - 2) Complete fine fraction detonation residue
 - 3) <125 micron fraction of detonation residue
 - 4) 150 micron – 180 micron fraction of residue
 - 5) 212 micron-300 micron fraction of residue
 - 6) >600 micron fraction of residue

- Set syringe pump to springtime outflow rate of 0.05 mL/hr
- Attach narrow gauge plastic tubing to syringes, secure the outflow end to a height of 1 cm above the fritted glass
- Collect outflow every 48 hours (2.4 mL) for EM analysis
- graph EM concentrations vs. grain size diameter

RESULTS

Figure 1 shows the EM concentration as a function of the grain size of the source term. Grain size has a very important effect on the concentration of the effluent. At a flow rate of 0.05 mL/hr, the dissolution kinetics of all three energetic materials tested is roughly linear with respect to grain size, with the effluent concentration a function of grain size according to the equations

$$[\text{TNT}] = -210.3 d + 135.7$$

$$[\text{RDX}] = -101.4 d + 61.3$$

$$[\text{HMX}] = -8.7 d + 7.2$$

Where d is the grain size diameter of the detonation residue.

As well, it was demonstrated that the maximum concentration in the effluent from the complete fine fraction (samples 1 and 2) is reached at around day 15 to 20 of the infiltration. The curve suggests that near-maximal concentrations may have been attained much faster than the measured results indicate. However, the very small quantities of liquid which were collected made any analysis prior to the 10 day period impossible. What is clear is that after 20 days of infiltration, the concentrations of all three energetic compounds begins to drop, as would be expected if the primary source of EM – the extreme fine fraction – slowly exhausted itself.

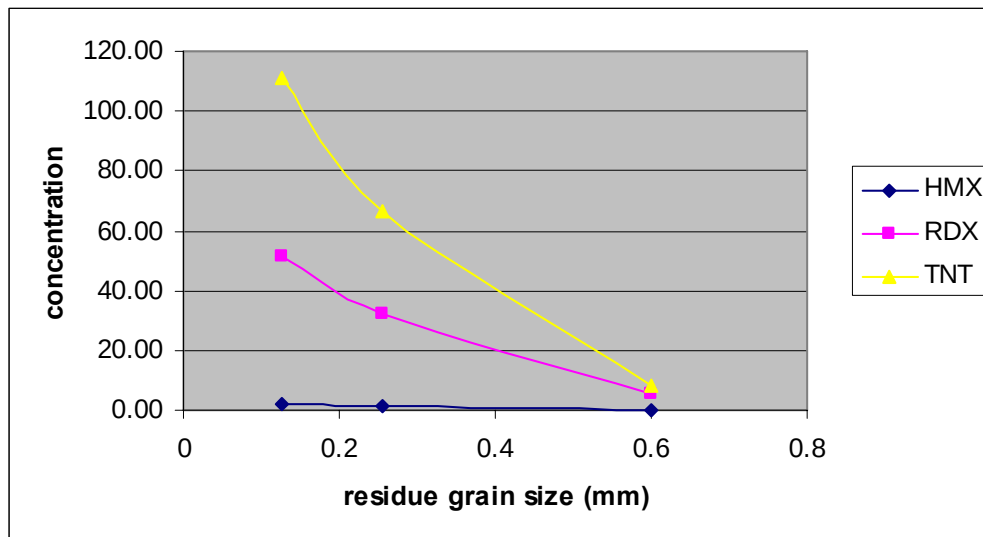


Figure 1: EM concentration vs. grain size of source term

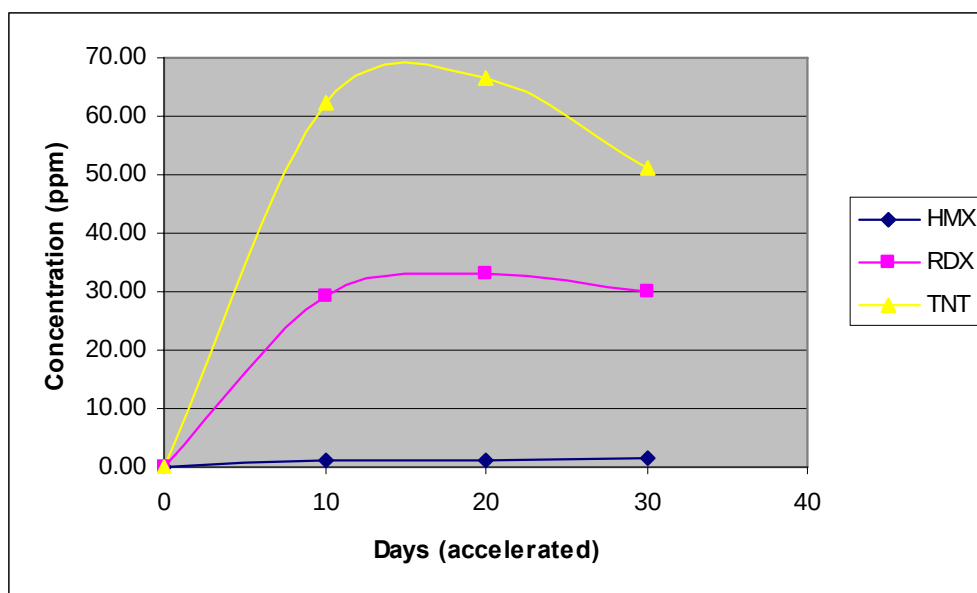


Figure 2. EM concentration vs. time

CONCLUSIONS

The kinetics of dissolution of the detonation residue follows a roughly linear relationship with respect to the grain size of the residue. For the complete fine fraction of detonation residue (samples 1 and 2), which reproduced the samples placed on the soils columns for the leaching tests, near maximal concentrations may have been achieved much earlier than the observed period of 10 days, but insufficient effluent was available prior to the 10 day period to analyze the sample reliably. After 20 days of infiltration, the concentrations of the complete fine fractions began to drop, which supported the observations of the leaching experiments.

APPENDIX 1. CR-10 PROGRAMS

Autumn Infiltration Period

```
;{CR10X}  
;-----  
;PROJET UX0  
;  
;INFILTRATION AUTUMN  
;  
;MESURE ET ENREGISTRE LES PARAMETRES DE BASE ET LES TENEUR EN EAU  
;CONTROLE ET ENREGISTRE LES PRECIPITATIONS DU SIMULATEUR DE PLUIE  
;-----
```

*Table 1 Program

01: 1800 Execution Interval (seconds)

; Permet le controle des valves lorsque le FLAG 1 est high
; Tout la journee, 24 hrs sur 24

1: Do (P86)
1: 11 Set Flag 1 High

; Permet la lecture des TEE lorsque le FLAG 2 est high

2: If time is (P92)
1: 0 Minutes (Seconds --) into a
2: 30 Interval (same units as above)
3: 30 Then Do

3: Do (P86)
1: 12 Set Flag 2 High

4: Else (P94)

5: Do (P86)
1: 22 Set Flag 2 Low

6: End (P95)

;MESURE LES PARAMETRES DE BASE
;-----

7: Batt Voltage (P10)
1: 1 Loc [Bat_Volt]

8: Signature (P19)
1: 2 Loc [Signature]

9: Internal Temperature (P17)
1: 3 Loc [Temp_int]

```

10: Thermocouple Temp (DIFF) (P14)
  1: 1      Reps
  2: 1      2.5 mV Slow Range
  3: 1      DIFF Channel
  4: 1      Type T (Copper-Constantan)
  5: 3      Ref Temp (Deg. C) Loc [ Temp_int  ]
  6: 4      Loc [ Temp_Ext  ]
  7: 1.0    Mult
  8: 0.0    Offset

;-----
; CONTROLE DU SIMULATEUR DE PLUIE (VALVES)

11: If Flag/Port (P91)
  1: 11     Do if Flag 1 is High
  2: 30     Then Do

; ACTIVE LE RELAIS BRANCHE AU PORT No.8 AUX 60 MINUTES

12: If time is (P92)
  1: 0      Minutes (Seconds --) into a
  2: 60     Interval (same units as above)
  3: 48     Set Port 8 High

13: Z=F (P30)
  1: 1      F
  2: 0      Exponent of 10
  3: 5      Z Loc [ Valve      ]

;+++++
; ENREGISTRE LES HEURES D'OUVERTURE DE LA VALVE

14: Do (P86)
  1: 10     Set Output Flag High (Flag 0)

15: Set Active Storage Area (P80)
  1: 1      Final Storage Area 1
  2: 2      Array ID

16: Real Time (P77)
  1: 111    Day,Hour/Minute,Seconds (midnight = 0000)

17: Sample (P70)
  1: 1      Reps
  2: 5      Loc [ Valve      ]

18: Do (P86)
  1: 20     Set Output Flag Low (Flag 0)

;+++++
;OUVRE LES VALVES PENDANT LE TEMPS A LA LIGNE 3

19: Excitation with Delay (P22)
  1: 1      Ex Channel
  2: 0      Delay W/Ex (units = 0.01 sec)
  3: 141    Delay After Ex (units = 0.01 sec)

```



```

4: 0000      mV Excitation

20: Do (P86)
1: 58      Set Port 8 Low

21: Z=F (P30)
1: 0      F
2: 0      Exponent of 10
3: 5      Z Loc [ Valve      ]

;+++++

; ENREGISTRE LES HEURES DE FERMETURE DE LA VALVE

22: Do (P86)
1: 10      Set Output Flag High (Flag 0)

23: Set Active Storage Area (P80)
1: 1      Final Storage Area 1
2: 2      Array ID

24: Real Time (P77)
1: 111     Day,Hour/Minute,Seconds (midnight = 0000)

25: Sample (P70)
1: 1      Reps
2: 5      Loc [ Valve      ]

26: Do (P86)
1: 20      Set Output Flag Low (Flag 0)
;+++++

27: End (P95)

```

```

;-----
;MESURE "La" AVEC LE TDR100
;-----

```

```

28: If Flag/Port (P91)
1: 12      Do if Flag 2 is High
2: 30      Then Do

29: TDR100 Measurement (P119)
1: 0      SDM Address
2: 0      La/L for Water Content
3: 3006   MMMP Mux & Probe Selection
4: 32     Waveform Averaging
5: 1      Vp
6: 251    Points
7: 12.5   Cable Length (meters)
8: 4      Window Length (meters)
9: 1      Probe Length (meters)
10: 0.0    Probe Offset (meters)
11: 6      Loc [ La_1      ]
12: 1.0    Mult
13: 0.0    Offset

```

```

30:  TDR100 Measurement (P119)
   1: 0          SDM Address
   2: 0          La/L for Water Content
   3: 1106       MMMP Mux & Probe Selection
   4: 32         Waveform Averaging
   5: 1          Vp
   6: 251        Points
   7: 14.5       Cable Length (meters)
   8: 4          Window Length (meters)
   9: 1          Probe Length (meters)
  10: 0.0        Probe Offset (meters)
  11: 12         Loc [ La_7      ]
  12: 1.0        Mult
  13: 0.0        Offset

```

```

31:  TDR100 Measurement (P119)
   1: 0          SDM Address
   2: 0          La/L for Water Content
   3: 2106       MMMP Mux & Probe Selection
   4: 32         Waveform Averaging
   5: 1          Vp
   6: 251        Points
   7: 14.5       Cable Length (meters)
   8: 4          Window Length (meters)
   9: 1          Probe Length (meters)
  10: 0          Probe Offset (meters)
  11: 18         Loc [ La_13     ]
  12: 1.0        Mult
  13: 0.0        Offset

```

```

; TRANSFORME "La" EN TENEUR EN EAU
; Dans un premier temps, on corrige les La obtenus avec les tiges
; de teflon pour qu'ils correspondent a des La avec tiges inox
;-----

```

```

32:  Beginning of Loop (P87)
   1: 0          Delay
   2: 18         Loop Count

```

```

; La (inox) = 1.3466 * La (tef) - 0.4265
; Puis on soustrait le OffSett 0.157

```

```

33:  Z=X*F (P37)
   1: 6          -- X Loc [ La_1      ]
   2: 1.3466     F
   3: 24         -- Z Loc [ TEE_1     ]

```

```

; 0.5835 = 0.4265 + 0.157

```

```

34:  Z=X+F (P34)
   1: 24         -- X Loc [ TEE_1     ]
   2: -0.5835    F
   3: 24         -- Z Loc [ TEE_1     ]

```

```
;Racine carre Ka = La/L, ou L=0.39
;Racine carre Ka = La * (1/L) = La * (1/0.39) = La * 2.5641
```

```
35:  Z=X*F (P37)
1: 24      -- X Loc [ TEE_1      ]
2: 2.56410  F
3: 24      -- Z Loc [ TEE_1      ]
```

```
36:  Z=X*Y (P36)
1: 24      -- X Loc [ TEE_1      ]
2: 24      -- Y Loc [ TEE_1      ]
3: 24      -- Z Loc [ TEE_1      ]
```

```
; MULTIPLIE Ka PAR 0.1 POUR UTILISER L'EQUATION POLUNOMIALE
```

```
37:  Z=X*F (P37)
1: 24      -- X Loc [ TEE_1      ]
2: 0.1      F
3: 24      -- Z Loc [ TEE_1      ]
```

```
; ON APPLIQUE L'EQUATION DE TOPP DU 3iem ORDRE
```

```
38:  Polynomial (P55)
1: 1      Reps
2: 24      -- X Loc [ TEE_1      ]
3: 24      -- F(X) Loc [ TEE_1      ]
4: -0.053  C0
5: 0.292   C1
6: -0.055  C2
7: 0.0043  C3
8: 0.0     C4
9: 0.0     C5
```

```
39:  End (P95)
```

```
; ENREGISTRE LES PARAMETRES
```

```
;-----
```

```
;Ici les donnees sont enregistrees aux trente minutes
```

```
40:  Do (P86)
1: 10      Set Output Flag High (Flag 0)
```

```
41:  Set Active Storage Area (P80)
1: 1      Final Storage Area 1
2: 1      Array ID
```

```
42:  Real Time (P77)
1: 1110    Year,Day,Hour/Minute (midnight = 0000)
```

```

43: Sample (P70)
   1: 4      Reps
   2: 1      -- Loc [ Bat_Volt  ]

44: Sample (P70)
   1: 36     Reps
   2: 6      -- Loc [ La_1      ]

45: Do (P86)
   1: 20     Set Output Flag Low (Flag 0)

46: End (P95)

```

```
;------
```

```

*Table 2 Program
 02: 0      Execution Interval (seconds)

```

*Table 3 Subroutines

End Program

```

-Input Locations-
1 Bat_Volt  5 1 0
2 Signature 9 1 0
3 Temp_int  9 1 1
4 Temp_Ext 25 1 1
5 Valve     17 2 4
6 La_1      5 1 1
7 La_2      1 1 0
8 La_3      1 1 0
9 La_4      1 1 0
10 La_5     1 1 0
11 La_6     1 1 0
12 La_7     1 1 1
13 La_8     1 1 0
14 La_9     1 1 0
15 La_10    1 1 0
16 La_11    1 1 0
17 La_12    1 1 0
18 La_13    1 1 1
19 La_14    1 1 0
20 La_15    1 1 0
21 La_16    1 1 0
22 La_17    1 1 0
23 La_18    1 1 0
24 TEE_1    7 7 6
25 TEE_2    11 1 0
26 TEE_3    11 1 0
27 TEE_4    11 1 0

```

28	TEE_5	11	1	0
29	TEE_6	11	1	0
30	TEE_7	11	1	0
31	TEE_8	11	1	0
32	TEE_9	11	1	0
33	TEE_10	11	1	0
34	TEE_11	11	1	0
35	TEE_12	11	1	0
36	TEE_13	11	1	0
37	TEE_14	11	1	0
38	TEE_15	11	1	0
39	TEE_16	11	1	0
40	TEE_17	11	1	0
41	TEE_18	19	1	0
42	_____	0	0	0
43	_____	0	0	0
44	_____	0	0	0
45	_____	0	0	0
46	_____	0	0	0
-Program Security-				
0000				
0000				
0000				
-Mode 4-				
-Final Storage Area 2-				
0				
-CR10X ID-				
0				
-CR10X Power Up-				
3				

Springtime Infiltration Period

```
;{CR10X}  
;-----  
;PROJET UX0  
;  
;INFILTRATION PRINTEMPS  
;  
;Dans la version quatre (ux04) tout le programme est dans la meme table.  
;  
;MESURE ET ENREGISTRE LES PARAMETRES DE BASE ET LES TENEUR EN EAU  
;CONTROLE ET ENREGISTRE LES PRECIPITATIONS PERIODES DU SIMULATEUR DE PLUIE  
;-----
```

*Table 1 Program

01: 900 Execution Interval (seconds)

```
;MESURE LES PARAMETRES DE BASE  
;-----
```

```
1: Batt Voltage (P10)  
  1: 1            Loc [ Bat_Volt  ]  
  
2: Signature (P19)  
  1: 2            Loc [ Signature ]  
  
3: Internal Temperature (P17)  
  1: 3            Loc [ Temp_int  ]  
  
4: Thermocouple Temp (DIFF) (P14)  
  1: 1            Repts  
  2: 1            2.5 mV Slow Range  
  3: 1            DIFF Channel  
  4: 1            Type T (Copper-Constantan)  
  5: 3            Ref Temp (Deg. C) Loc [ Temp_int  ]  
  6: 4            Loc [ Temp_Ext  ]  
  7: 1.0          Mult  
  8: 0.0          Offset  
;-----
```

```
; CONTROLE DU SIMULATEUR DE PLUIE (VALVES)
```

```
; Permet le controle des valves lorsque le FLAG 1 est high  
; Entre la 540 iem et la 960 iem minute de la journee  
;-----
```

```
5: If time is (P92)  
  1: 540          Minutes (Seconds --) into a  
  2: 1440         Interval (same units as above)  
  3: 11           Set Flag 1 High
```

```

6:  If time is (P92)
  1: 960      Minutes (Seconds --) into a
  2: 1440     Interval (same units as above)
  3: 21       Set Flag 1 Low

7:  If Flag/Port (P91)
  1: 11       Do if Flag 1 is High
  2: 30       Then Do

; ACTIVE LE RELAIS BRANCHE AU PORT No.8
8:  If time is (P92)
  1: 0        Minutes (Seconds --) into a
  2: 15       Interval (same units as above)
  3: 48       Set Port 8 High

9:  Z=F (P30)
  1: 1        F
  2: 0        Exponent of 10
  3: 5        Z Loc [ Valve      ]

;+++++
; ENREGISTRE LES HEURES D'OUVERTURE DE LA VALVE

10: Do (P86)
  1: 10       Set Output Flag High (Flag 0)

11: Set Active Storage Area (P80)
  1: 1        Final Storage Area 1
  2: 2        Array ID

12: Real Time (P77)
  1: 111      Day,Hour/Minute,Seconds (midnight = 0000)

13: Sample (P70)
  1: 1        Reps
  2: 5        Loc [ Valve      ]

14: Do (P86)
  1: 20       Set Output Flag Low (Flag 0)

;+++++

15: Excitation with Delay (P22)
  1: 1        Ex Channel
  2: 0        Delay W/Ex (units = 0.01 sec)
  3: 3000     Delay After Ex (units = 0.01 sec)
  4: 0000     mV Excitation

16: Do (P86)
  1: 58       Set Port 8 Low

```

```

17:  Z=F (P30)
    1: 0      F
    2: 0      Exponent of 10
    3: 5      Z Loc [ Valve      ]

;+++++
; ENREGISTRE LES HEURES DE FERMETURE DE LA VALVE

18:  Do (P86)
    1: 10     Set Output Flag High (Flag 0)

19:  Set Active Storage Area (P80)
    1: 1      Final Storage Area 1
    2: 2      Array ID

20:  Real Time (P77)
    1: 111    Day,Hour/Minute,Seconds (midnight = 0000)

21:  Sample (P70)
    1: 1      Reps
    2: 5      Loc [ Valve      ]

22:  Do (P86)
    1: 20     Set Output Flag Low (Flag 0)

;+++++

23:  End (P95)

;-----
;MESURE "La" AVEC LE TDR100
;-----

24:  TDR100 Measurement (P119)
    1: 0      SDM Address
    2: 0      La/L for Water Content
    3: 3006   MMMP Mux & Probe Selection
    4: 32     Waveform Averaging
    5: 1      Vp
    6: 251    Points
    7: 12.5   Cable Length (meters)
    8: 4      Window Length (meters)
    9: 1      Probe Length (meters)
   10: 0.0    Probe Offset (meters)
   11: 6      Loc [ La_1      ]
   12: 1.0    Mult
   13: 0.0    Offset

25:  TDR100 Measurement (P119)
    1: 0      SDM Address
    2: 0      La/L for Water Content

```



```

3: 1106      MMMP Mux & Probe Selection
4: 32        Waveform Averaging
5: 1         Vp
6: 251       Points
7: 14.5      Cable Length (meters)
8: 4         Window Length (meters)
9: 1         Probe Length (meters)
10: 0.0       Probe Offset (meters)
11: 12        Loc [ La_7      ]
12: 1.0       Mult
13: 0.0       Offset

```

```

26: TDR100 Measurement (P119)
1: 0         SDM Address
2: 0         La/L for Water Content
3: 2106      MMMP Mux & Probe Selection
4: 32        Waveform Averaging
5: 1         Vp
6: 251       Points
7: 14.5      Cable Length (meters)
8: 4         Window Length (meters)
9: 1         Probe Length (meters)
10: 0         Probe Offset (meters)
11: 18        Loc [ La_13     ]
12: 1.0       Mult
13: 0.0       Offset

```

```

; TRANSFORME "La" EN TENEUR EN EAU
; Dans un premier temps, on corrige les La obtenus avec les tiges
; de teflon pour qu'ils correspondent a des La avec tiges inox
;-----

```

```

27: Beginning of Loop (P87)
1: 0         Delay
2: 18        Loop Count

; La (inox) = 1.3466 * La (tef) - 0.4265
; Puis on soustrait le OffSett 0.157

```

```

28: Z=X*F (P37)
1: 6         -- X Loc [ La_1      ]
2: 1.3466     F
3: 24        -- Z Loc [ TEE_1     ]

; 0.5835 = 0.4265 + 0.157

```

```

29: Z=X+F (P34)
1: 24        -- X Loc [ TEE_1     ]
2: -0.5835    F
3: 24        -- Z Loc [ TEE_1     ]

```

```

;Racine carre Ka = La/L, ou L=0.39
;Racine carre Ka = La * (1/L) = La * (1/0.39) = La * 2.5641

```

```

30:  Z=X*F (P37)
   1: 24      -- X Loc [ TEE_1      ]
   2: 2.56410  F
   3: 24      -- Z Loc [ TEE_1      ]

31:  Z=X*Y (P36)
   1: 24      -- X Loc [ TEE_1      ]
   2: 24      -- Y Loc [ TEE_1      ]
   3: 24      -- Z Loc [ TEE_1      ]

; MULTIPLIE Ka PAR 0.1 POUR UTILISER L'EQUATION POLUNOMIALE

32:  Z=X*F (P37)
   1: 24      -- X Loc [ TEE_1      ]
   2: 0.1      F
   3: 24      -- Z Loc [ TEE_1      ]

; ON APPLIQUE L'EQUATION DE TOPP DU 3iem ORDRE

33:  Polynomial (P55)
   1: 1      Reprs
   2: 24      -- X Loc [ TEE_1      ]
   3: 24      -- F(X) Loc [ TEE_1      ]
   4: -0.053  C0
   5: 0.292   C1
   6: -0.055  C2
   7: 0.0043  C3
   8: 0.0      C4
   9: 0.0      C5

34:  End (P95)

; ENREGISTRE LES PARAMETRES
;-----

;Ici les donnees sont enregistrees aux trente minutes

35:  If time is (P92)
   1: 0      Minutes (Seconds --) into a
   2: 30      Interval (same units as above)
   3: 10      Set Output Flag High (Flag 0)

36:  Set Active Storage Area (P80)
   1: 1      Final Storage Area 1
   2: 1      Array ID

37:  Real Time (P77)
   1: 1110    Year,Day,Hour/Minute (midnight = 0000)

38:  Sample (P70)
   1: 4      Reprs
   2: 1      -- Loc [ Bat_Volt  ]

```

```

39: Sample (P70)
   1: 36      Repls
   2: 6      -- Loc [ La_1      ]

40: Do (P86)
   1: 20      Set Output Flag Low (Flag 0)
;-----

```

```

*Table 2 Program
  02: 0      Execution Interval (seconds)

```

*Table 3 Subroutines

End Program

```

-Input Locations-
1 Bat_Volt  5 1 0
2 Signature 9 1 0
3 Temp_int  9 1 1
4 Temp_Ext  25 1 1
5 Valve     17 2 4
6 La_1      5 1 1
7 La_2      1 1 0
8 La_3      1 1 0
9 La_4      1 1 0
10 La_5     1 1 0
11 La_6     1 1 0
12 La_7     1 1 1
13 La_8     1 1 0
14 La_9     1 1 0
15 La_10    1 1 0
16 La_11    1 1 0
17 La_12    1 1 0
18 La_13    1 1 1
19 La_14    1 1 0
20 La_15    1 1 0
21 La_16    1 1 0
22 La_17    1 1 0
23 La_18    1 1 0
24 TEE_1    7 7 6
25 TEE_2    11 1 0
26 TEE_3    11 1 0
27 TEE_4    11 1 0
28 TEE_5    11 1 0
29 TEE_6    11 1 0
30 TEE_7    11 1 0
31 TEE_8    11 1 0
32 TEE_9    11 1 0
33 TEE_10   11 1 0
34 TEE_11   11 1 0
35 TEE_12   11 1 0
36 TEE_13   11 1 0
37 TEE_14   11 1 0

```

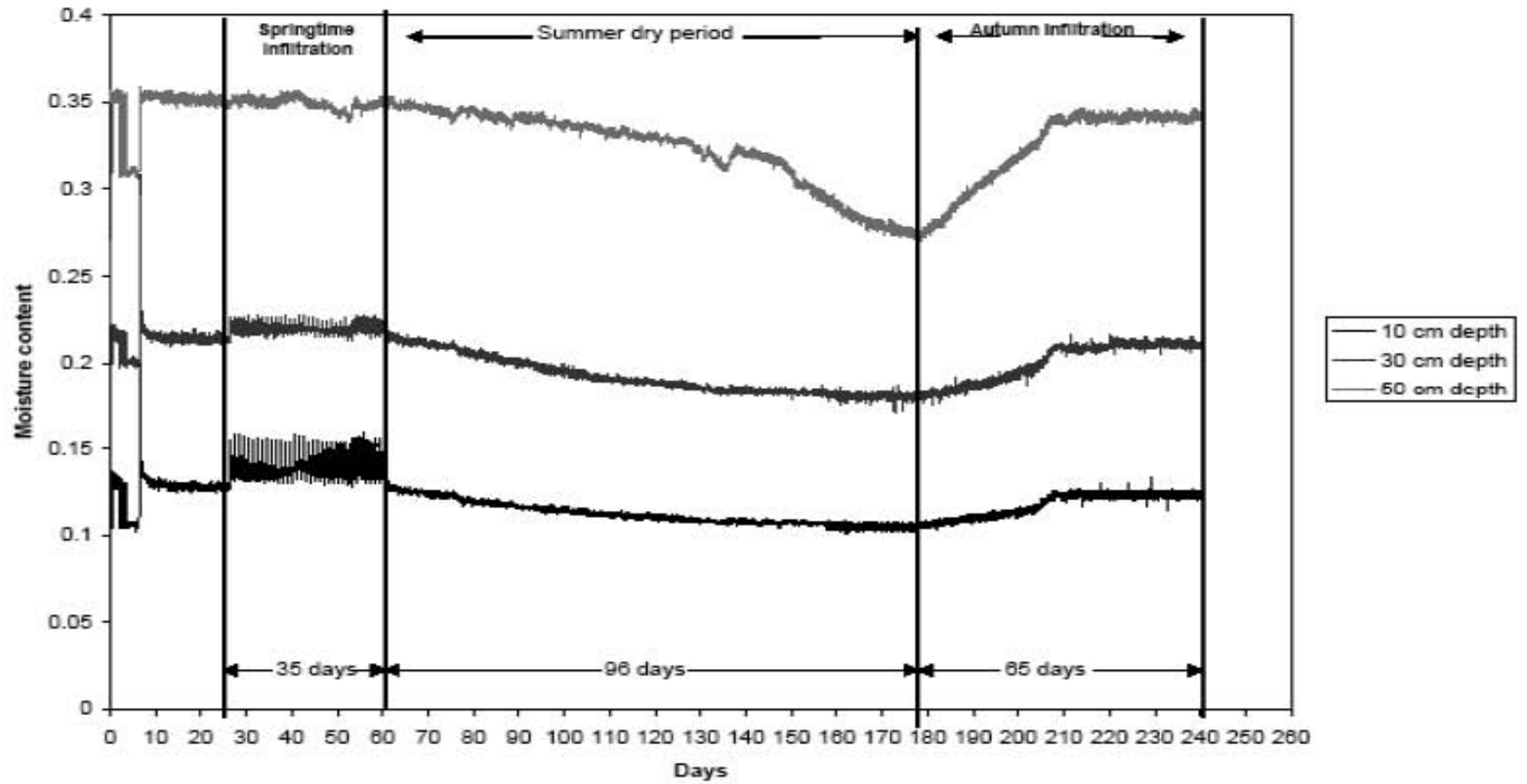
```

38 TEE_15      11 1 0
39 TEE_16      11 1 0
40 TEE_17      11 1 0
41 TEE_18      19 1 0
42 _____  0 0 0
43 _____  0 0 0
44 _____  0 0 0
45 _____  0 0 0
46 _____  0 0 0
-Program Security-
0000
0000
0000
-Mode 4-
-Final Storage Area 2-
0
-CR10X ID-
0
-CR10X Power Up-
3

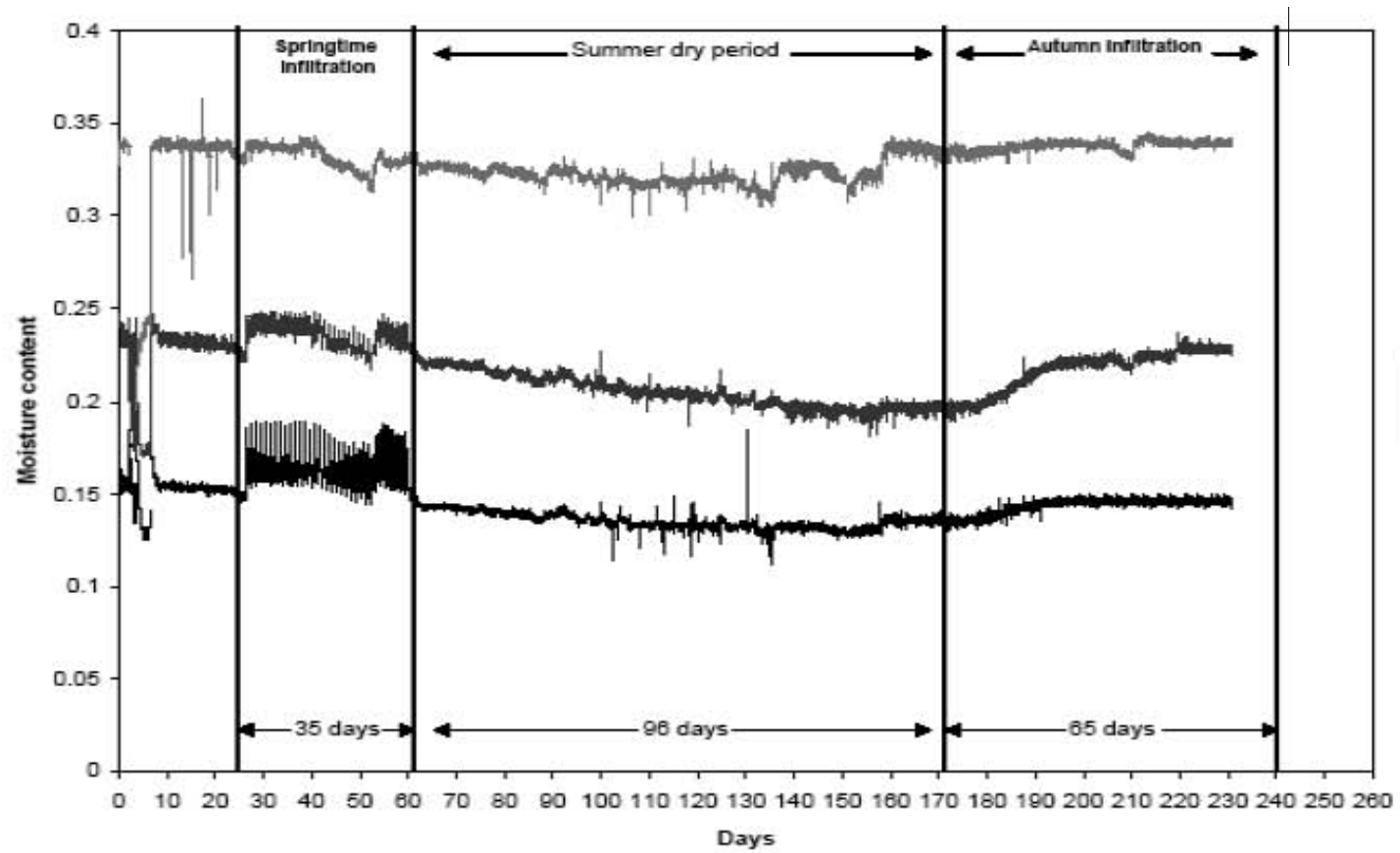
```

APPENDIX 2. COMPLETE TIME DOMAIN REFLECTOMETRY CHARTS

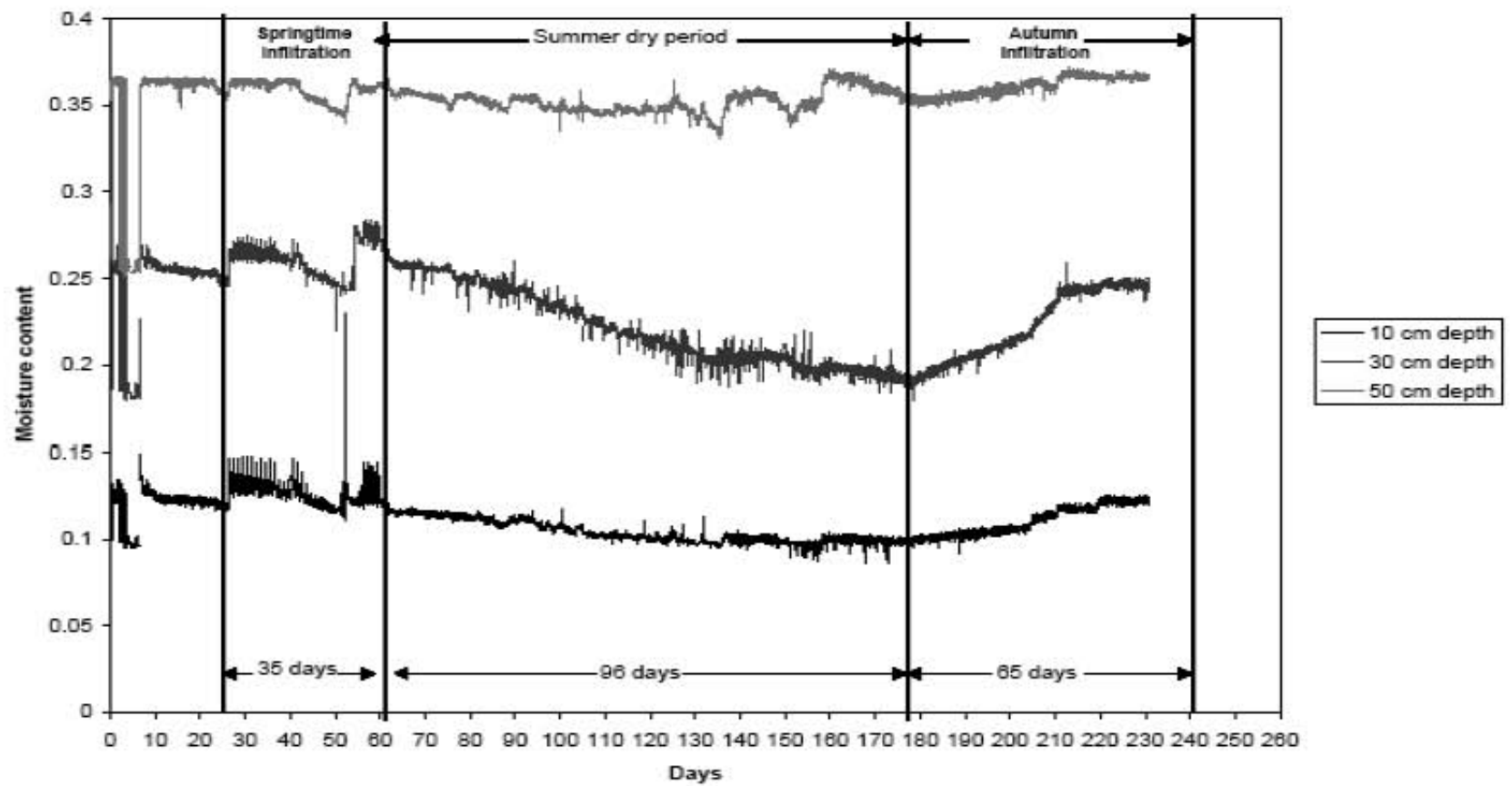
Moisture Content in Column B (Detonation Residue) at different depths



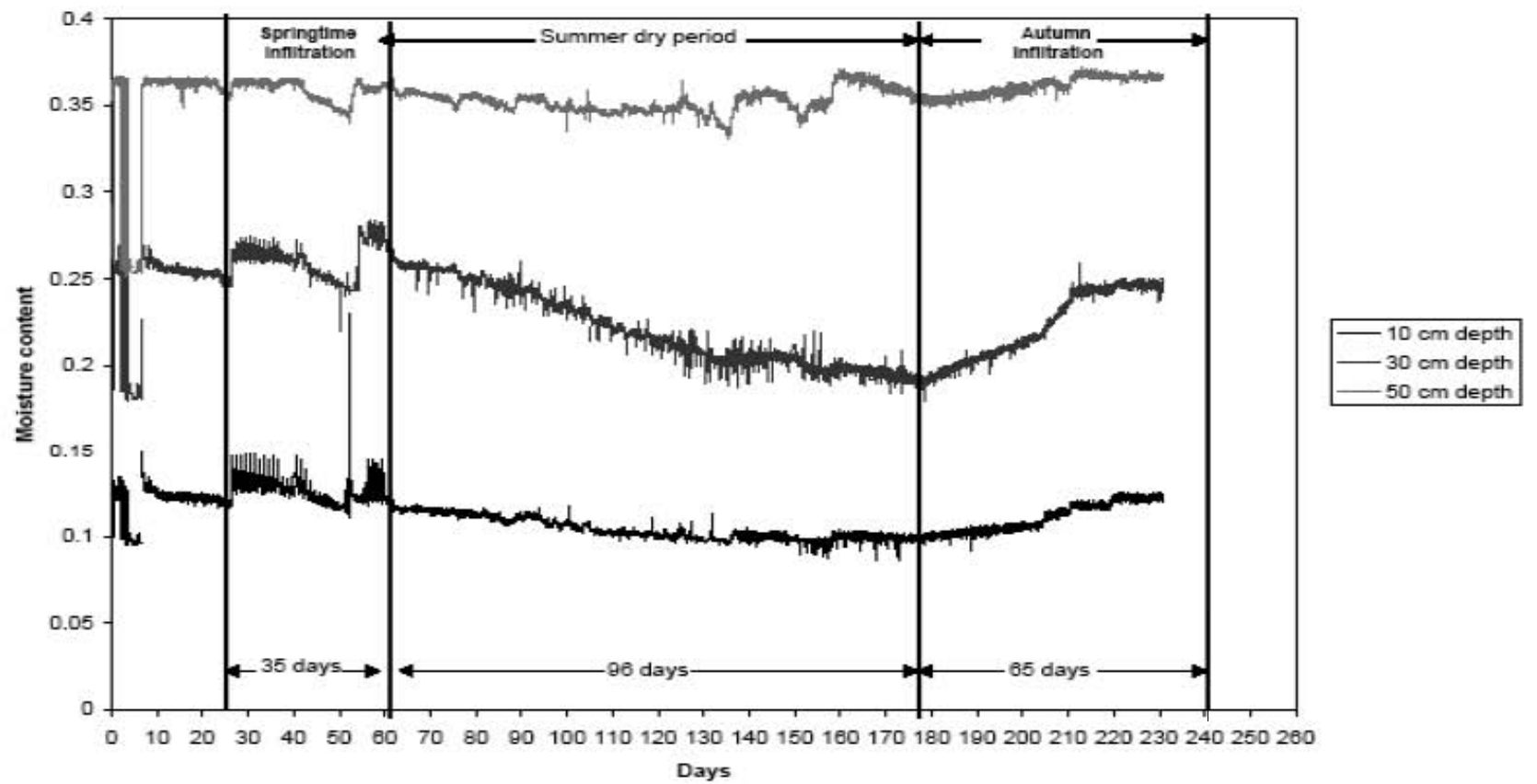
Moisture Content in Column C (Detonation Residue) at different depths



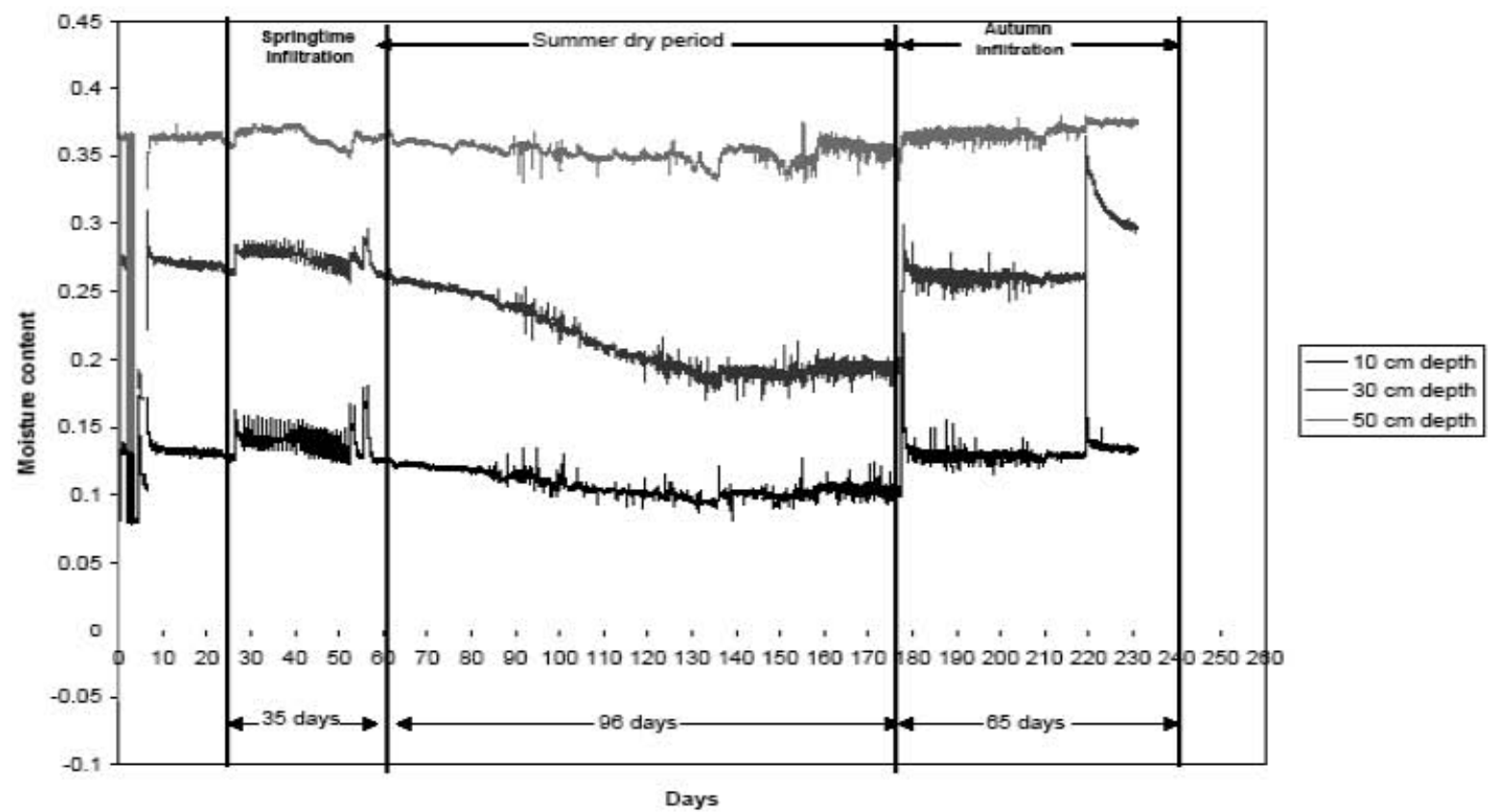
Moisture Content in Column D (Cracked Shell) at different depths



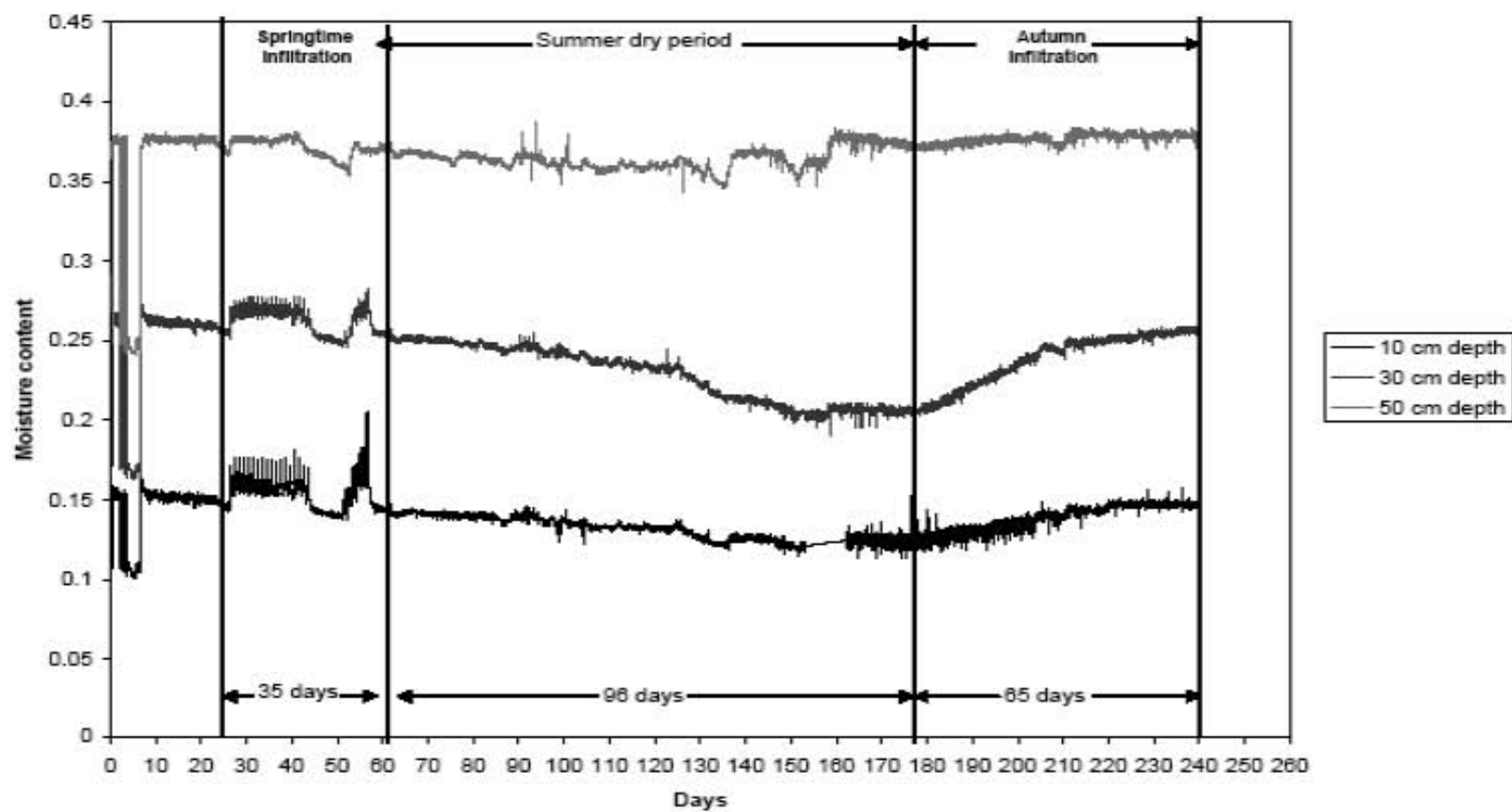
Moisture Content in Column D (Cracked Shell) at different depths



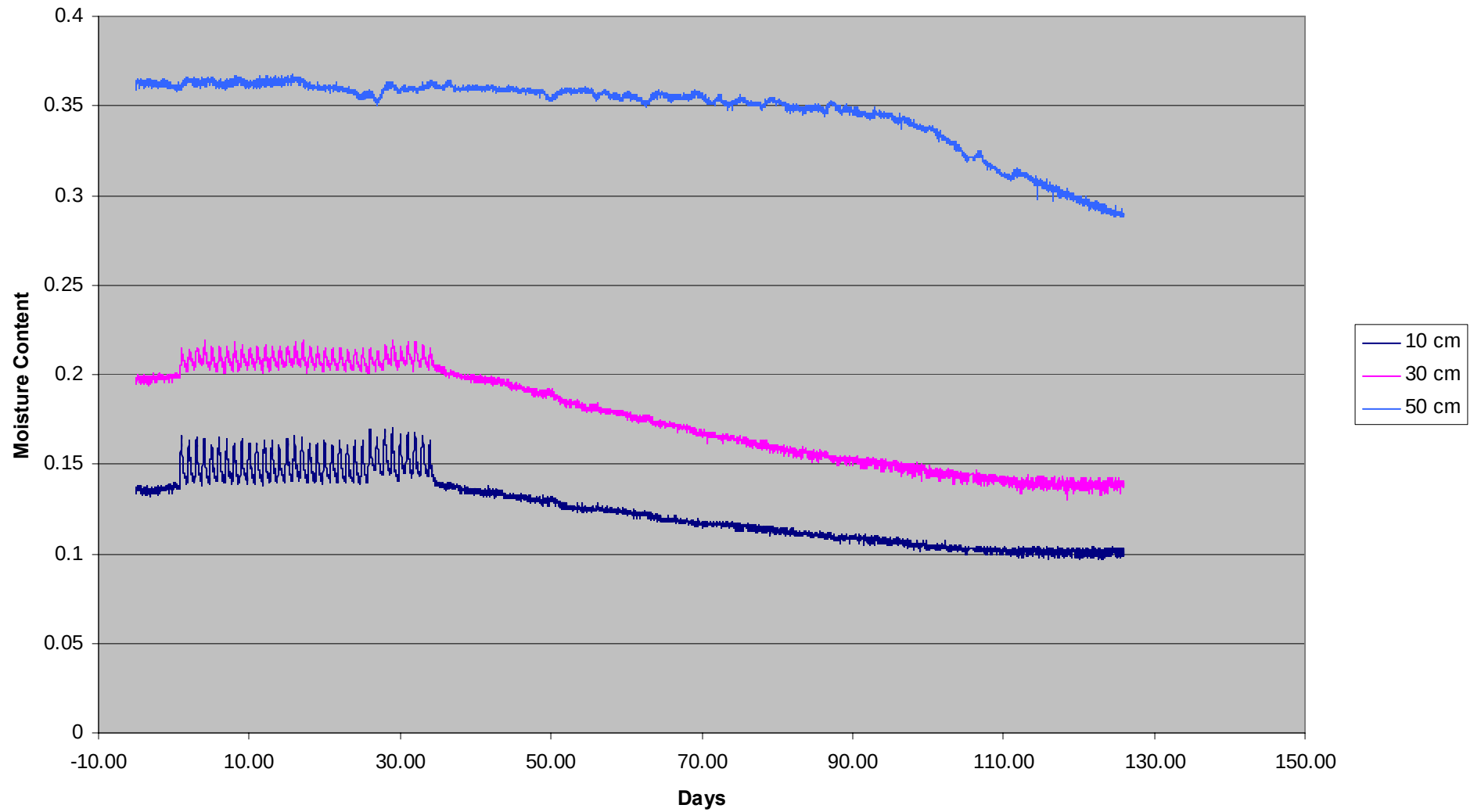
Moisture Content in Column E (Comp B) at different depths



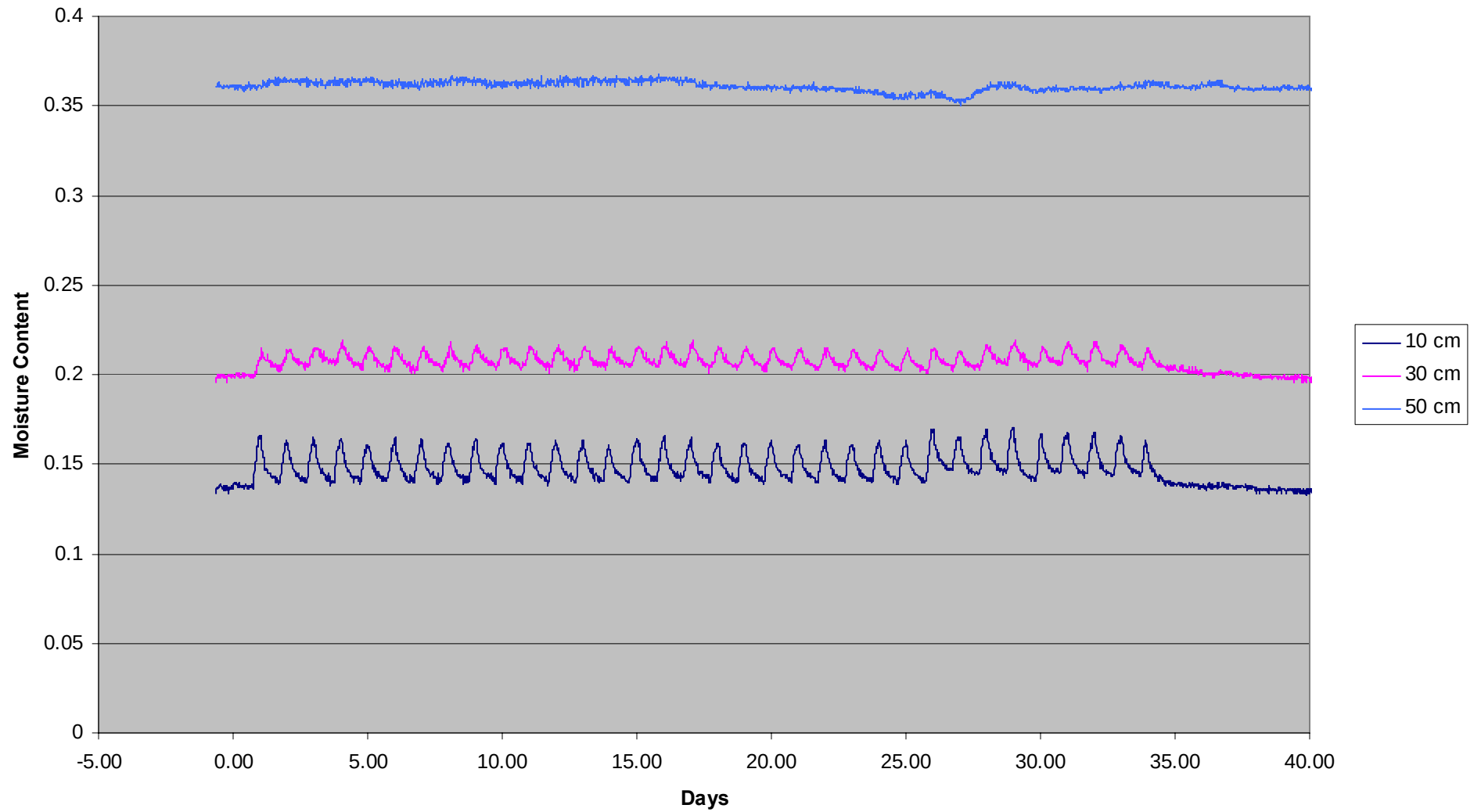
Moisture Content in Column F (Cracked Shell) at different depths



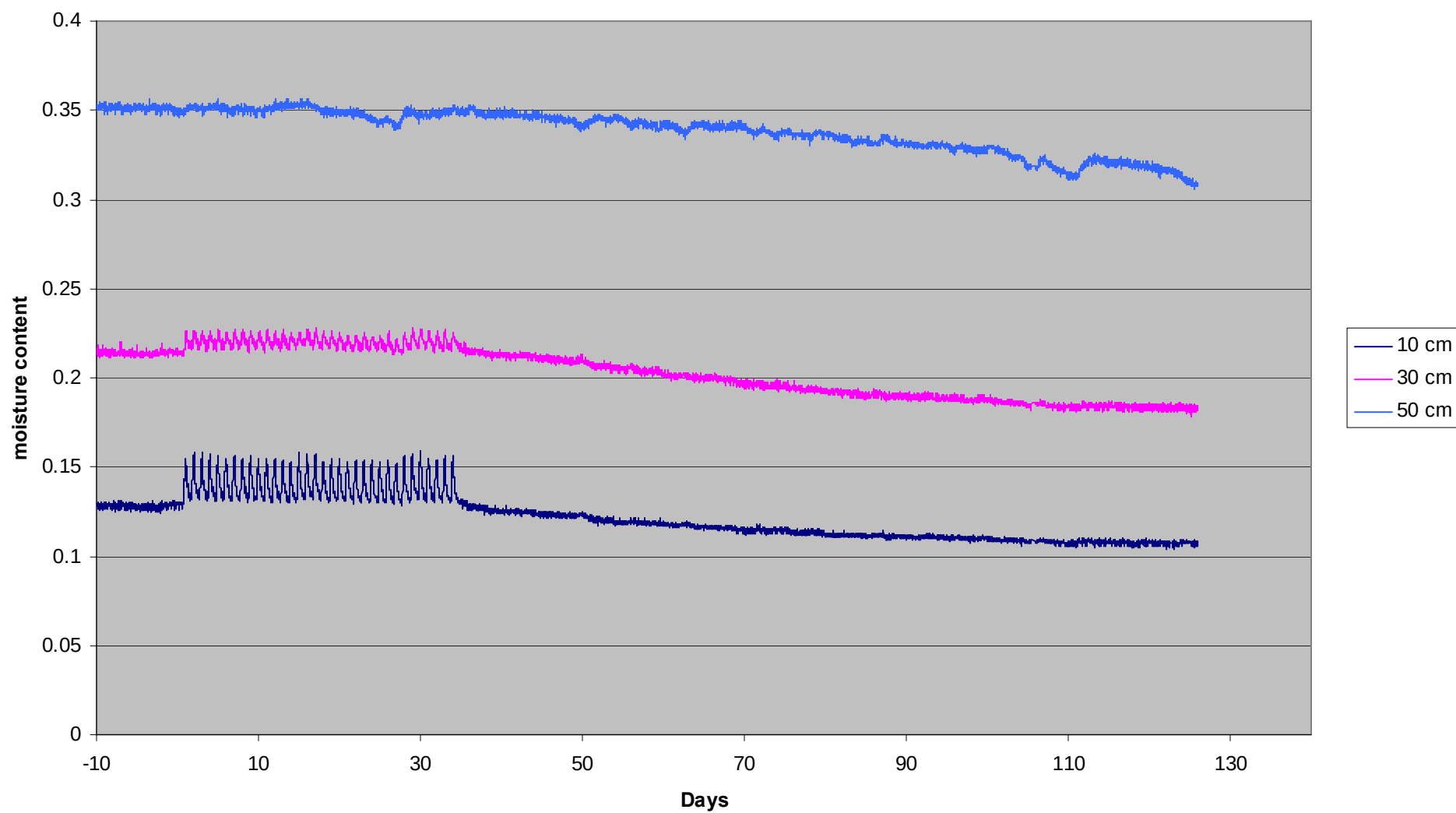
Column A - Springtime infiltration & summer dry period



