GROUNDWATER CONTAMINATION IN THE HIGHWAY ENVIRONMENT

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ABSTRACT

Groundwater is an important resource. There is an increasing demand from regulators for designers to consider the risk of developments with regard to groundwater quality.

There have been a number of studies considering the leaching potential from pavement materials, and the quality of highway runoff. However, there are very few that have considered these together within the context of a functional highway. To ensure prudent assumptions are made during risk assessment the interaction of these sources should be considered. This project has attempted to draw together these areas of study into an integrated model.

Laboratory testing has been undertaken to improve understanding of the interaction between pavement materials and runoff. This testing includes batch tests and infiltration tests, in which aggregates have been exposed to a range of artificial runoffs. Chemical analysis of the eluates from these tests has allowed an assessment of the likely interaction process, and the evaluation of appropriate modelling parameters.

The potential for sorption by the sub-grade has been identified as a key parameter in the assessing the extent of groundwater contamination relating to highways. A brief study has been undertaken to assess the sorption potential of local sandy soils, i.e. those that are most likely to be affected by groundwater contamination.

This study has verified the functionality of the commercially available software MODFLOW SURFACT in conjunction with Groundwater Vistas, for the purpose of modelling groundwater flow and contaminant transport in conditions encountered in the pavement sub-grade. These have then been used to carry out a parameter sensitivity study that considers the impact of a range of parameters on the potential for groundwater contamination. Following this a set of ‘case studies’ have been undertaken, incorporating data from the laboratory testing referenced above.

PUBLISHED PAPERS

Papers published in relation to the study detailed in this thesis include:

Dawson, A.R. & Boothroyd, P.G., 2005, 'Drainage in Reality – A Survey of Practicing Engineers', published in the proceedings of the *International Workshop on Water in Pavements – WIP'05*, 27th October, Madrid.

Dawson, A.R., Hill, A.R. & Boothroyd, P.G., 2006, 'The hydraulic and geo-environmental behaviour of the sub-pavement environment', published in *Pavement Mechanics and Performance – Geotechnical Special Publication 154*, ASCE.

Dawson, A.R., Boothroyd, P.G., Jie, M., Liming, H., 2008, 'Two-dimensional numerical simulation of groundwater contamination in the highway environment', published in the *International Journal of Pavement Engineering*, Taylor & Francis, London.

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NOTATION

BFS	blast furnace slag
DIST	distilled or deionised water
DoT	Department of Transport
HTM	representative of runoff with high traffic mean
IBAA	incinerator bottom ash aggregate
ICPMS	inductively coupled plasma mass spectroscopy
ISE	ion selective electrodes
HDPE	high density polyethylene
LS	limestone
LTM	representative of runoff with low traffic mean
MAX	representative of runoff with maximum contaminant concentrations
MSWI(B)A	municipal solid waste incinerator (bottom) ash
NAPL	non-aqueous phase liquid
OBFS	old (weathered) blast furnace slag
OIBAA	old (weathered) incinerator bottom ash aggregate
OLS	old (weathered) limestone
OMSWIA	old (weathered) municipal solid waste incinerator ash
ORFS	old (weathered) reclaimed foundry sand
PAH	poly-aromatic hydrocarbon
RFS	reclaimed foundry sand
A	section area
b	bed volume
C	chemical concentration
C_A	chemical concentration at point A
C_a	chemical concentration in gas phase
C_b	chemical concentration in bed volume ‘b’
C_i	chemical concentration in infiltration test inflow
C_{napl}	chemical concentration in NAPL phase
C_s	chemical concentration in solid phase
C_{si}	chemical concentration in solid phase at start of test
C_{sf}	chemical concentration in solid phase at end of test

$C_{s\,max}$	maximum possible chemical concentration in solid phase
C_w	chemical concentration in aqueous phase
C_{wi}	chemical concentration in aqueous phase at start of test
C_{wf}	chemical concentration in aqueous phase at end of test
d	depth of drainage layer
D	particle diameter
E	estimated van Genuchten error
E_{hc}	van Genuchten capillary head error
E_{se}	van Genuchten effective saturation error
F_s	shape factor for particle surface area
F_m	shape factor for particle mass
G_w	specific gravity of water
h or H	hydraulic head
h_{ap}	air pressure head
h_c	capillary head
h_w	depth of water above soil
i	hydraulic head gradient
i	‘y’ axis intercept of data points on test interpretation chart
k	biodegradation rate
k	permeability
K_d	soil/water sorption coefficient
k_{rw}	permeability at given saturation
K_S	saturated permeability
K_{sp}	solubility product
L	length of the drainage layer
m	gradient of data points on test interpretation chart
m	gradient of the drainage layer
M	mass of soil/aggregate sample
$M_{A\text{-}B}$	chemical mass flow from A to B
M_C	chemical mass in all phases
M_d	dry mass of soil/aggregate sample
M_g	mass of a given grain of soil/aggregate
M_S	mass of aggregate sample
M_s	saturated mass of soil/aggregate sample

M_w	mass of water in a soil/aggregate sample
n	Freundlich sorption parameter
n	porosity
N_g	number of soil/aggregate grains in a given sample
Q	water flow rate
R^2	goodness of fit factor
S	water content of soil/saturation
S_A	surface area of an individual soil/aggregate grain
SD	standard deviation
S_e	effective saturation
S_M	surface area for particles of mass 'M'
$\overline{S_M}$	average surface area of particles per unit mass
S_{mis}	minimum pavement base saturation
S_r	residual saturation
t	time
$t_{1/2}$	biodegradation half-life
v	bulk sample volume
V	test leachate volume
V_{A-B}	volume of water flow from A to B
v_v	volume of the void space in a sample
V_W	volume of water in a sample
w	edge drain depth
W	source strength i.e. rate of water ingress or egress at a given point by drainage or pumping
z	elevation
z	depth of saturated soil
α	gamma distribution parameter
α	van Genuchten distribution parameter
β	gamma distribution parameter
β	van Genuchten distribution parameter
γ	van Genuchten distribution parameter
μ	average (mean)
θ	water content by volume

θ_r	residual saturated water content by volume
θ_s	saturated water content by volume
χ^2	chi-squared goodness of fit value
ψ	capillary suction
ψ_a	air entry pressure

1. Introduction

In recent years there has been an increasing awareness of the adverse effect of many anthropocentric activities on both biodiversity and resource quality and availability. One of the most critical resources required for survival is water. With an increasing population and an expected future decrease in precipitation due to global warming (Hulme et al. 2002), there is likely to be a reduction in the available water supply from existing sources. Consequently, more new water sources will need to be developed to provide potable water.

Groundwater is an important source of potable water. According to the UK Groundwater Forum groundwater abstractions provide up to 72% of water in the south east of the United Kingdom, and typically between 40% and 50% across the central and eastern regions, indicating that it is a significant source and valuable resource. Given the dependence on groundwater and the likely need for the development of additional abstractions it is clear that groundwater bodies should be protected not only considering current abstractions but also the potential for future abstractions.

In response to this the regulating bodies, both at national and European level, are developing increasingly stringent laws and regulations. For example, the Water Framework Directive (WFD) has been passed by the European Union. This will come into effect in 2013, and will have a potentially significant impact on the management of water resources. The WFD shifts the focus of the national regulator from having acceptable limits for the discharge of contaminants to groundwater, to the assessment of aquifers as a whole with a view to maintaining a high standard of water quality, or improving the water quality where necessary.

As a result of this it is useful for highway design and construction engineers and regulators to have a good understanding of the potential impact of highways on groundwater. This can prevent overly conservative assumptions being made regarding the risk, and therefore unnecessary interventions. Where a significant risk is identified, modelling may be able to assist in choosing the most appropriate measures to minimise the risk of environmental harm.

There is currently very limited knowledge concerning the effect of highways on groundwater. Many contaminants are released in exhaust fumes, tyre and road surface abrasion, leaks and spillages, and by leaching of pavement materials. There is therefore some potential for highways to drain water of unacceptably low quality into aquifers.

To successfully understand the impact on water resources it is necessary to understand the movement of water in the highway environment, and the interaction between the contaminants, water, pavement materials and the sub-grade. This way models can be developed that would reasonably predict the extent of contamination in a variety of circumstances.

1.1. Project Aim & Objectives

The aim of this project is to assist in the understanding of how groundwater contamination can occur due to the construction and operation of roads, the extent to which groundwater can be contaminated, and how it can be prevented.

The specific objectives are as follows:

1. Review existing data on contaminant sources, transport and fate in the highway environment.
2. Select and verify a system for modelling the water flow in pavements and subgrade.
3. By means of sensitivity analysis and subjective evaluation of existing data consider processes in contaminant transport that require further study.
4. Identify scenarios in which there is a significant risk of groundwater contamination occurring as a result of road construction and use.
5. Carry out laboratory and in-situ studies to improve understanding of selected processes. In particular this was intended to address the behaviour of aggregates in the presence of contaminated run-off. Studies of aggregates to date have focused on their capacity to leach contaminants, however, in situ the water passing through them will be contaminated and a more significant measure of the acceptability may be their capacity to adsorb or absorb contaminants from the run-off. This is supported by studies (Legret 2005 & Wilson 2004) looking at the quality of water that has passed through sustainable urban drainage pavements (SUDs), which show there is a net sorbtion of contaminants in pavements. This will require the development of new testing procedures and a process of analysing results for their acceptability.
6. Model contaminant spread for selected scenarios. Modelling of contamination spread has been carried out in the past. However, as the understanding of contaminant movement in pavements is increased (as objective 4 is achieved)

a way must be found to integrate the new information into a contamination spread model to allow an assessment of its implication.

2. Background

This project looks at the movement of contaminants in the pavement and underlying soils. Pavement sub-base courses are usually unsaturated granular materials, and therefore very similar in behaviour, both mechanically and hydraulically to large grain soils. As a result, although this project deals with the movement of contaminants in pavements as well as in soils, it is fundamentally a geoenvironmental project.

Like any other geoenvironmental study the key aspects that need to be understood are the source, transport and fate of contaminants within the given environment. The source being the point or mechanism by which a contaminant enters the environment, transport the processes that result in any change in either location or characteristics of the contaminant, and the fate the point or mechanism at which the contaminant leaves the environment or has a negative effect.

2.1. Contaminant Sources

The sources of contaminants in the highway environment are important to consider as they determine which contaminants are present, the quantities of the contaminants and their initial location. A brief description of each of these is given in this section.

2.1.1. Contamination of Runoff

This section gives details of the major sources of contamination in pavement runoff and the contaminants they release.

2.1.1.1. Traffic and Cargoes

Highway traffic and cargo is a significant source. The contaminants can be released by vehicle exhaust emissions, vehicle component wear, road degradation, and littering and spills.

Vehicle exhaust emissions include contaminants from complete and partial combustion of fuel, lubricants used within the engine, fuel additives and engine wear. As a result of the many processes contributing to this contamination there are a wide range of contaminants produced. These may include hydrocarbons, nitrous oxides, heavy metals, and PAHs that may all settle on the highway surface. Carbon dioxide, carbon monoxide, sulphur dioxide and methane are also produced, however as these are gaseous at atmospheric temperatures they are therefore unlikely to enter the pavement or soil and affect the groundwater and are therefore outside the scope of this study.

There is also substantial wear of vehicles using the highway. This includes the abrasion of tyres and brake pads, as well as the corrosion of the vehicle body. This wear results in the deposition of many heavy metals, PAHs, and small rubber particles on the surface of the road.

As the vehicles pass over the surface of the highway, there will inevitably be some erosion of the pavement surface. The particles and contaminants released by this erosion are dependant upon the materials used to construct the pavement.

Spills and littering from vehicles also releases a wide range of contaminants. Oil and de-icing fluids are spilt from vehicles during normal operation along with a wide variety of litter that is deposited on the highway.

There are also large accidental spillages resulting from crashes or vehicle failure in which significant quantities of transported fluids or solids, such as petrol, milk, pesticides and alcohol, may be deposited on the highway surface. Although relatively rare these events have the potential to cause the most serious contamination when they do occur.

2.1.1.2. Maintenance and Operation Sources

Salts used for de-icing the road surface during winter months introduce large quantities of sodium, potassium, and chloride. Due to the large quantities of salts that are required to maintain highways in some areas this can be a very serious source of contamination. Studies by Kjensmo (1997) and Williams et al. (2000), summaries of which are given below, provide evidence that the salting of roads has a significant impact not just on water quality but also on local ecologies.

According to Kjensmo (1997) lake Svinsjøen in Norway is meromictically stable. That is, the deeper layer of the lake has a substantially higher salinity than the upper layer, and is therefore denser. The result of this is that the two layers do not mix and behave almost as two separate water bodies. In recent decades the upper layer has experienced a three-fold increase in the levels of sodium and chloride as a result of the use of de-icing salts. The presence of the salt in the upper layer has weakened the meromictic stability. Collapse of the meromixis would mean that the two layers were no longer separated, and that flows previously confined to the surface would no longer be so. These flows often carry nutrients vital to the lakes ecosystem, and their demise or redirection would prevent the nutrients from being suspended in the more biologically active upper layer of the lake.

Williams et al. (2000) carried out a study of springs in Canada, recording chloride contamination in excess of 1.2 g/l. The chloride was tested on macroinvertebrates to assess whether or not they could be used as an indicator. It was found that many were sensitive to chloride and could be used. This however also implies that the macroinvertebrates living in the spring water would also be affected. This could result in a reduction in the local biodiversity if the more sensitive organisms are killed off. As these organisms are likely to be close to the bottom end of a food chain their demise could also have an impact on higher-level life forms. This effect would be magnified if the organisms concerned played a major role in an ecosystem nutrient cycle.

It should be noted that the studies referenced above are based in countries that suffer much more severe winters than the UK. Consequently a much greater quantity of deicing salts are used and the associated risk of environmental damage is increased.

Although they are the most intensively studied, de-icing salts are not the only contaminants deposited in the highway environment. For example, control of the vegetation along highways can also result in the release of contaminants. Although banned in many countries, in those where they are still used, herbicides directly release toxic chemicals into the verge of the highway.

2.1.1.3. Outside Sources

There will also be the introduction of contaminants from outside sources. On any surface there will be the deposition of atmospheric contaminants. These contaminants may be derived from local or remote sources. An example of local source is pesticides from fields adjacent to the pavement while more remote sources might be industrial areas releasing sulfates and nitrates into the atmosphere which, in the form of sulphuric and nitric acid rain, is then deposited by precipitation over a large area.

2.1.1.4. Literature Values

For the purposes of this project the runoff entering the pavement as the source of contaminants. Although there are a wide range of individual sources, as already discussed, there is insufficient data available in literature to consider each individually. Their net effect on the pavement hydrology is to contaminate the runoff entering the pavement, and the quality of this runoff is well documented.

Kayhanian et al. (2003) carried out a study looking at the effect of traffic loading on pollutant concentrations in runoff. During this study measurements of concentrations were taken at a range of sites, for a wide range of contaminants. The results of this study have been compared to those of a range of previous studies (see Table 2.1). It can be seen that there is a significant range in pollutant concentrations recorded by each study. However, the minimum, average and maximum values vary relatively little between the different studies. A further range of studies such as Thomson et al. (1997), Barret et al. (1998), Hares and Ward (1999) and Moy et al. (2002) reported contaminant concentrations to be close to or within the range given by Kayhanian. The detected levels are shown in Table 2.1.

In almost all cases the averages are similar to the average concentrations recorded by Kayhanian and individual readings recorded levels are well within 1 order of magnitude. The exception to this is the study carried out by Hares and Ward. In this case the concentrations of most heavy metals are reported to be circa 20 times greater than the average reported by Kayhanian, and in some cases they exceed the maximum value. This is likely to be due to the fact that the samples have been taken from the M25, one of the most heavily trafficked roads in the UK (average annual daily traffic, AADT, for the sites monitored were 120,000 and 140,000), and therefore one on which there will be significant deposition of contaminants. This assumption is supported by Kayhanian's results that showed that the roads with an AADT exceeding 30,000 had concentrations in runoff typically ten times higher than those with an AADT less than 30,000.

The concentrations of contaminants are likely to vary between sites dependant upon a range of factors, such as the traffic loading, average annual rainfall, rainfall intensity, and presence of background sources of contaminants. At a given site there are likely to be variations due to antecedent dry period, rainfall intensity and rainfall duration.

		Kayhanian et al 2003		Thomson et al 1997		Barrett et al 1998	Hares & Ward 1999	Moy et al 2002		
Contaminant	Unit	Range	Mean	Mean	SD	Range of site medians	Range	Range of site means	Min/Max range	Mean
Characteristic Parameters										
Chemical Oxygen Demand	mg/L	2.4-480	123.8					70-138	28-458	90.16
Hardness	mg/L ($CaCO_3$)	2-448	49.5						0-619	145
pH	PH	5.1-10.1	7.3							
Temperature	^{O}C	4.8-18.7	13							
Total Dissolved Solids	mg/L	5-8,780	184.1	184	357.7					
Total Suspended Solids	mg/L	1-5,100	148.1	93	106.9	19-129		53-318	<1-1,350	117.1
Turbidity	NTU	1.1-2,620	310.1			37-130				
Total Organic Carbon	mg/L			23	21	20-46				
Metals										
Arsenic	μg/L	0.5-15.9	1.1							
Cadmium	μg/L	0.02-6.1	0.2				11.9-14.1		0-5.4	0.47
Chromium	μg/L	0.6-22	2.4				86-105		0-49.9	6.66
Copper	μg/L	1-121	14			12-37	248-274	24-64	<4-242	41
Iron	μg/L					249-2,824				
Lead	μg/L	0.2-414	5.4			3-53	70-81	4-45	0.2-178	25.66
Nickel	μg/L	0.6-52	3.6						0-40	5.92
Zinc	μg/L	3-1,017	72.7	150.5	153.6	24-222	188-208	53-222	21-688	140.3
Nutrients										
Ammonia - N	mg/L	0.08-6.4	1.1						0.25-0.73	0.05
Nitrate - N	mg/L	0.01-14.7	1.1			0.37-1.07				

Table 2.1 Contaminant Concentrations in Run-Off

		Kayhanian et al 2003		Thomson et al 1997		Barrett et al 1998	Hares & Ward 1999	Moy et al 2002		
		Range	Mean	Mean	SD	Range of site medians	Range	Range of site means	Min/Max range	Mean
Nitrite - N	mg/L	0.05-1.7	0.1							
Ortho - P	mg/L	0.01-1.03	0.1							
Total Kjeldahl nitrogen	mg/L	0.1-57	2							
Total phosphorus	mg/L	0.01-10	0.3			0.1-0.33				
Major Ions										
Calcium, total	mg/L	4.5-66.8	12.7							
Magnesium, total	mg/L	1-21.8	3.2							
Sodium, total	mg/L	1-56.0	11						0-2,100	171.66
Sulfate	mg/L	0.23-57.0	4.2							
Microbiological										
Total coliform	MPN/100ml	2-900,000	21,970							
Fecal coliform	MPN/100ml	2-205,000	6,083							
Oil and Grease	mg/L	1-226	10.6			0.4-4.2				
Pesticides										
Diazinon	µg/L	0.013-2.4	0.3							
Chlorpyrifos	µg/L	0.03-1	0.1							
Glyphosate	µg/L	6.4-220	27.8						0-17.5	0.87

Table 2.1 Contaminant concentrations in run-off (Continued)

2.1.2. Pavement and Embankment Materials

Materials used for the construction of pavements and embankments may also contain contaminants. These can be leached into water present within the pavement and embankment. Almost any contaminants may be leached including metals, carbonates, salts, nitrous compounds, sulphates, etc.

Which contaminants are released depends upon the constitution and history of the materials used, and the quantity of contaminant leached is dependant upon several factors including the surface area of the material, the material history, the pH of the leachate, and how the material has been treated (e.g. bound or unbound).

The surface area of the aggregate is important as it determines the area across which leaching can occur. Where leaching is occurring by means of solid diffusion, for example, the greater the area across which the diffusion can occur the greater the rate of that diffusion. In a scenario in which the contact time between leachate and aggregate is limited, such as a drained pavement sub-base, an increase in the rate of diffusion will lead to an increase in the total leached mass.

The history of the material used is also important. There is a limited quantity of contaminant available to be leached from any material and so, if that quantity has been depleted either through pre-treatment or weathering, then the leached quantity will be reduced.

The pH of the leachate has been shown in many laboratory tests to have an effect on the quantity of contaminant leached. Each contaminant will have its own relationship between pH and rate of leaching. Figure 2.1 (van der Sloot et al., 2001) is an example of diagrams showing the effect of pH on zinc and chromium concentrations leached from municipal solid waste incinerator bottom ash (MSWIBA) fill. In this example the variance of leached concentration is particularly pronounced for zinc. It varies by a factor of nearly 100 across the pH range typical of that in MSWIBA fill, and by a factor of over 10,000 across the full tested pH range. Leached chromium is less variable than zinc, but it still varies by almost a factor of 10 across the typical pH domain of MSWIBA fill, and a factor of approximately 100 across the full tested range.

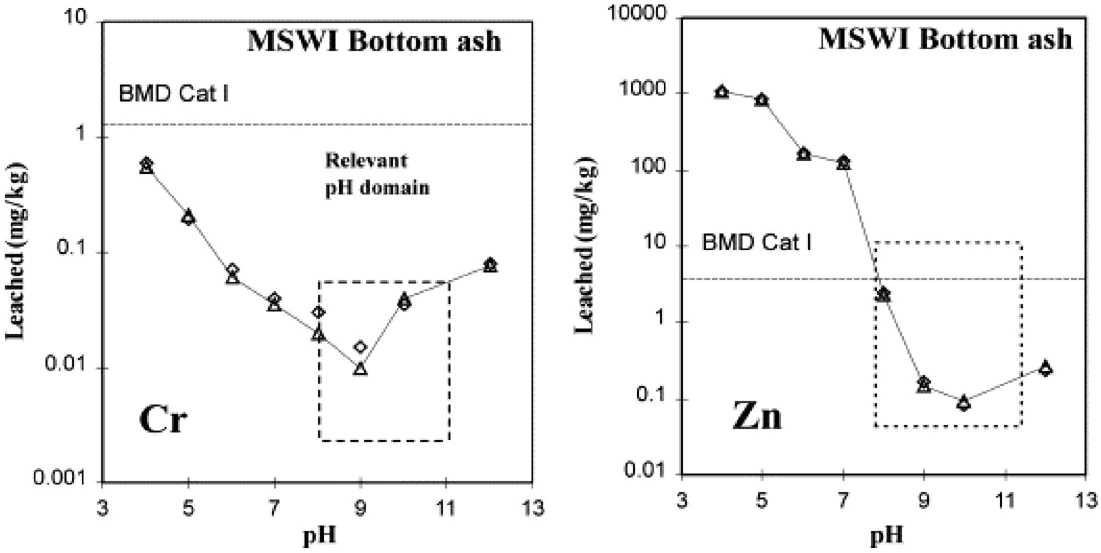


Figure 2.1: pH effect on leached concentrations of chromium and zinc from MSWIBA (taken from van der Sloot et al, 2001).

Hill (2004) carried out a study in which a number of leaching tests were undertaken on a range of alternative aggregates. The tests carried out included a rapid leaching test carried out to the NRA leaching test standard (now BS EN 13457) using an end over end agitator and a total liquid to solid ratio of 10 l/kg. Tank tests were also carried out on material samples graded as they would be in the pavement sub-base, these also included tests on compacted and bound samples. Following this permeameter leaching tests were carried out, in which the chemical constitution of leachate passed through a graded aggregate sample was assessed.

Finally lysimeter tests were undertaken in which samples of aggregates were graded and compacted, as they would be during highway construction, but within a 1m x 1m square inert box. These were placed in a rural outdoor environment in which they were exposed to precipitation. Samples of water that had infiltrated through the aggregates were analysed to determine the concentration of leached chemicals.

It was concluded that leaching tests on aggregates with a coarse grading, as is often used in-situ, exhibited lower leaching potential than those with a fine grading as specified for the rapid leaching test. It was noted that compaction and binding of aggregates also generally reduced leaching from the aggregates. The exception to this was where relatively inert aggregates were bound. In this case, although there is a reduced surface area for aggregate leaching the binder is assumed to have a higher leaching potential and therefore increases contaminant concentrations.

Permeameter and lysimeter leaching tests found that there was a progressive decrease in the leached concentration of contaminants with time. It was noted that for a similar liquid to solid ratio the total concentration of contaminants leached in the permeameter and lysimeter tests was less than that in the tank leaching test. This has been attributed to the reduced contact time between the leachate and aggregate where there is a dynamic flow regime.

A number of additional studies have been carried relating to the assessment of chemical concentrations in aggregate leachate including, Hjelmar et. al (2006), van der Sloot et al. (2000, 2001), Shim et al. (2003),

Although the concentrations of contaminants released in test conditions is well documented for a range of materials there is little information quantifying the nature of this release, or the concentrations that would be released in the conditions encountered in-situ. Only the study by Hill included testing that closely simulated the conditions found in the sub-pavement environment.

2.2. Contaminant Transport

To refine the project the focus of this study has been restricted to the area directly between the pavement surface and water table, and the opposite verges of the highway, as shown in Figure 2.2. The objective of this sub-chapter is to give the reader a generalised description of the processes involved in the transportation of contaminants in the pavement sub-base and sub-grade.

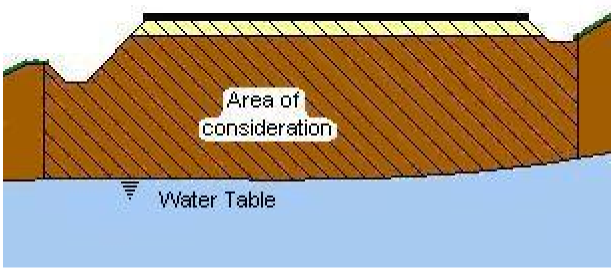


Figure 2.2, Pavement section considered in this project.

It should be noted that there are other potential routes by which contaminants could be released into the environment, for example the spread of air-borne contaminants. These have not been ignored because they are believed to be insignificant, it is done solely to restrict the scope of the project such that it can be realised within the available time frame.

2.2.1. Water Flow in Pavement Sub-base and Sub-grades

The pathways that could be followed by contaminants are extremely varied, however given the scope of this project then the pathways under consideration are those passing through the pores of the highway body and soil down to the water table, as shown in Figure 2.3. A more detailed description of hydraulic flow within the pavement is given in CIRIA Report 167 (Baldwin et al. 1997).

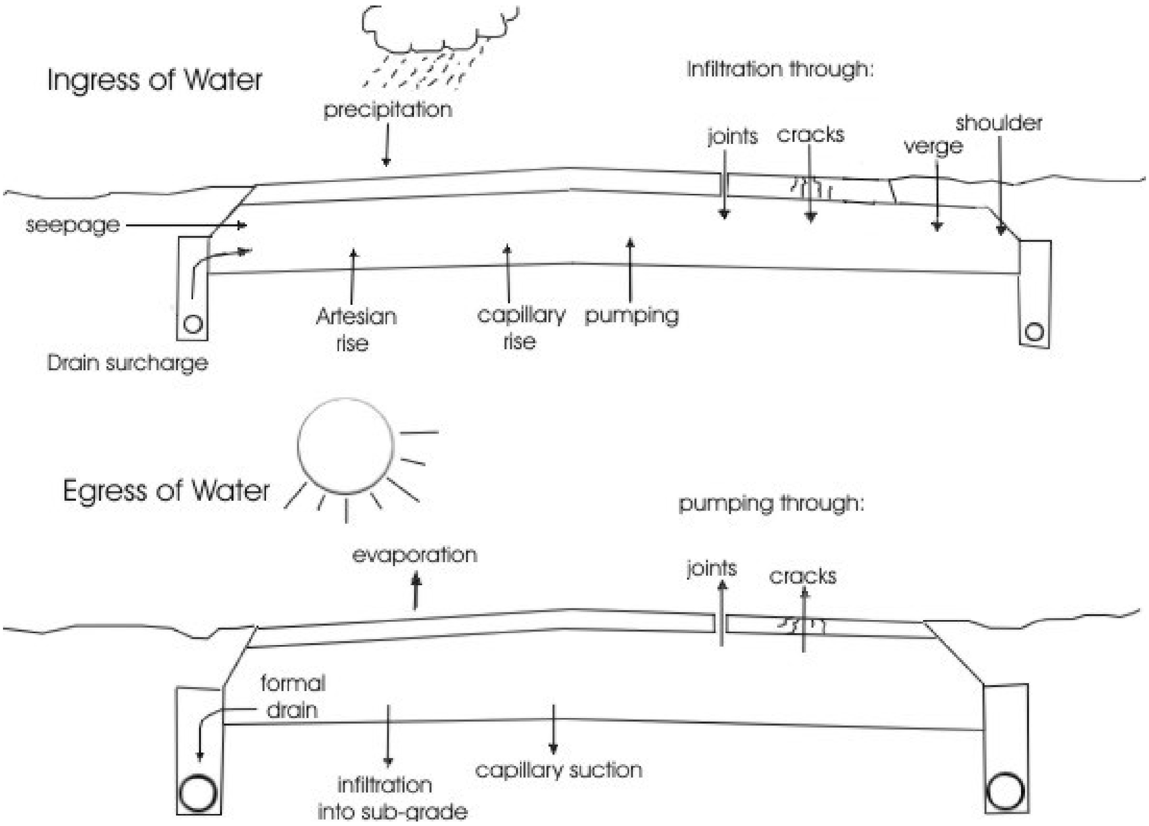


Figure 2.3, Water flow in the pavement sub-base

In the vast majority of cases the pavement design will be such that the quantity of water entering the pavement by artesian flow, capillary rise and pumping will not be significant. Flooding of the pavement sub-base is only likely to occur when there are failures in the drainage system or when there are particularly heavy precipitation events that exceed the design capacity of the drainage. Although unusual, these scenarios will need consideration to determine whether or not they are likely to have a significant effect on the spread of contaminants.

As a result the most significant source of water entering the pavement is likely to be the infiltration of precipitation through the pavement surface, verge and shoulder. For a period following the construction or resurfacing of a pavement the surface will have little or no cracking, and will therefore have a low permeability allowing little water to enter the sub-base. This being the case, there will be little water movement in the sub-base and sub-grade, and therefore little transport of contaminants except in an unsealed verge area. As the pavement surface begins to crack and fracture more water will be able to enter the pavement. Initially the effective permeability will be low and the entry of water into the pavement will be limited by the size and number of cracks. As the quantity and length of cracks increases the rate at which water can infiltrate will exceed the rate of precipitation, and thus rate precipitation will become the limiting factor.

In the UK a proportion of water leaves the pavement surface by evaporation. The rate of evaporation from the pavement surface is unknown. However, the MetOffice give rates of evaporation ranging from less than 450 to more than 630mm per annum for grass surfaces (MetOffice 2005), for which the areas where there is the least evaporation coincide with those where there is the most rainfall. For example, the difference between the two in West Scotland is circa 1000mm. This indicates that in these areas a substantial amount of water must be removed by means other than evaporation.

To improve the mechanical performance of the pavement, it will be designed to either lie above the water table, or there will be a drainage system to reduce the level of the water table below the pavement. Consequently there is unlikely to be significant ingress and egress of water due to horizontal artesian flow. Therefore the primary routes by which the remainder of the water leaves the pavement are through the drainage systems and infiltration into the sub-grade. The relative significance of each will depend upon the functionality of the drainage system and the permeability of the sub-grade. The rate at which water infiltrates into the sub-grade will depend upon its permeability, and the period over which it drains into the sub-grade depends upon the drainability of the sub-base (i.e. a function of the permeability of the sub-base and sub-grade, and the efficiency of the drainage system).

Respondents to the study 'Drainage in Reality' (Dawson & Boothroyd 2005) reported that there is uncertainty regarding the function of many drainage systems and that therefore there is a need to be cautious when making assumptions about the rate at which water can leave the pavement sub-base by that route. Complete failure of drainage systems refers to drainage pipes becoming completely blocked, such that water in the sub-base either cannot drain at all, or can only drain by infiltration into the sub-grade. It is believed that this is rare, and that when it does occur it will tend to lead to structural failure of the pavement, probably before environmental failure, and so is not considered for this study.

2.2.2. Contaminant Transport in Water

Contaminants can be transported within fluids by three different methods; advection, diffusion and advective dispersion. Advection is the movement of a contaminant resulting from the net flow of a fluid. Diffusion is the net movement of a contaminant across a concentration gradient resulting from the fluid's tendency to concentration equilibrium. Advective dispersion is the mixing of the fluid due to a flow passing through a material that is not perfectly heterogeneous. Figure 2.4, below, shows the different forms of contaminant transport, and Figure 2.5 (Rowe et al. 1997) shows typical ratios of contamination of effluent relative to influent with respect to time.

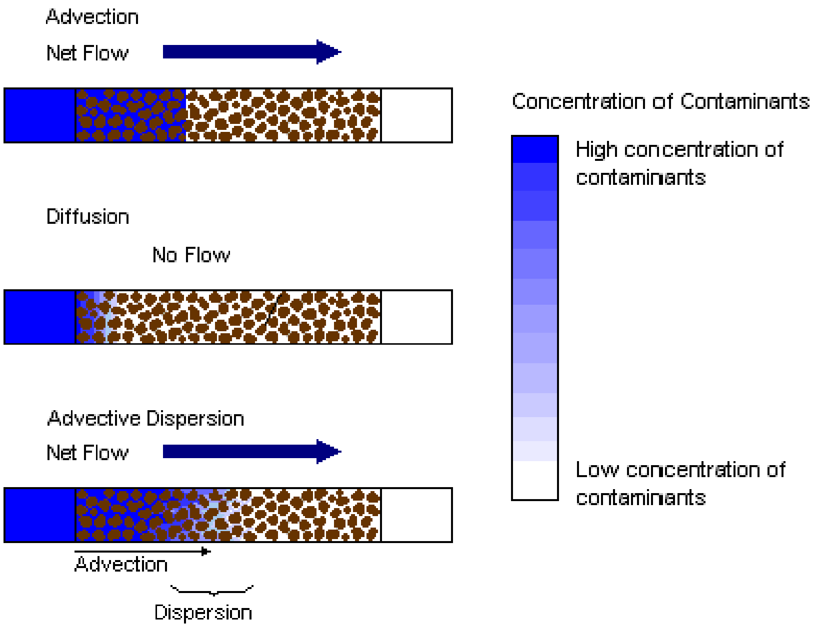


Figure 2.4 Modes of contaminant transport.

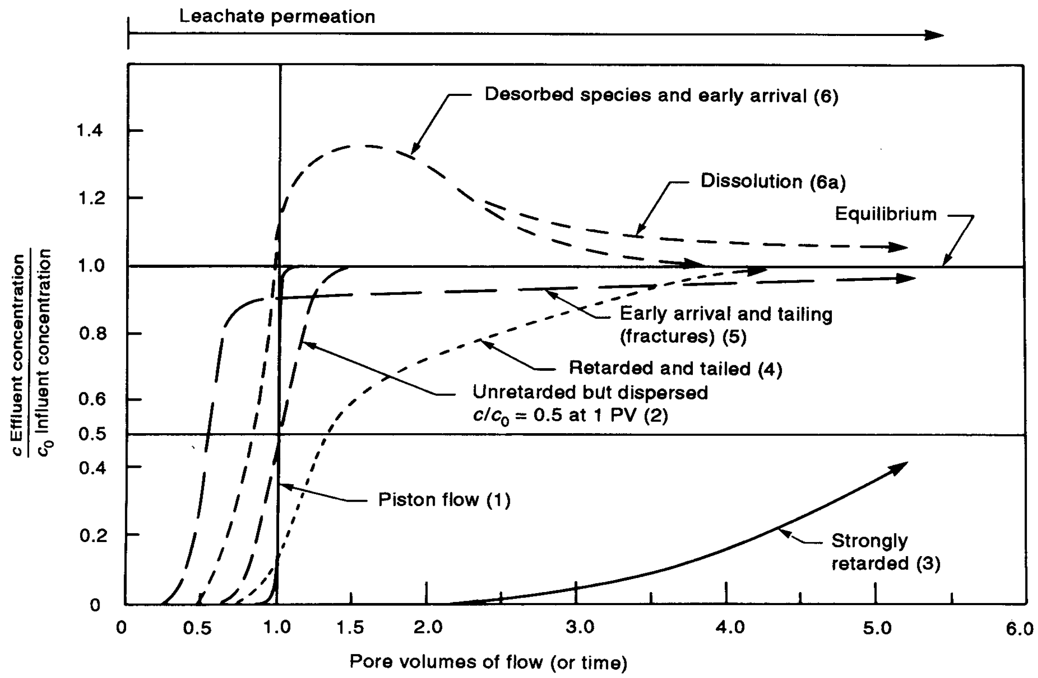


Figure 2.5 Ratios of contamination of effluent relative to influent with respect to time/flow volume (Rowe et al, 1997).

From the descriptions of the modes of transport it is possible to determine under which circumstances each will occur. The first condition is that there must be a concentration gradient for any to occur, for diffusion this must be within the fluid, for advection and advective dispersion this can also be a concentration gradient within the soil. For example, if a contaminated fluid is moving into a previously unsaturated soil the concentration within the soil will increase even if the fluid moving in has the same concentration as the fluid that was already present.

The second condition, for advection and advective dispersion is that there must be a flow of the fluid. Diffusion does not require this and will occur in any fluid within which there is a concentration gradient.

2.2.3. Chemical Processes

While the contaminants are in the highway environment they are susceptible to many chemical processes, which potentially include partitioning (e.g. sorption and desorption), volatilization and photolysis.

Sorption refers to the attachment of contaminant molecules to particles within the soil, typically due to van der Wahls, polar, or ionic electro-magnetic forces. This is generally a beneficial process for two reasons. The first reason is that while the contaminants are bound to particles they are only as mobile as the particles that they are bound to. In a tightly packed soil this is likely to mean that they will not move. The second reason is that while the contaminants are bound to the particles they are often not available to be absorbed or consumed by plants or animals. This effectively reduces their toxicity.

If a molecule has sufficient energy when it reaches the surface of a liquid it will break any bonds it has with the fluid and escape into the atmosphere as a gas. This process is referred to as volatilisation. With respect to the contamination of groundwater this can be considered a beneficial process as it removes the contamination. It should be noted however that, from a holistic perspective, this is not necessarily a real benefit. The contaminant is not eliminated and will travel through the atmosphere by advection and diffusion, and may re-enter the groundwater at a different point, or cause contamination elsewhere.

Sorption, leaching and volatilisation occur as a result of the tendency of contaminant concentrations to reach equilibrium between the water, solid, gas and oil (when present) phases, known as partitioning. Sorption refers to the net flow of contaminants from the liquid (aqueous) phase to the solid phase, leaching to the net flow from the solid to the liquid phase and volatilisation the net flow from the liquid to the gas phase. The contaminant mass flow from one phase to another is controlled by the contact area between the phases, the contaminant concentration in the phase from which it is flowing and into which it is flowing, and the isotherm (a function that describes the nature of the relationship between concentrations). In general, the greater the contaminant concentration is in one phase, the greater is the mass flow from that phase to the other.

The relative concentrations in each phase at equilibrium are often accurately described using the linear relationship:

$$C_s = K_d C_w \qquad \text{Equation 2.1}$$

For which K_d is the sorption coefficient (l/kg), C_s the concentration in the solid phase (mg/kg) and C_w the concentration in the liquid (aqueous) phase (mg/L).

If the concentration in either the liquid or the solid phase exceeds the equilibrium concentration there will be a net movement of contaminants from that phase into the other. This occurs rapidly and ceases when equilibrium is attained.

When contaminants are exposed to sunlight, the energy absorbed by the molecules can in some cases cause oxidisation, an irreversible change in the makeup of the molecules, this is known as photolysis. The changes induced can in some cases completely eliminate the toxicity of the contaminant thus removing it from the system. This project considers contamination within the pavement body and sub-base, i.e. not exposed to sunlight, and therefore photolysis is not considered further in this report.

2.2.3.1. Interactions Between Contaminants

Within the pavement sub-base and sub-grade there will be a range of contaminants from a range of different sources. These will interact with each other affecting their partitioning characteristics and consequently their concentrations in the liquid phase and therefore influencing their transport beneath the pavement.

When considering the pavement sub-base there is particular difficulty as the materials used can act both as a source of contaminants (due to leaching) and as part of the pathway for contaminated runoff that has infiltrated through the verge or wearing course.

A description is given below of leaching from aggregates and how this can be affected by additional contaminants present, in this case from runoff.

For leaching to occur the dry aggregate must have the contaminant that will be leached initially attached to its surface. In the presence of a polar solute, in this case water, the contaminant (A) will be able to attach and detach from the active sites on the surface of aggregate particles (see figure 2.6). After a period of time equilibrium will be attained, in that the rate at which the A leaves the active sites will be equal to the rate at which it re-attaches. At this point the concentration of the molecules attached and in solution will be constant. The ratio of the concentration fixed to the solids to the concentration in solution is the partitioning (or sorption) coefficient. This ratio can be affected by solute characteristics such as pH, and also the quantity of the molecule (and similar molecules) competing for the same sites. Where the proportion of contaminant initially present in the solution exceeds that dictated by the partitioning coefficient there will be a net movement of contaminants onto the aggregate, this process is known as sorption.