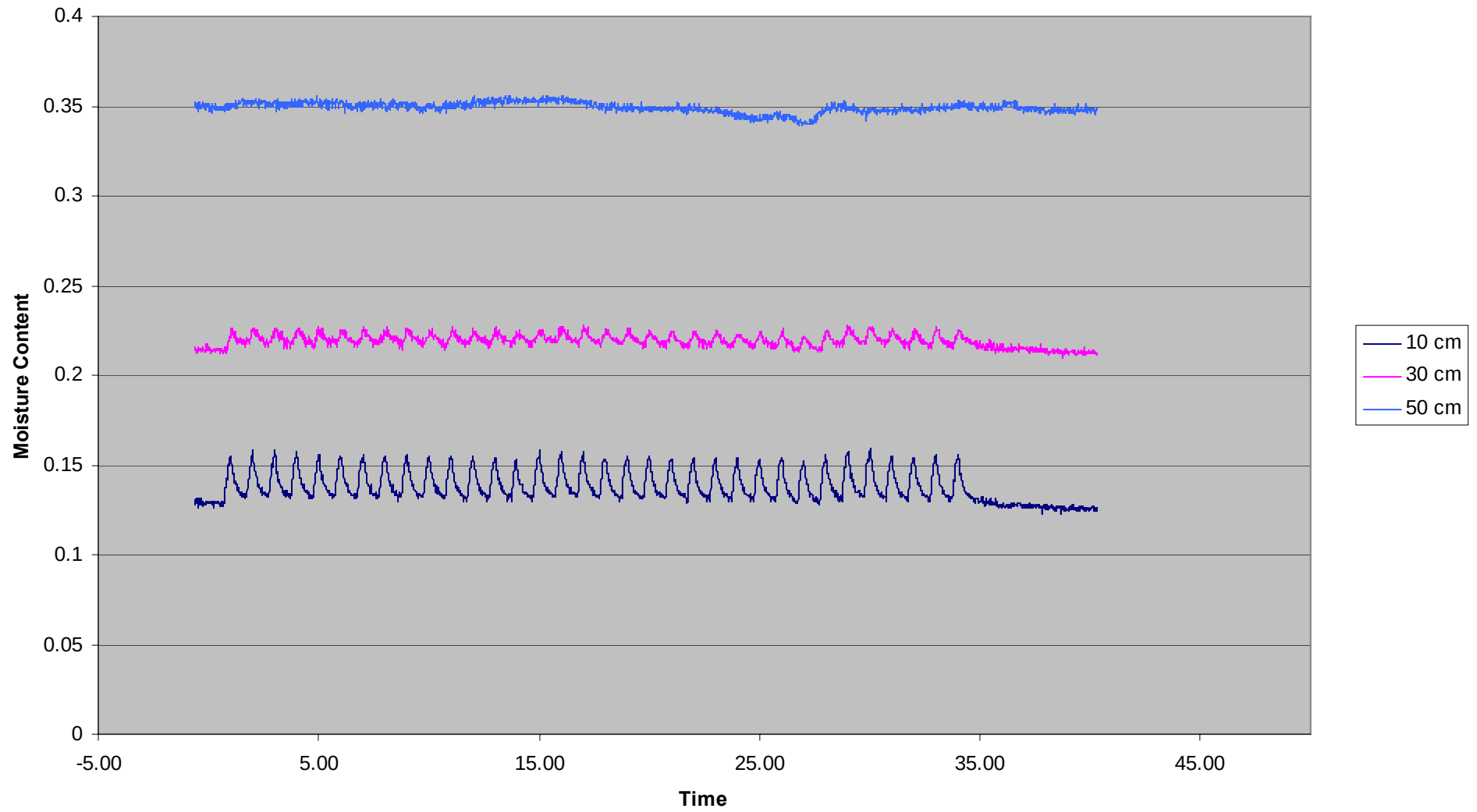
Column A Springtime Infiltration



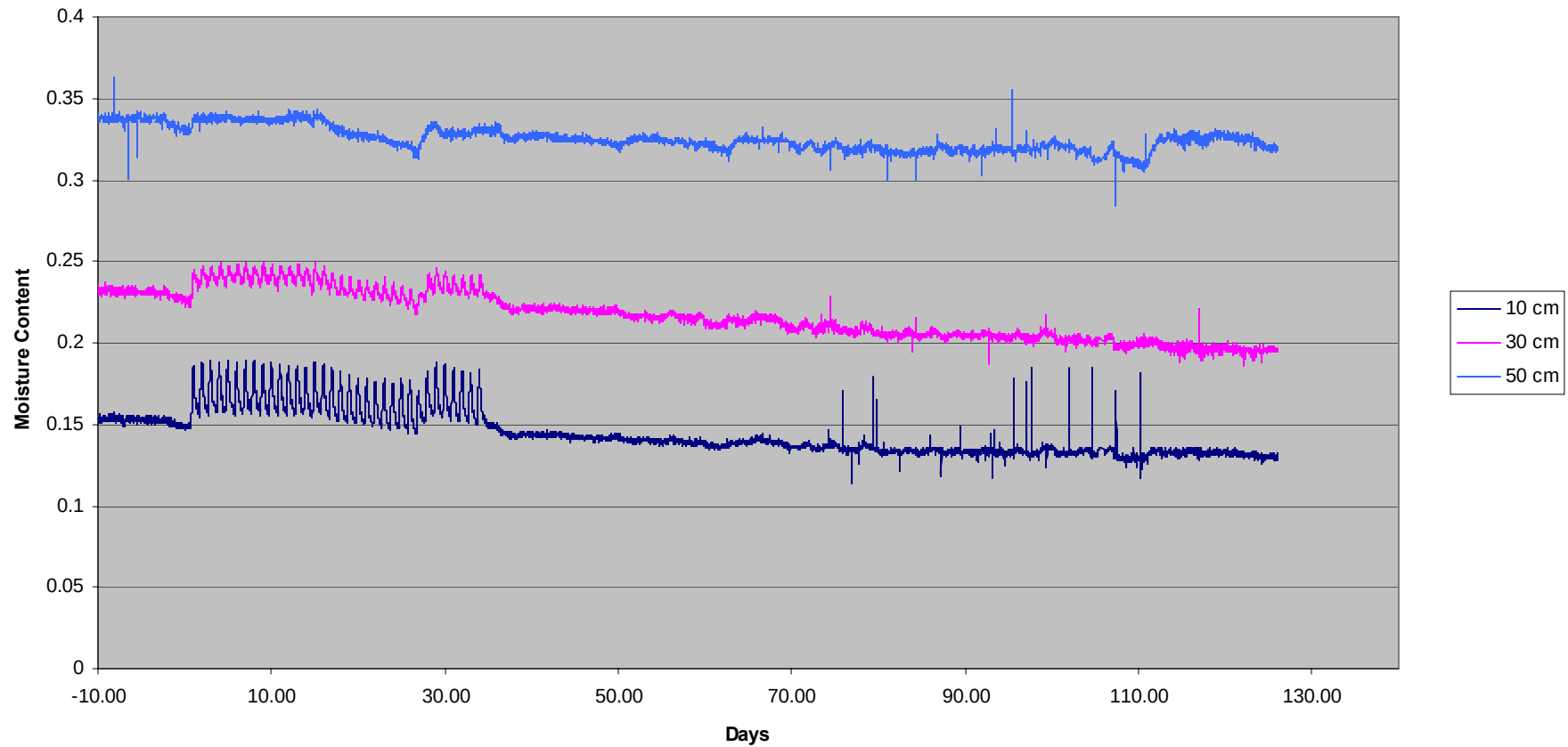
Column B - Springtime infiltration & summer dry period



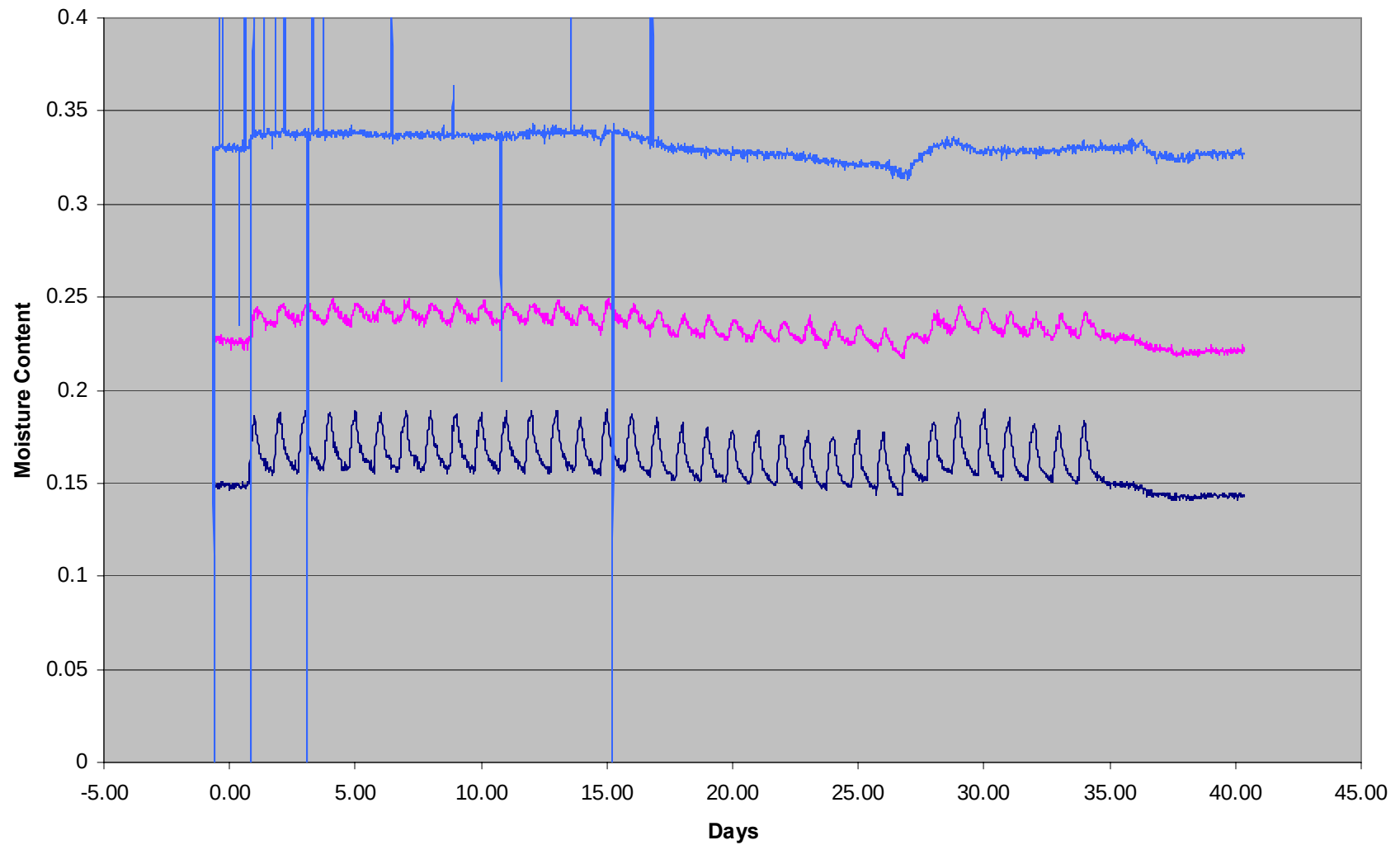
Column B - Springtime infiltration



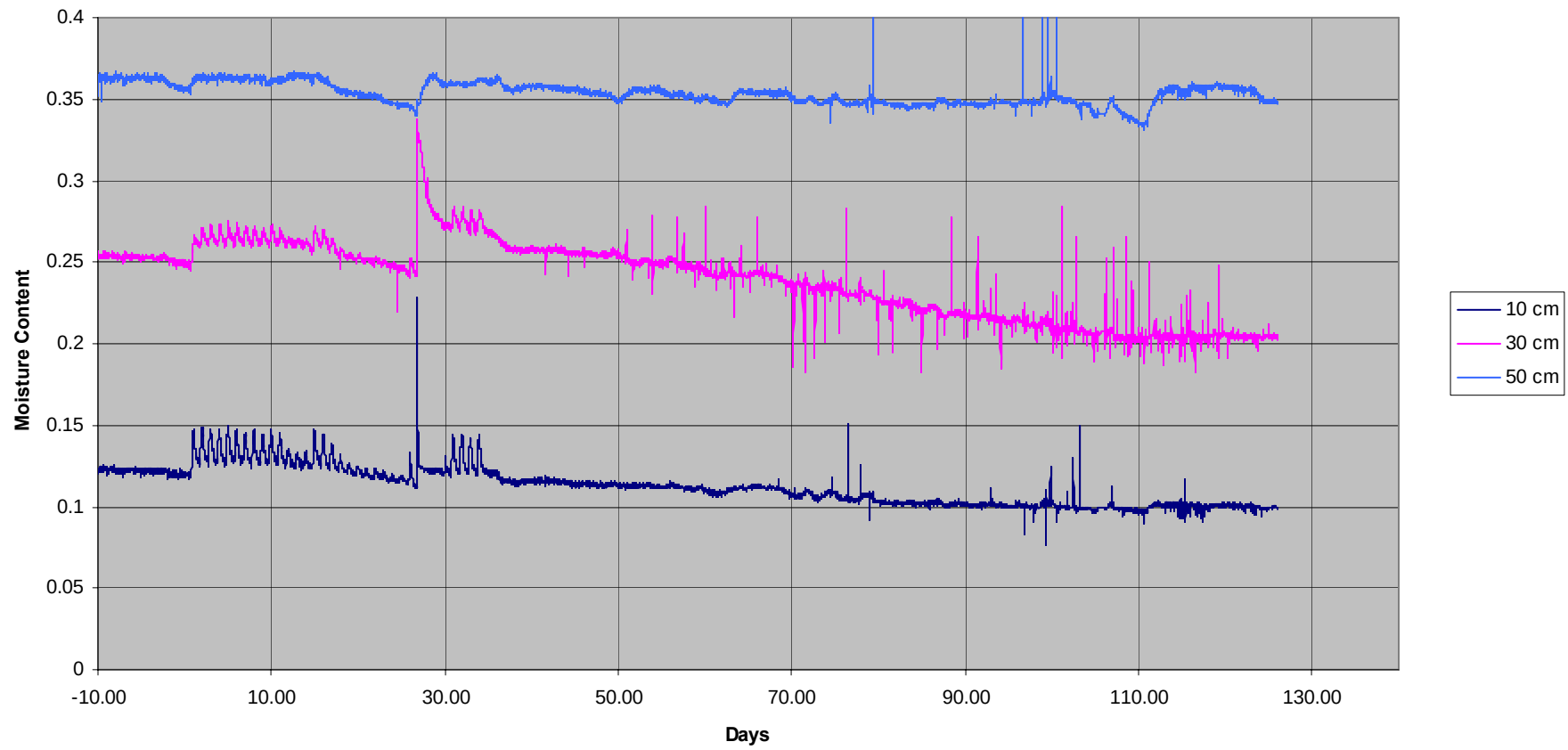
Column C - springtime infiltration & summer dry period



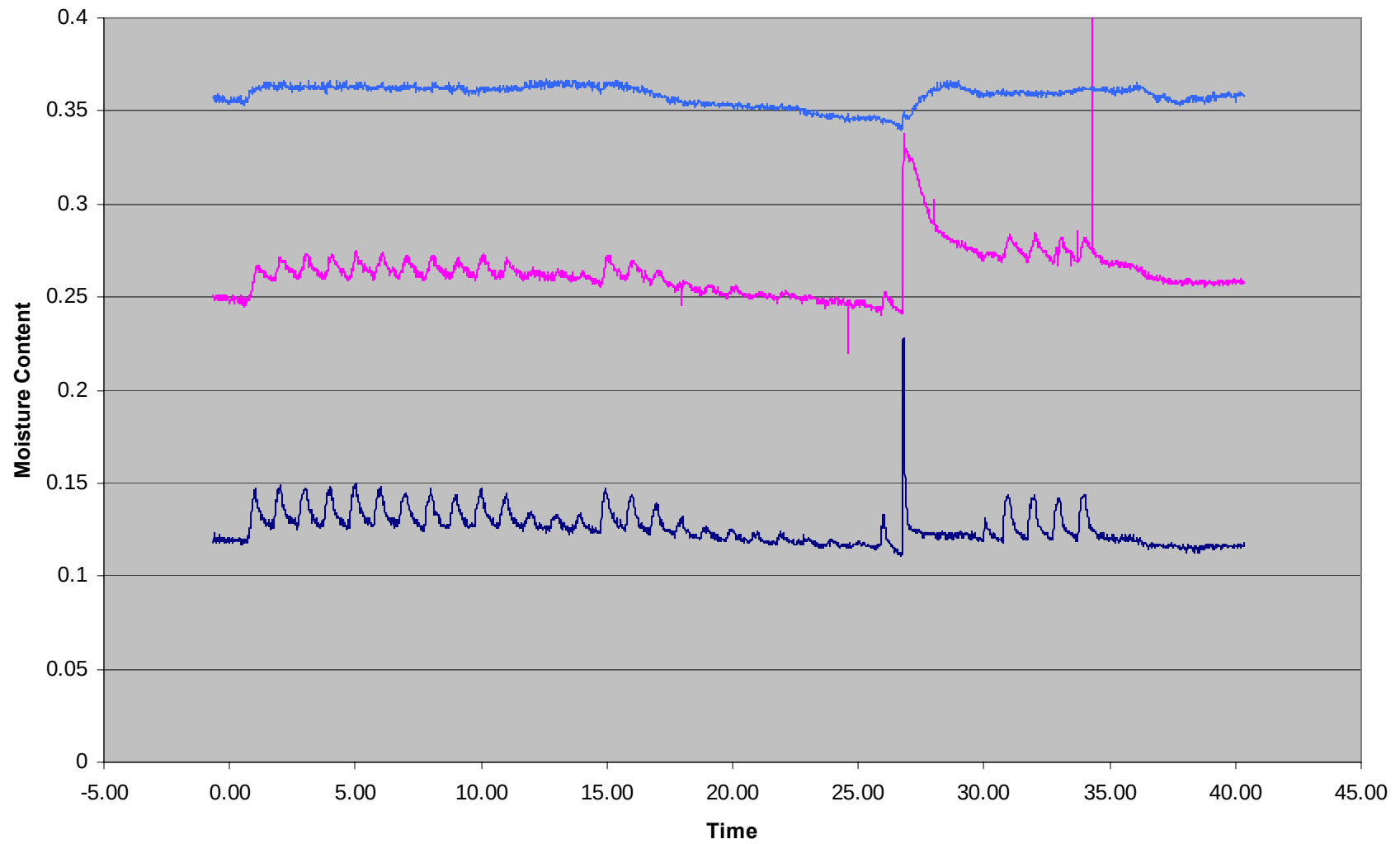
Column C - Springtime infiltration



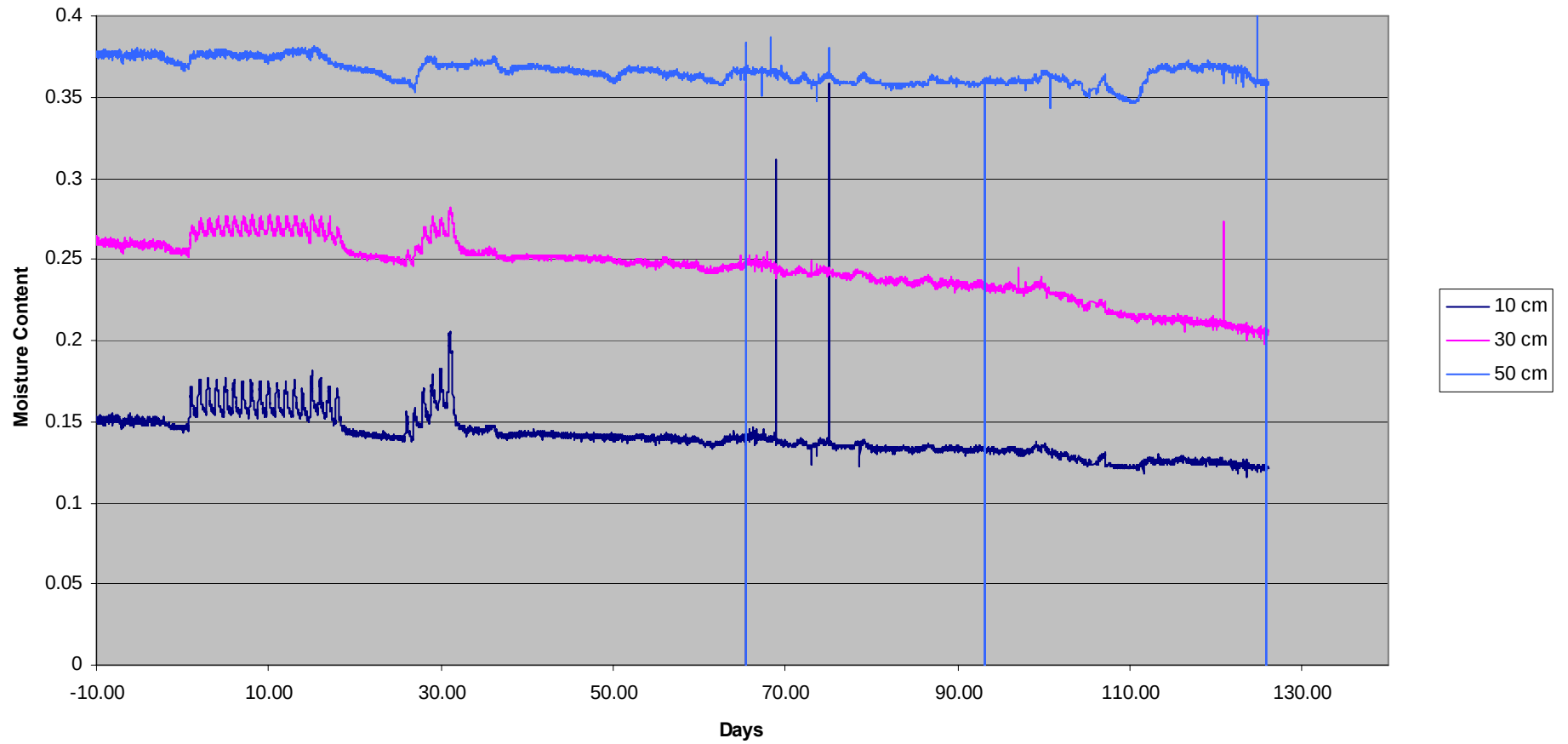
Column D - springtime infiltration & summer dry period



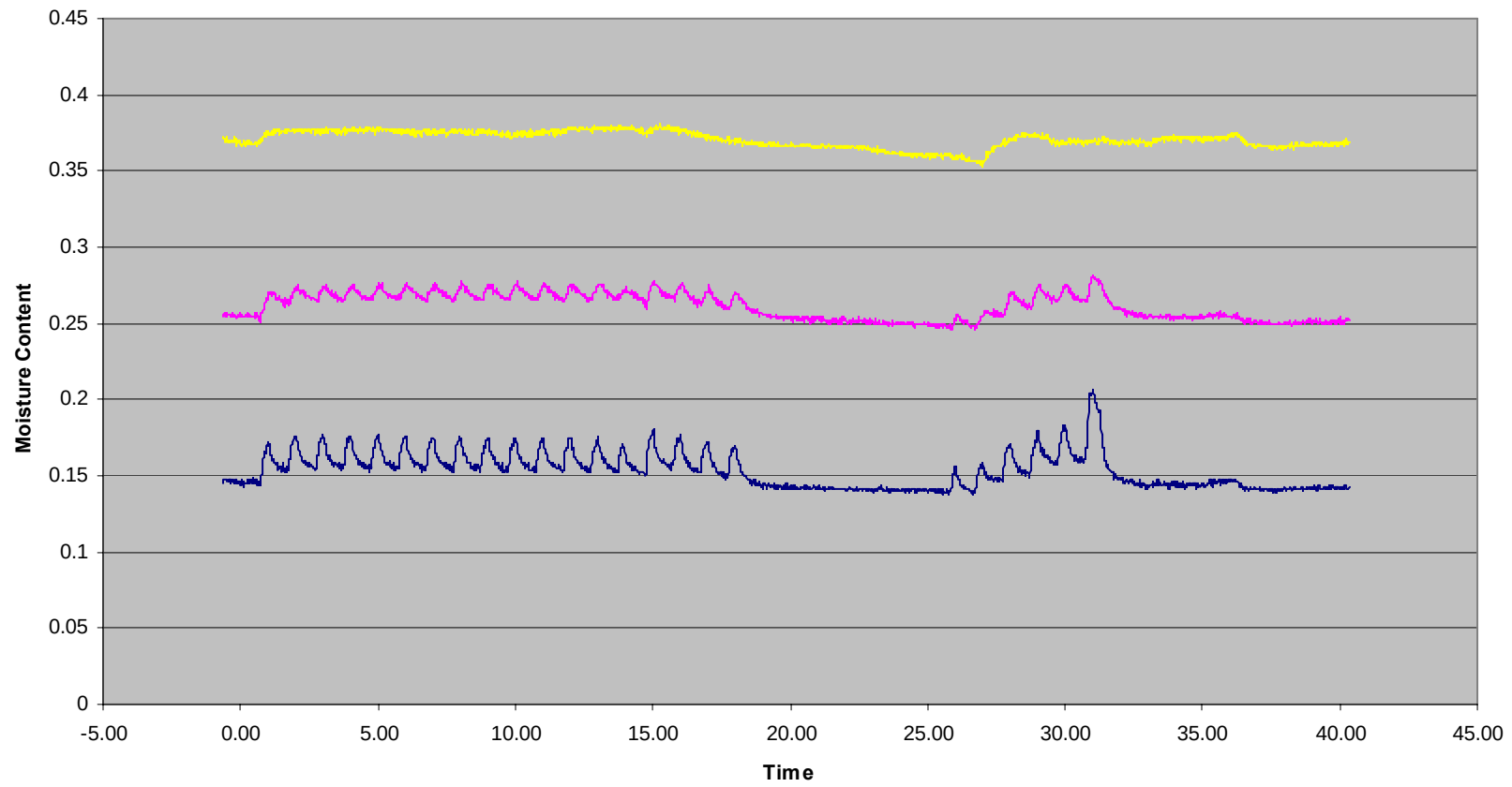
Column D - Springime infiltration



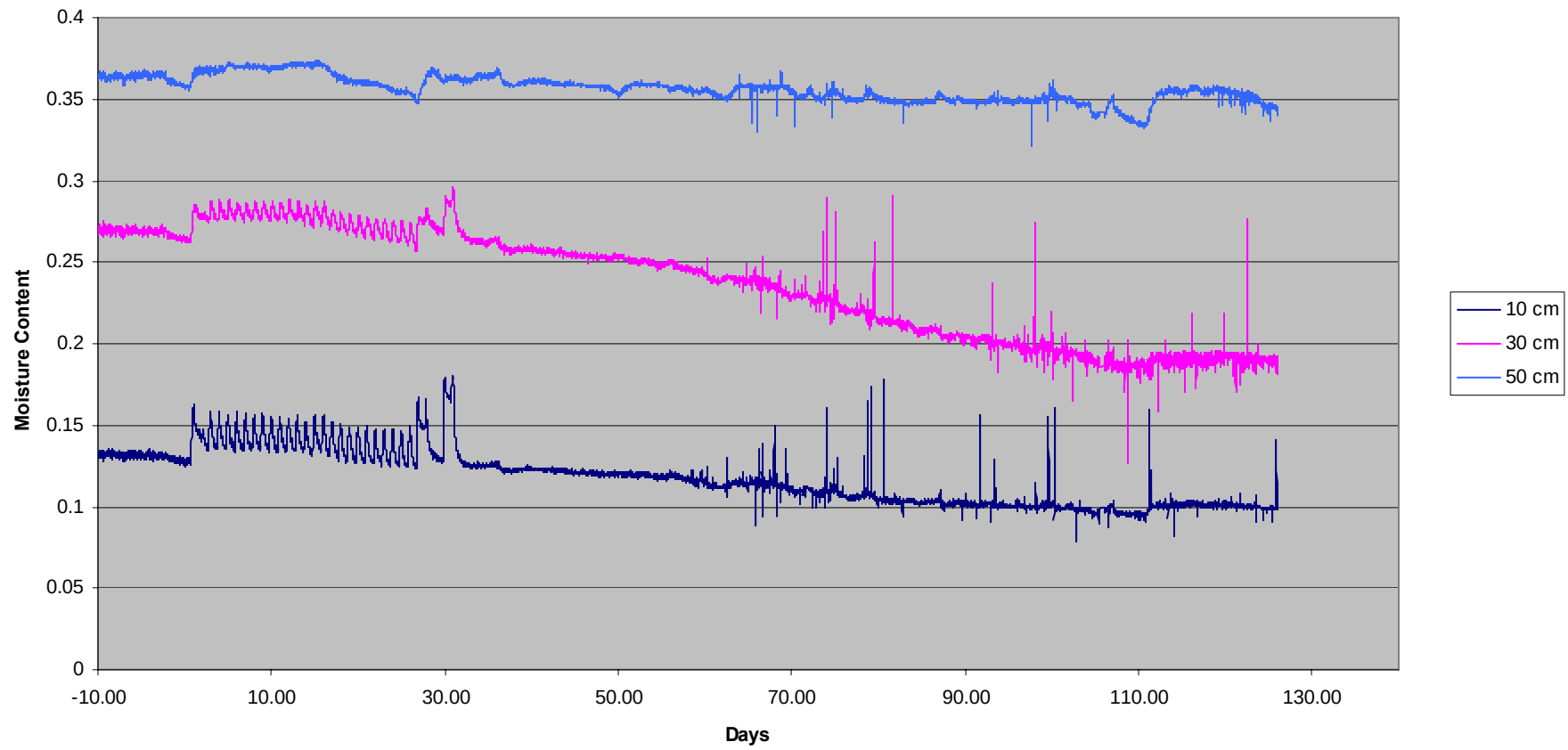
Column E - springtime infiltration & summer dry period



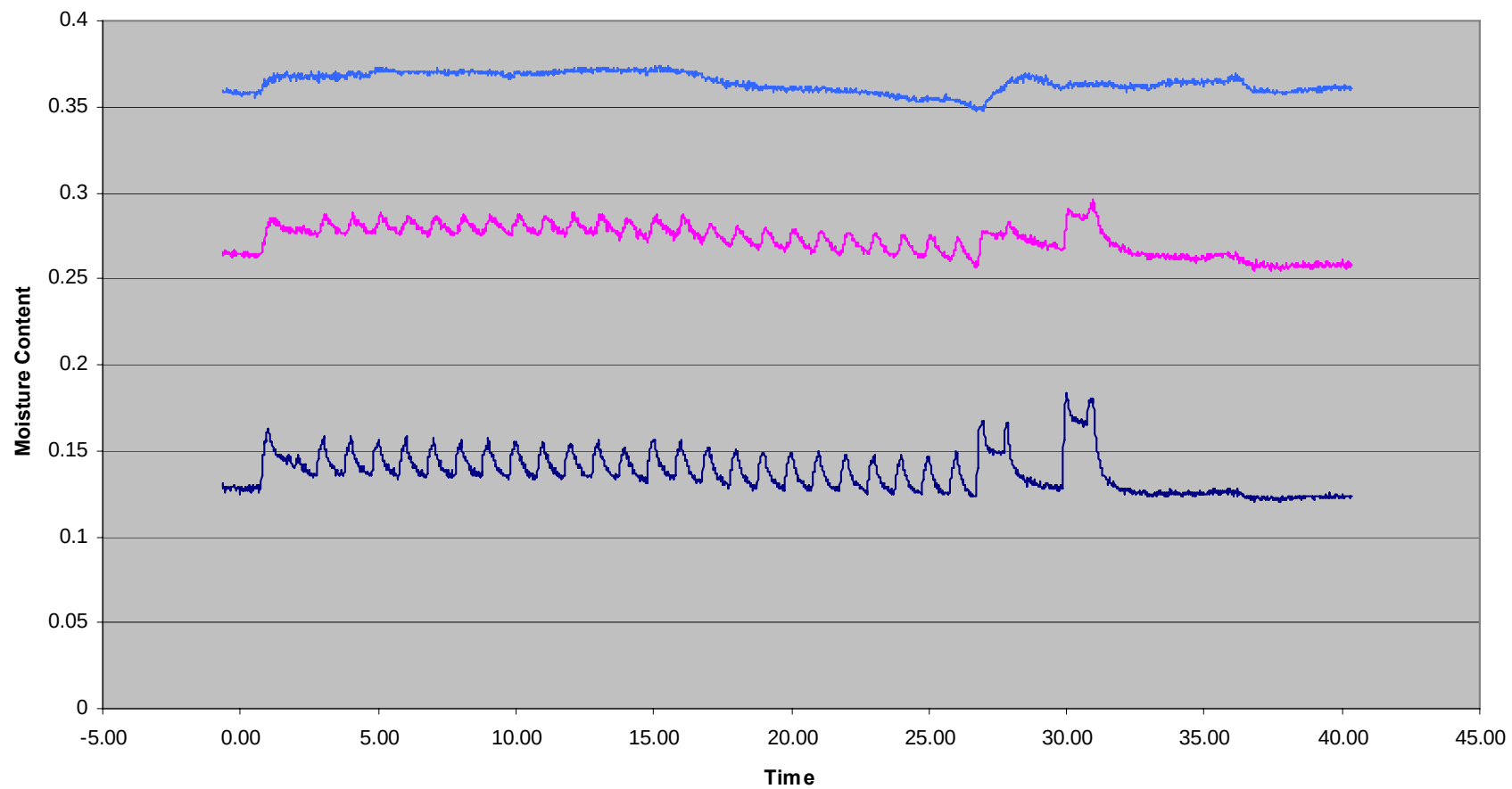
Column E - Springtime infiltration



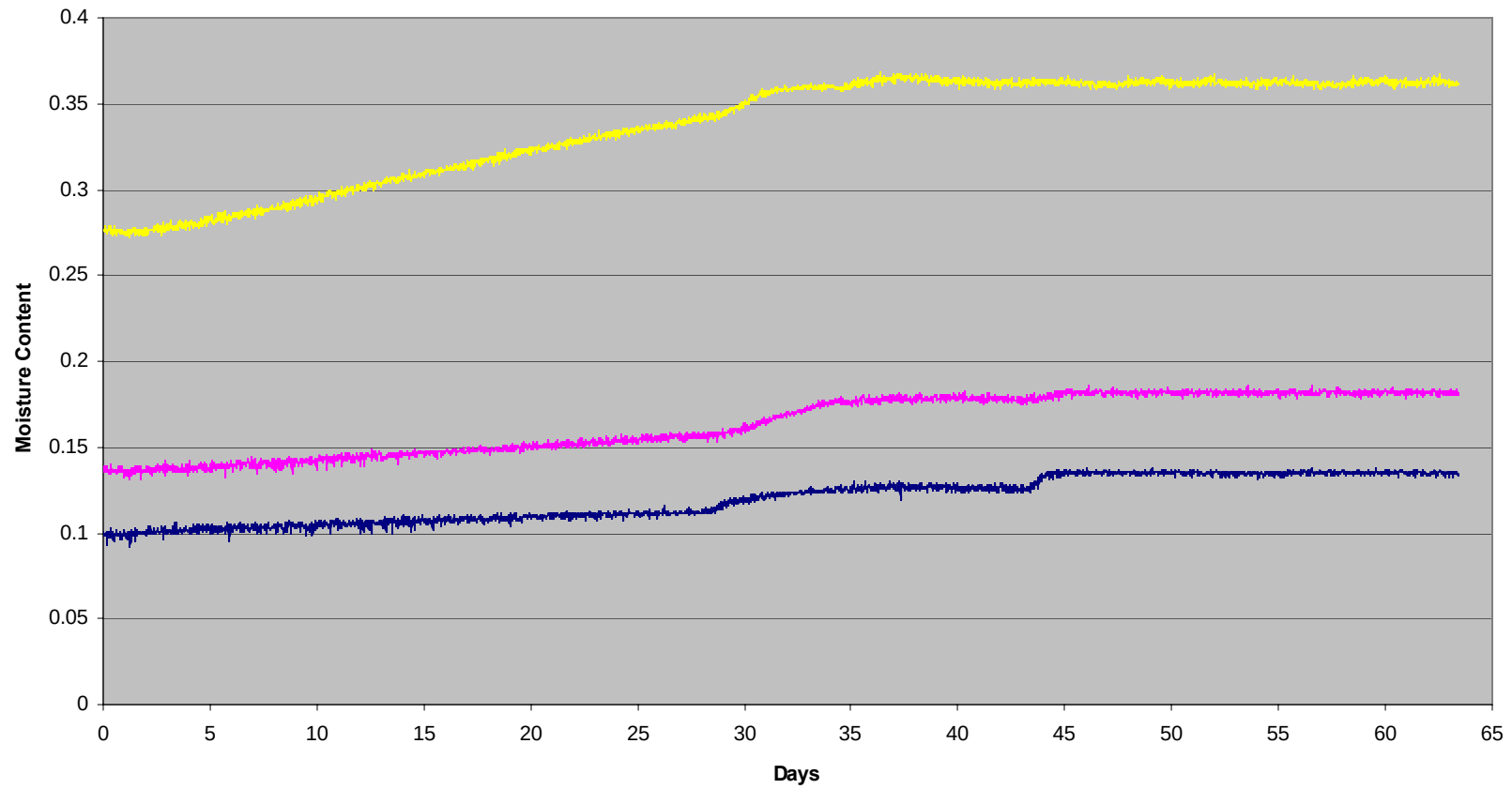
Column F - springtime infiltration & summer dry period