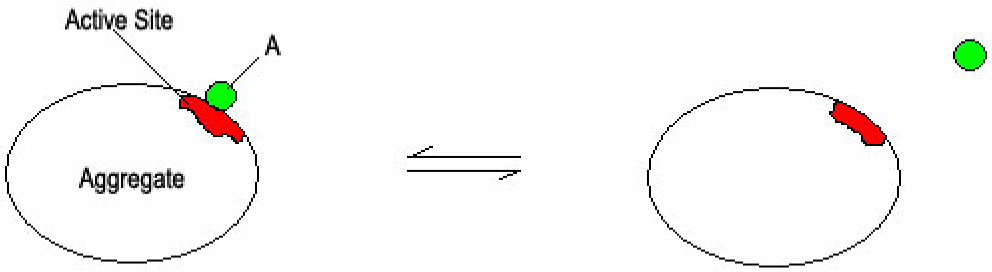


Figure 2.6 Contaminant leaching or sorption

When the solute contains a range of chemicals prior to leaching they can affect the leaching process in several ways.

The first is that an increase in the total amount of contaminant A's molecules/atoms will mean there is increased competition for the same sites on the aggregate particles (see figure 2.7). Depending upon the total amount of contaminant A relative to the number of active sites and the preference of A for the sites the affect of the additional contaminant will vary. As the proportion of sites free to be bound to by A decreases the greater will be the proportion remaining in solution.

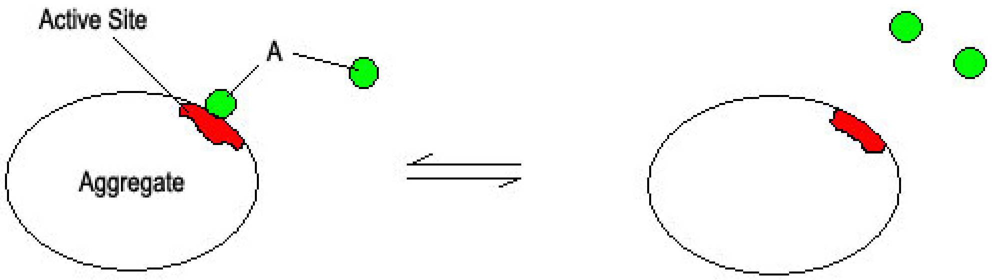


Figure 2.7 The effect of increased contaminant concentration

A similar effect to that described above can be achieved by the addition of contaminants, either not present or present in very small quantities in the leachate, but able to bind to the same sites (B). In this case there will be equilibrium between 3 states (see figure 2.8). Contaminant B will compete in a similar manner to that described above, but it may have a different aggregate water partitioning coefficient. The greater the preference for the alternative contaminant B, the more of A will be released into solution. The most extreme form of this is that B may bind permanently to active sites forcing the entirety of the original contaminant A into the solution.

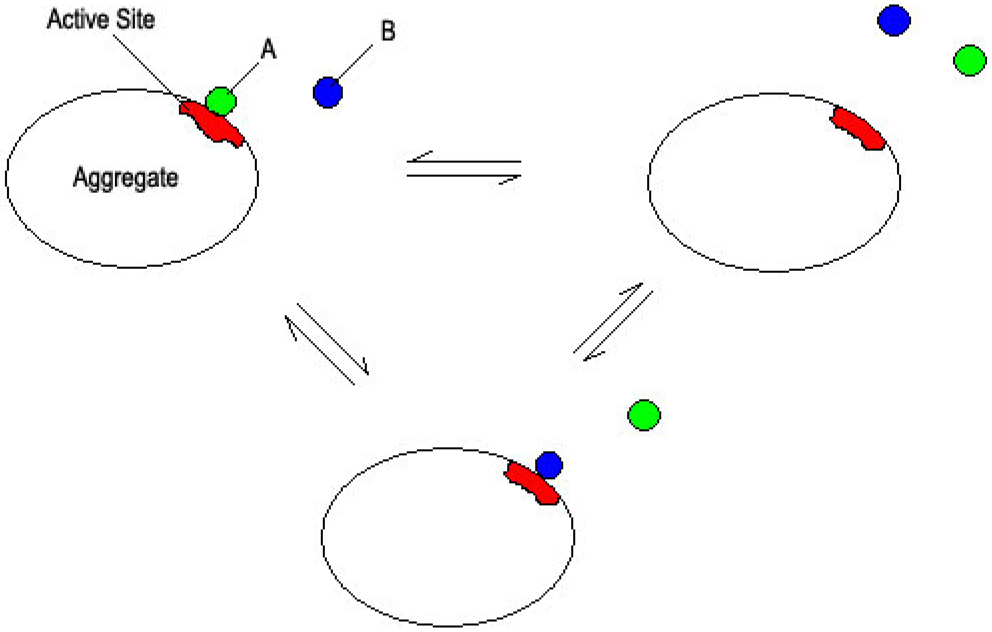


Figure 2.8 Cosorption - contaminants competing for the same active site

Alternatively an additional compound may react with the original compound rather than the active sites (C). This may involve the 2 contaminants becoming permanently bonded or altered, or could involve an equilibrium reaction similar to that between A and the active sites.

Where A becomes permanently bonded to C, or altered (A'), it is effectively removed from the system. However, it should be noted that in its place is a new compound that could pose a greater risk as a contaminant; either A-B or A'. Where the original compound forms a non-permanent bond with the additional compound equilibrium will eventually be reached and there will be partitioning between the aggregate, solute and C (see figure 2.9).

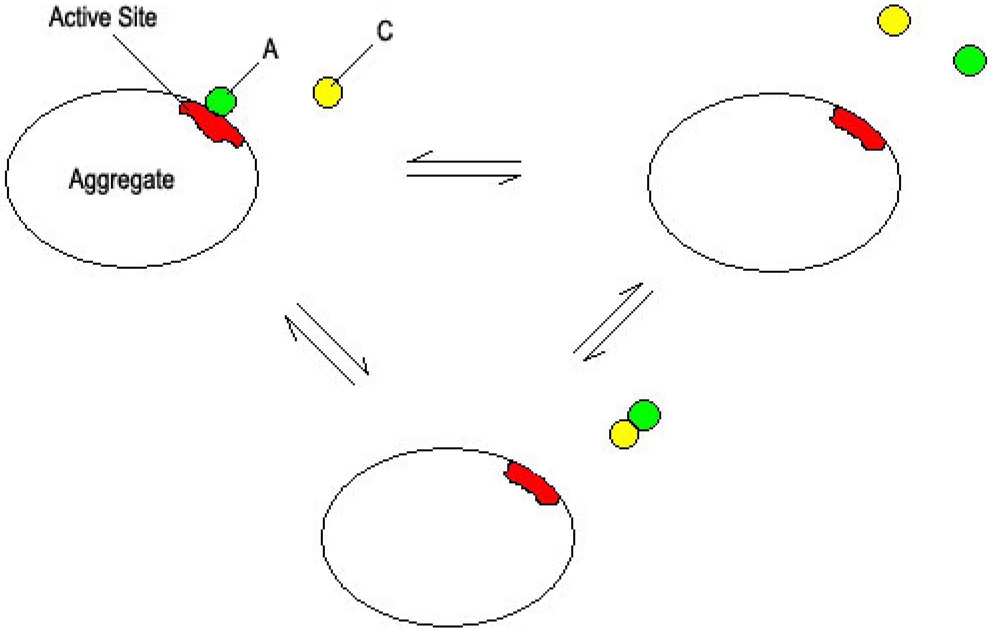


Figure 2.9 Complexation of contaminants.

The process described is referred to as complexation or precipitation. When contaminants A and B combine they form compound A-B, this is capable of forming a crystalline solid within the aggregate matrix if the concentration in the solute is above saturation. The equilibrium reactions will occur even in an unsaturated solution, but there will not be sufficient contaminants in the complex form to allow the growth of a crystal.

According to Senese (2005), the limit of solubility of two contaminants can be calculated using the solubility product (K_{sp}) of the salt produced by the complexation reaction.

$$K_{sp} = [A][B] \qquad \text{Equation 2.2}$$

For which [A] and [B] are the concentrations, in moles per litre, of the acid and sub-base contaminants. The units for K_{sp} vary depending upon the number of contaminants forming the complex.

The values of K_{sp} for common salts in water are well documented and readily available in literature and online. However they vary depending on the temperature, and the presence of other salts. Where other salts are present the solubility limit can increase or decrease, phenomenon known as salting-in and salting-out respectively. In addition to this where there is more than one salt added to a solution a range of new salts will exist. For example when salts A1B1 and A2B2 are added to a solution, it could be that salt A1B2 or A2B1 has a particularly low solubility reducing the concentration of it's constituent ions in solution, and allowing the ions A2 and B1 to remain in solution at a concentration greater than would have been possible in their original salt solution.

An example of the possible ways in which contaminants already present in the aggregate and run-off can interact is given for municipal solid waste incinerator ash in the following sub-chapter 2.2.3.2.

2.2.3.2. Interactions Between Contaminants in MSWIA

Leaching from Municipal Solid Waste Incinerator Ash (MSWIA) can be affected significantly by the presence of chemicals within the solute. Variations in pH, sorption competition (cosorption) and complexation of the chemicals present can cause significant variations in the final solute contaminant concentrations.

Variations of pH have been shown to affect leaching and complexation (van der Sloot et al 2001a and b, Christensen & Christensen 2000). Figure 2.1 shows the variation of leaching concentrations of Cr and Zn with variations in pH

The measurements of the pH of runoff, by Kayhanian et al (2003), range between 5.1 and 10.1. It is clear that the most acidic of these samples has a pH well below the standard range found in MSWIA; and from Figure 2.1 we can see that this would significantly increase the leaching of both Zn and Cr.

Where there is an increased concentration of a contaminant, or chemically similar contaminants, in the solution they may compete for the same sites on the aggregate. In the case of MSWIA, one of the active sites to which contaminants can be bound are alumino-silicate cenospheres (Shim et al. 2003). The surface of these is negatively charged, and cations are able to bind to it. However all cations are able to do so, and do so in competition. The affinity of cations increases with their ionic potential (ionic charge divided by the ionic radius), and as a result cations with a high ionic potential (e.g. Cd) can displace those with a lower potential (e.g. Zn). We would therefore expect that when leaching occurs in the presence of Cd contaminated run-off the Cd will be almost entirely adsorbed by the cenospheres, while there will be a disproportionate increase in the Zn concentration.

The presence of anions in run-off with a stronger affinity for cations (e.g. sulphate and nitrate) may reduce the concentration of cations in the leachate through complexation. Also any contaminant increasing the availability of Hydroxil ions is likely to increase the precipitation of heavy metal ions.

In summary, with so many on-going interdependent processes it is difficult to estimate what the concentrations of contaminants will be when MSWIA reacts with run-off rather than pure water. The presence of additional contaminants in the run-off and the reduced pH is likely to increase the leached concentration of contaminants. Preferential adsorption may reduce the increase in concentration of some contaminants at the expense of others.

2.2.4. Modelling Contaminant Transport

Having described the generalised water flow regime in pavements and contaminant transport mechanisms, it is next necessary to consider how these can be modelled. The following sections give details of the governing equations used for modelling hydraulic flow and contaminant transport.

2.2.4.1. *Saturated Flow*

According to Darcy's Law the flow of water through any given plane in the aggregate is given by,

$$q = -Aki \qquad \text{Equation 2.3}$$

For which q is the water flow rate across the plane, A is the area of the plane, k the coefficient of permeability of the aggregate (or the coefficient of hydraulic conductivity) and i is the hydraulic gradient. The hydraulic gradient is the gradient due to the sum of the elevation head (z), the capillary suction, and the pressure head, all divided by the flow path distance.

In reality the flow is 3 dimensional rather than 1 dimensional and frequently in unsaturated media. A number of solutions have been developed for this, generally based on the 3-dimensional resolution of Richard’s equation, which is shown in a simple format in Equation 2.5. MODFLOW, an example of software for modelling groundwater calculates flow within a 3-dimensional (x,y,z) space by resolving the equation:

$$\delta S \frac{\delta h}{\delta t} + W = \frac{\delta Q}{\delta x} + \frac{\delta Q}{\delta y} + \frac{\delta Q}{\delta z} \qquad \text{Equation 2.4}$$

For which Q is the flow rate in direction x, y or z, W the source strength (i.e. the ingress or egress of water directly to that point, e.g. a pumped well), S the amount of water stored at that point, h the hydraulic head, and t the time. The flow rates are calculated based on Darcy's equation.

Permeability increases with the saturation, so water flows more easily through a saturated aggregate than a partially saturated aggregate. The capillary suction of aggregate is reduced as it becomes more saturated. This means that the aggregate around a saturated area will have a tendency to draw water from the latter, the former's suction decreasing as it does so. The incompressibility of the water means that transitory loads on the aggregate will be carried by the water in place of the aggregate. This creates pressure differentials between the water where the load is applied and the water in adjacent areas where there is no load. The flow of water is therefore increased into those areas under transitory traffic loading, for example.

In summary, the overall effect of these processes is that groundwater flow is likely to be fastest in a saturated aggregate and that therefore contaminants will be transported more rapidly in such a material. In these circumstances the transport process will be dominated by advection and advective dispersion.

2.2.4.2. Unsaturated Flow

In an aggregate at residual saturation the permeability is greatly reduced, the capillary suction of the aggregate can increase hugely, holding water in, and there are no pressure gradients as the water is maintained at air pressure. The result of this is that there will be no flow of water from the aggregate. Due to this the contaminant transport will primarily be by diffusion.

The drainage behaviour of partially saturated aggregates will be somewhere between residual and saturated aggregates. Low saturation aggregates are likely to have low flows and therefore there will be some advection but transport will be heavily influenced by diffusion. As the saturation increases the influence of advection will increase.

In terms of contaminant destination the influence of advection is important. Diffusion will occur evenly in all directions in which the contaminant differential exists, while advection will transport contaminants wherever the water is draining, either into a fin drain, or down the vadose zone towards the phreatic surface.

In an unsaturated soil some of the void space is filled by gas. Contaminants may pass from the liquid phase into the gas phase by both volatilisation and by transport in water vapour. Contaminants within the gas will then be transported by diffusion and advection within the gas phase. Where there are significant gas phase flows this could result in substantial contaminant transport. The contaminants can be transferred back into the water or solid phase either by the precipitation, if the vapour moves into cooler soil, or by diffusion and the soil water's tendency to concentration equilibrium, if the vapour moves into less contaminated soil.

However, for the purposes of this project only contaminant transport in the fluid phase, and sorption to the solid phase are considered.

2.2.4.3. Precipitation

Where highways are well maintained and there is little cracking of the surface there is likely to be little penetration of water through the pavement. During a precipitation event some of the water will remain on the surface of the road and evaporate back into the atmosphere, while most of the rest will run across the surface to the verge where it will be collected in the drainage system. Any contaminants deposited on the surface of the highway are likely to become suspended or dissolved within the water and transported to the edge of the pavement when there is sufficient flow to transport them. Where there is cracking of the pavement surface, some of the water, and contaminants within it, will pass through the cracks into the pavement sub-base. The proportion of the rainfall that passes through the cracks varies dependant on the amount of cracking, the width of the cracks, the permeability of the base and sub-base layers, and the rainfall intensity.

Work undertaken by Jones & Jones (1989), Ridgeway (1976) and Taylor (2004) have either measured or estimated the ingress of water through the surface of a cracked but serviceable pavement to be between 2 and 20 litres/hour/m^2. Thus, pavement ingress could reach rates exceeding rainfall rates. Therefore, the pavement has the capacity to absorb all rainwater that falls on it, although this is only likely to apply for a relative short period prior to resurfacing.

Due to the rapid movement of water across the pavement surface, this form of contaminant transport is heavily dominated by advection.

Once the edge of the pavement has been reached the run-off will either be collected in a drain, a ditch, or allowed to infiltrate into the soil (although this is rare in the UK). If the run-off is collected in a drain or ditch then it will be transported away from the pavement to a site where it can be monitored and treated if necessary. Water infiltrating into the soil will penetrate slowly towards the saturated zone.

Modelling of precipitation has been carried out using data from the UK MetOffice on rainfall rates. For the purpose of this project it has been assumed that the rate at which runoff enters the pavement sub-base is equal to the rate at which it precipitates on the pavement surface. In reality this is not likely to be true. Even on a highly fractured pavement surface there will be some evaporation and some runoff running into formal drains.

Overestimating the quantity of runoff and therefore contamination entering the pavement entering the pavement is a conservative assumption, but in the absence of more reliable data it has been used for this project. In reality similar conditions will only be encountered for a short period prior to repair of the pavement surface or where permeable pavement surfaces are used (i.e. SUstainable Drainage Systems - SUDS).

2.2.4.4. Contaminant Mass Transport

When considering advection, if we can calculate the volume of water flowing from one point to another using Equation 2.3 or 2.4, and know the concentration of the contaminant at the first point we can also calculate the contaminant mass transport. In terms of advection it is sufficient to consider that if a volume of water $V_{A\text{-}B}$ flows from point A to point B and has a concentration of C_A. Then the contaminant mass moving from A to B ($M_{A\text{-}B}$) can be easily calculated and is given by,

$$M_{A-B} = V_{A-B} C_A \qquad \text{Equation 2.5}$$

This can be applied to both saturated and unsaturated flow.

2.3. Contaminant Fate

The fates of contaminants can be divided into three principal groups; retardation; removal; and pollution of targets. Retardation is a mechanism that slows the contaminant from being transported to a target. A target is a body or organism that can be affected negatively by the contaminant.

It is necessary for an engineer to consider the contaminant fate both in terms of its potential ecological impact and as well as in relation to environmental regulation.

2.3.1. Retardation

Retardation can occur either as a result of naturally occurring processes or due to artificial systems added with the intention of removing or minimising the environmental impact of the pavement. The principal mechanisms of retardation include biodegradation, volatilisation and sorption.

Biodegradation is the process by which contaminants are removed from the environment by organisms. This can include absorption by plant roots, the breakdown of toxic molecules or the construction of larger non-toxic molecules from contaminants.

Volatilisation and sorption are two aspects of partitioning, the division of contaminants between the liquid, solid and gas phases of the soil. This is discussed in more detail in Chapter 4.1.1 of this report.

2.3.2. Receptors

The possible targets include plants and animals in the area, and the ground water below the pavement which may be a potential or active water resource.

2.3.2.1. Human Health

A number of contaminants present within highway runoff and leachate from potential aggregates are known to be toxic in sufficient concentrations. The effects vary with each contaminant, but many have the potential to cause significant harm and even death. Some examples are given below.

Some hydrocarbons, such as benzene, are known to be carcinogenic even at relatively low concentrations. Consequently where a water source is affected it may increase the incidence of cancers for populations using the water.

The impact of heavy metals is variable. Cadmium has been considered as an example. According to the Material Safety Data Sheet for cadmium as supplied by J.T. Baker, chronic exposure to cadmium, even at relatively low concentrations, may have a wide range of effects including kidney damage, anemia, pulmonary fibrosis, emphysema, reduced fertility, and an increased risk of cancer of the lung and of the prostate. Short term exposure has a range of effects from irritation to death depending on the method of contact and amount of exposure.

2.3.2.2. Local Ecosystems

As with humans, many plants and animals can be adversely affected by contaminants in runoff and aggregate leachate.

Certain contaminants, such as heavy metals, in addition to being toxic to the receiving organisms are known to bioaccumulate. That is to say they are retained within organisms once adsorbed. As a result even when present at very low concentrations they may accumulate over time to the point that they become toxic.

2.3.3. Summary

It is clear when looking at the potential impact of chemicals present in runoff and aggregate leachate that there is potential for these to cause significant harm to human health and the environment. However, it is necessary to assess this risk, as in reality it may be highly improbable that these will be present in sufficient quantities to cause harm. Failure to acknowledge this may result in ‘solutions’ being implemented that have a more significant negative impact than the contaminants they are being used to control.

As an example the use of traditional aggregates may be preferred to recycled aggregates to avoid the potential for contamination. However, this will result in additional material being quarried for the development, and the alternative potentially going into landfill. If, following rigorous assessment, it can be demonstrated that the recycled aggregate poses no or negligible risk it could be used, avoiding these other negative impacts.

As a conservative assumption for initial assessment the target considered is the groundwater in the permanently saturated zone. If the water seeping down to the water table is sufficiently cleansed by retardation processes, then it will not affect the quality of the groundwater body, and from that the local eco-system. If, however, the groundwater becomes contaminated, plant and animal life in the immediate vicinity could potentially be affected, and the groundwater may become unsuitable to extract for human consumption. In this case further and more detailed risk assessment should be carried out, considering the specifics details of the groundwater and local receptors.

When considering the transport of contaminants to the water table it is important to ask the question ‘What is contamination?’. Almost all contaminants are naturally present in the environment, and it is excessive concentrations rather than merely the presence of these that causes damage. In fact in many cases low levels of contaminants are essential to life. As an example, iron is essential for the human body. It is used both for the transportation of oxygen and also for reduction and oxidation processes such as those in the production of adenosine triphosphate (ATP) the energy source used by cells. However, in excessive concentrations iron can cause damage to the liver, fatigue, joint disease and impotence, and it also increases the risk of diabetes, liver cancer, heart disease and arthritis.

2.3.3.1. Legal Framework

The government body regulating potential contamination is the Environment Agency. In relation to the development of highways there are principally two points at which they are able to influence the construction of the highway and the proposed schemes to limit or prevent contamination from occurring.

The first of these occurs during the planning stage. At this point proposals for the development are given to the appropriate local planning department, and where they feel it is appropriate the plans are forwarded to the Environment Agency. This generally occurs where the Environmental Health officer assessing the development considers there to be a risk to the environment. This generally occurs where the development includes construction or end-use processes that have a significant chance of causing contamination and also for particularly large projects.

Given the general scale of projects, proposals for the construction or redevelopment of highways are likely to be passed on to the Environment Agency. Small car parks and access roads included as part of other developments will not always be considered by the Environment Agency.

The acceptability of contaminant concentrations is considered in this project in relation to legal quality standards. United Kingdom legislation provides limits to contaminant concentrations acceptable in both drinking water and the environment. These include:

1. The Water Supply (Water Quality) Regulations 2000.
2. The EC Dangerous Substances Directive.
3. The EC Directive on Freshwater Fish.
4. The River Quality Objectives.
5. The Surface Waters (Surface Water Abstraction) Regulations 2006.
6. The Surface Waters (Dangerous Substances) Regulations 1989,1992, 1997 & 1998.
7. The Protection of Water Against Agricultural Nitrate Pollution Regulations 1996.

The contaminant concentration limits in these regulations are given either as an a maximum acceptable concentration (MAC), an annual average concentration (AA), or as a statistically calculated maximum, generally a limit that must not be exceed by more than $5^{\%}$ of samples. The full list of acceptable limits for drinking water, referred to in this thesis as Drinking Water Standards (DWSs), is as given by The Water Supply (Water Quality) Regulations 2000. A list of the environmental limits, referred to in this report as Environmental Quality Standards (EQSs), for direct and indirect discharges to groundwater has been compiled by the Environment Agency and can be obtained through their website.

Some consideration should also be given to potential changes in the law as a result of the Water Framework Directive that has been approved by the EC but has not yet been fully implemented. The objective of this legislation is to move away from the current system of quality standards, which the EC considers to be accepted levels of pollution. The proposed system is for groundwater improvement, in which the background levels of contamination in aquifers are protected where water quality is high and improved to 'normal' background levels in contaminated aquifers. Changes in the regulation of direct and indirect discharge to groundwater are due to be implemented in 2013.

2.3.3.2. Procedures for Contamination Risk Assessment

The Environment Agency has produced a number of documents detailing the methods by which the risks to human health and the environment from contaminated land should be assessed. The principal document is Contaminated Land Report 11 'Model Procedures for the Management of Land Contamination'.

The first stage of the risk assessment is to carry out a preliminary risk assessment. This will include a review of all data available, and the development of a conceptual model that includes all potential sources of contamination, pathways by which these may migrate and receptors that may be affected. Where there are no potential sources or receptors, or no viable pathway between the two there is negligible risk of damage and no further assessment is required. Where there is a potential risk a second stage of assessment is required.

The second stage is to carry out a generic quantitative risk assessment. This involves the collection of quantitative data such as the concentration of contaminants in leachate derived from a potential source. If this can be shown to be below generically accepted levels (e.g. drinking water standards or environmental quality standards) then the source would be assumed to be safe and no further assessment would be required. Where generic criteria a third stage of assessment is required.

The third stage of assessment is to carry out a detailed risk assessment. This may considers data obtained from the stage 2 assessment, and possibly additional data collected for the phase 3 assessment within a more detailed model. For this the possible concentration of contaminants reaching receptors is calculated (for example using modelling software such as ConSim) and the risk to the receptors is calculated based on this. If the assessment indicates an acceptable level of risk then the proposals are likely to be accepted. However, if the third stage of risk assessment indicates unacceptable risk alternative proposals should be considered.

2.4. Specific Topics Considered in this Thesis

The previous sub-chapters provided a general overview of the issues relating to groundwater contamination in the highway environment. Further detail is provided in this sub-chapter of the specific topics considered in this study.

2.4.1. Aggregate Runoff Interaction

As described previously in this chapter a number of studies have been carried out that consider the potential of runoff or aggregate leaching as a source of contamination in the highway environment. However, none were identified that considered the potential interaction between contaminated runoff and aggregates used for the pavement body. In reality, it is possible that adsorption of contaminants already present in runoff will have a more significant impact on water quality than the leaching of additional contaminants.

Pandey et al. (2002) carried out tests that considered the use of various alternative materials for use as substrates in treatment filters, designed to remove contaminants from highway runoff prior to discharge. Tests were carried out by placing samples of the materials in a 600mm by 60mm inert pipe. An artificial runoff was then pumped through the pipe, with comparisons made of the contaminant concentrations of water flowing into and out of the pipe.

The results provided are for copper, lead, zinc, fluoranthene and pyrene. Bottom ash was included in the testing, and this may also be used as an aggregate for highway construction. The results included showed that bottom ash adsorbed in excess of 90$^{\%}$ of each contaminant present in the artificial runoff. This indicates that adsorption of contaminants from runoff is likely to be a significant process.

In addition to this in-situ studies such as Legret (2005) have been carried out that compare contaminant concentrations in runoff with those of leachate that has passed through the pavement body. These studies have demonstrated that there is generally a reduction in contaminant concentrations. It can therefore be assumed that contaminant sorption rather than contaminant leaching is generally the dominant process within the pavement body. It should be noted however that these studies do not indicate where in the pavement body the sorption processes are occurring, and what part of it, if any, is attributable to pavement aggregates.

2.4.2. Soil Sorption

Sorption of contaminants within the sub-grade has been identified by the sensitivity study carried out as part of this project to be a critical parameter in determining the mobility of contaminants.

A large number of studies have been carried out considering the sorption of contaminants by natural soils, including Christensen et al. (2000), Chang et al. (2001), Tran et al. (2002) & Zytner et al. (1995). In addition to these, papers such as Krupka et al. (1999) have been published that bring together data from a number or sources, in this case in excess of 200, and give ranges of sorption coefficients for different chemicals and soil types.

While each of these provides real soil sorption data it is noted that the soils fitted into very broad classifications, and sorption parameters provided vary by several orders of magnitude. When simulating contaminant transport the choice of sorption parameter will have a very significant impact on the extent of contaminant transport.

2.4.3. Modelling of Contamination in the Highway Environment

Previously simulations have been carried out by Apul (2005) considering the movement of contaminants within the pavement structure and sub-grade. Analysis was carried out considering a pavement section with an impermeable surface, and contaminants derived from aggregate leaching.

Modelling demonstrated that in these circumstances, despite the impermeable surface there was migration of contaminants from the underlying aggregate. However, this migration was very limited and indicated that even after a period of 20 years only a small area of the sub-grade was affected.

This provides a useful model for academic study and a good starting point for further modelling. However, the assumptions that the pavement surface is impermeable, and that water infiltrating into the pavement is clean are both favourable rather than conservative, and that the simulations will potentially underestimate the concentrations and extent of contamination underlying real highways.

The additional testing and modelling carried out as part of the project described in this report has, to an extent, addressed this.

3. Chemical Interaction Between Aggregates and Runoff - Testing

As described previously the pavement sub-base plays a complex role in the contaminant source-pathway-fate processes. It is possible for the sub-base aggregates to act as a source of contaminants that are leached and then infiltrate into the sub-grade; it can also act as a pathway as contaminants either already leached, by aggregates 'upstream', or present in infiltrating runoff pass through it, and the fate of many contaminants could be sorption to aggregates particles.

Most work that has been undertaken to date has considered the pavement sub-base in only one of its possible roles described above. For example those considering the impact of alternative aggregates, such as Hill & Dawson (2000 and 2004) and van der Sloot et al. (2001a and 2001b), tend to look at the potential for contaminant leaching, however in-situ studies, such as Legret (2005) and Wilson (2004), tend to show that there is in reality a general reduction of contaminant concentrations as runoff infiltrates through pavements, although they do not quantify the role of the pavement sub-base course in this reduction, nor do they consider the use of alternative aggregate materials.

A series of tests were carried out in an attempt to determine, for a range of contaminants and aggregates, the nature of the sorption and leaching processes that occur in the pavement sub-base. This series included simple tank tests and advective tests using a permeameter. Based on this testing, appropriate modelling techniques and parameters were determined. The analysis by which these are determined is described in the following chapter.

3.1. Test Materials

3.1.1. Aggregates used

A wide range of materials was selected for analysis. These can be divided into ‘new’ and ‘old’ aggregates as well as conventional and alternative aggregates.

The ‘old’ aggregates are those that have been reclaimed from previous lysimeter testing, described briefly in chapter 2.1.2 of this report, undertaken by Hill and reported in Hill (2004), Hill & Dawson (2000) and Dawson et al. (2006). The ‘new’ aggregates are those provided by aggregate suppliers and are therefore in the condition they would be expected to be when new, i.e. at the time of pavement construction.

Since their installation in the lysimeters the old aggregates have been exposed to both weathering and biological action, and they are used to represent aggregates that have been in situ for a period of several years. However, it is important to note that there are some significant differences between these aggregates and those that have actually been used in pavement construction. The first of these is that the aggregates have been exposed directly to precipitation not pavement runoff, the second is that they have been exposed to a much greater degree of biological action than they would have been had they been used in a pavement (see Figure 3.1). In addition to this the aggregates have been covered with a permeable gravel allowing more water to enter than would be the case underlying an impermeable asphalt surface.

Figure 3.1, Photo showing plant growth in the lysimeter containing municipal solid waste incinerator ash.

The precipitation weathering the aggregates is likely to contain lower concentrations of contaminants than runoff, and as a consequence they may have leached more, or adsorbed and absorbed fewer contaminants during their time in the lysimeter. The most obvious form of biological action, as can be seen from Figure 3.1, is the growth of plants within the lysimeter, and the consequent presence of their roots within the aggregate. The roots will have many effects on the aggregates including changing the water flow regime by drawing up water, breaking down the structure of the aggregate, and reducing the porosity and consequently the permeability. Plant roots and bacteria may also be present in pavement aggregates. However, given the condition of the lysimeters roots are likely to be present in much smaller quantities in pavement aggregates.

With regard to conventional and alternative aggregates, conventional aggregates are those that are traditionally used in pavement construction (such as quarried limestone and granite), while alternative aggregates cover those obtained from alternative sources; often these are recycled materials or by-products of other processes. For this project limestone is used as an example of a conventional aggregate.

According to the British Geological Survey (2005) approximately 250-270 million tonnes of aggregate are used each year for construction; of this only about 50 million tonnes are obtained from alternative sources, the rest was quarried. Of the quarried rock the majority, 141 million tonnes in 2005, was crushed rock aggregate, the limestone used in this project is of this nature and from a source frequently used for highway aggregate.

The aggregates used for this project were obtained in January 2006 and are as shown in Table 3.1:

Material	Abbreviation	Description
Limestone	LS	Limestone is a sedimentary rock consisting principally of calcium carbonate. The limestone used for this project has been extracted from Dene quarry in Derbyshire.
Municipal Solid Waste Incinerator Bottom Ash	MSWIBA	MSWIBA is made up of the ash residue that is left after the incineration of municipal waste. Also referred to as Incinerator Bottom Ash Aggregate (IBAA).
Reclaimed Foundry Sand	RFS	Foundry sand is used for the production of casts used in the brass casting industry. When heated the sand fuses and forms a mould which is capable of withstanding the high-temperatures used in metal casting. Reclaimed foundry sand is that which is spilt or fails to set during the heating process.
Old Limestone	OLS	Limestone is a sedimentary rock consisting principally of calcium carbonate. The limestone used for this project has been extracted from Dene quarry in Derbyshire.
Old Municipal Solid Waste Incinerator Ash	OMSWIA	MSWIA is made up of the ash residue that is left after the incineration of municipal waste. Also referred to as Old Incinerator Bottom Ash Aggregate (OIBAA).
Old Reclaimed Foundry Sand	ORFS	Foundry sand is used for the production of casts used in the brass casting industry. When heated the sand fuses and forms a mould which is capable of withstanding the high-temperatures used in metal casting. Reclaimed foundry sand is that which is spilt or fails to set during the heating process.
Old Blast Furnace Slag	OBFS	Blast furnace slag is a by-product of the iron manufacturing industry. It is non-mettalic and consists mainly of silicates, aluminosilicates and calcium-alumina-silicates.

Table 3.1, Aggregates used

The aggregates have been prepared such that they are graded as they would be when used in highway construction. The limestone, blast furnace slag and incinerator bottom ash aggregate are mixed to DoT type 1 sub-base grading (Highways Agency, 2006), while the foundry sands is tested at the grading provided by the supplier. For the permeameter tests the specification was used for particle sizes below 2mm. Figure 3.2 shows the grading limits for a DoT type 1 aggregate and test samples.

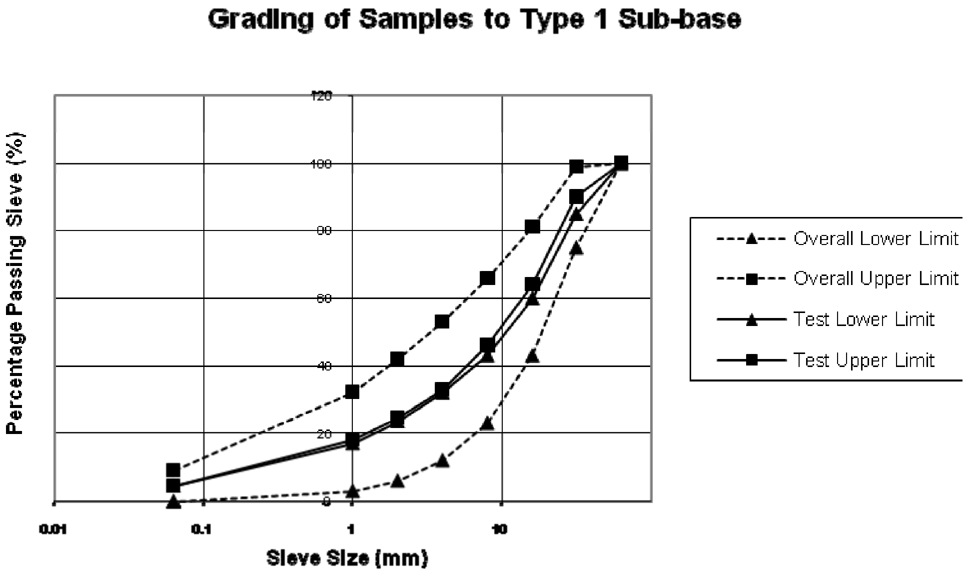


Figure 3.2, Grading of type 1 sub-base samples, the test upper and lower limits represent the variations in samples used for the tests.

3.1.2. Leachates used

In looking at the relative significances of sorption and leaching within the pavement sub-base it is necessary not only to consider a range of different aggregates, but also to consider a range of different leachates. The contaminant concentrations in runoff entering the pavement are likely to vary depending upon many factors such as; the quantity of traffic; the dry period between rainfalls; the presence of other local contaminant sources; and climatic conditions (e.g. in cold climates de-icing salts are likely to be used).

There have been several studies looking at the concentration of contaminants in runoff, including Kayhanian et al. (2003), Thomson et al. (1997), Barrett et al. (1998), Hares & Ward (1999) and Moy et al. (2002), as referenced in Chapter 2.1.1.4 of this report. These show a large range of concentrations detected but consistency in the limits to this range and average values, and as a result it was not deemed necessary for further measurements to be taken as a part of this study. The most comprehensive of the studies listed above is that by Kayhanian et al. (2003). Consequently the concentrations used in the different leachates have been based on the results of this study.

The leachates used include a purified water (WAT) deionised using a chemical filter, to provide a comparison to previous leaching tests. In addition leachates have been used with contaminant concentrations representative of a low traffic road (LTM), a high traffic road (HTM) and the maximum detected concentrations (MAX), as measured by the studies referenced above. The full list of contaminants and their concentrations in each of the leachates is given in Table 3.2. These concentrations were selected to be close to those values detected by Kayhanian, and allowing for the production method. That is, the chemicals were added as salts rather than individually and therefore the amount added was based on the final concentration of both chemicals in the salt.

The number of contaminants considered in this study was limited compared to those found in real runoff for several reasons. The principal reason for this is that it would be impractical to produce a pseudo runoff with all of the contaminants, while using real runoff would be unreliable due to the variations in contaminant concentrations from one sample to the next, and also because they would be biologically and chemically unstable.

The contaminants selected for analysis in this study were those that were:

- Present in runoff and/or leachate in significant concentrations.
- Detectable using ion selective electrodes (ISEs).
- Representative of a range of contaminant types – de-icing salts, metals and nutrients.

The contaminant mixtures selected were as follows:

Contaminant	**Artificial Runoff**			
	DIST	**LTM**	**HTM**	**MAX**
Na^+ (mg/l)	0	21.2	42.3	211.8
Cl^- (mg/l)	0	35	66.4	332.6
NH_4^+ (mg/l)	0	1.3	0.6	3.76
NO_2^- (mg/l)	0	0	0.14	1.84
NO_3^- (mg/l)	0	0.6	1.22	14.8
SO_4^- (μg/l)	0	10.6	21.2	196.5
Cu^{2+} (μg/l)	0	7	14	130
Cd^{2+} (μg/l)	0	0	0.45	9
Pb^{2+} (μg/l)	0	1.5	8	510

Table 3.2, Ionic concentrations in synthetic runoff

In reality there are likely to be trace concentrations of all elements even in the deionised sample. However, these are likely to be present at negligible concentrations that are significantly below detectable limits.

An additional set of tests was carried out on the limestone and MSWIBA using a more comprehensive list of contaminants. These were as shown in table 3.3.

Contaminant	**Artificial Runoff**			
	DIST	**LTM**	**HTM**	**MAX**
Al^{3+} (mg/l)	0	2.79	1.23	20.67
Ni^{2+} (μg/l)	0	8.64	9.88	49.40
Cd^{2+} (μg/l)	0	1.09	1.09	6.09
Cu^{2+} (μg/l)	0	31.81	58.54	127.26
Pb^{2+} (μg/l)	0	46.92	93.84	406.63
Zn^{2+} (μg/l)	0	64.84	226.94	972.60
Na^{+} (mg/l)	0	69.49	101.66	1,227.32
Cl^{-} (mg/l)	0	118.23	161.75	1,974.76
Simazine (μg/l)	0	0	0.12	0.9
Diuron (μg/l)	0	0.33	0.33	2.02
Benzo(a)pyrene (μg/l)	0	0.15	0.15	0.7
Indeno(1,2,3-c,d)pyrene (μg/l)	0	0.1	0.09	0.9
Naphthalene (μg/l)	0	0.17	0.17	4.75

Table 3.3, Chemical concentrations in synthetic runoff for additional testing

Due to the increased cost of analysis, the extended list of contaminants was only used in the two sets of tests.

3.1.2.1. Leachate synthesis

The mixture of chemicals used in the artificial runoff leachates is not frequently used, and as a result the solution needed to be mixed from base salts and their solutions. It is for this reason that there is some minor variation between the concentrations used and the concentrations given in literature, i.e. Kayhanian et al. (2003). The salts and quantities measured out for the synthesis of the leachates were as shown in Table 3.4. These were mixed with 20 litres of deionised water.

Chemical	**Artificial Runoff**		
	LTM	**HTM**	**MAX**
NaCl	1.07 g	2.14 g	10.72 g
NH_4Cl	7.43 mls of 10g/l solution	3.72 mls of 10g/l solution	223 mg
$NaNO_2$	0	4.14 mls of 1g/l solution	5.52 mls of 10g/l solution
HNO_3	1 ml of 0.01M HNO_3	2 mls of 0.01M HNO_3	2.4 mls of 0.2M HNO_3
$CuSO_4$	3.51 mls of 0.1g/l solution	7.18 mls of 0.1g/l solution	6.38 mls of 1g/l solution
$PbNO_3$	0.4 mls of 0.1g/l solution	1.99 mls of 0.1g/l solution	1.32 mls of 10g/l solution
$CdNO_3$	0	1.42 mls of 0.01g/l solution	2.84 mls of 0.1g/l solution

Table 3.4, Chemicals added to purified water to create synthetic runoff

The salts and quantities measured out for the synthesis of the more comprehensive leachates were as shown in Table 3.5. These were mixed with 1.8 litres of deionised water.

Chemical	**Artificial Runoff**		
	LTM	**HTM**	**MAX**
NaCl	0.1767g	0.2584g	3.12g
$CuSO_4$	2.25 mls of 0.1g/l solution	4.14 mls of 0.1g/l solution	9 mls of 0.1g/l solution
$PbNO_3$	1.35 mls of 0.1g/l solution	2.7 mls of 0.1g/l solution	11.7 mls of 0.1g/l solution
$CdNO_3$	0.54 mls of 0.01g/l solution	0.54 mls of 0.01g/l solution	3.02 mls of 0.01g/l solution
$AlCl_3.6H_2O$	4.5 mls of 10g/l solution	1.98 mls of 10g/l solution	0.333g
$NiCl_2.6H_2O$	0.63 mls of 0.1g/l solution	0.72 mls of 0.1g/l solution	3.6 mls of 0.1g/l solution
Simazine	0	0.108 mls of 2μg/ml solution	0.81 mls of 2μg/ml solution
Diuron	0.297 mls of 2μg/ml solution	0.297 mls of 2μg/ml solution	1.82 mls of 2μg/ml solution
Benzo(a)pyrene	0.135 mls of 2μg/ml solution	0.135 mls of 2μg/ml solution	0.63 mls of 2μg/ml solution
Indeno(1,2,3-c,d)pyrene	0.09 mls of 2μg/ml solution	0.081 mls of 2μg/ml solution	0.81 mls of 2μg/ml solution
Naphthalene	0.173 mls of 2μg/ml solution	0.173 mls of 2μg/ml solution	4.275 mls of 2μg/ml solution

Table 3.5, Chemicals added to purified water to create synthetic runoff

3.2. Eluate analysis

The eluates were analysed to determine the concentration of a range of chemicals, as well as the conductivity and pH of the sample solutions.

The pH and conductivity were measured using a PH-009 (111) meter and the Jenway 3540 meter respectively.

Various methods were considered for the analysis of eluate samples. These were divided into internal analysis using ion selective electrodes (ISEs) and external analysis. The external analysis was carried out at laboratories that specialise in the analysis of the chemical constitution of water samples. A range of methods are used by these laboratories dependent on the chemical being assessed and the level of accuracy required. There are significant advantages and disadvantages regarding these as listed in Table 3.6.

	Advantages	Disadvantages
ISEs	Cheap to use. Once the equipment has been bought it can be used as frequently as desired.	The detection limits are greater than those for Mass Spectrometry.
		There can be interference between detected ions reducing the precision.
	Consequently more readings per test can be taken and more tests can carried out on a restricted budget.	Other factors, such as Ionic Strength, of the solution can effect readings and consequently reduce precision.
		Analysis is time consuming.
External Analysis	Greater precision than ISEs.	As work is carried out externally, the cost of running a range of tests is much greater.
	Lower detection limits and consequently greater accuracy when analysing trace concentrations, such as those typically found for metals.	
	Analysis is carried out externally and therefore is not time consuming.	

Table 3.6, Advantages and disadvantages of ISEs and external analysis

The majority of the analysis done during this project was carried out internally using the ISEs. Two additional sets of tests were carried out, one on limestone and one on the incinerator bottom ash aggregate. There were two principal reasons for doing this: the first was that it provided confirmation of the results obtained using the ISEs; the second that it allowed a wider range of contaminants to be considered. It would have been preferable to run all the tests with the more comprehensive artificial runoff, however sufficient funding was not available to carry out such an analysis.

3.2.1.1. Internal Analysis (ISEs)

When two electrodes are placed in a liquid and a charge is placed across those electrodes it will create a current. Within the liquid the current is transferred by the movement of ions, within the metals by the movement of electrons. At the liquid solid interface the ion flow is converted into electron flow, e.g. Cd^{2+} will become become Cd and draw in 2 electrons, while Cl^- would become Cl and release an electron.

An ion selective electrode works on this principal. However, as shown in Figure 3.3, the difference is that the electrode is contained in a liquid separated from the sample solution by a selectively permeable membrane. The membrane prevents the entry of other ions so that the reading obtained is based purely on the movement of, and therefore the concentration, of the ion being measured. The equipment used for analysis with ion selective electrodes is as shown in Figure 3.4.

These membranes are not 100% effective and in some cases do let other ions in. The reading can also be affected by other factors that influence the conductivity of the solution, such as the ionic potential and pH.

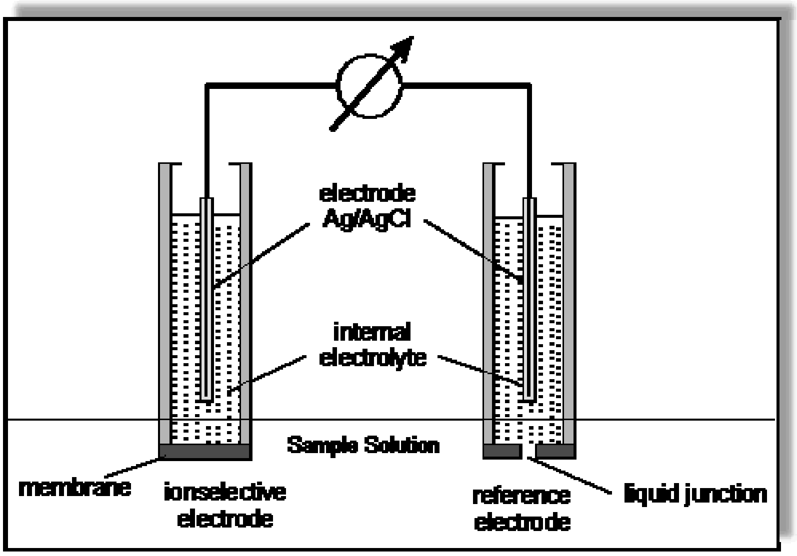


Figure 3.3, Components of an ion selective electrode. Taken from www.nico2000.net.

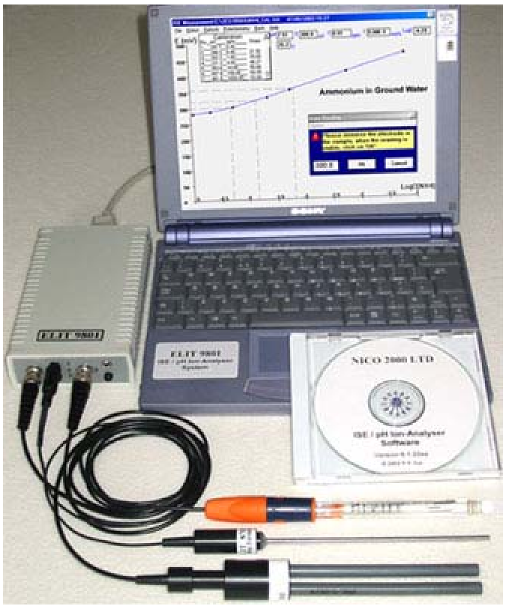


Figure 3.4, Equipment used for ion selective electrode analysis. Taken from www.nico2000.net.

For the ISEs the charge is not imposed, but generated by ions diffusing through the membrane. As the charged ions move across the membrane there will be a change in the net charge on either side. For example if the membrane were accepting the flow of positively charged ions then the internal electrolyte would become positively charged and the sample solution negatively charged. The greater the concentration of the ion in the sample solution, the greater is the rate at which those ions diffuse across the membrane and the greater is the charge. By measuring the current generated by this charge the concentration of ions in the sample solution can be calculated.

The limitations of the electrodes are as given in Table 3.7

Ion		**Concentration Detection Limits (ppm)**		**pH Limits**	
Detected	Interference	Min	Max	Min	Max
NH_4^+	K^+	0.9	9,000	0	8.5
NO_2^-	Cl^-, CN^-	0.5	460	4.5	8
NO_3^-	BF_4^-, ClO_4^-, Cl^-, NO_2^-, I^-	0.4	62,000	2	11
Na^+	Most Cations	0.2	20,000	3	10
Cl^-	Ag^+, Br^-, CN^-, I^-, S^{2-}	1	35,500	1	12
Cu^{2+}	Ag^+, Br^-, Cd^{2+}, Cl^-, Fe^{2+}, Hg^{2+}, S^{2-}, I^-	0.006	64,000	2	7
Pb^{2+}	Ag^+, Cd^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+},Hg^{2+}, S^{2-}	0.2	20,800	3	7
Cd^{2+}	Ag^+, Cu^{2+}, Fe^{2+}, Fe^{3+},Hg^{2+}, Pb^{2+}, S^{2-}	0.1	11,200	3	7

Table 3.7, Limitations of ion selective electrodes used for this project.

As can be seen many of the ISEs being used in this project will be affected by other ions present in the eluates being analysed. However, the rate at which the interfering ions pass across the membrane is generally much lower than that for the detected ion, and consequently their impact on the charge and the reading taken based on that charge is in most cases insignificant. As an example, taken from the data sheets supplied with the ISEs (nico 2000), chloride would have to be present at a concentration ten times greater than nitrate in order to cause an error of 5.6% in the reading.

The pH of samples can also affect the reading taken by the ion selective electrodes, and a number of the samples collected during the testing were above the usable limits for some of the ion selective electrodes. Where this occurred, hydrochloric acid was added to the solution to reduce the pH to an appropriate level. None of the samples had a pH exceeding 12, and it was therefore possible to take readings of the chloride concentration prior to the addition of the acid.

3.2.1.2. External Analysis

When analysed externally, a range of analytical techniques are used that vary dependent on the chemicals that require detection, and the degree of accuracy required. For this project the following have been used:

- Inductively coupled plasma mass spectroscopy (ICPMS). This was used for analysis of the metal concentrations in the solutions.
- Gas chromatography. This was used for analysis of the PAHs naphthalene, indeno(1,2,3-c,d)pyrene and benzo(a)pyrene.
- Colorimetry. This was used for the analysis of chloride.
- Triazines and Subureas. This was used for the analysis of pesticides simazine and diuron.

Using these methods it was possible to analyse a much wider range of contaminants and to a much greater degree of accuracy. The contaminants assessed using these methods, and the detection limits for each are as shown in Table 3.8. It can be seen from the table that the detection limits are much lower for the external analysis than for internal analysis using ISEs. In many cases the detection limit varies by more than an order of magnitude, for example cadmium has a detection limit of 0.1 mg/l using ISEs but a much lower value of 0.5 µg/l using ICPMS.

Chemical	**Method**	**Detection Limit (µg/l)**
Al^{3+}	ICPMS	20
Ni^{2+}	ICPMS	5
Cd^{2+}	ICPMS	0.5
Cu^{2+}	ICPMS	5
Pb^{2+}	ICPMS	5
Zn^{2+}	ICPMS	5
Na^{+}	ICPMS	200
Cl^{-}	Colorimetry	2000
Simazine	Triazines and Subureas	0.05
Diuron	Triazines and Subureas	0.05
Benzo(a)pyrene	Gas Chromatography	0.01
Indeno(1,2,3-c,d)pyrene	Gas Chromatography	0.01
Naphthalene	Gas Chromatography	0.01

Table 3.8, Contaminants analysed and limits of detection.

The eternal analysis was carried out by Severn Trent Laboratories Ltd and further information on the analytical techniques can be found on their website at www.stl-ltd.co.uk.

3.3. Tank Testing

Batch leaching tests were carried out on each of the aggregates. These were based on the standard leaching test BS EN 1744-3:2002 ‘Leaching from Aggregates’. However, the tests were modified such that they considered not only the potential for leaching from the aggregates, but also their potential to adsorb contaminants.

The tests were run in accordance with the standard, with the exception that the purified water leachate was substituted for the range of artificial runoffs described in section 3.1.2, and the test was run over an elongated period with periodic sample collection to ensure that equilibrium was obtained prior to the test being completed.

3.3.1. Tank Test Equipment

This sub-chapter gives details of the equipment used for the analysis of the interaction between aggregates and runoff.

The equipment used for aggregate preparation comprised:

- Sieves at 75mm, 20mm, 5mm, 2mm, 1mm, 0.6mm and 0.075mm.
- Weighing scales accurate to 0.1g.
- Oven set to 105^0C.

The equipment used for leachate preparation comprised:

- Chemical salts.
- Weighing scales accurate to 0.0001g.
- Water purifier (de-ionisation, purified water conductivity <20 μS).
- Pipettes and pi-pump accurate to 0.02ml.
- Glass beaker for mixing.
- Measuring jug with a capacity of 100ml, accurate to 1ml.

The equipment used for leaching test comprised:

- Leaching tanks.
- Aggregate stands.
- HDPE Sample bottles.

3.3.2. Tank Test Methodology

The purpose of the tests was to determine whether leaching or sorption was the dominant process when contaminated aggregate comes into contact with contaminated runoff. The tests were run in accordance with BS EN 1744-3:2002, with the exception that the distilled leachate was substituted for the range of leachates described in section 3.2, the tank was not agitated and the test was run over a longer period, with samples collected periodically to ensure that equilibrium was obtained.

The steps in the tests are as follows:

1. For each run 5 tanks are prepared, 1 each for the 4 leachates and 1 blank as a control.
2. Set up testing tanks as described in the standard, and prepare 20ltrs of each of the leachates as described in section 4.2.1. The leachate used in the control tank was alternated for each round of testing, such that by the end of the testing control readings were available for each of the leachate types.
3. Weigh out 4 batches of 1kg of dry aggregate then place on sample stands.
4. Collect samples from tanks to check that initial chemical concentrations are correct. Lower the stands into the tanks containing the leachates.
5. After 24 hrs pour out the first sample – this must be at least 100ml.
6. Measure the pH of the sample. If it exceeds 7 then split the sample and acidify (by addition of 0.1M hydrochloric acid in increments of 1ml) 1 half of it until the pH is reduced below 7.
7. Measure the conductivity of the non-acidified sample using the relevant meter, and the chemical concentrations of the samples using the ion selective electrodes.
8. Take further samples after 3, 5, 7 and 14 days and for each repeat steps 6 and 7. If two consecutive samples show no change in chemical concentrations, i.e. equilibrium has been obtained, no further samples are required. If equilibrium is not obtained in this period continue taking samples at 14 day intervals until equilibrium is obtained.

3.3.3. Tank Test Limitations

3.3.3.1. Repetition

There are several limitations regarding the methodology of the tank tests. The first was that the tests were not repeated. Due to limitations in terms of available space, number of tanks and time required to run each test it was simply not possible to do so within the time available for this project. However there are several factors that mitigate this. The first is that when each material was tested 4 tests were run on that material, one with each of the artificial runoffs. Consequently, if there is any heterogeneity in the material the differences will be observed by the variations of the reactions in the different tanks. Where external factors may have an impact on the results, such as temperature and other atmospheric conditions, this will be observed in the control tanks. A control tank was run with each set of samples, and any influential variations in the background conditions would be likely to affect these control tanks. In fact, there was very little variation either between the behaviour of the different samples, or in the readings from the control tanks and it is therefore concluded that the results, despite the absence of repetition, are in this regard reliable.

3.3.3.2. Segragation Effects in Eluate

The second limitation is that it was found during the initial tests that there were some anomalies in the leachate samples taken during the early stages of the test, typically in the pre-test samples and those collected on days 1-7. The concentration of chemicals seemed to decrease in the control tanks during the early stages of the test, and in the tanks containing aggregate there was an early peak in the concentrations followed by a gradual decline, see Figure 3.4.

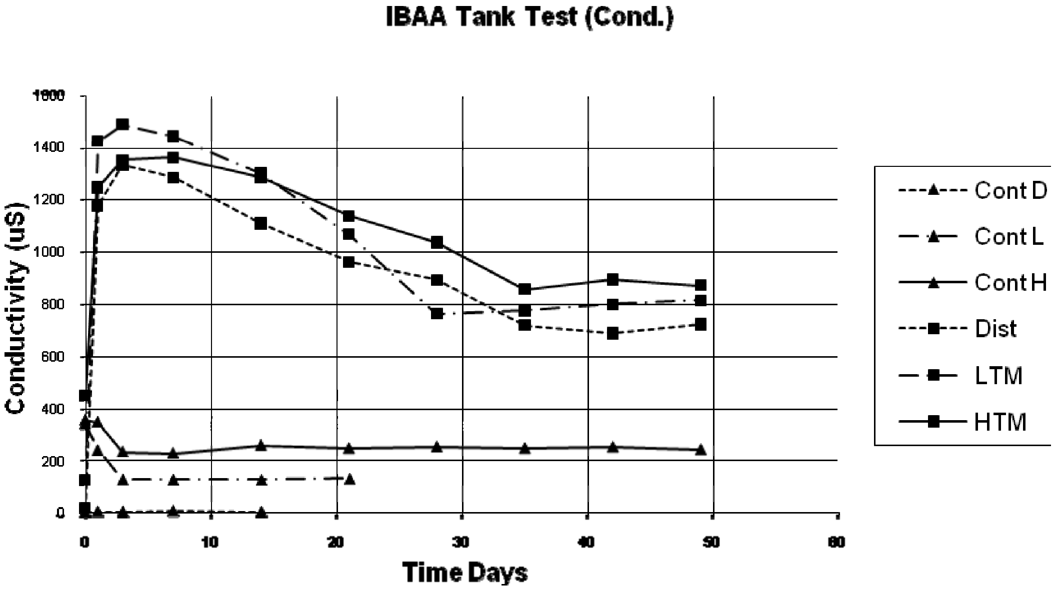


Figure 3.5, Typical variation in contaminant concentrations.

It was concluded that these results were significantly affected by segregation, possibly related to diffusion and density dependent flows within the tank. In the tanks containing artificial runoff, it was observed that the contaminants were not evenly dispersed within the tank. A possible explanation is that the more contaminated water had a greater density and 'sank' to the bottom of the tank. Where there was leaching from the aggregate the contaminated water would sink to the bottom of the tank from the aggregate generating a density dependent flow as the leaching occurred, this was followed by a period of diffusion as shown in Figure 3.6. The taps used to collect samples were situated at the bottom of the tanks, and consequently when the contaminants were not evenly dispersed within the leachate the samples collected would have chemical concentrations that were greater than expected, and not representative of the average in the tank.

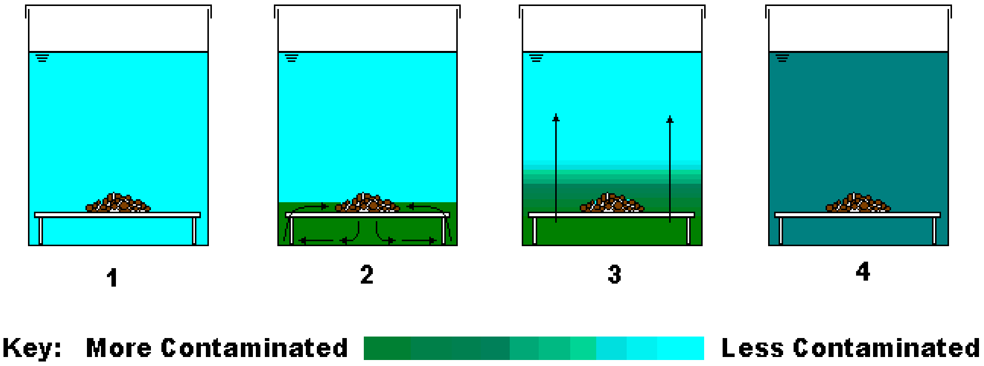


Figure 3.6, Stages of tank leaching test. 1 – initial conditions, no leaching has occurred. 2 – period dominated by leaching (up to 7 days). 3 – period of diffusion (up to 6 weeks). 4 – equilibrium attained.

These hypothetical explanations are strongly supported by additional tests that were carried out, with the specific intention of exploring this issue. 3 tests were undertaken looking at this and were as follows:

- A ‘normal’ tank test, but with samples taken from the top and the bottom of the tank to identify any variation in the in the contaminant concentrations within the tank.
- An agitated tank test, run as described in the methodology but using a stirrer to maintain an even dispersion of contaminants within the leachate.
- A suspended sample tank test, run as described in the methodology except that the aggregate sample was suspended at the top of the tank such that it was only just submerged by the leachate.

The first of these tests demonstrated clearly that there was a significant variation in the chemical constitution of the leachate within the tank. Initially readings from the top and bottom of the tank showed huge variations in the conductivity, however as the test progressed the contaminants became more diffused (see Fig 3.7).

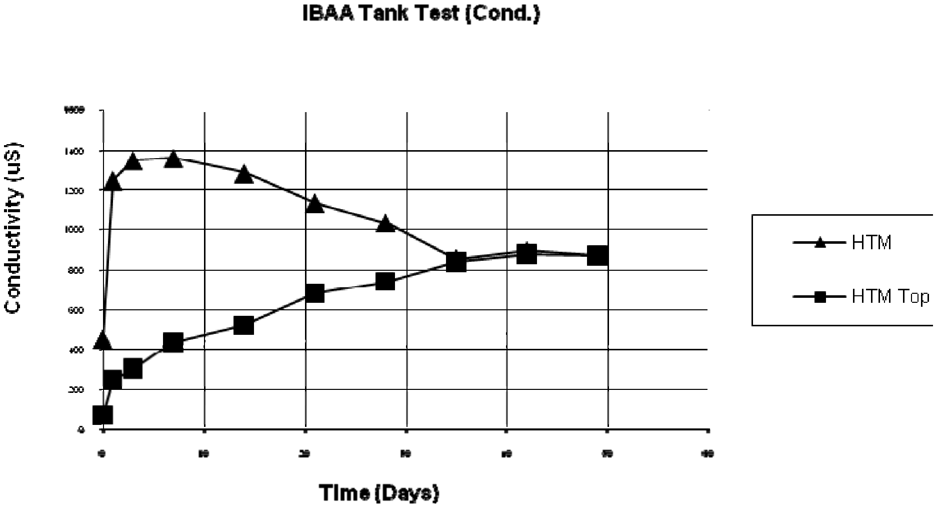


Fig 3.7, Graph showing variations in conductivity with respect to time, in samples taken from the top and bottom of the leaching tank.

The second set of tests using agitation and a suspended sample also confirmed the influence of segregation in the tank. In these cases the contaminants were well diffused within the eluate at all points in the test. In the case of the first as a result of the agitation and in the case of the second as a result of the density dependent flow occurring across the entire volume of the artificial runoff within the tank. The results for these tests (see Fig. 3.8) clearly show some variation in the early stages of the test. Both the agitated and suspended samples demonstrate a progressive release of contaminants leading up to a point of equilibrium. In the case of the standard test it is likely that the same progressive release occurs, but the uneven distribution of contaminants within the solution mask this.

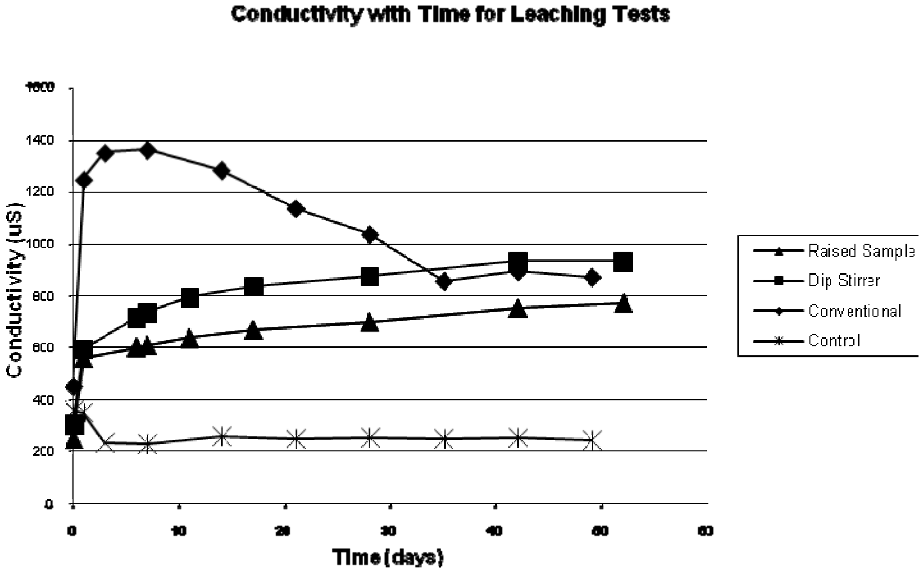


Fig 3.8, Graph showing variations of conductivity with time in tanks with a dip stirrer, suspended sample and a normal test.

3.3.3.3. Metal Analysis

The third major limitation of the test procedure was that it was not possible to get reliable readings for the metals in the leachate. The interference from the other ions present were generating greater errors in the readings than the readings themselves. As a result no results are available for the metals in the tank tests. In response to this, a series of metal sorption tests were carried out in an attempt to determine reasonable modelling parameters for the metals, and to gain some understanding of the interaction between the runoff and metals. These are described in the next sub-chapter.

3.3.3.4. Test Conditions

In additional to the limitations of the test methodology there were also limitations inherent to the principles of the test. There are fundamental variations between the conditions that the aggregate is subjected to in-situ and those in the test. These differences include differences in the hydrology, such as the complete saturation of the aggregate, the liquid to solid ratio and hydrostatic conditions, as well as potential variations in the physical state of the aggregate, such as compaction and loading, and the chemical state, such as pH of the groundwater. In reality it is likely that some or all of these will have an impact on the contaminant concentrations in the leachate. Van der Sloot et al. (2003) have suggested that the tank test to be an inadequate method of characterising the leaching process and assessing the suitability of the aggregate on this basis.

Despite these issues tank-leaching tests are documented in previous works, such as Hill (2004) and Peploe & Dawson (2006), as being a reasonable method for determining the potential leachability of unbound aggregates.

The use of aged aggregates in addition to new aggregates addresses many of the concerns raised regarding the reliability of the test in assessing the long-term performance of the material.

The alternative leaching tests proposed by van der Sloot et al. are a percolation test, and a pH dependence test. In addition to the tank test, percolation type tests have also been included in this project, and the results of these tests are compared in the following chapter of this report.

pH dependence tests have not been used in this project. However, both tank and percolation tests have been carried out on samples of both weathered and 'new' aggregates. As part of the weathering process much of the acid neutralisation capacity of the aggregates is used up. Consequently the weathered and new aggregates give an indication of the behaviour of the aggregates at their natural acidity and in their neutralised state. As an example tests on new MSWIBA had a typical pH of 11.3, while the weathered MSWIBA had a pH of approximately 8. Although these tests do not provide any data on the interim states it means that the tests carried out do provide data on both the initial and the long-term behaviour of the aggregates.

3.4. Metal Sorption Tests

In the batch tests it was found that the analysis for metals was impossible either due to the concentration of metals in the eluates being below the detection limit, or due to interference from other chemicals, present in much greater quantities, causing an unacceptable error in the reading. In response to this a series of metal sorption tests were carried out for the aggregates. Tests were carried out for each metal individually, and the initial solution contained a concentration significantly greater than that found in runoff (see Table 3.9) to ensure that the eluate would have a concentration that could be measured reliably.

Chemical	Concentration (mg/l)	
	Low	High
Copper	100	1000
Cadmium	10	100
Lead	10	100

Table 3.9, Concentrations used for metal sorption tests

Due to the increased concentration of the metals and their toxicity, in particular for Cadmium and Lead it was decided that smaller samples would be used to simplify the process of disposing of the samples following testing. Consequently 50g of aggregate sieved to 2mm down and 100ml of leachate were used.

3.4.1. Metal Sorption Testing Equipment

The equipment used for aggregate preparation comprised:

- Sieves at 75mm, 20mm, 5mm, 2mm, 1mm, 0.6mm and 0.075mm.
- Weighing scales accurate to 0.1g.
- Oven.

The equipment used for leachate preparation comprised:

- Chemical salts.
- Weighing scales accurate to 0.0001g.
- Water purifier (de-ionisation, purified water conductivity <20 μS).
- Pipettes and pi-pump accurate to 0.02ml.
- Glass beaker for mixing.
- Measuring jug with a capacity of 100ml, accurate to 1ml.

The equipment used for the metal sorption test comprised:

- HDPE bottles, 250mls.
- Weighing scales accurate to 0.1g.
- Vacuum pump and 45µm filter.

3.4.2. Metal Sorption Test Methodology

The metal sorption tests were carried out using a simple sorption test methodology that was as follows:

1. The aggregate was graded and 7 representative samples were taken with a particle size of 20mm down, and a mass of 50g.
2. The aggregate samples were added to 250ml HDPE bottles.
3. 7 sets of 100ml solutions were prepared; 1 deionised water, 2 with cadmium nitrate (10 and 100 mg/l Cd), 2 with copper sulphate (100 and 1000 mg/l Cu) and 2 with lead nitrate (10 and 100 mg/l Pb)
4. The solutions were then added to the bottles containing the aggregate.
5. The aggregate and solution mixtures were left for 24 hours +/- 30 mins, in a dark area at 20^{o}C +/-1^{o}C.
6. The solutions were then separated from the aggregates by passing through a 45µm filter.
7. The filtered solutions were then analysed using ISEs to determine the change in the metal concentrations.

3.4.3. Metal Sorption Test Limitations

The metal sorption tests were carried out in response to the limitations to the tank test procedure, more specifically those concerning the analysis of the eluates. The procedure was designed to by-pass these, but in so doing it has created limitations of its own.

The first and foremost is that the aggregate is no longer being tested in relation to an artificial runoff. To ensure that the final metal concentrations are measurable, each of the initial solutions contains only one metal ion and at a concentration several orders of magnitude greater than that found in runoff. As a result any sorption that occurs cannot be assumed to be equal to that that would occur when runoff comes into contact with aggregate.

However, the results do give some indication of the nature of the sorption process and the scale of the model parameters. The results are generally supported by commercial tests carried out on the MSWIBA and limestone where contaminant concentrations were relatively high, i.e. in the HTM and MAX leachates.

The tests also suffer from many of the same limitations as the tank tests, such as the complete saturation, unrealistic liquid to solid ratio and no loading or compaction. It is possible that changes in these conditions in-situ would have some effect on the sorption characteristics of the aggregates.

3.5. Infiltration Testing

While the batch tests provide a simple method for analysing the interaction between the aggregate and runoff, they are not an accurate representation of the conditions found in-situ. In-situ there is likely to be a much lower liquid to solid ratio, and a water flow regime with cyclic draining and replenishment of the water in the aggregate layer.

Infiltration tests were designed to provide a more accurate representation of the hydraulic conditions found in the pavement subsurface environment.

3.5.1. Infiltration Testing Equipment

The equipment used for aggregate preparation comprised:

- Sieves at 75mm, 20mm, 5mm, 2mm, 1mm, 0.6mm and 0.075mm.
- Weighing scales accurate to 0.1g.
- Drying oven.

The equipment used for leachate preparation comprised:

- Chemical salts.
- Weighing scales accurate to 0.0001g.
- Water purifier (de-ionisation, purified water conductivity <20 µS/cm).
- Pipettes and pi-pump accurate to 0.02ml.
- Glass beaker for mixing.
- Measuring jug with a capacity of 100ml, accurate to 1ml.

The equipment used for the permeameter testing comprised:

- Flexible wall permeameter.
- Vacuum pump.
- Pressurised air supply.
- Pressurised water supply.

3.5.2. Infiltration Testing Methodology

The objective of the infiltration tests was to investigate the impact of more realistic liquid to solid ratios than those generated in the tank tests. The infiltration test also gives some indications of how this interaction varies over time.

The test is run using a flexible wall permeameter. The permeameter is set up as shown in Figure 3.7.

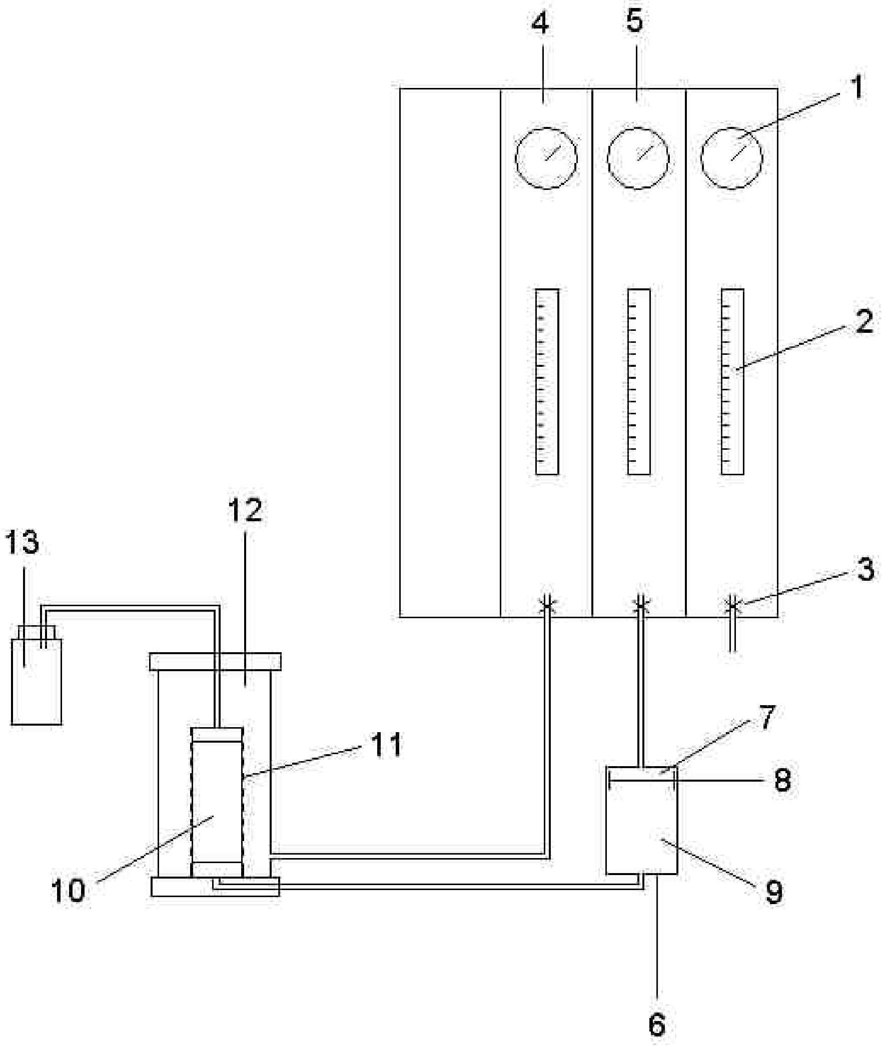


Figure 3.7, Flexible Wall Permeameter.

1, Pressure gage and controls; 2, pipette measuring outflow volume; 3, outflow tap; 4, pressure tank control panel; 5, leachate inflow control panel; 6, leachate tank; 7, water; 8, sliding divider membrane; 9, leachate; 10, aggregate sample; 11, flexible membrane; 12, pressure tank; 13, eluate collection bottle.

Once the equipment has been set up the infiltration test is run as follows:

1. 4 litres of leachate is prepared. Only the HTM leachate has been used for this test.
2. Prepare the aggregate sample in the permeameter. This should be graded to DoT type 1 sub-base then sieved to remove particles >2mm diameter. Ensure that the mass of aggregate used for the test is recorded. Apply a vacuum to the sample.
3. Construct the pressure cell around the sample.
4. Fill the pressure cell with water and apply a pressure of 25 KPa.
5. Fill the leachate tank with the artificial runoff.
6. Set a pressure of 20 KPa on the leachate inflow control panel.
7. Slowly fill the sample. Record the volume of water required to fill the sample – i.e. one bed volume.
8. Leave the sample to stand for 30 minutes.
9. Open up the leachate inflow tap and allow one bed volume of leachate to flow into the sample. Collect the eluate in a sample bottle.
10. Repeat steps 8 and 9 a further 7 times.
11. Leave the sample to stand for 18 hours.
12. Open up the leachate inflow tap and allow one bed volume of leachate to flow into the sample. Collect the eluate in a sample bottle.

3.5.3. Infiltration Testing Limitations

There are a range of limitations affecting the infiltration tests carried out for this project.

In reality the water in the sub-base and sub-grade is likely to be not only flowing, but it will also often be unsaturated and consequently in suction. It is possible that this capillary water will behave differently to that which not only saturates, but also completely submerges and pressurises the sample in the batch test.

The duration of the contact time between aggregate and runoff is also set in these experiments to 30 minutes for the first 7 bed-volumes, and 18 hours for the 8th bed volume. In-situ the contact time between the aggregate and runoff will vary dependent on a whole range of factors, such as the function of the drainage system, the permeability of the aggregate, the permeability of the sub-base, the saturation of the aggregate and sub-base, and the nature and intensity of the rainfall.

Simulations carried out as part of this project and described in Chapter 6.3.1.2 of this report were used to calculate outflow hydrographs for a pavement sub-base drain. The lag between the start of precipitation and the peak of the outflow hydrograph was approximately 30 minutes. Consequently this has been used as a reasonable approximation for the typical contact time for water infiltrating through the sub-base.

The principle limitation of the flexible wall permeameter test is that it can only test small particles, not the full range of particle sizes as expected in a DoT type 1 pavement sub-base aggregate. The type 1 sub-base course aggregate contains particles with dimensions of up to at least 32mm

In the case of the reclaimed foundry sands and crumbed rubber the particles are all of a size that can be used within the permeameter. However, in the case of the type 1 aggregates, i.e. the blast furnace slag, municipal solid waste incinerator bottom ash aggregates and limestones, only the fine particles were assessed (those that passed a 2mm sieve).

Despite the above limitations it is possible to make an educated guess as to the behaviour of the larger particles and the material as a whole. In the case of homogeneous materials, such as limestone, it can be reasonably assumed that the surface of the larger grains will behave in the same manner as the fines. The relative surface area of the larger grain particles, and consequently the relative impact of these particles, can be estimated by using a simple mathematical model and by making several simple assumptions.

The assumptions are:

- That the particles are the same shape irrespective of size.
- That the grading of particles trapped between any two sieves is evenly distributed between the upper and lower limit.

Given the above assumptions then it can be assumed that the surface area (S_A) of any given particle is given by:

$$S_A = F_s D^2 \qquad \text{Equation 3.1}$$

For which F_s is a shape factor that remains constant for the material in question and D is the diameter of the particles.

The mass of any given particle (M_g) is then given by the function:

$$M_g = F_m D^3 \qquad \text{Equation 3.2}$$

and the number of grains (N_g) per unit mass is given by:

$$N_g = \frac{1}{M_g} = \frac{1}{F_m D^3} \qquad \text{Equation 3.3}$$

For which F_m is a constant mass factor that would be a function of the density of the material and the shape of the particles.

From this it can be deduced that the surface area for a group of particles of unit mass (S_m) is given by:

$$S_m = N_g S_A = \frac{F_s}{F_m D} \qquad \text{Equation 3.4}$$

Going back to the original statements it has been assumed that there is an even distribution of particles trapped between two sieves (a lower sieve size of D_1 and an upper sieve size of D_2). Based on this the average surface area of the particles per unit mass is calculated as being:

$$\overline{S}_m = \frac{\frac{F_s}{F_m}\left(\ln D_2 - \ln D_1\right)}{D_2 - D_1} \qquad \text{Equation 3.5}$$

If $\overline{S}_m$, derived from Equation 3.5, is multiplied by the mass of particles (M) trapped between the two sieves it will give the surface area of those particles. Although the shape and mass factors, F_s and F_m respectively, are unknown by assuming they are constant for all particle sizes they can be cancelled out to determine relative surface areas using Equation 3.6.

$$S_R^{\frac{A}{B}} = \frac{\sum_{i=1}^{i=n} M_i^A \frac{\left(\ln D_{i+1}^A - \ln D_i^A\right)}{\left(D_{i+1}^A - D_i^A\right)}}{\sum_{i=1}^{i=n} M_i^B \frac{\left(\ln D_{i+1}^B - \ln D_i^B\right)}{\left(D_{i+1}^B - D_i^B\right)}} \qquad \text{Equation 3.6}$$

For which $S_R^{A/B}$ is the surface area of sample ‘A’ relative to sample ‘B’. The sub-script i indicates the number of the sieve, with 1 being the smallest, 2 the second smallest, etc, with n being the total number of sieves used for the grading. The superscript A and B indicate which sample is being considered.

Equation 3.6 was used to determine the minimum possible surface area of fines as a fraction of the total for a type 1 aggregate. This was calculated as $34.5^{\%}$ on the assumption that the grading was as shown in Table 3.10 for the minimum fine fraction. For a more typical grading, also as shown in Table 3.10, the approximate surface area of the fine particles was calculated as $95.2^{\%}$.

Sieve Size (mm)	Type 1 % Passing		Minimum Fines	Typical Grading
	Min	Max		
63	100	100	100	100
31.5	75	99	99	87
16	43	81	81	62
8	23	66	66	44.5
4	12	53	53	32.5
2	6	42	6	24
1	3	32	3	14.5
0.063	0	9	0	4.5
% surface area on fraction <2mm	-	-	34.5	95.2

Table 3.10, Type 1 Aggregate Gradings (Highways Agency, 2006)

From the above it can be assumed that in most cases the majority of the surface area for a typical pavement sub-base is likely to be on the particles of sand size and smaller (<2mm). By testing this fraction the flexible wall permeameter test is likely to provide a close representation of what occurs in the sub-base.

Where the non-fines fraction of the aggregate accounts for a significant proportion of the surface area it may be possible to estimate the impact of the larger particles by using the assumption that the surface area is predicted accurately using the above methodology, and that the particles' surfaces will behave in much the same manner as that of the fines.

This has been supported by rapid leaching tests, carried out on limestone and IBAA graded to DoT type 1 aggregate sub-base. Two 180g samples of each graded aggregate were tested with one sieved to 2mm to remove the larger particle sizes. These were then placed in an end over end agitator with 1.8 litres of purified water, and agitated for a period of 24 hours. The conductivity of the samples was then measured, providing an indication of the overall ionic content of the solutions.