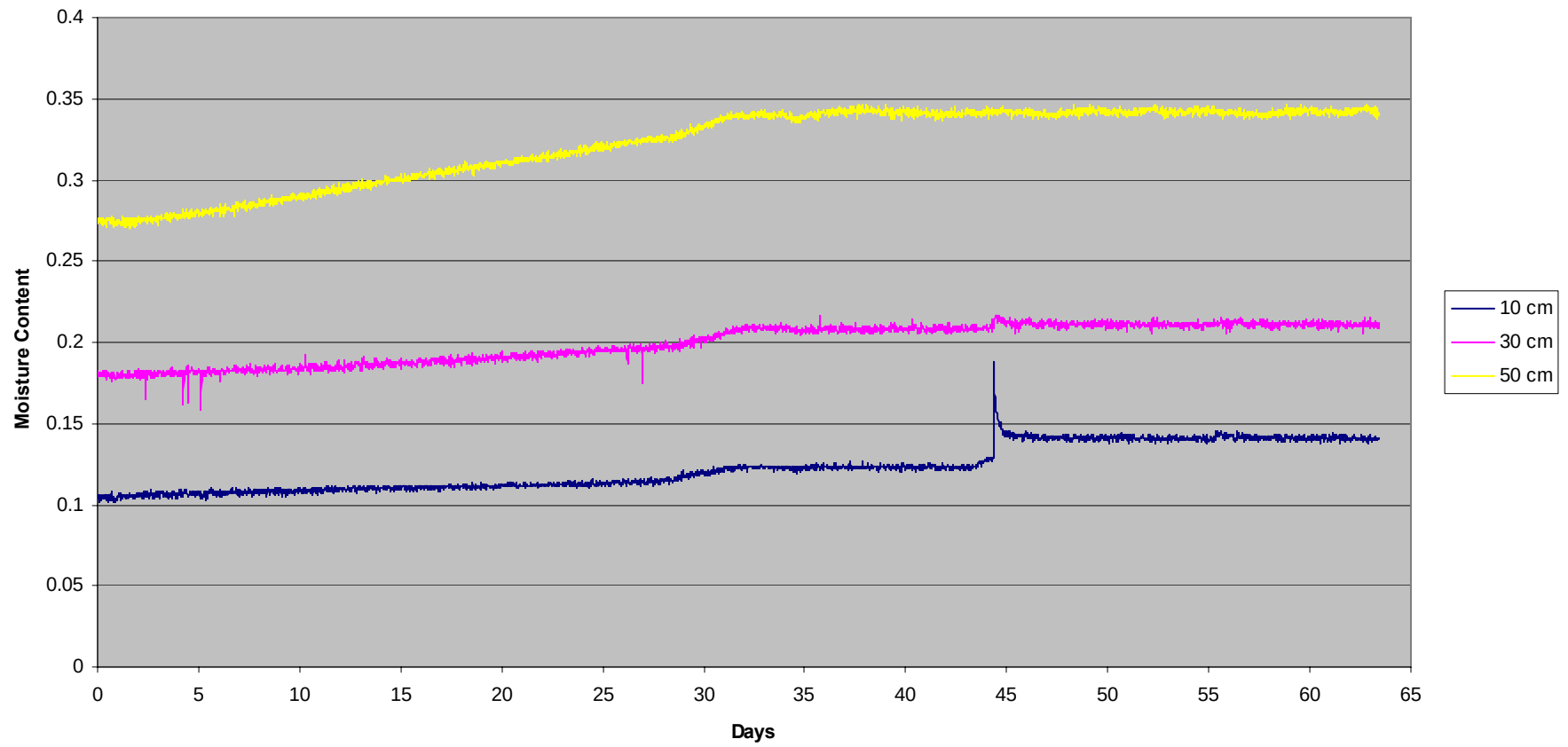
Column F - Springime infiltration



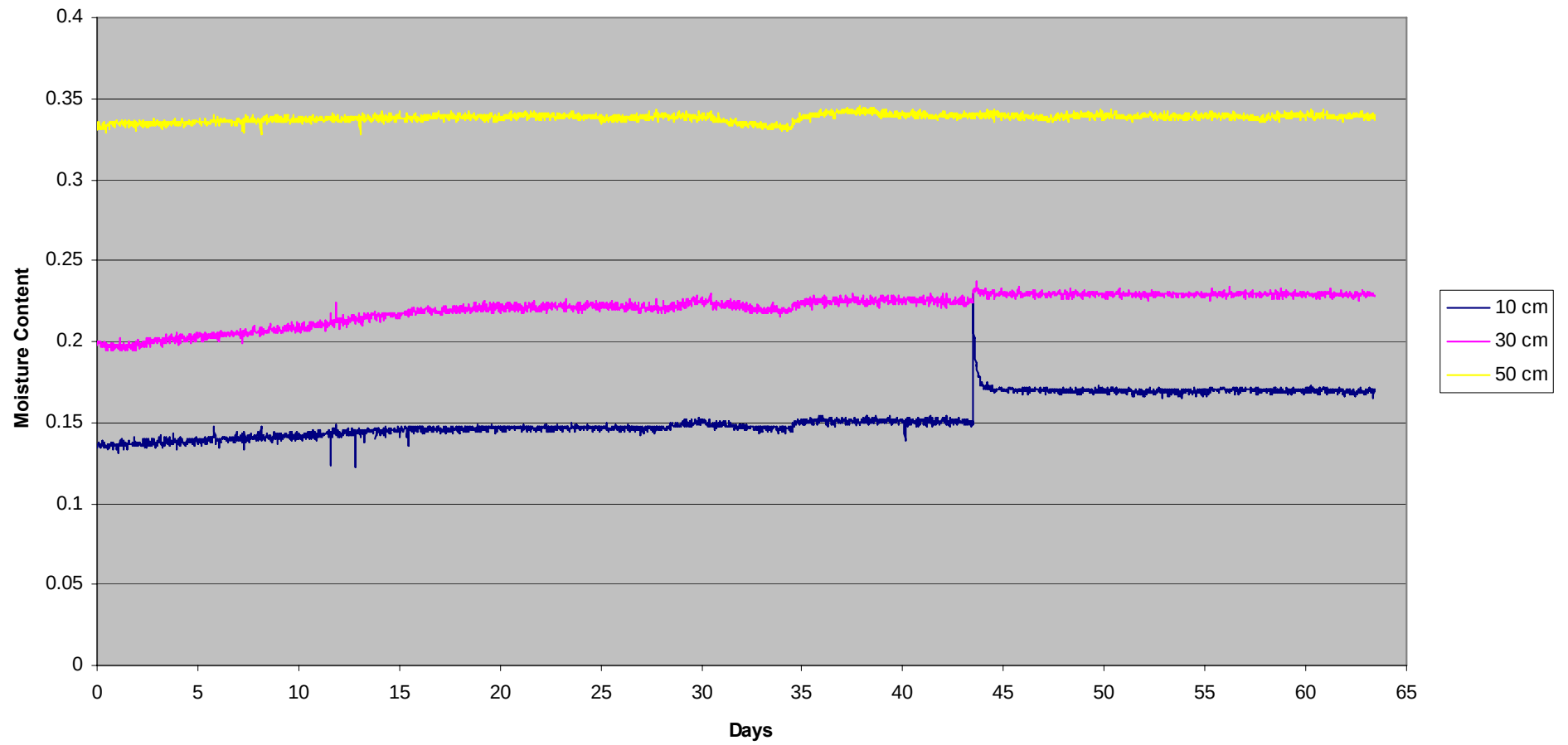
Autumn Infiltration Column A



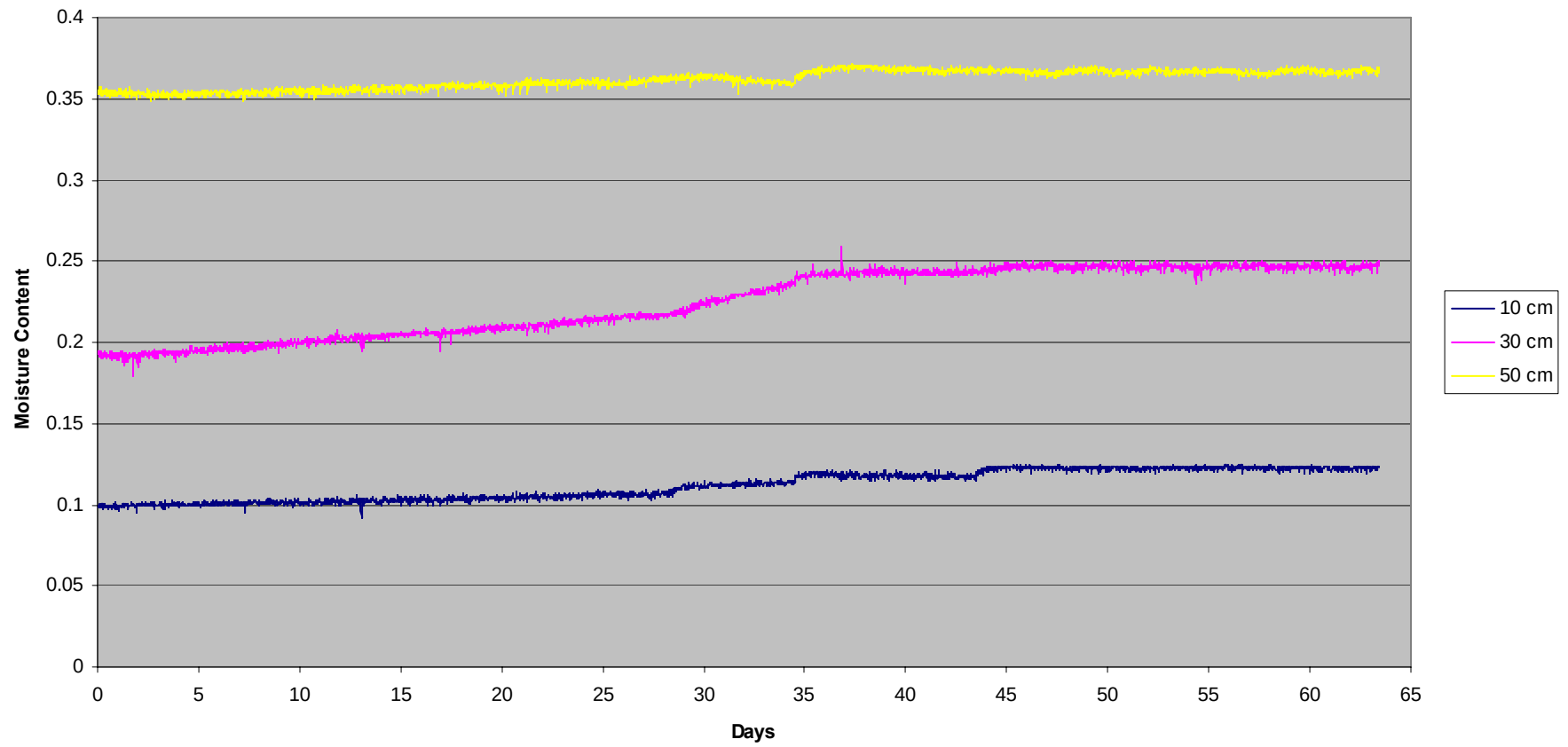
Autumn Infiltration Column B



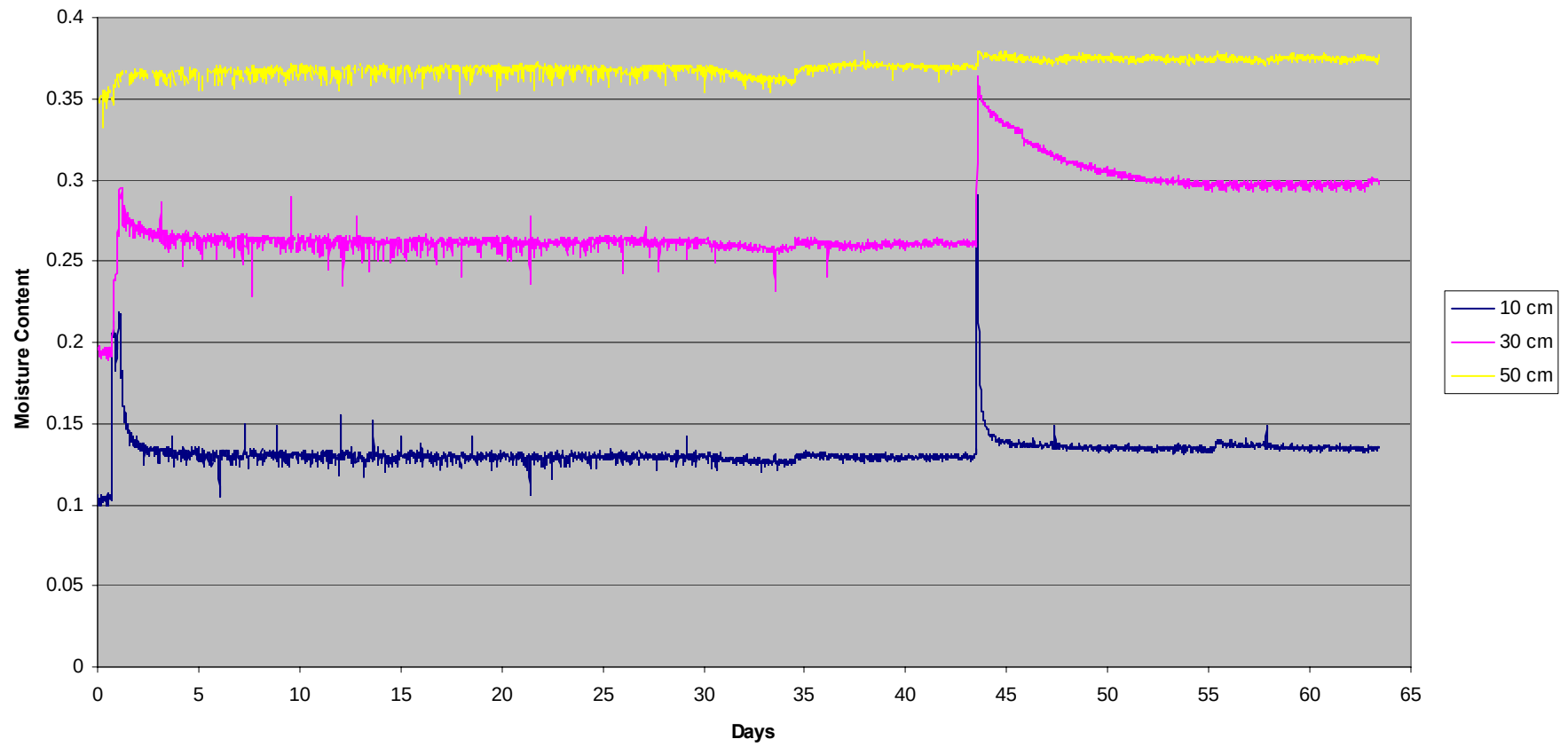
Autumn Infiltration Column C



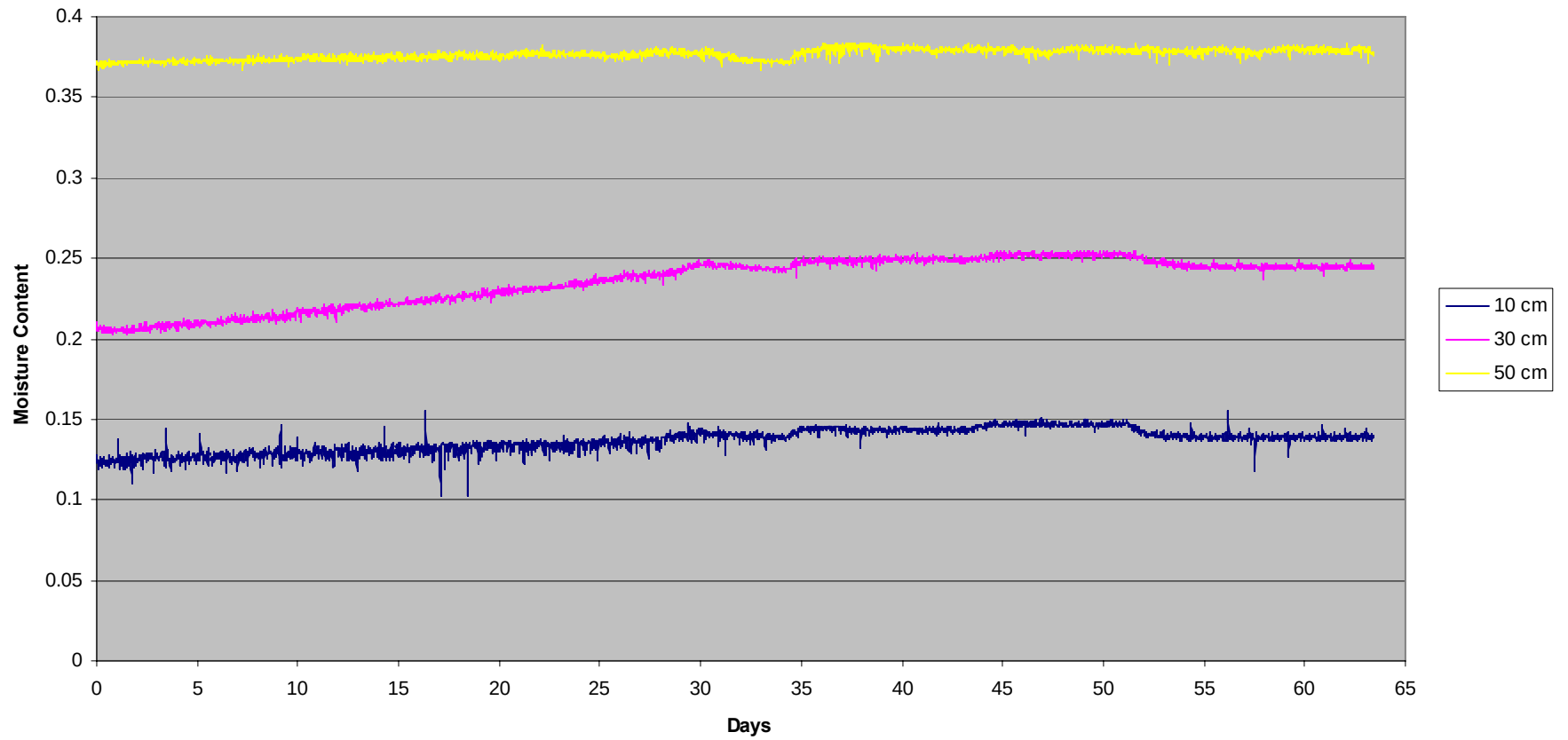
Autumn Infiltration Column D



Autumn Infiltration Column E

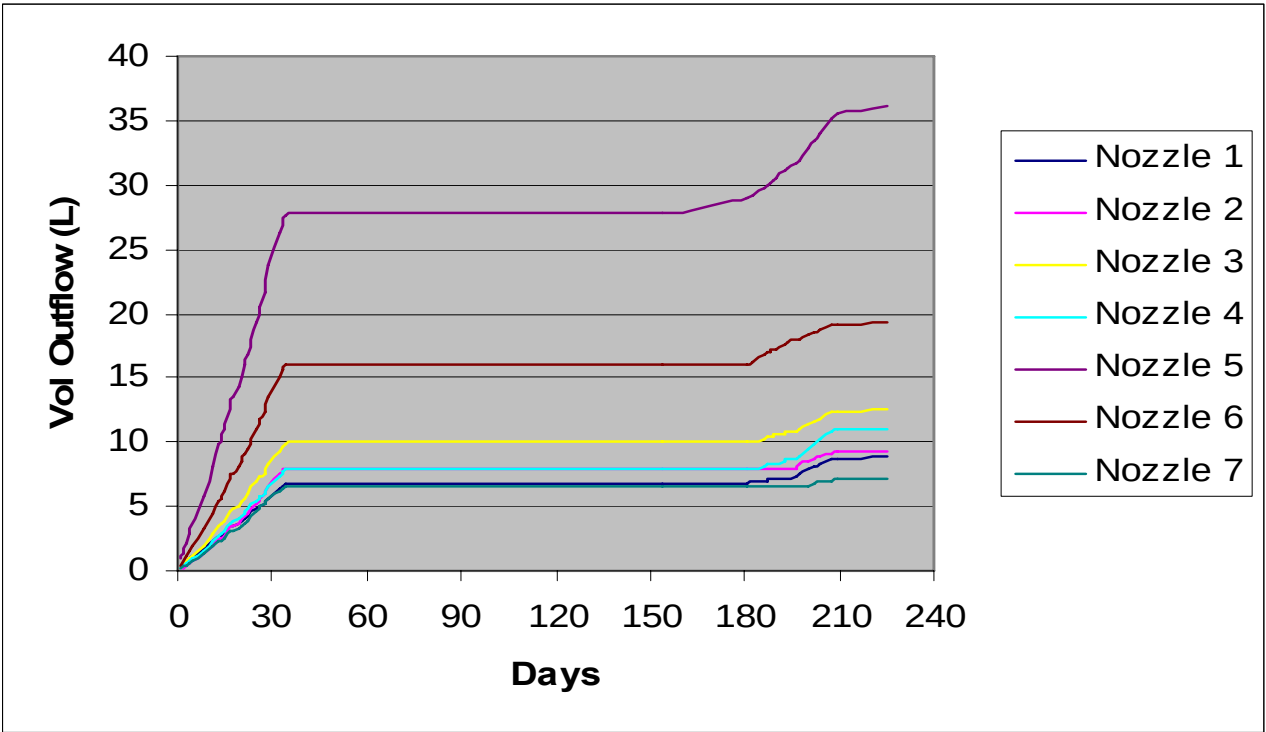


Autumn Infiltration Column F

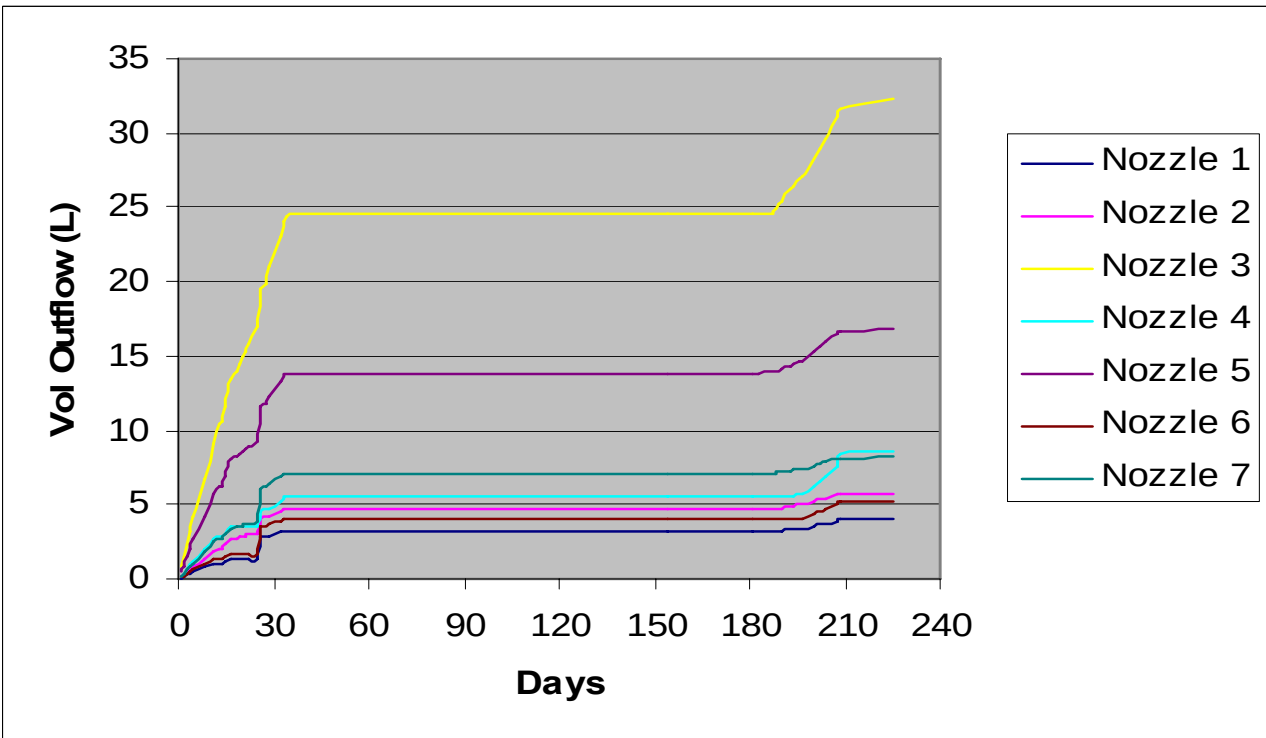


APPENDIX 3. COMPLETE AUTUMN OUTFLOW CHARTS
BY NOZZLE

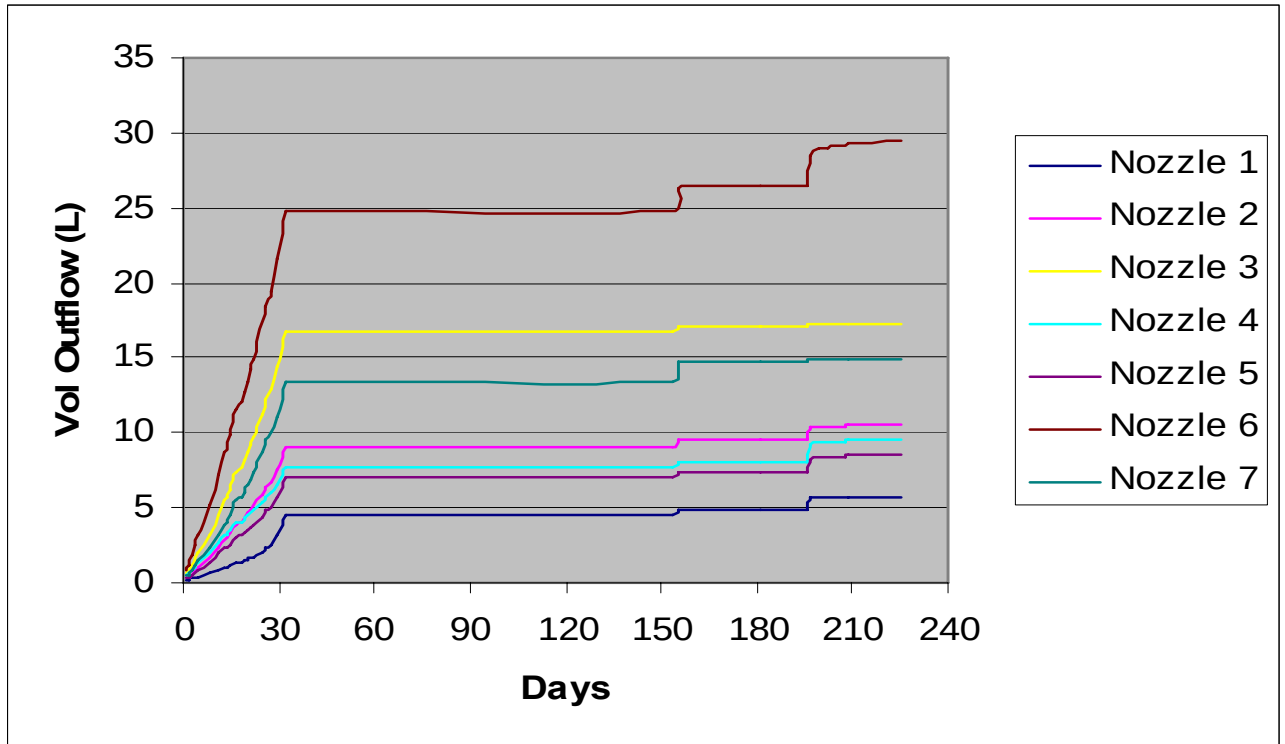
Column C



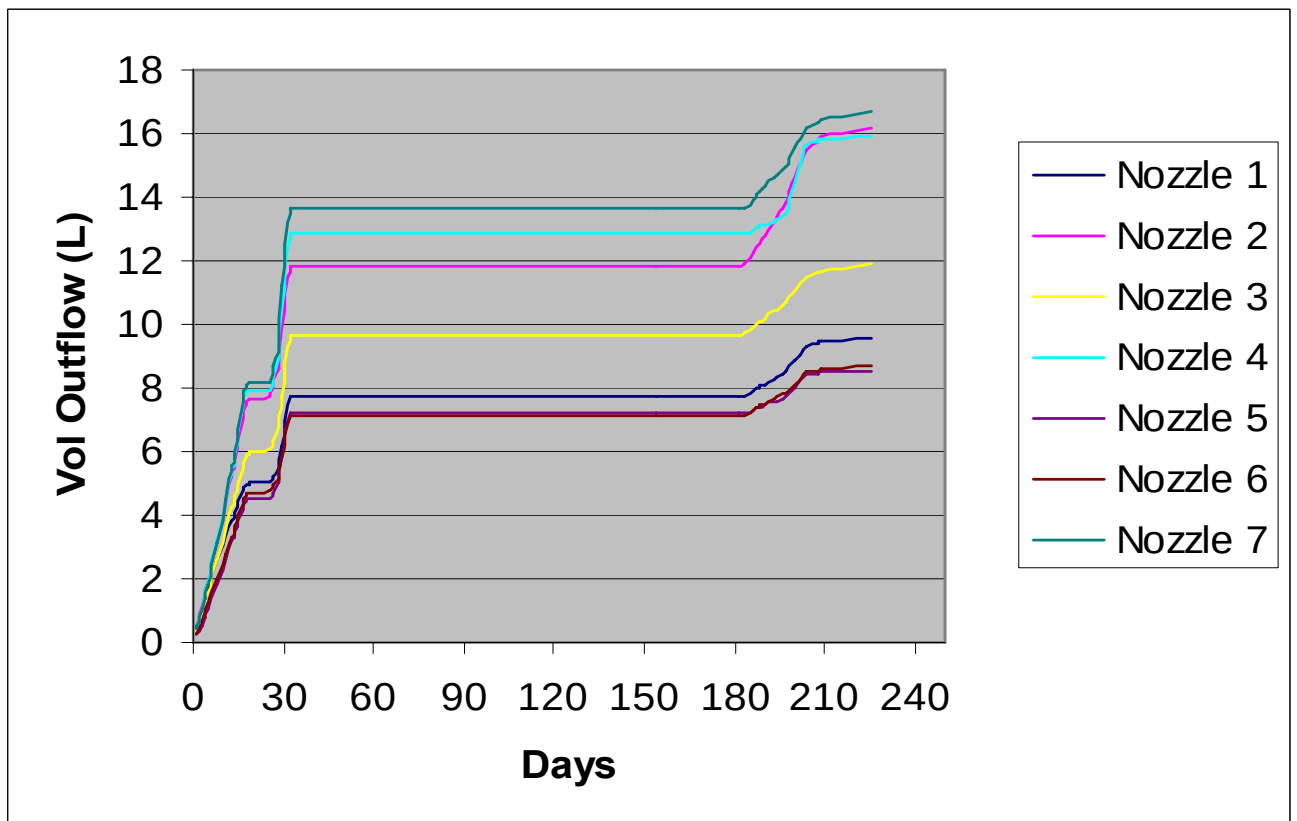
Column D



Column E

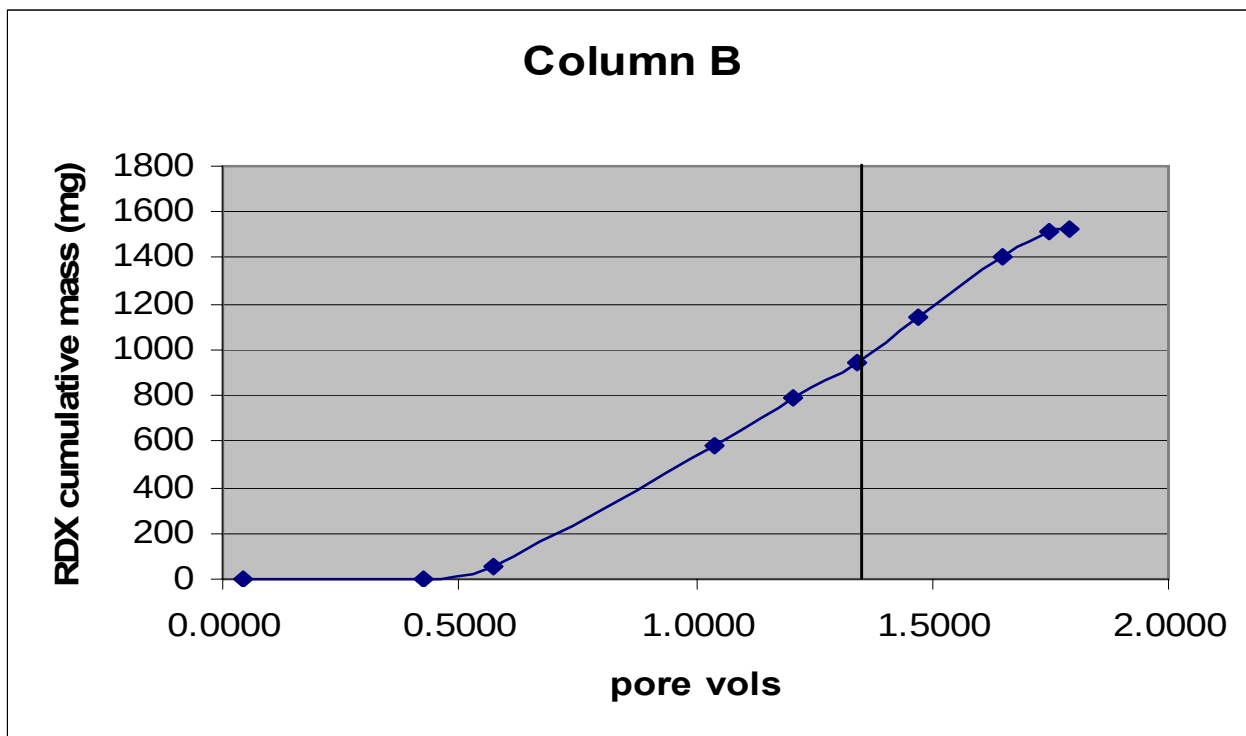
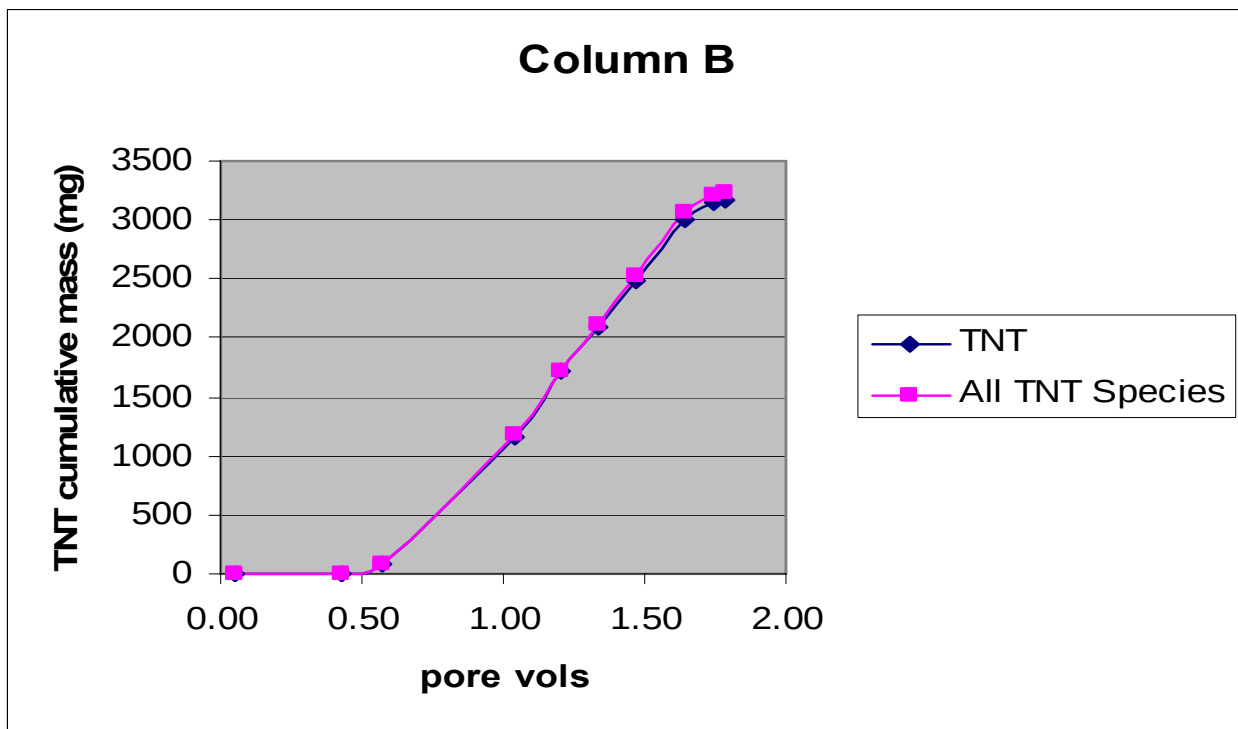


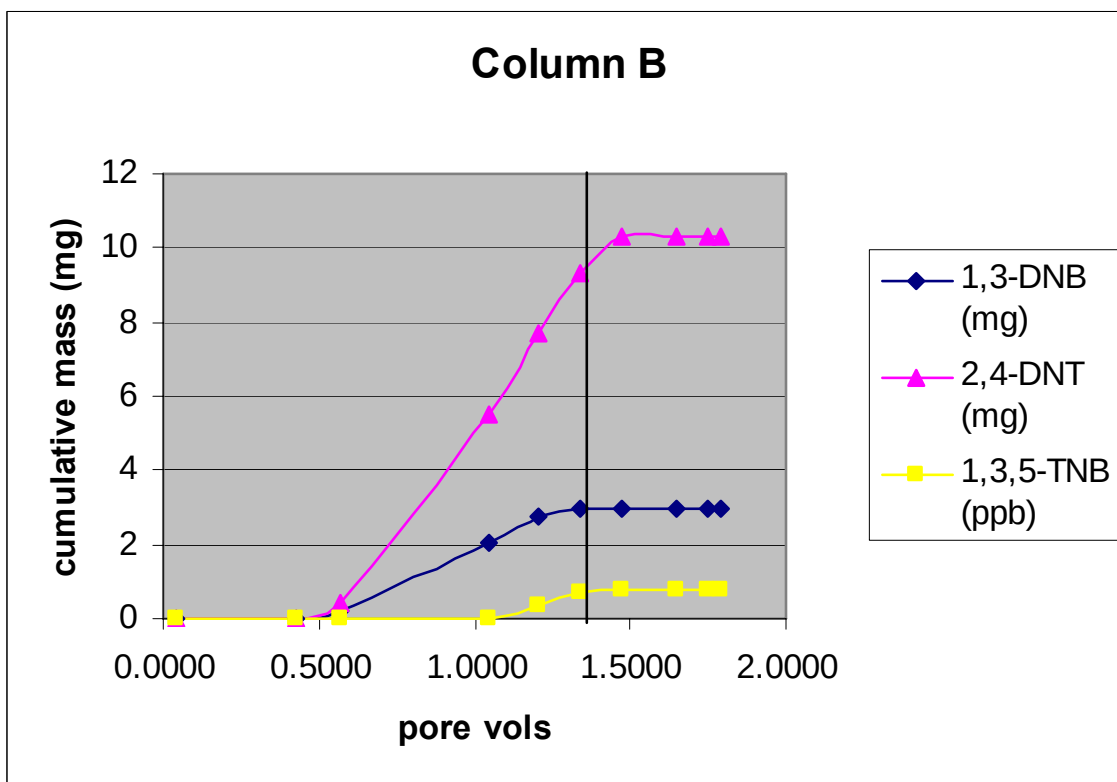
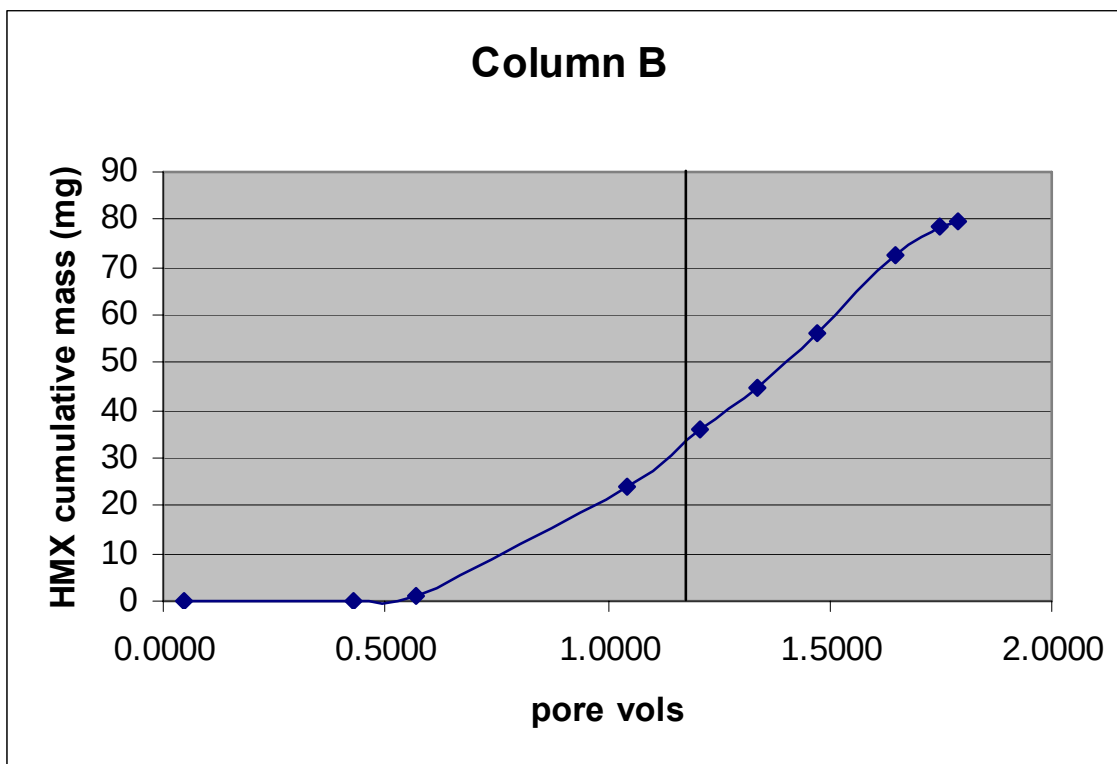
Column F



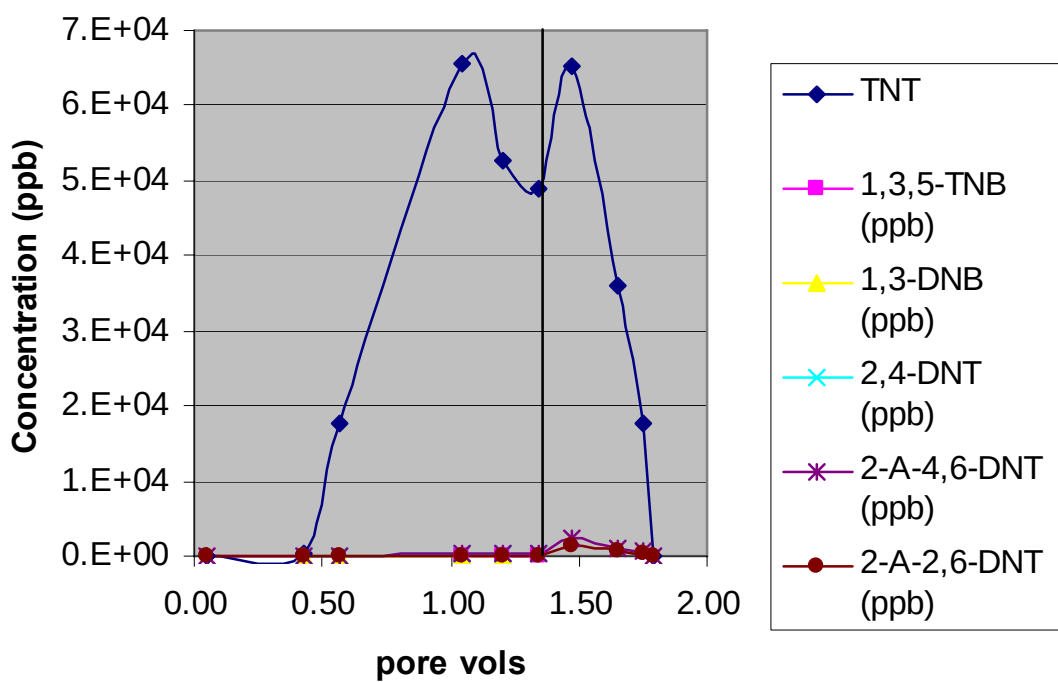
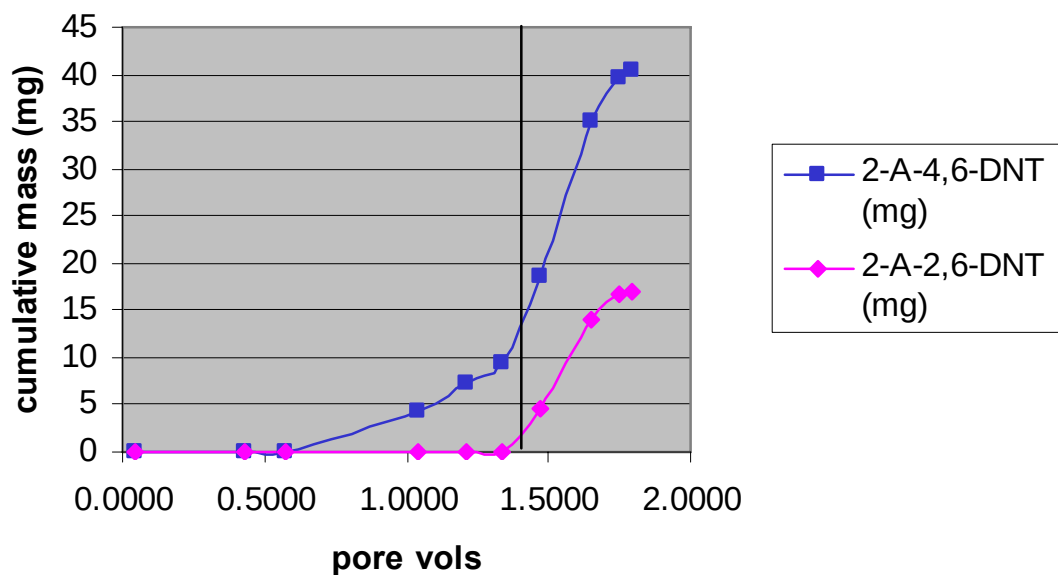
APPENDIX 4. COMPLETE ENERGETIC MATERIAL OUTFLOW

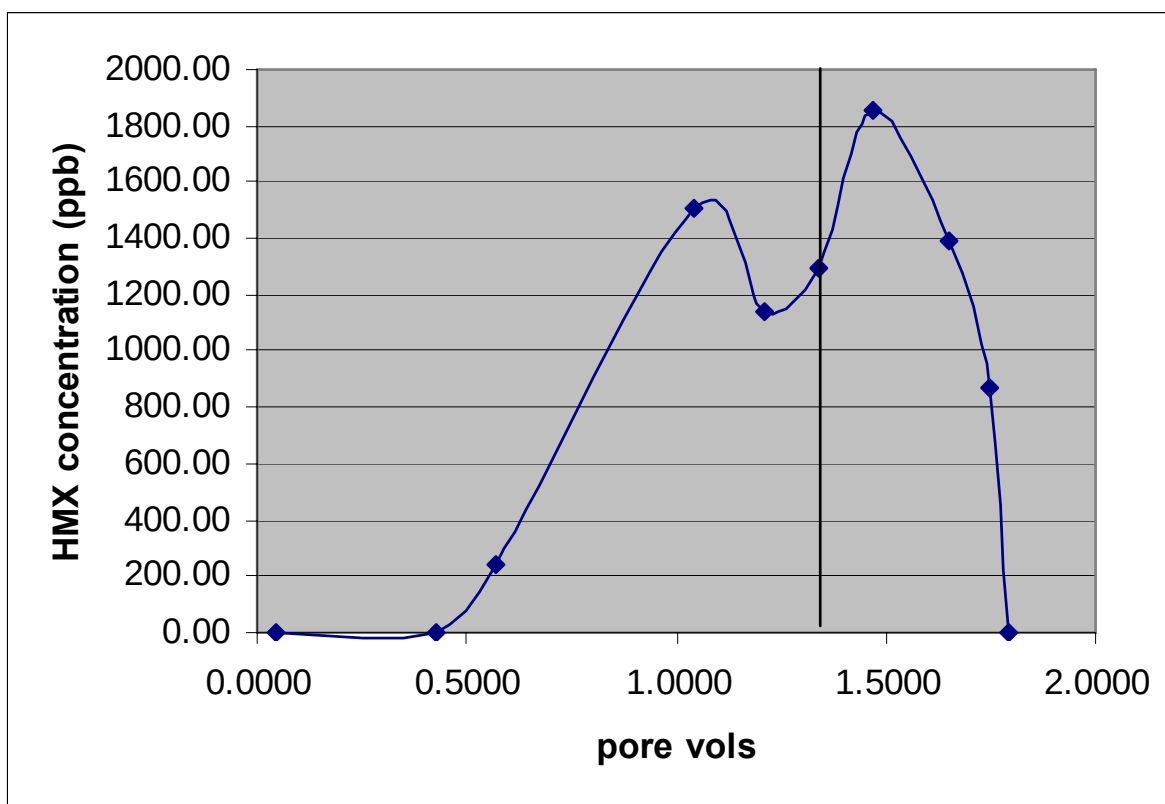
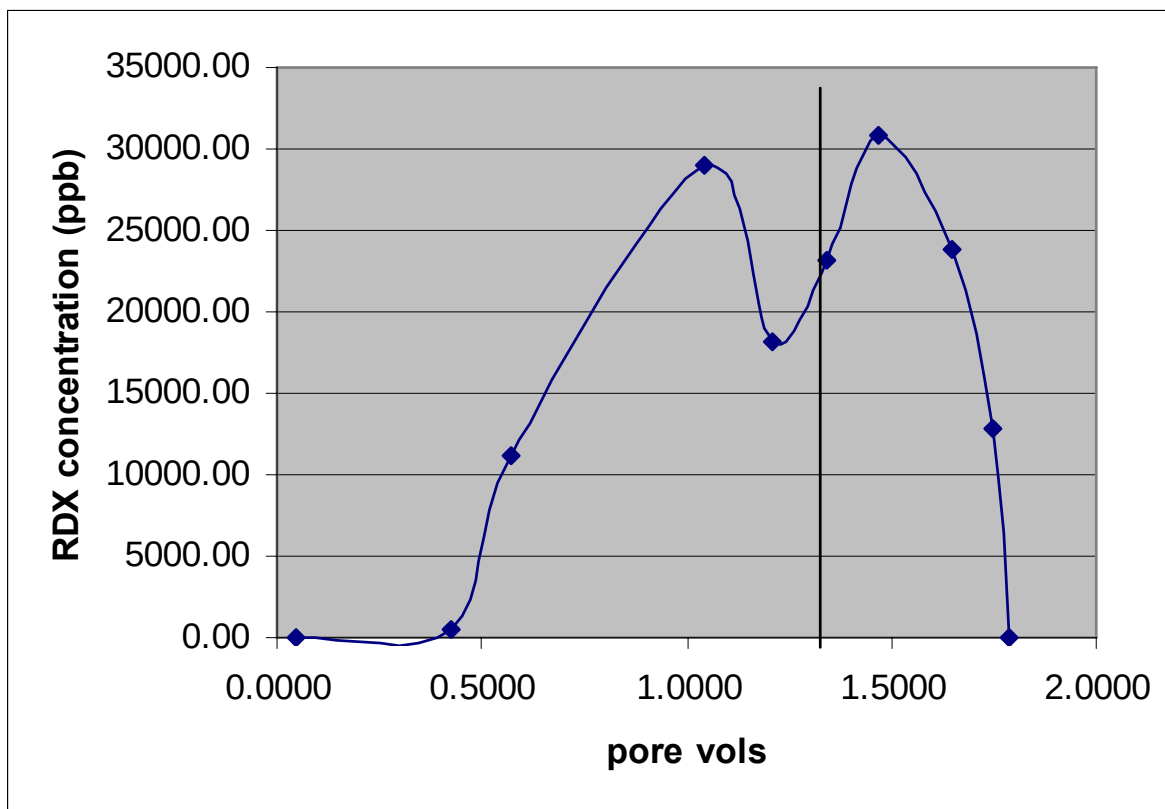
CHARTS

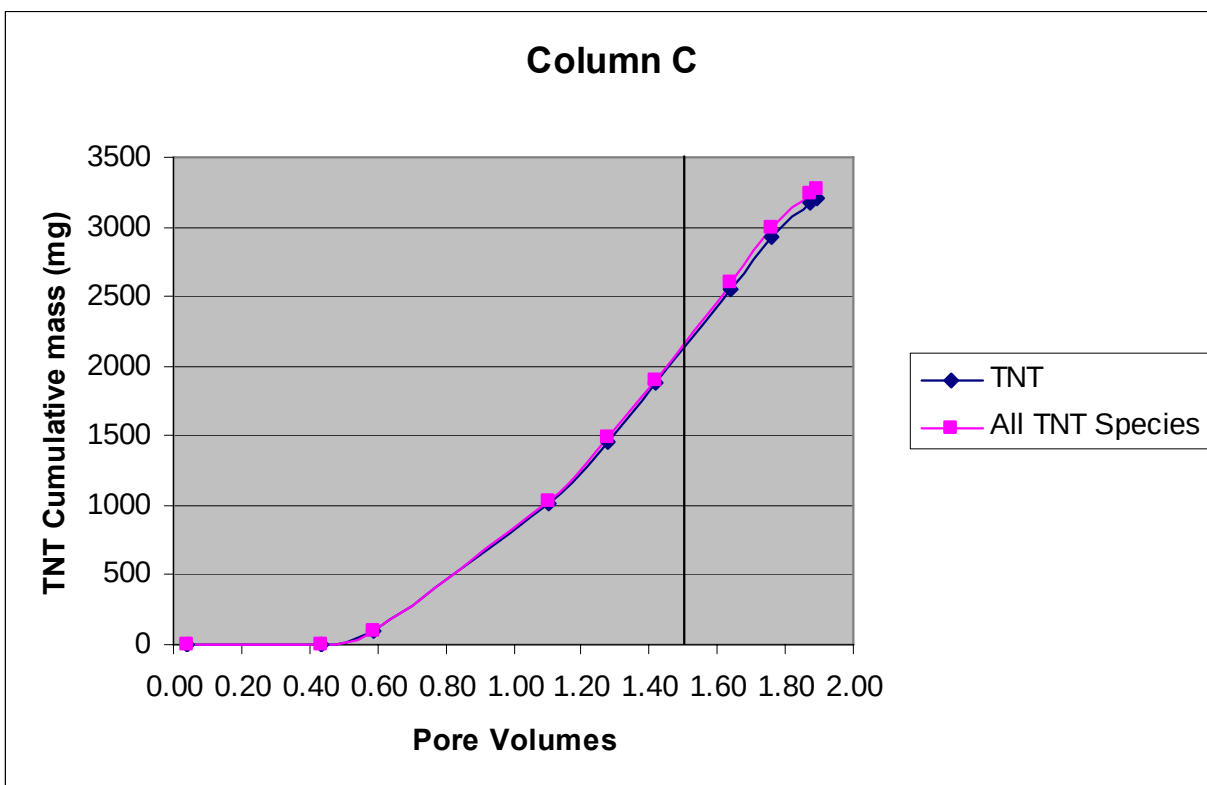
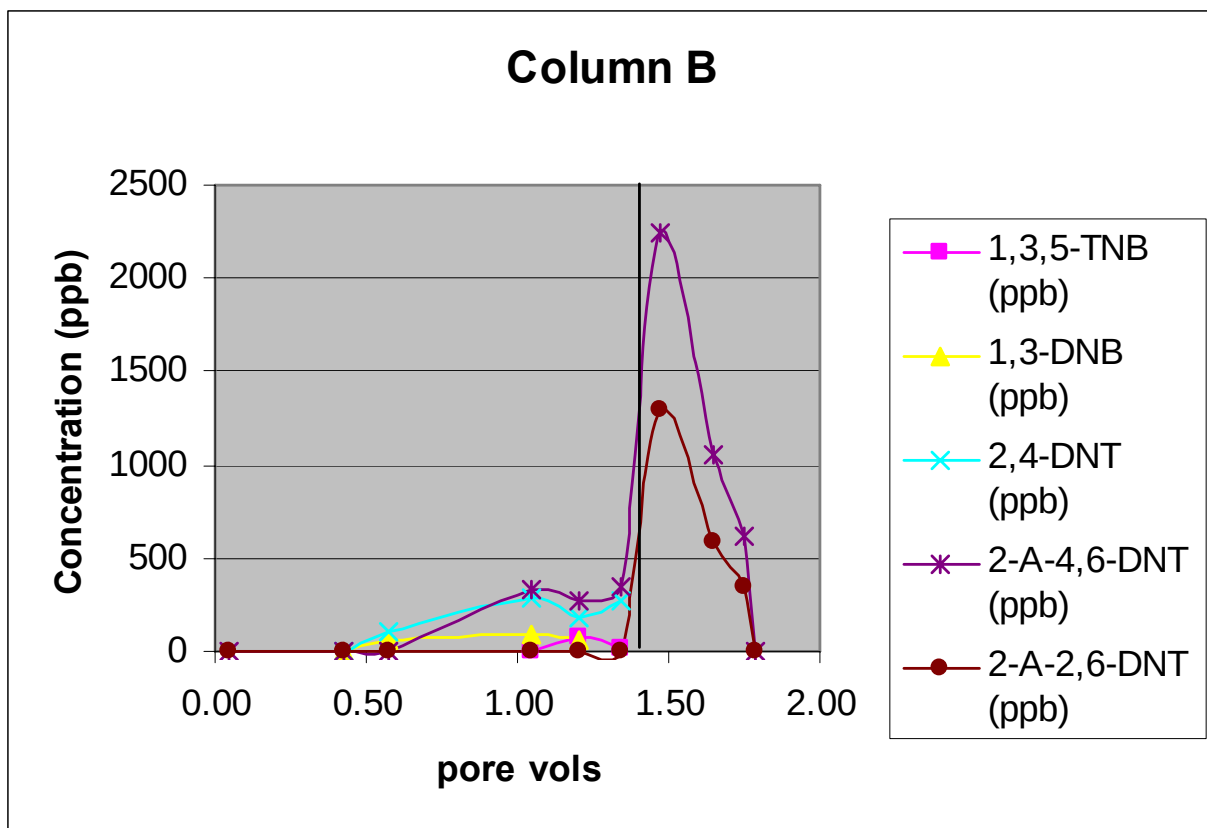


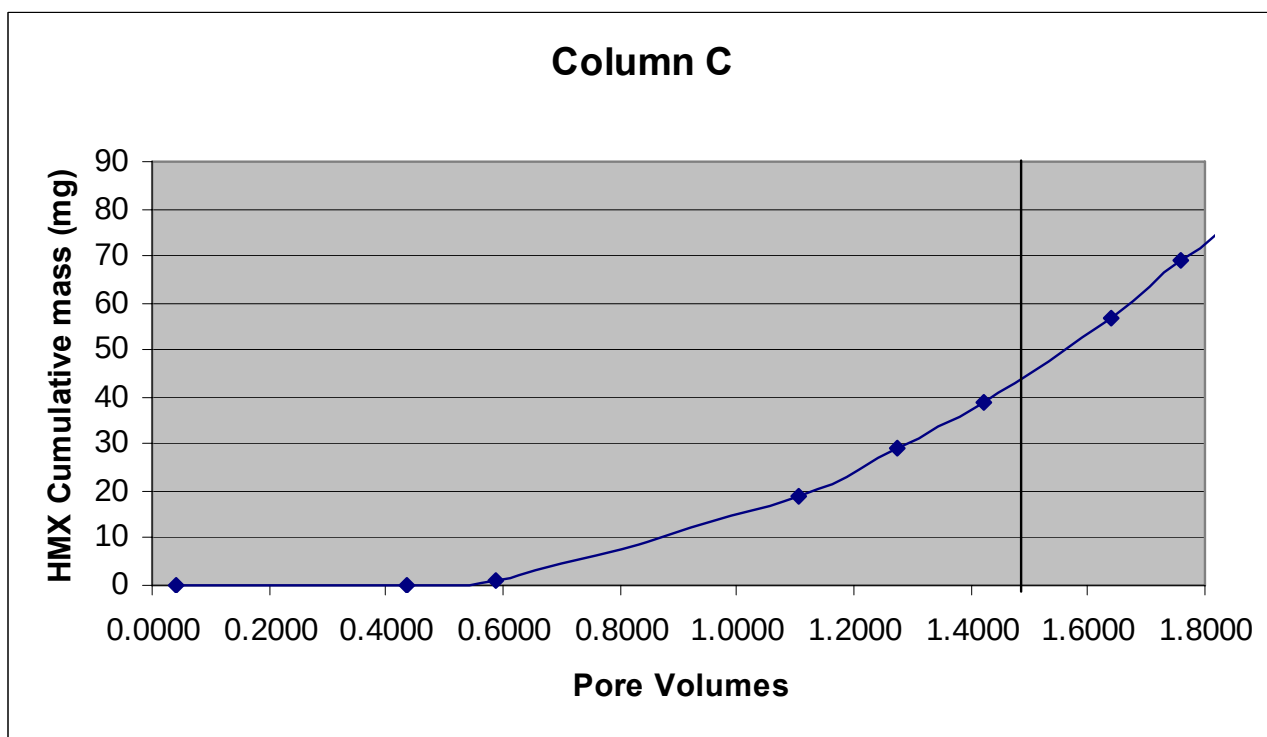
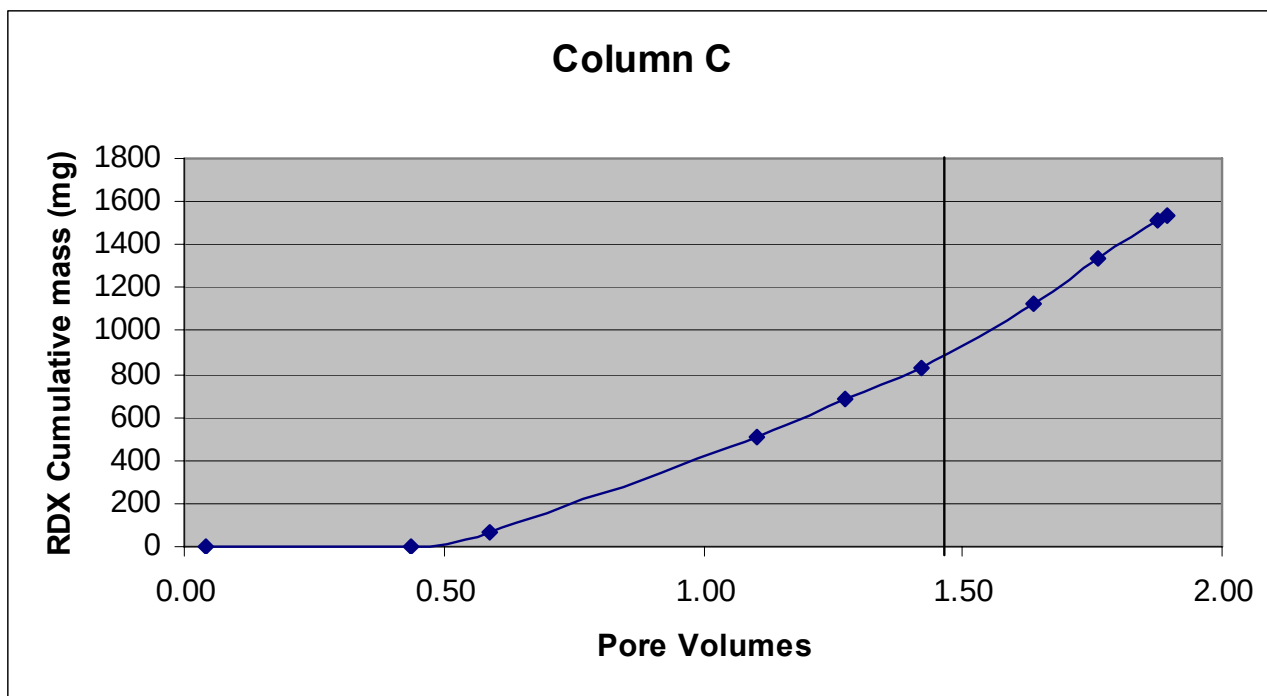


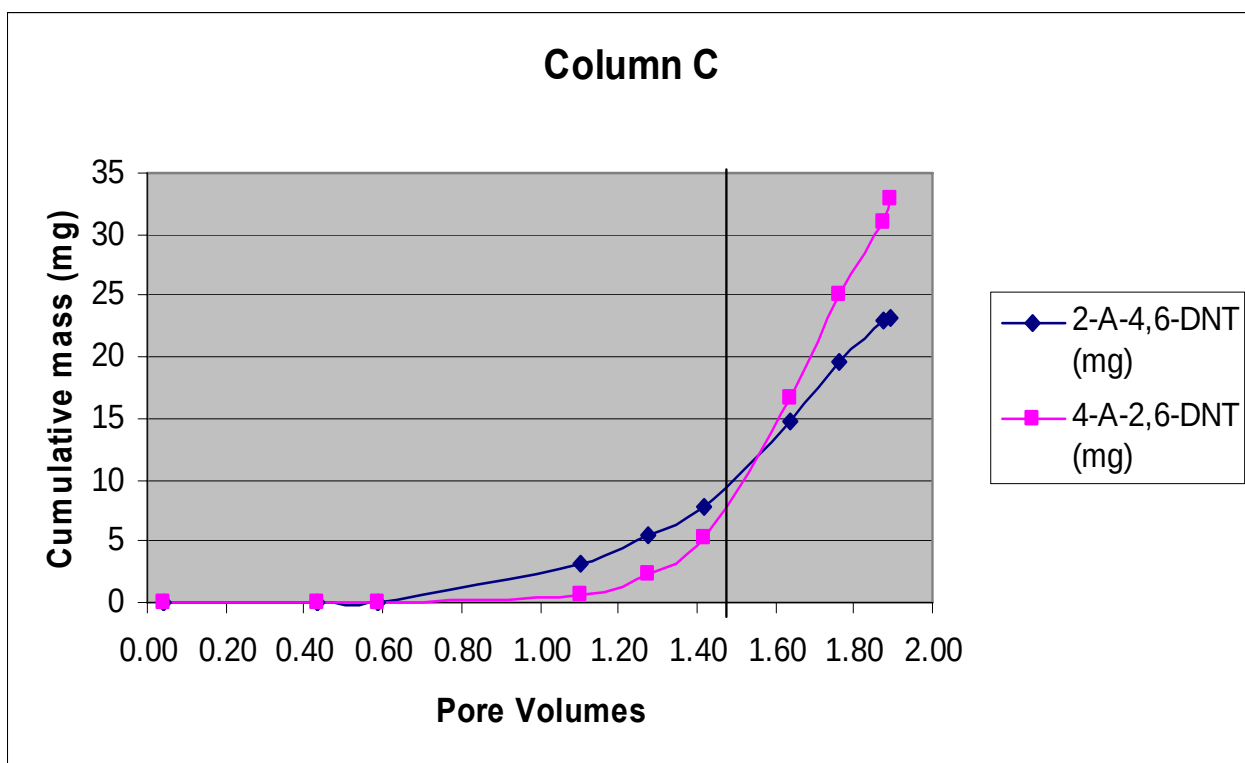
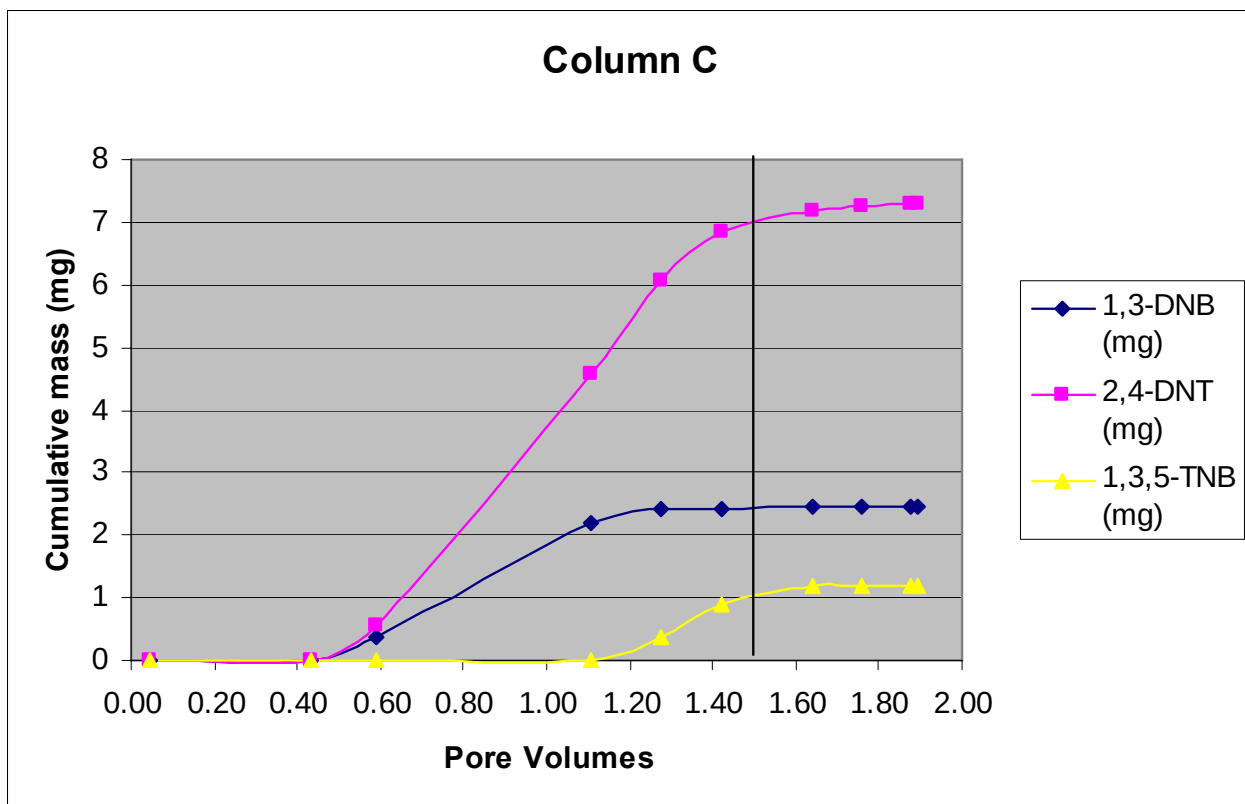
Column B

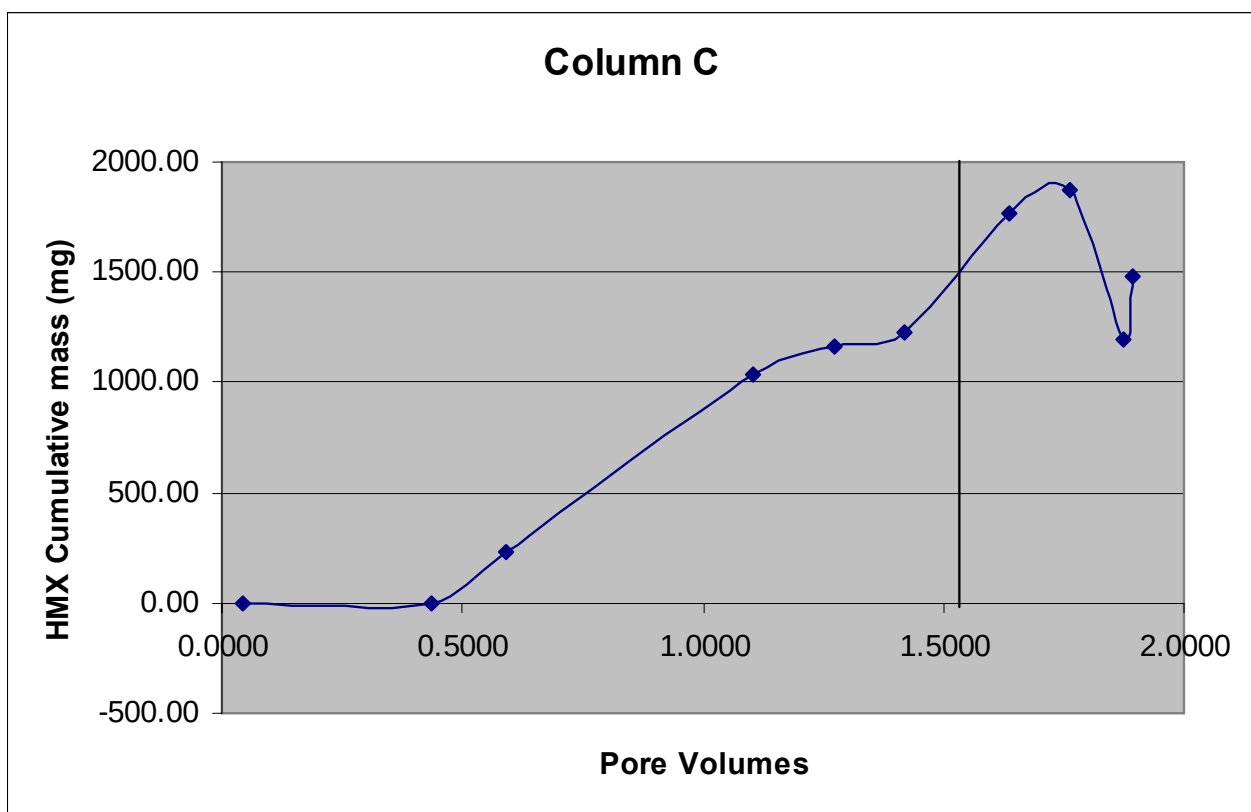
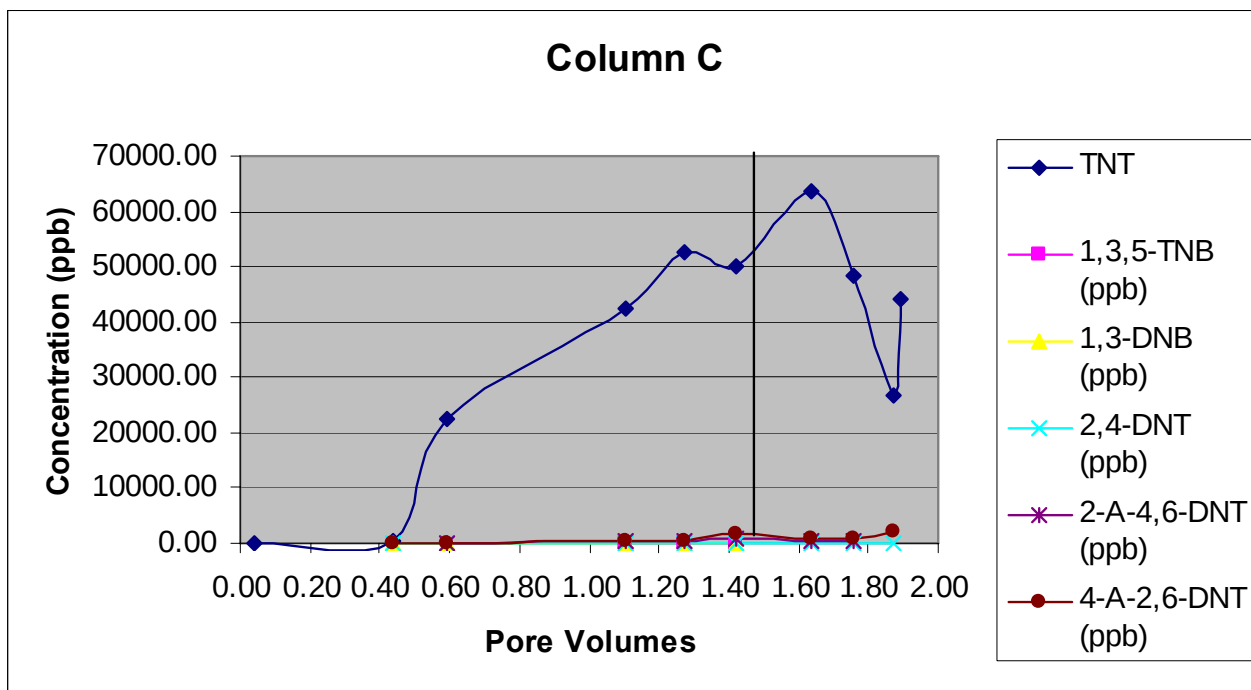


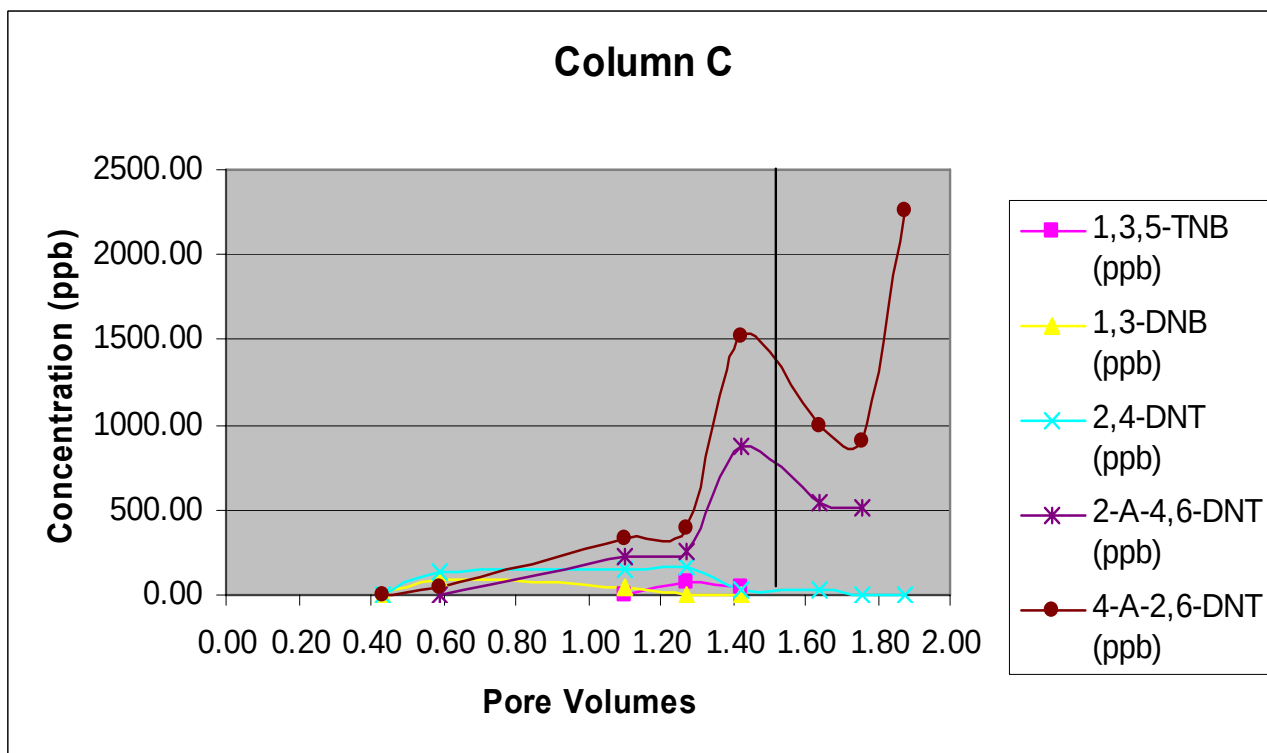
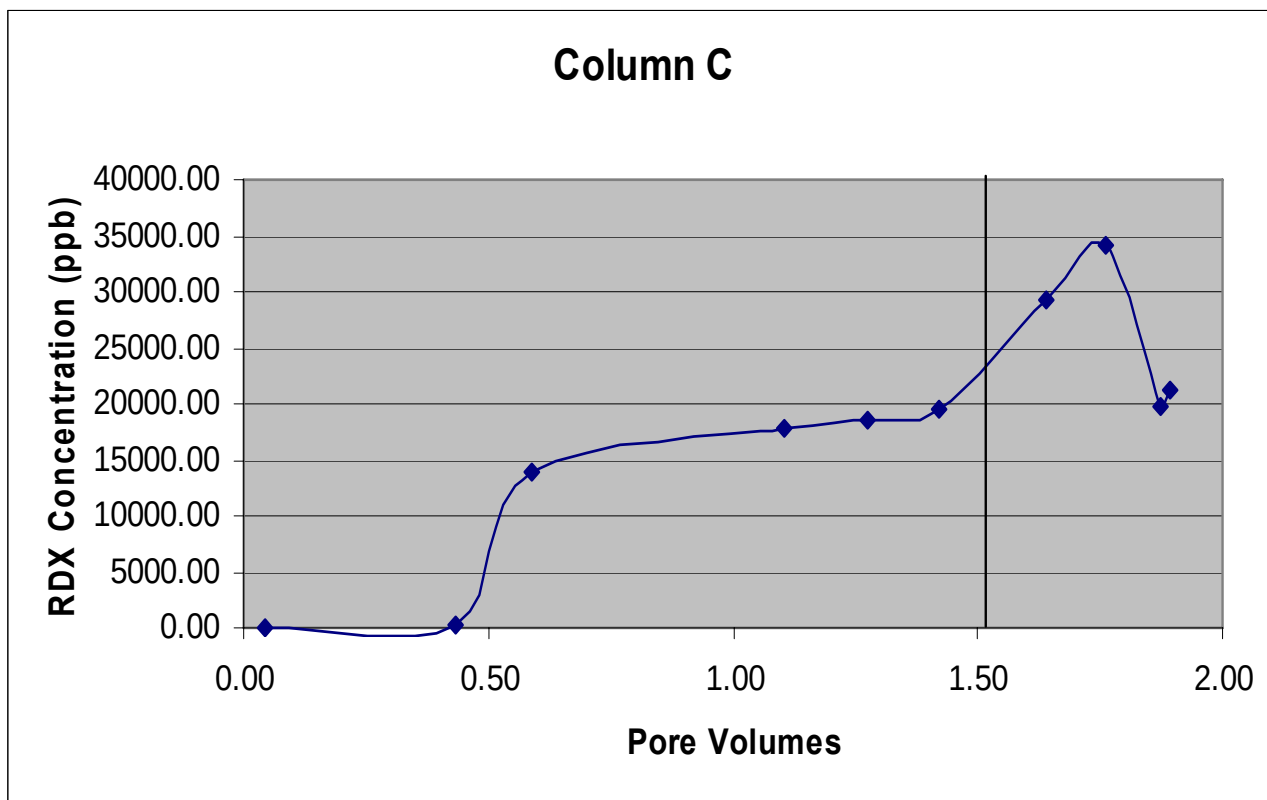


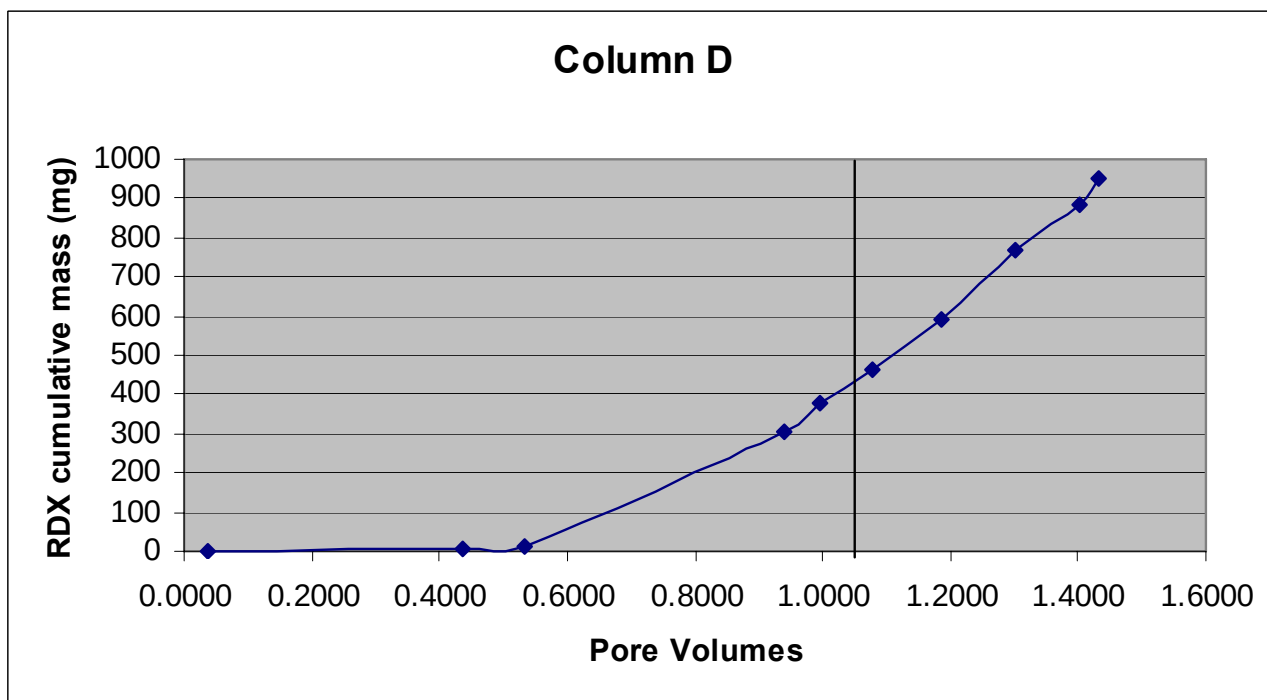
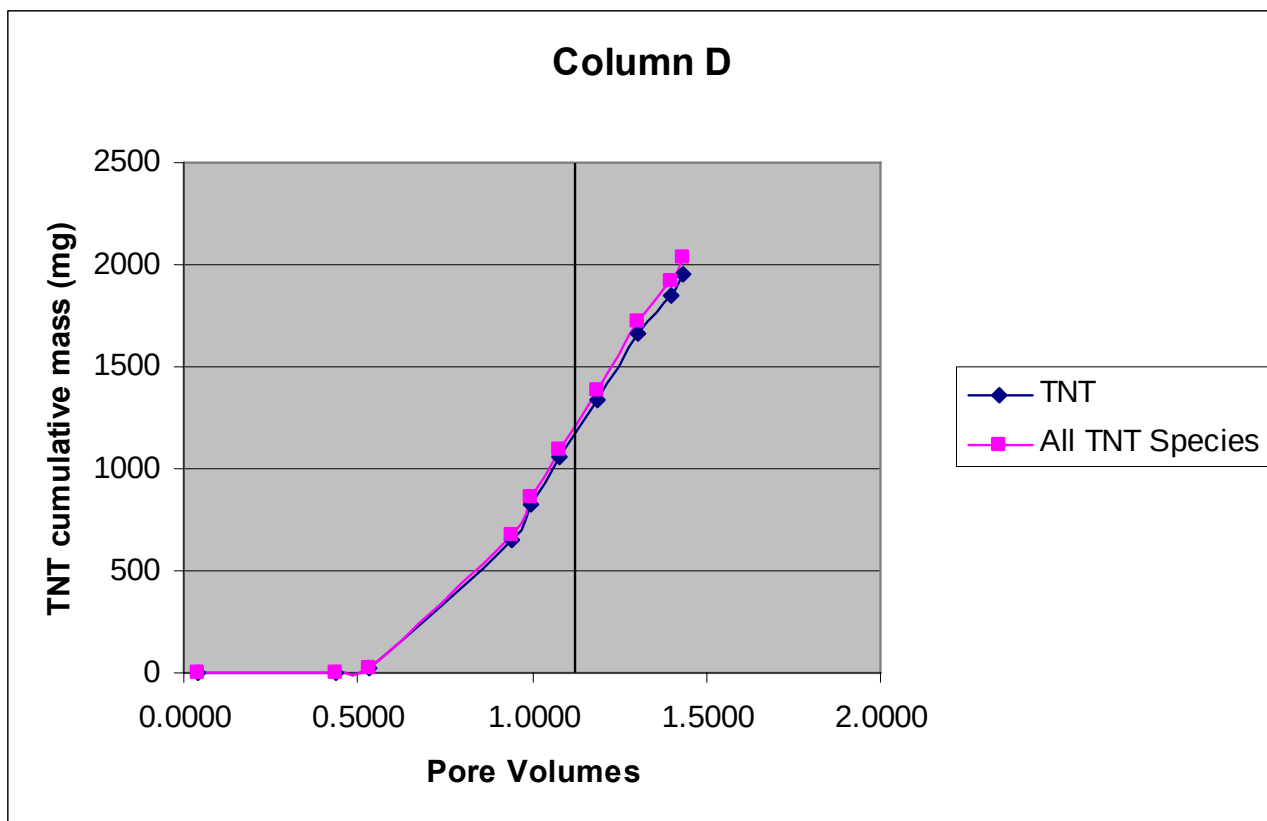


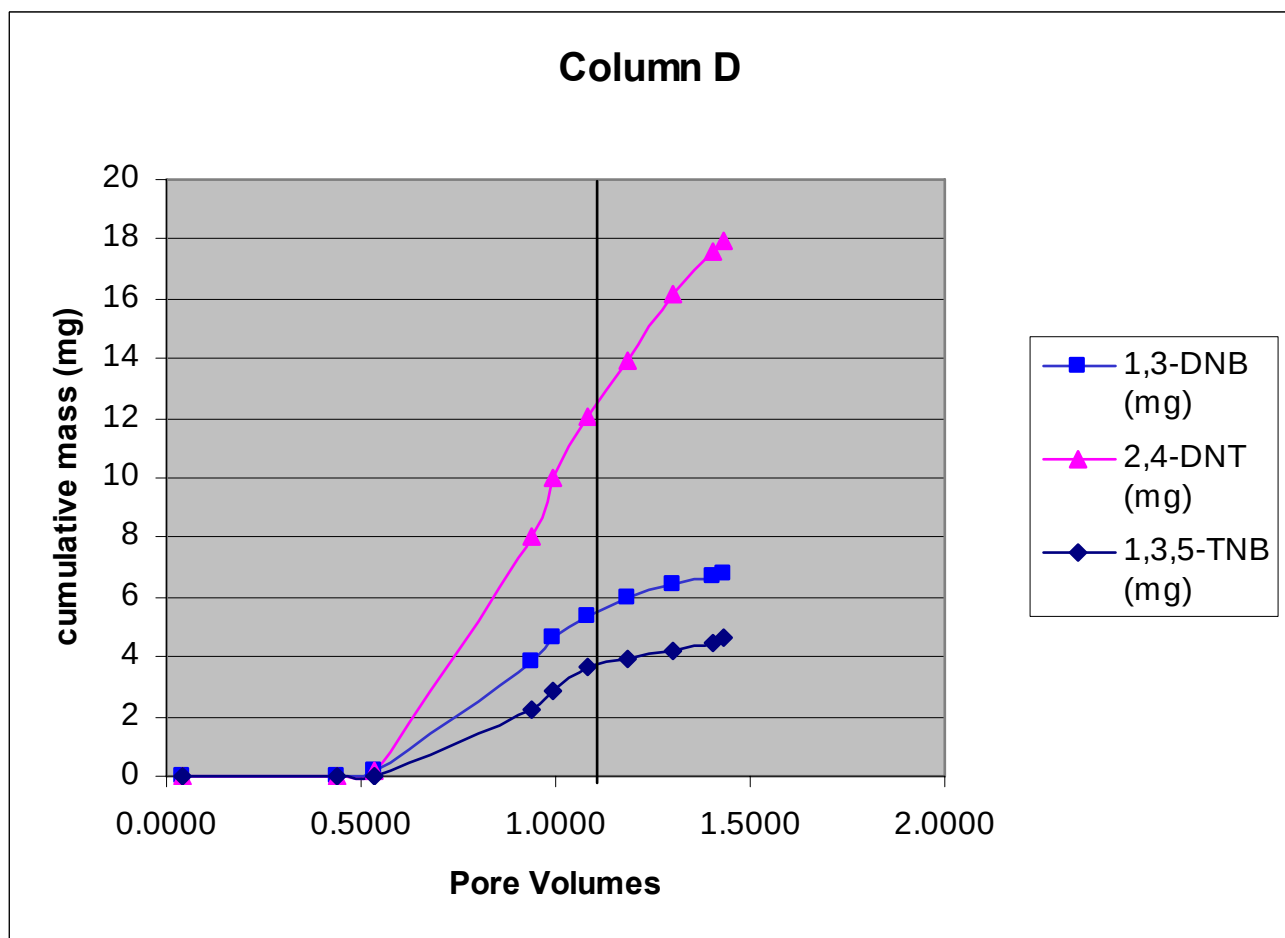
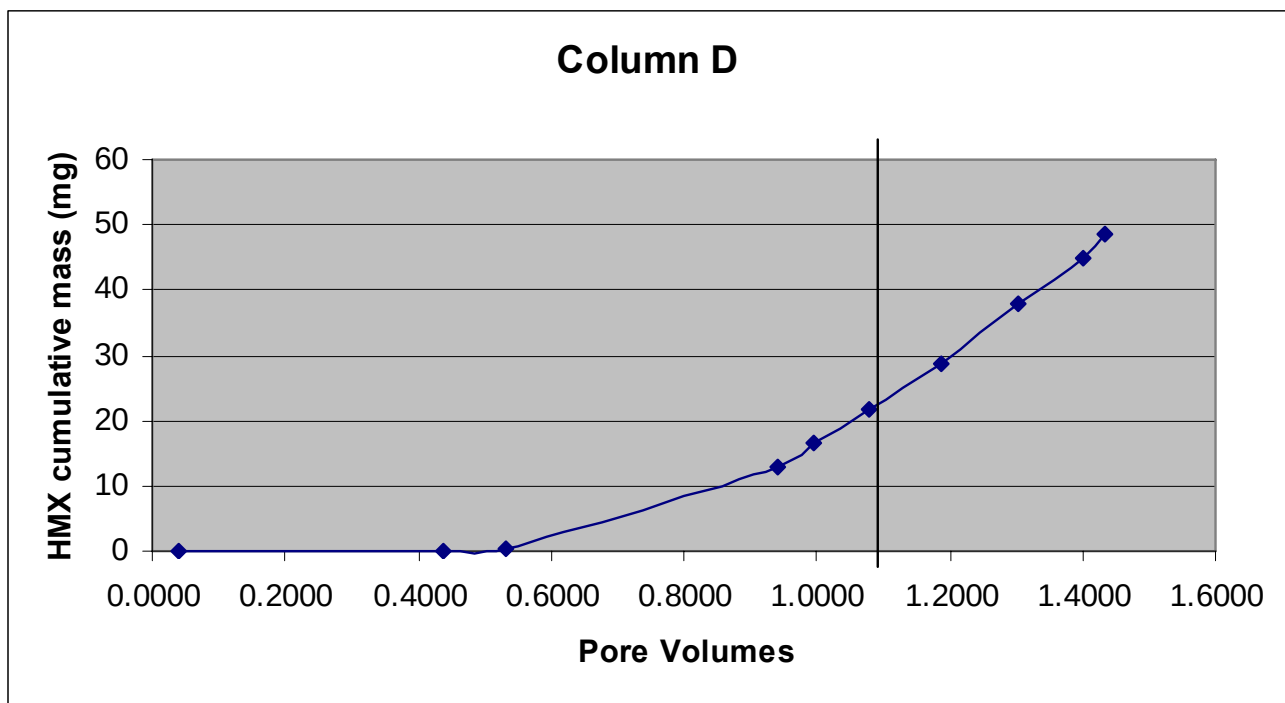


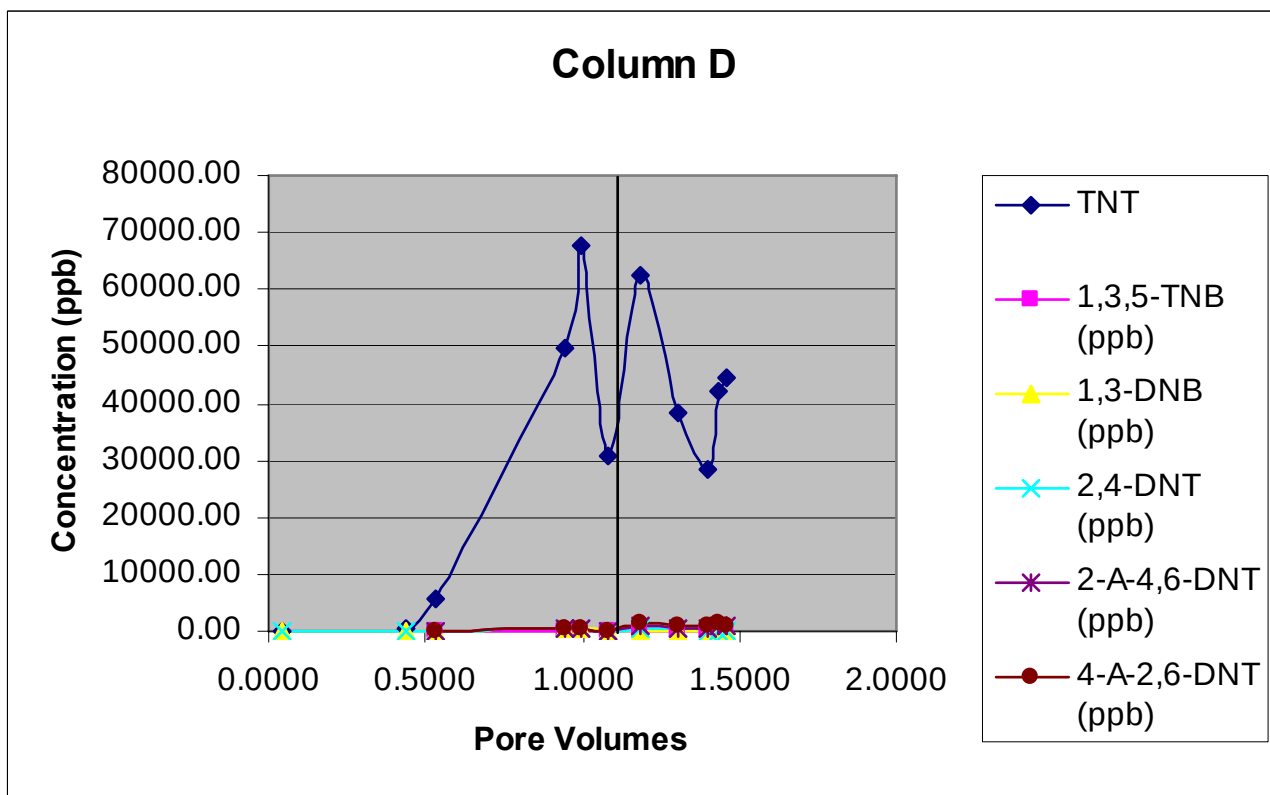
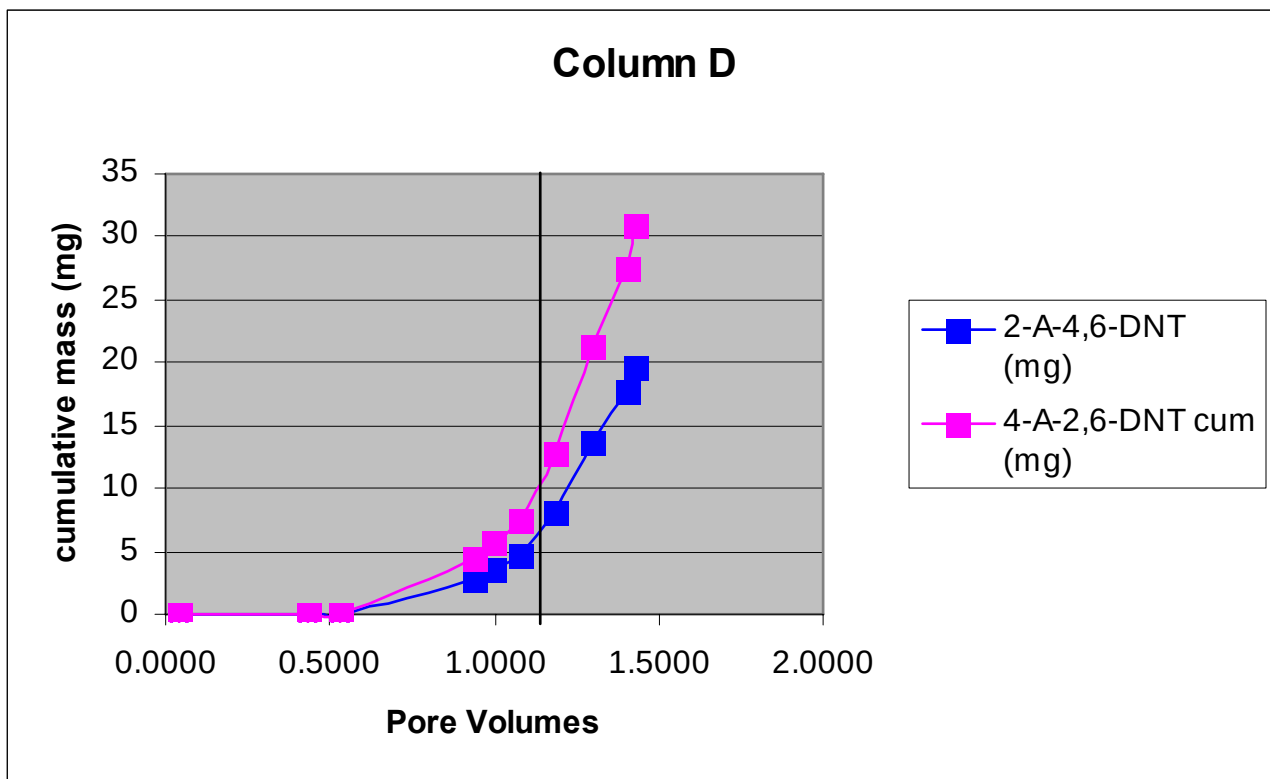


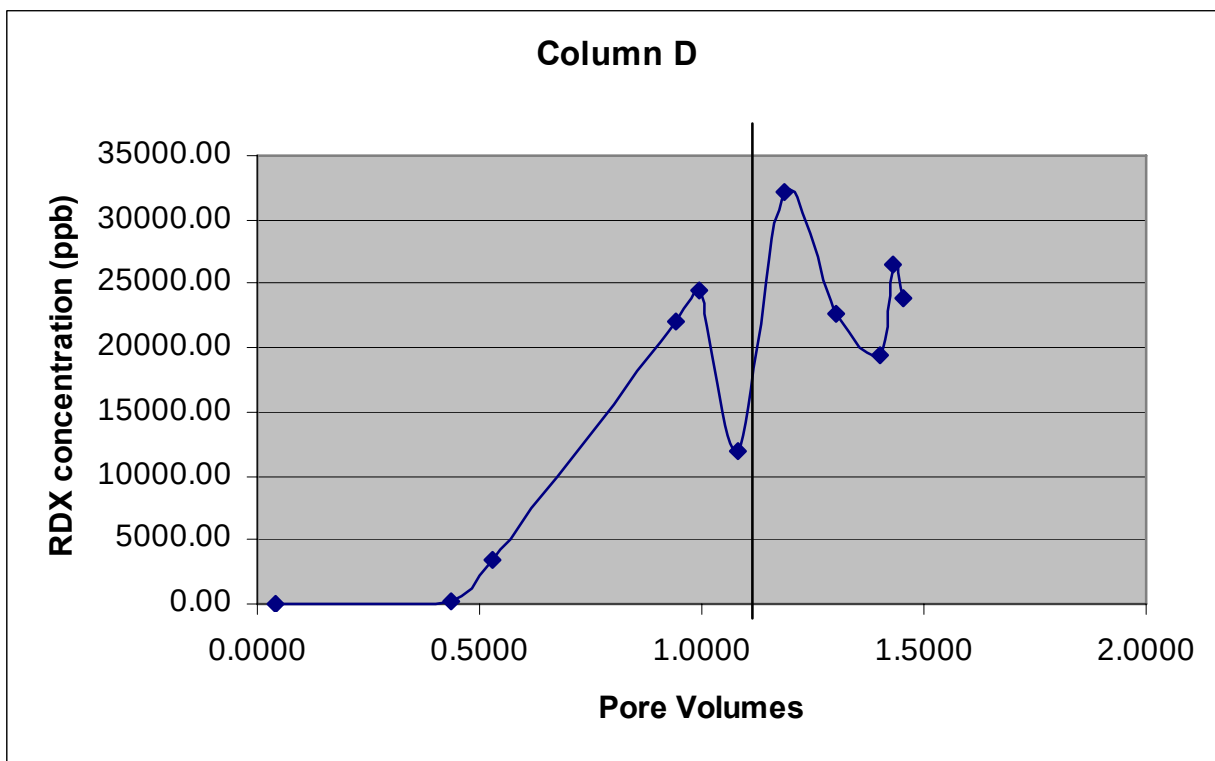
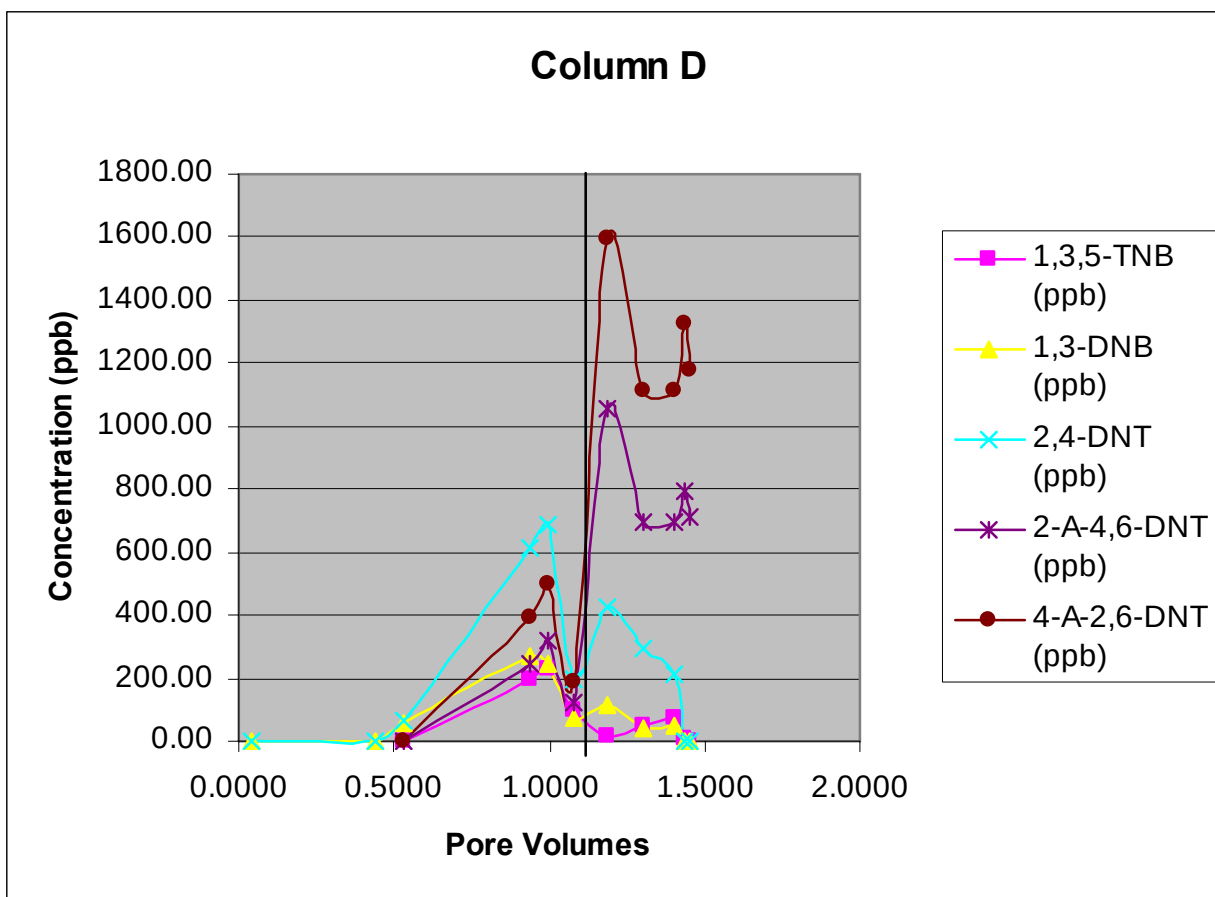


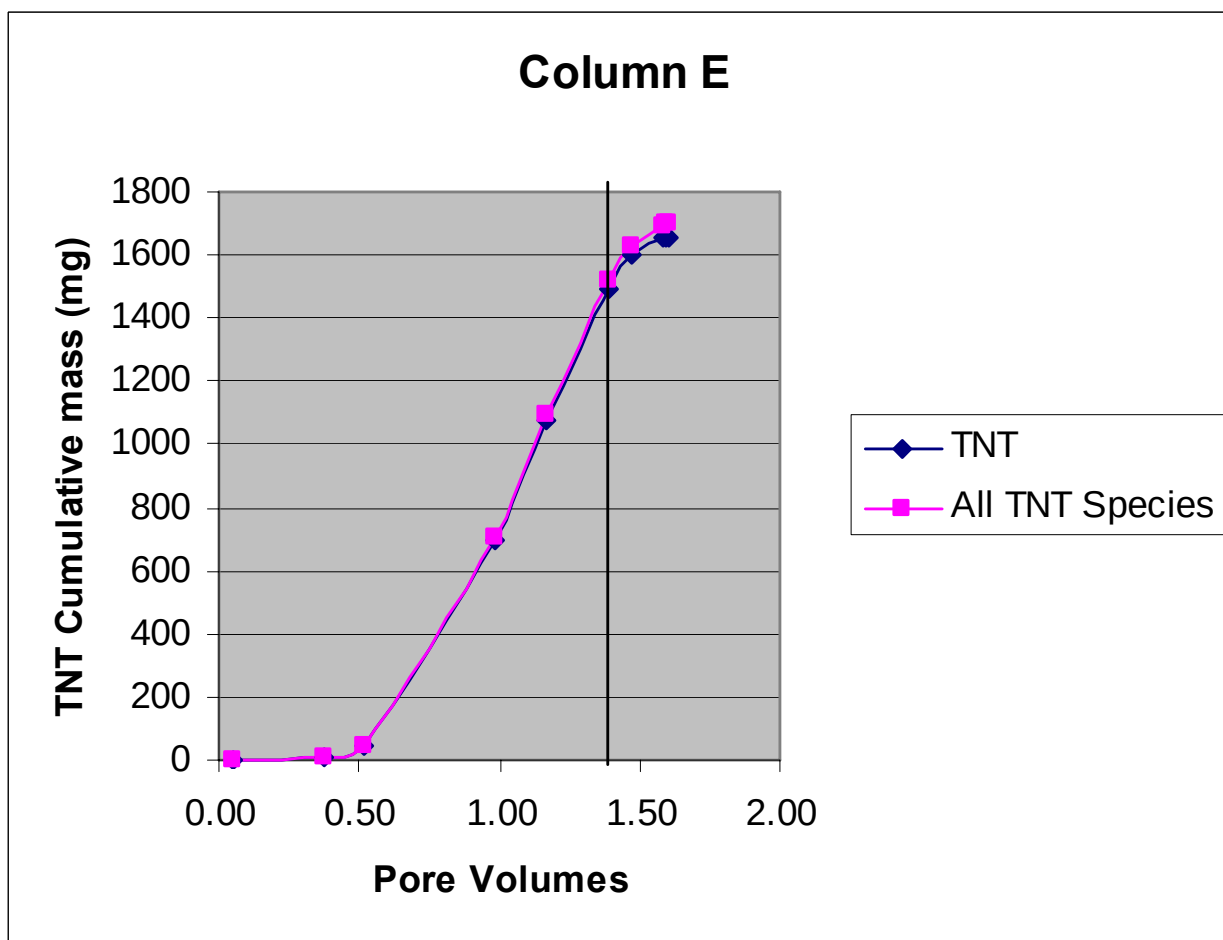
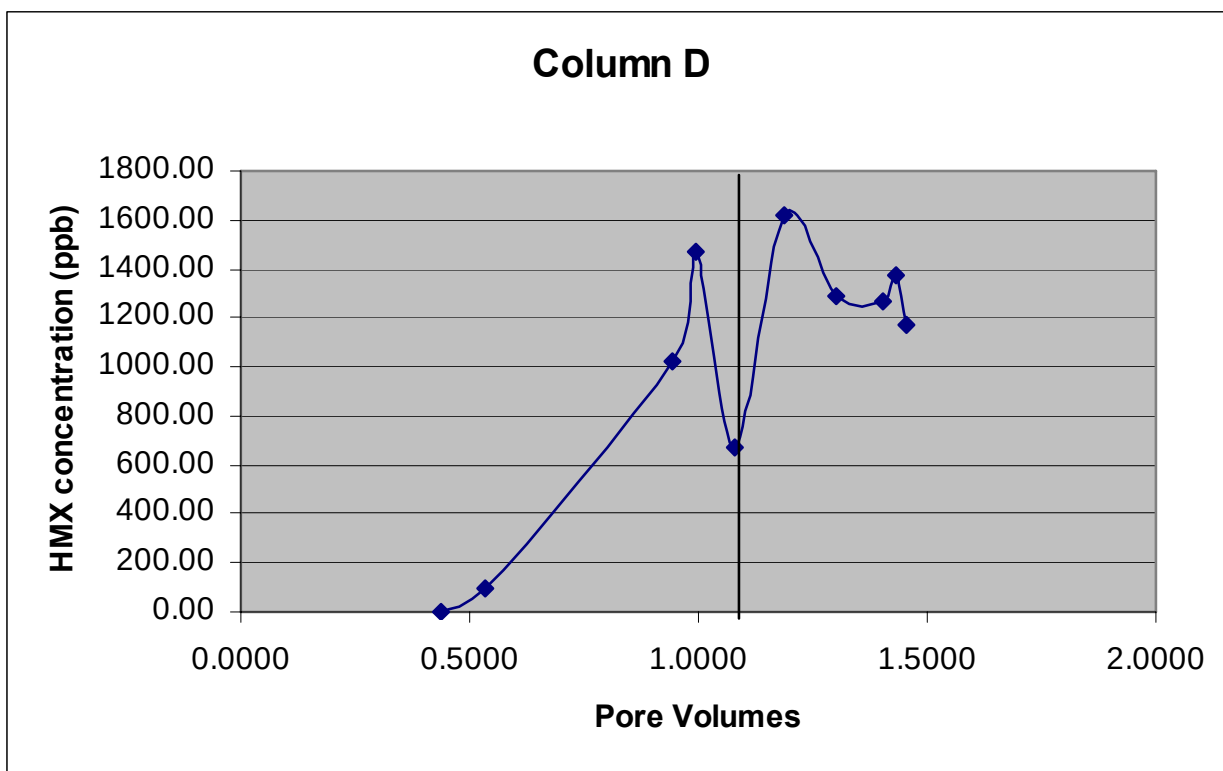


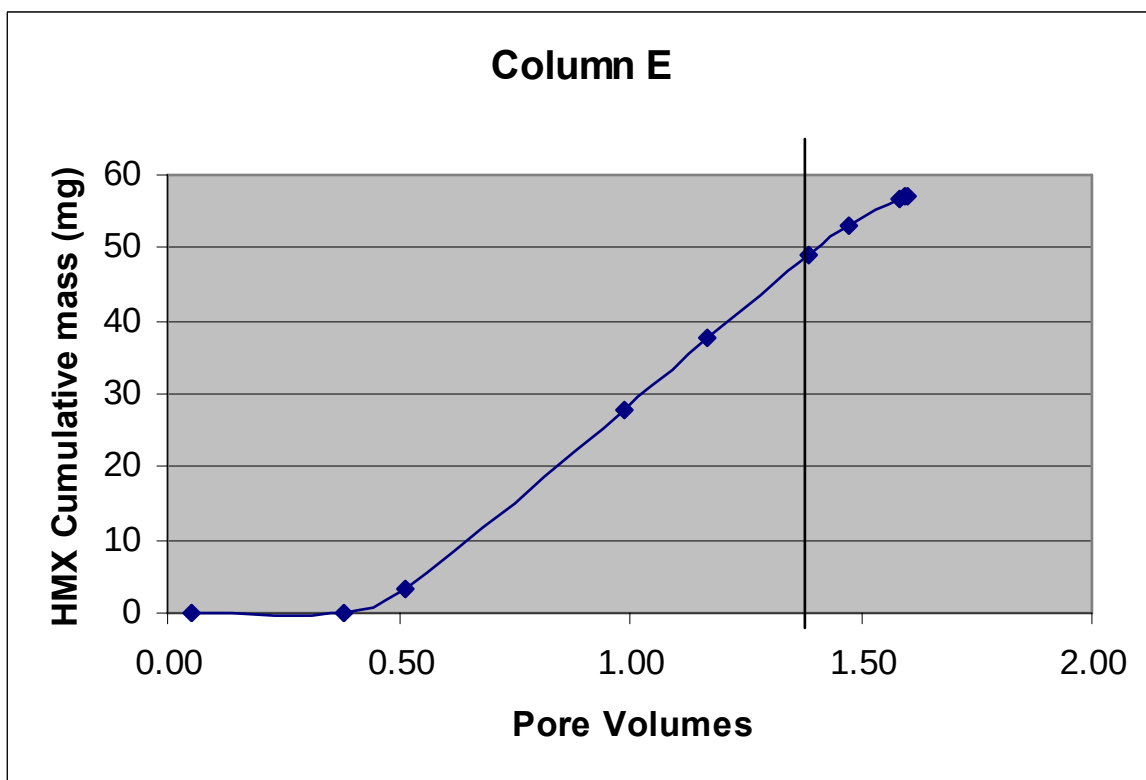
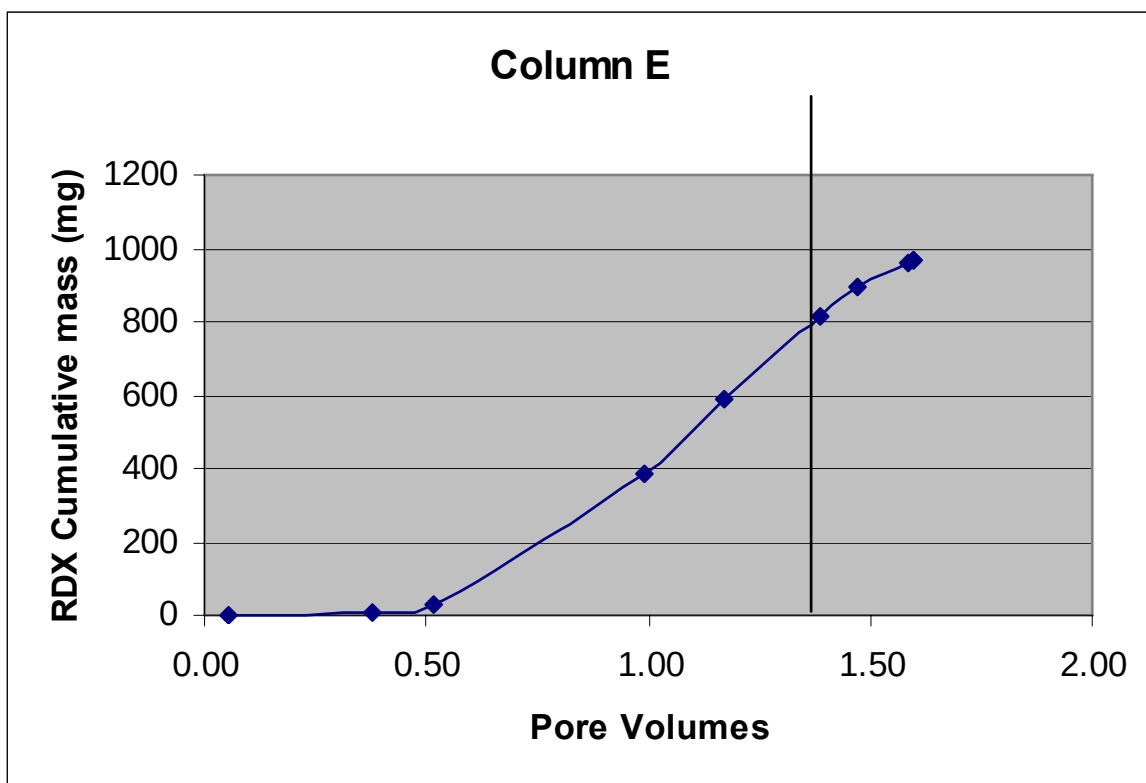


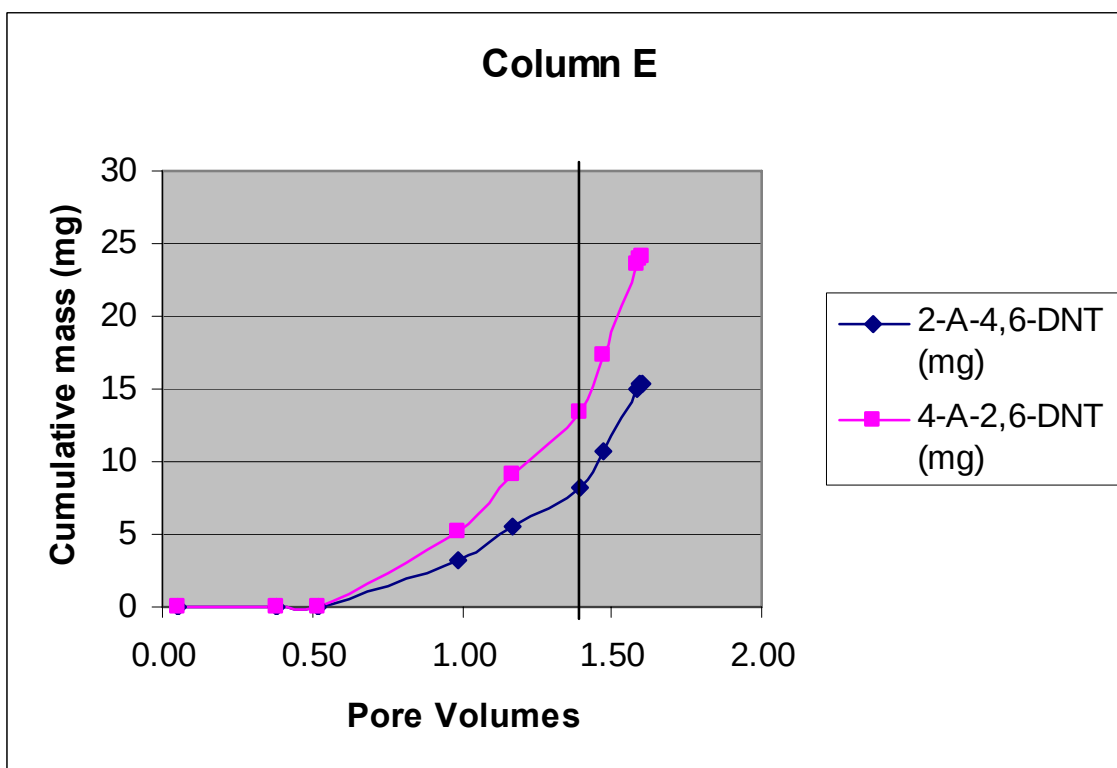
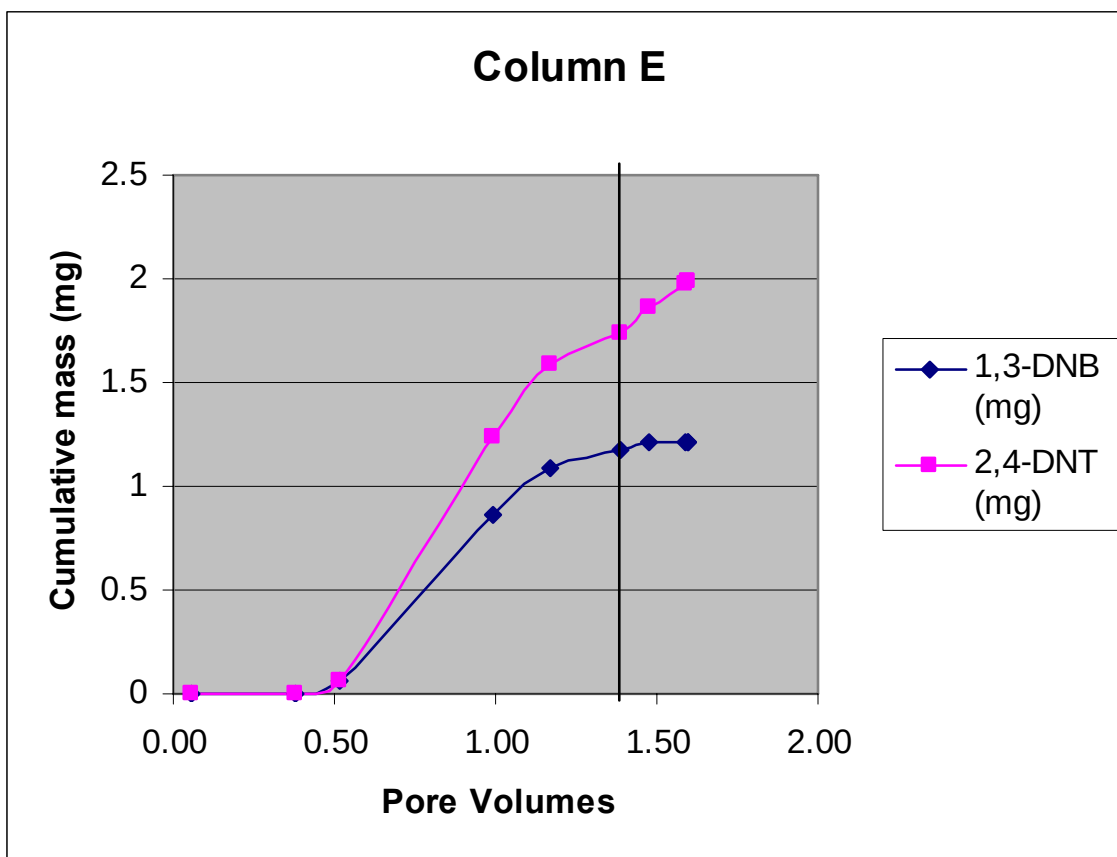


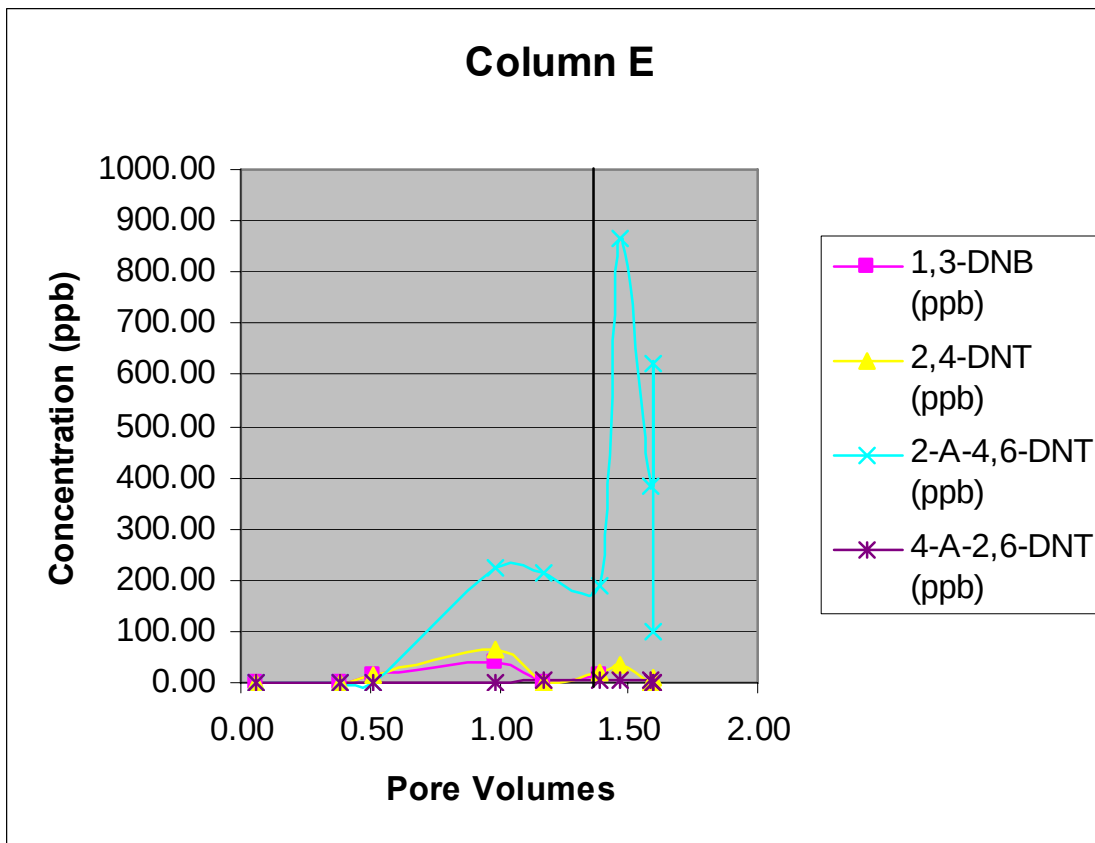
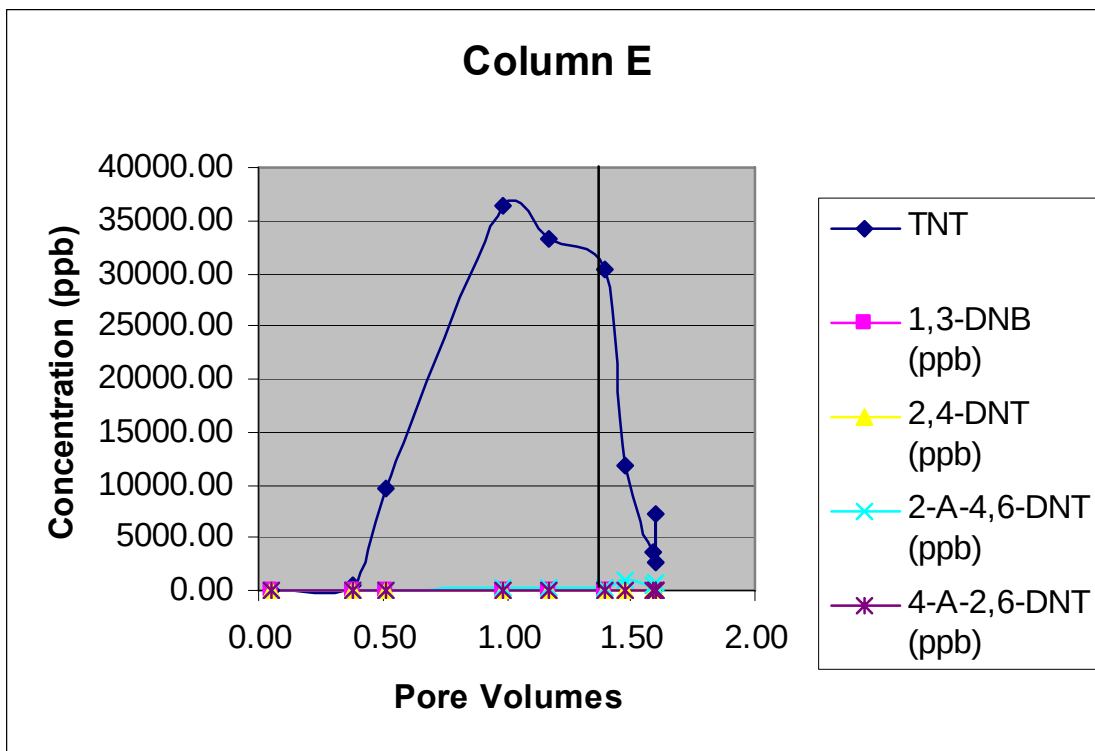


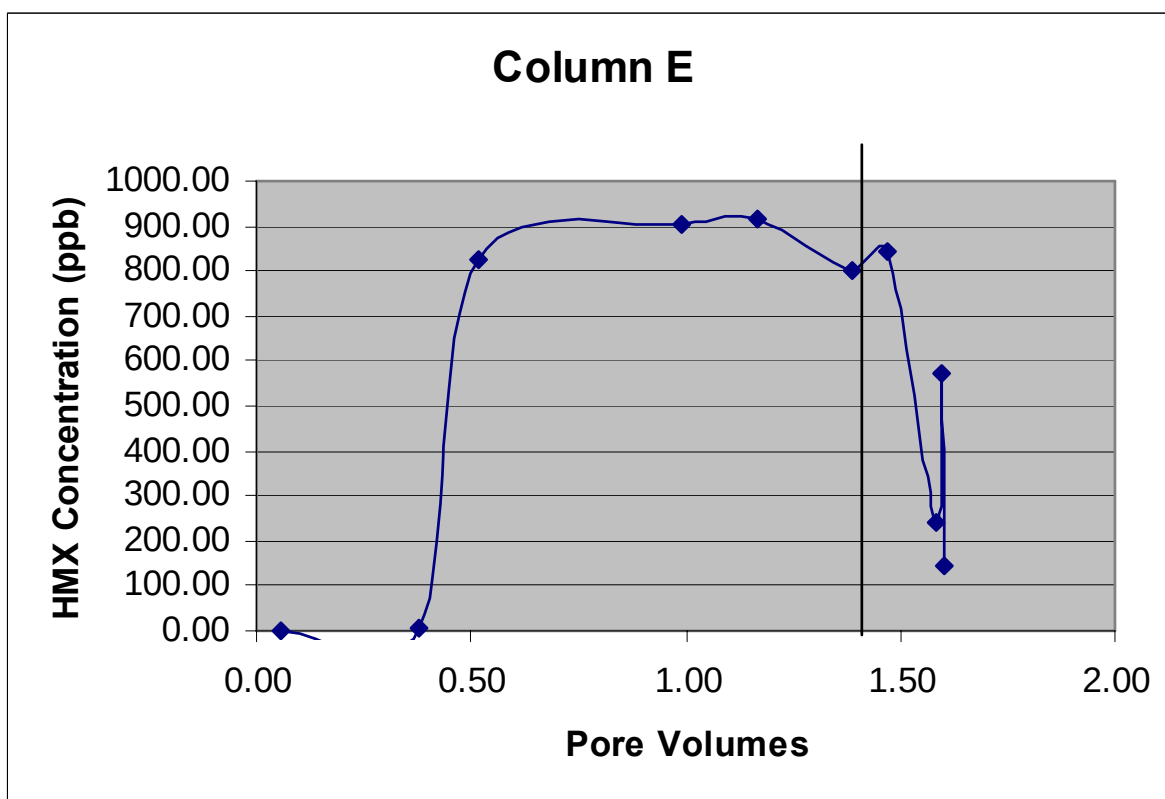
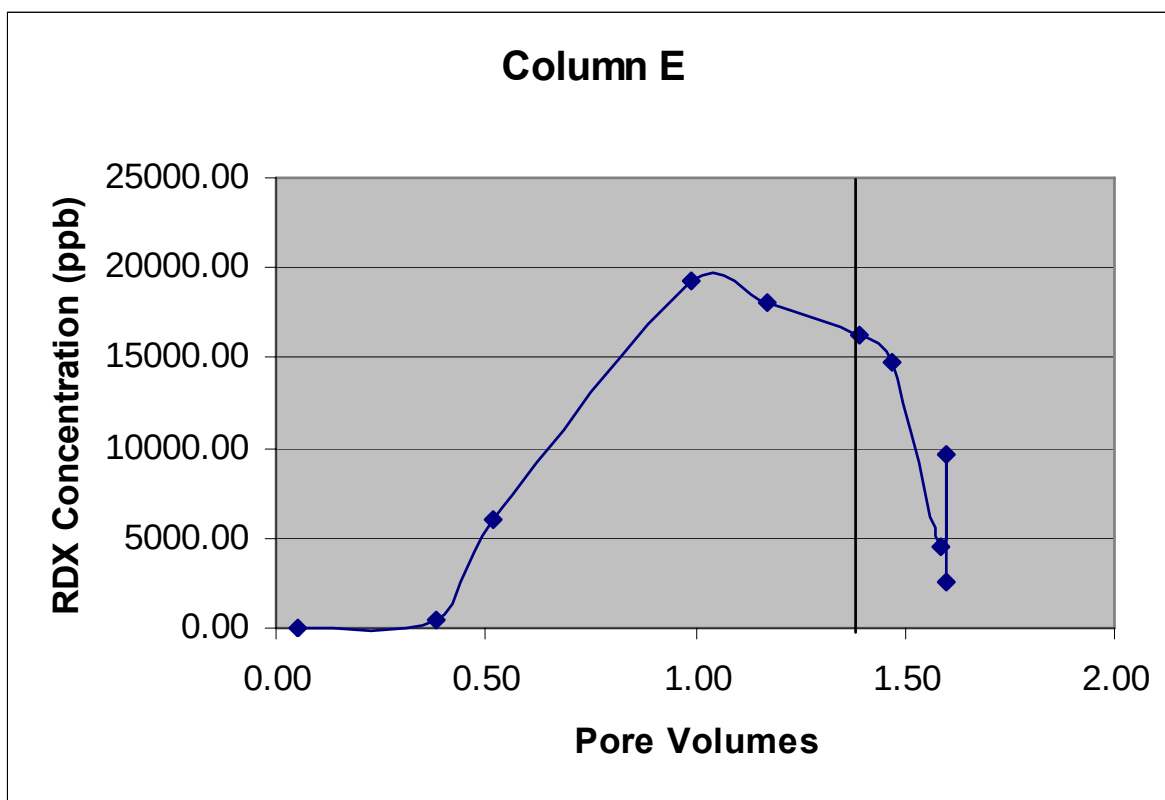