Despite the sieved samples having 24% of the mass content of the un-sieved samples the change in conductivity was approximately equal for the Type 1 and fine samples. Results are as shown on Table 3.11. It is noted that the increase in conductivity is broadly similar for both the sieved and the unsieved samples, indicating that almost all the activity is occurring within the fines fraction of the aggregate.

	Limestone		IBAA	
	Coarse	Fine	Coarse	Fine
Conductivity (µS/cm)	132.9	118	343	357

Table 3.11, Conductivity of Eluate from Leaching Tests on Fine and Type 1 Aggregates.

4. Chemical Interaction Between Aggregates and Runoff - Analysis

Having carried out tests, as described in chapter 3, it is next necessary to consider the results of these tests and their implications. The testing was undertaken to derive modelling parameters for the simulation of contaminant transport in the highway environment. This chapter details first the chemical processes that may occur when an aggregate comes into contact with runoff, it then describes the methodology by which modelling parameters have been determined from the test results, and the results of this analysis.

4.1. Aggregate Sorption and Leaching Theory

Where runoff comes into contact with an aggregate there are likely to be chemical reactions occurring between the two. These reactions are likely to result in changes in the concentration of chemicals dissolved in the runoff. When modelling contaminants in the pavement sub-surface it is important to consider not only the spatial movement of the contaminants, but also these chemical reactions that may cause them to be absorbed or adsorbed by or leached from the aggregate and soil.

A range of processes and the theoretical models which can be used to describe them are now introduced. Sorption and leaching processes are described in the following sub-chapter, including partitioning, salt solution and precipitation, biodegradation and time controlled release together with other processes that may influence their behaviour.

4.1.1. Partitioning

Partitioning is used as an expression to describe the net effect of processes causing sorption and desorption. Krupka et al. (1999) carried out a study considering the processes involved in soil sorption. They identified complexation, reduction/oxidation, adsorption, ion exchange and precipitation as processes that may contribute to contaminants movement between the solid and liquid phase within a soil.

As a result of these and other processes, chemicals are divided between the solid phase (generally the solid-liquid interface), the aqueous phase, the gas phase and, where present, non-aqueous phase liquids (NAPLs). The theory is that when a chemical is present in a granular material, the concentration of the chemical will reach equilibrium between the different phases in which the concentration of the chemical in each phase is in balance. i.e.:

$$C_s = f[C_w] = f'[C_a] = f''\lfloor C_{napl}\rfloor \qquad \text{Equation 4.1}$$

Where C_s is the concentration of the chemical on the solid, C_w the concentration in the water, C_a the concentration in air and C_{napl} the concentration in the NAPL, with f, f' and f'' representing different functions.

For this project the presence of NAPLs in the soil is not considered. NAPLs may be present in soils and the pavement sub-base as a result of oil leakage from vehicles, however, except where major spills have occurred they are likely to be present in relatively low quantities compared to the water and are therefore not likely to have a major impact on the flow of other contaminants within the water. Kayhanian et al. (2003) and Barret et al. (1998) detected maximum levels of oil and grease in runoff of 226 mg/l and 4.2 mg/l respectively.

The concentration of contaminants in the gas phase is also not considered in this study. The contaminants considered in this study are all ions, and consequently they are strongly attracted to the bi-polar water molecules and only a small proportion will become volatised. As a result the concentration in the gas phase will be very low compared to that in the liquid, or on the solid, and the transport of contaminants in the gas phase is likely to be insignificant compared to that in the liquid phase.

However, it should be noted that where soils and aggregates are not fully saturated there is likely to be some contaminant flow in the gas phase. Furthermore, when considering the flow of volatile contaminants that may be found in runoff (e.g. benzene, toluene, ethylbenzene and xylene) the gas phase contaminant flow regime may be the dominant method of contaminant transport.

As a result of the above, for the purposes of this project the only partitioning relationship being considered is that between the concentration in the solid-liquid interface and the concentration in the liquid phase for which:

$$C_s = f[C_w] \qquad \text{Equation 4.2}$$

There are three frequently used functions to describe the relationship between these two concentrations, they are:

- Linear

$$C_s = K_d C_w \qquad \text{Equation 4.3}$$

- Freundlich

$$C_s = K_d {C_w}^n \qquad \text{Equation 4.4}$$

- Langmuir

$$C_s = \frac{C_{s\max} K_d C_w}{1 + K_d C_w} \qquad \text{Equation 4.5}$$

For which K_d and n are model sorption parameters and C_{smax} the maximum possible sorbed concentration as used by the Langmuir isotherm.

Deciding which relationship provides the most accurate model of partitioning must be done on a case-by-case basis, as each contaminant will react differently with different soils and liquids. For the simulations carried out in this project only the linear relationship has been used. The contaminant concentrations in the highway environment are likely to be relatively low compared to other 'contaminated land' scenarios where there may be significant known environmental harm. According to Charbeneau (2000) at low concentrations most partitioning relationships are well represented by the linear model. Chang (2001) assessed the linear, Langmuir and Freundlich models and found all to provide a good fit with experimental data.

4.1.1.1. Sorption and Desorption Modelled as Partitioning

When a liquid and solid come into contact it is highly unlikely that they will initially be in a state of chemical equilibrium, as defined by Equations 4.3 to 4.5. That is to say, considering the linear model:

either,

$$C_s < K_d C_w \qquad \text{Equation 4.6}$$

or,

$$C_s > K_d C_w \qquad \text{Equation 4.7}$$

In the first case, to obtain equilibrium, some of the contaminant will become adsorbed on the solid surface reducing the concentration in the liquid phase, and increasing that on and in the solid (i.e. sorption will occur). In the second case the contaminants will be released from the liquid solid interface reducing the concentration in/on the solid and increasing the liquid concentration (i.e desorption or leaching will occur).

For equilibrium to be achieved the contaminant must be both released from the liquid solid interface, and then diffuse through the fluid and each of these takes time. Where a test period is less than the time required to obtain equilibrium the formulae given will have reduced accuracy. However, work by Bajracharya et al. (1996) indicates that the time taken for equilibrium to be attained for cadmium in soils is so low as to be insignificant, that is to say, even at high groundwater flow rates (up to Darcy's velocity $6x10^{-4}ms^{-1}$) there is sufficient contact time for equilibrium at any point to be obtained. The time required to reach equilibrium for other contaminants may vary, but it is reasonable to assume that other metals with similar chemical characteristics are likely to behave in a similar manner.

Where sorption occurs it can be considered a beneficial process by which the contaminant is removed from the system and prevented from reaching and contaminating groundwater. However, it should be noted that if, in the future, the soil or aggregate comes into contact with cleaner water the equilibrium concentrations will change, and some or all of the contaminant will then be released back into that water and continue to migrate towards the water table.

4.1.2. Salt Dissolution and Precipitation

In addition to partitioning there is also the possibility that dissolution and precipitation of salts will occur in pavement base courses and sub-grades.

In the case of salts, for each salt there is a limit of solubility. That limit being the maximum concentration that a fluid can hold. Below this limit, and given sufficient time, a salt will dissolve completely; above that limit, any salt will remain in its crystalline form and further salt will precipitate until the equilibrium concentration is reached..

The value of the limit of solubility varies however, not only between different liquids but also with temperature, pH and the presence of other chemicals. All of which are highly variable in the highway environment. In general the greater the temperature the greater the solubility limit. The effect of variations in pH and the presence of other chemicals is dependent upon the salt in question, and the other chemicals present. For example, many heavy metals have minimum solubility at pH 9-11 and are more soluble at both higher and lower values.

In some situations a runoff containing a dissolved salt may be exposed to a change of conditions that lead to a reduction in the solubility limit. If the limit is reduced below the concentration of salt in the liquid the excess salt will precipitate forming crystals in the fluid.

4.1.2.1. Literature Values

As mentioned above the solubility limits of salts vary dependent upon a wide range of factors. However, literature values are available for the solubility of salts in standard conditions. Pure water at 20^{o}C is frequently used. Table 4.1 gives values of the solubility limits for the salts used in this project.

Solubility (g/l at 20°C unless otherwise stated)				
	NO_3^-	NO_2^-	Cl^-	SO_4^-
Na^+	900	820	360	-
NH_4^+	1410	-	-	770 (25°C)
Cu^{2+}	138	-	-	203
Cd^{2+}	2150	-	1680	1130
Pb^{2+}	343	-	-	0

Table 4.1, Salt solubility limits – taken from Material Safety Data Sheets as supplied by Fisher Scientific.

4.1.3. Bioremediation

Bioremediation refers to the biological processes that act to prevent contaminants from affecting receptors. This includes bio-uptake or biofixing which refers to the processes by which bacteria and other flora and fauna may remove contaminants from the aggregate runoff mixture by uptake of the contaminants or binding to inert organic compounds. In addition to the above there is also the possibility of biodegradation. Biodegradation refers to the breakdown of the contaminants' chemical structure by bacteria within the soil.

According to Liu & Liptak (2002), one way to model biodegradation is to assume that the rate of contaminant degradation is proportional to the contaminant concentration. That is:

$$\frac{dc}{dt} = -kCc \qquad \text{Equation 4.8}$$

In which c is the contaminant concentration, t is time and k the biodegradation rate.

The rate of biological degradation can also be expressed in terms of its half-life ($t_{\frac{1}{2}}$), i.e. the period of time over which half of the contaminant biodegrades. Knowing the rate of degradation the half-life can be calculated using:

$$t_{\frac{1}{2}} = \frac{0.693}{k} \qquad \text{Equation 4.9}$$

It should be noted however that for Equations 4.8 and 4.9 to apply it is assumed that the population of bacteria able to degrade contaminants will increase proportionally with the contaminant concentration. In many cases this will be a close approximation to the real situation as the contaminant acts as a food source for the bacteria and a larger supply can support a larger population.

However, in some cases the contaminant supply is not the limiting factor for the bacteria population. Where there is a limited supply of oxygen or other necessary nutrients these will limit the population and consequently limit the rate of degradation.

It is also assumed that other contaminants present within the aggregate and runoff are not toxic to the bacteria. Where such toxins are present the rate of degradation may be reduced or stopped completely.

4.1.4. Time Controlled Release

Many processes are time controlled. As discussed above relatively little time is needed for partitioning equilibrium, while salt dissolution and biodegradation are processes by which contaminants may be taken-up or released gradually over time.

Other examples of the time-dependent activity can be seen in the short term time controlled release of salts within the aggregate matrix. Slower release mechanisms include processes such as solid diffusion.

In the case of rapid release mechanisms, such as time required for salt dissolution, this is most likely to have an impact and be observed in the infiltration test, as described in Chapter 3.5, as this has the minimum contact time between aggregate and runoff. This can be observed by comparison of the concentrations in the 7th and 8th steps, as these have contact times of 30 mins and 18 hours respectively.

Slow release mechanisms, such as solid diffusion, may be detected in the tank leaching tests, in which scenario the equilibrium condition will be a constant rate of change in concentration rather than a constant concentration.

4.1.5. Combined

In reality the surface of some aggregate particles is likely to be highly heterogeneous, and in some cases all or none of the above processes may be going on at some point within the aggregate and runoff mixture. In addition to the quantitative methods, as described in the following sub-chapter, qualitative analysis is also required to balance the results set for each material and assess which are likely to be the dominant processes. There is also the possibility that, due to heterogeneity between samples, even for different specimens of the same material not all specimens will behave in the same manner.

4.2. Analytical Methods for Interpretation of Results

Laboratory testing was carried out as described in the previous chapter, and the known interaction processes are governed by the principles outlined in the previous sub-chapter. Based on this it is next necessary to understand how the relevant processes, and their associated parameters, may be identified from the results of the tests.

4.2.1. The Tank Test

The principle test used for analysing the interaction between the selected aggregates and the potential contaminants sodium, chloride, nitrate and ammonium was the tank test. To determine parameters for the interaction processes, for each material a plot was produced showing the variations in the equilibrium concentration in the leachate compared to that of the eluate. In addition to this the total leached or sorbed concentration was calculated.

4.2.1.1. Partitioning

The tank test is a form of batch sorption/leaching test. Other batch tests include agitated leaching tests and metal sorption tests as described in the previous chapter. In each of these tests a known quantity of water is mixed with a known quantity of aggregate. The concentration of contaminants in the water at the start of the test is established as described in the previous chapter. The unknown parameters in these tests are the initial concentration of contaminants in the aggregate, and the sorption coefficient.

Taking a sample of water with a known contaminant concentration and adding a solid also with a known contaminant concentration it is possible to calculate C the total concentration of the contaminant, i.e. both the liquid and solid phase, with relation to the volume of water.

If the initial concentration in the water is C_{wi}, that in/on the solid C_{si}, the water volume V and the solid mass M_S, then the total contaminant mass M_C is given by:

$$M_C = C_{wi}V + C_{si}M_S \qquad \text{Equation 4.10}$$

Unless biodegradation has occurred we can assume that the final contaminant mass is equal to the initial mass and that the final aqueous and solid concentrations (C_{wf} and C_{sf} respectively) are accurately calculated using the linear partitioning coefficient. Thus:

$$M_C = C_{wf}V + K_d C_{wf} M_S \qquad \text{Equation 4.11}$$

Combining Equations 4.10 and 4.11 it can be shown that:

$$C_{wf} = \frac{C_{wi}}{\left(1 + \frac{K_d M_s}{V}\right)} + \frac{C_{si} M_s}{\left(V + K_d M_s\right)} \qquad \text{Equation 4.12}$$

Assuming a linear sorption coefficient then the relationship between C_{wi} (x axis) and C_{wf} (y axis) is linear with the gradient (m) given by:

$$m = \frac{1}{\left(1 + \frac{K_d M_s}{V}\right)} \qquad \text{Equation 4.13}$$

And the intercept (i) given by:

$$i = \frac{C_{si} M_s}{\left(V + K_d M_s\right)} \qquad \text{Equation 4.14}$$

Based on this it is possible to calculate C_{si} and K_d from the plot of C_{wi} against C_{wf} for a variety of different concentrations.

4.2.1.2. Salt Dissolution

Where salt dissolution occurs, and assuming that samples are homogeneous, then it is anticipated that an equal mass of contaminant will be released into the leachate, except where the maximum solubility would be exceeded.

Within the batch test, the initial concentration in the water, C_{wi}, is known. However, the concentration in the solid phase, C_{si}, and the solubility limit, C_{lim}, are unknown. Given this, where the limit concentration is not exceeded the final concentration in the water, C_{wf}, is given by:

$$C_{wf} = C_{wi} + \frac{M_s C_{si}}{V} \qquad \text{Equation 4.15}$$

Based on this it can be seen that considering the plot of C_{wf} against C_{wi} will be a straight line for which:

$$m = 1 \qquad \text{Equation 4.16}$$

And,

$$i = \frac{M_s C_{si}}{V} \qquad \text{Equation 4.17}$$

Based on this it is possible to calculate the initial solid concentration. Where the limiting limit concentration would be exceeded, the final concentration will be equal to the limiting concentration.

4.2.1.3. Biodegradation

As stated previously the rate at which biodegradation occurs is assumed to be proportional to the concentration of the contaminant, and the rate of degradation is as given by Equation 4.8. By integrating this for the period of the test it is possible to calculate the degradation coefficient using:

$$k = -\frac{1}{t}\ln\left(\frac{C_{wi}}{C_{wf}}\right) \qquad \text{Equation 4.18}$$

For which C_{wi} is the initial concentration and C_{wf} the final concentration. The half life of the contaminant can also be calculated from the rate of degradation using Equation 4.8.

It should be noted however that this assumes that there is no salt dissolution, or initial leaching or sorption by means of precipitation. Where these have occurred it is possible to use the equation:

$$k = -\frac{1}{t}\ln\left(\frac{\Delta C_{wi}}{\Delta C_{wf}}\right) \qquad \text{Equation 4.19}$$

For which $\left(\frac{\Delta C_{wi}}{\Delta C_{wf}}\right)$ is equal to the gradient of the plot of C_{wi} against C_{wf}.

4.2.1.4. Solid Diffusion

Where solid diffusion is occurring there will be continual dissolution of the chemical into the leachate. The rate of dissolution is likely to vary with time, but may vary little over the relatively short test period. Where this occurs, the equilibrium conditions at the end of the test will be a continually increasing contaminant concentration rather than a constant concentration. This can be identified by considering the relationship between the contaminant concentration in the leachate and time.

4.2.2. Infiltration Test

While the tank test has been used initially to determine parameters for simulations, the infiltration test has been used to provide verification of these parameters in conditions more closely representative of those found in-situ, and aid in identifying the dominant processes. Given the impact of time limited interaction between the runoff and aggregate, and the affects of advective dispersion within the sample it is not possible to use the infiltration test alone to determine values for K_d and C_{si}. However, as the test conditions are more alike to those found in-situ, the test does provide evidence that the results obtained in the tank tests are broadly similar to those that would be encountered in practice.

When comparing the results of the tank test and infiltration test the first aspect considered is the overall mass of contaminant sorbed or leached from the sample ($M_{\Delta C}$). This is given by:

$$M_{\Delta C} = \sum_{b=i}^{8} \left(C_b - C_i\right)V \qquad \text{Equation 4.20}$$

For which b is the number of the bed volume, C_b the concentration in the outflow of bed volume ‘b’, C_i the concentration of the inflowing water and V the bed volume.

As described in the previous chapter, samples used in the infiltration tests are taken from a Type 1 sub-base that has been passed through a 2mm sieve, excluding the reclaimed foundry sand. This must be considered as it has a significant impact on the relative surface area per unit mass of the sample. For the Type 1 grading used in this study $24^{\%}$ passes the 2mm sieve, and is therefore used in the infiltration test. However, this portion of the aggregate makes up 95.2% of the aggregate surface area, as described in Chapter 3.5.3. Therefore where a sample is comprised of $100^{\%}$ material passing the 2mm sieve it will have $397^{\%}$ of the surface area of an equivalent mass of unsieved sample, i.e. the ratio of aggregate mass in the infiltration tests and tank test of equal surface area is 1:3.97.

Using this, the effective concentration, per kg of Type 1 sub-base aggregrate, leached or sorbed during the infiltration test (ΔC_a) can be calculated using Equation 4.21, assuming that the magnitude of the reaction relates directly to the available surface area over which it may occur.

$$\Delta C_s = \frac{3.97 M_{\Delta C}}{8 M_s V} \qquad \text{Equation 4.21}$$

This value can be compared to the values derived from the tank leaching test. For each material different values can be obtained assuming both salt dissolution and partitioning.

4.2.2.1. Partitioning

Where partitioning occurs it is assumed that it will be governed by Equation 4.3 as described previously. The theoretical value for the effective leached concentration, assuming partitioning is the dominant process, can be calculated using the derived parameters and based on the following relationship:

$$\Delta C_s = \frac{C_{wi} V}{\left(\dfrac{V}{K_d} + M_s\right)} + \frac{C_{si} M_s}{\left(\dfrac{V}{K_d} + M_s\right)} - C_{si} \qquad \text{Equation 4.22}$$

However, it should be noted that this assumes that equilibrium conditions are obtained by the end of the infiltration test. In reality this may not always be the case. It is possible to estimate the progression towards equilibrium by considering the change in outflow concentration in each step of the infiltration test.

Where equilibrium has not been obtained the magnitude of the effective leached or sorbed concentration will be less than that obtained in the tank test.

4.2.2.2. Salt Dissolution

Given the reduced liquid to solid ratio, where salt dissolution occurs it will result in a more significant increase in the chemical concentrations than in the tank test. Assuming that the solubility limit of the solution is not reached, there is sufficient time for dissolution to occur and that salt dissolution is the dominant process, it is anticipated that the effective leached concentration will be the same as that in the tank test.

4.2.2.3. Biodegradation & Solid Diffusion

It is possible that biodegradation and solid diffusion will also occur during the infiltration test. However, given the test period this is unlikely to have a noticeable impact on contaminant concentrations. Consequently these have not been considered in the analysis.

4.2.3. Metal Sorption Test

With regard to the principles of the test procedure and the governing equations, the metal sorption tests are the same as the tank tests. What variation there is between these two tests, lies primarily in the nature of the materials being tested. In the case of the metal sorption tests the mass of metals in the leachate are significantly greater than the mass within the aggregate.

4.2.3.1. Partitioning

The metal sorption test is in principle a batch test and the results may be interpreted in the same manner as the tank test. However, it is noted that particularly high concentrations of the metals were used in the test liquid and in general these are absorbed strongly by the solid phase. Where the initial contaminant mass in the liquid is significantly greater than that in/on the solid phase, it is possible to estimate the sorption coefficient from a single result rather than the trends produced by a set of results.

i.e. based on Equation 4.12 if;

$$C_{wi}V >> C_{si}M_s \qquad \text{then} \qquad C_{wi} >> \frac{C_{si}M_s}{V + K_d M_s} \qquad \text{Equation 4.23}$$

then;

$$C_{wi} \cong C_{wf}\left(1 + \frac{K_d M_s}{V}\right) \qquad \text{Equation 4.24}$$

and;

$$K_d \cong \frac{V\left(\frac{C_{wi}}{C_{wf}} - 1\right)}{M_s} \qquad \text{Equation 4.25}$$

4.2.3.2. Salt Dissolution

Where salt dissolution occurs the interaction between the aggregate and runoff will be the same as that identified for the tank test. The concentration of salts within the solid matrix may be calculated using Equations 4.16 to 4.17.

4.2.3.3. Biodegradation and Solid Diffusion

As with the infiltration test it is possible that biodegradation and solid diffusion will also occur during the metal sorption test. Due to the test period this is unlikely to have a noticeable impact on contaminant concentrations. Consequently this is not considered in the analysis.

4.3. Results

Full results of the tests carried out are included in Appendices A to C. These have been analysed using the methods described above, and the results of this analysis are summarised in this sub-chapter.

Appendix A relates to the tank tests and includes charts showing the variation in the chemical determinants (contaminant concentrations, pH and conductivity) with time. Appendix B shows the changes in the chemical determinants between the leachate entering the sample and that leaving it, i.e. a positive value indicates that leaching has occurred and a negative value that sorption has occurred. Appendix C shows the analysis charts plotting the initial concentration in the tank and metal tests in relation to the final concentration. A control line is also shown for which the initial concentration is equal to the final concentration, i.e. values above the line indicate net leaching and values below the line indicate net sorption.

Tables 4.2 to 4.5 give the modelling parameters derived from the tank (partitioning, salt dissolution and biodegradation) and metal sorption tests (partitioning). These give the calculated modelling parameters for each process, and where possible the R^2 measurement of the goodness of fit for that process.

It is assumed for the metals that partitioning is the dominant process. Although no additional infiltration testing has been carried out to confirm this it is supported by in-situ monitoring (Legret 2005), during which significant adsorption was noted to occur as runoff infiltrated through the pavement body.

Aggregate		Sodium			Chloride			Nitrate			Ammonia		
		K_d (l/kg)	C_{si} (mg/kg)	R^2	K_d (l/kg)	C_{si} (mg/kg)	R^2	K_d (l/kg)	C_{si} (mg/kg)	R^2	K_d (l/kg)	C_{si} (mg/kg)	R^2
Limestone	New	0.58	53.62	0.999	1.19	351.27	0.994	-	-	-	84.71	59.58	0.738
	Old	1.01	32.82	0.999	4.10	90.05	0.999	-	-	-	57.22	20.77	0.950
IBAA	New	0	807.8	0.992	0	1783	0.998	-	-	-	0	52.18	0.999
	Old	0.02	125.09	0.999	0.55	182.28	0.995	-	-	-	101.95	122.80	0.275
RFS	New	2.68	562.13	1.000	0	84.66	0.999	0	29.6	0.957	68.11	597.71	0.967
	Old	0	51.96	1.000	1.30	159.70	1.000	0	20.8	0.895	33.19	57.77	0.903
BFS	Old	0.04	0	0.999	1.61	161.13	0.999	-	-	-	0	37.228	0.025

Table 4.2 , Results of tank test analysis assuming partitioning.

Aggregate		Sodium		Chloride		Nitrate		Ammonia	
		C_{si} (mg/kg)	R^2	C_{si} (mg/kg)	R^2	C_{si} (mg/kg)	R^2	C_{si} (mg/kg)	R^2
Limestone	New	16.2	0.999	207.6	0.995	124.3	0.840	-	-
	Old	-	-	-	-	82.8	0.762	-	-
IBAA	New	1404.1	0.957	3109.1	0.943	22.4	0.854	80.5	0.978
	Old	124.1	1.000	118.7	0.999	30.7	0.834	-	-
RFS	New	339.3	0.993	203.1	0.998	29.1	0.986	103.0	0.976
	Old	155.3	0.997	13.7	0.997	50.7	0.913	-	-
BFS	Old	-	-	-	-	108.5	0.864	-	-

Table 4.3 , Results of tank test analysis assuming salt dissolution.

Aggregate		Sodium		Chloride		Nitrate		Ammonia	
		k mg/day	$T_{1/2}$ days	k mg/day	$T_{1/2}$ days	k mg/day	$T_{1/2}$ days	k mg/day	$T_{1/2}$ days
Limestone	New	0.0005	1366.5	0.001	673.4	-	-	0.030	23.4
	Old	0.0009	789.0	0.003	208.3	-	-	0.024	28.7
IBAA	New	-	-	-	-	-	-	-	-
	Old	0.00001	38789	0.0005	1417.8	-	-	0.032	21.5
RFS	New	0.002	309.1	-	-	-	-	0.026	26.2
	Old	-	-	0.001	616.6	-	-	0.017	39.7
BFS	Old	1.58 x10^{-5}	43726	0.0006	1075.6	-	-	-	-

Table 4.4 , Results of tank test analysis assuming biodegradation.

Aggregate		Copper		Cadmium		Lead	
		Kd Low	Kd High	Kd Low	Kd High	Kd Low	Kd High
Limestone	New	35.59	11109	1.40	69.43	28.30	10.11
	Old	28.86	15.72	331.33	87.29	18.62	5.84
IBAA	New	25.55	234.13	20.73	8.67	1.41	25.62
	Old	11.78	26.37	12.93	5.49	2.43	3.65
RFS	New	498.0	90.20	2855	268	>500	9998
	Old	4.85	0.74	16.18	16.71	-0.82	0.55
BFS	Old	78.97	3.67	6.89	4.94	9.98	23.25

Table 4.5, Metal Sorption Results

Low and high concentrations used in tests are as detailed in Chapter 3.4.

It is clear from the results shown in Tables 4.2 to 4.5 that in some cases the behaviour demonstrated in the tank tests could be reasonably explained by several processes. To assist in determining which is the most significant, the results of the infiltration tests are compared with those predictions based on the tank test for partitioning and salt dissolution. These values are as shown in Table 4.6.

Aggregate		Effective Leached Concentration (mg/kg)											
		Sodium			Chloride			Nitrate			Ammonia		
		m	p	s	m	p	s	m	p	s	m	p	s
Limestone	New	17	29	16	82	273	208	6	-	124	0.7	-40	-
	Old	4	-10	-	4	-181	-	0.5	-	83	2	-47	-
IBAA	New	682	808	1404	1892	1783	3109	14	0	22	20	52	81
	Old	32	124	124	22	146	119	1	0	31	0.7	2	-
RFS	New	99	448	19	-2	85	203	16	30	29	22	517	103
	Old	-12	52	3	-14	74	14	-0.2	21	51	1	19	-
BFS	Old	1.1	23	-24	22.8	-51	-17	1.9	-	108	1.7	-	-10

Table 4.6, Results of infiltration test analysis.

m is the measured effective leached concentration, p the calculated result assuming partitioning and s the calculated result assuming salt dissolution.

The above results have been assessed qualitatively to determine which is most likely to be the dominant interactive process for each material, and what values can be used when modelling that are both realistic and conservative. The results of this analysis are shown in Table 4.7 and 4.8.

Where results were similar for all models or none provided a good fit, the salt dissolution model has been selected. Using this model there is generally a slight decrease in the available concentration of contaminants. However, as none will be retained in the solid matrix this will generally provide a more conservative approximation.

To determine appropriate modelling parameter for metal sorption the average K_d value was taken for both the new and old samples of each material and contaminant. The lesser of the values for the new and old samples was used to ensure a conservative approximation for modelling.

Aggregate	Interaction Type and Parameters			
	Na	Cl	NO_3	NH_4
Limestone	P ($K_d = 0.58$, $C_{si} = 53.62$)	P ($K_d = 1.19$, $C_{si} = 351.27$)	S ($C_{si} = 124.3$)	B ($k = 0.029$)
IBAA	S ($C_{si} = 807.8$)	S ($C_{si} = 1783$)	S ($C_{si} = 22.4$)	P ($K_d = 101.95$, $C_{si} = 122.8$)
RFS	S ($C_{si} = 339.3$)	S (Csi = 203.1)	S ($C_{si} = 29.1$)	P ($K_d = 33.19$, $C_{si} = 597.71$)
BFS	P ($K_d = 0.04$, $C_{si} = 0$)	P ($K_d = 1.61$, $C_{si} = 161$)	S ($C_{si} = 108.5$)	P ($K_d = 0$, $C_{si} = 37.2$)

Table 4.7 , Anticipated interactive processes for each material and contaminant, and modelling parameters.

For the interaction type P is partitioning, S is salt dissolution and B biodegradation.

Aggregate	Kd (mg/l)		
	Cu	Cd	Pb
Limestone	22.29	12.23	209.31
IBAA	19.08	10.20	3.04
RFS	2.80	16.45	-
BFS	41.32	5.92	16.62

Table 4.8, Modelling parameters for metal partitioning.

4.4. Conclusions

Conclusions have been reached based on the analysis described in this chapter and are as follows.

Firstly, that a range of reactions may be occurring when aggregate and runoff come into contact. However, it is not always clear which, if any, is dominant.

Modelling parameters have been identified for each of the processes and a qualitative assessment has identified which seems to best fit the available data. This analysis has not considered which is likely to be the most conservative of the viable options.

Secondly significant sorption has been found to occur when some aggregates and contaminants interact. This supports the theory that aggregate sorption may have a significant impact on the contaminant transport regime, and the use of leaching tests alone may be overly conservative when assessing the potential impact of a highway on groundwater.

It should be noted that only a limited number of interactive processes have been considered by this study. These processes have been selected as they are those that are used by the modelling software described in Chapter 6 of this report, and the testing was carried out with the intention of deriving suitable modelling parameters to be used with this software. Future work could give consideration to alternative degradation processes, e.g. a constant rate of biodegradation that may be encountered where biodegradation is controlled by the availability of oxygen.

5. Soil Sorption Analysis

During the initial stages of this project a range of simulations were carried out that considered the impact of various parameters on the transport of contaminants in the pavement sub-grade. These are described in Carretta (2007) and chapter 7.1 of this thesis. These parameter analyses indicated that the single most significant parameter in determining the extent of contaminant spread was the sorption coefficient of the sub-grade.

This parameter was identified as being the most variable of those included in the sensitivity study. It also had the most significant impact on the extent of contamination. As a result of this it was decided that a study should be carried out to consider the methodology for the determination of suitable values to be used for this parameter.

Using parameter values based on literature relating to previous studies the modelling described above identified a sandy sub-grade as being the only soil type in which there is a significant risk of groundwater contamination occuring. As a result this study focused on local sandy soils although two other soil types, both a clay and a loam, were considered to provide confirmation of this.

As well as focusing on sandy soils, the range of contaminants considered in this study was also restricted. Only sodium, chloride and cadmium were considered. The reasoning for this is that based on the literature review and the results of the runoff and aggregate interaction study, these were considered to be the most mobile of the contaminants considered, and therefore those most likely to cause contamination.

Additional emphasis has been placed on the analysis of the results for cadmium sorption. The literature review indicated the sorption coefficient for cadmium is highly variable, and consequently accurate determination of appropriate modelling parameters is likely to have a more significant impact on the results of modelling.

Many additional studies looking at the sorption of contaminants by soils were found. Although none of these looked at either the contaminant mixtures typically found in runoff or leachate from aggregates, i.e. similar to those that may be encountered in the highway environment, they do give some impression of the potential variation in parameter values. The values for Kd vary hugely between the different contaminants and different soils.

Christensen et al. (2000) carried out a study looking at the sorption of cadmium and nickel by sandy aquifer materials. 18 samples were taken from 12 different sites in Denmark, all predominantly sand in their constitution. Despite the soils having similar classifications the sorption coefficient varied significantly; over three orders of magnitude between the upper and lower limit values. In the case of cadmium the sorption coefficient varied between 2-1770 l/kg, for nickel it varied between 3-7250 l/kg.

Chang et al. (2001) carried out a study looking at the sorption of copper and cadmium by predominantly silty clayey soils. In this case the samples were taken from a single site but at a range of depths. In this case it was found that the soil sorption parameter varied little with values ranging between 5.33-9.63 l/kg for copper and 2.71-5.04 l/kg for cadmium.

5.1. Sites

A range of sites was considered for this study. The sites and the soils collected from these sites are described below.

5.1.1. Sand

The sandy soils used for this study were all collected from sites overlying the Sherwood Sandstone bedrock. As well as providing a local source of sandy soil for the analysis, the Sherwood Sandstone is the underlying bedrock to sections of the M1 and A1; two of the principal North-South highways in the UK. It is also an important local aquifer with the associated area being classified as a total catchment groundwater protection zone. There are a number of groundwater abstraction points within the aquifer, with associated inner and outer source protection zones. Some of these underlie the A1 and M1. As a result, the parameters derived from this study can be used as a reasonable estimate of those that may be encountered beneath the relevant sections of those highways.

Once collected the samples were analysed for their particle size distribution using dry sieving for the sand and gravel particles and hydrometer sedimentation for the fines (according to BS 1377-2:1990). Atterberg limits were also determined for the samples. This has allowed more detailed characterisation of the soils, as well as comparison of the sorption coefficients with other soil characteristics.

5.1.1.1. Blidsworth, Nottinghamshire.

This site is located within a rural area and samples were excavated using a hand auger. A small road is located a short distance to the south of the augerholes and agricultural fields to the north south and west. Two holes were excavated at this site approximately 10m apart, and samples of the sandy soil were taken from these at a depth of circa 0.5m. The soil at this site was a dark brown non-cohesive loosely packed gravelly silty fine to coarse sand. Gravel was generally rounded and of various lithotypes.

5.1.1.2. Haywood, Nottinghamshire.

This site is located within a rural area and samples were excavated using a hand auger. A crossroad is located a short distance to the west of the augerholes with agricultural fields in all directions. Two augerholes were excavated at this site, approximately 10m apart and samples of the sandy soil were taken from these at a depth of circa 0.5m. The soil at this site was a dark grey brown non-cohesive loosely packed gravelly silty fine to coarse sand. Gravel was generally rounded and of various lithotypes.

5.1.1.3. Lichfield, Nottinghamshire.

The site is located within a residential area of an army barracks. Samples were taken from an excavation at this site into the Sherwood Sandstone bedrock. Samples were taken from depths of 0.5m and 1.5m. The soil was a red weathered silty gravelly sand. Gravel included angular red sandstone and rounded grains of various lithotypes.

5.1.2. Finer soils

In addition to the sand sampled for this study, samples of a loam and clay with a greater fine content were also collected, to act as a reference.

5.1.2.1. University Campus, Nottingham.

A single borehole was excavated on the university campus, and a dark brown non-cohesive loose silty clayey sand sample was collected at a depth of 0.5m

5.1.2.2. Leeming, Yorkshire.

The site was located within a residential area, adjacent to a tennis court. A trial pit was excavated to a depth of 2m, with a sample taken at a depth of 1.2m. The sample taken was a firm blue grey clay, derived from a glacial lake deposit.

5.2. Test Procedure

The following sub-chapter gives details of the test procedure used for the soil sorption analysis.

5.2.1. Equipment

The equipment required for the collection of samples comprised:

- 2m manual auger with 70mm auger head.
- Sealable sample storage bags.

The equipment required for the preparation of the soil comprised:

- Oven set to 105°C.
- Sample trays.
- Scales accurate to 0.1g.
- High-density polyethylene sample bottles.

The equipment required for preparation of the sorption solutions comprised:

- Sodium chloride and cadmium nitrate salts.
- Purified water.
- Scales accurate to 0.001g.
- 100ml glass measuring cylinder accurate to 1ml.
- Glass beaker.
- 2ml pipettes accurate to 0.01ml.
- Pi-pump.

The equipment used to carry out the sorption tests comprised:

- High-density polyethylene test bottle.
- Timer accurate to 1s over a period of 24 hours.
- Vacuum filter to 0.45 microns.
- Ion selective electrodes for analysis.

5.2.2. Methodology

The methodology for the tests was as follows:

1. 20 no. 50g soil samples were weighed out and bottled seperately.
2. 5 no. 100ml solutions were prepared of each of 1,000ppm NaCl, 100ppm NaCl, 100ppm Cd and 10ppm Cd were prepared.
3. The solutions were added to the soil samples.
4. Each bottle was agitated manually for 10 seconds.
5. The bottles were then left to stand for 24 hours +/- 1 hour.
6. After 24 hours the solutions were separated from the soils by filtration.
7. The ion concentrations in the solutions were then measured using the ion selective electrodes.

5.2.3. Limitations

There are several limitations relating to this test procedure. The test conditions are such that the soil is completely saturated with a high liquid to solid ratio, the solution contains only one chemical salt at concentrations greater than those encountered in highway runoff and aggregate leachate, it has hydrostatic conditions, a controlled contact time, it is carried out at room temperature, etc. In-situ conditions are likely to vary significantly from this being unsaturated with a low liquid to solid ratio, infiltrating water is likely to have a complex chemical constitution, the water will be moving, and the remaining parameters will be highly variable.

The variability between the test conditions and those found in-situ mean that it is very difficult to draw definitive material characteristics from this study. However, these limitations are, to some extent, mitigated by the objectives of the study. In this case the principal objective is not to characterise the Sherwood Sandstone and overlaying soils for specific detailed assessment, but rather to assess the general material variability with regards to sorption both within sites and between different sites overlying the Sherwood Sandstone geological stratum.

As described in the previous chapters there are also limitations regarding the accuracy of the electrodes used to analyse the solutions.

The limitations listed above should be considered when analysing results.

5.3. Results

The objective of this study was to assess the sorption coefficient (Kd) of sandy soils. It has been necessary to calculate this from the concentrations resulting from the sorption tests. In doing this it has been assumed that there is no pre-existing contamination of the soil sample. Based on this assumption the sorption coefficient can be calculated using Equation 4.25, as described in the previous chapter of this thesis.

The results of this analysis are summarised in Table 5.1 showing the mean and standard deviations of the calculated sorption coefficients.

		Kd (Cd)		Kd (Na)		Kd (Cl)	
		Mean	SD	Mean	SD	Mean	SD
Blidsworth A	Hi	81.72	15.74	0.45	0.05	n/a	n/a
	Lo	43.47	17.07	2.49	0.16	n/a	n/a
Blidsworth B	Hi	20.65	6.08	0.48	0.12	n/a	n/a
	Lo	6.82	1.67	3.79	0.30	n/a	n/a
Haywood A	Hi	68.28	27.23	0.38	0.11	n/a	n/a
	Lo	26.85	8.23	1.17	0.23	n/a	n/a
Haywood B	Hi	29.09	3.81	0.27	0.03	n/a	n/a
	Lo	57.30	14.61	0.91	0.33	n/a	n/a
Lichfield	Hi	5.83	2.20	0.45	0.06	n/a	n/a
	Lo	9.23	2.74	3.15	0.15	0.03	0.09
University Park	Hi	146.8	56.5	0.8	0.19	0.2	0.18
Leeming	Hi	84.3	33.0	-	-	-	-

Table 5.1, Soil sorption values for samples from each site.

Hi represents the high concentration mixture, Lo the low concentration mixture, Mean the average, and SD the standard deviation. Kd values are in l/kg.

Statistical analysis has also been carried out on the results from each site in an attempt to characterise the range of sorption values encountered, such as distribution type, mean, and standard deviation. The distribution for each site has been compared to the normal, log normal and gamma distributions. The χ^2 test has been used to assess the goodness of fit. The χ^2 test gives a value ranging between 0 and 1, for which 0 indicates no fit between the hypothetical model and the data and 1 indicates a perfect fit. The results of this analysis are summarised in Table 5.2 and 5.3.

	Normal			Lognormal			Gamma		
	μ	SD	χ^2	μ	SD	χ^2	α	β	χ^2
Blidsworth	38.2	31.1	0.477	1.41	0.43	0.908	1.51	25.4	0.734
Haywood	45.4	23.5	0.049	1.60	0.22	0.138	3.72	12.2	0.040
Lichfield	5.83	2.20	0.561	0.745	0.18	0.553	6.53	1.15	0.556

Table 5.2, Statistical distribution of Cd sorption at each site.

μ is the mean, SD the standard deviation (both in l/kg), α and β the gamma distribution parameters and χ^2 the probability of a set of values drawn from such a distribution deviating as much as the actual distribution.

	Normal			Lognormal			Gamma		
	μ	SD	χ^2	μ	SD	χ^2	α	β	χ^2
Blidsworth	1.80	1.46	0.011	0.075	0.43	0.136	1.53	1.18	0.011
Haywood	0.68	0.43	0.112	-0.255	0.29	0.091	2.57	0.27	0.091
Lichfield	1.80	1.43	0.027	0.073	0.45	0.027	1.59	1.13	0.004

Table 5.3, Statistical distribution of Na sorption at each site.

μ is the mean, SD the standard deviation (both in l/kg), α and β the gamma distribution parameters and χ^2 the probability of a set of values drawn from such a distribution deviating as much as the actual distribution. A negative value indicates that leaching has occurred.

It should be noted that only 10 samples each were tested from Lichfield, Nether Broughton and University Park. This reduces confidence that the distribution parameters are representative of those found in-situ.