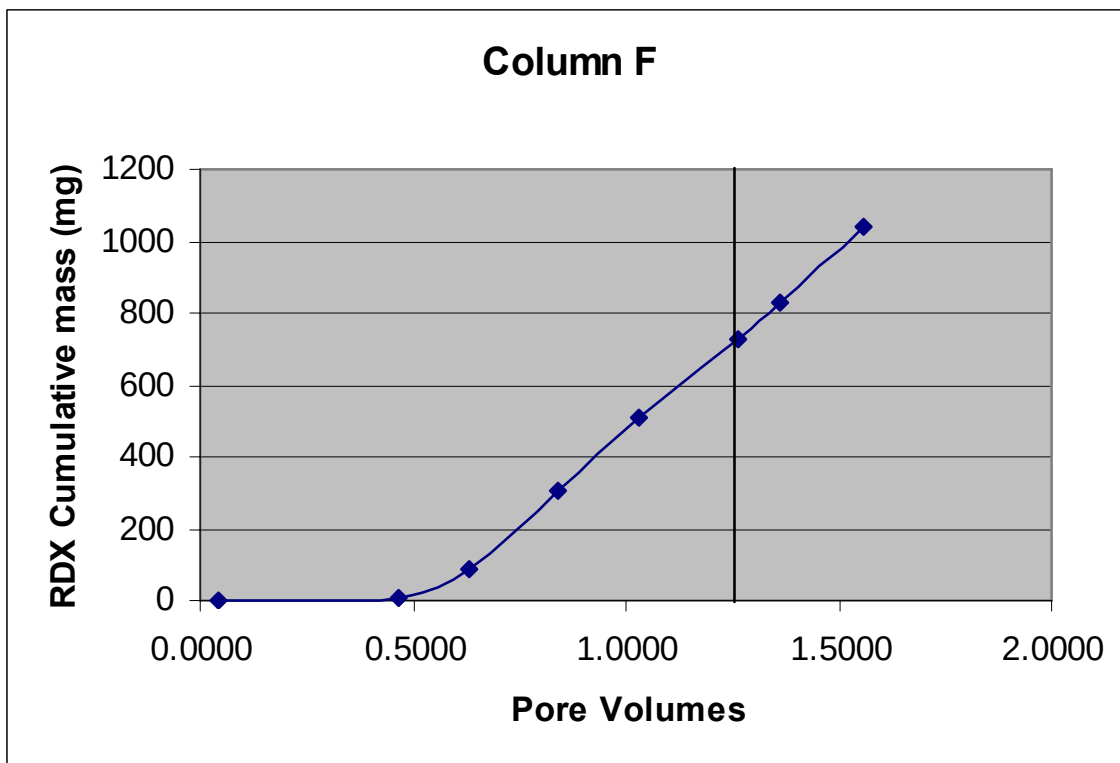
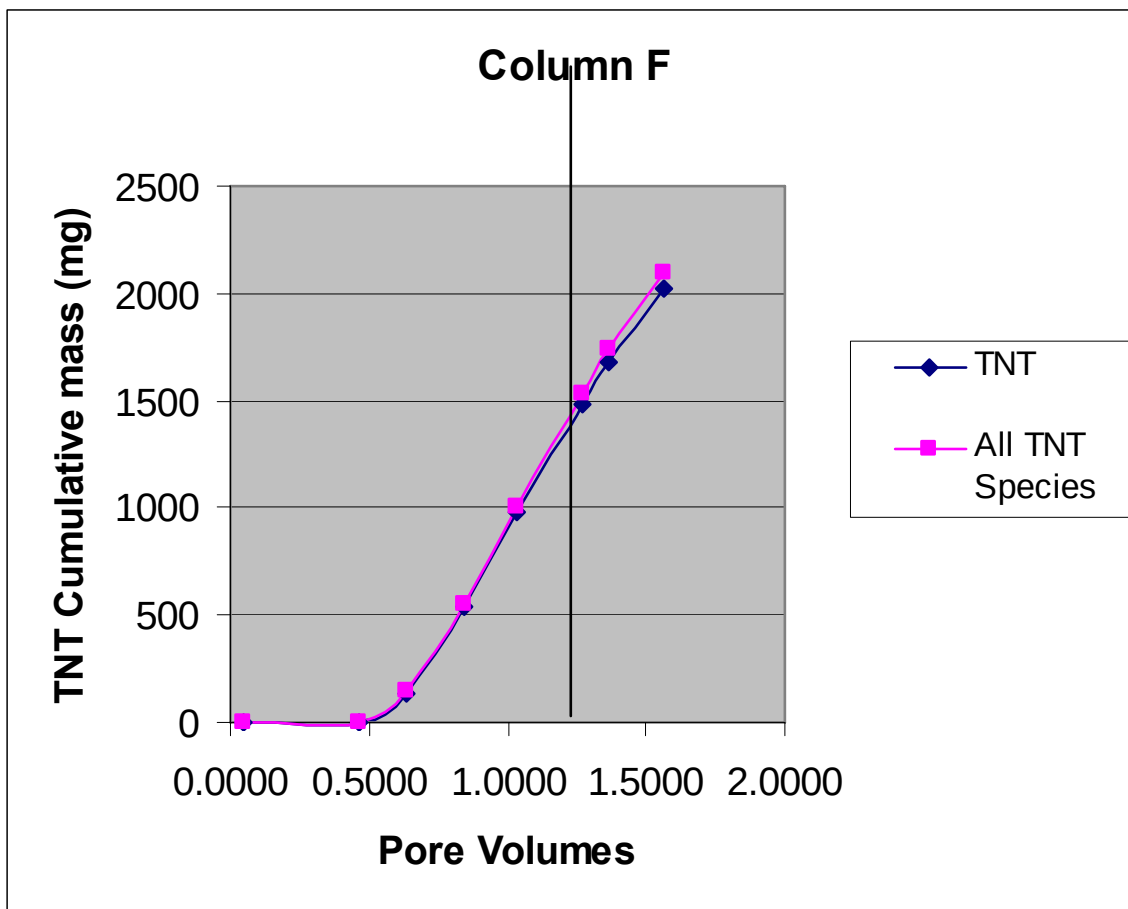


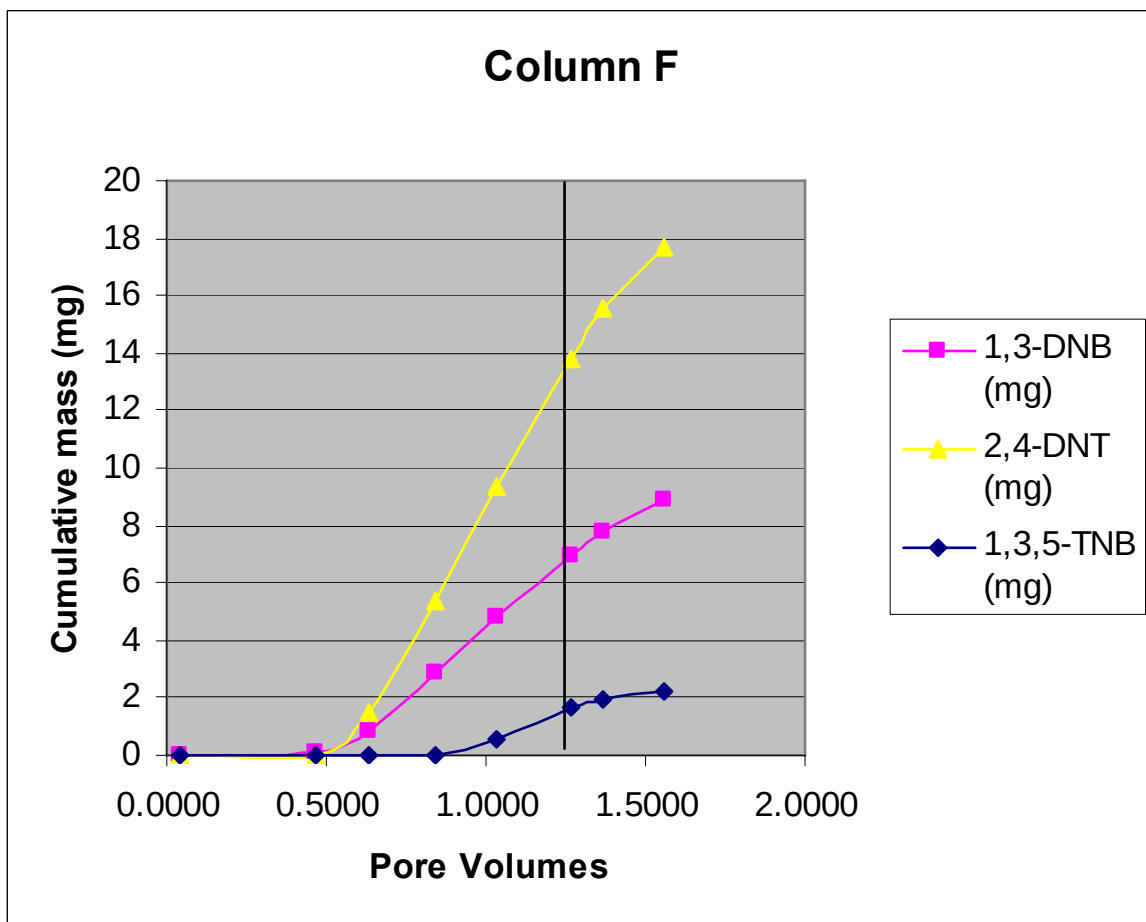
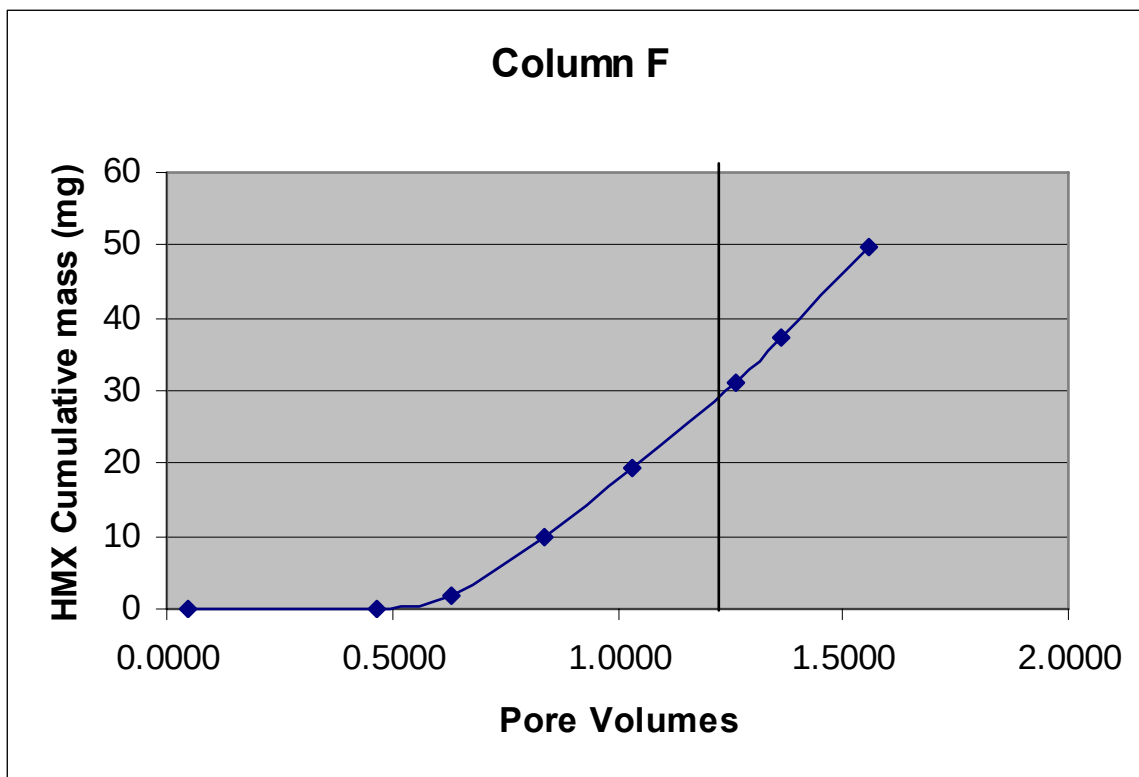


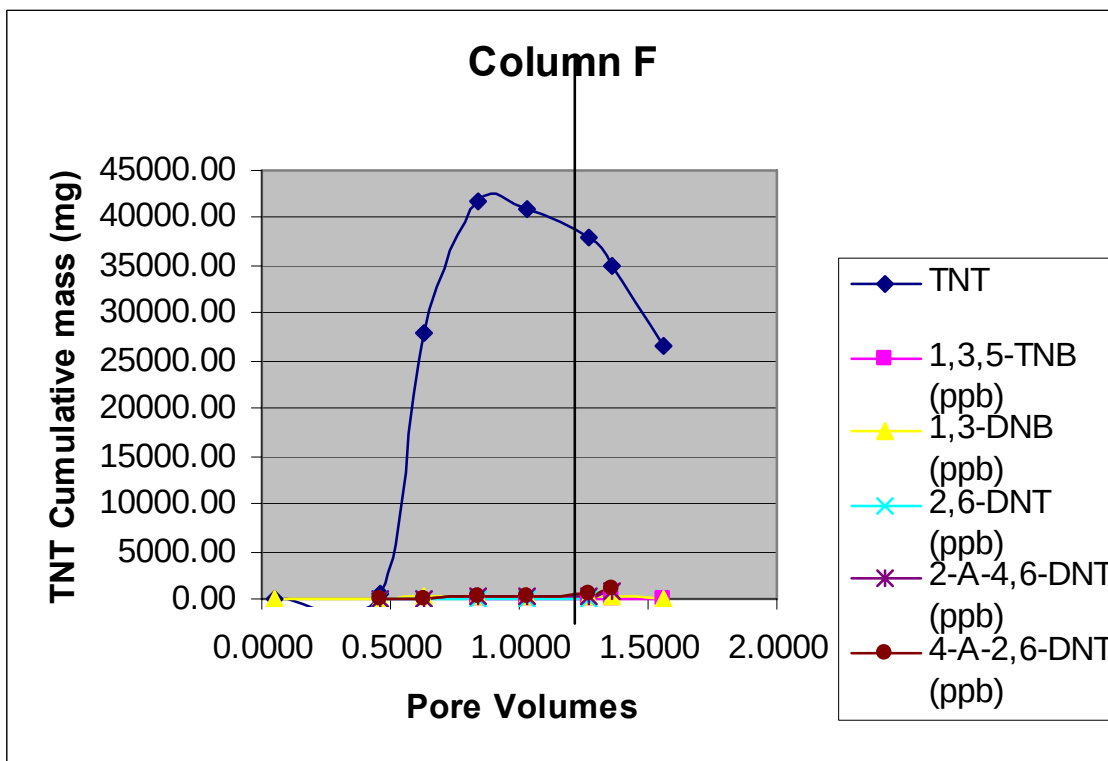
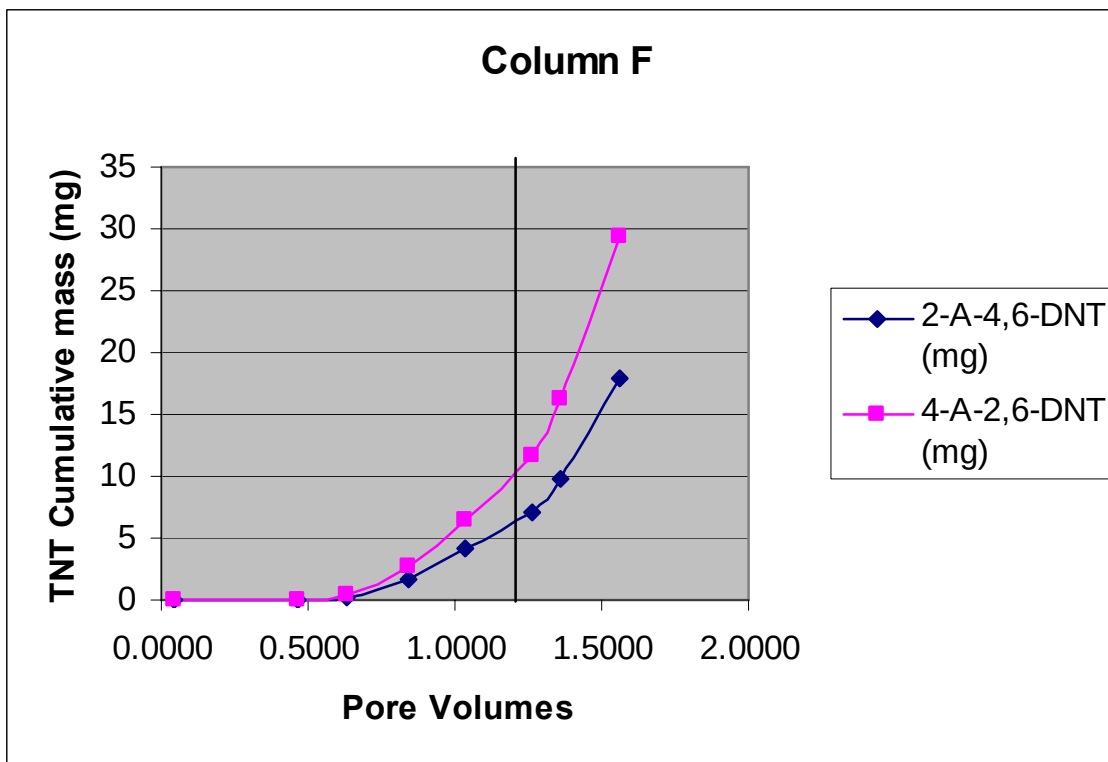


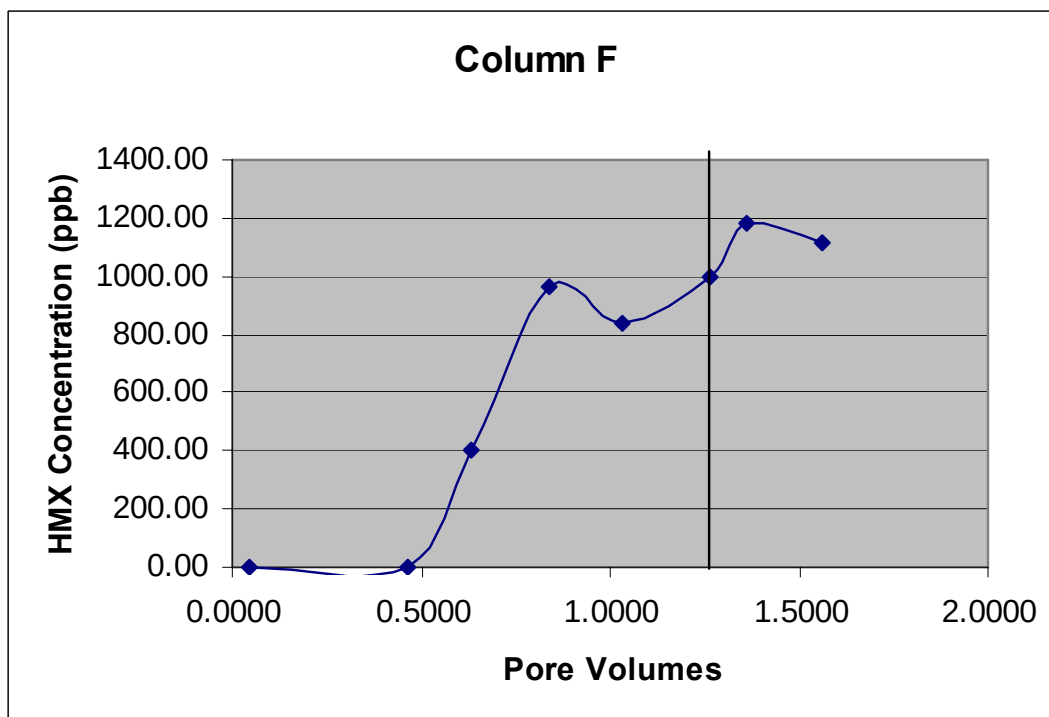
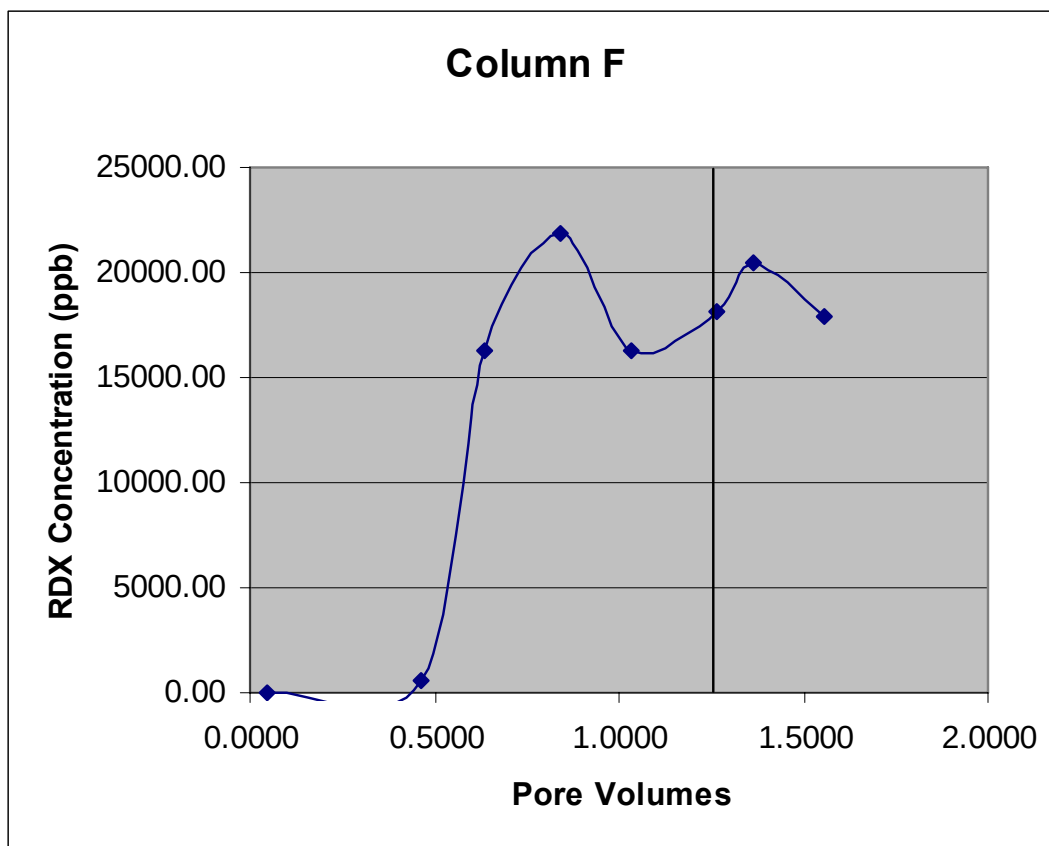


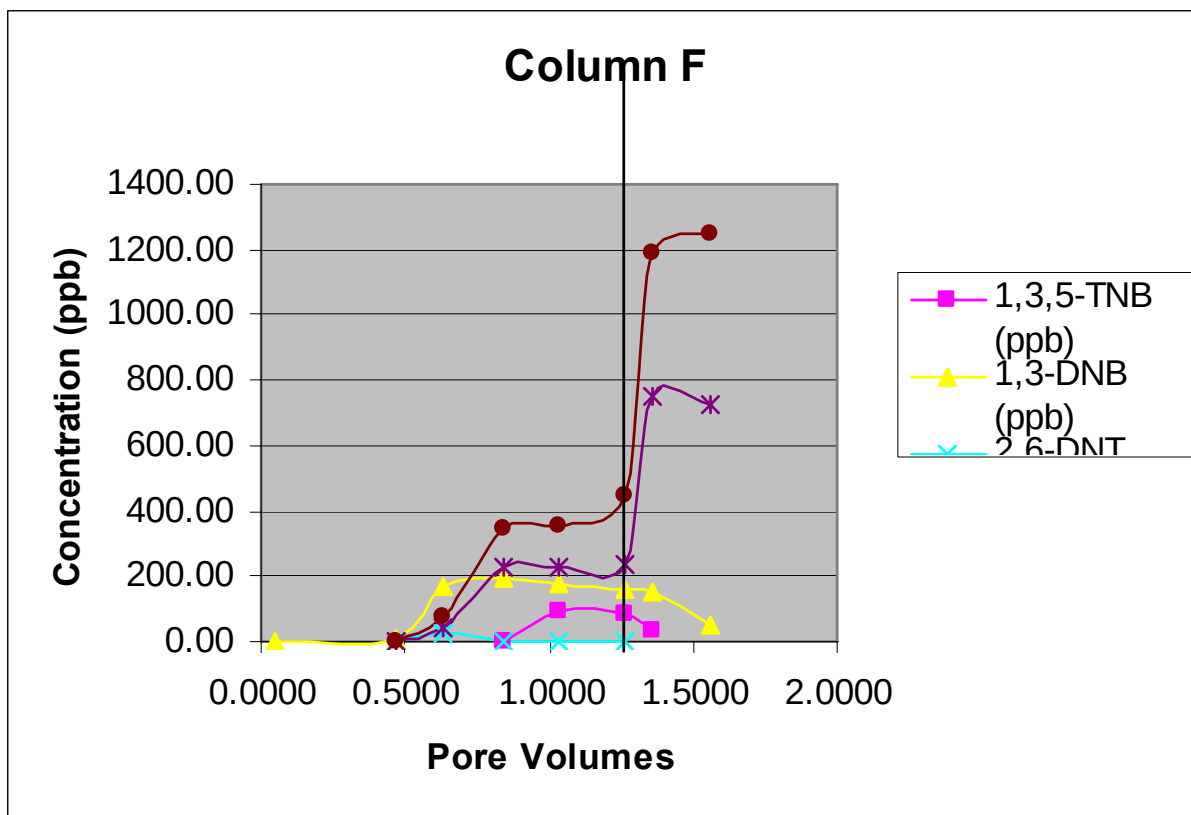






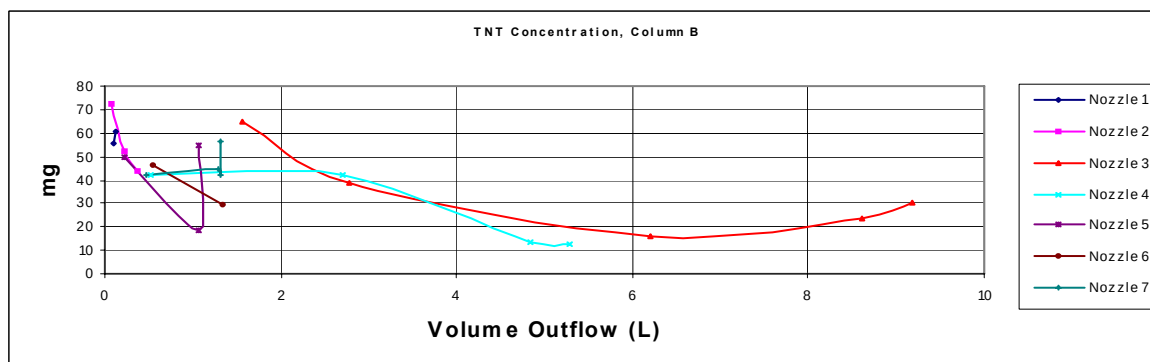
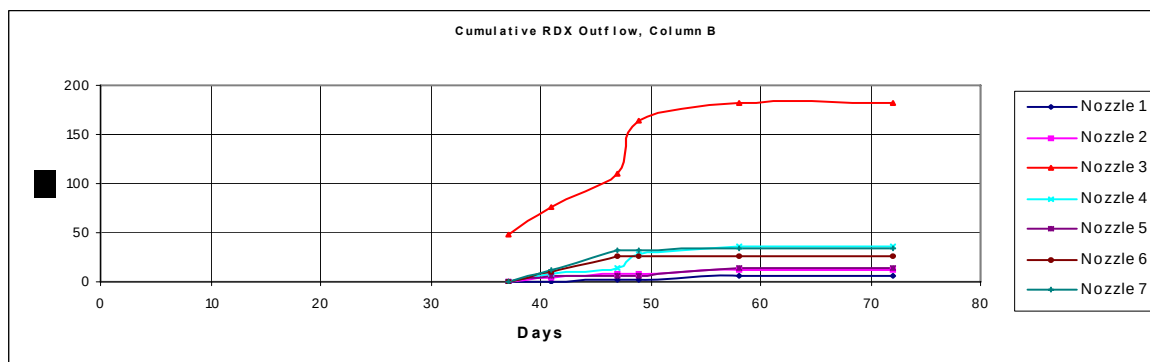
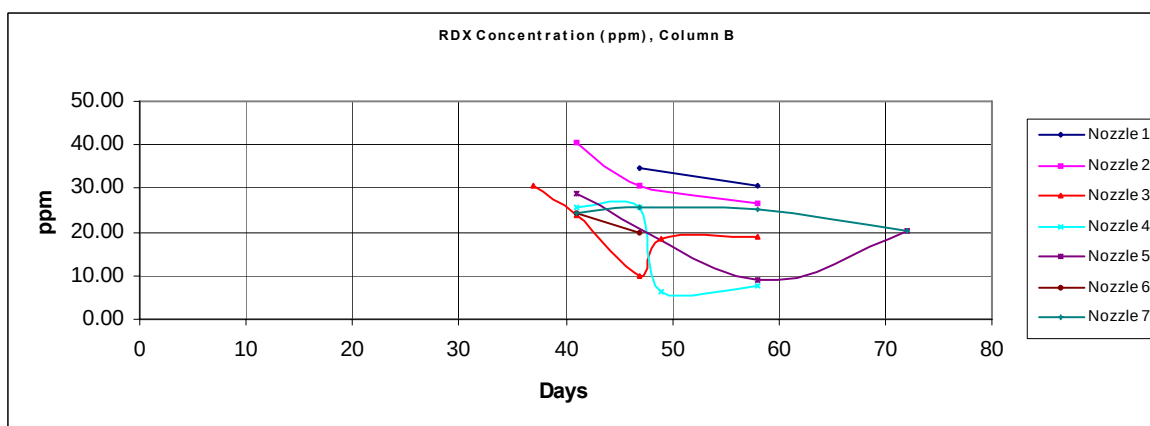
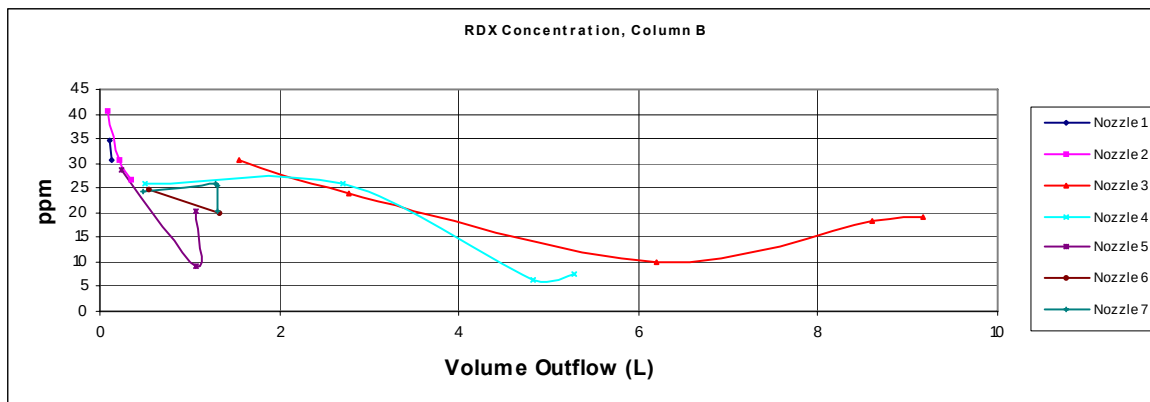


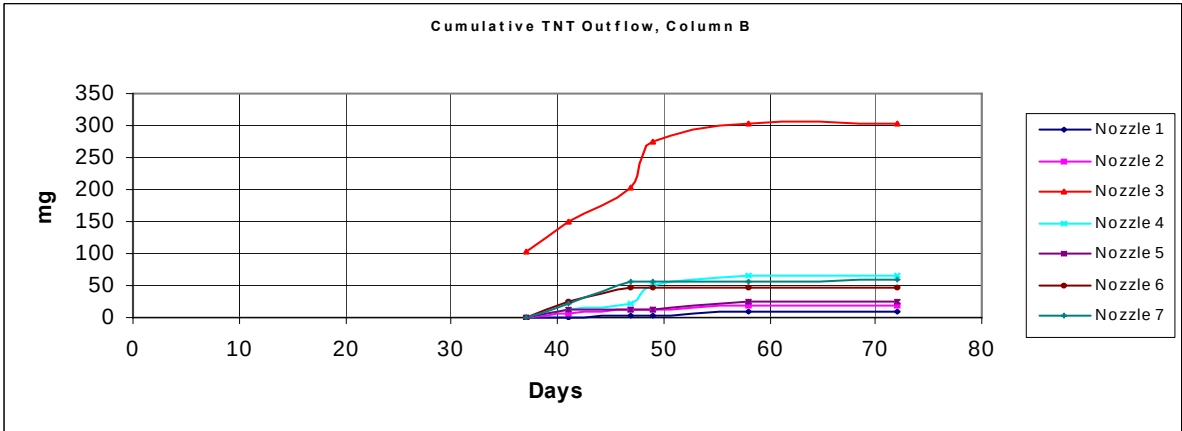
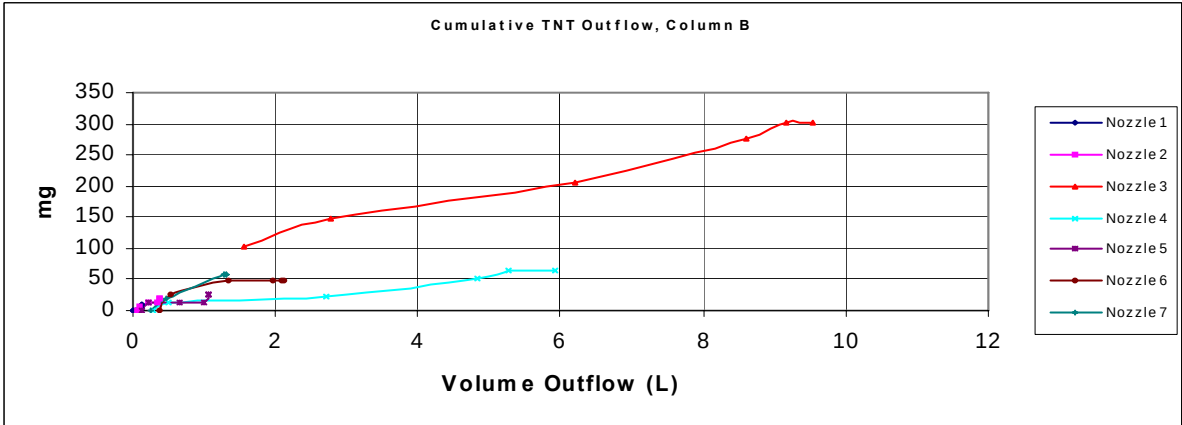
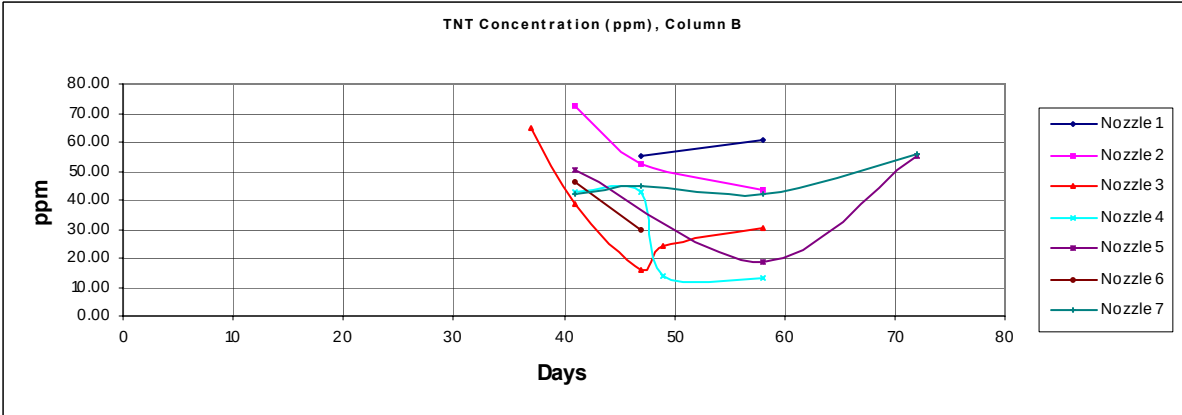
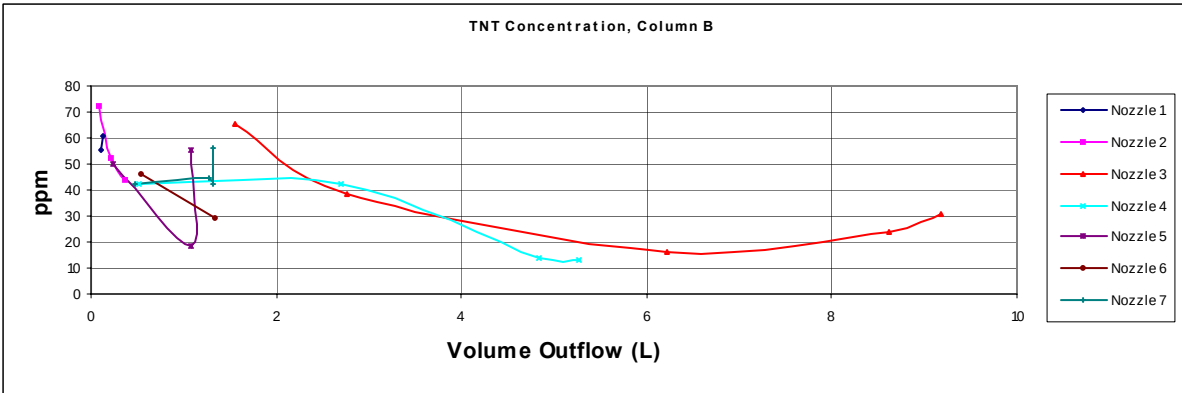


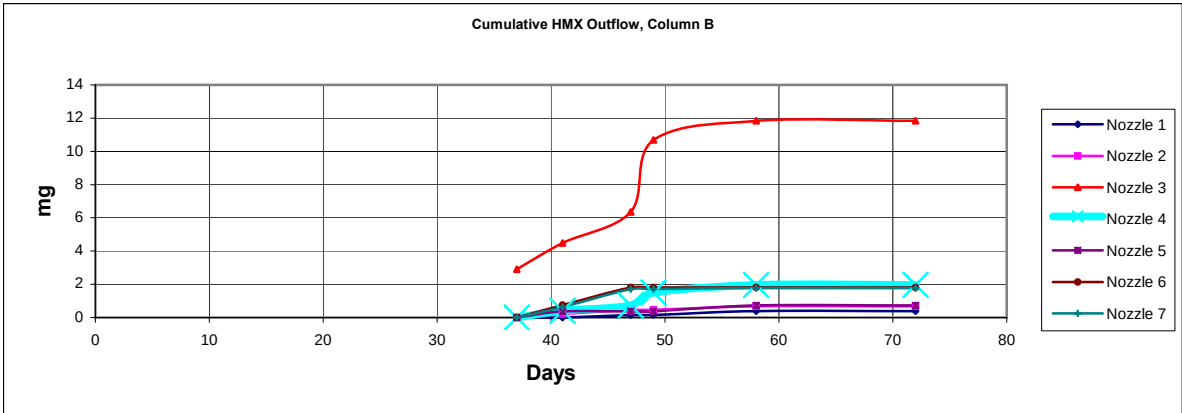
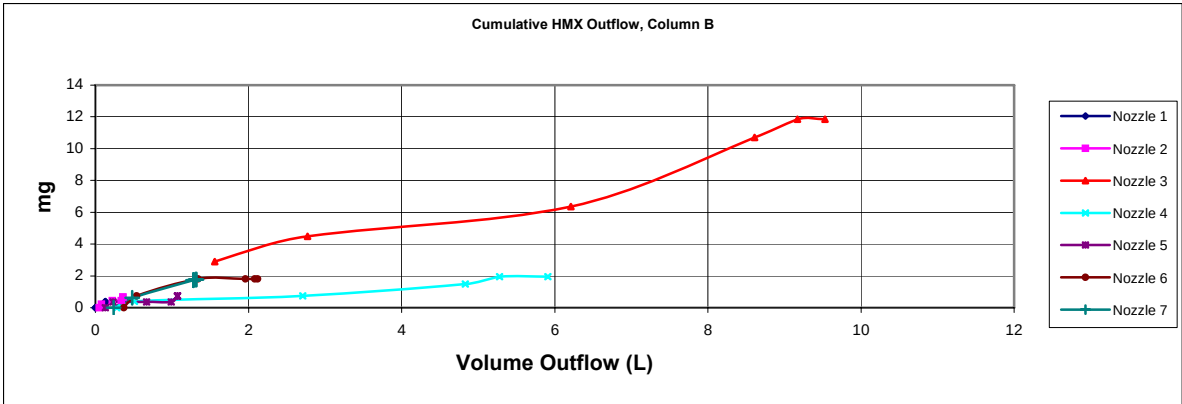
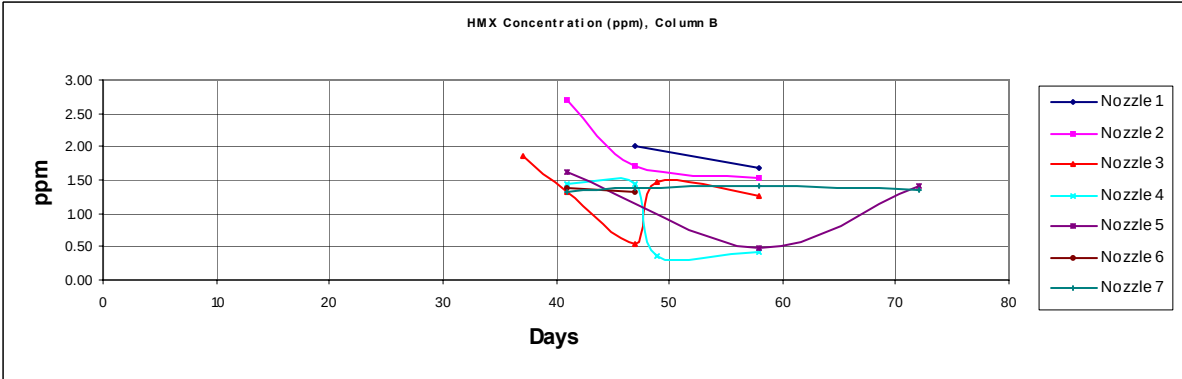
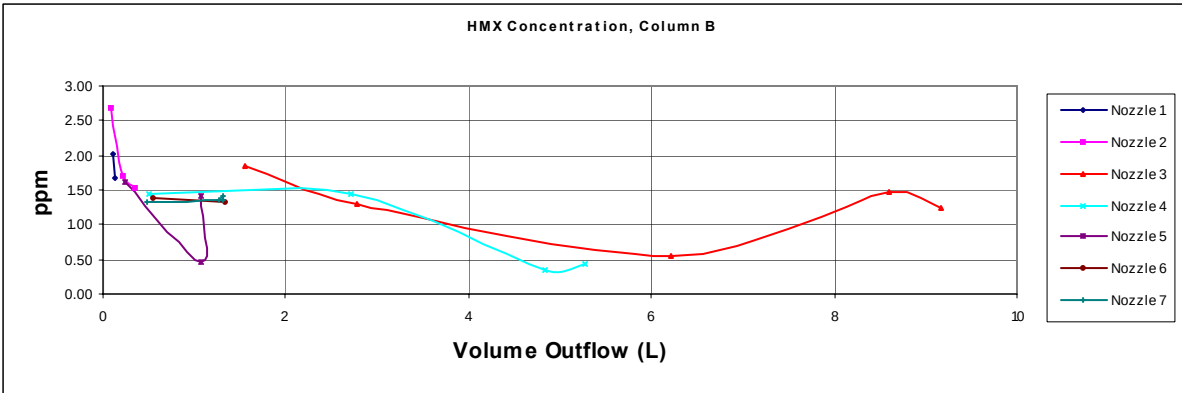


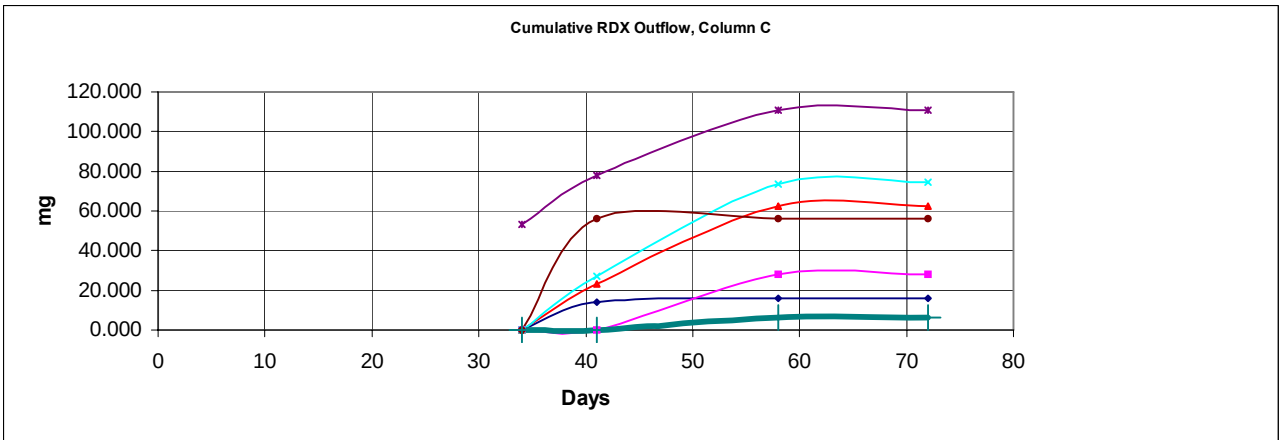
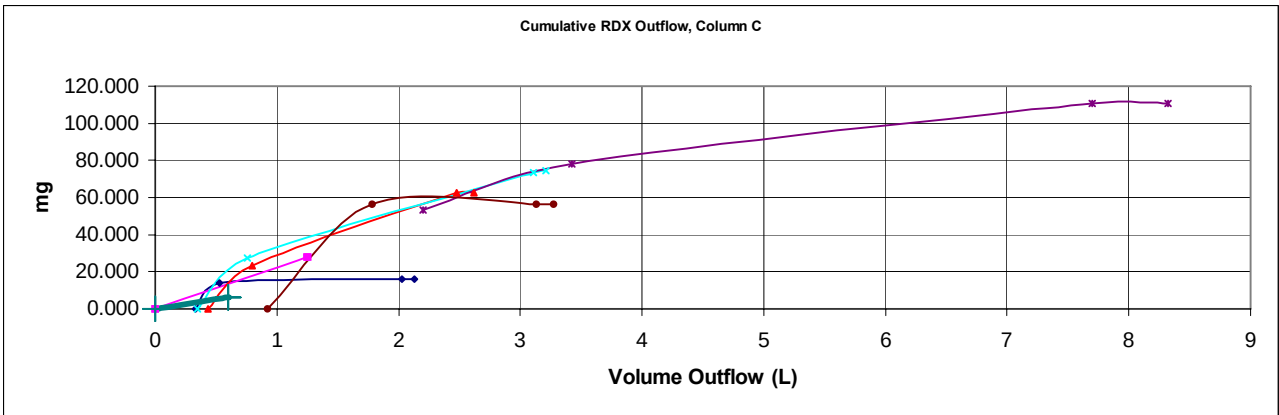
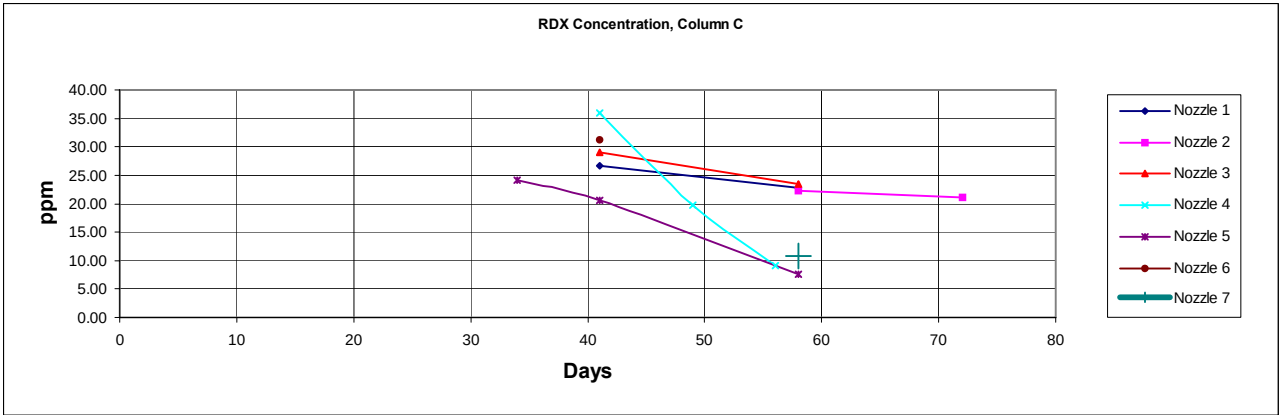
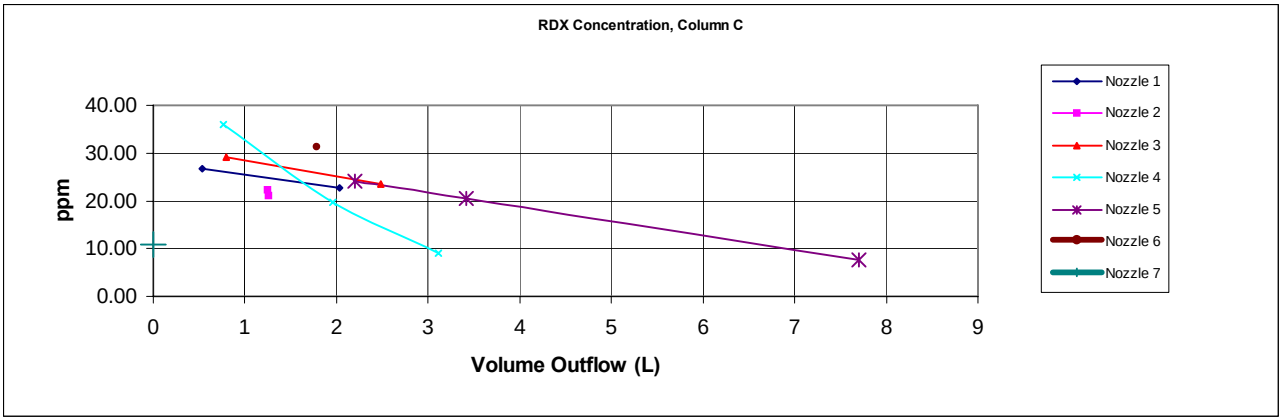
APPENDIX 5. AUTUMN EXPLOSIVES LEACHATE OUTFLOW

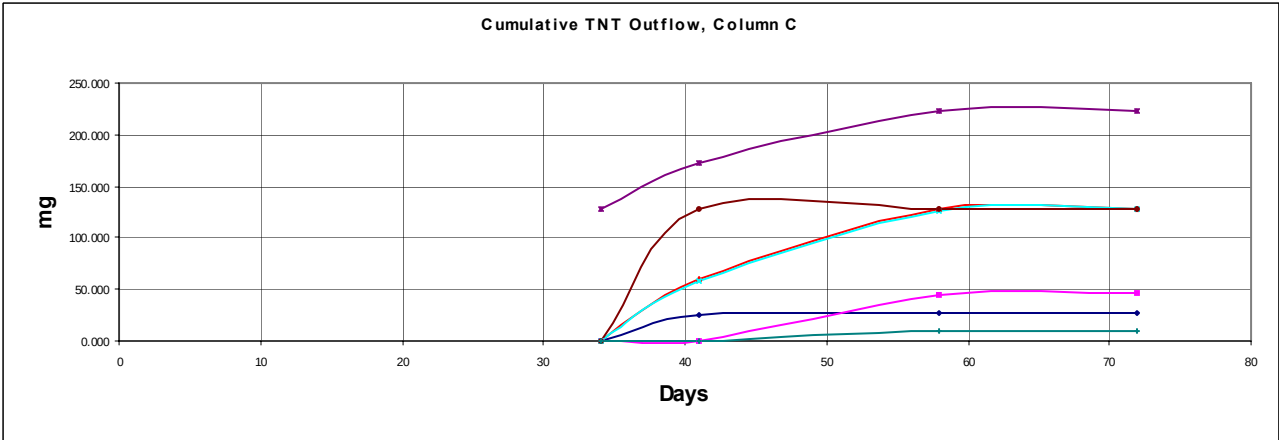
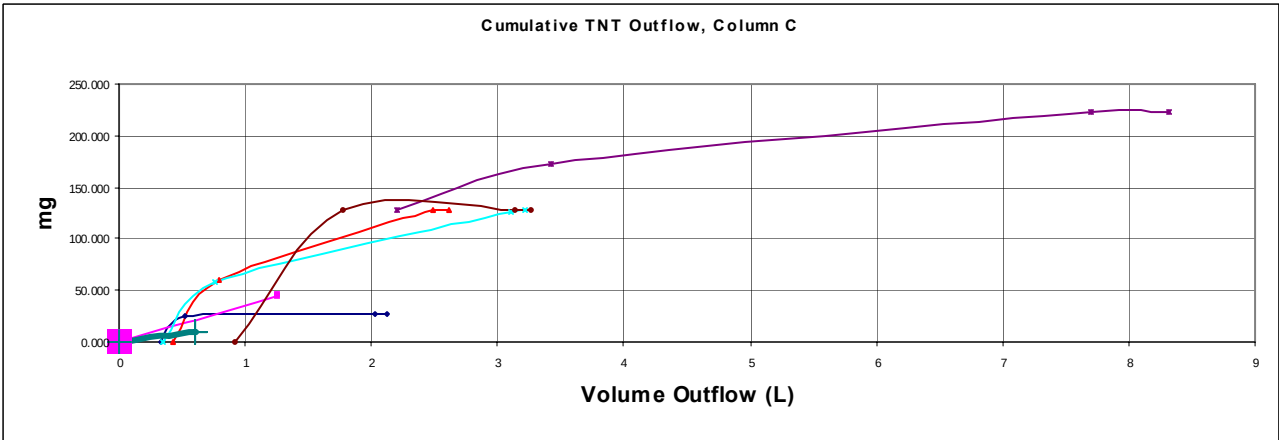
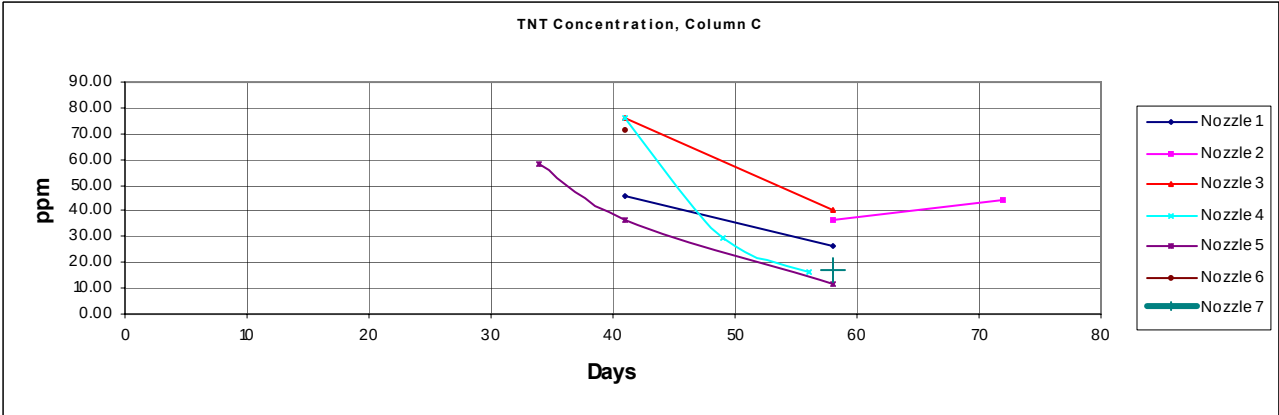
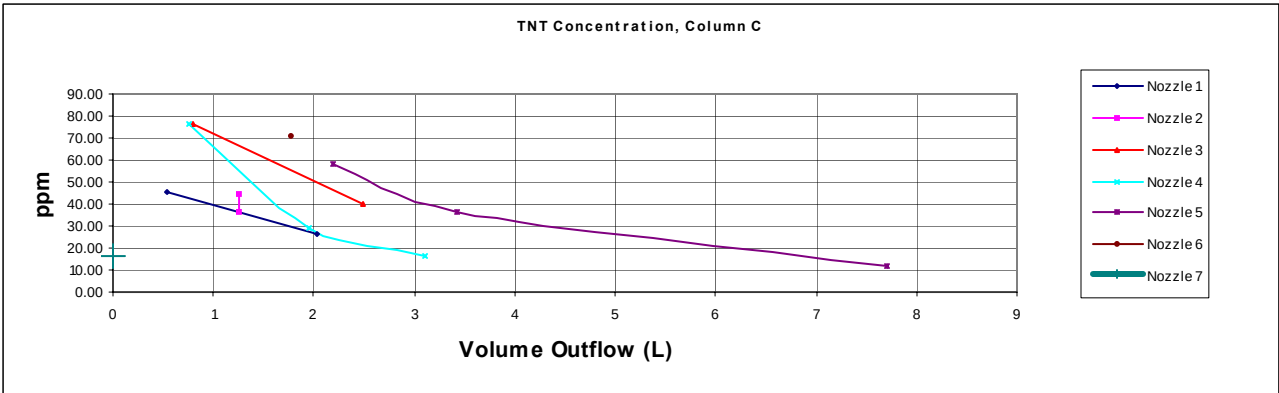
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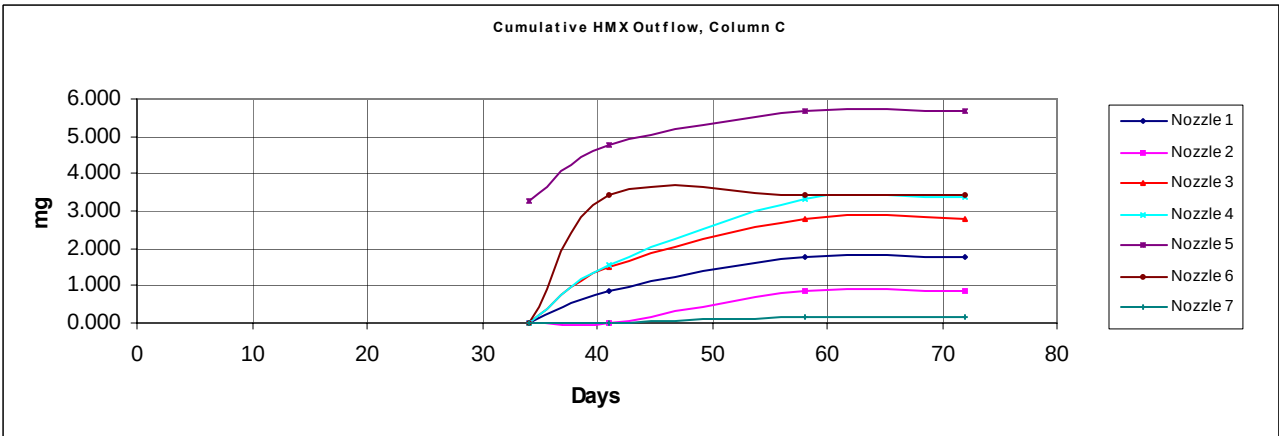
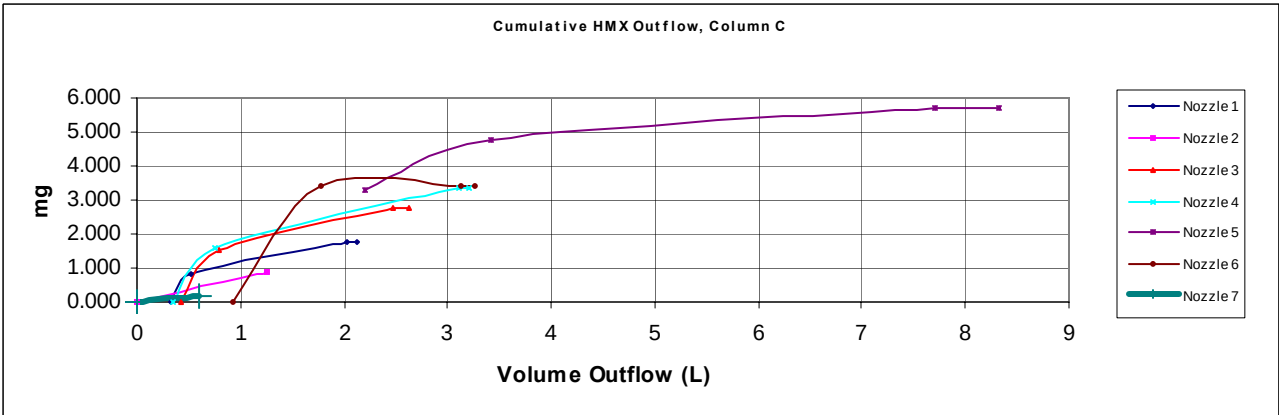
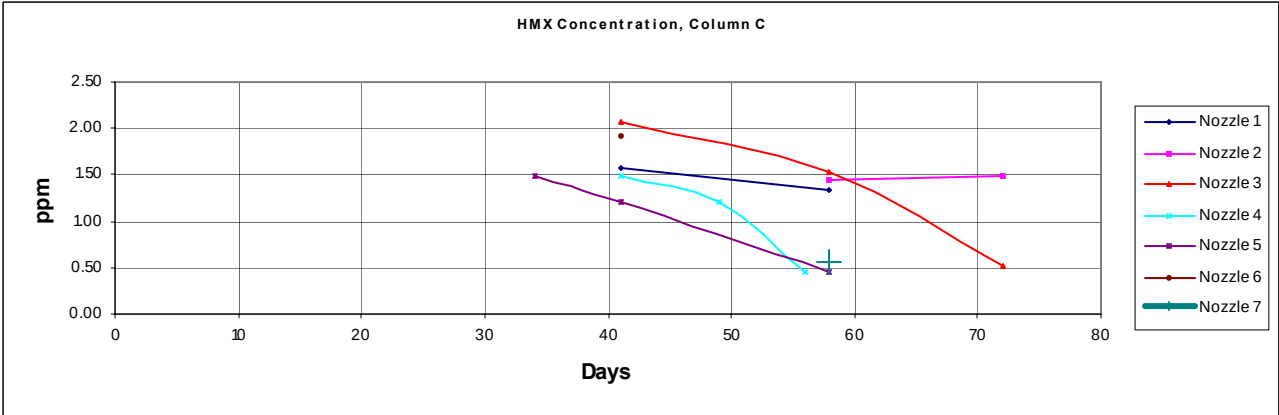
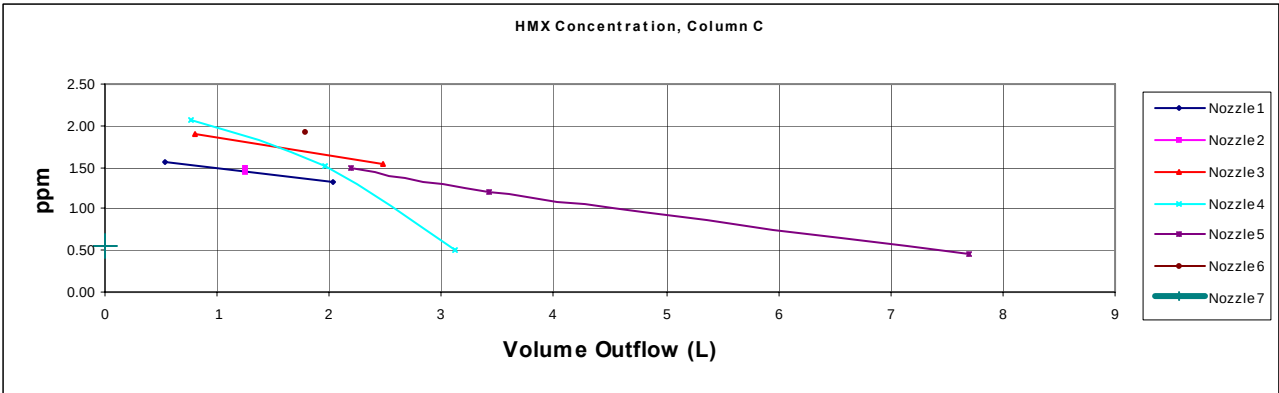


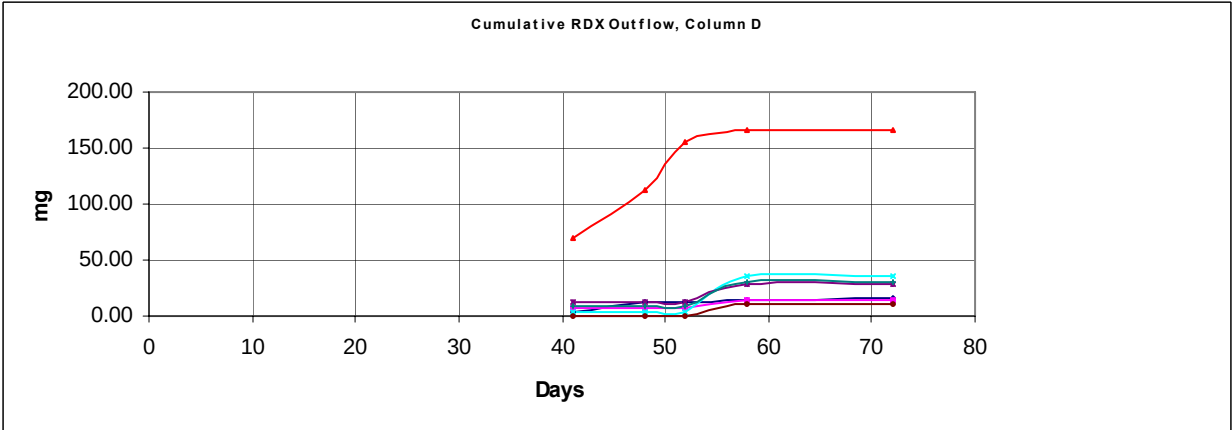
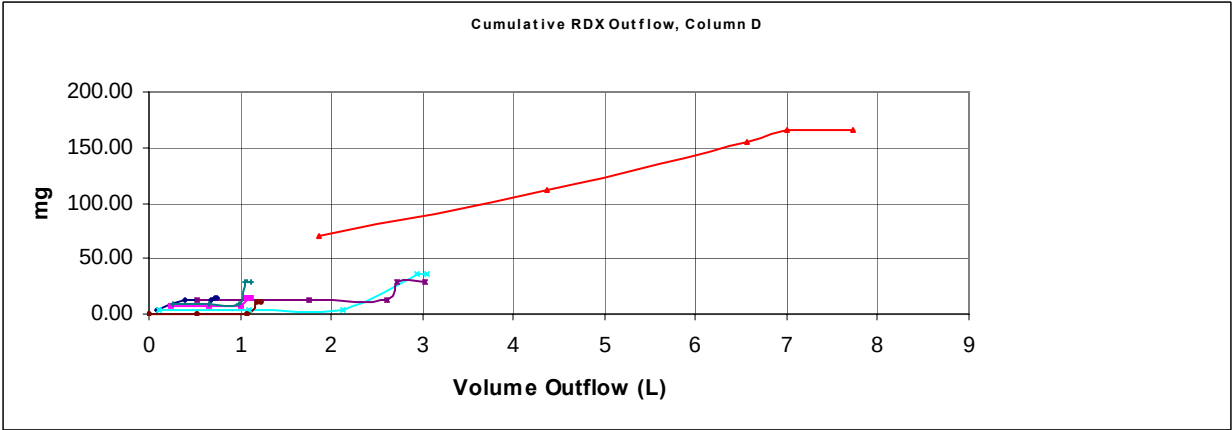
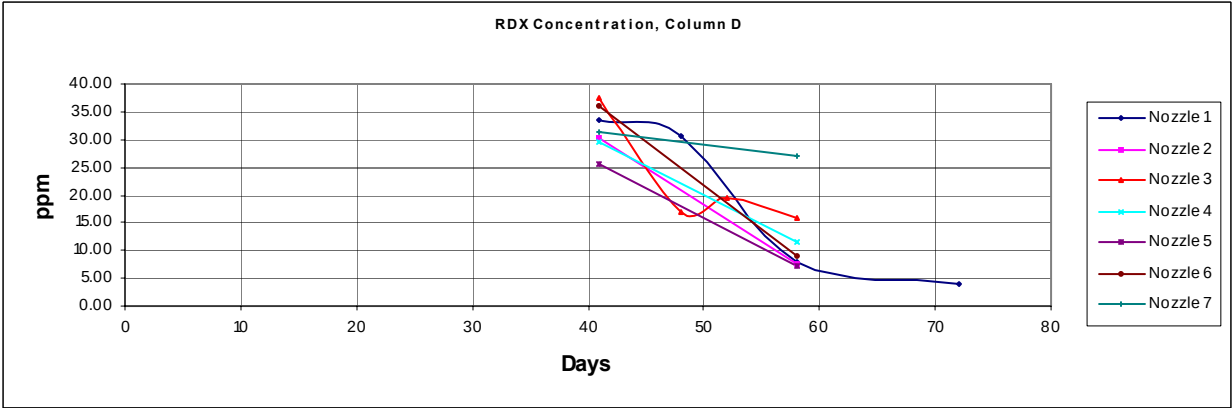
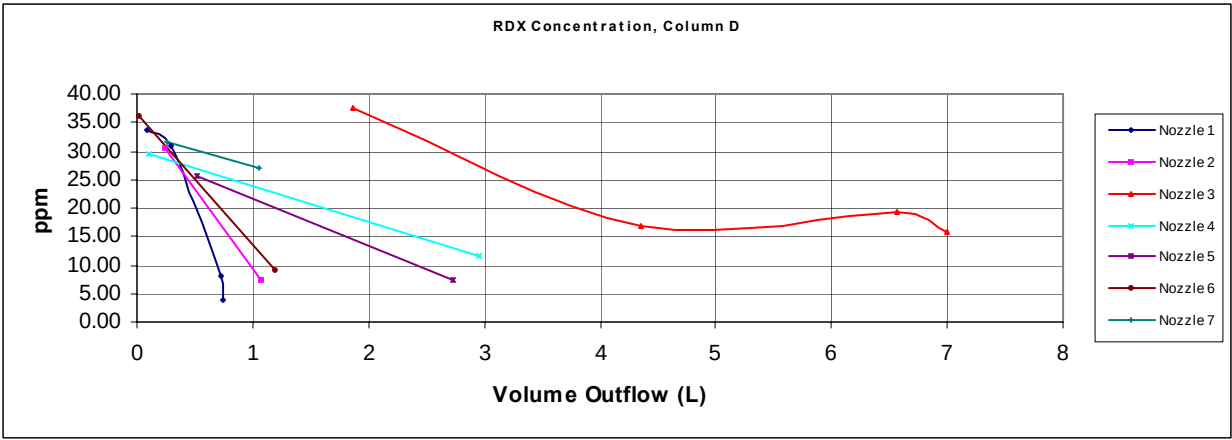


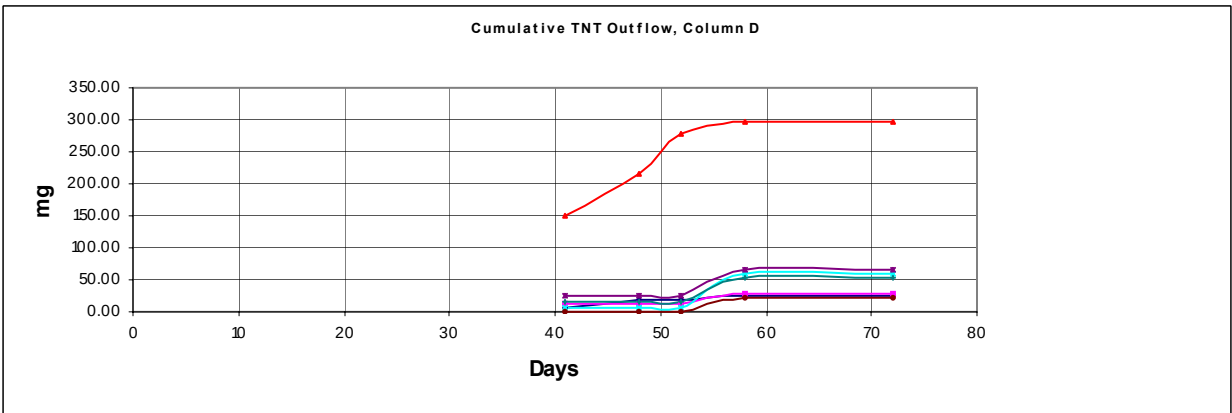
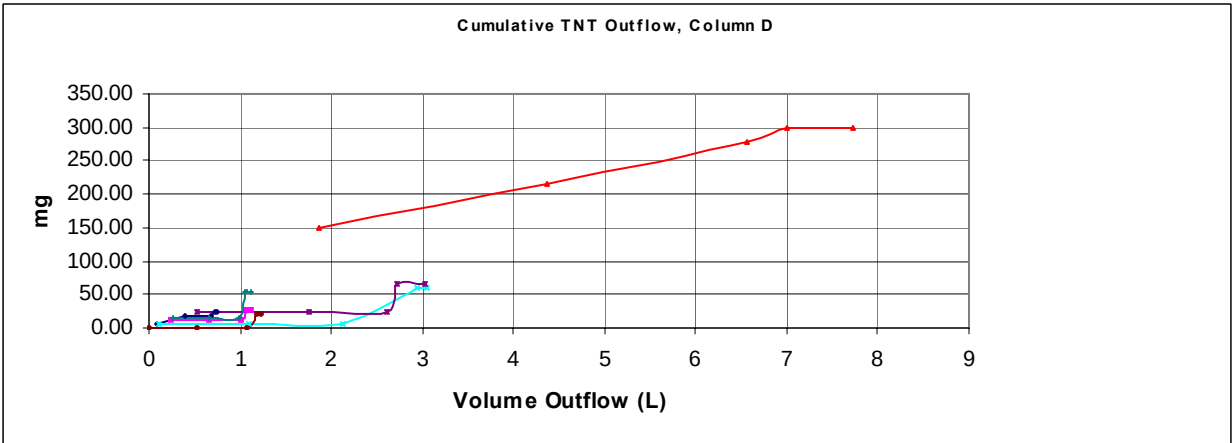
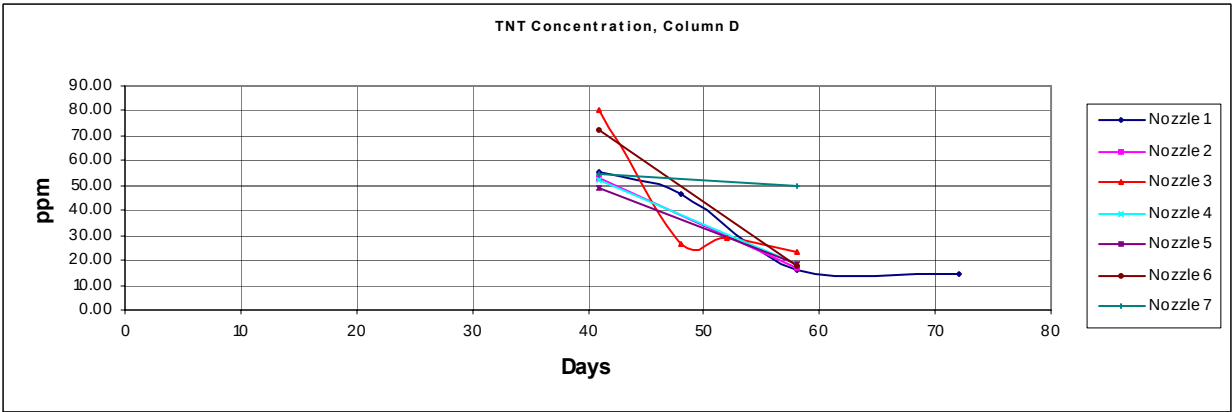
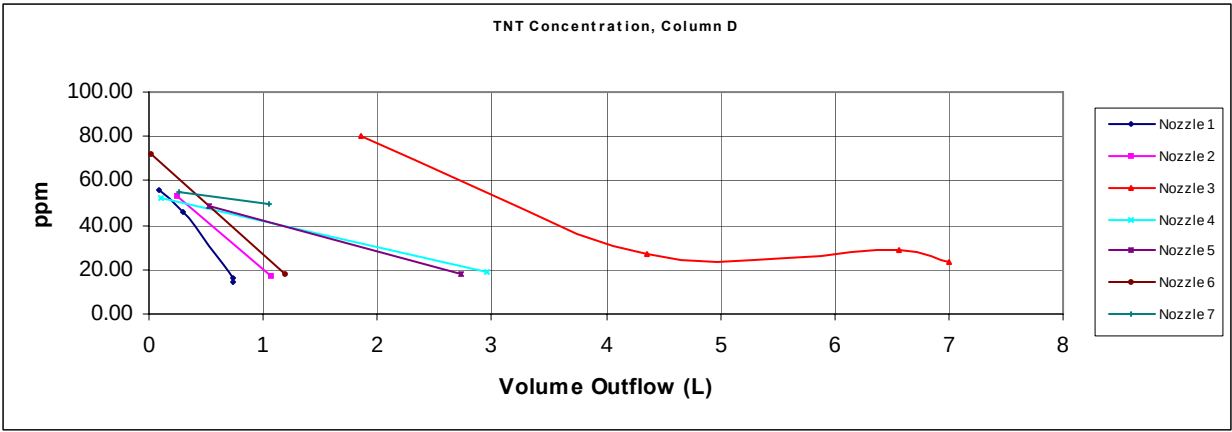


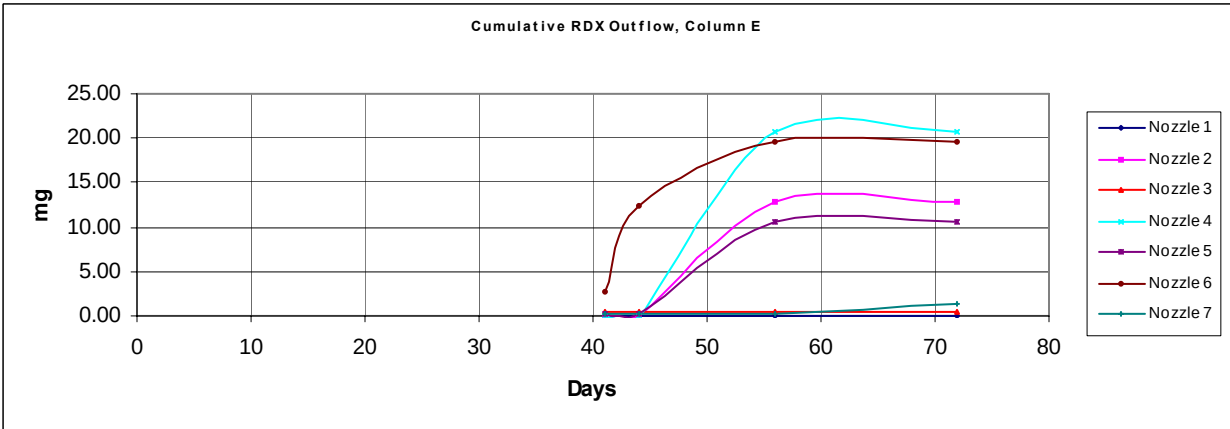
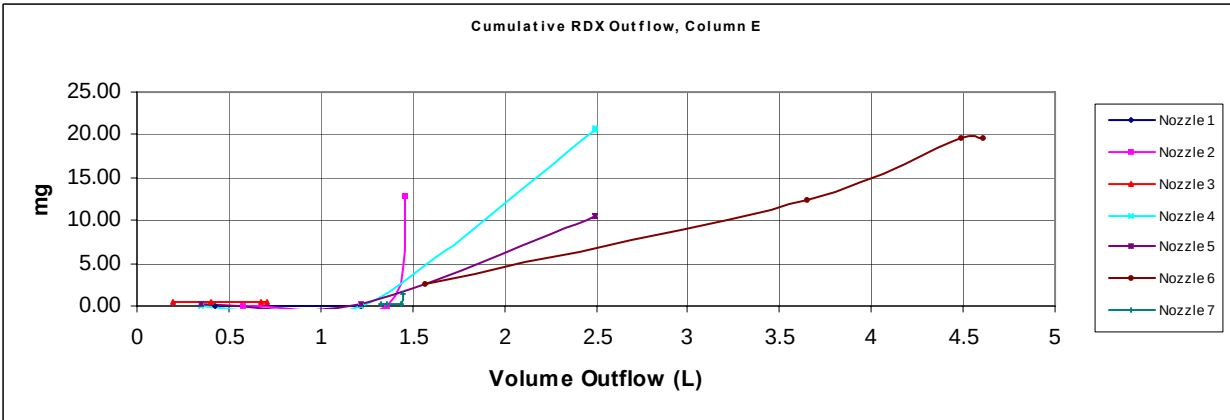
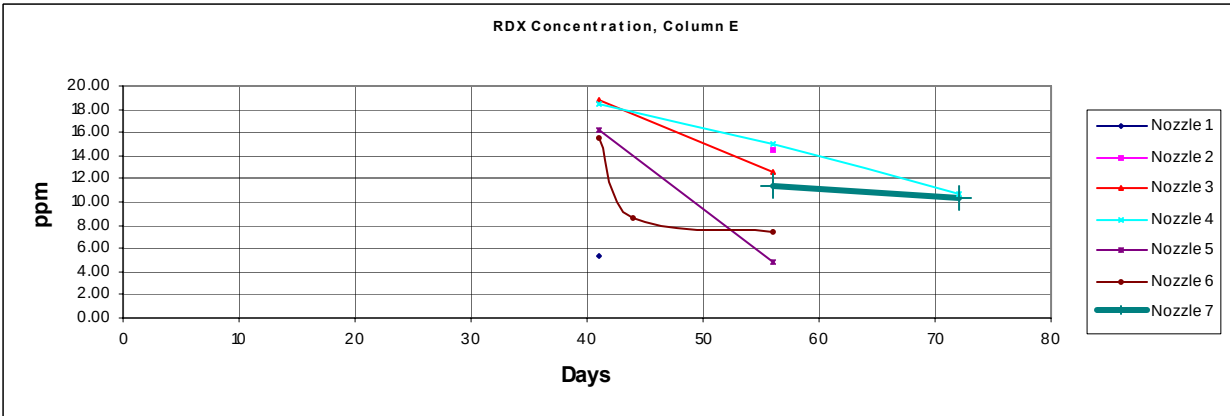
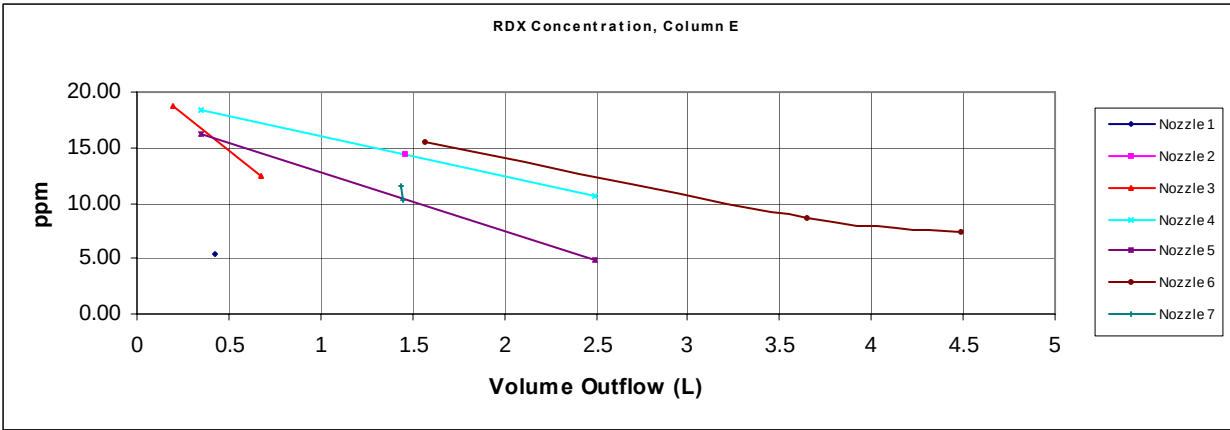


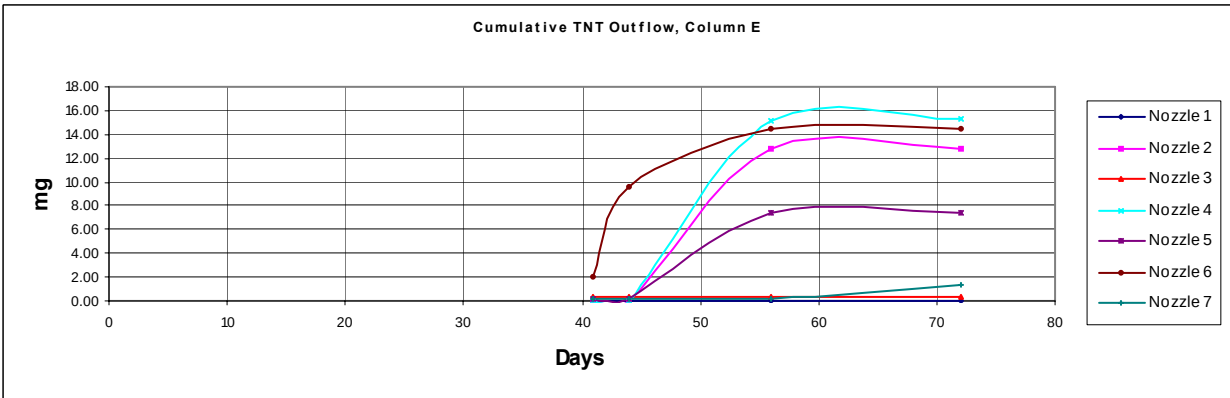
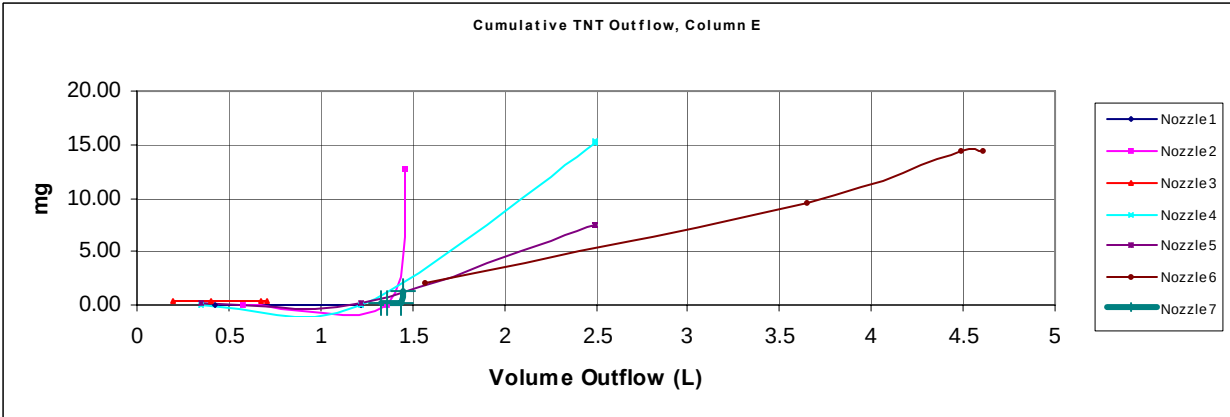
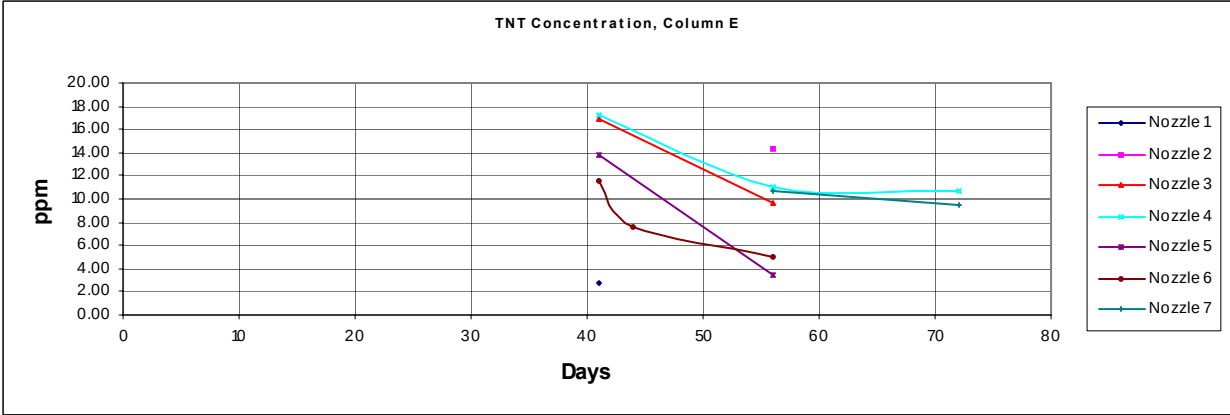
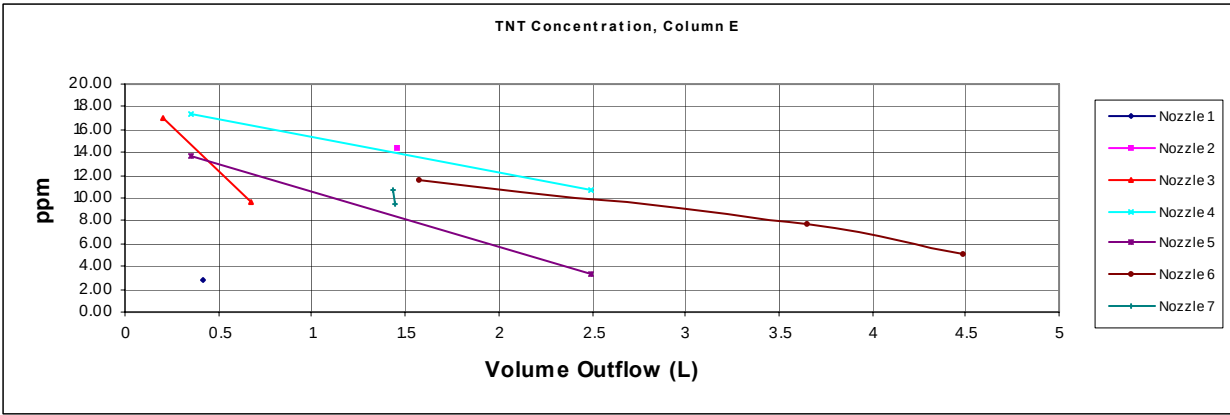


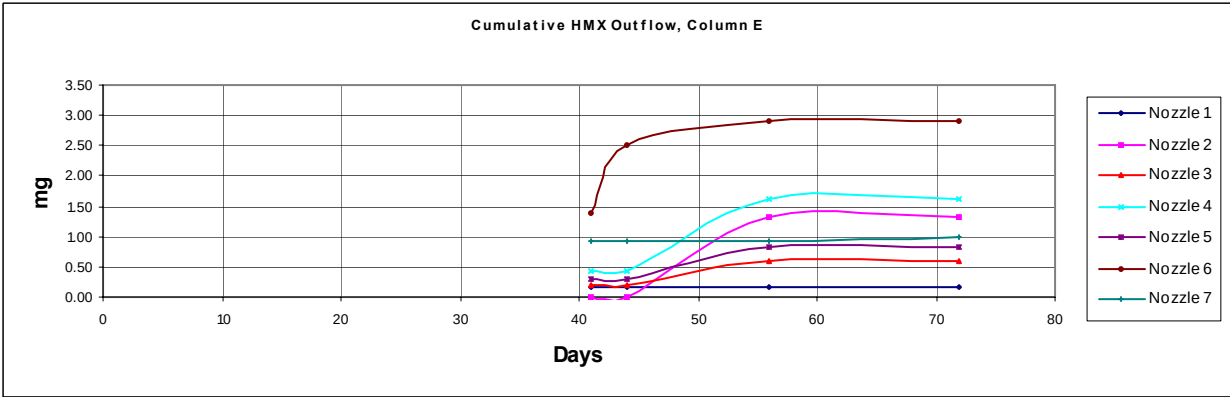
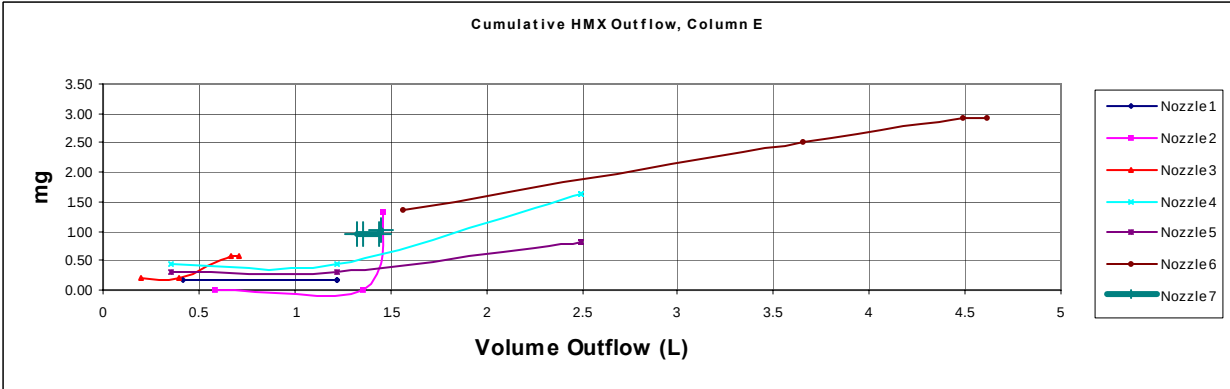
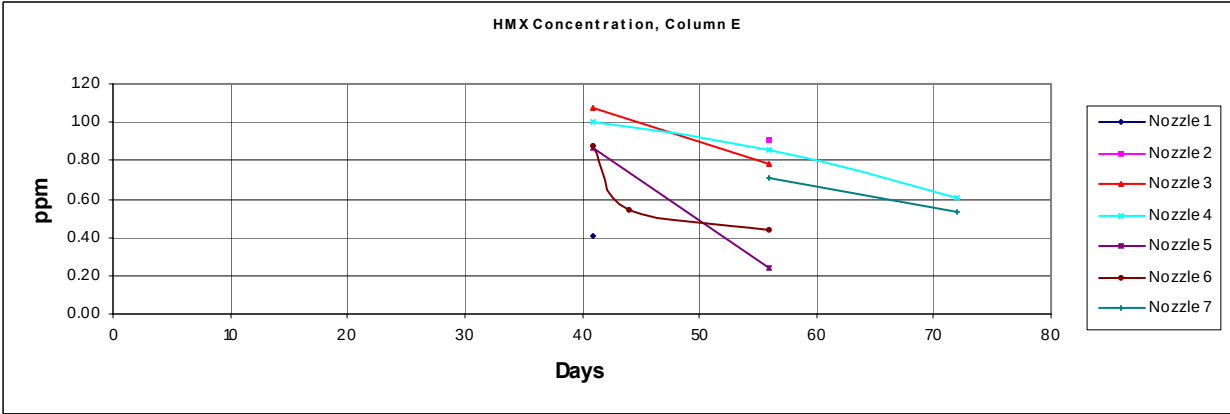
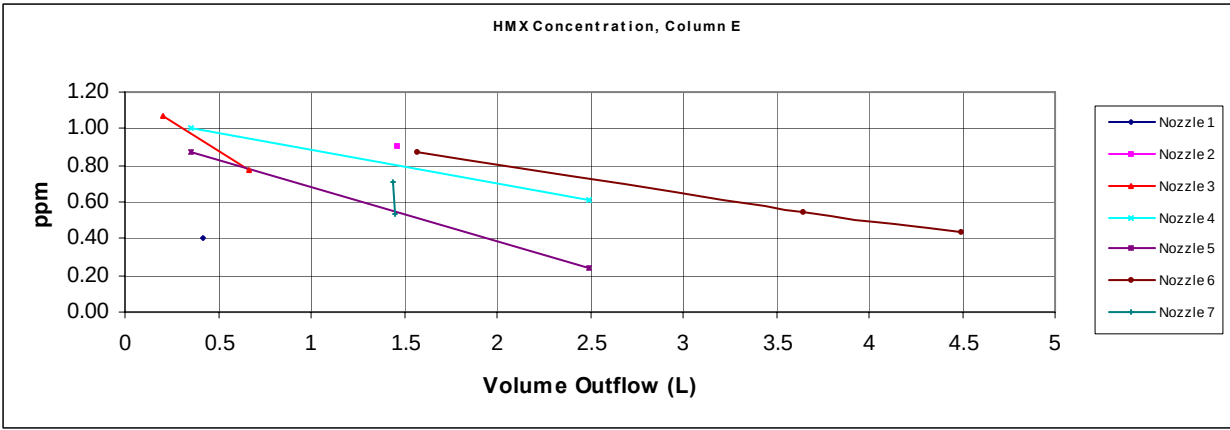


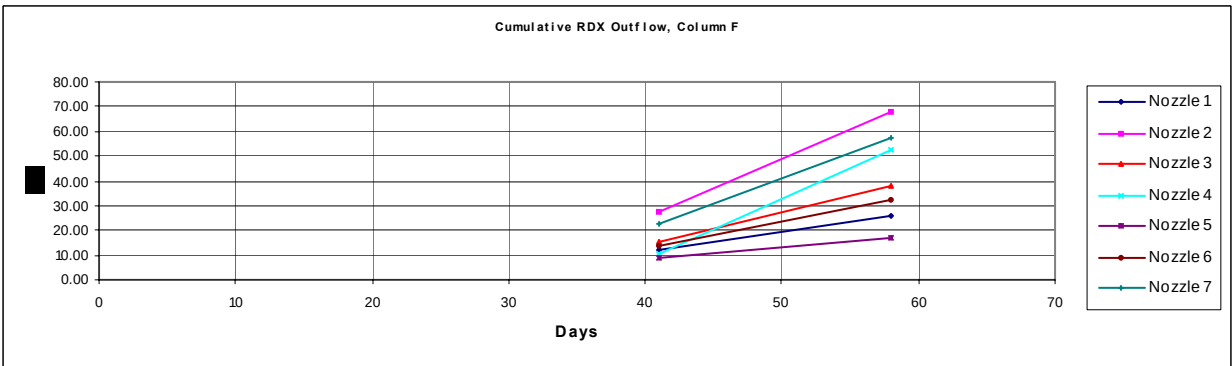
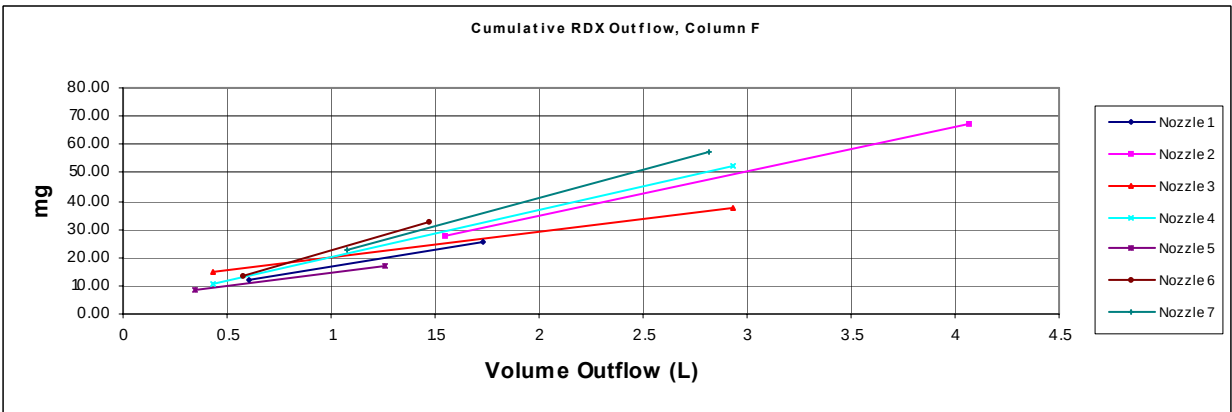
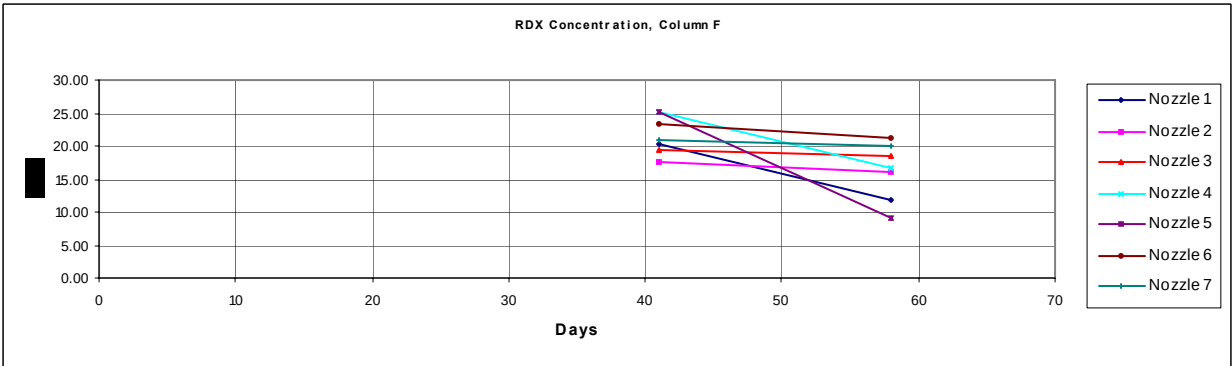
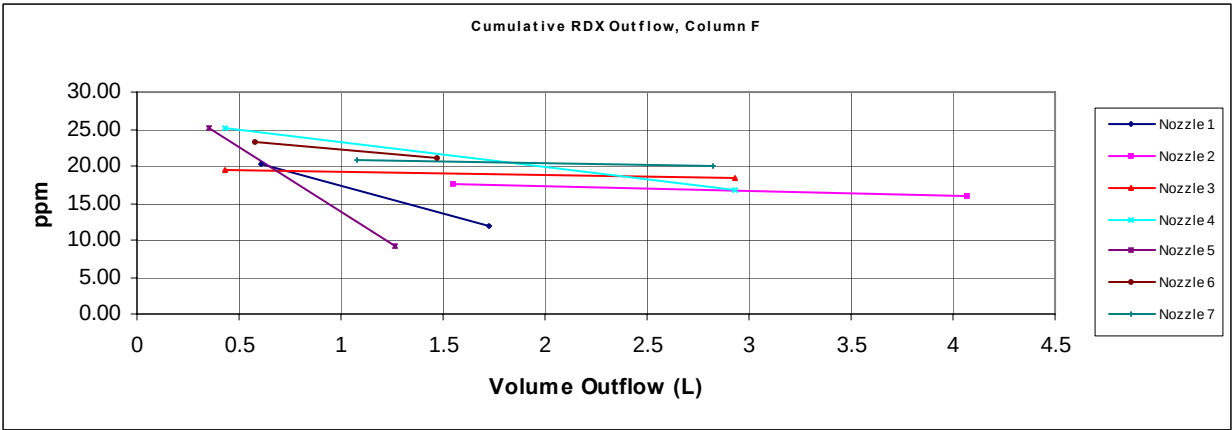


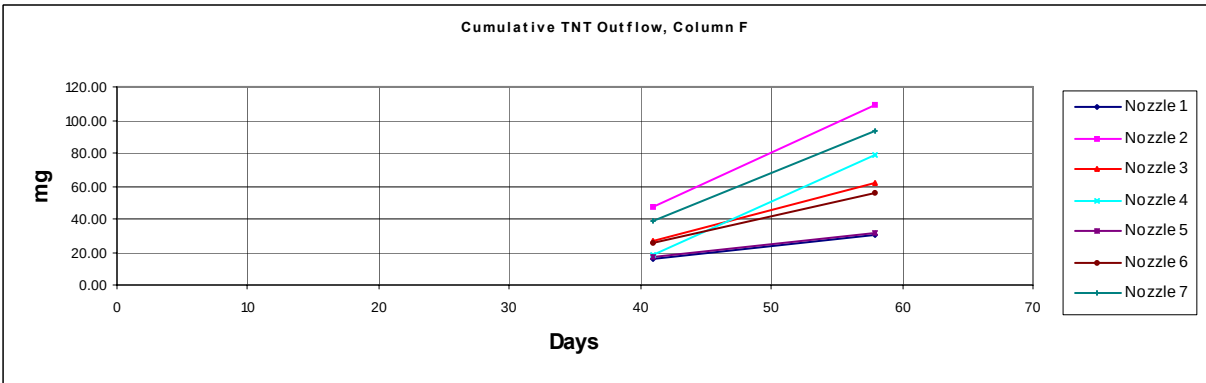
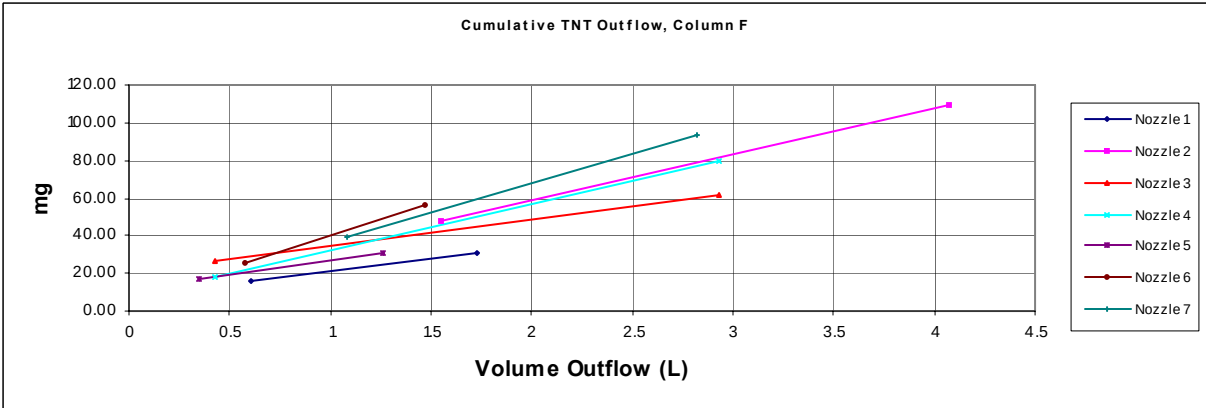
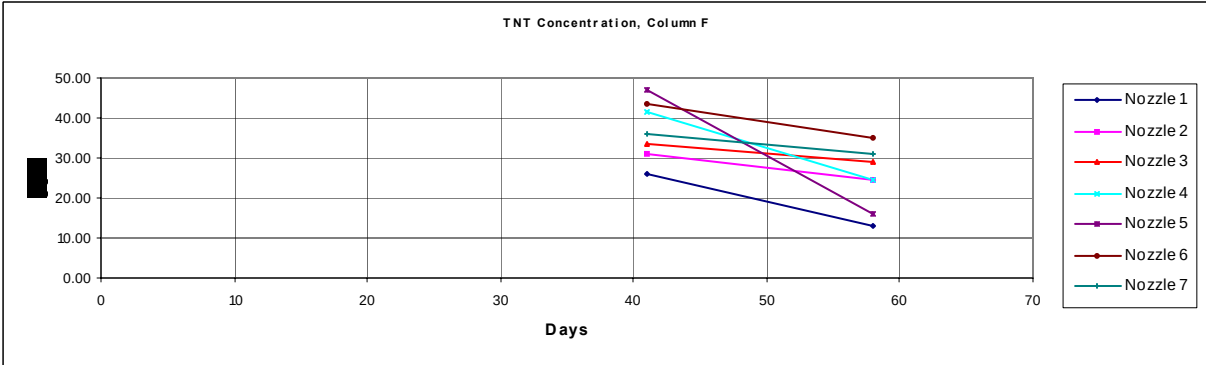
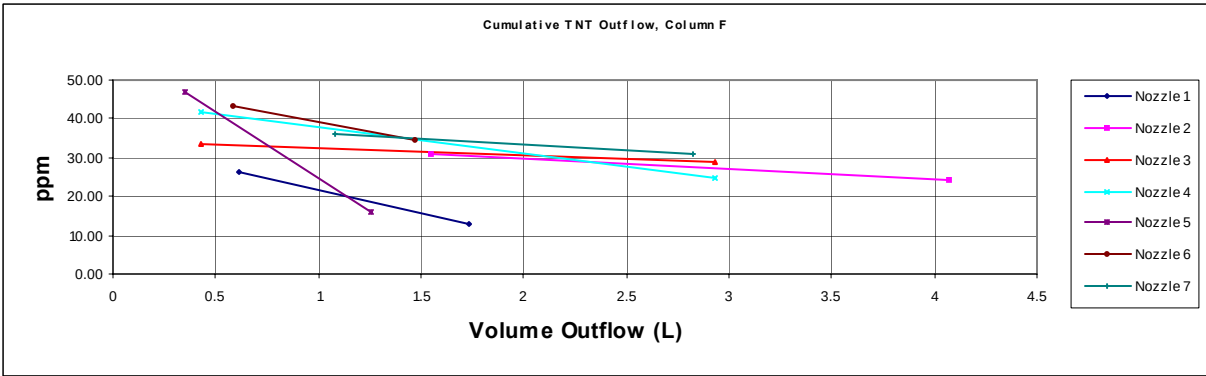


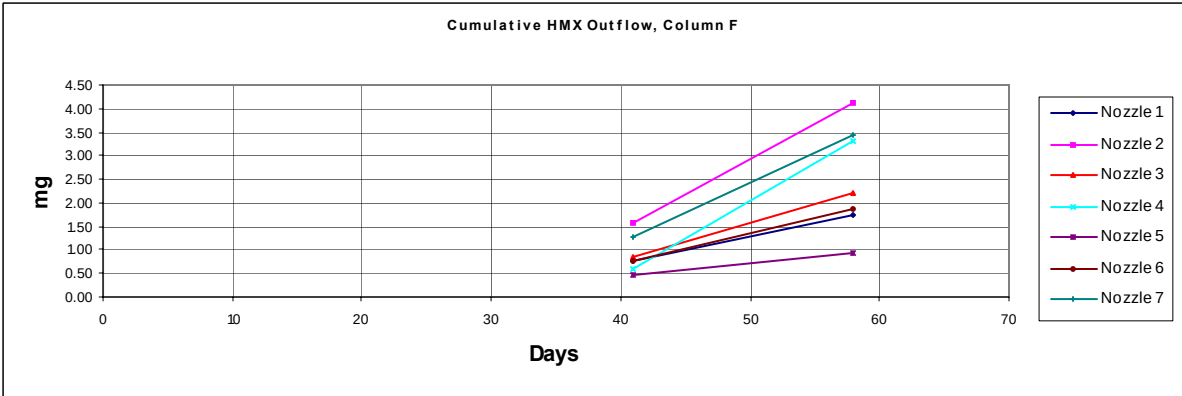
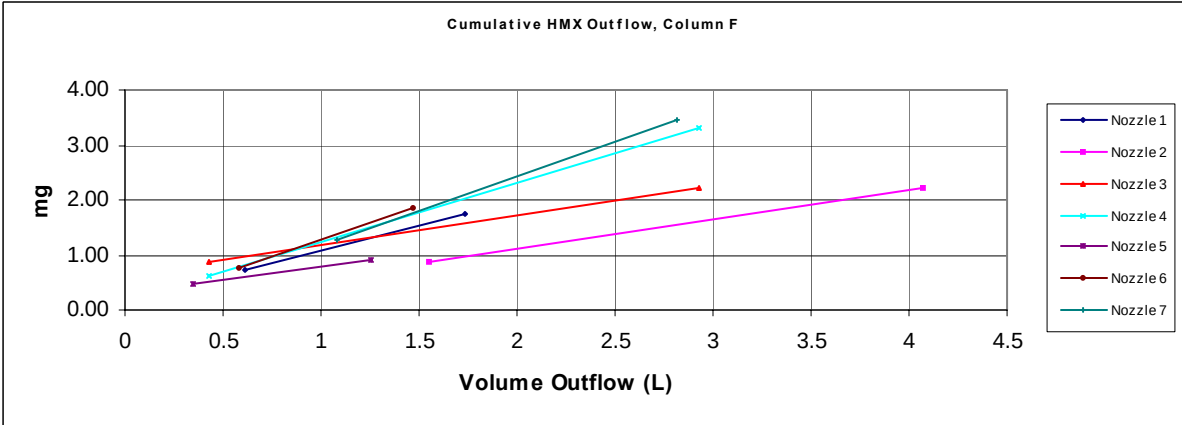
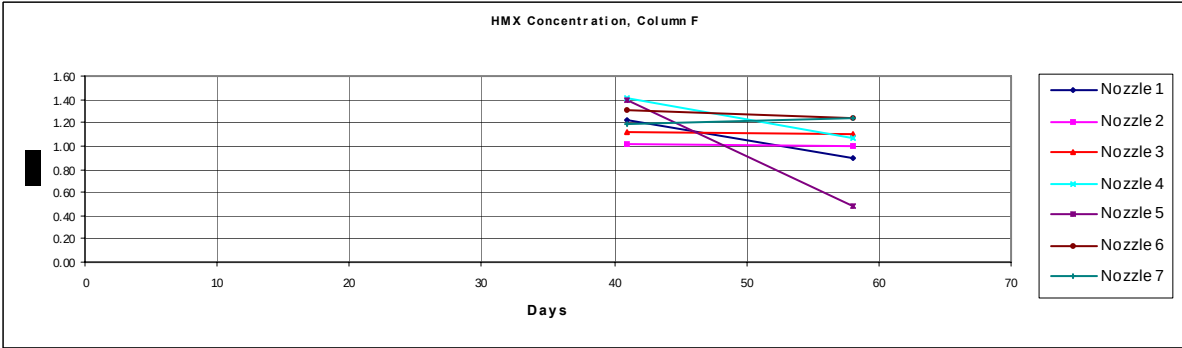
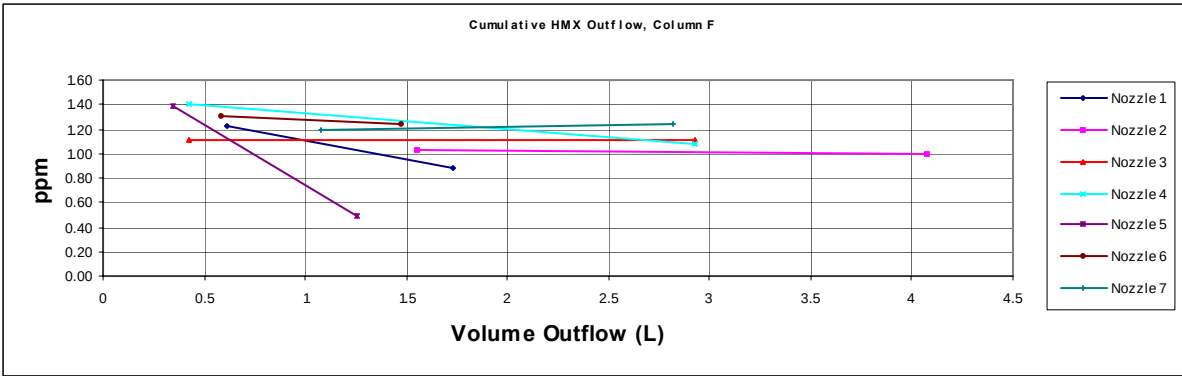












APPENDIX 6 HPLC EPA METHOD 8330

METHOD 8330

NITROAROMATICS AND NITRAMINES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

1.0 SCOPE AND APPLICATION

1.1 Method 8330 is intended for the trace analysis of explosives residues by high performance liquid chromatography using a UV detector. This method is used to determine the concentration of the following compounds in a water, soil, or sediment matrix:

Compound	Abbreviation	CAS No ^a
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX	2691-41-0
Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX	121-82-4
1,3,5-Trinitrobenzene	1,3,5-TNB	99-35-4
1,3-Dinitrobenzene	1,3-DNB	99-65-0
Methyl-2,4,6-trinitrophenylnitramine	Tetryl	479-45-8
Nitrobenzene	NB	98-95-3
2,4,6-Trinitrotoluene	2,4,6-TNT	118-96-7
4-Amino-2,6-dinitrotoluene	4-Am-DNT	1946-51-0
2-Amino-4, 6-dinitrotoluene	2-Am-DNT	355-72-78-2
2,4-Dinitrotoluene	2,4-DNT	121-14-2
2,6-Dinitrotoluene	2,6-DNT	606-20-2
2-Nitrotoluene	2-NT	88-72-2
3-Nitrotoluene	3-NT	99-08-1
4-Nitrotoluene	4-NT	99-99-0

a Chemical Abstracts Service Registry number

1.2 Method 8330 provides a salting-out extraction procedure for low concentration (parts per trillion, or nanograms per liter) of explosives residues in surface or ground water. Direct injection of diluted and filtered water samples can be used for water samples of higher concentration (See Table 1).