5.4. Analysis and Conclusions

There are several conclusions that can be drawn from the results of this study. The first is that there is significant variability in the sorption values, even comparing samples taken from the same auger hole. The sorption coefficient generally varied by up to one order of magnitude between the minimum and maximum values. This would seem to indicate that there is likely to be significant variation in in-situ sorption parameters not only between different sites, as indicated by previous studies, but also within sites. The potential impact of this variability is considered in the following sub-chapter.

The second conclusion is that there appears to be limited correlation between sorption coefficient and the fines content of soils. It is noted that the soil taken from University Park and Leeming, that have a greater fine content than the sandy soils, also have a greater sorption coefficient. Likewise the sample from Lichfield has a particularly low fines content and has a lower sorption coefficient. However, as shown by Figures 5.1 and 5.2 there is still significant deviation from the correlation relationship. It is expected, where the soil contains more fine particles it will have a greater sorption coefficient as it will have a greater surface area onto which the contaminants can be adsorbed. The lack of correlation relating to samples collected from Haywood and Blidsworth may relate to the limited variation in the clay fraction of the samples. As the fine content is reasonably similar it is possible that other unrelated factors are have a more significant influence of the results.

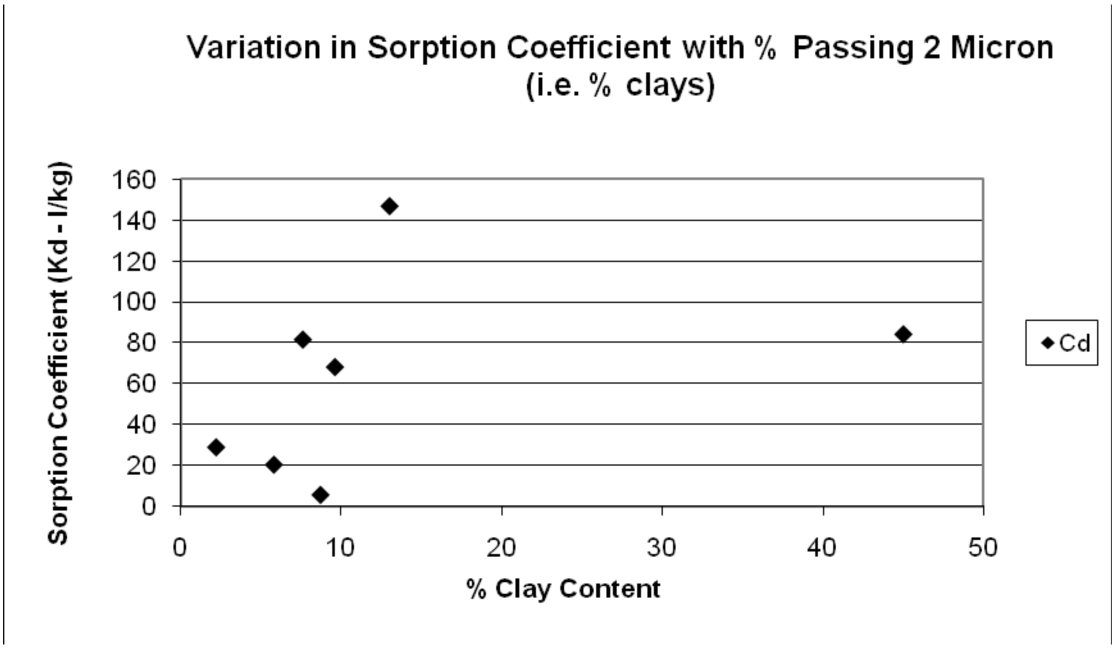


Figure 5.1, Plot of clay content against average sorption coefficient for cadmium

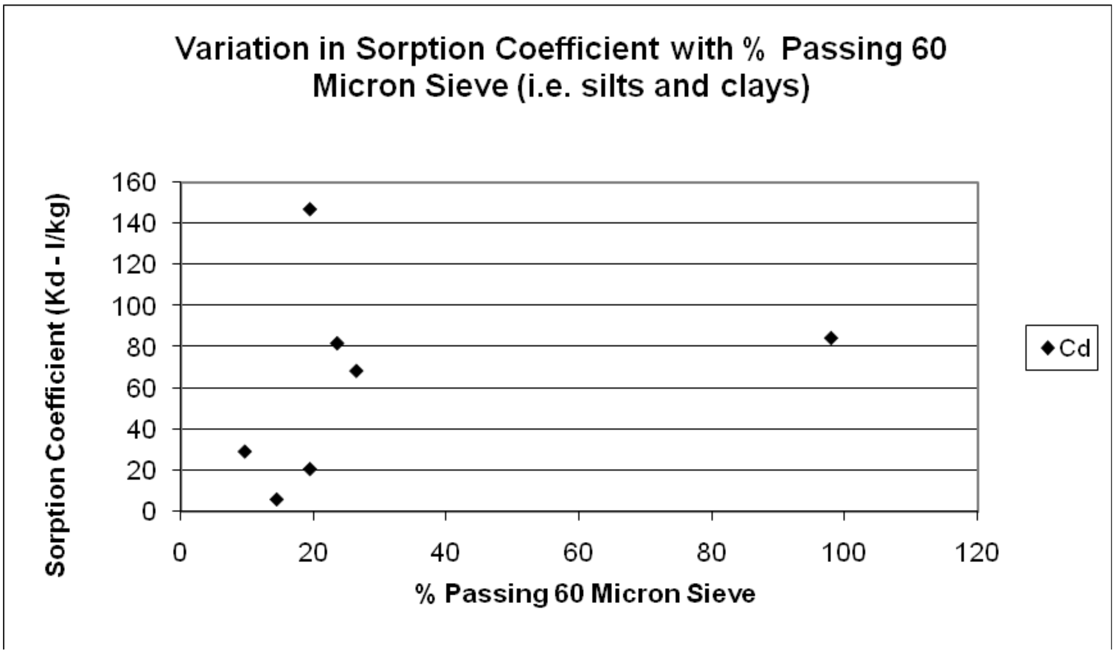


Figure 5.2, Plot of fines content (fraction passing 63 micron sieve) against average sorption coefficient for cadmium.

The third conclusion is that there is a poor fit between the sample distributions and the fitted distributions. It is possible that this relates to the use of varying contaminant concentrations in the solutions being tested. This is a significant modification to the test conditions and consequently even when identical samples are taken, some variation is expected.

Where different concentrations are used there are two known ways in which they can have an impact on the measured Kd value of the soil.

The first is that there is a potential for error in the readings of the concentrations. The software used to measure the voltages recorded across the ion selective electrodes assumes a linear relationship between voltage and concentration, however in reality the relationship is non-linear. As a result of this, where the concentration is particularly low the electrodes will often overestimate the reading leading to an artificially low sorption value.

The second is in the chemical interaction between the contaminant and the soil. Although a linear Kd has been assumed, i.e. the same proportion of contaminant is adsorbed irrespective of the concentration, this is not always the case in reality. It is often the case that as the concentration of the contaminant increases, more of the sorption sites on the soil particles will be ‘occupied’ and there will be fewer free sites remaining. This leads to greater competition between the contaminants remaining in solution for the available sites and consequently a smaller proportion being adsorbed. In some cases there will also be more sorption at higher concentrations, for example where the sorption occurs as a result of precipitation and the solubility in solution rather than sorption to the soil particles is limited.

It most cases it is likely that both of the above processes will be having an impact on the results. Depending on which has the most significant impact the test will indicate either higher or lower sorption at lower concentrations. Where the test indicates higher sorption this is a reasonable estimate of the likely sorption within the sub-grade as it caused by an actual increase in the sorption at the lower concentration. Given that the maximum concentrations detected as a result of leaching or present in runoff are several orders of magnitude less than those used in the test, it is reasonable to use the increased value as a conservative estimate.

5.4.1. Analysis of the impact of a random distribution to model sorption

This variation in sorption capacity will have a significant impact on the potential for groundwater pollution within the sub-grade. Simulations undertaken prior to this study (Dawson et al. 2006, Dawson et al. 2008) have made the conservative assumption that most sensitive sub-grades can be represented using the lower bound values for the sorption coefficient as found in literature review. However, this study would seem to indicate that such a sub-grade may be better represented by a distribution of values for which the lower bound value corresponds with that found in literature.

It is not possible based on the data available in literature at this time to determine a generic range of sorption values for the most sensitive sites. However, using the samples obtained for this study it has been possible, as described previously, to produce distributions for the sites visited.

The impact of using a distribution, as an alternative to a constant value based on the lower bound, is assessed using a simple 1-dimensional model. The model considers sorption within a generic column, with generic units (i.e. l = length, v = volume = l^3, m = mass, t = time) for a real column these can be substituted for appropriate units provided that consistency is maintained.

The transport of a generic contaminant is considered across a column of length 100l divided into 100 elements, with the sorption coefficient for each stochastically generated from the appropriate distribution. In this case the log-normal distribution is used, with parameters as given for soil samples from the Blidsworth site, shown in Table 5.2. 50 of the columns have been randomly generated. Each has then been modelled using a finite element model to simulate the flow of water through the column with a concentration of 100. The volume of contaminated water required to obtain a concentration of 50 at the far end of the section was recorded, i.e. the volume of contaminated water required for the mid-point of the contaminant front to reach the base of the column.

The distribution used for this case study is that of the log normal distribution at Blidsworth. This has been selected as it had the best fit of any of the tested distributions. In reality there is likely to be a wide range of distribution parameters for different soils, these will vary significantly with soil type and both recent and geological history.

The values determined for the flush volume required for the contaminant front to reach the base of the column were then analysed. As with the Kd values for the soil, the log normal distribution was shown to have the closest fit to the actual distribution, see Table 5.4.

Normal			Lognormal			Gamma		
μ	SD	χ^2	μ	SD	χ^2	α	β	χ^2
6408	3771	0.000	3.758	0.194	0.434	2.88	2219	0.034

Table 5.4, Statistical distributions of flush volume required for contaminant front to reach the base.

μ is the mean, SD the standard deviation (both in l/kg)

Having determined the statistical distributions for both the soil partitioning coefficient, and the flush required for a soil column randomly generated using that distribution. It was also possible to simulate a soil column using a single partitioning coefficient parameter, this was done for the $1^{\%}$, $2^{\%}$, and $5^{\%}$ values for Kd. The flush required for the contaminant front to reach the base of this column was then compared to that of the equivalent stochastically generated columns. The results are as shown in Table 5.5.

Column Type	Probability (%)	Flush
Stochastically Generated Kd	99%	1616200
	95%	1192800
	$50^{\%}$	573000
	$5^{\%}$	275300
	$1^{\%}$	211900
Constant Kd	99%	9674853
	95%	2509341
	$50^{\%}$	96602
	$5^{\%}$	3719
	$1^{\%}$	962

Table 5.5, Comparison of low probability flushes for stochastically generated and constant Kd columns.

It is noted that using a stochastically generated sorption coefficient there is a reduction in the range of calculated flush volumes at each probability. Considering a conservative case, i.e. 1% or 5% probability of occurrence, it is noted that the required flush volume obtained using variable stochastically generated values of Kd are several orders of magnitude greater than those using a constant Kd. From this it can be assumed that the use of a single value for Kd may be excessively conservative.

6. Modelling of Contaminant Transport in Pavements

In addition to carrying out tests to better understand the interaction between aggregates and runoff, this project has also considered the application of this test data to simulations.

Due to the complexity of the simulations it would be impractical, within the time limitations of this project, to develop software capable of analysing water flow and contaminant transport. For this reason it was decided that modeling would be carried out using commercially available software.

This chapter provides details of:

- the requirements of the software for it to be able to accurately model contaminant flow within the pavement sub-base and sub-grade.
- available software for modeling hydraulic flow and contaminant transport.
- the software chosen for use in this in project, including details of modelling parameters and verifications of its functionality.

6.1. Selection of Software for Modelling Contaminant Transport

A number of programs are available commercially for the purpose of modelling groundwater flow and contaminant transport. This sub-chapter describes the requirements of the software to be used in this project, the software available at the time of selection, and details of the software selection.

6.1.1. Project Requirements of Software

For the software to be suitable for this project it was necessary for the software to be able to simulate the conditions found within the highway structure and sub-grade. These conditions are as follows:

- Hydraulic flow in both saturated and unsaturated soils.
- Contaminant leaching and sorption.
- Contaminant advection.
- Transient conditions (i.e. rainfall).
- 3-Dimensional flow.

6.1.2. Commercially Available Software

The following software are a selection of those that were available at the time of investigation.

FEFLOW: This is a finite element flow modelling program. The engine used is based on a Galerkin finite element method for unstructured meshes. The program is capable of dealing with saturated and unsaturated flow, heat and mass transport, 2D and 3D problems, multiple free surfaces, density dependant flow, steady state and transient conditions, advection, hydrodynamic dispersion, linear and non linear sorption and first order chemical non equilibrium.

3D FEMFAT: This is a finite element flow modelling program that uses the Galerkin finite element method to resolve problems. The program is capable of dealing with saturated and unsaturated flow, 2D and 3D problems, density dependant flow, steady state and transient conditions, advection and linear and non linear sorption.

Groundwater Vistas (with MODFLOW SURFACT): This is a program that uses a finite difference method to resolve problems. The engine used is MODFLOW (original, 2000 or SURFACT), Groundwater Vistas serves as an interface to create and visualise input and output data sets. The program is capable of dealing with saturated and unsaturated flow, 2D and 3D problems, density dependant flow, non-aqueous phase liquid (NAPL) flow, linked air and fluid flow, steady state and transient conditions, advection, linear and non linear sorption, and linear and non linear decay.

Chemflux 3D: This is a program that uses the Galerkin finite element method to resolve problems. It is capable of dealing with saturated and unsaturated flow, 2D and 3D problems, steady state and transient conditions, advection, diffusion, linear and non linear sorption and radioactive or biological decay.

SVFLUX 3D: This program uses the Galerkin finite elemet analysis to model problems. The software is capable of dealing with saturated and unsaturated flow, 2D and 3D problems, steady state and transient conditions, anisotropic analysis at any angle, transport and retardation can also be included when combined with Chemflux 3D.

Visual MODFLOW (with MODFLOW SURFACT): This is a program that uses a finite difference method to resolve problems. The engine used is MODFLOW (96 or SURFACT). Visual MODFLOW acts as an interface providing 3D visualisation of input and output files. The program is capable of dealing with saturated and unsaturated flow, 2D and 3D problems, density dependant flow, NAPL flow, linked air and fluid flow, density dependant flow, steady state and transient conditions, advection, linear and non linear sorption, and linear and non linear decay.

HYDRUS 2D: This program uses a finite element method to resolve problems. It uses Richard's equation for saturated and unsaturated flow, and Fickian based advection/dispersion equations for heat and solute transport. The program is capable of dealing with saturated and unsaturated flow, 2D problems, linear and non linear partitioning between the solid, liquid and gas phases, and steady state and transient boundary conditions.

Further information on the above software can be found at the producers and vendors websites as shown in Table 6.1.

	FEFLOW	**3D FEMFAT**	**Groundwater vistas + MODFLOW SURFACT**	**Chemflux 3D**	**SVFLUX 3D**	**Visual MODFLOW + MODFLOW SURFACT**	**MODFLOW SURFACT**	**HYDRUS 2D**
www.scisoftware.com	✓	✓	✓	✓	✓	✓	✓	
www.surfacewater.com	✓	✓	✓				✓	
www.rockware.com	✓		✓	✓	✓	✓	✓	
www.wasy.de	✓							
www.esinternational.com			✓					
www.soilvision.com				✓	✓			
www.waterloohydrogeologic.com	✓					✓	✓	
typhoon.mines.edu								✓

Table 6.1, Websites for supply and more details of modelling software

6.1.3. Software Chosen for this Project

Groundwater Vistas, 3D FEMFAT and Visual MODFLOW, were all capable of simulating the key processes in contaminant transport required for this project. Groundwater Vistas and Visual MODFLOW were favoured over 3D FEMFAT as their capabilities extended further than the key processes. This left open the option of including additional processes (for example biological decay), that although not originally anticipated as an essential aspect of this study, help to increase the realism of simulations, and allows the software to be used for future work in which this may be relevant. Of these Groundwater Vistas (with MODFLOW SURFACT) was chosen for use in this project as it was cheaper yet had the same capabilities.

6.2. Modelling Parameters

This sub-chapter lists the parameters required for modelling groundwater flow and contaminant sorption with MODFLOW SURFACT, how these parameters can be obtained in laboratory and in-situ tests, and typical values based on available literature.

6.2.1. Permeability

Darcy's law dictates that the rate at which water flows through a material is directly proportional to the hydraulic head gradient and the area across which the flow is occurring, the factor linking the two is referred to as the permeability. That is, the greater the permeability the more rapidly a fluid can pass through the material. In mathematical form Darcy's Law is written as:

$$Q = Ak\frac{\delta H}{\delta x} \qquad \text{Equation 6.1}$$

In which Q is the flow of the water, A the area being considered, k the permeability, H the hydraulic head and x distance in the direction of flow.

Although k is often treated as a constant in geotechnical work it can vary depending on the viscosity of the fluid and the saturation. MODFLOW SURFACT allows alternative values to be input for non aqueous liquids to take account of different viscosities. It also allows changes in permeability to be accounted for using the Van Genuchten model, which relates the saturation to both the capillary suction and the permeability (for more details on this model see the section on the Van Genuchten parameters).

6.2.1.1. Experimental Determination of Permeability

Permeability of soil/aggregate samples can be determined by both laboratory and in-situ experiments.

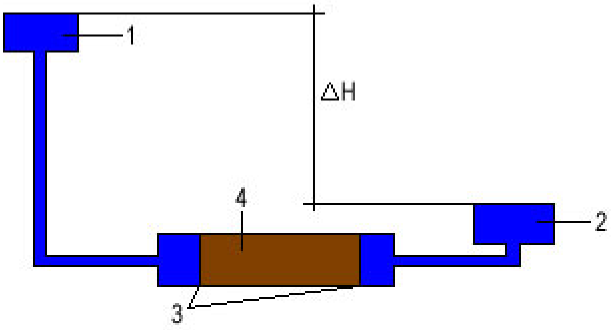


Figure 6.1, Constant head permeameter

A common form of determining the permeability in the laboratory is to use a constant head permeameter (see Fig. 6.1 - 1 and 2 are water tanks, 3 the cell in which the sample is contained and 4 the test sample). By adjusting the elevation of the water tanks a pre-determined head differential (ΔH) can be applied across the sample. To ensure that the head difference remains constant each tank has an overflow, and the elevated tank has water flowing into it at a rate greater than the rate it flows through the sample. As water flows through the sample it overflows from the lower water tank and can be measured at this point.

Knowing the dimensions of the cell (from which the area of flow and the length can be calculated) and the flow rate through the sample, the permeability can be calculated using equation 6.1.

This method of determing the permeability has several substantial drawbacks. The first is that because the soil sample has been excavated from the ground and then placed within a container suitable for the testing equipment, it will have been significantly disturbed and may no longer have the same permeability as it did in-situ. Also the pressure head across the sample is limited by the maximum difference in elevation of the water tanks. In materials with low permeability the flow may be so small that it takes a substantial period of time to obtain a measurable volume of outflow. Another problem is that it only gives the permeability in one direction; in many soils the permeability may vary between the horizontal and vertical planes. Finally, the experiment only gives you an indication of the permeability of the soil at the point it was taken from. Soils generally have significant spacial variations in their permeability, something that is only represented if you take a range of samples to show the distribution of the permeability. It should be noted that for engineered fill there is likely to be much less variation in permeability than there would be for the in-situ soils in the sub-grade.

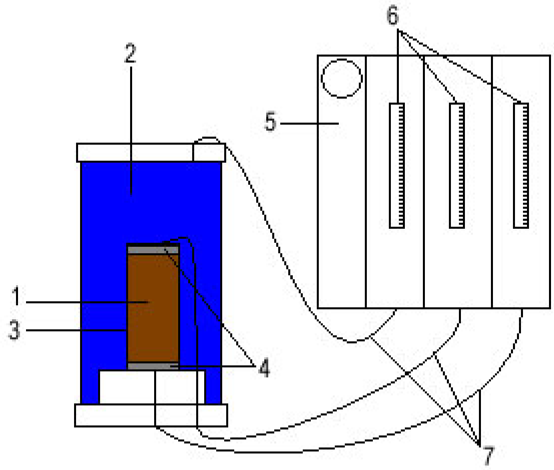


Figure 6.2 Flexible Wall Permeameter

Where the permeability is so low that it is impractical to use a constant head permeameter, it is possible to use a flexible wall permeameter (see Figure 6.2). The basic principles for this are the same as the constant head permeameter. However, in this case the sample (1) is contained within a high pressure cell (2). The confining pressure of the cell allows much higher pressures to be applied to the sample, and therefore a much more significant head difference can be applied across it, the increased hydraulic gradient means that a larger flow of water can be obtained - decreasing the time required to run the test. It should be noted however that the hydraulic gradient obtained will be much greater than those which would occur in roads.

A flexible membrane (3) is used to hold the sample, allowing the pressure in the cell to be transferred onto it. A pressure transducer (5) is used to apply pressure to both the cell and the porous plates (4) above and below the sample. The pressure transducer has separate panels controlling the pressures in the cell and in each of the plates. Each panel is connected by a pipe (7) to the relevant part of the test apparatus to allow the flow of water and the transfer of pressure. The volume of water that has flowed to or from each panel can be measured on the pipettes (6) on each panel. The volume of water flowing from the high pressure end of the sample should be equal to the volume flowing into the low pressure end, and is the volume that has flowed across the sample.

The permeability of soils can be measured in-situ using a double ring permeameter. The apparatus for this is as shown in Figure 6.3.

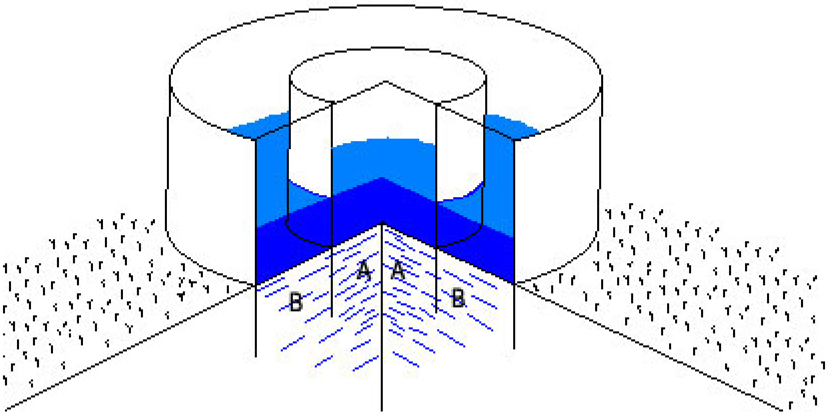


Figure 6.3, A double-ring permeameter.

The two rings are filled with water at the start of the experiment and as the experiment progresses the water infiltrates into the soil below. The rate at which water infiltrates into the soil depends upon the depth of water above the soil (h_w), the capillary suction of the soil (ψ) and the depth of saturated soil below the ring (z).

The purpose of the experiment is to measure the permeability by assessing the rate at which water infiltrates into the soil from the inner of the two rings. The rate of infiltration from the inner ring can be measured using a depth gauge in the inner ring to measure the change in depth with respect to time.

The calculations for this experiment assume that the flow of water is one dimensional, i.e. it only flows vertically. However in reality when water enters a soil at a point it will flow vertically and horizontally. As the surrounding soil will have a lower saturation it will have a stronger capillary suction and will draw water into it from the source. The purpose of the outer ring is to reduce the impact of this suction on the flow of the inner ring. By saturating the surrounding soil it ensures that the major force acting on the water beneath the inner ring is gravity and the accuracy of the one dimensional model is increased.

According to Darcy's Law the rate of infiltration due to gravity is,

$$q = -K\frac{\psi - z - h_w}{z} \qquad \text{Equation 6.2}$$

Initially all three variables have a significant impact on the infiltration of the water. However, as the experiment continues the depth of saturated soil (z) will increase, reducing the significance of the capillary suction of the soil and the head of water in the permeameter.

When z becomes much greater than ψ and h_w then

$$\frac{\psi - z - h_w}{z} \cong 1 \qquad \text{Equation 6.3}$$

and therefore, $q \cong -K$ Equation 6.4

From this we can see that after the experiment has been running for a long period of time the rate of infiltration will become constant and be equal to the permeability of the material being tested.

There are limitations with this experiment that should be noted when it is being used.

The first is that the experiment assumes that the effects of capillary suction and the water pressure head on the surface are negligible when the permeability is calculated. Although their significance may decrease as the experiment continues to run they will always slightly increase the rate of infiltration and as a result lead to overestimation of the permeability.

The second limitation is that the experiment is only feasible for soils within a range of hydraulic conductivities. If the hydraulic conductivity is too high it would be difficult to prepare the test as the rings would drain as fast as, or faster than, they are filled. However, if the hydraulic conductivity is too low the period of time required to allow the infiltration of sufficient water would be too great and other factors, such as the evaporation of water from the rings would begin to have an effect.

The third limitation is that the depth of water in the outer ring should remain as close as possible to that of the inner ring for the duration of the experiment. If there is a variation in these depths then the pressure differential beneath the rings will result in small flows between the rings as well as infiltration into the soil.

Other methods of measuring permeability in-situ include the CSIRO permeameter and the Guelph permeameter.

6.2.1.2. Literature Values of Permeability

Tables 6.2 to 6.4 contain values of saturated permeability (K_s in m/s) from a range of literature sources.

	Terzaghi et al. 1996 typical range		Meyer et al. 1997	
	upper limit	lower limit	μ	SD
Sand	10^{-2}	10^{-5}	8.22×10^{-5}	4.39×10^{-3}
Silt	10^{-5}	10^{-9}	4.89×10^{-7}	2.76×10^{-5}
Clay	10^{-9}	10^{-11}	3.65×10^{-7}	1.08×10^{-8}

Table 6.2, Soil permeability (m/s) by grading classification.

Where μ is the mean and SD the standard deviation

	Lambe & Whitman 1979	
	Min	Max
Fluvial Deposits	2×10^{-4}	4×10^{-3}
Glacial Deposits	$<1 \times 10^{-6}$	2×10^{-2}
Wind Deposits	1×10^{-6}	3×10^{-3}

Table 6.3, Soil permeability (m/s) by formation type.

	Apul et al. 2002*		Jones & Jones 1989		
	Min	Max	Min	Max	μ
Sub-Base Course Aggregates	5.03×10^{-5}	5.85×10^{-2}	1.4×10^{-3}	5.8×10^{-2}	1.7×10^{-2}

Table 6.4, Permeability (m/s) of sub-base aggregates

** Apul et al cited a range of reports giving field measurements of the permeability of sub-base materials, with the minimum and maximum values as given here.*

6.2.2. Porosity

The porosity of a material refers to the proportion of that material that is filled with voids. In geotechnics the porosity generally refers only to those voids that are interconnected, that is those that allow the flow of air and water, as it is these voids that have the greatest impact on the behaviour of the material. In mathematical form;

$$n = \frac{V_v}{V} \qquad \text{Equation 6.5}$$

For which n is the porosity, V_v the volume of interconnecting voids in the soil and V the volume of the soil.

The factors affecting the porosity of a material are the grading of the particle sizes, the particle shapes and the degree of compaction.

6.2.2.1. Experimental Determination of Porosity

To determine the porosity of a material a sample of a known volume is required, this is normally achieved by filling a container of known dimensions and therefore volume. The sample is then fully saturated, and weighed (M_s). After the sample has been weighed it is heated to remove all water in the soil structure and the dry sample is then weighed (M_d). The difference between the saturated and dry weight of the sample is the mass of water in the saturated sample (M_w).

$$M_w = M_s - M_d \qquad \text{Equation 6.6}$$

Knowing the specific gravity of water (G_w) it is possible to then calculate the volume of water (V_w) in the sample.

$$V_w = \frac{M_w}{G_w} \qquad \text{Equation 6.7}$$

As the pores are filled with water when the sample is saturated the void volume (V_v) is equal to the water volume. Based on this, and knowing the total volume of the sample, the porosity (n) can be calculated using Equation 6.5.

6.2.2.2. Literature Values of Porosity

Tables 6.5 and 6.6 contain values of porosity from a range of literature sources.

	Hodnett and Tomasella 2002		Meyer et al 1997	
	μ	SD	μ	SD
Sand	0.410	0.051	0.430	0.060
Loamy Sand	0.438	0.071	0.410	0.090
Sandy Loam	0.461	0.117	0.410	0.090
Loam	0.521	0.124	0.430	0.100
Silt Loam	0.601	0.122	0.450	0.080
Silt	-	-	0.456	0.110
Sandy Clay Loam	0.413	0.074	0.390	0.070
Clay Loam	0.519	0.132	0.410	0.090
Silty Clay Loam	0.586	0.143	0.430	0.070
Sandy Clay	0.460	0.070	0.380	0.050
Silty Clay	0.570	0.117	0.360	0.070
Clay	0.546	0.084	0.380	0.090

Table 6.5, Porosity of soils according to grading.

For which μ is the mean and SD the standard deviation.

	Jones and Jones 1989			Jessep 1998		
	Mean	Min	Max	Mean	Min	Max
Sub-Base Aggregates	0.184	0.130	0.242	0.346	0.250	0.489

Table 6.6, Porosity of base course aggregates.

6.2.3. Van Genuchten Parameters

As stated earlier, the Van Genuchten model predicts changes in the permeability and capillary suction with relation to the saturation of a material. The equation used to predict the permeability of the material is (from MODFLOW-SURFACT version 2.2 manual):

$$k_{rw} = K_s S_e^{\frac{1}{2}} \left[1 - \left(1 - S_e^{\frac{1}{\gamma}} \right)^{\gamma} \right]^2 \qquad \text{Equation 6.8}$$

In which k_{rw} is the permeability for the given saturation (units are length/time), K_s the saturated permeability, γ a dimensionless parameter derived from the input β as shown below, and S_e the effective saturation given by the equation below (from MODFLOW-SURFACT version 2.2 manual) in which S is the saturation and S_r the residual saturation (saturation is unitless).

$$S_e = \left(\frac{S - S_r}{1 - S_r} \right) \qquad \text{Equation 6.9}$$

$$\gamma = 1 - \frac{1}{\beta} \qquad \text{Equation 6.10}$$

The relationship between pressure head (ψ) and water saturation is approximated using the following equation:

$$S_e = \frac{1}{\left[1 + (\alpha h_c)^{\beta} \right]^{\gamma}} \text{ for } \Psi < 0 \qquad \text{Equation 6.11}$$

$$S_e = 1 \text{ for } \Psi \geq 0 \qquad \text{Equation 6.12}$$

In which α (units are 1/length) and β (unitless) are constant parameters for each given material that can be input into the model, and h_c is the capillary head defined as h_c =

h_{ap} - ψ, h_{ap} being the air pressure head, assumed to be atmospheric (i.e. 0) by MODFLOW SURFACT.

6.2.3.1. Experimental Determination of Van Genuchten Parameters

For the parameters to be estimated it is necessary to run a laboratory experiment that measures the variation of either capillary suction or hydraulic conductivity with the saturation of the material.

One method of determining the relationship between suction and saturation is to use a column of the material and analyse its capillary fringe after it has either drawn-in or drained water.

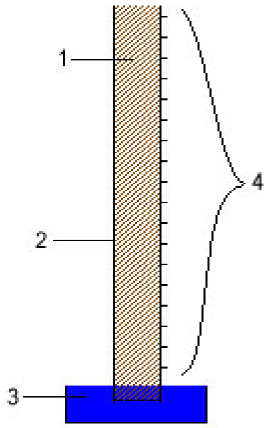


Figure 6.4, Column for the determination of van Genuchten parameters.

Figure 6.4 shows the column test apparatus. The soil/aggregate sample (1) is compacted into the test column (2). The lower end of the column is then placed in a water tank (3) and the material is left undisturbed for a predetermined period of time while it either drains or draws up water. The time period should be sufficient to allow the water to reach static conditions. After this period the saturation should be measured at a range of elevations (4) above the water level.

The lower end of the column should be fitted with a porous cover. The pores should be large enough to allow water to move freely between the column and water tank but small enough to prevent the test material leaching out of the column.

The saturation can be measured either by extracting samples at various elevations and comparing the dry and wet weights, or in the column using time domain reflectometry. The capillary head can be considered equal to the elevation above the water surface. This assumes that the air pressure in the column is atmospheric (i.e. air pressure = 0).

Once the saturation at various capillary heads has been measured, the values can be used to approximate the van Genuchten Parameters.

This has been done by carrying out a least squares analysis of the error (E) in terms of effective saturation and capillary head. For this project three error estimation methods have been used. One looking at the errors in the saturation and capillary head combined, another looking at just the error in the saturation, and one approximating the minimum error to the soil water characteristic curve.

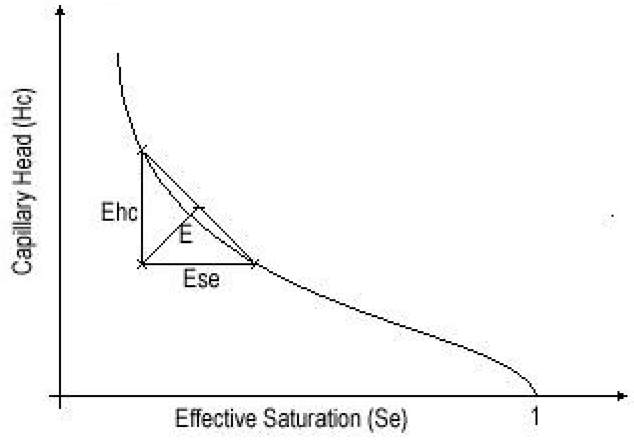


Figure 6.5, Graphical representation of error approximations (E=approximate minimum error)

for the effective saturation and:

$$S_e - \frac{1}{\left[1 + (\alpha h_c)^{\beta}\right]^{\gamma}} = E_{se} \qquad \text{Equation 6.13}$$

for the capillary head:

$$\frac{\left[\left(\frac{1}{S_e}\right)^{1/\gamma} - 1\right]^{1/\beta}}{\alpha} - h_c = E_{hc} \qquad \text{Equation 6.14}$$

As the saturation and capillary head are known an iterative solution can be used to find the optimal values for α and β. The solution is that pair of values which minimizes the squares of the errors (E^2), given:

for the sum of saturation and capillary head errors:

$$E_{hc+se}^{2} = \frac{1}{n} \times \sum_{i=1}^{n} \left[\left(E_{se}^{i} \right)^{2} + \left(E_{hc}^{i} \right)^{2} \right] \qquad \text{Equation 6.15}$$

for the saturation errors:

$$E_{se}^{2} = \frac{1}{n} \times \sum_{i=1}^{n} \left(E_{se}^{i} \right)^{2} \qquad \text{Equation 6.16}$$

for the approximated minimum error:

$$E^{2} = \frac{1}{n} \times \sum_{i=1}^{n} E_{hc}^{i} \cos\left(\tan^{-1}\left[\frac{E_{se}^{i}}{E_{hc}^{i}} \right] \right) \qquad \text{Equation 6.17}$$

From a mathematical perspective, it seems that the first and the third methods would provide the most accurate approximations of the Van Genuchten parameters, as they account for errors in both the saturation and capillary head. However, in reality the most useful approximation is the saturation error. The reason for this is that in most modelling and experimental applications the capillary head is known, and the saturation is being calculated based on this. Therefore the principle interest is how well the model predicts the saturation.

6.2.3.2. Literature Values of Van Genuchten Parameters

The parameters used in the Van Genuchten model have been approximated in many papers for a range of different soil types. Although MODFLOW SURFACT uses the residual saturation (S_r) most of these papers refer to the residual volumetric water content (θ_r). Using the residual water content and the porosity/saturated water content the residual saturation can be calculated as:

$$S_r = \frac{\theta_r}{\theta_s} \qquad \text{Equation 6.18}$$

Table 6.7 gives a range of values for van Genuchten parameters from various sources, α is given in units of m^{-1}, β and θ_r are unitless.

		Hodnett and Tomasella 2002		Meyer et al 1997		Jessep 1998	
		μ	SD	M	SD	Min	Max
Sand	α	3.80	1.53	14.7	2.55		
	β	2.47	0.92	2.67	0.27		
	θ_r	0.04	0.02	0.05	0.01		
Loamy Sand	α	8.37	27.1	12.5	4.04		
	β	1.67	0.34	2.27	0.21		
	θ_r	0.06	0.05	0.06	0.01		
Sandy Loam	α	3.96	3.51	7.57	3.68		
	β	1.55	0.29	1.89	0.16		
	θ_r	0.11	0.07	0.06	0.02		
Loam	α	2.46	1.53	3.67	2.02		
	β	1.46	0.29	1.56	0.11		
	θ_r	0.16	0.08	0.08	0.01		
Silt Loam	α	1.91	1.43	1.93	1.15		
	β	1.64	0.60	1.41	0.12		
	θ_r	0.22	0.12	0.07	0.01		
Silt	α	-	-	1.78	0.01		
	β	-	-	1.38	0.04		
	θ_r	-	-	0.04	0.00		
Sandy Clay Loam	α	6.44	9.52	5.72	3.37		
	β	1.54	0.57	1.48	0.13		
	θ_r	0.15	0.06	0.10	0.01		
Clay Loam	α	3.92	3.38	1.90	1.53		
	β	1.44	0.19	1.32	0.10		
	θ_r	0.23	0.06	0.10	0.01		
Silty Clay Loam	α	2.98	3.10	1.04	0.01		
	β	1.51	0.49	1.23	0.06		
	θ_r	0.27	0.12	0.09	0.01		
Sandy Clay	α	5.09	3.63	2.70	1.64		
	β	1.40	0.20	1.28	0.08		
	θ_r	0.20	0.05	0.10	0.01		
Silty Clay	α	2.58	3.06	0.41	0.26		
	β	1.47	0.24	1.16	0.05		
	θ_r	0.28	0.11	0.07	0.02		
Clay	α	4.63	4.86	0.62	0.76		
	β	1.51	0.65	1.13	0.07		
	θ_r	0.27	0.09	0.07	0.03		
Granite Aggregates	α					5.8	333.4
	β					1.27	2.51
	θ_r					0	1.7
Limestone Aggregates	α					8.8	348.4
	β					1.24	3.08
	θ_r					0	6.4

Table 6.7, Van Genuchten parameters for a range of soils and pavement sub-base aggregates.

**To provide parameters for typical highway sub-base aggregates data was taken from Jessep (1998). Jessep carried out column draw up and drainage experiments to look at capillary rise in limestone and granite aggregates. The results of these experiments related the moisture content (proportion by mass) to the capillary rise (cm). The saturation has been calculated from the moisture content, and this has been used together with the capillary rise to estimate the parameters for the aggregates.*

6.2.4. *Retardation Parameters*

When modelling contaminant transport MODFLOW SURFACT is able to model retardation of contaminants by both sorptive partitioning and biodegradation.

The sorption models used by MODFLOW SURFACT are the linear model and the Freundlich model. Biodegradation is modelled using a linear decay model.

Each of these processes and the methods by which values can be determined are detailed in the previous chapters of this thesis.

6.3. Verification of Software Functionality

Having chosen the software to be used for this project, and investigated the parameters required for its use it was next necessary to verify the functionality of the software.

6.3.1. *Limits of Modelling Parameters*

When carrying out simulations using the software, there are two sets of parameters that must be considered. The first set is the material parameters such as permeability, porosity and sorption coefficient as described in the previous sub-chapter. The second set of parameters is the modelling parameters.

The modelling parameters are those set by the user for the resolution of the simulation. In the case of Groundwater Vistas and MODFLOW SURFACT the software is a finite difference model. That is, the software models material behaviour by considering the simulation are as a network of nodes and then resolving the contaminant flow and transport equations between those nodes. The equations are resolved using an iterative method, with the first iteration accepted for which the model error is reduced below a set limit.

The variables that may be set by the user include the distance between nodes, the acceptable error for each set of iterations, and the time interval over which the flow is being resolved.

6.3.1.1. Acceptable Error Limit and Time Interval

Although the acceptable error and time interval may be set by the user it has been decided not to modify these for the simulations being undertaken. In the case of the acceptable error the potential impact is apparent, in that results obtained are likely to have a greater degree of variability where the error is increased. In the case of the magnitude of the time interval the user does not define a specific value, but rather the limits to a range of values. The software then automatically modifies the time interval within these limits to ensure that results fall within the acceptable error limit.

6.3.1.2. *Finite Difference Grid*

In the case of the distance between nodes this is defined by the user and was investigated as it may have a significant impact on simulation results.

To investigate the potential impact a series of simulations were carried out with the grid size, and therefore the distance between nodes varying between simulations. Simulations considered a single rainfall event affecting a highway with dimensions as shown in Figure 6.6, and material parameters as shown in Table 6.8.