1.3 All of these compounds are either used in the manufacture of explosives or are the degradation products of compounds used for that purpose. When making stock solutions for calibration, treat each explosive compound with caution. See NOTE in Sec. 5.3.1 and Sec. 11 on Safety.

1.4 The estimated quantitation limits (EQLs) of target analytes determined by Method 8330 in water and soil are presented in Table 1.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of HPLC, skilled in the interpretation of

chromatograms, and experienced in handling explosive materials. (See Sec. 11.0 on SAFETY.) Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Method 8330 provides high performance liquid chromatographic (HPLC) conditions for the detection of ppb levels of certain explosives residues in water, soil and sediment matrix. Prior to use of this method, appropriate sample preparation techniques must be used.

2.2 Low-Level Salting-out Method With No Evaporation: Aqueous samples of low concentration are extracted by a salting-out extraction procedure with acetonitrile and sodium chloride. The small volume of acetonitrile that remains undissolved above the salt water is drawn off and transferred to a smaller volumetric flask. It is back-extracted by vigorous stirring with a specific volume of salt water. After equilibration, the phases are allowed to separate and the small volume of acetonitrile residing in the narrow neck of the volumetric flask is removed using a Pasteur pipet. The concentrated extract is diluted 1:1 with reagent grade water. An aliquot is separated on a C-18 reverse phase column, determined at 254 nm, and confirmed on a CN reverse phase column.

2.3 High-level Direct Injection Method: Aqueous samples of higher concentration can be diluted 1/1 (v/v) with methanol or acetonitrile, filtered, separated on a C-18 reverse phase column, determine at 254 nm, and confirmed on a CN reverse phase column. If HMX is an important target analyte, methanol is preferred.

2.4 Soil and sediment samples are extracted using acetonitrile in an ultrasonic bath, filtered and chromatographed as in Sec. 2.3.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences.

3.2 2,4-DNT and 2,6-DNT elute at similar retention times (retention time difference of 0.2 minutes). A large concentration of one isomer may mask the response of the other isomer. If it is not apparent that both isomers are present (or are not detected), an isomeric mixture should be reported.

3.3 Tetryl decomposes rapidly in methanol/water solutions, as well as with heat. All aqueous samples expected to contain tetryl should be diluted with acetonitrile prior to filtration and acidified to pH <3. All samples expected to contain tetryl should not be exposed to temperatures above room temperature.

3.4 Degradation products of tetryl appear as a shoulder on the 2,4,6-TNT peak. Peak heights rather than peak areas should be used when tetryl is present in concentrations that are significant relative to the concentration of 2,4,6-TNT.

4.0 APPARATUS AND MATERIALS

4.1 HPLC system

4.1.1 HPLC - equipped with a pump capable of achieving 4000 psi, a 100 μ l loop injector and a 254 nm UV detector (Perkin Elmer Series 3, or equivalent). For the low concentration option, the detector must be capable of a stable baseline at 0.001 absorbance units full scale.

4.1.2 Recommended Columns:

4.1.2.1 Primary column: C-18 Reverse phase HPLC column, 25 cm x 4.6 mm (5 μ m), (Supelco LC-18, or equivalent).

4.1.2.2 Secondary column: CN Reverse phase HPLC column, 25 cm x 4.6 mm (5 μ m), (Supelco LC-CN, or equivalent).

4.1.3 Strip chart recorder.

4.1.4 Digital integrator (optional).

4.1.5 Autosampler (optional).

4.2 Other Equipment

4.2.1 Temperature controlled ultrasonic bath.

4.2.2 Vortex mixer.

4.2.3 Balance, $\pm$ 0.0001 g.

4.2.4 Magnetic stirrer with stirring pellets.

4.2.5 Water bath - Heated, with concentric ring cover, capable of temperature control ($\pm$ 5°C). The bath should be used in a hood.

4.2.6 Oven - Forced air, without heating.

4.3 Materials

4.3.1 High pressure injection syringe - 500 μ L, (Hamilton liquid syringe or equivalent).

4.3.2 Disposable cartridge filters - 0.45 μ m Teflon filter.

4.3.3 Pipets - Class A, glass, Appropriate sizes.

4.3.4 Pasteur pipets.

4.3.5 Scintillation Vials - 20 mL, glass.

4.3.6 Vials - 15 mL, glass, Teflon-lined cap.

4.3.7 Vials- 40 mL, glass, Teflon-lined cap.

4.3.8 Disposable syringes - Plastipak, 3 mL and 10 mL or equivalent.

4.3.9 Volumetric flasks - Appropriate sizes with ground glass stoppers, Class A.

NOTE: The 100 mL and 1 L volumetric flasks used for magnetic stirrer extraction must be round.

4.3.10 Vacuum desiccator - Glass.

4.3.11 Mortar and pestle - Steel.

4.3.12 Sieve - 30 mesh.

4.3.13 Graduated cylinders - Appropriate sizes.

4.4 Preparation of Materials

4.4.1 Prepare all materials to be used as described in Chapter 4 for semivolatile organics.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination.

5.1.1 Acetonitrile, CH_3CN - HPLC grade.

5.1.2 Methanol, CH_3OH - HPLC grade.

5.1.3 Calcium chloride, CaCl_2 - Reagent grade. Prepare an aqueous solution of 5 g/L.

5.1.4 Sodium chloride, NaCl , shipped in glass bottles - reagent grade.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Stock Standard Solutions

5.3.1 Dry each solid analyte standard to constant weight in a vacuum desiccator in the dark. Place about 0.100 g (weighed to 0.0001 g) of a single analyte into a 100 mL volumetric flask and dilute to volume with

acetonitrile. Invert flask several times until dissolved. Store in refrigerator at 4°C in the dark. Calculate the concentration of the stock solution from the actual weight used (nominal concentration = 1,000 mg/L). Stock solutions may be used for up to one year.

NOTE: The HMX, RDX, Tetryl, and 2,4,6-TNT are explosives and the neat material should be handled carefully. See SAFETY in Sec. 11 for guidance. HMX, RDX, and Tetryl reference materials are shipped under water. Drying at ambient temperature requires several days. DO NOT DRY AT HEATED TEMPERATURES!

5.4 Intermediate Standards Solutions

5.4.1 If both 2,4-DNT and 2,6-DNT are to be determined, prepare two separate intermediate stock solutions containing (1) HMX, RDX, 1,3,5-TNB, 1,3-DNB, NB, 2,4,6-TNT, and 2,4-DNT and (2) Tetryl, 2,6-DNT, 2-NT, 3-NT, and 4-NT. Intermediate stock standard solutions should be prepared at 1,000 µg/L in acetonitrile when analyzing soil samples, and in methanol when analyzing aqueous samples.

5.4.2 Dilute the two concentrated intermediate stock solutions, with the appropriate solvent, to prepare intermediate standard solutions that cover the range of 2.5 - 1,000 µg/L. These solutions should be refrigerated on preparation, and may be used for 30 days.

5.4.3 For the low-level method, the analyst must conduct a detection limit study and devise dilution series appropriate to the desired range. Standards for the low level method must be prepared immediately prior to use.

5.5 Working standards

5.5.1 Calibration standards at a minimum of five concentration levels should be prepared through dilution of the intermediate standards solutions by 50% (v/v) with 5 g/L calcium chloride solution (Sec. 5.1.3). These solutions must be refrigerated and stored in the dark, and prepared fresh on the day of calibration.

5.6 Surrogate Spiking Solution

5.6.1 The analyst should monitor the performance of the extraction and analytical system as well as the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard and reagent water blank with one or two surrogates (e.g., analytes not expected to be present in the sample).

5.7 Matrix Spiking Solutions

5.7.1 Prepare matrix spiking solutions in methanol such that the concentration in the sample is five times the Estimated Quantitation Limit (Table 1). All target analytes should be included.

5.8 HPLC Mobile Phase

5.8.1 To prepare 1 liter of mobile phase, add 500 mL of methanol to 500 mL of organic-free reagent water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Follow conventional sampling and sample handling procedures as specified for semivolatile organics in Chapter Four.

6.2 Samples and sample extracts must be stored in the dark at 4°C. Holding times are the same as for semivolatile organics.

7.0 PROCEDURE

7.1 Sample Preparation

7.1.1 Aqueous Samples: It is highly recommended that process waste samples be screened with the high-level method to determine if the low level method (1-50 µg/L) is required. Most groundwater samples will fall into the low level method.

7.1.1.1 Low-Level Method (salting-out extraction)

7.1.1.1.1 Add 251.3 g of sodium chloride to a 1 L volumetric flask (round). Measure out 770 mL of a water sample (using a 1 L graduated cylinder) and transfer it to the volumetric flask containing the salt. Add a stir bar and mix the contents at maximum speed on a magnetic stirrer until the salt is completely dissolved.

7.1.1.1.2 Add 164 mL of acetonitrile (measured with a 250 mL graduated cylinder) while the solution is being stirred and stir for an additional 15 minutes. Turn off the stirrer and allow the phases to separate for 10 minutes.

7.1.1.1.3 Remove the acetonitrile (upper) layer (about 8 mL) with a Pasteur pipet and transfer it to a 100 mL volumetric flask (round). Add 10 mL of fresh acetonitrile to the water sample in the 1 L flask. Again stir the contents of the flask for 15 minutes followed by 10 minutes for phase separation. Combine the second acetonitrile portion with the initial extract. The inclusion of a few drops of salt water at this point is unimportant.

7.1.1.1.4 Add 84 mL of salt water (325 g NaCl per 1000 mL of reagent water) to the acetonitrile extract in the 100 mL volumetric flask. Add a stir bar and stir the contents on a magnetic stirrer for 15 minutes, followed by 10 minutes for phase separation. Carefully transfer the acetonitrile phase

to a 10 mL graduated cylinder using a Pasteur pipet. At this stage, the amount of water transferred with the acetonitrile must be minimized. The water contains a high concentration of NaCl that produces a large peak at the beginning of the chromatogram, where it could interfere with the HMX determination.

7.1.1.1.5 Add an additional 1.0 mL of acetonitrile to the 100 mL volumetric flask. Again stir the contents of the flask for 15 minutes, followed by 10 minutes for phase separation. Combine the second acetonitrile portion with the initial extract in the 10 mL graduated cylinder (transfer to a 25 mL graduated cylinder if the volume exceeds 5 mL). Record the total volume of acetonitrile extract to the nearest 0.1 mL. (Use this as the volume of total extract [V_t] in the calculation of concentration after converting to μL). The resulting extract, about 5 - 6 mL, is then diluted 1:1 with organic-free reagent water (with pH <3 if tetryl is a suspected analyte) prior to analysis.

7.1.1.1.6 If the diluted extract is turbid, filter it through a 0.45 - μm Teflon filter using a disposable syringe. Discard the first 0.5 mL of filtrate, and retain the remainder in a Teflon-capped vial for RP-HPLC analysis as in Sec. 7.4.

7.1.1.2 High-Level Method

7.1.1.2.1 Sample filtration: Place a 5 mL aliquot of each water sample in a scintillation vial, add 5 mL of acetonitrile, shake thoroughly, and filter through a 0.45- μm Teflon filter using a disposable syringe. Discard the first 3 mL of filtrate, and retain the remainder in a Teflon-capped vial for RP-HPLC analysis as in Sec. 7.4. HMX quantitation can be improved with the use of methanol rather than acetonitrile for dilution before filtration.

7.1.2 Soil and Sediment Samples

7.1.2.1 Sample homogenization: Dry soil samples in air at room temperature or colder to a constant weight, being careful not to expose the samples to direct sunlight. Grind and homogenize the dried sample thoroughly in an acetonitrile-rinsed mortar to pass a 30 mesh sieve.

NOTE: Soil samples should be screened by Method 8515 prior to grinding in a mortar and pestle (See Safety Sec. 11.2).

7.1.2.2 Sample extraction

7.1.2.2.1 Place a 2.0 g subsample of each soil sample in a 15 mL glass vial. Add 10.0 mL of acetonitrile, cap with

Teflon-lined cap, vortex swirl for one minute, and place in a cooled ultrasonic bath for 18 hours.

7.1.2.2.2 After sonication, allow sample to settle for 30 minutes. Remove 5.0 mL of supernatant, and combine with 5.0 mL of calcium chloride solution (Sec. 5.1.3) in a 20 mL vial. Shake, and let stand for 15 minutes.

7.1.2.2.3 Place supernatant in a disposable syringe and filter through a 0.45- μ m Teflon filter. Discard first 3 mL and retain remainder in a Teflon-capped vial for RP-HPLC analysis as in Sec. 7.4.

7.2 Chromatographic Conditions (Recommended)

Primary Column: C-18 reverse phase HPLC column, 25-cm x 4.6-mm, 5 μ m, (Supelco LC-18 or equivalent).

Secondary Column: CN reverse phase HPLC column, 25-cm x 4.6-mm, 5 μ m, (Supelco LC-CN or equivalent).

Mobile Phase: 50/50 (v/v) methanol/organic-free reagent water.

Flow Rate: 1.5 mL/min

Injection volume: 100- μ L

UV Detector: 254 nm

7.3 Calibration of HPLC

7.3.1 All electronic equipment is allowed to warm up for 30 minutes. During this period, at least 15 void volumes of mobile phase are passed through the column (approximately 20 min at 1.5 mL/min) and continued until the baseline is level at the UV detector's greatest sensitivity.

7.3.2 Initial Calibration. Injections of each calibration standard over the concentration range of interest are made sequentially into the HPLC in random order. Peak heights or peak areas are obtained for each analyte. Experience indicates that a linear calibration curve with zero intercept is appropriate for each analyte. Therefore, a response factor for each analyte can be taken as the slope of the best-fit regression line.

7.3.3 Daily Calibration. Analyze midpoint calibration standards, at a minimum, at the beginning of the day, singly at the midpoint of the run, and singly after the last sample of the day (assuming a sample group of 10 samples or less). Obtain the response factor for each analyte from the mean peak heights or peak areas and compare it with the response factor obtained for the initial calibration. The mean response factor for the

daily calibration must agree within $\pm 15\%$ of the response factor of the initial calibration. The same criteria is required for subsequent standard responses compared to the mean response of the triplicate standards beginning the day. If this criterion is not met, a new initial calibration must be obtained.

7.4 HPLC Analysis

7.4.1 Analyze the samples using the chromatographic conditions given in Sec. 7.2. All positive measurements observed on the C-18 column must be confirmed by injection onto the CN column.

7.4.2 Follow Sec. 7.0 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence. If column temperature control is not employed, special care must be taken to ensure that temperature shifts do not cause peak misidentification.

7.4.3 Table 2 summarizes the estimated retention times on both C-18 and CN columns for a number of analytes analyzable using this method. An example of the separation achieved by Column 1 is shown in Figure 1.

7.4.4 Record the resulting peak sizes in peak heights or area units. The use of peak heights is recommended to improve reproducibility of low level samples.

7.4.5 Calculation of concentration is covered in Sec. 7.0 of Method 8000.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500.

8.2 Quality control required to validate the HPLC system operation is found in Method 8000, Sec. 8.0.

8.3 Prior to preparation of stock solutions, acetonitrile, methanol, and water blanks should be run to determine possible interferences with analyte peaks. If the acetonitrile, methanol, or water blanks show contamination, a different batch should be used.

9.0 METHOD PERFORMANCE

9.1 Table 3 presents the single laboratory precision based on data from the analysis of blind duplicates of four spiked soil samples and four field contaminated samples analyzed by seven laboratories.

9.2 Table 4 presents the multilaboratory error based on data from the analysis of blind duplicates of four spiked soil samples and four field contaminated samples analyzed by seven laboratories.

9.3 Table 5 presents the multilaboratory variance of the high concentration method for water based on data from nine laboratories.

9.4 Table 6 presents multilaboratory recovery data from the analysis of spiked soil samples by seven laboratories.

9.5 Table 7 presents a comparison of method accuracy for soil and aqueous samples (high concentration method).

9.6 Table 8 contains precision and accuracy data for the salting-out extraction method.

10.0 REFERENCES

1. Bauer, C.F., T.F. Jenkins, S.M. Koza, P.W. Schumacher, P.H. Miyares and M.E. Walsh (1989). Development of an analytical method for the determination of explosive residues in soil. Part 3. Collaborative test results and final performance evaluation. USA Cold Regions Research and Engineering Laboratory, CRREL Report 89-9.
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7. Jenkins, T.F., P.W. Schumacher, M.E. Walsh and C.F. Bauer (1988b) Development of an analytical method for the determination of explosive

residues in soil. Part II: Further development and ruggedness testing. USA Cold Regions Research and Engineering Laboratory, CRREL Report 88-8.

8. Leggett, D.C., T.F. Jenkins and P.H. Miyares (1990) Salting-out solvent extraction for preconcentration of neutral polar organic solutes from water. *Analytical Chemistry*, 62: 1355-1356.
9. Miyares, P.H. and T.F. Jenkins (1990) Salting-out solvent extraction for determining low levels of nitroaromatics and nitramines in water. USA Cold Regions Research and Engineering Laboratory, Special Report 90-30.

11.0 SAFETY

11.1 Standard precautionary measures used for handling other organic compounds should be sufficient for the safe handling of the analytes targeted by Method 8330. The only extra caution that should be taken is when handling the analytical standard neat material for the explosives themselves and in rare cases where soil or waste samples are highly contaminated with the explosives. Follow the note for drying the neat materials at ambient temperatures.

11.2 It is advisable to screen soil or waste samples using Method 8515 to determine whether high concentrations of explosives are present. Soil samples as high as 2% 2,4,6-TNT have been safely ground. Samples containing higher concentrations should not be ground in the mortar and pestle. Method 8515 is for 2,4,6-TNT, however, the other nitroaromatics will also cause a color to be developed and provide a rough estimation of their concentrations. 2,4,6-TNT is the analyte most often detected in high concentrations in soil samples. Visual observation of a soil sample is also important when the sample is taken from a site expected to contain explosives. Lumps of material that have a chemical appearance should be suspect and not ground. Explosives are generally a very finely ground grayish-white material.

TABLE 1
ESTIMATED QUANTITATION LIMITS

Compounds	Water (µg/L)		Soil (mg/kg)
	Low-Level	High-Level	
HMX	-	13.0	2.2
RDX	0.84	14.0	1.0
1,3,5-TNB	0.26	7.3	0.25
1,3-DNB	0.11	4.0	0.25
Tetryl	-	4.0	0.65
NB	-	6.4	0.26
2,4,6-TNT	0.11	6.9	0.25
4-Am-DNT	0.060	-	-
2-Am-DNT	0.035	-	-
2,6-DNT	0.31	9.4	0.26
2,4-DNT	0.020	5.7	0.25
2-NT	-	12.0	0.25
4-NT	-	8.5	0.25
3-NT	-	7.9	0.25

TABLE 2
RETENTION TIMES AND CAPACITY FACTORS ON LC-18 AND LC-CN COLUMNS

Compound	Retention time (min)		Capacity factor (k)*	
	LC-18	LC-CN	LC-18	LC-CN
HMX	2.44	8.35	0.49	2.52
RDX	3.73	6.15	1.27	1.59
1,3,5-TNB	5.11	4.05	2.12	0.71
1,3-DNB	6.16	4.18	2.76	0.76
Tetryl	6.93	7.36	3.23	2.11
NB	7.23	3.81	3.41	0.61
2,4,6-TNT	8.42	5.00	4.13	1.11
4-Am-DNT	8.88	5.10	4.41	1.15
2-Am-DNT	9.12	5.65	4.56	1.38
2,6-DNT	9.82	4.61	4.99	0.95
2,4-DNT	10.05	4.87	5.13	1.05
2-NT	12.26	4.37	6.48	0.84
4-NT	13.26	4.41	7.09	0.86
3-NT	14.23	4.45	7.68	0.88

* Capacity factors are based on an unretained peak for nitrate at 1.71 min on LC-18 and at 2.00 min on LC-CN.

TABLE 3
SINGLE LABORATORY PRECISION OF METHOD FOR SOIL SAMPLES

	Spiked Soils			Field-Contaminated Soils		
	Mean Conc. (mg/kg)	SD	%RSD	Mean Conc. (mg/kg)	SD	%RSD
HMX	46	1.7	3.7	14	1.8	12.8
				153	21.6	14.1
RDX	60	1.4	2.3	104	12	11.5
				877	29.6	3.4
1,3,5-TNB	8.6	0.4	4.6	2.8	0.2	7.1
	46	1.9	4.1	72	6.0	8.3
1,3-DNB	3.5	0.14	4.0	1.1	0.11	9.8
Tetryl	17	3.1	17.9	2.3	0.41	18.0
2,4,6-TNT	40	1.4	3.5	7.0	0.61	9.0
				669	55	8.2
2,4-DNT	5.0	0.17	3.4	1.0	0.44	42.3

TABLE 4
MULTILABORATORY ERROR OF METHOD FOR SOIL SAMPLES

	Spiked Soils			Field-Contaminated Soils		
	Mean Conc. (mg/kg)	SD	%RSD	Mean Conc. (mg/kg)	SD	%RSD
HMX	46	2.6	5.7	14 153	3.7 37.3	26.0 24.0
RDX	60	2.6	4.4	104 877	17.4 67.3	17.0 7.7
1,3,5-TNB	8.6 46	0.61 2.97	7.1 6.5	2.8 72	0.23 8.8	8.2 12.2
1,3-DNB	3.5	0.24	6.9	1.1	0.16	14.5
Tetryl	17	5.22	30.7	2.3	0.49	21.3
2,4,6-TNT	40	1.88	4.7	7.0 669	1.27 63.4	18.0 9.5
2,4-DNT	5.0	0.22	4.4	1.0	0.74	74.0

TABLE 5
MULTILABORATORY VARIANCE OF METHOD FOR WATER SAMPLES^a

Compounds	Mean Conc. (µg/L)	SD	%RSD
HMX	203	14.8	7.3
RDX	274	20.8	7.6
2,4-DNT	107	7.7	7.2
2,4,6-TNT	107	11.1	10.4

^a Nine Laboratories

TABLE 6
MULTILABORATORY RECOVERY DATA FOR SPIKED SOIL SAMPLES

Laboratory	Concentration (µg/g)						
	HMX	RDX	1,3,5-TNB	1,3-DNB	Tetryl	2,4,6-TNT	2,4-DNT
1	44.97	48.78	48.99	49.94	32.48	49.73	51.05
3	50.25	48.50	45.85	45.96	47.91	46.25	48.37
4	42.40	44.00	43.40	49.50	31.60	53.50	50.90
5	46.50	48.40	46.90	48.80	32.10	55.80	49.60
6	56.20	55.00	41.60	46.30	13.20	56.80	45.70
7	41.50	41.50	38.00	44.50	2.60	36.00	43.50
8	52.70	52.20	48.00	48.30	44.80	51.30	49.10
True Conc	50.35	50.20	50.15	50.05	50.35	50.65	50.05
Mean	47.79	48.34	44.68	47.67	29.24	49.91	48.32
Std Dev	5.46	4.57	3.91	2.09	16.24	7.11	2.78
% RSD	11.42	9.45	8.75	4.39	55.53	14.26	5.76
% Diff*	5.08	3.71	10.91	4.76	41.93	1.46	3.46
Mean % Recovery	95	96	89	95	58	98	96

* Between true value and mean determined value.

TABLE 7
COMPARISON OF METHOD ACCURACY FOR SOIL AND AQUEOUS SAMPLES
(HIGH CONCENTRATION METHOD)

Analyte	Recovery (%)	
	Soil Method*	Aqueous Method**
2,4-DNT	96.0	98.6
2,4,6-TNT	96.8	94.4
RDX	96.8	99.6
HMX	95.4	95.5

* Taken from Bauer et al. (1989), Reference 1.

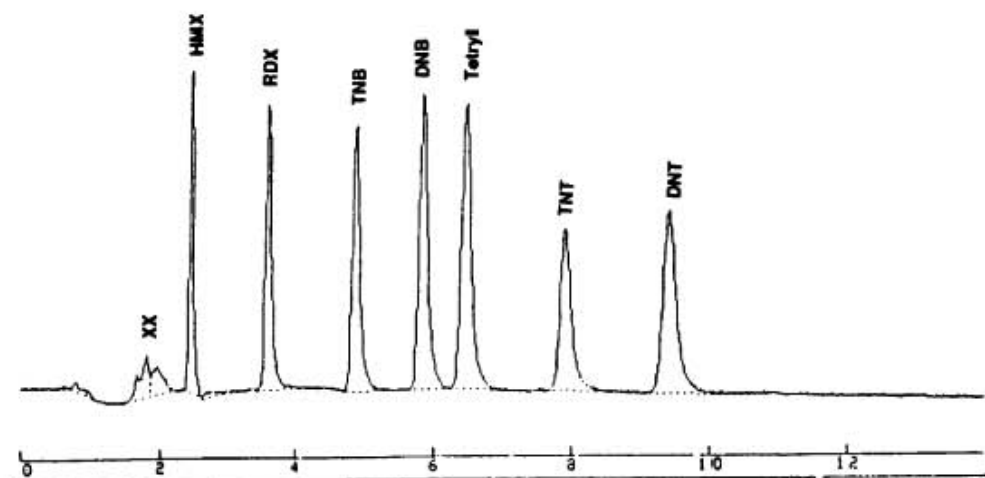
** Taken from Jenkins et al. (1984), Reference 3.

TABLE 8
PRECISION AND ACCURACY DATA FOR THE SALTING-OUT EXTRACTION METHOD

Analyte	No. of Samples ¹	Precision (% RSD)	Ave. Recovery (%)	Conc. Range (µg/L)
HMX	20	10.5	106	0-1.14
RDX	20	8.7	106	0-1.04
1,3,5-TNB	20	7.6	119	0-0.82
1,3-DNB	20	6.6	102	0-1.04
Tetryl	20	16.4	93	0-0.93
2,4,6-TNT	20	7.6	105	0-0.98
2-Am-DNT	20	9.1	102	0-1.04
2,4-DNT	20	5.8	101	0-1.01
1,2-NT	20	9.1	102	0-1.07
1,4-NT	20	18.1	96	0-1.06
1,3-NT	20	12.4	97	0-1.23

¹Reagent water

**EXPLOSIVES ON A
C18 COLUMN**



**EXPLOSIVES ON A
CN COLUMN**

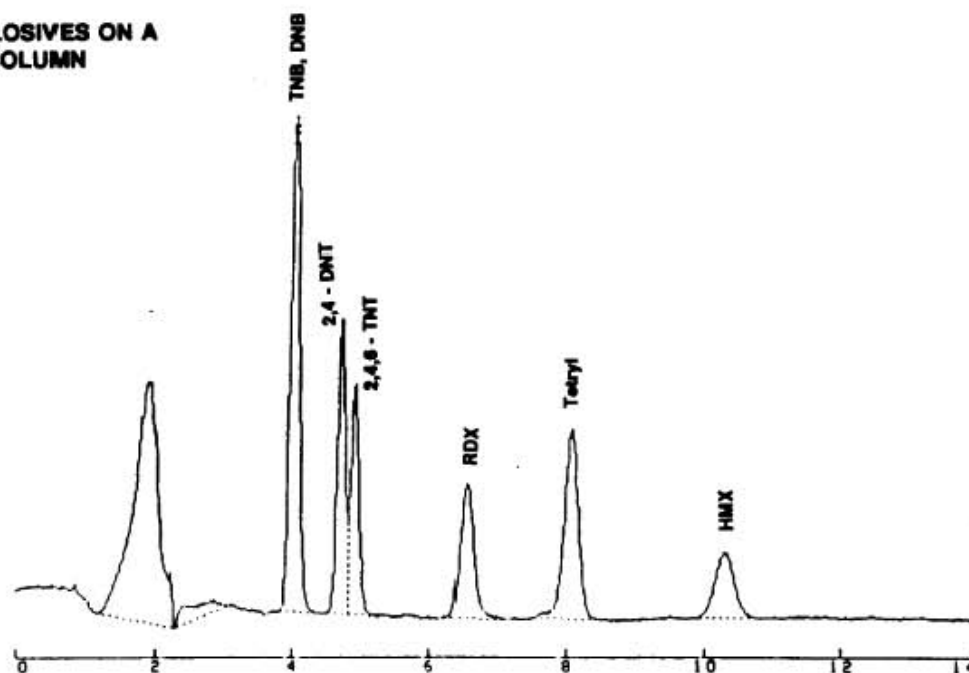
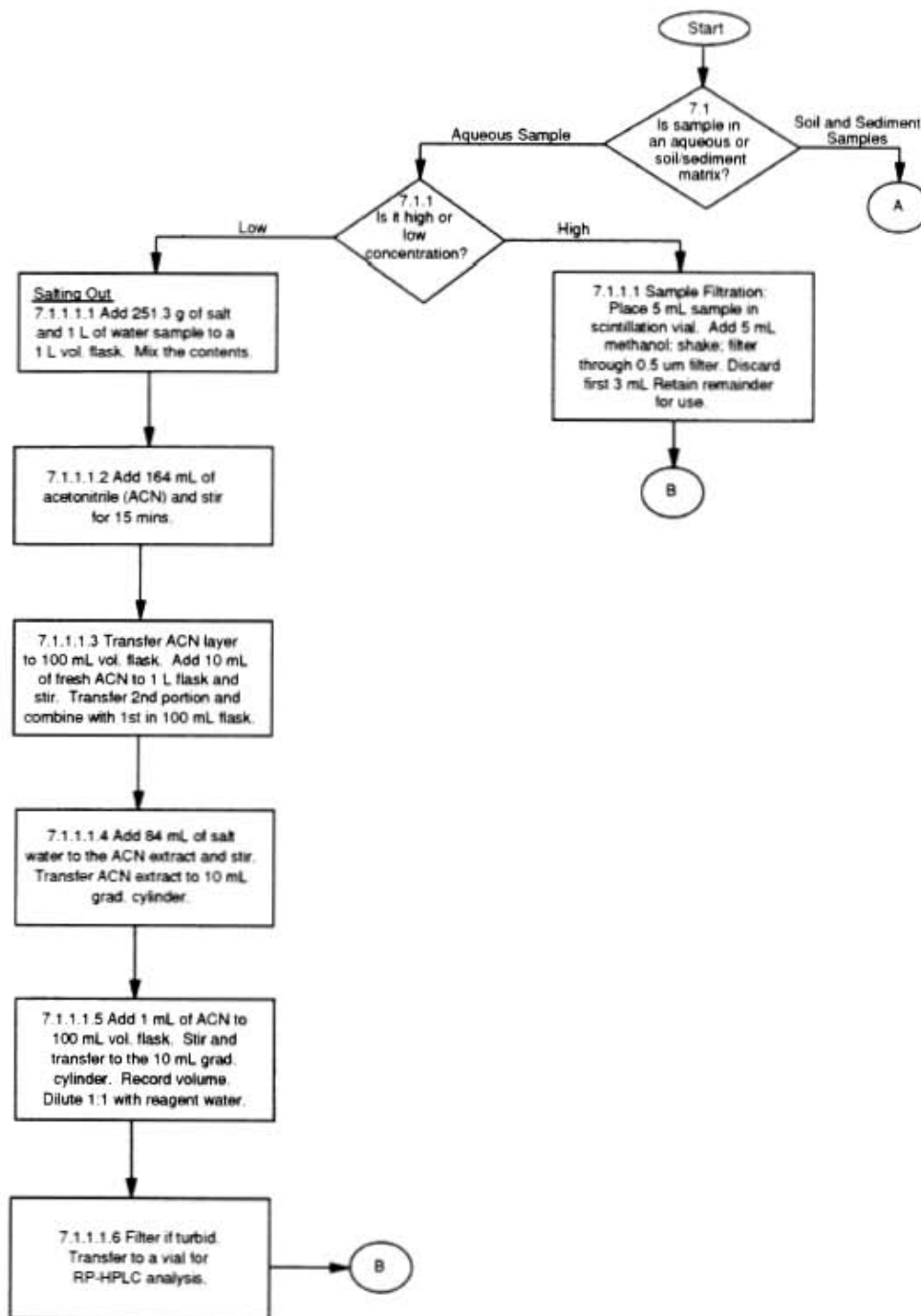
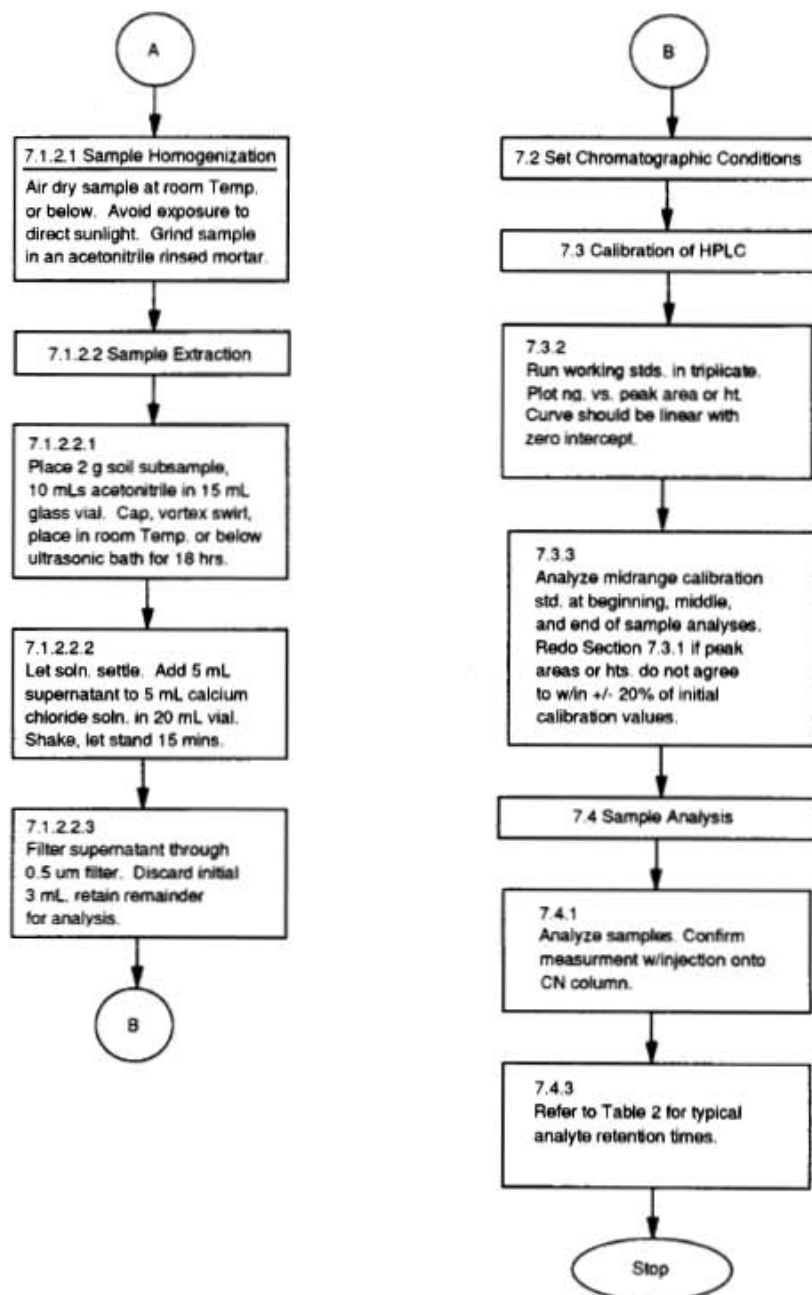


FIGURE 1
CHROMATOGRAMS FOR COLUMNS DESCRIBED IN Sec. 4.1.2.
COURTESY OF U.S. ARMY CORPS OF ENGINEERS, OMAHA, NE.

METHOD 8330
NITROAROMATICS AND NITRAMINES BY HIGH
PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)



METHOD 8330
(continued)



APPENDIX 7 BROMIDE IC ANALYSIS NIOSH METHOD 6011

BROMINE

6011

See CHLORINE, Method 6011, for procedure

Br₂

MW: 159.82

CAS: 7726-95-6

RTECS: EF9100000

METHOD: 6011, Issue 2

EVALUATION: FULL

Issue 1: 15 May 1989

Issue 2: 15 August 1994

OSHA : 0.1 ppm
NIOSH: 0.1 ppm; STEL 0.3 ppm
ACGIH: 0.1 ppm; STEL 0.3 ppm
(1 ppm = 6.53 mg/m³)

PROPERTIES: liquid; d 3.119 g/mL @ 20 °C;
BP 58.78 °C; VP 23.3 kPa (175 mm Hg)
@ 20 °C vapor density (air=1) 5.5

SYNONYMS: None.

SAMPLING		MEASUREMENT	
SAMPLER:	PREFILTER + FILTER (PTFE, 0.5-µm + silver membrane, 25-mm, 0.45-µm)	TECHNIQUE:	ION CHROMATOGRAPHY, CONDUCTIVITY
FLOW RATE:	0.3 to 1 L/min	ANALYTE:	bromide ion (Br ⁻)
VOL-MIN:	8 L @ 0.1 ppm	EXTRACTION:	3 mL 6 mM Na ₂ S ₂ O ₃ , 10 min
-MAX:	360 L	INJECTION VOLUME:	50 µL
SHIPMENT:	routine, protect from light	COLUMN:	Dionex HPIC-AG4A guard, HPIC-AS4A separator, MFC-1 precolumn, AMMS anion suppressor
SAMPLE STABILITY:	≥30 days at 25 °C [1]	DETECTOR SETTING:	10 µS full scale
BLANKS:	2 to 10 field blanks per set	ELUENT:	0.25 mM NaHCO ₃ /4 mM Na ₂ CO ₃ /0.78 mM p-cyanophenol, 2 mL/min
ACCURACY		CALIBRATION:	standard solutions of Br ⁻ in deionized water
RANGE STUDIED:	0.07 to 1.42 mg/m ³ (72-L samples)	RANGE:	5 to 150 µg Br ⁻ per sample [1]
BIAS:	- 1.2%	ESTIMATED LOD:	1.6 µg Br ⁻ per sample [1]
OVERALL PRECISION ($\bar{S}_{\overline{r}}$):	0.069 [1]	PRECISION ($\bar{S}_p$):	0.045 @ 5 to 100 µg per sample [1]
ACCURACY:	± 13.6%		

APPLICABILITY: The working ranges for Br₂ and Cl₂ are 0.008 to 0.4 ppm (0.06 to 2.6 mg/m³) and 0.007 to 0.5 ppm (0.02 to 1.5 mg/m³) respectively for a 90-L air sample. The method has sufficient sensitivity for STEL samples.

INTERFERENCES: Hydrogen sulfide gives a negative interference. HCl gives a positive interference upon a maximum of 15 µg per sample. HBr gives a positive interference as it is sampled continuously [1].

OTHER METHODS: P&CAM 209 (colorimetric) [2], OSHA Methods ID-101 [3] and ID-108 [4] are alternative methods.

CHLORINE

6011



MW: 70.91

CAS: 7782-50-5

RTECS: FO2100000

METHOD: 6011, Issue 2		EVALUATION: FULL		Issue 1: 15 May 1989 Issue 2: 15 August 1994	
OSHA : C 1 ppm NIOSH: 0.5 ppm; STEL 1 ppm ACGIH: 0.5 ppm; STEL 1 ppm (1 ppm = 2.90 mg/m ³ @ NTP)		PROPERTIES: gas; d 3.214 g/L at 0 °C; BP -34.6 °C; vapor density (air = 1) 2.5			
SYNONYMS: None.					
SAMPLING			MEASUREMENT		
SAMPLER:	PREFILTER + FILTER (PTFE, 0.5-µm + silver membrane, 25-mm, 0.45-µm)		TECHNIQUE:	ION CHROMATOGRAPHY, CONDUCTIVITY	
FLOW RATE:	0.3 to 1 L/min		ANALYTE:	chloride ion (Cl ⁻) or bromide ion (Br ⁻)	
VOL-MIN:	2 L @ 0.5 ppm		EXTRACTION:	3 mL 6 mM Na ₂ S ₂ O ₃ , 10 min	
-MAX:	90 L		INJECTION VOLUME:	50 µL	
SHIPMENT:	routine, protect from light		COLUMN:	Dionex HPIC-AG4A guard, HPIC-AS4A separator MFC-1 precolumn, AMMS anion suppressor	
SAMPLE STABILITY:	≥30 days at 25 °C [1]		DETECTOR SETTING:	10 µS full scale	
BLANKS:	2 to 10 field blanks per set		ELUENT:	0.25 mM NaHCO ₃ /4 mM Na ₂ CO ₃ /0.78 mM p-cyanophenol, 2 mL/min	
ACCURACY			CALIBRATION:	standard solutions of Cl ⁻ in deionized water	
RANGE STUDIED:	0.35 to 6.77 mg/m ³ (15-L samples)		RANGE:	2 to 50 µg Cl ⁻ per sample [1]	
BIAS:	- 1.4%		ESTIMATED LOD:	0.6 µg Cl ⁻ per sample [1]	
OVERALL PRECISION ($\bar{S}_r$):	0.075 [1]		PRECISION ($\bar{S}_r$):	0.067 @ 5.3 to 100 µg per sample [1]	
ACCURACY:	± 14.8%				
APPLICABILITY: The working ranges for Br ₂ and Cl ₂ are 0.008 to 0.4 ppm (0.06 to 2.6 mg/m ³) and 0.007 to 0.5 ppm (0.02 to 1.5 mg/m ³) respectively for a 90-L air sample. The method has sufficient sensitivity for STEL samples.					
INTERFERENCES: Hydrogen sulfide gives a negative interference. HCl gives a positive interference up to a maximum of 15 µg per sample. HBr gives a positive interference as it is sampled continuously [1].					
OTHER METHODS: P&CAM 209 (colorimetric) [2], OSHA Methods ID-101 [3] and ID-108 [4] are alternative methods.					

REAGENTS:

1. Sodium thiosulfate, reagent grade.
2. Water, deionized.
3. Extraction solution: 6 m M $\text{Na}_2\text{S}_2\text{O}_3$. Dissolve 0.474 g $\text{Na}_2\text{S}_2\text{O}_3$ in 500 mL deionized water.
4. Eluent: 0.25 m M NaHCO_3 /4 m M Na_2CO_3 /0.78 m M *p*-cyanophenol. Dissolve 0.041 g NaHCO_3 , 0.848 g Na_2CO_3 and 0.186 g *p*-cyanophenol in 2 L filtered deionized water.
5. Suppressor regenerant, 0.025 N H_2SO_4 . Dilute 2.8 mL conc. H_2SO_4 to 4 L with deionized water.*
6. Calibration stock solutions, 1 mg/mL (as anion).
 - (1) Dissolve 0.149 g KBr in 100 mL deionized water
 - (2) Dissolve 0.21 g KCl in 100 mL deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Silver membrane filter,* 25-mm, 0.45- μm , (Costar/Nuclepore, Poretics, or equivalent) with porous plastic support pad (Costar/Nuclepore); prefilter, PTFE with PTFE support, 0.5- μm (Gelman Zefluor, SKC, or equivalent), or polyester, 0.4- μm (Costar/Nuclepore) with porous plastic support pad; three-piece, 25-mm carbon-filled polypropylene cassette (opaque) with 50-mm extension (Costar/Nuclepore or Gelman) (Fig. 1).
 - a. In the outlet piece of cassette, place porous plastic support pad and cleaned silver filter. Insert 50-mm extension (cowl) securely.
 - b. At the inlet (top) of the extension, place porous plastic support pad and prefilter. Insert inlet cassette piece securely.
 - c. Seal each connection with shrinkable bands or tape.
2. Personal sampling pump, 0.3 to 1 L/min, with flexible connecting tubing.
3. Ion chromatograph with Dionex MFC-1, HPIC-AG4A, HPIC-AS4A columns, AMMS anion micromembrane suppressor, conductivity detector and integrator (page 6011-1).
4. Bottles, 30-mL, wide mouth with screw caps, amber or opaque polyethylene.
5. Micropipettes, with disposable tips.
6. Volumetric flasks, 10- and 100-mL.
7. Repipet reagent dispensers, 0 to 10-mL.
8. Syringes, 10-mL, polyethylene, luer-tip.
9. Forceps.

* Silver membrane filters must be cleaned prior to use (see APPENDIX A).

NOTE: Some lots of silver membrane filters contain excessively high chloride background levels. Please screen before field use.

SPECIAL PRECAUTIONS: Sulfuric acid is extremely corrosive to skin, eyes, and mucous membranes. Wear protective clothing. Handle in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.3 and 1 L/min for a total sample size of 8 to 360 L for bromine or 2 to 90 L for chlorine.
4. Seal ends of sampler with plugs. Pack securely for shipping.

SAMPLE PREPARATION:

- NOTE: Silver halides are photosensitive. Protect from light during transfer and desorption.
5. Under very dim or red light, open cassette and transfer the silver filter with forceps to amber bottle. Add 3 mL 6 M $\text{Na}_2\text{S}_2\text{O}_3$ and cap.
NOTE: Prefilter may be analyzed for particulate halides, or discarded.
 6. Allow samples to stand a minimum of 10 min with occasional swirling.
NOTE: Once desorbed, samples are no longer photosensitive.
 7. Uncap the sample bottles and add 7 mL deionized water for a total solution volume of 10 mL.
 8. Pour sample into 10-mL plastic syringe for manual injection or into autosampler vials.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards covering the range of 0.2 to 15 μg bromide and/or 0.05 to 5 μg chloride per mL of sample.
 - a. Add known aliquots of calibration stock solution to deionized water in 10-mL volumetric flasks and dilute to the mark with deionized water.
 - b. Prepare fresh working standards biweekly.
 - c. Analyze working standards together with samples and blanks (steps 11 through 13).
 - d. Prepare a calibration graph (peak height vs. μg of anion per sample).
10. Analyze three quality control spikes, three analyst spikes and media blanks to ensure that calibration graph is in control.

MEASUREMENT:

11. Set ion chromatograph according to manufacturer's instructions and to conditions given on page 6011-1.
NOTE: Excessive amounts of Ag^+ and $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ deteriorate column performance. Use a metal free column (MFC-1) prior to the chromatographic columns and recondition the column every 100 to 150 analyses (See APPENDIX B).
12. Inject 50- μL sample aliquot manually or with autosampler. For manual operation, inject 2 to 3 mL of sample from syringe to ensure complete rinse of the sample loop.
13. Measure peak height. If sample peak height exceeds linear calibration range, dilute with deionized water, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

14. From the calibration graph, determine the mass of Br^- or Cl^- in each sample, W (μg), and in the average blank, B (μg).
15. Calculate the concentration, C (mg/m^3), of Br_2 or Cl_2 in the air volume sampled, V (L):

$$C = \frac{W - B}{V}, \text{ mg}/\text{m}^3.$$

EVALUATION OF METHOD:

The method was evaluated by sampling generated atmospheres of Br_2 and Cl_2 at both high (80%) and low (20%) relative humidities [1]. Samples were taken at four concentration levels ranging from 0.007 to 1.42 mg/m^3 for Br_2 and 0.354 to 6.77 mg/m^3 for Cl_2 . Overall recovery for Br_2 was 98.8% with total overall precision, $\hat{S}_{\text{RT}}$, of 6.8%. Overall recovery for Cl_2 was 98.6% with total overall precision, $\hat{S}_{\text{RT}}$, of 6.7%. Samples for Cl_2 were stable at least 30 days at 25 °C (103 $\pm$ 4% Recovery) and up to 60 days at 5 °C (101 $\pm$ 3% Recovery). The Br_2 samples were stable up to 60 days at 25 °C (99.2 $\pm$ 10.1% Recovery).

REFERENCES:

- [1] Cassinelli, M.E. Development of Solid Sorbent Monitoring Method for Chlorine and Bromine with Determination by Ion Chromatography, Appl. Occup. Environ. Hyg., 6:215-226 (1991).
- [2] NIOSH Manual of Analytical Methods, 2nd ed.; Taylor, D.G., Ed.; V. 1, P&CAM 209; U.S. Department of Health Education and Welfare, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health; DHEW (NIOSH) Publication No. 77-157, 1977.
- [3] Occupational Safety and Health Administration Analytical Laboratory: OSHA Analytical Methods Manual, Method No. ID-101). American Conference of Governmental Industrial Hygienists: Cincinnati, OH, 1985; Publ. No. ISBN: 0-936712-66-X.
- [4] Occupational Safety and Health Administration Analytical Laboratory: OSHA Analytical Methods Manual, (Method No. ID-108). American Conference of Governmental Industrial Hygienists: Cincinnati, OH, 1985; Publ. No. ISBN: 0-936712-66-X.

METHOD WRITTEN BY:

Mary Ellen Cassinelli, NIOSH/DPSE

APPENDIX A: CLEANING PROCEDURE FOR SILVER MEMBRANE FILTERS

NOTE: Some lots of silver membrane filters contain extremely high chloride background levels. If excessively high this cleaning procedure will not remove all of the chloride, even if repeated several times. Screening is necessary for each lot before being used for this method. Screening may be done by following this procedure at least twice, or by analyzing by XRD.

- 1. Place each filter in a 30-mL, wide-mouth bottle, and add 3 mL 6 M $\text{Na}_2\text{S}_2\text{O}_3$.
- 2. Allow to stand for a minimum of 10 min with occasional swirling.
- 3. Discard solution and rinse thoroughly with deionized water. Allow the filters to stand in last rinse for a few minutes.
- 4. Remove filters from bottles and dry between layers of absorbent laboratory towels.
- 5. Store cleaned filters between paper disks in manufacturer's container. Filters are stable for at least 8 months.

APPENDIX B: COLUMN RECONDITIONING PROCEDURE

In the following order, pump through the analytical columns at 2 mL/min:

- a. 30 mL deionized water to rinse;
- b. 60 mL 1 M HNO_3 to remove contaminants;
- c. 30 mL 0.1 M Na_2CO_3 to remove the NO_3^- ;
- d. Eluent to equilibrate.

Reconditioning is recommended after 100 to 150 analyses.

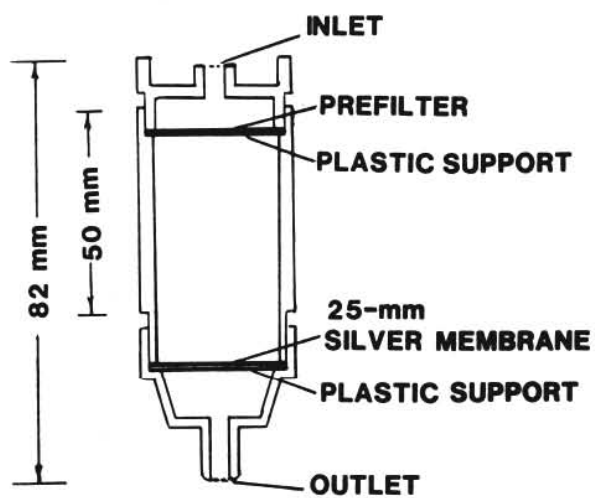


Figure 1. Silver Filter Sampler

ATTACHMENT 1. SERDP INTERIM REPORT 4 CHAPTER 7

Assessment of the Long Term Fate and Transport of Energetic Materials in the Vadose Zone Using Cracked 81 mm Mortars as a Source Term

Introduction

The long term fate and transport of energetic materials through the vadose zone is important for understanding how explosives ultimately reach the water table. If contaminants in the vadose zone are immobile, remediation or removal becomes fairly straightforward. However, once a contaminant enters the groundwater, clean up becomes much more challenging and costly. Therefore, the mechanisms of transport through the vadose zone are key to the development of remediation efforts. This study will seek to better define the parameters influencing the fate and transport of energetic materials in the vadose zone using cracked munitions as a source term. The goal of this work is to provide a link between laboratory scale studies and range characterization studies. Laboratory work tends to be theoretical. Many practical questions are left unanswered using this approach, such as: how much explosive will dissolve in the rain when a round low-orders? What is the rate of the dissolution? How much of the dissolved explosive from a cracked munition will sorb on the soil? How quickly will this dissolved explosive reach the water table? This experiment will use an engineering approach to try to reproduce what is being seen in the field, and to answer some of these pragmatic questions.

The explosives contained in the munitions have potentially negative impacts on the environment. The build-up of explosives residues in the soil may result in the contamination of groundwater [1]. Such a situation has been encountered at the Massachusetts Military Reservation (MMR) in the United States where the Environmental Protection Agency (EPA) suspended training because low RDX concentrations were found in the groundwater [2]. RDX and other high explosives have been identified as potential carcinogens [3]. At MMR, RDX is thought to originate from leaking UXOs, low-order detonations, residues

of past munitions disposal, or from accumulated residues over the years. The contamination caused by functioning munitions and munitions blown-in-place has been studied by various research teams in field conditions [4-8]. However, no work has been performed on leaching of explosives from UXOs or cracked munitions.

The leaching study will be conducted for a minimum of 12 months starting in Sept 2004; therefore, these results are not currently available. The experimental production of the cracked shells will be emphasized in this abstract as this phase of work was successfully completed in January 2004. However, the experimental plan of the hydrogeological leaching study will be presented as well. For clarity, the production of the cracked shells will be referred to as Phase I and the hydrogeological study will be referred to as Phase II

The objective of phase I of this study was to create the UXOs which would act as source terms for phase II. One key requirement was that the steel shell of the munitions be breached, exposing the explosives inside. This meant that the explosives could not detonate or burn completely, and that a large fraction of the explosive remained in or around the broken shell. An unexpected result of the experimental setup of phase I was the identification of a new type of UXO, which we have named the cracked shell. Cracked shells were subsequently used as the source term during phase II of the study.

The objectives of phase II are to produce fate and transport parameters for the energetic materials produced in phase I and to identify which fraction of explosives produced by the cracked shells results in the greatest amount of contamination to the vadose zone. This data will be compared to both an inert tracer and to pure granulated Composition B to come up with a clear picture of how cracked shells and their detonation residues contribute to subsurface energetic material contamination.

Phase I: Generation of Cracked 81 mm mortars

Phase I - Experimental

a) Materials

The Canadian 81-mm C70A1 mortar was used for all trials. The choice of the 81-mm offered several advantages. First, it is used both in Canada and the United States. Second, the composition B explosive fill contained in the projectile is the same in both countries and is widely used in other munitions. Third, the shell was an ideal size to fit in the columns during phase II. The 81-mm mortar is filled with 0.9 kg of Composition B (59.5% RDX, 39.5% TNT and 1% wax) [9]. Prior to detonation, the propellant was removed because it is completely consumed during launch; thus, it would not be present in either UXOs or normally detonating rounds. The fuze was also removed for safety purposes. The fuze was not replaced with an inert fuze for most tests, to increase the likelihood of obtaining cracked shells. An inert plug was used for one test only.

The trials chosen for use during phase II were performed on snow, with the detonation residue collected by removing a 2-5 cm thick layer of snow and storing it in large plastic bags. The cracked shell itself was also collected. The bags of snow were later freeze-dried in the laboratory to separate the residue from the snow without exposing the residue to liquid water, eliminating the possibility of losses due to dissolution. By holding the pressure below the triple point, water vapor can be drawn off the solid ice. This process is commercially used to preserve food products.

b) Method 1: C4 Attack

Composition C4 in sub-critical quantities, in blocks or in linear shaped charges, was applied to the outside of the shell to simulate the blow-in-place of unexploded ordnances (UXOs) by ammunition technicians. The shaped charges were Canadian military issues (Mk 7 series) [10] hand-filled with C4. Method 1 represents what would happen if the wrong amount of explosives or the wrong type of charge were used in range clearance operations. This method could also

represent the attack of munitions by a strong non-fragmentary blast very close to the item.

Table 1: Experimental Conditions Used in Method 1

Trial #	Type of attack	Position	Amount of C-4 used (g)
1	Mk 7 Mod 1 shaped charge	Longitudinal, 0 stand-off	15.1
2	Mk 7 Mod 1 shaped charge + C4 ball	Longitudinal, 0 stand-off	16.3 + 5.7*
3	Mk 7 Mod 2 shaped charge + C4 ball	Longitudinal, 0.5-cm stand-off	15.4 + 7.7*
4	Mk 7 Mod 3 shaped charge + C4 ball	Longitudinal, 0 stand-off	24.7 + 5.0*
5	Mk 7 Mod 2 shaped charge + C4 ball	Perpendicular, 2.9-cm stand-off	16.0 + 7.0*
6	Mk 7 Mod 4 shaped charge cut in half	Perpendicular, 1.5-cm stand-off	27.1 + 6.0*
7	Mk 7 Mod 8 shaped charge cut in half	Perpendicular, 9.5-cm stand-off	71.0
8	C4 ball	In fuze well	20.0
9	C4 ball	In fuze well, 2.5 cm stand-off	10.0
10	C4 block	Outside, at the nose	72.3
11	C4 block	Outside, at the nose	72.0
12	C4 block	Outside, at the nose	72.0
13	C4 block	Outside, at the nose + plug fuze	70.2
14	C4 block	Outside, at the nose	72.1
15	C4 block	Outside, at the nose	90.0
16	C4 block	Outside, at the nose	80.0
17	C4 hemisphere	Outside, at the nose	80.0
18	C4 hemisphere	Outside, at the nose	80.0
19	C4 hemisphere on cracked shell	Outside, at the nose	80.0
20	C4 hemisphere	Outside, at the nose	80.0
21	C4 hemisphere on cracked shell	Outside, at the nose	80.0
22	C4 hemisphere on cracked shell	Outside, at the nose	63.2
23	C4 hemisphere on cracked shell	Outside, at the nose	64.0

* Amounts refer to mass of C4 in shaped charge + mass of C4 ball which was required to seat detonator on shaped charge

Finally, by placing C4 near the nose of the round, the effect of a strong impact by a non-functioning round with a hard target (e.g. rock, other round, target) could be simulated.

The C4 was applied in various amounts and at various positions on the outside of the mortar round. Various sizes of shaped charges were used, with different stand-off distances. Table 1 summarizes the experimental conditions used. Figure 1 shows several different configurations for Method 1.

Twenty-three trials of Method 1 were performed in January 2004 at the DRDC Valcartier trial site on the Canadian Force Base Valcartier. The early trials were done on a thick metal plate until the right conditions were found to crack shells. The successful ones were then repeated on snow to ensure a maximum recuperation of the explosives and a minimum contamination by soil. This approach was taken to maximize the number of trials. Preparation of the snow-pack was very time consuming and we only had two weeks to complete our work. The surface area of the snow-pack, was roughly 3 m x 3 m. A large metal plate was buried in the middle of the snow pack under approximately 30 cm of fresh packed snow.



Figure 1: Configurations used in Method 1. Top left: small shaped charge longitudinal, minimal stand-off. Top right: larger shaped charge, large stand-off. Bottom left: Small block of C4 at the nose. Bottom right: Hemispherical configuration of C4 at the nose.

PCB 113B52 pressure gauges were placed at 10 meters from the detonation point to measure the overpressure generated by the events. The overpressure data suggests whether the round detonated completely, or a low-order detonation was produced. The gauges were triggered by an ionization pin placed in the C4.

c) Method 2: Fragment Attack

The second method consisted in detonating a mortar shell next to another similar round, in order to simulate the attack of a UXO by another incoming round that functions. It is similar, in many ways, to a sympathetic detonation trial [11]. A booster charge of 40-g of C4 was employed in all trials. Two 81-mm mortar

projectiles (A and B) were used for each trial. Projectile A was the intentionally detonated projectile, which simulated a round that functions normally (see Figure 2). Projectile B served as a UXO lying on the ground in the vicinity of the point of impact of an incoming round (Projectile A).

The two 81-mm mortars were placed one over the other (Figure 4), one was laid on a metal plate and the other was suspended by chains. The first objective was to determine the distance at which the reaction would change from a detonation of Projectile B to the production of a cracked shell. The second objective was to determine the distance at which Projectile B would remain intact. The third objective was to determine the effects of placement of Projectile B in the ground, on snow and underwater.

To maximize the number of fragments from projectile A hitting Projectile B, and to simulate the worst-case scenario, the fragmentation pattern of the 81 mm mortar was analyzed¹. The zone for a maximum number of fragments was determined to be between 85° and 105°, where 0° was at the nose of the projectile and 180° was at the tail end. Thus, projectile A was placed parallel to B, with an angle of 95° between the driving band (roughly the larger diameter) and the point of impact on projectile B (see Figure 2). The point of impact selected for Projectile B was at 5.5-cm from the projectile nose. At this spot, the wall of Projectile B was the thickest. This spot appeared to be the ideal place in order to be able to crack the projectile. Table 2 shows the distances between the projectiles for the various experiments.

For a small number of trials, the conditions were changed to reflect situations that are found in the field. For one experiment, the round was placed on fresh snow instead of on the metal plate. In this trial, the

¹ Personal Communication, Fragmentary pattern of 81mm mortar, C. Fortier, DRDC-Valcartier, Sept 2004

detonation residue was collected as in Method 1 and stored for use in Phase 2. For other trials, Projectile B was covered by various depths of sand, with or without an angle of entry. Finally, one trial was performed in which the round was immersed in water, a situation that was reported by ammunition technicians as common in some of our training ranges where UXOs are found in small ponds. PCB 113B52 pressure gauges were placed at 10 meters from the detonation to measure the overpressure generated by the events.

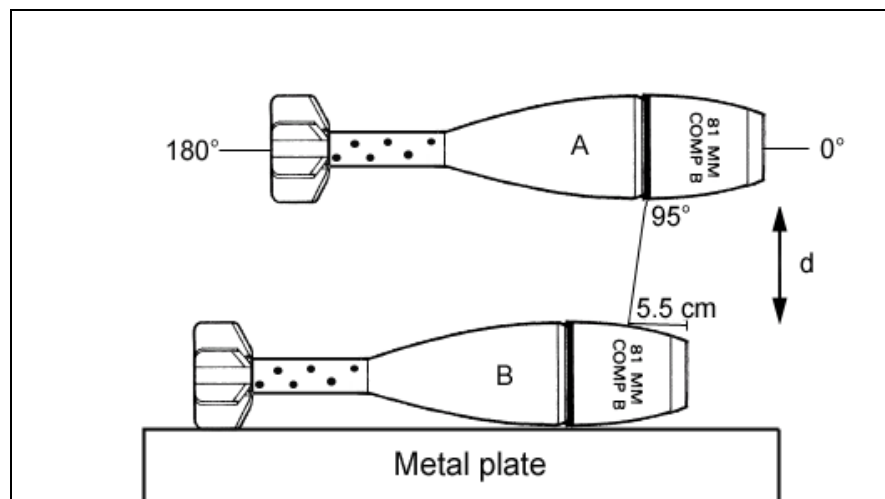


Figure 2: Experimental Set-up for Method 2



Figure 3: Photo of the Experimental Set-up for Method 2

Table 2: Experimental Conditions Used in Method 2

Trial #	Distance between projectiles (cm)	Material underneath Projectile B	Material above Projectile B
1	0	Metal plate	-
2	20	Metal plate	-
3	15	Metal plate	-
4	10	Metal plate	-
5	13	Metal plate	-
6	15	Metal plate	-
7	15	Metal plate	-
8	25	Metal plate	-
9	45	Metal plate	-
10	100	Metal plate	-
11	157	Metal plate	-
12	15	Snow	-
13	15	Sand	Sand 2.5 cm
14	15	Sand	Sand flush with top
15	15	Sand	Sand at mid-depth
16	15	Sand	Sand (proj. planted at 45°)
17	15	Sand	Water 5 cm

Phase I - Results

a) Method 1: C4 Attack

In general, the shaped charges did not generate cracked shells (Table 3). The shaped charges were not powerful enough to penetrate the metal casing of the shell, and failed to significantly expose the Comp. B filler. An example of such an event is shown in Figure 4. Only the larger shaped charge (trial # 7) pierced the mortar round significantly. This was not deemed acceptable for the subsequent hydrogeological leaching studies with the shells, since an insufficient amount of Composition B was exposed. C4 placed on the nose of the projectile, however, proved very successful. The C4 removed the metal in the fuse cavity and exposed the Composition B contained inside of the mortar rounds (Figure 5). This was considered acceptable, and some of the trials were repeated on clean snow. These projectiles and the detonation residue surrounding them were kept for the leaching study. The upper limit of this method was determined in trial #15 when the projectile detonated with a larger amount of C4 (90 g). The number of detonations was rather low (only 2). No low-order events resulted in large amounts of explosives being scattered around the site. Creating cracked shells was surprisingly easy with 81-mm mortars, an indication that this may also occur in the field during firings or range clearances.

Table 3: Results for Method 1

Trial	Resulting Condition of Projectile B
1	No effect
2	Groove blasted into projectile casing
3	Thick groove blasted into projectile casing
4	Long thick groove blasted into projectile casing
5	Thin groove blasted into projectile casing
6	Thick groove blasted into projectile casing
7	Thick groove, casing opened, Comp. B exposed
8	Detonation
9	Exposed Comp. B in the fuze well
10	Cracked, exposed Comp. B
11	Cracked, exposed Comp. B
12	Cracked, exposed Comp. B

13	Partial Crack at the nose & plug fuze
14	Cracked, exposed Comp. B
15	Detonation
16	Cracked, exposed Comp. B
17	Cracked, exposed Comp. B
18	Cracked, exposed Comp. B
19	Cracked, exposed Comp. B
20	Cracked, exposed Comp. B
21	Cracked, exposed Comp. B
22	Cracked, exposed Comp. B
23	Cracked, exposed Comp. B

b) Method 2: Fragment Attack

The attack by fragments seemed to be a very efficient way of obtaining cracked shells and exposing explosives, and was more effective than Method 1. For the trials done on the metal plates, when the distance between the projectiles was smaller than 15 cm, a sympathetic detonation occurred and both rounds were destroyed (Table 4). Above that distance, even at distances up to 157 cm (which was the maximum for our set-up), the projectiles were damaged and the explosives were exposed. At such long distances, the number of fragments hitting Projectile B was much lower, resulting in less damage. However, those fragments that hit were able to penetrate the casing. This is an indication that, in an impact area with many UXOs, the likelihood of a UXO being hit by a fragment is rather high given that incoming rounds potentially generate thousands of fragments. Examples of the cracked projectiles obtained at short and long distances between the rounds are shown in Figures 7 and 8.

Results of the trial done on snow (# 12) did not produce significantly different results. The sand, at a thickness of 2.5 cm, protected the projectile (# 13) from the fragments and acted as confinement in the case of trial # 14, when a low-order detonation was observed. Water did not protect the projectile from the fragments, and also acted as confinement to cause a low-order detonation. In both cases of low-order reactions, the likelihood of getting this result in the impact area seems quite high.



Figure 4: Effect of a shaped charge, showing groove blasted into projectile casing (trial #2)



Figure 5: Cracked shell produced by C4 on the nose (trial # 22)

Table 4: Results for Method 2

Trial	Resulting Condition of Projectile B
1	Detonation
2	Cracked and explosives scattered
3	Cracked and explosives scattered
4	Detonation
5	Detonation
6	Cracked and explosives scattered
7	Cracked and explosives scattered
8	Cracked and explosives scattered
9	Cracked and explosives scattered
10	Pierced and bare explosives exposed
11	Pierced and bare explosives exposed
12	Cracked and explosives scattered
13	Lost its shape but not pierced
14	Low order detonation and explosives scattered
15	Cracked and explosives scattered
16	Cracked and explosives scattered (Only the exposed part and 3 cm of the buried part)
17	Low order detonation and explosives scattered



Figure 6: Projectile attacked by fragments at a short distance (trial #6)



Figure 7: Projectile attacked by fragments at a long distance (trial # 11)

Phase 1 - Conclusion

Cracked 81-mm mortars were obtained using two methods. Remnants of these are now available for the study on the transport of explosives during phase II. The use of a small amount of C4 on the nose of the munitions was an effective means of producing cracked shells during Method 1 attacks. However, superior results were obtained by fragmentary attacks during Method 2. Shrapnel from a donor shell easily produced cracked shells and low-order detonations at standoff distances greater than 15 cm. Both methods produced reproducible cracked shells. The 81 mm mortars were easy to break open without causing detonation.

The initial hypothesis was that a sympathetic reaction caused by the pressure from an incoming round would be the best way to generate cracked shells and that fragments would tend to detonated rounds upon impact. The study demonstrated instead that fragments are more efficient than pressure at creating the cracked shells found in real firing situations.

The results suggest that cracked shells could be the cause of significant contamination by explosives on training ranges. If true, the frequency and methods of training and range clearance may require modification, particularly at fixed firing

positions used for many years which tend to create a high UXO density at the point of impact.

Phase II – Hydrogeological Leaching Trials

Phase II – Experimental

a) Materials

The hydrogeological leaching aspect of this study has been initiated in six separate soil columns, 60 cm in diameter and 75 cm deep (Figure 8). These columns are located in a dedicated laboratory refrigerated to 8 degrees Centigrade. The soil in the columns was obtained from a firing range on Canadian Force Base Valcartier near Quebec City and is a silty sand. Granulometry is scheduled to determine the precise composition of the soil. Qualitatively, it closely resembles the sandy soil commonly found on several other Canadian Forces bases such as Canadian Forces Base (CFB) Shilo, Wainwright, Suffield and Cold Lake. The soil was thoroughly mixed to eliminate any heterogeneities. This was followed by screening to remove any stones larger than 0.7 cm in diameter.

The columns were manufactured of ¼” thick 304 stainless steel lined with Teflon (Figure 8). This heavy gauge material was required because of the stresses placed on the column during compaction of the soil. All parts were rinsed with acetone prior to addition of the soil. The soil was added to the column in uniform 1700 g layers, which corresponded to a 1 cm compacted thickness. It was then compacted thoroughly with the jack drill, and the surface was scarified to provide a hydraulic connection between the sand layers. This was repeated until the sand level was 75 cm deep. Care was taken to produce homogenous conditions in all six columns. The columns are each fitted with an automated spray system, which simulates the annual water infiltration cycle for the Quebec City region.

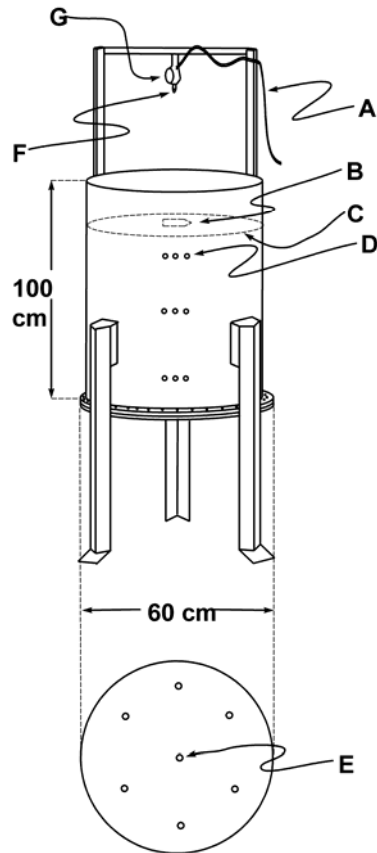


Figure 8. Schematic of Column. A is the water feed line. B is the cracked shell source term. C represents the surface of the soil. D are the access holes for the Time Domain Reflectometers (TDR). E are the leachate outflow nozzles. F is the infiltration spray nozzle, and G is the electric valve controlling flow.

b) Instrumentation

The columns were each instrumented using time domain reflectometers (TDR) connected to a Campbell datalogger (model CR-10) via three multiplexers. This system allows the real-time measurement of the volumetric water content (θ) of the soil and has the advantage of being non-destructive. Measurements can be taken without disturbing the system. The TDR probes were coated in Teflon, and inserted through the column wall via drilled holes. The TDR's were installed during the sand compaction, and will remain inside the columns for the duration of the experiment.

c) Hydraulic conductivity

Following the sand compaction, the hydraulic conductivity was determined for each column using a Guelph permeameter (Figure 9). The infiltration rate was measured at 3-5 different tensions varying from -250 mm to -10 mm. A porous plate was used in conjunction with the Guelph permeameter, and this plate created a hydraulic link with the surface of the soil. The rate of descent of the water level in the main reservoir was the information used to calculate the hydraulic conductivity.

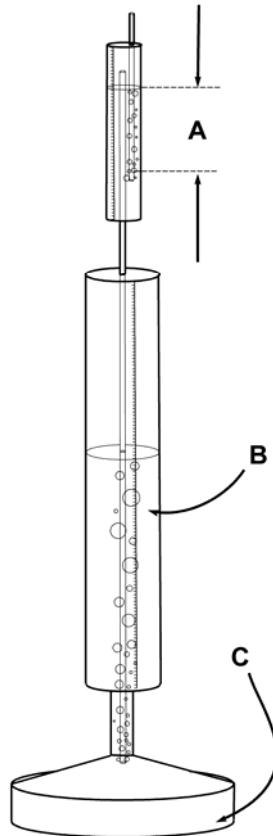


Figure 9. Guelph Permeameter: A shows tension measurement, B shows main reservoir and C shows the porous plate

d) Spray system

The spraying system to infiltrate the columns was selected to produce uniform spray coverage over the surface of the column (a diameter of 60 cm) at a very low flow rate. The spray nozzle which best fit our needs was the UniJet model TG 0.3, which at 30 psi produces 0.197 litres per minute. In the Quebec City area, there are only two periods of significant water infiltration. The first and most significant is in the springtime, when the when the snowpack melts and the second is in the autumn with two

months of heavy rainfall. Other infiltration events during the year are not significant compared to these two and will not be considered. The spray cycle for springtime infiltration is 1.5 minutes per hour from 9 am to 4 pm for (the period of the day above zero degrees Centigrade) for 30 days (the month of April). During the autumn infiltration period, the spray cycle is 6.6 seconds/hour, 24 hours per day for 61 days (October-November). Such short timeframes required substantial control over the spray system. An electric valve was installed between the water feed line and the spray nozzle. This valve was controlled by the CR-10.

The electric valve on each of the six columns is connected to its own dedicated 20 L water reservoir (Figure 10). The six reservoirs were constructed of schedule 80 PVC and were each equipped with a fill valve, pressure hose inlet, outflow valve connected to the water feed line and a transparent scale tube to monitor the water level. The pressure hoses on all six reservoirs were connected to a single manifold which distributed the pressurized air equally. Therefore, even if there was an unexpected variation in air pressure, it would change equally for each of the columns, and no difference in water volume sprayed should be encountered. As well, all water feed lines were cut the same length to prevent variations in resistance caused by different lengths of tubing. Table 5 shows the experimentally measured flow rates from each of the spray nozzles.

The water used for infiltration is simulated rainwater consisting of distilled water pH adjusted to 4.7, which is the annual mean pH for rain in the Quebec City region. PH adjustment was accomplished with concentrated HCl.

Table 5. Flow Rates of Spray nozzles

Volume mL	Time to fill graduated cylinder to volume indicated (sec)					
	Column A	Column B	Column C	Column D	Column E	Column F
50	16	16	16	15	17	17
70	23	22	21	21	23	22
90	28	28	27	27	29	28
110	34	35	33	33	36	34
130	40	40	39	39	42	40
150	45	47	45	45	49	47
250	75	76	76	76	80	75

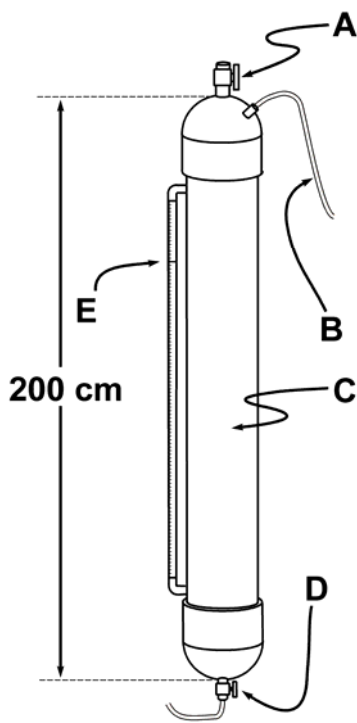


Figure 10 – Pressurized Water Reservoir: A is the fill valve, B is the pressure hose inlet, C is the schedule 80 PVC pipe, D is the outflow valve connected to the water feed line, E is a transparent scale tube to monitor the water level

Table 6 Source terms

Column	Source Term
A	Potassium Bromide (Inert Tracer)
B	25 g Granulated Comp B (Control)
C	25 g Detonation residue (Soot, Comp B particles, metal particles)
D	25 g Detonation residue (Soot, Comp B particles, metal particles)
E	Cracked shell & 25 g detonation residue
F	Cracked shell

e) Experimental Design

Each column will be monitored continuously for the volumetric water content using the TDRs. Leachate flowing from the column from the outflow nozzles will be collected in graduated cylinders and the volumes tabulated. Five hundred mls of water will be drawn from the outflow for chemical analysis on a regular basis, dictated by the rate of leachate outflow.

The detonation residue used in the columns will be a composite of residue from 5 different crack shell trials. This is necessary to have enough homogenous residue to split between four columns and still retain enough for laboratory analyses to allow complete characterization of the residue. Twenty five g of the composite detonation residue will be used in each of the four columns. Table 6 shows the source terms for each column. The cracked shells to be used as source terms used were those obtained in trials 12 and 15 of Method 2, fragment attack.

Phase II – Discussion

The fate and transport parameters for four different energetic material source terms will be produced. The detonation residues are hypothesized to have the shortest breakthrough time because it consists of very fine particles with an extremely high surface area. High surface area increase the rate of dissolution of the energetic materials

as compared to source terms with less surface area (such as in the cracked shells). However, the mass of the residue is very small compared to the 500-750g of Comp B remaining in the cracked shells. Despite the large mass of the cracked shells, the Comp B is in large chunks. One of the questions which these trials should help answer is which source is more significant – the detonation residue or the cracked shells themselves? Depending on the answer, approaches to remediation would be very different.

Infiltration data for the Quebec City region will be used for the water application protocol [14]. In Quebec, no infiltration occurs between December and March, as the ground is frozen. Statistically, no infiltration takes place from June-September because of the dry summer months. Therefore, as long as a year may be required to achieve breakthrough of the energetic materials in the outflow collected below the columns if realistic flow rates are applied. Therefore, the infiltration cycle will be accelerated in order to obtain results more quickly. An obvious disadvantage to accelerating the cycle is that the risk of producing unrealistic conditions that may negatively affect the reliability of the fate and transport parameters. A compromise was achieved by shortening the two dry cycles between infiltration seasons. The dry season is postulated to contribute little to the fate and transport of contaminants in the vadose zone, and that the vast majority of transport activity occurs during infiltration events. The infiltration cycle will, therefore, be doubled with two years of activity occurring in one year. This is achieved not by increasing the rate of infiltration i.e., doubling the rate of water sprayed on the column, but halving the dry periods between infiltration events. The reduced experimental duration will also reduce the likelihood of fungal growth in the column, a problem observed in longer duration studies².

Phase 2 was started 17 Sept 2004 with the initial infiltration of water to bring the water content in the columns up to the field capacity. The volumetric water content in

² Personal communication, Problems encountered with long term vadose zone column trials, J. Caron, Ph.D., University of Laval, Québec, 2004

the columns was uniform as measured by the TDRs, with the top 25 cm in each column registering around 17%, the middle 25 cm 27% and the bottom 25 cm registering around 36%.

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8 (b) Transport of Residues from Cracked Unexploded Ordnance Through the Vadose Zone During Springtime Aquifer Recharge

Introduction

High explosive compounds such as 2,4,6-trinitrotoluene (TNT), cyclotrimethylene-trinitramine (RDX) and cyclotetramethylene-tetranitramine (HMX) have entered the environment where these compounds have been manufactured, stored, disposed-of, or used (Best et al. 1999). TNT has been associated with abnormal liver function and anemia, while both TNT and RDX have been classified as potential human carcinogens (ATSDR a & b, 1996). There is currently limited information available concerning the health effects of HMX (ATSDR c, 1996). In response, the U.S. Environmental Protection Agency has established lifetime exposure drinking water health advisory limits for TNT, RDX, and HMX at 2, 2 and 400 µg/L, respectively (Crockett et al. 1999).

Of particular interest are the explosive compounds in unexploded ordnance (UXO) found on former and current military training ranges (MacDonald, 2001). UXO are produced when military ordnance fails to detonate, or fails to detonate completely. These unexploded projectiles are often difficult to locate, and may be scattered randomly over hundreds of square kilometres. Due to the kinetic energy they have when they strike the ground, they are often buried which complicates clean up efforts. They may be physically damaged upon impact, or they may be ruptured from a low-order detonation. Given enough time, they may be penetrated by corrosion. Recently, it has been speculated that unexploded ordnance may be damaged and cracked open by other rounds that detonate nearby (Pennington et al. 2005). This heterogeneity in physical condition and spatial distribution greatly complicates clean up and modeling efforts.

The bulk charge in all Canadian and US army fragmentary ordnance is either TNT or

Composition B. Composition B is a 60%/39% compound of RDX and TNT which contains ~ 1% wax. However, all weapons grade RDX contains 8-10% HMX as an impurity, which means that Composition B is actually composed of about 55.2% RDX, 39% TNT, 4.8% HMX and 1% wax. Composition B has been used in military ordnance since WW II due to its high explosive yield and melt cast characteristics.

Dissolution is the primary method by which solid explosive compounds are made available to the environment (Brannon et al. 1999). The dissolution of RDX rather than its aqueous transport probably controls the entry of this compound into the environment. This is because its adsorption coefficient in soil is quite low, indicating that it will travel through the vadose zone at the infiltration rate (Brannon et al, 1999). Several studies have measured the dissolution rate of Composition B (Lynch et al. 2001, 2002. Phelan et al 2003, Lever et al, in publication) and Lynch et al (2002) published data on the effects of component interactions on the dissolution of Composition B.

Brannon and Pennington (1999) have compiled a comprehensive summary of the fate and transport process descriptors for energetic materials. Unfortunately, there has been no work to date on possible component interactions on the adsorption coefficients (K_d) or transformation rate coefficients (K) for energetic compounds such as Composition B.

In this paper, we expand the laboratory findings to try and identify the extent and rate which a buried, cracked UXO will contaminate the pore water of the vadose zone with energetic materials. Although this experiment is tailored to the conditions at Canadian Forces Base (CFB) Valcartier near Quebec City, the results are applicable to many other bases in Canada that have sandy soil, including CFB Wainwright, Shilo, Suffield, Petawawa and Cold Lake. We have constructed large scale unsaturated columns of soil and housed them in a refrigerated laboratory. With this set-up, we attempted to reproduce the conditions found in the vadose zone below the frost line. In Quebec City, the frost line is found at a depth of between 1.4 to 1.8 m.

An automated sprinkler system was designed to reproduce the annual aquifer recharge cycle in Quebec City. We have used cracked unexploded ordnance and detonation residues as source terms, rather than pure explosives in an attempt to measure the mass of

energetic materials which may be expected to infiltrate the vadose zone and subsequently the water table from a single cracked 81 mm mortar shell. With this apparatus, we were able to periodically measure the concentration of the explosive species found in the pore water in the vadose zone around buried, cracked unexploded ordnance and extrapolate from this the mass of energetic materials lost in the effluent. We compared these results to published data on the fate and transport parameters of TNT, RDX and HMX and used this information to suggest a dissolution model for detonation residue, which could explain these results.

Experimental

Source Terms

The explosives source terms used in this experiment were derived from cracked 81 mm mortar rounds. The production of these cracked rounds was complex, and is described in detail in chapter 7 of the 2004 SERDP annual report. The hypothesis that guided this work was that UXOs might be cracked open by other rounds that detonate nearby. By being cracked open in this fashion, the UXO's would be expected to scatter substantial amounts of explosive filler or detonation residue into the surrounding area. This work was described in chapter 7 of the 2004 SERDP Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 4. The rounds used were 81 mm mortar rounds, and the detonation trials were performed on uncontaminated snow. Jenkins et al (2000) discuss the advantages of collecting detonation residue on snow. Following each detonation, the explosive filler and detonation residue was collected by scraping the snow down to a depth of 10 cm and collecting the contaminated snow in opaque plastic bags. The surface area of the snow that was collected was measured in order to calculate the concentration of detonation residue per square meter. The collected snow samples were stored frozen in commercial freezers, and the detonation residues were subsequently extracted by freeze-drying the snow using a LABCONCO Lyph-Lock 4.5 freeze dry system which operated at a vacuum of 5 to 8 microns Hg and temperatures of -40°C to -50°C . Freeze drying allowed collection of the solid detonation residue without ever exposing it to liquid water. As a result, the physical structure of the detonation residue was not lost through dissolution. The detonation residue was separated into a fine fraction (< 0.5 cm diameter) and a coarse fraction (> 0.5 cm diameter) in order to improve grain size characterization of the finer fraction.

Both an inert tracer and pure composition B were used as controls. The inert tracer was a brine of 10.00g potassium bromide dissolved in 200 mL of distilled water. The pure composition B was weapons grade, and was crushed to a powder on a milling machine. The grain size distribution of the composition B was heterogeneous, and varied from 5 microns to 0.85 mm. Table 1 describes the source terms that were used on each column.

Apparatus

The soil used in the columns was sieved prior to use to remove all stones larger than 0.8 cm. The soil was uncontaminated quartz sand obtained near an active range on Canadian Forces Base Valcartier. This sand comes from an alluvial formation around the Jacques Cartier River, shown on the map in Figure 1. The sand was well mixed and screened manually prior to use to ensure homogeneity and to remove any stones larger than 0.7 cm diameter. The soil was then loaded into the columns in 4600 g lifts, and was compacted with a jackhammer fitted with a metal ram. Each lift was approximately 1 cm in thickness, and following compaction the surface of each layer was lightly scarified to provide hydraulic linkage. The grain size distribution of the sand is shown in Figure 2.

Six stainless steel columns packed with this soil were used for the leaching trials. These cylindrical columns were TeflonTM-lined and measured 0.62 m in diameter and 0.6 m in depth. A schematic is shown in Figure 3. Each column was constructed with seven outflow nozzles on the bottom of the column. These outflow nozzles were equipped with fibreglass wicks, which were embedded in the sand. The capillary action of these wicks provided a head of ~3 cm, which was sufficient to draw out the unsaturated pore water and cause it to flow from the column. A graduated cylinder was placed under each nozzle and the water level was measured daily in order to calculate the rate of flow from each nozzle, and from the column as a whole.

Three triple-pronged time domain reflectometers (TDR's) were inserted in each column at depths of 10, 30 and 50 cm from the surface to measure the saturation of the soil at these depths. The data from the TDR's was recorded automatically at 15 min. intervals for the duration of the experiment.

An automated system sprayed distilled water pH adjusted to 4.7 (simulated rainwater) onto the surface of the columns in a cycle designed to reproduce annual springtime groundwater recharge for the Quebec City area. Inflow rate is shown in Figure 4.

Figure 1. Surficial Deposits around CFB Valcartier (adapted from Natural Resources of Canada surficial deposits map of Canada)

Table 1. Source terms used on columns

Column	Detonation residue fine fraction (<0.75 mm dia.)	Detonation residue coarse fraction (>0.75 mm dia.)	Cracked Mortar	Pure crushed Composition B	Inert Tracer (KBr)
A	0	0	No	0	200 mL
B	20.00 g	25.00 g	No	0	0
C	20.00 g	25.00 g	No	0	0
D	20.00 g	25.00 g	Yes	0	0
E	0	0	No	20.00	0
F	20.00 g	25.00 g	Yes	0	0

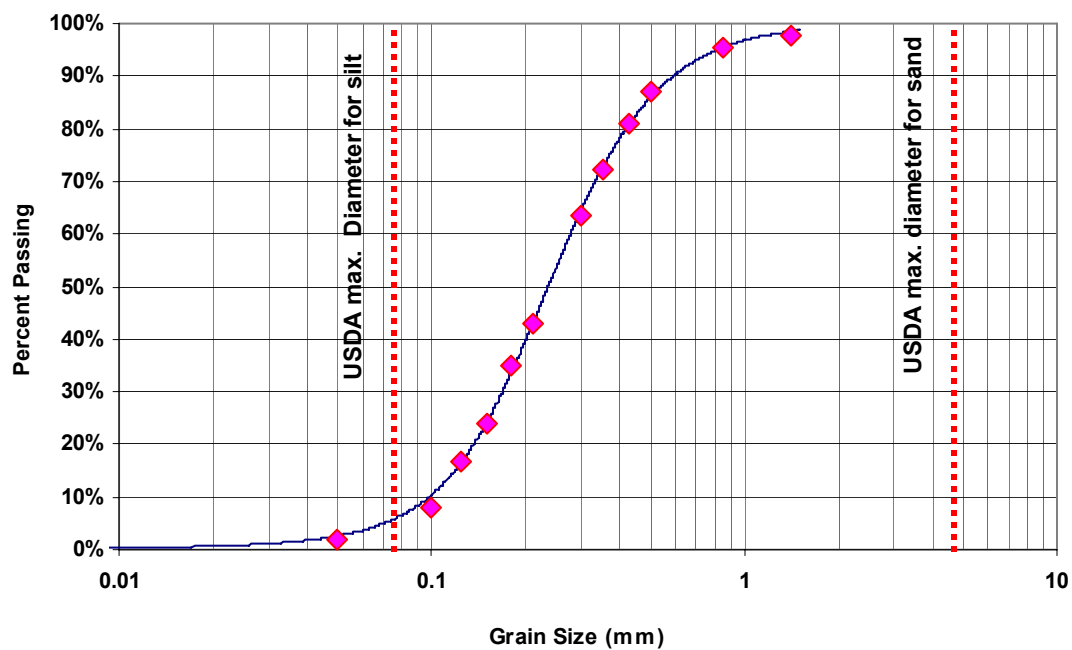


Figure 2. Grain size distribution of soil used in unsaturated column

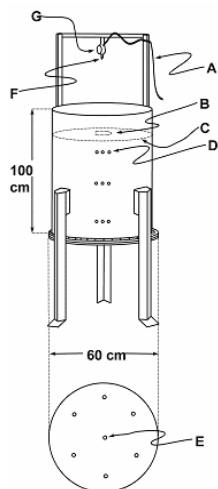


Figure 3. Soil Column Apparatus. A: Inflow tube B: Cracked UXO C: Soil Surface D: TDR access holes E: Outflow nozzle F: Spray nozzle G: Electric Valve

Method

The columns were brought to a steady state (spray inflow = leachate outflow) and refrigerated to 8° Centigrade (the perennial deep subsurface temperature in Quebec City) prior to the experimental source terms being deposited in the columns.

Simulated springtime recharge started immediately once the source terms were placed in the soil columns. For the Quebec City area, the springtime aquifer recharge caused by the snowmelt is 253 mm of water (Mailloux, 2002). This snowmelt occurs over a period of roughly 30 days in the months of March and April. The columns, having surface areas of 0.322 square meters, required a total of 81.3 litres to be sprayed over this 30 day period.

The spray cycle was programmed to operate only between the hours of 08:00 hrs and 16:00 hrs, which are typically the hours when it is above zero in the springtime. The cumulative inflow is shown in Figure. 4. A daily log was kept to monitor both the inflow to each column and outflow from each individual nozzle. 500 mL composite samples of the leachate were collected six times over the 30 day period. These samples were analyzed for energetic materials with HPLC according to EPA method 8330. The samples from column A, which contained the bromide tracer, were collected the same

way as the other columns, but the leachate was analyzed with a Dionex ICS using a AS14 column for bromides (details of NIOSH Method 6011 for Bromide and Chloride given in Appendix 7). Total energetic material outflow was extrapolated by correlating the six values of measured outflow concentrations with the total outflow volumes.

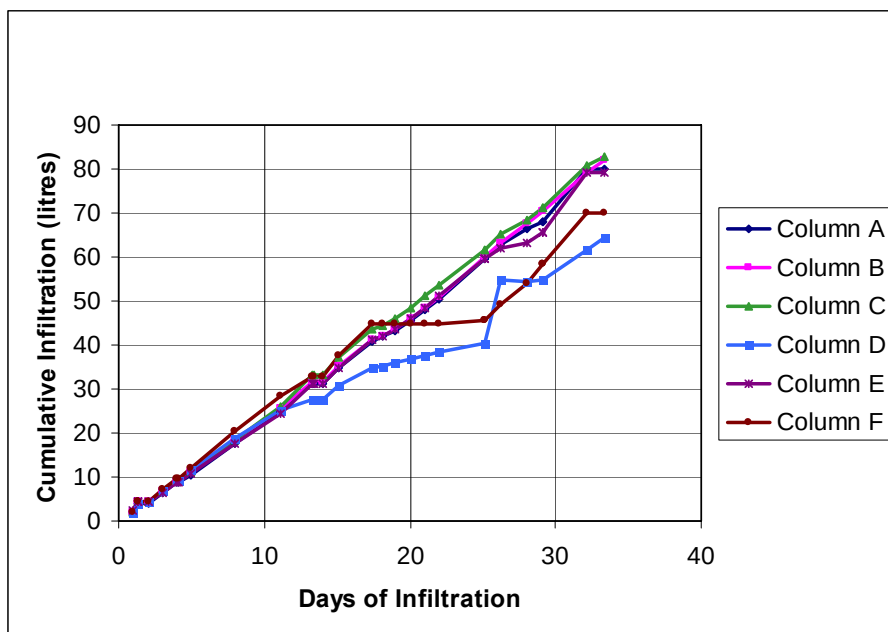


Figure 4. Cumulative inflow to columns

Results and Discussion

The automated spray apparatus proved difficult to control. As shown in Figure 4, the cumulative inflow to Column F and Column D was erratic due to difficulties with the electric valves. Both valves failed on the 17th day of infiltration, and were repaired on the 25th day. Rather than increase the flow rate in these two columns to catch up to the volumes sprayed in the other four columns during this period, it was decided to maintain the same flow rate. For this reason, columns D and E had 10 litres less of infiltration during the simulated spring recharge.

The grain size of the residue was heterogeneous, and varied between 5 microns to several cm in diameter, with the largest pieces being pure composition B. Figure 5 shows the grain size distribution plot of the composite detonation residue. Pieces of explosive larger than 5 mm were removed prior to the measurement of the grain size distribution.

This was because grain size distribution is measured on a mass basis and one or two large pieces could skew the results in a non-reproducible fashion.

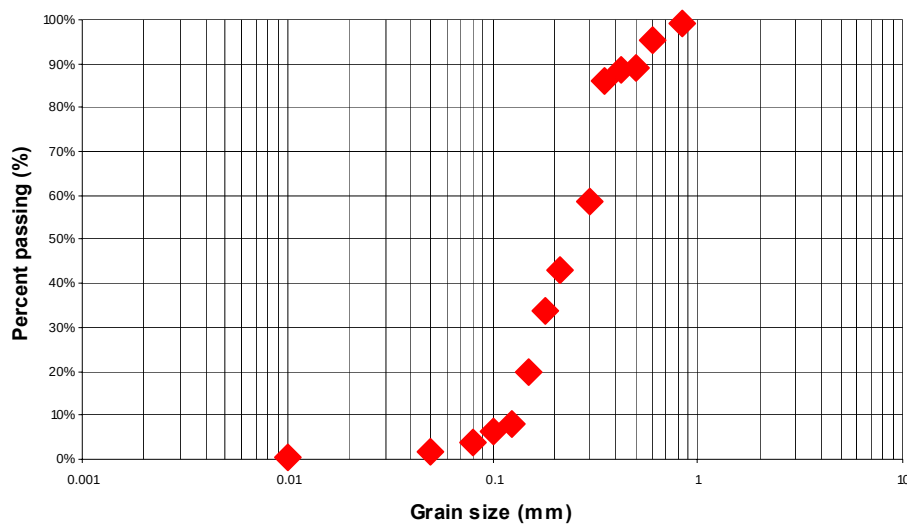


Figure 5. Grain size distribution of detonation residue

Cumulative outflow volumes are shown in Figure 6. The outflow of the columns is nearly identical to the inflow (Figure 4), as the columns were brought to steady state conditions prior to the start of the experiment. The saturated hydraulic conductivity (K_{sat}) of the columns was measured using Guelph permeameters to be on the order of 10 cm/hr. Unsaturated hydraulic conductivity of the columns was calculated to be between 1 cm/hr at a moisture content of 0.05 and 8 cm/hr for a moisture content of 0.2. The permeameter readings that these figures are based upon had an error range of $\pm 25\%$. The calculated conductivities therefore only indicate the order of magnitude of the conductivities, but these conductivities are consistent with the observed breakthrough times observed for the inert tracer KBr.

The time domain reflectometers showed that steady state unsaturated conditions were maintained in the columns for the duration of the experiment, with moisture contents in all columns remaining at 0.15 ± 0.02 at a depth of 10 cm, 0.24 ± 0.03 at a depth of 30 cm, and 0.35 ± 0.02 at a depth of 50 cm. Even the columns D and F which experienced failure of the inflow valves showed very little change in the unsaturated moisture content of the soil during the period which they did not undergo infiltration.

Elution curves of the concentration of TNT, RDX and HMX in the outflow with respect to the volume of inflow are shown in Figs 7, 8, and 9. The elution curve for the inert tracer in Column A is shown in Figure 10. TNT transformation products were detected as well, but the concentrations of these were two or three orders of magnitude below the concentration of TNT itself. This suggests that as expected, transformation, biodegradation and photolysis processes had a minimal effect on this experimental setup. For clarity and brevity, TNT transformation products will not be addressed here.

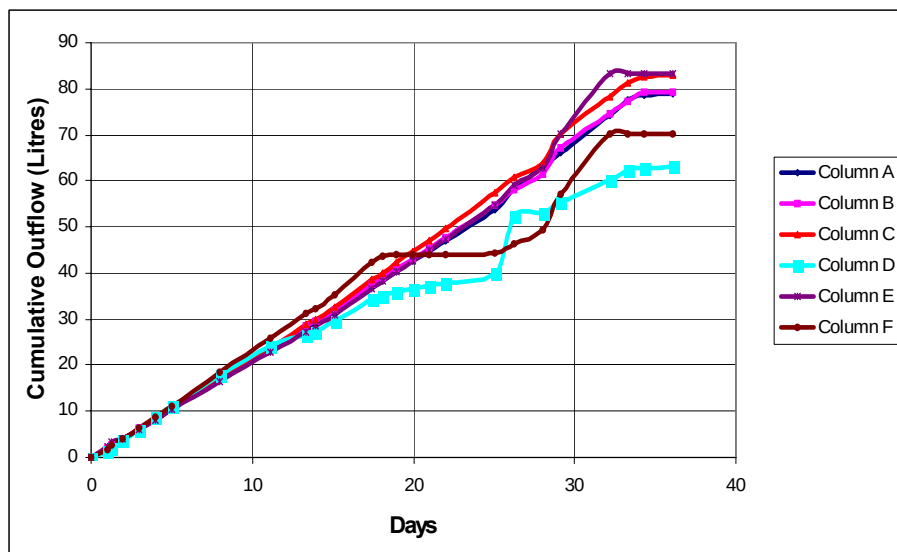


Figure 6. Cumulative outflow from columns

The data in figures 7, 8 and 9 suggests that there is a significant and probably unique mobilization of energetic materials during the first groundwater recharge event following detonation or partial detonation. Energetic material concentrations are detected at infiltration volumes of approximately 24 litres for all explosive species. In comparison, the inert KBr has breakthrough at 10 litres.

The retardation factor R_f may be calculated from this data. The retardation factor describes how many times faster a nonsorbing tracer is moving relative to the contaminant being sorbed. Since all columns have the same physical dimensions and the same infiltration rate, the outflow rate (L/hr) is a direct function of the hydraulic conductivity (m/hr). The inert tracer will travel through the column faster than a species that is being sorbed, so breakthrough for the inert tracer will occur at a lower volume of

cumulative outflow. Therefore, the ratio between the outflow volumes at which breakthrough occurs will be the inverse of the ratio of transport velocities. This ratio, R_f , is called the retardation factor. In the experimental columns, R_f is therefore 1.25L / 0.8 (non-dimensional).

$$R_f = 1 + \left(\frac{1-n}{n} \right) \rho_s K_d$$

Equation 1. Retardation factor R_f as a function of porosity n , bulk soil density ρ_s and adsorption coefficient K_d (Equation 18.5 in Domenico & Schwartz 1990)

R_f may also be defined according to the retardation equation (Domenico & Schwartz, 1990) This equation allows us to calculate K_d if we know the porosity (n) and the bulk density (ρ_s) For the soil used in the column study, it had a measured porosity of 0.38 and a bulk density of 1.3 g/cm³. This gives us a calculated K_d of 0.24 mL/g (or L/kg) for all energetics, TNT, RDX and HMX. This value fits closely with the literature values for K_d in sand for TNT of 1.5 L/kg (Townsend et al, 1996), 0.47 L/kg (Brannon et al, 1992) and 1.3 L/Kg (Cattaneo et al, 2000). Fewer literature values are available for the K_d of RDX and HMX in sand, but available values are also on the order of magnitude of 0 L/kg to 1 L/kg (Brannon and Pennington 2002).

Myers et al (1998) reported 100% recovery of RDX and HMX during saturated column studies using Ottawa sand, and 97.5% recovery of TNT. The subsurface, alluvial soil that was used for this experiment, while not being as homogenous as the river sand used in Myer's experiment, was a medium to fine sand (Figure 3) with a very small silt fraction and effectively zero clay content. The comparison with Myers river sand which had 0% clay content should therefore be reasonably good. Myers' results indicate that in both batch and column experiments in the saturated regime, energetic materials will not undergo significant transformation or adsorption in sands. Although Myers' source term was already dissolved prior to injection into the columns and his columns operated in the saturated regime, our observations are very complementary. We measured very low concentrations of TNT transformation products, and a substantial recovery of energetic

materials in the effluent. The measured transformation product concentrations were 2-3 orders of magnitude below measured TNT concentrations.

Given the weak adsorption and transformation of RDX, HMX and TNT in sandy soils, the rate-limiting step to contaminant transport in our columns should be dissolution. Lynch et al. (2001) published solubility data for TNT, RDX and HMX over a range of pH's and temperature. From Lynch's data, predicted solubility at pH 4.7 and 8°C is 61.6 mg/L (ppm) for TNT, 21.0 mg/L (ppm) for RDX and 1.58 mg/L (ppm) for HMX (shown as dashed lines in Figures 7, 8 and 9). From this we can see that our measured concentrations approach or surpass predicted solubility with a peak value occurring when approximately 50 L of water has flowed through the columns. The concentrations then tend to drop off. This is suggestive of a slug type input, as opposed to continuous input, which we would expect if a solid source were dissolving in a uniform fashion and at a uniform rate. One explanation for this is that the extremely fine fraction of detonation residue is dissolving preferentially due to its very high surface area, creating a "slug" of dissolved energetic material. This hypothesis will be further explored later in the text.

The extrapolated cumulative energetic material mass transport during the spring infiltration period is shown in Figs 11, 12 and 13. The figures indicate that despite the weak solubility of TNT, RDX and HMX, a substantial amount of energetic material flowed out in the effluent. It is clear from observing the sharp drop in the elution curves in Figures 7, 8 and 9 that this rate of recovery will not be sustained. Table 3 shows the concentrations of energetic materials measured during the first outflow of the autumn infiltration, which took place 4 months after the spring infiltration described in this paper. The measured concentrations are in general two orders of magnitude lower than the peak concentrations detected during the spring infiltration, and one order of magnitude lower than the final springtime analyses. Further autumn effluent analyses support this observation. The peak in energetic material concentration seen in the springtime infiltration was not reproduced in the autumn infiltration event, indicating it is a one-time occurrence. This supports the fine-fraction dissolution hypothesis.

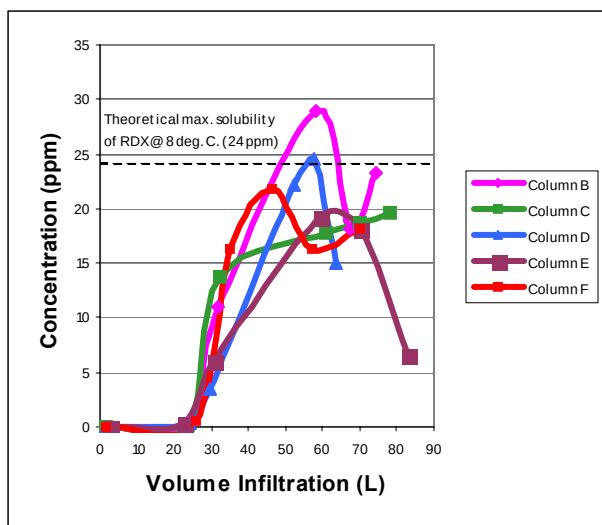


Figure 7. RDX outflow concentrations

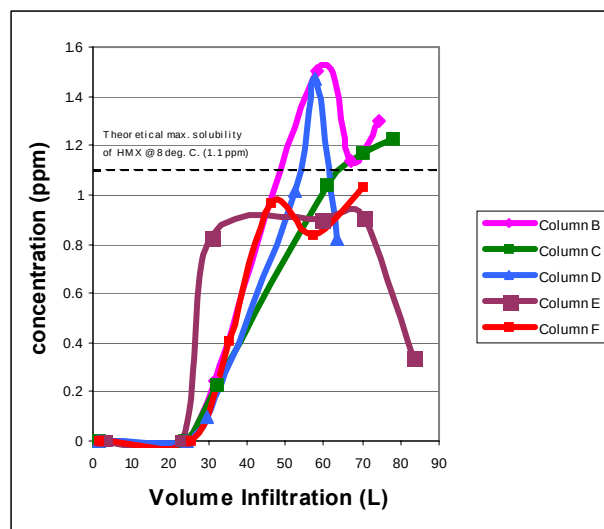


Figure 8. HMX outflow concentrations

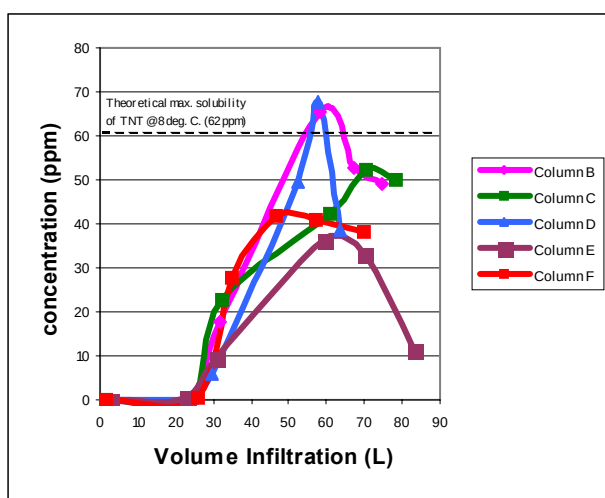


Figure 9. TNT outflow concentrations

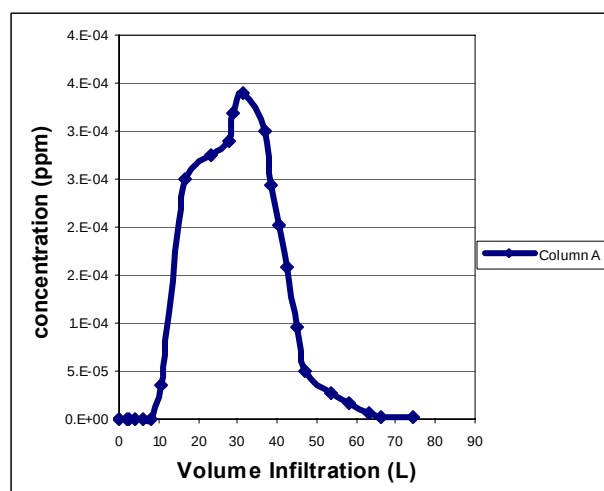


Figure 10. Br outflow concentrations

The columns with energetic materials as source terms all show essentially the same results. The differences between the curve of columns B & C and D & F, whose source terms were identical, suggests that the most important features of these curves are the uniform breakthroughs, the concentrations which approach saturation, and the drop off in concentrations towards the end of the infiltration period. Small variations in the curves, such as the small increase in concentrations observed in the final analyses of columns B and F should be interpreted with caution, since there are observed variations in the curves between columns having identical source terms. For example, the energetic material in column C appears to be somewhat slower in achieving maximum concentration, and

Figure 9 suggests that peak concentrations were reached just as the springtime infiltration came to an end. However, Column B, which had the exact same source term, showed the most pronounced peak and the highest concentrations of all columns. Similarly, column D shows a very sharp peak in concentration followed by a rapid decline, while column F achieved its peak earlier than all other columns. These differences are likely related to such factors as small differences in the bulk density of the soil achieved during compaction, small differences in the outflow nozzles, and of course the troubles

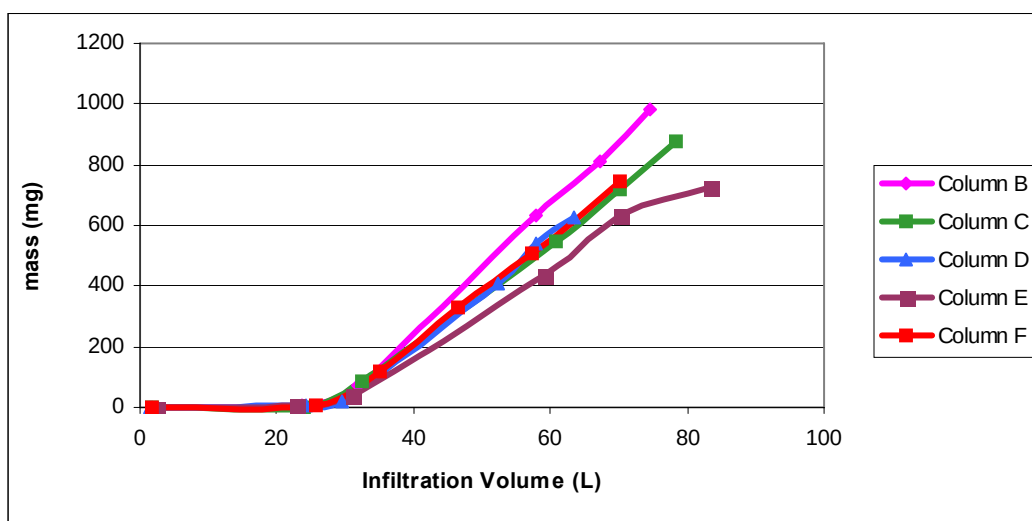


Figure 11. Cumulative mass transport of RDX in spring effluent

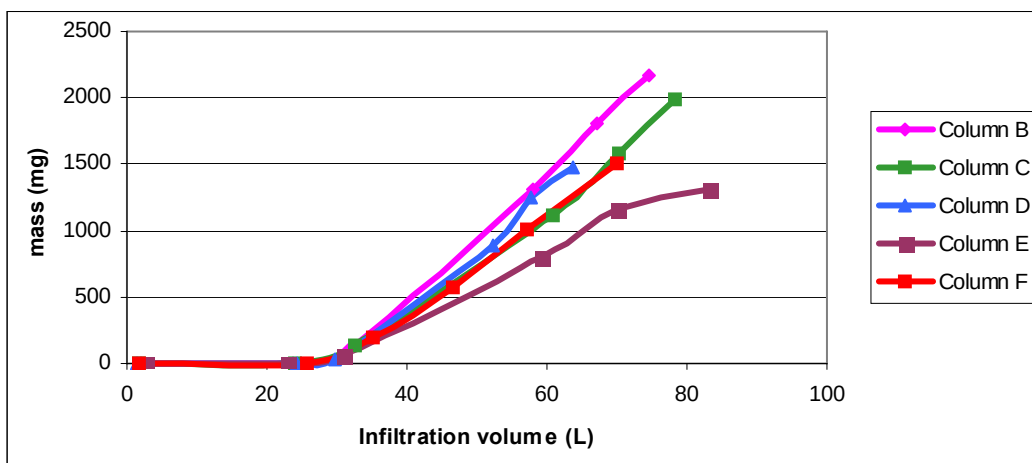


Figure 12. Cumulative mass transport of TNT in spring effluent

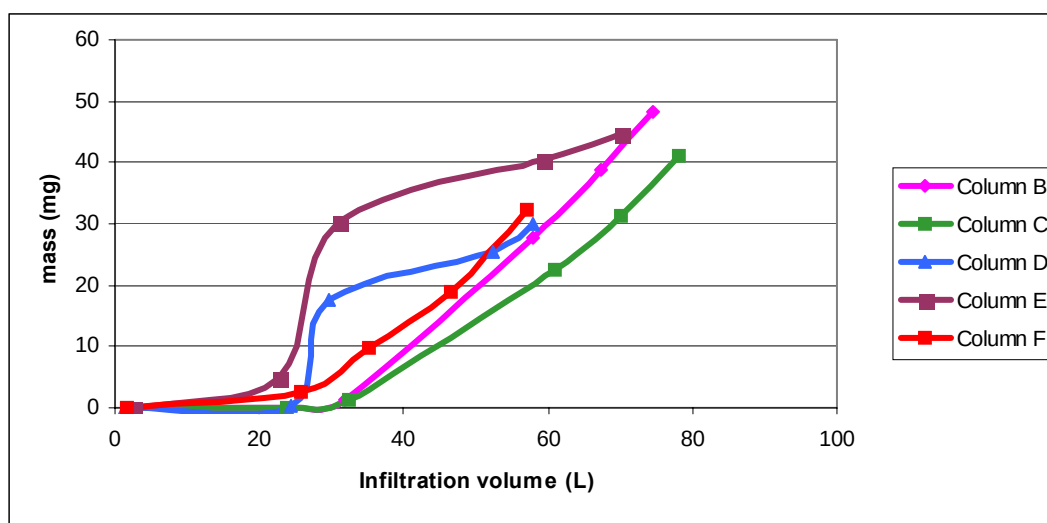


Figure 13. Cumulative mass transport of HMX in spring effluent experienced with the inflow spray system. Given these factors, small changes in the effluent concentration curves in Figures 7, 8 and 9 should not be interpreted.

The detonation residue in columns B, C, D, and F did not show effluent concentrations that were substantially differently from the control: the pure, crushed composition B that was placed on column E. This suggests that the small amounts of impurities found in the detonation residue (soot, metal fragments) do not have a substantial impact on mass transport. Similarly, the cracked shell mortars in columns D and F did not show any substantial impact on mass transport when compared with columns B and C, which did not contain the UXOs. While the cracked shells themselves represent a large potential source of energetic materials, it would appear that the small surface area of the solid energetic material filling and the protection afforded by the metal casing prevent the energetic materials inside the munition from contributing to the initial slug of dissolved explosives. The energetic material found inside the shell may be a long-term source of explosives, but they do not contribute substantially during the first infiltration event.

The observations concerning the high concentrations of energetic materials found in the effluent, coupled with the mass transport of TNT, RDX and HMX in the effluent supports the hypothesis that the extremely fine detonation particles are dissolving preferentially. These fine particles should enter into solution quite quickly, and once they are gone, the concentration in the effluent should drop off. This is what was observed.

The data in Figures 11, 12 and 13 indicates that up to 1000 mg of RDX, 2200 mg TNT and 48 mg HMX may be lost through the effluent in the springtime infiltration. The total mass of energetic materials lost from column B is therefore around 3.2 g out of an initial mass of 45 g., or 7.1%. This rate of mass transport would appear unsustainable, or very little energetic materials would be found on the surface of training ranges – it would all be transported through the vadose zone within 15 years. This is not the case (Thiboutot et al, 1998). If the fine fraction of explosives is dissolving preferentially, then we would anticipate a high initial rate of mass transport followed by a significant slow down when the fine fraction is exhausted. This would suggest that substantial amounts of the coarser fractions of detonation residue would still be found in surface soils, which is the case.

Table 3 Energetic Material concentrations in first autumn outflow

Column	TNT Concentration (ppb)	RDX Concentration (ppb)	HMX Concentration (ppb)
B	364.58	211.5	12.0
C	Not Available	278.1	40.76
D	263.1	146.3	35.29
E	5281	2857	158.2
F	393.9	232.0	13.31

Conclusion

High concentrations of energetic materials were found in the effluent of the soil columns during the initial groundwater recharge event that reproduced the springtime snowmelt. The retardation factor was measured to be 2.4 and the K_d of the sandy soil was calculated to be 0.94 L/kg. for TNT, RDX and HMX. No significant difference was observed between the three energetic materials in terms of the volume of infiltration prior to breakthrough at the bottom of the sand column. Very little transformation of TNT occurred as it passed through the sand, with TNT transformation species concentrations 2 to 3 orders of magnitude lower than the concentration of TNT.

It was proposed that the dissolution behaviour of the energetic materials may be explained by the fine fraction of energetic materials dissolving preferentially due to their very high surface areas.

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