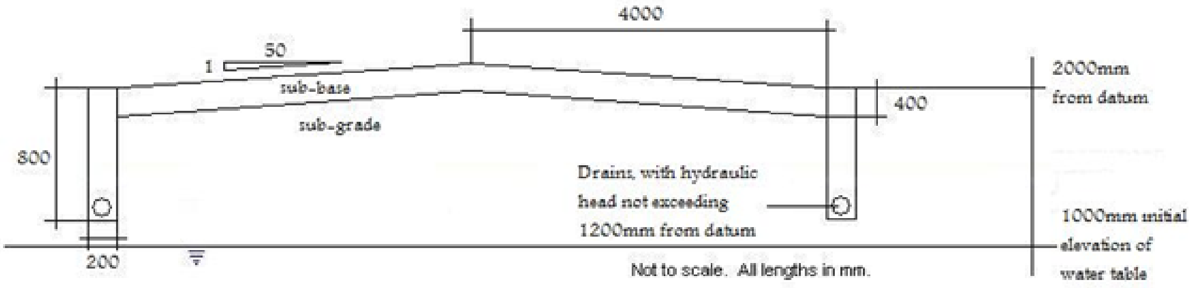


Figure 6.6, Dimensions and characteristics of highway used for simulations.

Material	Permeability (m/s)	Porosity	Van Genuchten Parameters		
			θ_r	α	β
Sub-base	1.7×10^{-4}	0.43	0.01	1	2
Sub-grade	1×10^{-8}	0.43	0.05	0.147	2.67

Table 6.8, Material parameters used for simulations.

The simulation considered a period of 24 hours, with a single rainfall event in the initial 2.5 hours during which the recharge rate is 4mm/hr. All rainfall is assumed to penetrate into the pavement structure, a conservative estimation but may be similar to a pavement with a permeable or highly fractured surface. Simulations were carried out using grid sizes of 20cm, 10cm, 5cm, 1cm and a variable grid with dimensions between 5 and 20cm.

The outflow hydrographs in the drains were plotted for each simulation and are as shown in Figure 6.7.

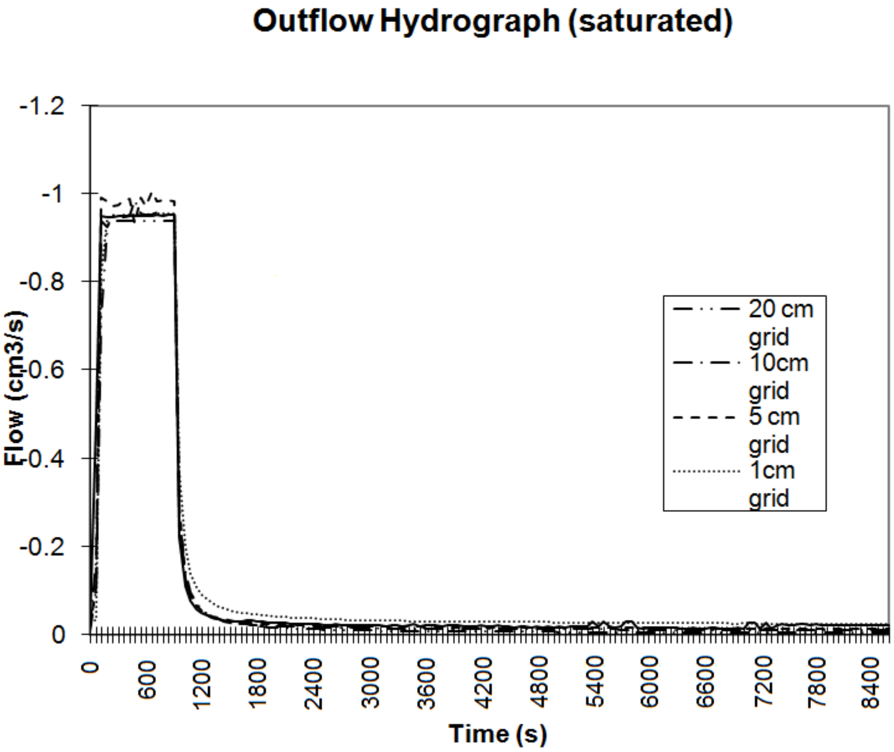


Figure 6.7, Outflow hydrographs for simulated pavement.

It is noted from these results that there is very little difference in the results, irrespective of the grid size used. Further where there are variations in the values obtained there is no link between the variation and the grid size. This would indicate that any grid size within the range assessed is likely to provide similar results.

However, while the numerical data obtained is similar for all grid sizes, the time required to generate the results is not. While the 20cm grid took several minutes to simulate the 24 hour period, the 1cm grid required several days. Consequently it seems apparent that in terms of practical terms a 20cm grid is more efficient for simulations than smaller grids. It is impractical to use larger grid sizes as the grid must have sufficient resolution to allow the model to represent the highway structure.

6.3.2. Verification with Laboratory Test Data

Following the assessment of the software and determination of the limits to modelling parameters, the software has next been compared to laboratory test data. This allows results obtained using the modelling software to be compared to real data for soils and aggregates.

6.3.2.1. Comparison with Column Drying and Wetting

The first verification is of the unsaturated flow modelling capabilities, and involves simulations based on drawdown experiments run by Jessep (1998). Using the results of these experiments the van Genuchten unsaturated flow parameters for the material were estimated. The parameters were calculated for a range of minimum errors (as described in the previous sub-chapter) for both the wetting and the drying curves. The material property was then assumed to be the mean of the parameters calculated by each method.

The calculated parameters were then used as input for Groundwater Vistas to simulate column draw up and down. The time period for the simulation was set at the same time period for which the experiment ran; 24 hours. Although permeability measurements had not been taken for the aggregate used in Jessep (1998), it is known that the 'granite ½' used for the drawdown pipe being simulated, was a coarse aggregate. A value of 0.017 ms^{-1} was chosen as a reasonable value to represent this, based on the literature review and the knowledge that it was a coarse aggregate likely to have a relatively high permeability. The results of these simulations are shown in figure 6.8.

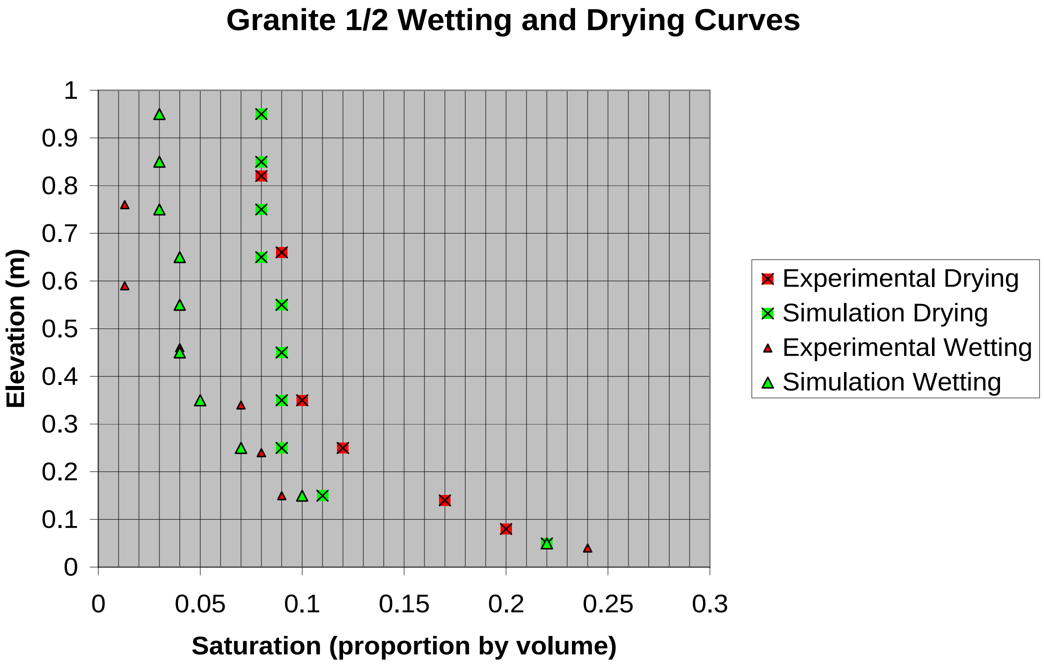


Figure 6.8, Granite 1/2 (coarse grading) experimental and simulated drying and wetting curves, after Jessep (1998).

Given that there is a degree of uncertainty in many of the approximations made for this simulation the results are surprisingly accurate. It can be seen that the simulation accurately predicted the saturation in both wetting and drying. Of particular significance is that the results of the simulation are almost identical to those from the experiment for aggregate drying at an elevation above 0.3m. As the pavement sub-base is more likely to reach residual saturation by drying after rainfall, and the pavement sub-base should be at least 0.3m above the water table, these are the conditions most likely to be encountered in pavement sub-base courses.

6.3.3. Comparison with Alternative Models

Having compared the software with the results of laboratory tests it has next been compared with alternative numerical models for the analysis of unsaturated hydraulic flow and contaminant transport. While the laboratory models verify that the software can reasonably model soil and aggregate behaviour, comparison with alternative models demonstrates that it can simulate the conditions encountered in the pavement structure and sub-grade.

6.3.3.1. Comparison to Numerical Mode

The third verification compared the drainage of a pavement sub-base layer with an exact, analytical, solution provided by McEnroe (1994). According to McEnroe the average minimum pavement sub-base saturation S_{min} can be calculated using; S_r the residual saturation, ψ_a the air entry pressure, w the depth of the edge drain, d the depth of the drainage layer, L the length of the drainage layer, and m the gradient of the drainage layer slope.

Using the same aggregate properties as had been determined for the previous verification, and assuming a drainage layer 7m wide, 0.1m deep, at a gradient of 0.02 and with the drain 0.3m below the bottom of the drainage layer a calculation was carried out using the method given by McEnroe. These dimensions were selected as they are very similar to those used by McEnroe, the only difference being that the drain depth is 0.3m rather than 0.1m. This meant that having carried out an initial calculation that could be verified against the published calculations, little change was required for the calculation for the simulated drain.

A simulation was then set up modelling the same drainage layer, using the same material properties in MODFLOW SURFACT. The simulation was run for a range of periods until the saturation became constant.

Using McEnroe's analytical method the minimum pavement sub-base saturation was 12.09$^{\%}$. Using MODFLOW SURFACT the minimum pavement sub-base saturation was 12.65$^{\%}$. The variation between these results is only 4.63$^{\%}$.

6.3.3.2. Comparison with Hydrus 2-D

A simulation has been carried out based on that described in Apul et al. 2005. This used Hydrus 2-D to simulate the transport of contaminants within the pavement sub-surface.

Complete data is not available for the Hydrus 2-D simulation, consequently there will inevitably be some variation between the two models attributable to the variation in modelling parameters. However, this does provide an opportunity to compare the generalised flow regime.

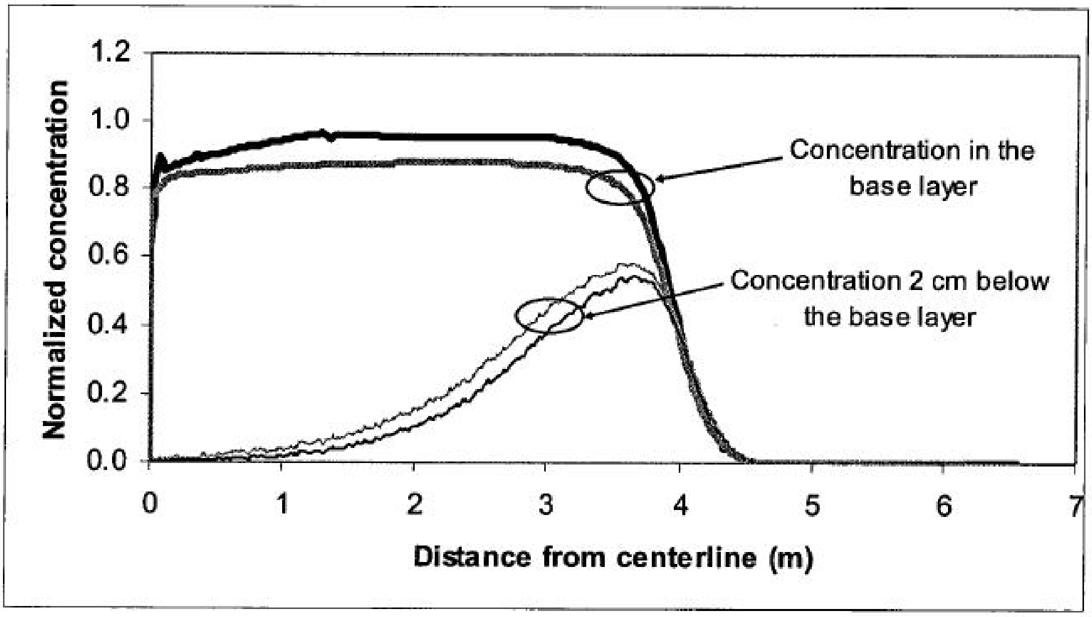


Figure 6.9, Migration of salts underlying pavement using Hydrus 2-D – from Apul 2005.

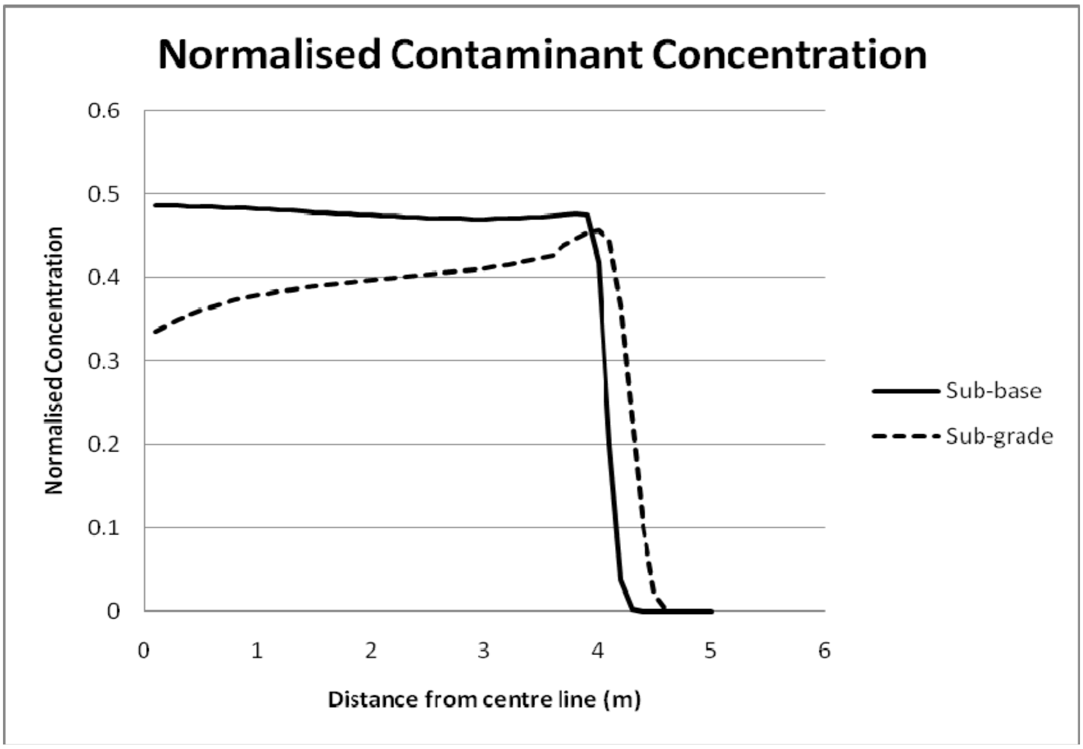


Figure 6.10, Migration of salts underlying pavement using Groundwater Vistas and MODFLOW SURFACT.

It can be seen from Figures 6.9 and 6.10 that there is significant variation in the extent of contamination between the two models. That run using MODFLOW SURFACT and groundwater vistas shows a significant increase in the extent of contamination within the sub-grade, and subsequent reduction in the sub-base course. However, the general form of the results (i.e the most extensive leaching to the right hand side where water enters the sub-grade via the shoulder), is similar to that predicted by Hydrus 2-D, and it is reasonable to assume that the differences may be related to the use of different modelling parameters.

6.3.4. Summary

Modelling hydraulic flow and contaminant transport within unsaturated soils and aggregates is a complex analysis involving a significant number of approximations and simplifications. Despite this, the verifications carried out indicate that Groundwater Vistas and MODFLOW-SURFACT are able to simulate the processes involved in water flow and contaminant transport within the highway environment.

Further work should consider the comparison of simulation results with data with from an instrumented highway to confirm that the modelling assumptions made are sufficiently representative of an actual highway.

7. Simulations of Contaminant Transport in the Highway Environment

Having undertaken a number of laboratory tests to better understand the nature of the materials in the highway environment, and verified the function of the selected software, the final stage of this project was to carry out simulations in contaminant transport in and around the highway structure. The objective of these models was two-fold; first to gain an understanding of the variations in the pavement and environment and how these affect contaminant transport and secondly to simulate specific sensitive scenarios and assess the associated risks.

The software used for the modelling is Groundwater Vistas, in combination with MODFLOW-SURFACT. These are as described in the previous chapter.

Where they are available modelling parameters have been derived from the tests carried out as part of this project. Where such data is not available parameters are based on values given in available literature.

7.1. Parameter Sensitivity Study

The first part of this study was the assessment of the simulation's sensitivity to a range of parameters.

Parameters relating to the pavement geometry have been studied by Carretá (2007) with assistance from the author of this thesis. Carretá carried out a range of simulations that looked at the impact of the pavement width, depth and crossfall gradient. The finding of this study was that the pavement geometry had little impact on the transport of contamination into the sub-grade.

Natural parameters including rainfall patterns, soil hydraulic and sorption parameters were assessed separately and are reported in Dawson et al. (2008), and summarised below.

It is noted that the parameter sensitivity study was carried out in the early stages of this project, prior to the completion of testing described in the previous chapters of this report. Consequently the results of these tests have not been incorporated into this study.

7.1.1. Scenarios Assessed

7.1.1.1. Parameters for Study

The scenarios assessed considered a range of parameters. The first of these is the contamination source, i.e. runoff, leaching or both. Values of contaminant concentrations in runoff have been measured by several authors. The values obtained by Kayhanian (2003) have been taken as typical and were selected as the basis of the input values for the simulations reported in this paper. Leachate concentration values were obtained from an earlier study by Hill (2004). The relevant values are given in Table 7.1.

Material	Cadmium (μg/l)	Zinc (μg/l)	Copper (μg/l)
Runoff (Mean) (Kayhanian, 2003)	0.9	203.4	51.3
Runoff (Max.) (Kayhanian, 2003)	13	2400	9500
Runoff values adopted in this paper	13	2400	9500
Limestone (Hill, 2004)	<6	75	<19
Municipal Solid Waste Incinerator Ash (MSWIA) (Hill, 2004)	<6	19	2546
Foundry Sand (Hill, 2004)	<6	303	1533
China Clay Sand (and cement) (Hill, 2004)	<6	107	19
Initial leaching values adopted in this paper	6	303	2546

Table 7.1, Adopted runoff and initial leaching contaminant concentrations

The second set of parameters considered are the hydraulic parameters, i.e. permeability and van Genuchten parameters. The parameter values are based on a range of soil types comprising sand, silt and clay and are based on values identified during the literature review, see Tables 7.2 to 7.5. Parameter values for a typical aggregate are also included, although variations in these have not been considered.

	Terzaghi et al. 1996 Typical range		Meyer et al. 1997	
	upper	lower	μ	SD
Sand	10^{-2}	10^{-5}	$8.22\ \mathrm{x}10^{-5}$	$4.39\ \mathrm{x}10^{-3}$
Silt	10^{-5}	10^{-9}	$4.89\ \mathrm{x}10^{-7}$	$2.76\ \mathrm{x}10^{-5}$
Clay	10^{-9}	10^{-11}	$3.65\ \mathrm{x}10^{-7}$	$1.08\ \mathrm{x}10^{-8}$

Table 7.2, Soil permeability by grading classification (m/s)

Where μ = mean value and SD = standard deviation

Jones and Jones 1989			Apul et al. 2002	
μ	Max	Min	Max	Min
$1.7\mathrm{x}10^{-2}$	$5.8\mathrm{x}10^{-2}$	$1.4\mathrm{x}10^{-3}$	$5.85\mathrm{x}10^{-2}$	$5.03\mathrm{x}10^{-5}$

Table 7.3, Permeability of sub-base course aggregates (m/s)

Where μ = mean value

Laboratory		In situ	
Max	Min	Max	Min
$5.8\mathrm{x}10^{-2}$	$1.4\mathrm{x}10^{-3}$	$5.85\mathrm{x}10^{-2}$	$5.03\mathrm{x}10^{-5}$

Table 7.4, Permeability of permeable sub-base (Roy & Sayer, 1989) (m/s)

		Hodnett and Tomasella, 2002		Meyer et al, 1997		Jessep, 1998†	
		μ	SD	μ	SD	Max	Min
Sand	α	3.80	1.53	14.7	2.55		
	β	2.47	0.92	2.67	0.27		
	θ_r	0.04	0.02	0.05	0.01		
Loam	α	2.46	1.53	3.67	2.02		
	β	1.46	0.29	1.56	0.11		
	θ_r	0.16	0.08	0.08	0.01		
Clay	α	4.63	4.86	0.62	0.76		
	β	1.51	0.65	1.13	0.07		
	θ_r	0.27	0.09	0.07	0.03		
Granite Aggregates	α					333.4	5.8
	β					2.51	1.27
	θ_r					1.7	0

Table 7.5, van Genuchten parameters for a range of soils and pavement sub-base aggregates.

Where μ = mean value and SD = standard deviation

Note: the unit of α is m^{-1}; β and θ_r are unitless.

† Values have been fitted to Jessep's published wetting curve data as described in Chapter 6.23.

For the purpose of identifying the impact of a range of parameters and values, the data sets used in the simulation are shown in Table 7.6, largely based on the range of values given in the previous Tables.

Layer	Type	Data Set	θ_s	Bulk Density (kg/dm^3)	Permeability (m/s)	Van Genuchten		
						α (1/m)	β	θ_r
Sub-grade	Sand	A1	0.43	1.62	1.00E-05	14.7	2.67	0.05
	Loam	A2	0.43	1.62	1.00E-06	3.67	1.56	0.08
	Clay	A3	0.38	1.62	1.00E-07	0.62	1.13	0.07
Sub-base Course	Aggregate	B	0.43	N/A	1.00E-03	5.8	1.27	0

Table 7.6, Values of permeability and van Genuchten parameters adopted

Note: the unit of α is m^{-1}; β, θ_s and θ_r are unitless.

The third set of parameters considered are the soil sorption parameters. The parameters used assume linear sorption (K_d, that has units of $l.kg^{-1}$). Different metals such as copper, zinc and cadmium are chosen to illustrate the effect of linear sorption. The selected values and the literature sources on which these are based are given in Tables 7.7 and 7.8.

Species	Min	Max
Copper	5.33[2]	10,800[1]
Zinc	6[1]	22,800[1]
Cadmium	2.71[2]	200[3]

Table 7.7, Partition coefficients for copper, zinc and cadmium; K_d *(l/kg)*

[1]Christensen (2000), [2]Chang (2001), [3]Tran (2002)

	Data Set		
Species	C1	C2	C3
Copper	5	200	10,000
Zinc	6	300	20,000
Cadmium	3	20	200

Table 7.8, Adopted partition coefficients for copper, zinc and cadmium; K_d *(l/kg)*

To evaluate the effects of contaminants in runoff and contaminants leached from sub-base course aggregates, three simple situations (D1 to D3) were analysed:

1. Contaminated runoff + no aggregate leaching + subgrade sorption (D1);
2. Clean runoff + aggregate leaching + subgrade sorption (D2);
3. Contaminated runoff + aggregate leaching + subgrade sorption (D3).

There was insufficient time to allow all combinations of soil and contaminant data sets (A, C and D) to be investigated, so a limited range of scenarios was selected with the purpose of demonstrating the impact of each set of parameters. The scenarios simulated were as follows:

1. To study the relative impacts of contaminated runoff and aggregate leaching, sand sub-grade and low sorption coefficient assumed in all cases:

   I D1 + A1 + B + C1 - contaminated runoff and no aggregate leaching

   II D2 + A1 + B + C1 - clean runoff and aggregate leaching

   III D3 + A1 + B + C1 - contaminated runoff and aggregate leaching

2. To study permeability and van Genutchen parameters, contaminated runoff and aggregate leaching is assumed in all cases:

   III D3 + A1 + B + C1 - sand and low sorption coefficient

   IV D3 + A2 + B + C2 - loam and intermediate sorption coefficient

   V D3 + A3 + B + C3 - clay and high sorption coefficient

   VII D3 + A3 + B + C1 - clay and low sorption coefficient

3. To study the sorption characteristics:

   III D3 + A1 + B + C1 - sand and low sorption coefficient

   IV D3 + A2 + B + C2 - loam and intermediate sorption coefficient

   V D3 + A3 + B + C3 - clay and high sorption coefficient

   VIII D3 + A1 + B + C3 - sand and high sorption coefficient

4. To study the effect of rainfall pattern:

   III D3 + A1 + B + C1 - 1 hour rain burst then 34 hour dry interval

   VI D3 + A1 + B + C1 - 2 hour rain burst then 68 hour dry interval

7.1.1.2. Simulated Pavement Design

In reality, pavements are three dimensional objects. However, on level ground, there is a large degree of symmetry in the longitudinal direction such that two dimensional (2D) cross-sections of the pavement can be expected to provide a reasonably reliable geometrical representation of the complete pavement. For this reason, 2D numerical simulations were performed using the cross-section of a typical pavement sub-structure as shown in Figure 7.1. Because the pavement cross-section is symmetric about its centre line, the model grid is as illustrated in Figure 7.2.

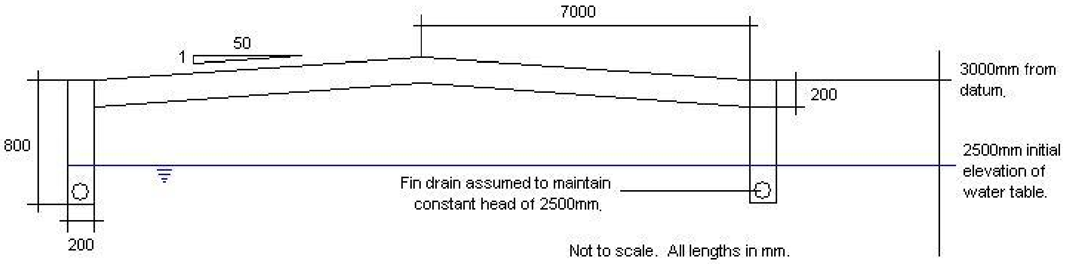


Figure 7.1, The simulated pavement design

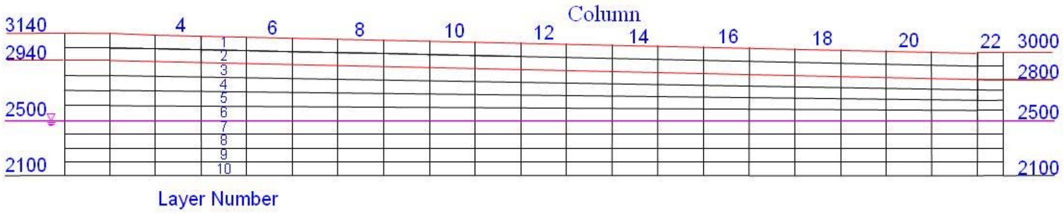


Figure 7.2, Model grid (vertical dimensions in mm, 2100mm is base of simulation)

7.1.1.3. Boundary Conditions

Initially, all the cells were given a head that was hydrostatic relative to an assumed phreatic surface at the 2500mm level (Figure 7.1). Thereafter the head value was determined by the simulation.

The cells in column 22 (layers 7-10) are arranged such that, if during the calculation, the water head of the cell is higher than 2500 mm, water will drain out of the cell. Otherwise, the cell is set to be dry. By this means a drain that never lowers the phreatic surface beneath its original level is provided.

As a worst-case, a permeable pavement surface is assumed to be allowing all the rainfall to enter the pavement. This is a conservative approximation as in reality much of the rainfall fall on the surface will run across the pavement and be collected by the surface drainage system. Conditions may be similar to this where the pavement is designed to be permeable (i.e. SUDS). Also, for non porous asphalt or concrete, there may be a short period prior to reinstatement where the surface is significantly cracked allowing rainfall to penetrate into the pavement body.

In principle the rainfall rate can be varied to simulate different climates, and different rates of infiltration through the pavement surface. However, a typical UK annual average rainfall rate of 1000mm per annum has been used.

The rainfall patterns are selected according to the statistical data for the UK. A simple pattern (1) was initially adopted, which had a one-hour-long burst of totalling 4 mm with an interval of 34 hours between rainfalls. There were 1000 cycles of such periods in total, giving a total simulated time of 2 years (see Figure 7.3). Another pattern (2) was chosen to simulate the same total time of 2 years and the same gross rainfall but falling in a different pattern. By this means it is hoped to assess the potential impact of rainfall pattern on contaminant transportation. The second pattern included rain in two-hour-long bursts totalling 8 mm with an interval of 68 hours between storms (see Figure 7.3).

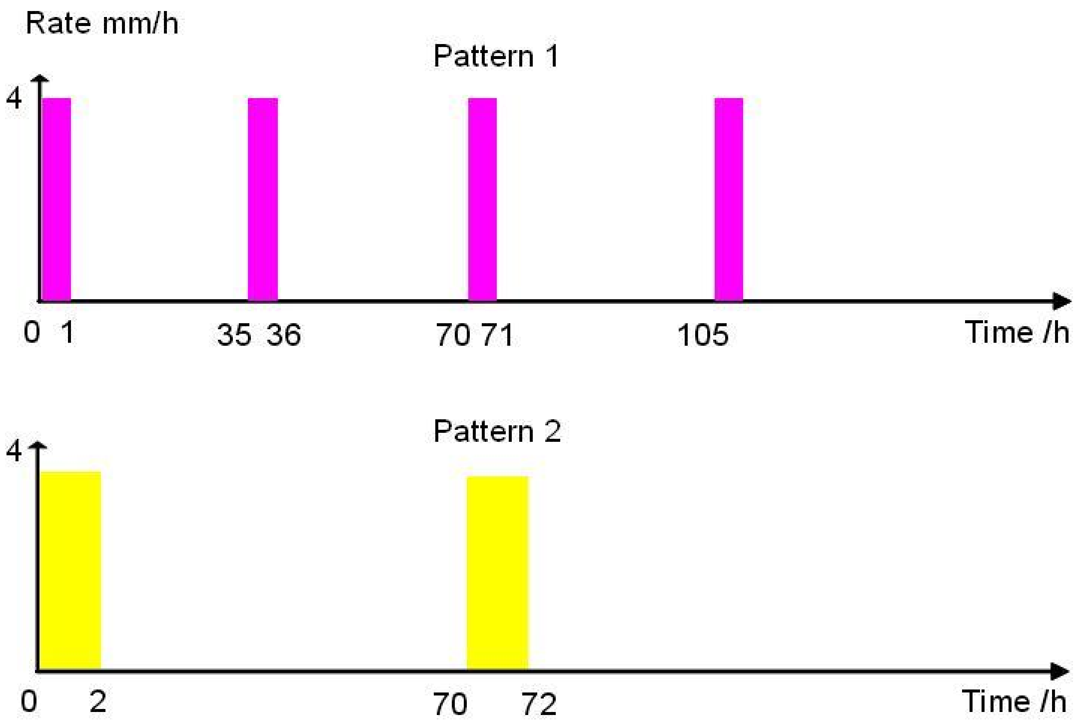


Figure 7.3, Rainfall patterns used in the simulation

7.1.2. Simulation Results

7.1.2.1. Typical Water Head

Figure 7.4 shows the typical water head during a simulation. The results are as would be expected, in accordance with the basic principles of water movement in the ground. Water flow is largely vertical in the upper part of the aggregate layer and runs largely horizontally towards the drain in the lower part of this layer at the interface with the relatively low permeability sub-grade. In the sub-grade water moves first vertically to the water table, and then laterally to the drain. Impermeable boundaries (imposed by the limited extent of the simulation) lead to some artificiality in the flow regime at the bottom and right lower parts of the mesh, but the points of interest are well removed from this area.

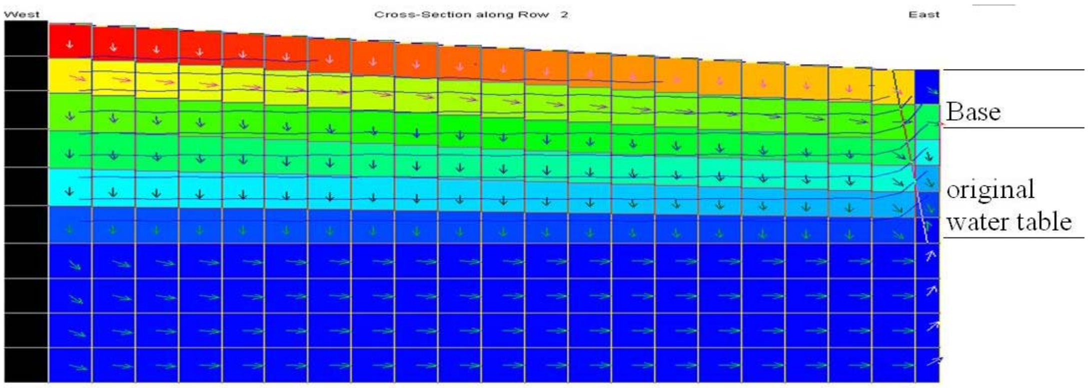


Figure 7.4, Typical water head in a simulation (not to scale, vectors indicate direction of flow only)

7.1.2.2. Contamination region

After the two-year simulation, the groundwater at the water table was not found to be polluted. However, the contaminant front had penetrated significantly into the sub-grade. The simulation was then re-run for an extended period of 4 years prior to groundwater contamination occurring. For the 'worst-case' soil conditions (A1 and C1) with 'worst-case' runoff and 'worst-case' leaching, all three contaminants eventually infiltrated into the groundwater and, thus, this pollution cannot be neglected on this basis. The contaminant concentration in the seventh layer from the top (the top of groundwater) is shown in Table 7.9 for scenario III as an example.

	Column of simulation									
Metal	3	5	7	9	11	13	15	17	19	21
Cd	4.59	8.60	11.01	12.31	12.91	12.79	11.39	7.08	2.35	9.20
Cu	11.92	214.33	617.85	1004.57	1194.92	1037.72	571.33	170.03	96.48	4461.44
Zn	0.03	2.52	18.04	40.29	53.66	44.56	19.57	5.75	3.60	1010.73

Table 7.9, Contaminant concentrations at the water table (7th layer) for Scenario III – contaminated runoff and leaching, at 4 years (µg/l)

The digit in the first row is the column number of model grid (see Figure 7.2). For comparison, drinking water maxima are 5µg/l for Cd, 2000 µg/l for Cu and 5000 µg/l for Zn.

From the table we can see that:

- The left columns show low contamination. This is because they are close to a no-flow boundary so receive little from columns to the left, while the supply at the top in a vertical direction only includes contaminants entering in the current column and columns to the left – of which there are very few.
- The groundwater had been polluted, and the degree of contamination depends on the individual contaminants' input concentration. The top layer of the groundwater had Cadmium concentrations that exceeded water quality maxima (taken to be those exceeding permitted drinking water values) in most columns of the simulation, while for copper the water quality maxima was only exceeded adjacent to the drain and for zinc the maxima were not exceeded.
- The partition coefficient has a major impact. The K_d of Cadmium is the lowest and the concentration relative both to the input concentrations and to the drinking water maxima is the highest, indicating that this is the critical contaminant of those considered.
- Initially contamination levels are higher adjacent to the drain (column 21) as a consequence of more heavily contaminated water entering into the sub-grade, at

the groundwater table, from the drain. That water which has infiltrated downwards has had much of the contamination removed by soil sorption.

- Contamination levels are a little higher near the centre of the pavement (column 11). This is thought to be because it represents the point at which the contribution of contaminant from adjacent columns to the left, together with ingress from the aggregate above, is greatest. Further to the right it becomes easier for contaminants to move to the drain through the aggregate. Further left the issue described in the first bullet point applies.

7.1.2.3. Contamination development with time

Due to sorption, controlled by the partition coefficient, K_d, the arrival of a pollutant at the water table takes some time. To illustrate this, consider Scenario III having the most permeable sub-grade. Because each metal moves with runoff in the sub-base course and sub-grade in a similar manner, only one contaminant, say cadmium, is selected here to demonstrate the effect of the transport mechanism. Table 7.10 and Figure 7.5 characterise the progress. Note that the final contaminant level (almost 20 μg/l) is, in effect, the sum of the cadmium concentrations in the runoff (13 μg/l) and that which comes from the aggregate by leaching (6 μg/l).

		Columns									
Months	Layer	3	5	7	9	11	13	15	17	19	21
6	3	8.81	10.01	10.74	11.16	11.34	11.20	10.59	9.15	6.06	2.14
	7	0	0	0	0	0	0	0	0	0	1.76
12	3	14.62	15.76	16.34	16.65	16.79	16.71	16.30	15.03	11.11	4.16
	7	0	0	0	0	0	0	0	0	0	3.22
18	3	17.50	18.19	18.48	18.62	18.71	18.72	18.58	17.90	14.68	6.06
	7	0	0	0.01	0.01	0.02	0.02	0.02	0.01	0.01	4.38
24	3	18.85	19.18	19.28	19.32	19.37	19.44	19.48	19.24	16.99	7.81
	7	0	0.02	0.10	0.23	0.32	0.29	0.18	0.10	0.06	5.34
36	3	19.79	19.74	19.66	19.62	19.64	19.75	19.95	20.18	19.38	10.88
	7	0.49	2.17	3.98	5.24	5.79	5.41	3.84	1.53	0.74	7.09
48	3	19.99	19.79	19.67	19.61	19.63	19.75	19.99	20.37	20.36	13.37
	7	4.59	8.60	11.01	12.31	12.91	12.79	11.39	7.08	2.35	9.20

Table 7.10, Cadmium transportation under the ground as a function of time from scenario III extended to 48 months (Concentration µg/l Cd)

Layer 3 = top of subgrade; Layer 7 = top of original water table

Concentration in runoff is 13 µg/l. Concentration due to leaching of aggregate is 6 µg/l.

Drinking Water Limit is 5 µg/l.

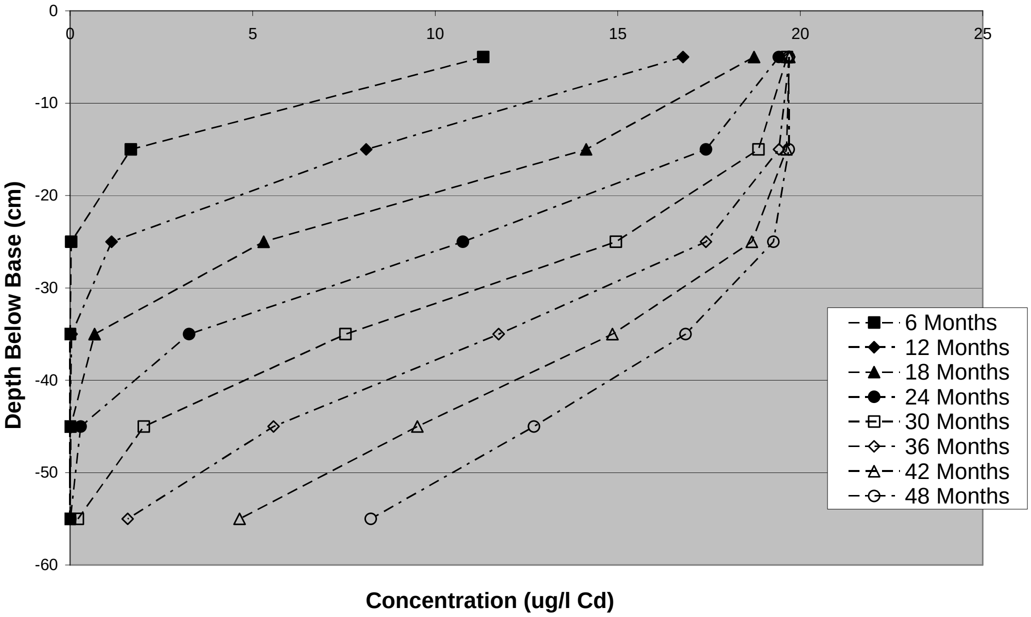
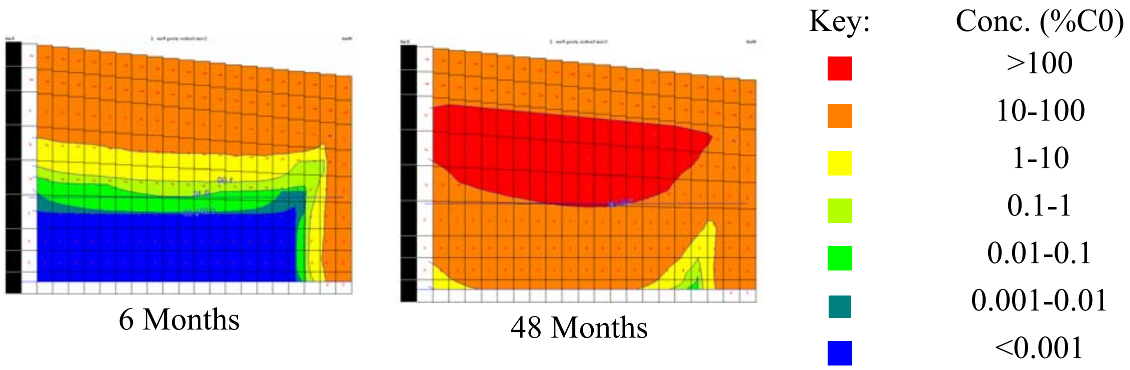


Figure 7.5, Graph of Cd Contamination Vertical Profile in Sub-Grade, for Scenario III.

Note that the top of the water table is at a depth of 40cm.



6 Months

48 Months

Figure 7.6, Image of Cd Contaminant Front Progression in Sub-Grade, for Scenario III.

From Table 7.10, Figure 7.5 and Figure 7.6, we can observe that, for these 'worst-case' conditions being investigated:

- It took the top of the sub-grade relatively little time, 6 months at most, to be significantly polluted but at this time, the sub-grade or soil under the water table appeared to be completely uncontaminated. The reason undoubtedly lies in the relatively high permeability and poor sorption capacity assumed for the sub-base course aggregate allowing contaminants to rapidly reach the sub-grade surface. Beyond this point the contaminant front progression is slowed by both the decreased permeability and increased sorption capacity.

- According to the above results, a reasonable estimate is that the degree of contamination of the sub-grade or soil under the water table would significantly decrease for the same time periods if the sub-grade soil were clay in which case the permeability, k, would be much lower and the K_d bigger. For this example only the lowest K_d values have been used (C1 in Table 7.8). If, as seems likely, advection controls the movement of contaminants and the water flow pattern is little changed with reducing permeability, then a 10 times reduction in permeability alone would be likely to delay arrival times by a similar factor of 10.

- For the same rainfall pattern, the real time simulated plays a key role in the contamination of groundwater. The longer the time, the more significantly the groundwater is contaminated.
- Initially, contamination is somewhat higher near the drain (columns 15-19) but, towards the end of the simulation, concentrations are highest at the level of the water table towards the centre of the pavement. This seems to suggest that horizontal contaminant movement becomes less important as time passes.

7.1.2.4. Impact of rainfall pattern on the contaminant transport

The two rainfall patterns considered produce the same total water inflow but over different time periods. Table 7.11 shows that there is no large difference between the effects of the two patterns. In practice, higher volume but less frequent rain storms (similar to Pattern 2) might be expected to lead to a smaller total volume of water entering a pavement and more running off into the surface water drainage system. If such is the case then a significant reduction in contamination might be expected, but the simulation done here has not modelled this eventuality as it requires that all water enters the pavement.

Scenario	Layer	3	5	7	9	11	13	15	17	19	21
III	3	12.9	13.2	13.3	13.4	13.4	13.5	13.5	13.6	13.1	9.4
	7	0.00	0.04	0.12	0.23	0.33	0.42	0.42	0.33	0.20	0.05
VI	3	13.6	13.9	13.9	13.9	13.9	14.0	14.1	14.2	14.1	11.6
	7	0.00	0.01	0.04	0.09	0.14	0.20	0.26	0.28	0.27	0.21

Table 7.11, Cadmium concentrations in the groundwater due to different rainfall patterns (µg/l Cd)

7.1.2.5. Interaction between runoff and sub-base aggregates

The three simple situations (D1, D2 & D3 – see Section 4, i.e. Scenarios I, II and III) are now compared. In-situ both sorption and leaching may take place in the sub-base, but in the simulations the sorption capacity of the sub-base was neglected so as to provide a conservative assumption. It is very important to quantify the impact of sorption by the sub-base on the movement of contaminants for the economy of engineering, but limited aggregate sorption data made this difficult at the time of analysis. Additional tests data has been included in the simulations described in the following sub-chapter.

Modelling of aggregate leaching from the sub-base layers was achieved by assigning an emission concentration equal to the maximum value indicated by lysimeter leaching tests (Hill, 2004). Modelling of contaminated water infiltrating into the surface is intrinsic to the software used. Scenario III which had both contaminated runoff and leaching from the aggregate was modelled by adding the concentrations of the two models. As the hydraulic flow regime is the same for each and sub-grade sorption is modelled using the linear sorption parameter, this seems a reasonable approach.

An example of the results of contaminant transport over the simulated period of two years is as shown in Tables 7.12 and 7.13 and Figures 7.7 and 7.8. It can be seen that the rate at which the contaminant front progresses is the same in each scenario (curve shapes are similar), but that the magnitude varies dependant upon the input concentration (size of curve varies widely). Note that the Scenario III results are, as noted earlier, a simple addition of the Scenario I and Scenario II results in any particular layer and column (see Table 7.12).

The overwhelming effect of contamination in runoff can be easily seen – contaminant levels at the top of the sub-grade are very high for Scenarios I and III, whereas Scenario II with clean runoff leads to much lower contaminant levels in the sub-grade. In this analysis, a constant leaching concentration has been assumed. In reality, most leaching reduces with time as the more mobile ions are moved first. Therefore, for the 'worst-case' conditions being studied here, the Scenario II curve in Figure 7.7 may, even so, be considered an over-estimate.

		Column									
Scenario	Layer	2	4	6	8	10	12	14	16	18	20
I	3	13.10	13.33	13.38	13.42	13.47	13.53	13.61	13.51	12.04	5.52
	7	0.00	0.04	0.12	0.23	0.33	0.42	0.42	0.33	0.20	0.05
II	3	5.77	5.89	5.94	5.96	5.96	5.95	5.92	5.78	4.98	2.35
	7	0.00	0.01	0.03	0.07	0.10	0.13	0.12	0.09	0.06	0.01
III	3	18.88	19.21	19.32	19.37	19.42	19.49	19.53	19.28	17.02	7.87
	7	0.00	0.05	0.15	0.30	0.43	0.55	0.54	0.42	0.26	0.06

Table 7.12, Cadmium concentrations in different scenarios (µg/l Cd)

Layer 3 = top of subgrade; Layer 7 = top of original water table

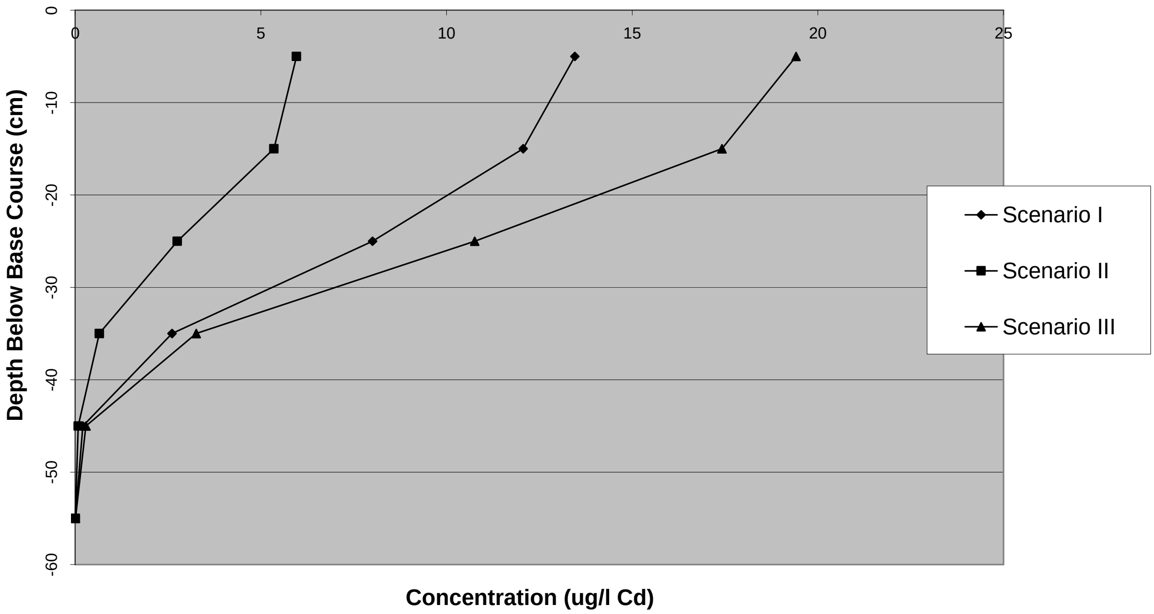


Figure 7.7, Cd contaminant fronts at 2 years, for scenarios I, II and III.

7.1.2.6. Sensitivity analysis

From the above results, we can primarily infer that the permeability and van Genuchten parameters, partition coefficient, and the rainfall quantity are important factors that affect the transport of contaminant underground, whereas the rainfall pattern has little effect. Accordingly, further simulations were run to assess the sensitivity of the simulation to these important factors.

The hydraulic and sorption parameters were varied as shown in Tables 7.6 and 7.8. Scenarios III, IV and V provide simulations of progressively finer soils from sand to silt to clay, with corresponding changes in the sorption and hydraulic parameters. Scenario VII has typical hydraulic parameters, but the same sorptive capacity as III to demonstrate the impact of changes in hydraulic conditions alone. Scenario VIII has the same hydraulic parameters as III, but a much greater sorption parameter to allow the impact of sorption parameter alone to be assessed. The simulation performed for a real time of 2 years gave results as shown in Table 7.13.

			Column									
Scenario	*k* (m/s)	K_d	2	4	6	8	10	12	14	16	18	20
III	1E-5	3	18.88	19.21	19.32	19.36	19.42	19.49	19.53	19.28	17.02	7.87
IV	1E-6	20	2.95	3.33	3.62	3.87	4.12	4.35	4.54	4.24	3.40	1.72
V	1E-7	200	0.07	0.08	0.09	0.10	0.11	0.11	0.11	0.10	0.06	0.03
VII	1E-7	3	3.86	4.46	4.96	5.40	5.77	6.03	6.05	5.41	3.83	1.64
VIII	1E-5	200	0.40	0.46	0.51	0.53	0.54	0.53	0.50	0.42	0.27	0.09

Table 7.13, Cadmium concentrations in the third layer after 2 years (μg/l Cd)

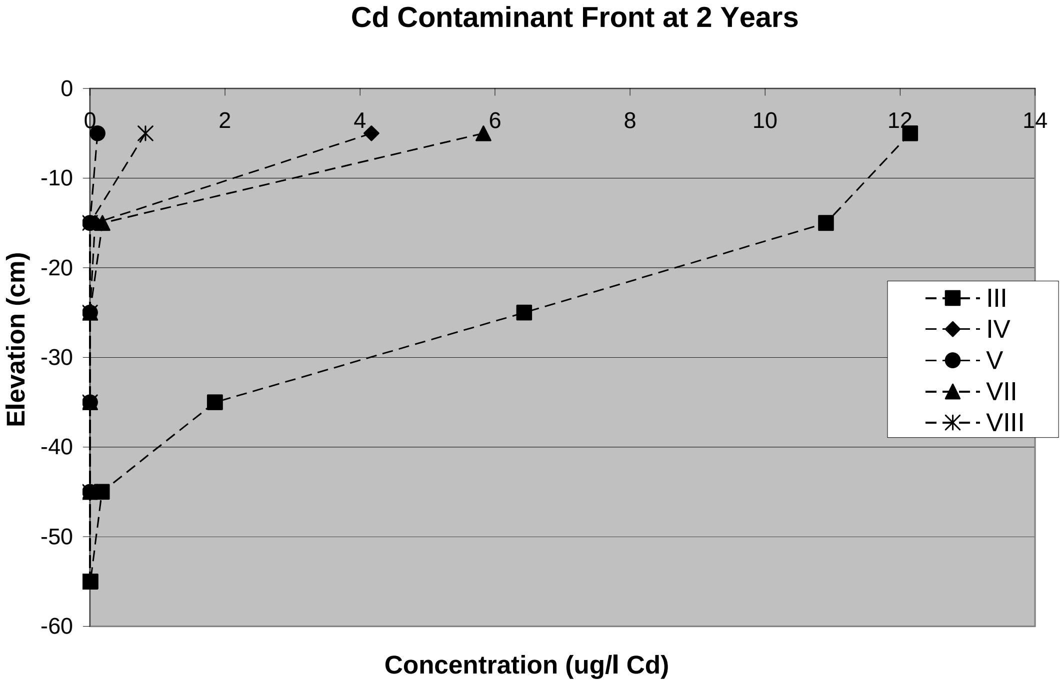


Figure 7.8, Cd contaminant fronts at 2 years, for scenarios III, IV, V, VII and VIII.

Water is the carrier of contaminants under the ground surface considered by these simulations. When the permeability of the sub-grade soil decreases, more water flows through the sub-base to the drain and is drained out. Thus there is less chance for groundwater to be contaminated. However, this will increase the concentration of contaminants in the water in the drain. Where there is also an increase in the sub-grade sorption capacity, the water still flowing through the subgrade is also cleaned of its contaminants much more effectively.

Looking at Figure 7.8 the contamination of the sub-grade for scenario VII is clearly much greater than that for VIII. This implies that the progression of the contaminant front is impacted on most significantly by the sorption parameter assumed for the sub-grade. In fact the contamination in scenario VIII is practically negligible. Even at the surface of the sub-grade, where the worst contamination would be expected, the concentration is still significantly below the drinking water quality maxima for cadmium. As can be seen from other results, a much lower concentration would be expected at the ground water level.

Table 7.14 shows the contamination of the sub-grade at various times for scenarios III, VII and VIII. The objective was to quantify, if possible, the change in the contamination of the sub-grade based on changes in the sorption capacity and hydraulic parameters.

It was hypothesised that the rate at which the sub-grade is contaminated would be inversely proportional to the sorption parameter, and proportional to the permeability. The basis for these is that the greater the permeability the greater the quantity of water that will be able to infiltrate into the sub-grade rather than the drainage system and consequently the more contaminated it becomes, whereas the greater the sorption capacity the greater the time taken for the sub-grade to become saturated with contaminants and consequently the contamination front will progress more slowly.

On this basis the contamination for scenario VII at 24 months would be expected to be the same as that for scenario III at 0.24 months as the permeability is 100 times greater in scenario III. The contamination for scenario VIII at 20 months would be expected to be similar to that for scenario III at 0.3 months as the sorption capacity is 66.6 times greater in scenario VIII.

The results shown in Table 7.14 seem to show that the hypothesis regarding sorption appears to be reasonably accurate while that for permeability is not. It is likely that the reason that the hypothesis does not fit for permeability is that it does not take account of the fact that the sub-grade and sub-base are of variable saturation. During the initial stages of a rainfall event a significant part of the water entering the pavement may be drawn into the sub-grade by the soil's capillary suction. This suction is likely to be greater in soils with a lower permeability due to smaller pore sizes and will therefore cancel out some of the impact of the reduced permeability.

			Columns									
Months	Scenario	Layer	3	5	7	9	11	13	15	17	19	21
0.24	III	3	0.30	0.35	0.38	0.40	0.41	0.40	0.37	0.31	0.19	0.07
		7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
24	VII	3	3.86	4.46	4.95	5.40	5.77	6.02	6.06	5.41	3.82	1.64
		7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.3	III	3	0.38	0.45	0.49	0.52	0.53	0.52	0.48	0.40	0.25	0.09
		7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20	VIII	3	0.47	0.54	0.59	0.62	0.63	0.62	0.58	0.49	0.32	0.12
		7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 7.14, Cadmium transportation under the ground as a function of time from scenarios III, VII and VII (μg/l Cd)

Layer 3 = top of subgrade; Layer 7 = top of original water table

7.1.3. Conclusions

2-Dimensional numerical simulations are an economical way to assess the factors that affect the movement of contaminated water. The potential impact of runoff and sub-base aggregate leaching were also modelled in the simulations. The results show that:

- Over the simulated period of 2 years water quality maxima are not exceeded in any of the scenarios even though some assumptions are very conservative. For the sand with low sorption these maxima are exceeded below the water table after 2.5 years. In some cases this could be of concern to pavement engineers, future work may help to identify whether this is due to overly conservative assumptions or is a genuine risk. For the present it would suggest that, over the most permeable and least sorptive subgrades, further study is needed.

- For other soils, contaminant movement is very limited and of no real concern over the length of the study period.
- Based on the values used in this study, contaminated runoff is likely to play a more significant role in groundwater contamination than aggregate leaching.
- The permeability of sub-grade soil, van Genuchten parameters and the partitioning coefficient are significant factors affecting the transport of water in the pavement foundation.
- The pattern of rainfall infiltration had little effect on groundwater contamination. Sealing of a pavement's surface, and variations in the total annual rainfall could have a significant impact.
- The sorption capacity seems to have the most significant impact on contaminant spread. Future work should therefore be targeted at this to ensure that assumed values are not overly conservative. This could result in the risk of unacceptable groundwater contamination being identified where in reality it is unlikely to occur.
- The role of the lateral drain in carrying contaminated seepage water away from the pavement should be given more detailed consideration. The simulation suggests that, in some circumstances, it could act as a concentrating source of contaminants to the groundwater table – contaminants which have, in other respects, been successfully removed from the pavement structure.
- The additive contamination from runoff and from leaching was necessary given the inputs. In reality, the aggregate may act as a significant means of sorbing contaminants from the runoff, meaning that the results presented here could be unnecessarily conservative.

7.2. Case Study Analysis

Following the parameter sensitivity study, laboratory testing was carried out to improve understanding of the interaction between runoff and aggregates, and the sorption potential of local sensitive soils. The results of these tests have been incorporated into hypothetical case studies, considering real soils and aggregates but not in relation to any proposed or existing highways.

Using the results of these simulations the impact of using alternative methods of modelling the aggregate/runoff interaction has been considered.

7.2.1. Scenarios Assessed

The scenarios simulated include the aggregates assessed in the laboratory testing (i.e. Incinerator Bottom Ash Aggregate - IBAA, Reclaimed Foundry Sand – RFS, Limestone – LS and Blast Furnace Slag – BFS). The sub-grade is assumed to be a sandy soil with low sorptive capacity, as determined for local samples derived from weathered Sherwood Sandstone.

As a result of the limited time available for this project it has not been possible to carry out simulations for all contaminants covered in the tank leaching test. The contaminants considered in these case studies are cadmium and sodium. These have been selected to allow one example of a chemical for which partitioning is generally the dominant process, and one for which salt dissolution is generally the dominant process.

Simulations have been considered for each of the runoff mixes considered in this project, i.e. clean deionised water (DEI), low traffic mean concentrations (LTM), high traffic mean concentrations (HTM) and the maximum concentrations (Max).

7.2.1.1. Environment Parameters

The environmental parameters set for the simulations include hydraulic and sorption parameters relating to the sub-grade, rainfall patterns and contaminant concentrations, and the hydrology.

As identified by the parameter sensitivity study, sand sub-grades provide the most conservative conditions. The modelling parameters used for the simulation of the sub-grade are as shown in Table 7.15.

Permeability (k- m/s)	Porosity (n-v/v)	Van Genuchten Parameters		
		θ_r (v/v)	α (m^{-1})	β
$1x10^{-5}$	0.43	0.05	14.7	2.67

Table 7.15, Soil hydraulic parameters for simulation.

The sorption parameters for the sandy soil vary for the two contaminants considered and are as shown in Table 7.16.

Soil Type	Sorption Parameter (K_d l/kg)	
	Na	Cd
Sand	0.27	5

Table 7.16, Soil sorption parameters for simulations.

The period of the simulations is 5 years, and each year 100 storm events are simulated each of 10mm rainfall over a period of 1 hour and evenly spaced. The concentration of the contaminants in the runoff entering the highway during each storm period are as shown in Table 7.17, and correspond to the values previously identified and used during the laboratory testing.

Runoff	Concentration	
	Na (mg/l)	Cd (ug/l)
DEI	0	0
LTM	21.2	0
HTM	42.3	0.45
MAX	211.8	9

Table 7.17, Contaminant concentrations in simulated runoff.

In addition to the duration and intensity of storms it is also necessary to consider the boundary conditions applied to the model to simulate drainage. To do this a fin drain has been simulated using the drain function built into the software. The potential for infiltration to an aquifer has been modelled by applying a constant head boundary condition to the base of the simulated area of sub-grade, in this case 1.6m below the sub-base. The constant head boundary is pressurised such that it generates a water table 0.8m below the sub-base in hydrostatic conditions.

7.2.1.2. Highway Parameters

The highway parameters set for the simulation include the hydraulic and sorption parameters relating to the sub-grade, and the geometry of the pavement structure. The pavement structure being considered is the same as that used in the parameter sensitivity study, i.e. as shown in Figure 7.1.

The modelling parameters used for the simulation of the sub-grade are as shown in Table 7.18. As all materials are being considered as a DoT type 1 aggregate, a single set of parameter values has been used.

Soil Type	Permeability (k – m/s)	Porosity (n – v/v)	Van Genuchten Parameters		
			θ_r (v/v)	α (m^{-1})	β
Type 1 Aggregate	$1x10^{-3}$	0.43	0.0	5.8	1.27

Table 7.18, Soil hydraulic parameters for simulation.

The sorption parameters for the aggregates are based on the values obtained in the tank tests carried out during this project and are as shown in Table 7.19.

Soil Type	Sorption Parameter (K_d l/kg)		Initial Concentration (C_{si} mg/kg)	
	Na	Cd	Na	Cd
IBAA	0	11	800	0
Limestone	0.5	12	50	0
RFS	0	16	560	0
BFS	0.04	5.92	0*	0

Table 7.19, Soil sorption and leaching parameters for simulations.

**No data is available for a new sample. In reality this parameter is likely to be significantly greater than indicated for a new sample.*

7.2.2. Simulation Results

The results of the simulation have been considered in two formats, the first is a direct measure of the contaminant concentrations in the groundwater both at the top of the sub-grade and at the top of the water table. The second is to consider the progression of the contaminant front into the sub-grade.

Where the contaminant concentration has been measured at the top of the sub-grade and water table, the value used is that for the central node across the width of the simulated pavement. Where the progression of the contaminant front is recorded, the central nodes have also been used.

7.2.2.1. Sodium

As stated previously, sodium has been considered as an example of a contaminant for which leaching is the dominant process. In the case of the aggregates considered the leaching of the sodium has been modelled as a salt dissolution for Incinerator Bottom Ash Aggregate and Reclaimed Foundry Sand, and due to partitioning for Limestone.

For each of the above the concentrations at the top of the sub-grade, 0.2m below the pavement surface, and at the top of the water table, 1.0m below the pavement surface have been calculated. The results are summarised in Table 7.20.

Aggregate	Runoff	Location	Concentration (mg/l) at time				
			12 months	24 months	36 months	48 months	60 months
limestone	Dist.	Sub-grade	0.14	0	0	0	0
		Water table	0.01	8.93	0.02	0	0
	LTM	Sub-grade	22.41	20.81	20.81	20.81	20.81
		Water table	0.01	22.11	21.3	21.25	21.25
	HTM	Sub-grade	44.72	41.62	41.62	41.62	41.62
		Water table	0	42.65	42.5	42.5	42.51
	Max	Sub-grade	223.96	208.09	208.09	208.09	208.09
		Water table	0.01	221.08	212.5	212.49	212.49
IBAA	Dist.	Sub-grade	0	0	0	0	0
		Water table	0.14	0.8	0	0	0
	LTM	Sub-grade	20.84	20.74	20.74	20.74	20.74
		Water table	0.14	22.44	21.41	21.34	21.34
	HTM	Sub-grade	40.16	41.48	41.48	41.48	41.48
		Water table	0.1	43.9	42.78	42.68	42.68
	Max	Sub-grade	208.36	208.9	208.26	208.16	208.16
		Water table	0.17	217.74	213.37	213.5	213.5
RFS	Dist.	Sub-grade	0	0	0	0	0
		Water table	0.1	0.56	0	0	0
	LTM	Sub-grade	20.84	20.74	20.74	20.74	20.74
		Water table	0.1	22.21	21.34	21.34	21.34
	HTM	Sub-grade	41.68	41.48	41.48	41.48	41.48
		Water table	0.1	43.9	42.68	42.68	42.68
	Max	Sub-grade	208.37	208.09	208.13	208.3	208.2
		Water table	0.14	217.64	213.39	213.51	213.53
BFS	Dist.	Sub-grade	0	0	0	0	0
		Water table	0	0	0	0	0
	LTM	Sub-grade	20.89	20.76	20.76	20.76	20.76
		Water table	0.01	21.74	21.32	21.32	21.32
	HTM	Sub-grade	41.79	41.53	41.51	41.51	41.51
		Water table	0.02	43.48	42.63	42.63	42.63
	Max	Sub-grade	209.44	207.53	207.54	207.53	207.53
		Water table	0.07	217.56	213.17	213.17	213.17

Table 7.20, Sodium concentrations at the top of the sub-grade and water table.

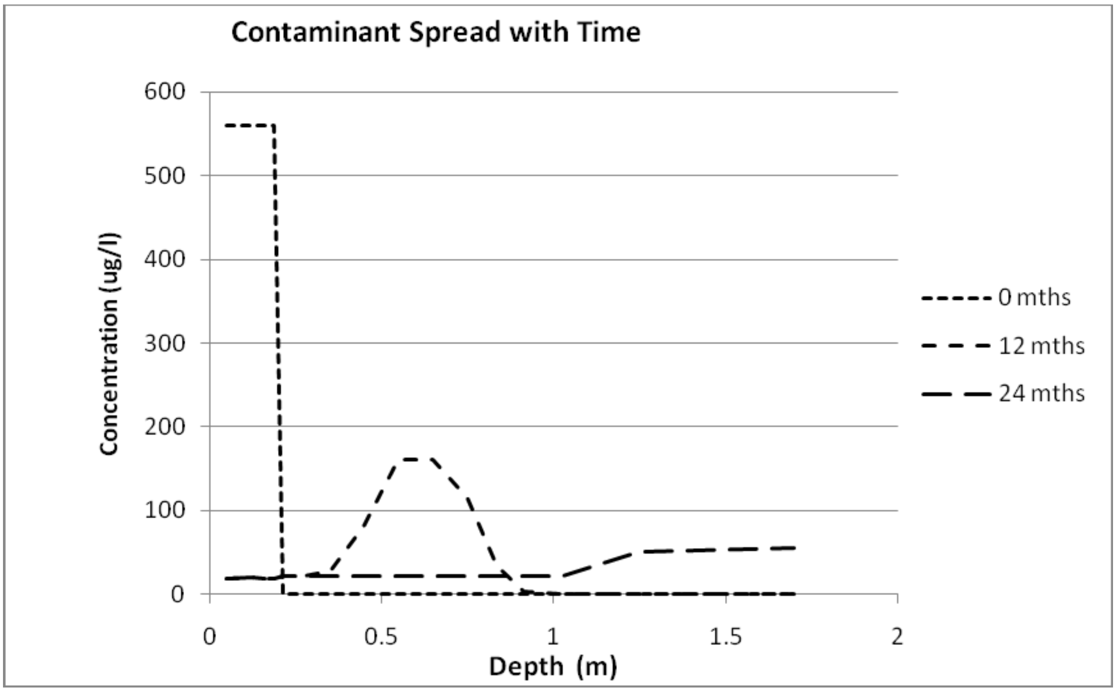


Figure 7.9, Sodium front progression with a reclaimed foundry sand sub-base.

Looking at the contaminant front progression shown in Figure 7.9 it can be noted that the peak contaminant concentration reduces as the contaminant front progresses into the sub-grade. The reduction in the contaminant concentration is likely to be attributable to several processes. The first is that the contaminant movement is not one-dimensional, much of the contaminated water will be removed laterally into the drainage system and will not migrate vertically down. In addition to this, as the contaminated water migrates down dispersion and dilution 'spreads out' the contamination. This increases the depth of the contaminated zone, but decreases the peak concentration.

Figure 7.10 shows the contaminant fronts for blast furnace slag, reclaimed foundry sand, incinerator bottom ash aggregate and limestone following 12 months of simulation. It can be seen that the contaminant fronts for the different aggregates all progress into the sub-grade at the same rate. However the magnitude of the peak increases with the concentration of contaminant in the aggregate.

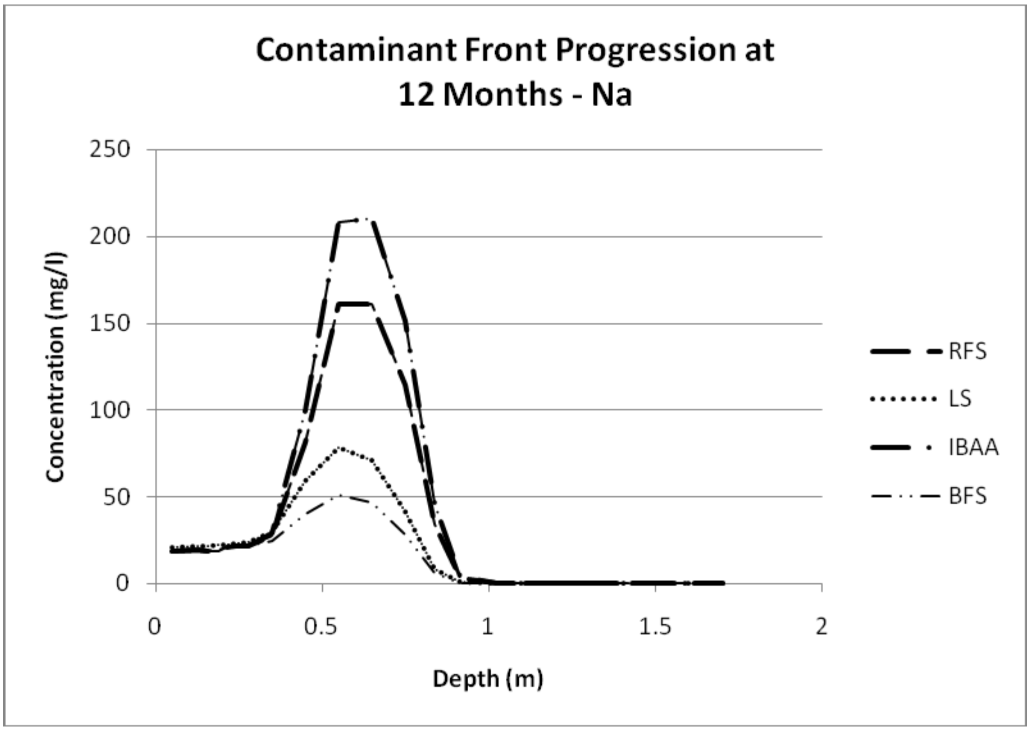


Figure 7.10, Sodium contaminant front at 12 months

7.2.2.2. Cadmium

As stated previously, cadmium has been considered as an example of a contaminant for which sorption is the dominant process. The leaching and sorption of cadium has been modelled using the partitioning relationships for all aggregates.

For each of the above the concentrations at the top of the sub-grade, 0.2m below the pavement surface, and at the top of the water table, 1.0m below the pavement surface have been calculated. The results are summarised in Table 7.21.

Aggregate	Runoff	Location	Concentration (µg/l) at time				
			12 months	24 months	36 months	48 months	60 months
Limestone	Max	Sub-grade	0.02	0.69	2.39	4.3	5.87
		Water table	0	0	0	0	0
IBAA	Max	Sub-grade	0.02	0.87	2.83	4.85	6.39
		Water table	0	0	0	0	0
RFS	Max	Sub-grade	0	0.26	1.15	2.5	3.94
		Water table	0	0	0	0	0
BFS	Max	Sub-grade	0.3	3.98	6.85	8.14	8.65
		Water table	0	0	0	0	0

Table 7.21, Sodium concentrations at the top of the sub-grade and water table

It is noted from the results that cadmium has not reached the water table in any of the simulations. Further, except for blast furnace slag, it takes in excess of 4 years for the concentration of cadmium at the top of the sub-grade to exceed the drinking water limit and environmental quality standard, both 5 µg/l.

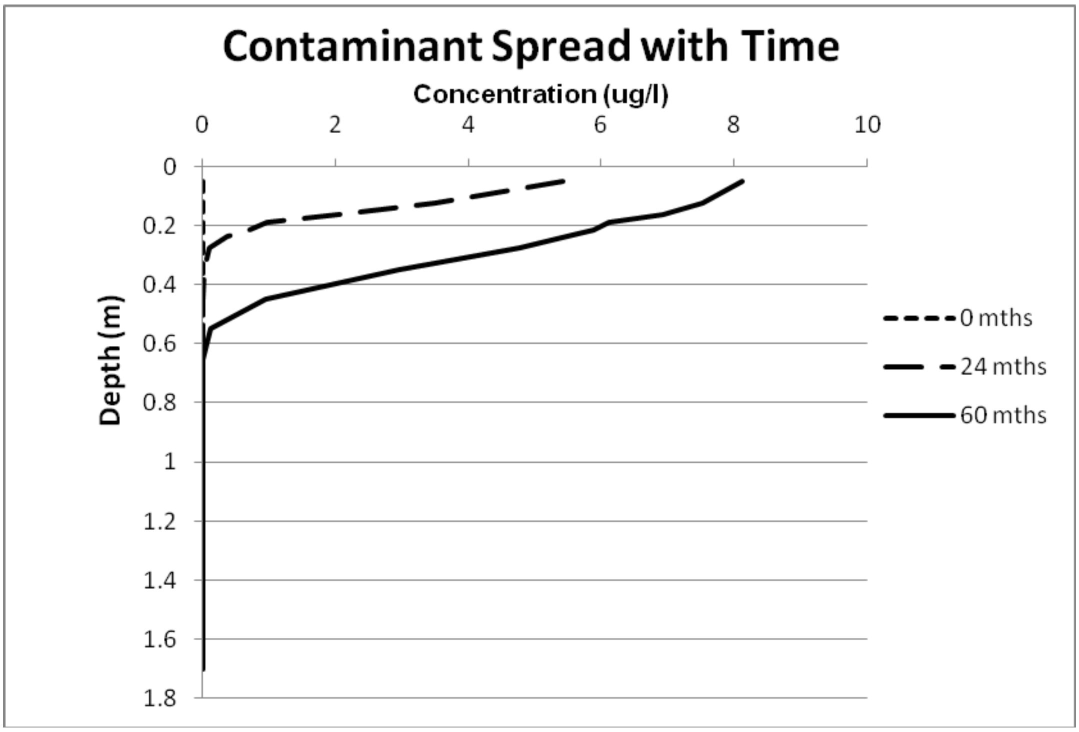


Figure 7.11, Cadmium contaminant front progression with a limestone sub-grade.

Figure 7.11 shows an example of the cadmium contaminant front progression through the sub-base and sub-grade. It can be seen that even after 5 years attenuation has reduced the cadmium concentration below the water quality maxima at a depth of approximately 0.25m. Simulations produced similar results for the IBAA, reclaimed foundry sand and blast furnace slag.

7.2.3. Conclusions

Based on the results the following observations have been made:

- Where there is an increase in the sorption coefficient of either the sub-base or sub-grade, there is a decrease in the rate at which the contaminant front progresses, but not in the maximum concentration.
- Where there is an increase in the concentration of a contaminant – either in the sub-base or runoff there is an increase in the magnitude of the contaminant front, but not in the rate at which it progresses.
- Even with a relatively low sorption coefficient no cadmium has reached the water table after a period of 5 years.
- Sodium within the sub-base is rapidly dissolved, with the dissolved sodium leaving the sub-base through the fin drain and infiltration into the sub-grade. Concentrations exceeding the water quality maxima are only encountered for the simulations considering the maximum concentration in runoff.

7.3. Discussion

The following sub-chapter considers the results of the simulations carried out within the context of highway design, planning and construction. It also advises, where appropriate, on the potential applications of simulating contaminant transport.

7.3.1. Limitations of Results

There are a number limitations relating to the simulations that would need to be addressed for specific data to be used by highways Engineers.

7.3.1.1. Contaminants Considered

The first is that only a limited number of contaminants have been considered, these being zinc, lead, cadmium and sodium.

These are examples of salt and heavy metals and it may be reasonably anticipated that other chemicals in these categories will behave in a similar fashion. However, in reality a much wider range of potential contaminants will be encountered, some of which may be more harmful to the environment and therefore more critical to the design.

Also chemicals from different categories may be controlled by different processes and behave in a very different fashion. As an example, hydrocarbons are likely to be present in runoff and the retardation of these is likely to be more dependent on biodegradation than sorption.

Further study would need to be applied to a wider range of chemicals to develop a comprehensive model.

7.3.1.2. *Highway Drainage*

It is noted that only one generalised highway section has been considered in this report, of particular significance is that this includes functioning sub-surface drainage. The removal of contaminated water by the drainage system reduces the flow of contaminanted water into the sub-grade, and as a result reduces its impact on the groundwater. In reality some highways will be constructed without sub-surface drainage or may have failures in the drainage system that prevent or reduce this effect.

In addition, the simulated case models an edge drain, into which water in the sub-base can flow. In practice a variety of drainage systems are used, and the choice of drainage system is likely to have an impact on the efficiency.

Further analysis should be carried out to assess the impact this has on the contaminant flow regime.

7.3.1.3. *Pavement Surface*

The pavement surface has been assumed to allow all rainwater to penetrate into the sub-base. In reality this will not occur, even where a permeable surface is used some of the rain will evaporate rather than infiltrate into the sub-base. However, it is assumed that this is a close approximation to conditions where a permeable pavement (i.e. SUDS) is used. Where a non-porous asphalt is used and the pavement surface is highly fractured there may be significant infiltration of water into the sub-grade.

However, this is only likely to apply during a relatively short period prior to reinstatement of the pavement surface.

Where an impermeable surface is used and there is little or no fracturing there will be very little infiltration into the sub-base, if any at all. This will result in a significant reduction in the infiltration of contaminated water into the sub-grade. In this scenario the effects of diffusion may be critical to the contaminant flow regime, and further analysis would be required to quantify this effect. Though clearly in this case there would be a significant reduction in the extent of contamination of the sub-grade and groundwater.

7.3.1.4. Geology and Hydrogeology

The simulations carried out have only considered a relatively simple 2-dimensional model of the pavement body and the sub-grade to a depth of 2m, and with a uniform soil type and hydrology.

When assessing the wider impact on a real groundwater body it will be necessary to consider the in-situ conditions. This may mean that a much larger area will need to be considered with variations across that area in terms of soil type, and depth of groundwater. In addition the rainfall patterns may vary significantly in terms of duration, intensity and the interval between rainfalls.

Given the potential for variation of these parameters it is probable that each site should be considered on its own merit, initially by a qualitative assessment and where this indicates a possible risk then a quantitative model, such as those described in this sub-chapter, which incorporates site specific details.

7.3.2. Context of Results

The results of the simulations carried out during the parameter sensitivity study and case study analysis have assessed the rate at which contamination spreads into the sub-grade underlying a hypothetical highway. It has been shown that where there is a both a sufficiently permeable sub-grade and low contaminant sorption, contaminants may reach the water table at concentrations exceeding relevant water quality maxima, see Chapter 2.3.3.1 and Table 7.22.

Contaminant	Drinking Water Standards	Environmental Quality Standards	
	Maximum	95th Centile	Average
Sodium (mgNa/l)	200	n/a	n/a
Cadmium (µCd/l)	5	n/a	5
Lead** (µPb/l)	25*	n/a	4
Zinc** (µZn/l)	5000	30	8

Table 7.22, Water quality maxima

*The water quality maxima for lead will be reduced to 10 µPb/l from the 25th December 2013.

**The maxima are variable depending on the hardness of the receiving water, the minimum values are shown. Values obtained from the Environment Agency website.

However, exceeding the water quality maxima does not necessarily mean that the extent of the contamination is unacceptable. Where this occurs, further assessment should be carried out to assess whether or not there is a significant risk of unacceptable contamination, and consequently whether or not intervention is required.

7.3.2.1. Environmental

The potential environmental damage that may be caused by contamination of the groundwater includes:

- Reducing the quality of the groundwater as a water resource.
- Reducing the quality of local surface water bodies receiving water from the groundwater body.
- Harm to ecosystems dependent on affected groundwater or surface water.

When considering the potential of the groundwater as a water resource the first point to consider is whether or not it is within an existing source protection zone and, if not, the Environment Agency classification of the aquifer status.

Source protection zones are categorised as 'inner', 'outer' and 'total catchment'. The inner source protection zone covers the area within which pollution can travel to the abstraction point within 50 days. The outer source protection zone covers the area within which pollution can travel to the abstraction point within 400 days. The total catchment area covers the remaining area within which contamination may reach the abstraction. Within a source protection zone the potential for contamination affecting the water abstraction will need to be assessed.

Where the groundwater is not within an existing source protection zone, the aquifer classification and vulnerability status should be considered. Where the underlying geology is classified as a non-aquifer it has negligible permeability and is not suitable for water abstractions. Where it is defined as a major or minor aquifer it is possible that it will be used as a water source in the future.

In assessing the potential impact on local surface water bodies a number of factors should be considered, including the proximity of the surface water body, the water quality designation, and the size of the catchment area feeding the water body. In most cases it is anticipated that the water body will be a significant distance from the highway, and there will be sufficient attenuation and dilution of contamination that there will be a negligible increase in chemical concentrations.

To prevent harm to ecosystems it should be ensured that discharges to any water bodies on which they are dependent do not exceed the relevant environmental quality standards. It should be noted however that these are not exhaustive, and the potential toxicity of contaminants present but not covered as List I or List II substances should also be considered.

7.3.2.2. Legal

The legal framework relating to potential contamination is imposed in two ways. The first is during the planning process, a part of which involves satisfying the local Environmental Health Officer and Environment Agency Officer that the development does not provide excessive risk to human health or the environment. Where they are not satisfied of this, conditions may be applied to the planning application or the application may be rejected.

In relation to the planning process it is noted that in most cases the relevant Environment Agency officer is not likely to consider the infiltration of contaminants into the sub-grade to be a significant source of contamination, and it is unlikely that they would deny or place conditions on an application in the standard case. However, concern may be expressed either where the highway is located overlying a source protection zone (or other sensitive site, e.g. a Site of Special Scientific Interest) or where non-standard construction methods and materials are used.

In some of these cases, such as within an inner source protection zone, it is likely that discharges to the groundwater, including infiltration through the pavement and sub-grade will be prohibited if contaminant concentrations exceed strict water quality standards, i.e. the drinking water standards. In this case it may be necessary to design in systems to prevent the migration of contaminants irrespective of the model behaviour.

In areas with a reduced sensitivity, such as an outer source protection zone or total catchment, it is likely that an assessment will be required considering the risk of unacceptable contamination occurring. In many cases a qualitative assessment is likely to be sufficient to demonstrate that the contamination presents a negligible risk to the environment. In some cases quantitative assessment will be required. This may include carrying out simulations such as those described in this report but perhaps considering a wider area.

During and following the construction of the highway, and in the event that significant contamination occurs, the highway engineer and others may be prosecuted under Part IIa of the Environmental Protection Act, if it is judged that their actions contributed to the incident occurring.

7.3.2.3. Intervention Measures

In some cases it will be decided that intervention measures are required to prevent the flow of contaminants into the sub-grade. This may occur as a result of the Engineer's assessment or planning conditions imposed by the Environment Agency.

Potential measures that may be installed to reduce the infiltration of contaminants into the sub-grade include:

- Installing an impermeable barrier between the sub-base and sub-grade preventing infiltration into the underlying groundwater. This could comprise either an artificial membrane or a layer of clay. This could create a perched water table within the sub-base adversely affecting the mechanical properties.
- Designing an impermeable pavement surface and specifying regular monitoring and maintenance to minimise the development of fractures. This will reduce the flow of water into the pavement body and therefore reduce infiltration.
- The use of a cement or binder on the sub-base aggregates to reduce leaching of contaminants.

7.4. Summary

This chapter describes a number of simulations that have been carried out to calculate the extent of contamination associated with the construction and operation of highways. These simulations are at an early stage and there are a number of limitations as described in section 7.3.1. However, the simulations should provide a general indication of the extent of contamination within the pavement and sub-grade.

Two sets of simulations were carried out; the first to assess the sensitivity of the simulations to a range of parameters; and the second considering a range of hypothetical sensitive sites and incorporating data from the laboratory testing detailed in chapters 3 to 5 of this thesis.

The parameter sensitivity study demonstrated that for the contaminants considered where there are fine-grained sub-grades, i.e. those with a high silt of clay content, there is likely to be little spread of contamination. Only in scenarios where there is a sand and/or gravel sub-grade, is there potential for significant contamination reaching the water table.

The second set of simulations, considering sensitive sites, demonstrated that even in these cases there was limited spread of the contaminants considered. However, concentrations of cadmium exceeding water quality limits were calculated at the water table, indicating that there is a risk of some contamination that may need to be considered further by future work.

8. Conclusions

8.1. Aggregate/Runoff Interaction

A number of conclusions have been reached based on the laboratory testing to investigate the interaction between aggregates and runoff:

- The nature of the interaction between contaminants in runoff and aggregates varies for each contaminant and runoff mixture.
- In all cases sorption of heavy metals was noted. This indicates that sorption within the pavement sub-base is likely to have a significant impact on the movement of metals, and potentially other contaminants, in the highway environment.
- There was little sorption of salts sodium and chloride by the aggregates.
- In some cases it was possible to derive appropriate modelling parameters based on the test data. However, in many cases the data provided by the tests could reasonably be explained by several different processes.

8.2. MODFLOW SURFACT and Groundwater Vistas

MODFLOW SURFACT and Groundwater Vistas have been used during this study to simulate the flow of groundwater and associated contaminant transport. The following observations have been made based on the results of the work undertaken:

- Simulations carried out using the software have been compared to laboratory test data, numerical models and simulations with alternative software. In each case the software provided a reasonable prediction of other results. This indicates that the software is able to reasonably model unsaturated flow and contaminant transport in the pavement sub-base and sub-grade.

- Although the software has been validated by comparison with other software and laboratory testing it has not been compared to field data. This should be considered as a part of any future work.

8.3. Contaminant Transport in the Sub-pavement Environment

Based on the simulations carried out using the above software the following has been concluded:

- For the contaminants considered there is negligible risk of groundwater contamination over the simulated period (up to 5 years) for all soils other than those with a low sorption capacity and high permeability.
- Simulations relating to soils with a low sorption capacity and high permeability indicate that water infiltrating to the water table will exceed water quality maxima. It should however, be noted that a shallow water table has been considered. In reality the water table may be present at much greater depth, and this should be taken into account during any site specific assessment.
- Where water quality maxima are exceeded it is generally by relatively small margins and it is therefore possible that they will be reduced to acceptable

levels within a short distance from the road due to attenuation within the aquifer and dilution.

- Variations in the sub-grade sorption coefficient and permeability have a significant impact on the rate at which contaminated water infiltrates. In addition the parameters themselves are highly variable, ranging by several orders of magnitude.
- Variations in the pavement geometry and rainfall pattern appear to have little impact on the migration of contaminants.
- Where there is leaching from the sub-base the concentration of the contaminant can be significantly reduced in the period it takes to travel from the sub-base to the water table.

8.4. Future Work

While the works carried out for this project provide a useful insight into the potential migration of contaminants within the highway environment, there are a number of areas in which the work undertaken could be improved with further study.

- Due to the use of ion selective electrodes the aggregate/runoff interaction testing was limited both in terms of the range of contaminants considered, and the precision of data collected. Further studies using alternative methods for chemical analysis would allow a wider range of contaminants to be assessed and provide more accurate results.
- More realistic testing, either using a lysimeter set up to receive artificial runoff or a test road with groundwater sampling points would provide data on the in-

situ behaviour of aggregates exposed to runoff. Data from this could be used as further verification of both the laboratory testing and simulation software, or may highlight currently unforeseen issues that could have a significant impact on real roads.

- Simulations could be carried out to consider a wider range of scenarios. Scenarios such as an impermeable or low permeability pavement surface, failures to the sub-base drainage system, or the use of an alternative drainage system are not uncommon and may have a significant impact on contaminant transport. However, they have not been considered during this study.

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APPENDIX A – TANK TEST RESULTS

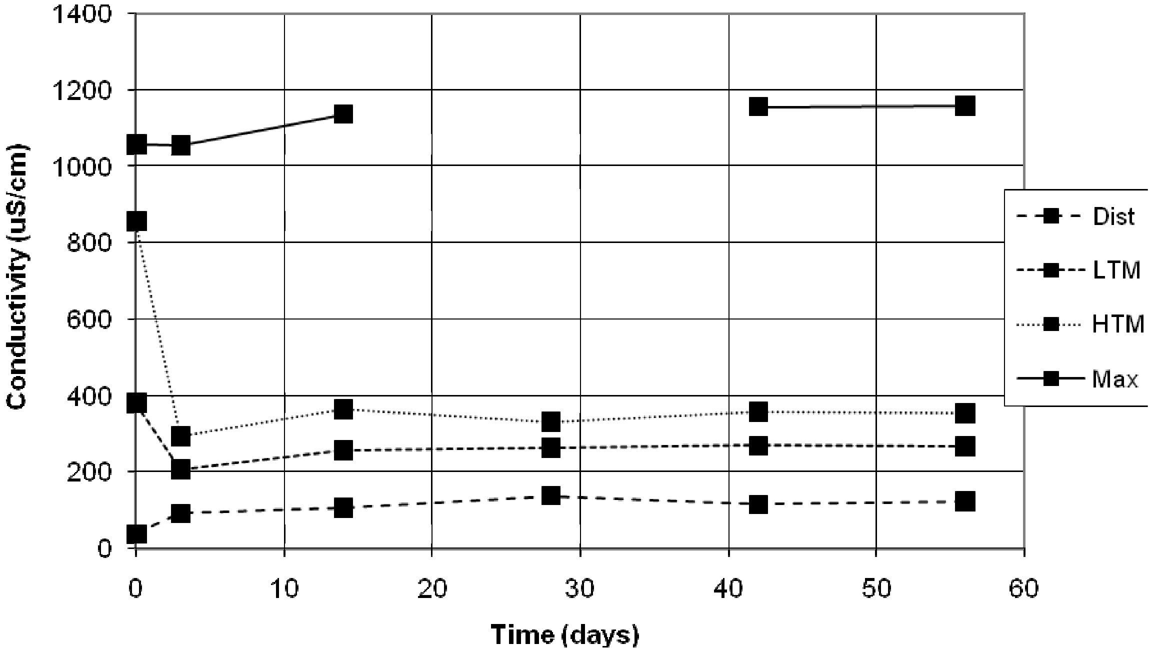
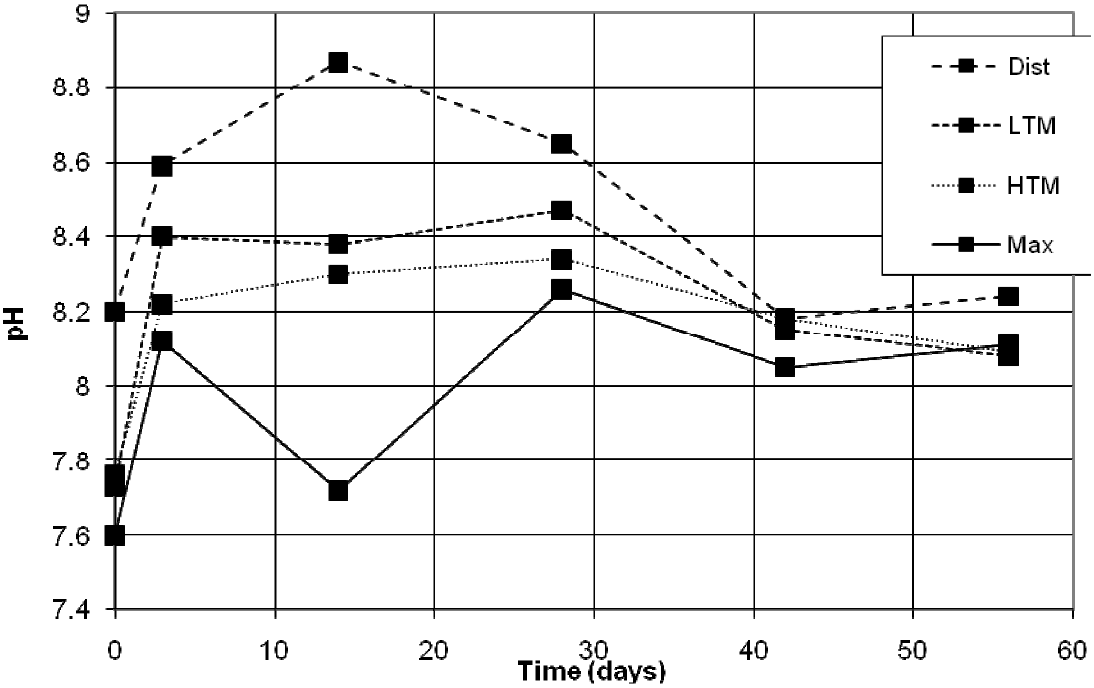


Figure A.1, Conductivity in Limestone Tank Tests.



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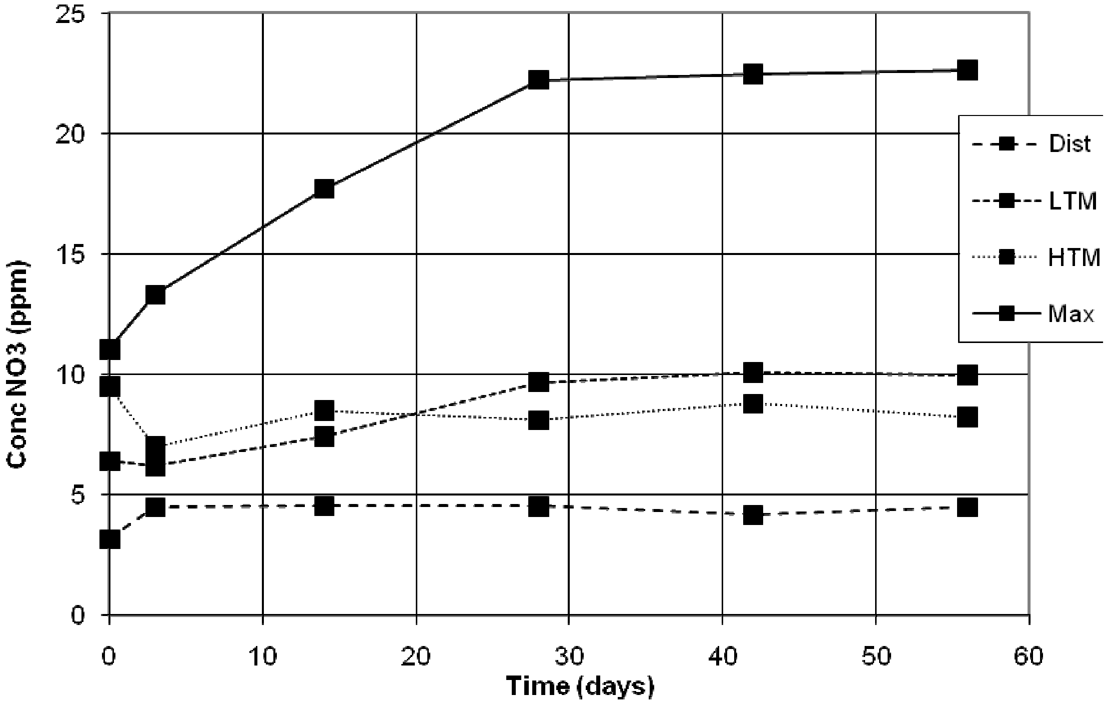


Figure A.3, Nitrate Concentration in the Limestone Tank Test.

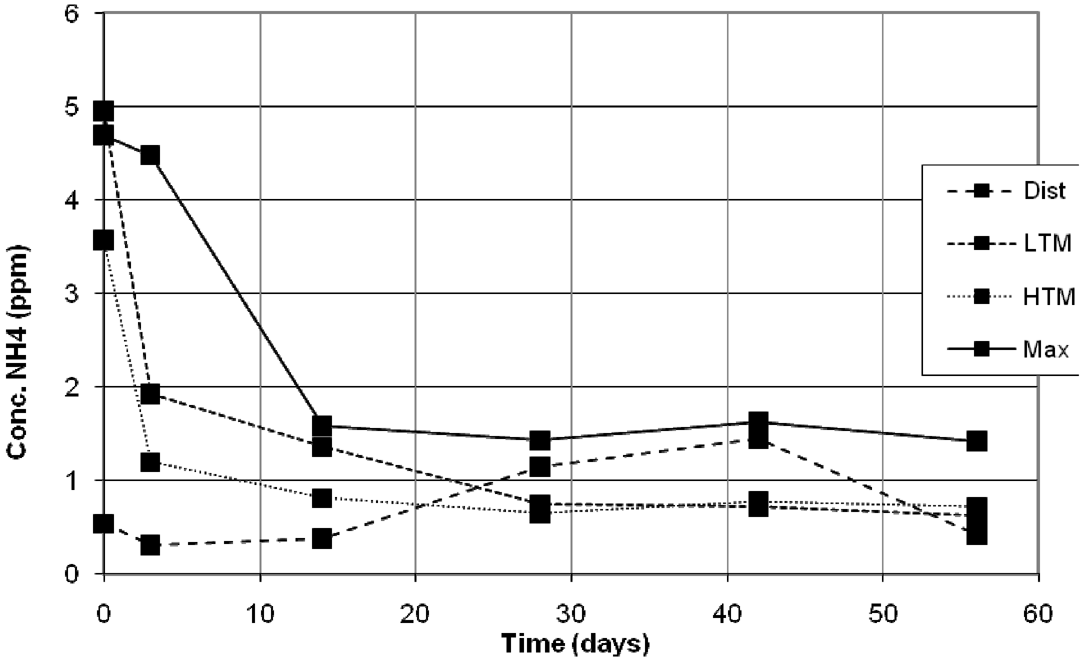


Figure A.4, Ammonium Concentration in the Limestone Tank Test

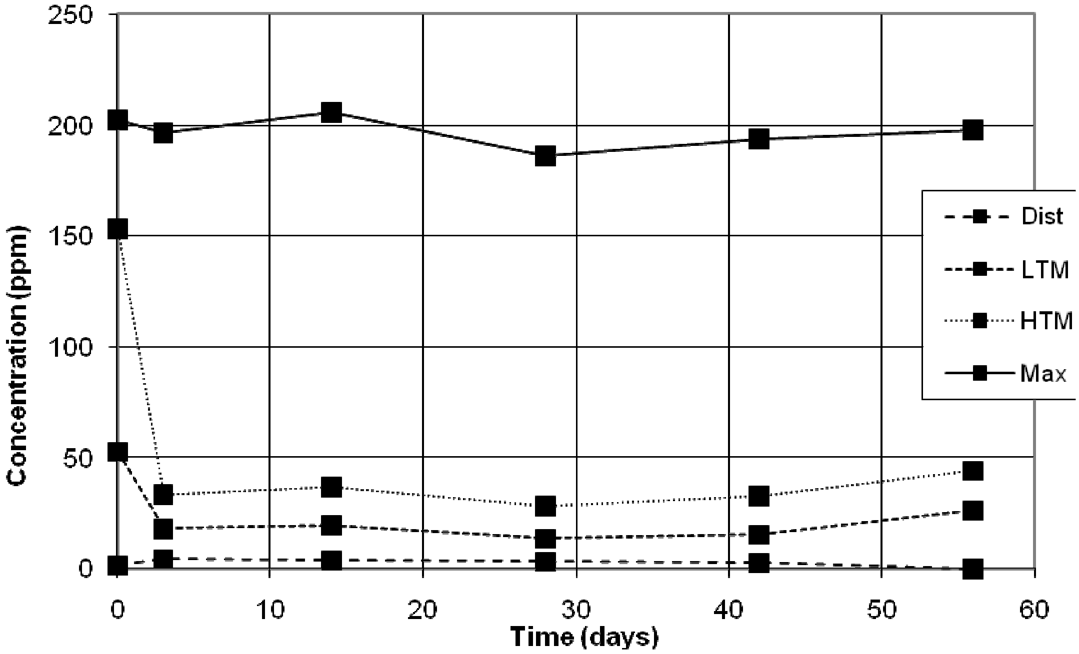


Figure A.5, Sodium Concentrations in the Limestone Tank Test

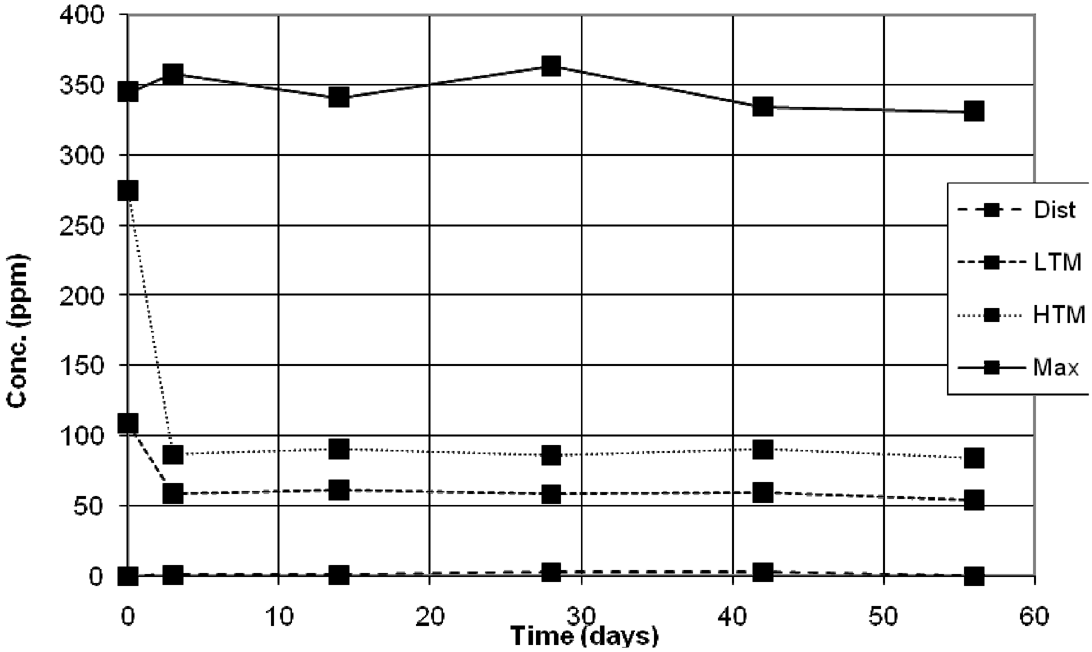


Figure A.6, Chloride Concentrations in Limestone Tank Test.

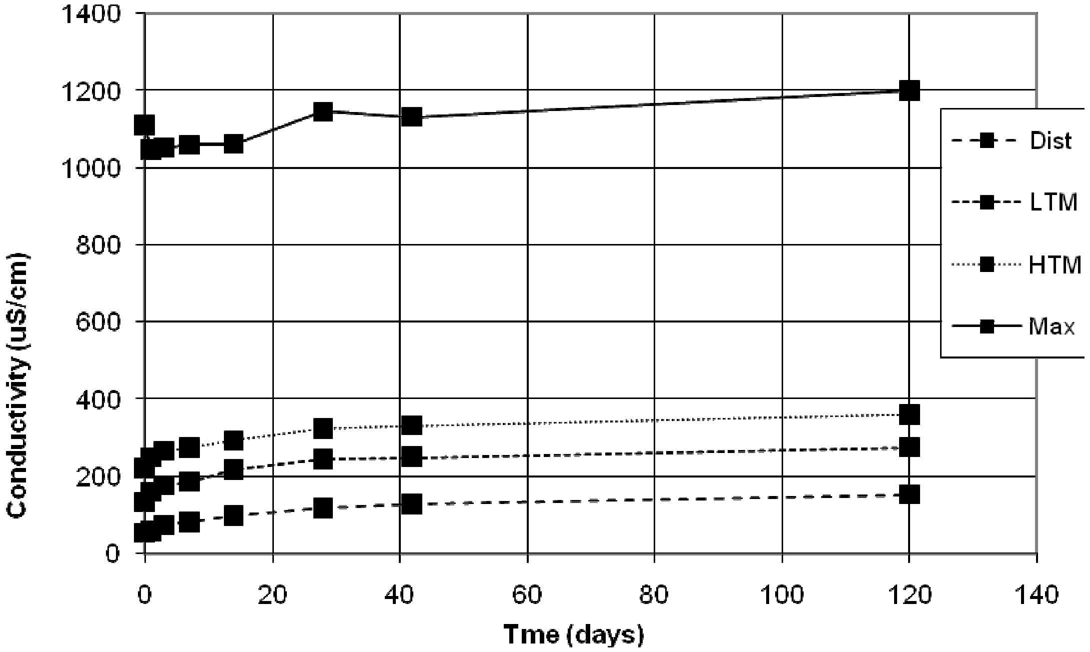


Figure A.7, Conductivity in the Old Limestone Tank Test.

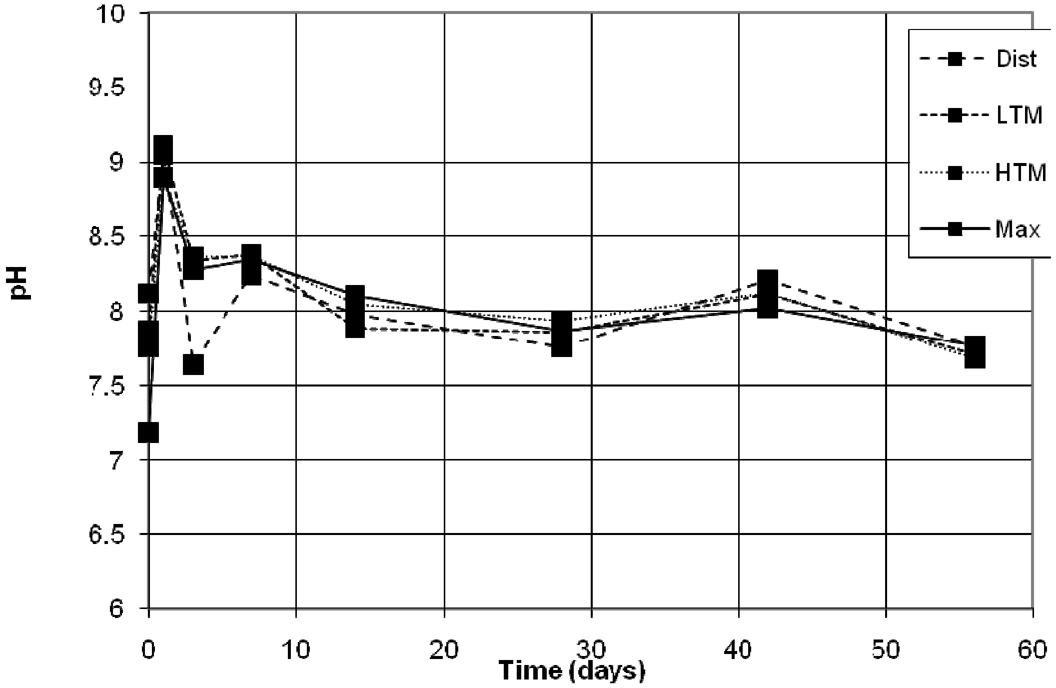


Figure A.8, pH in the Old Limestone Tank Test

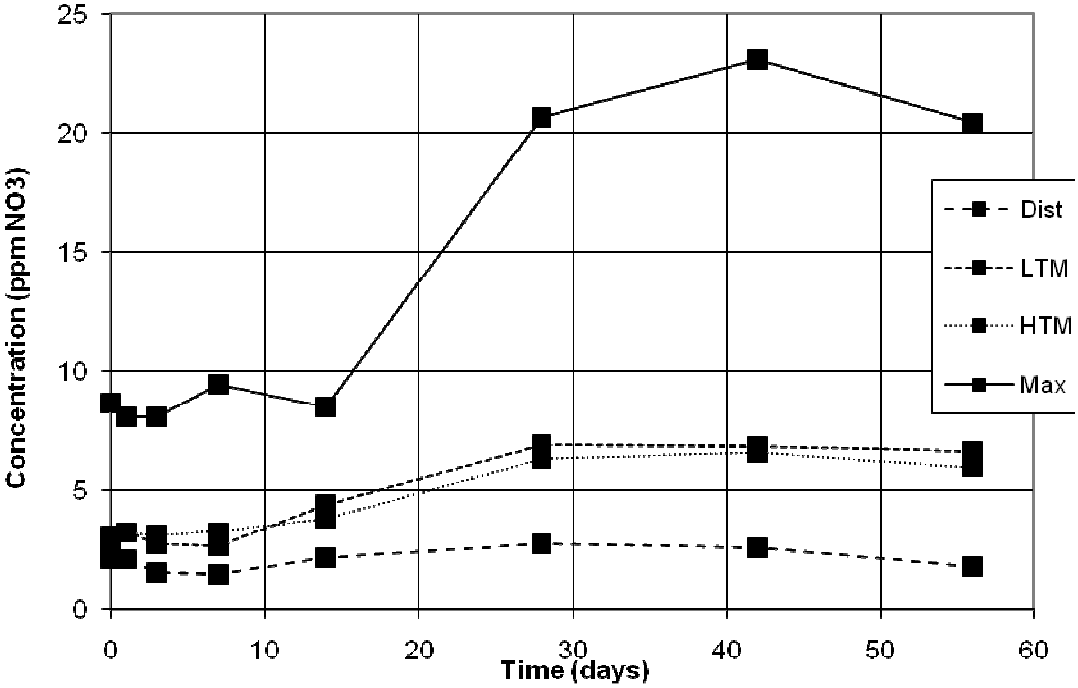


Figure A.9, Nitrate in the Old Limestone Tank Test.

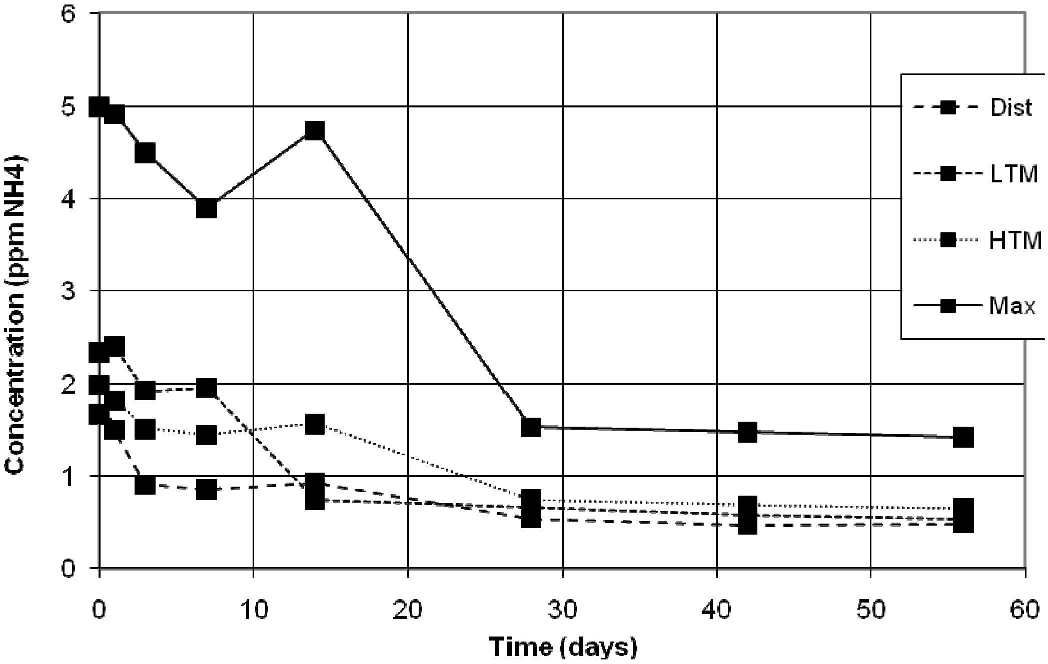


Figure A10, Ammonium in the Old Limestone Tank Test

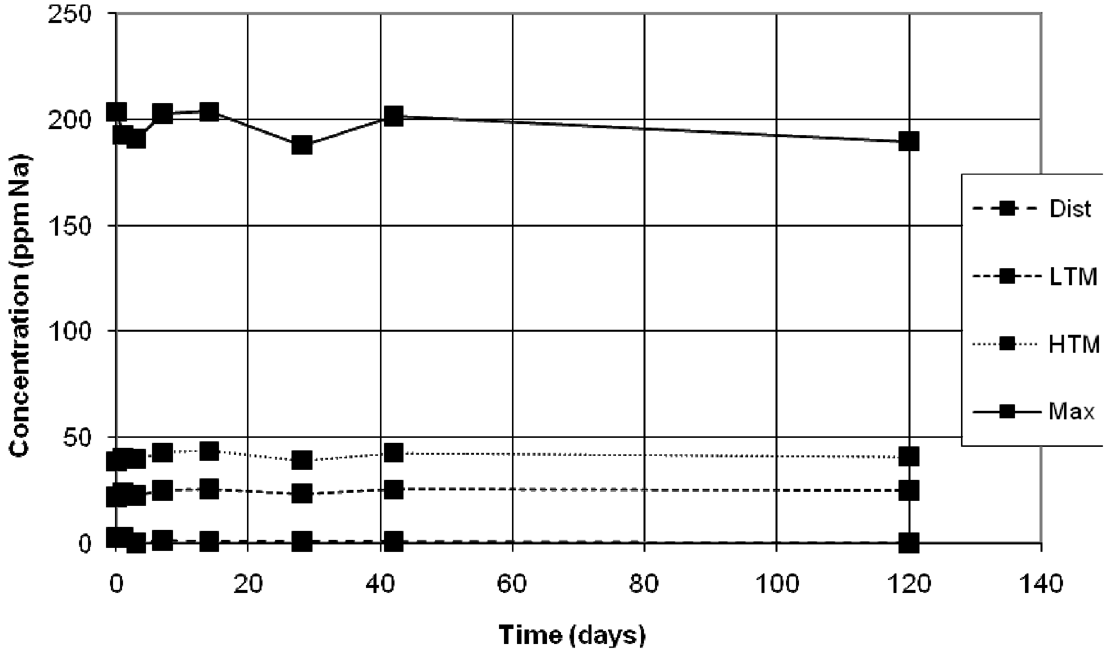


Figure A.11, Sodium in the Old Limestone Tank Test.

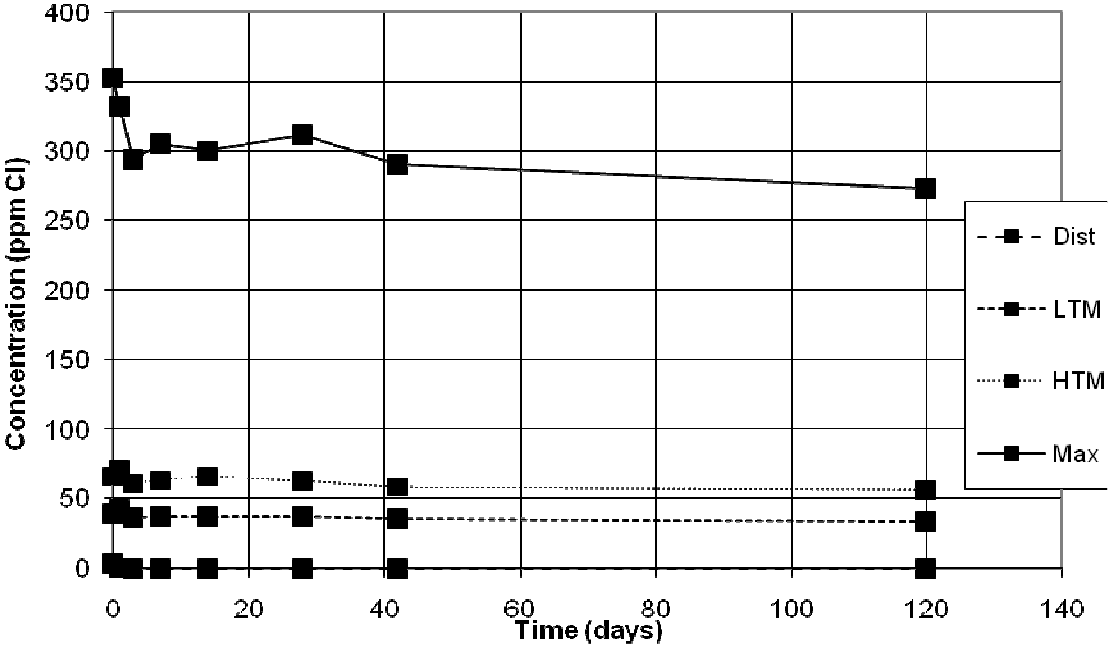


Figure A.12, Chloride in the Old Limestone Tank Test.

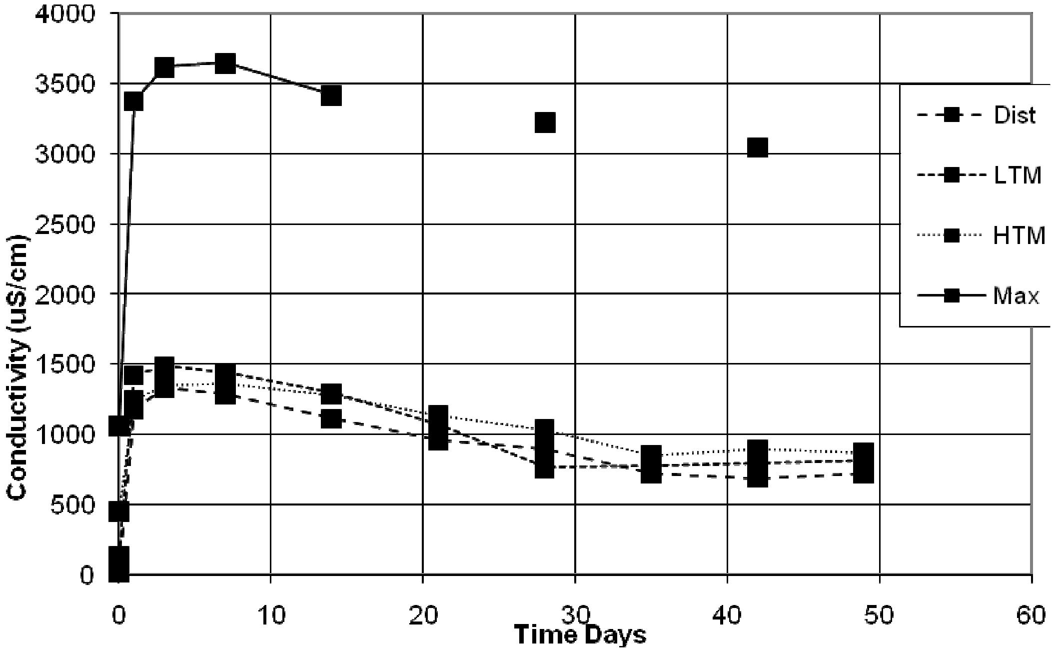


Figure A.13, Conductivity in the IBAA Tank Test.

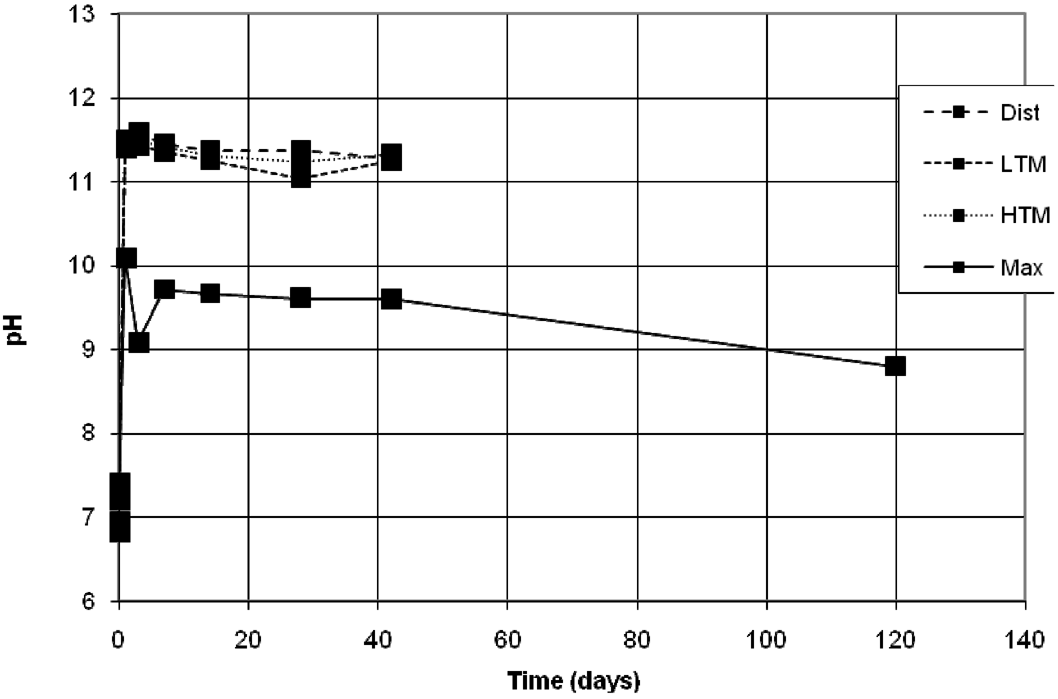


Figure A.14, pH in the IBAA Tank Test

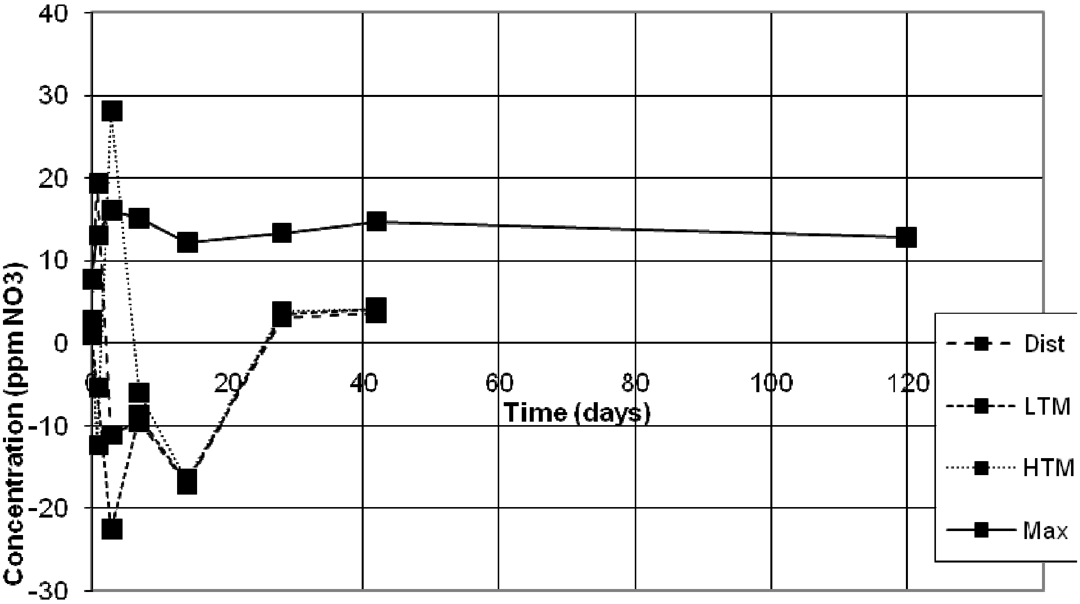


Figure A.15, Nitrate in the IBAA Tank Test

Note that negative readings relate to errors following the addition of nitric acid to modify the pH. All readings for the Max test, and readings from 28 days onwards in the others used hydrochloric acid instead of nitric acid and are consequently unaffected by this error.

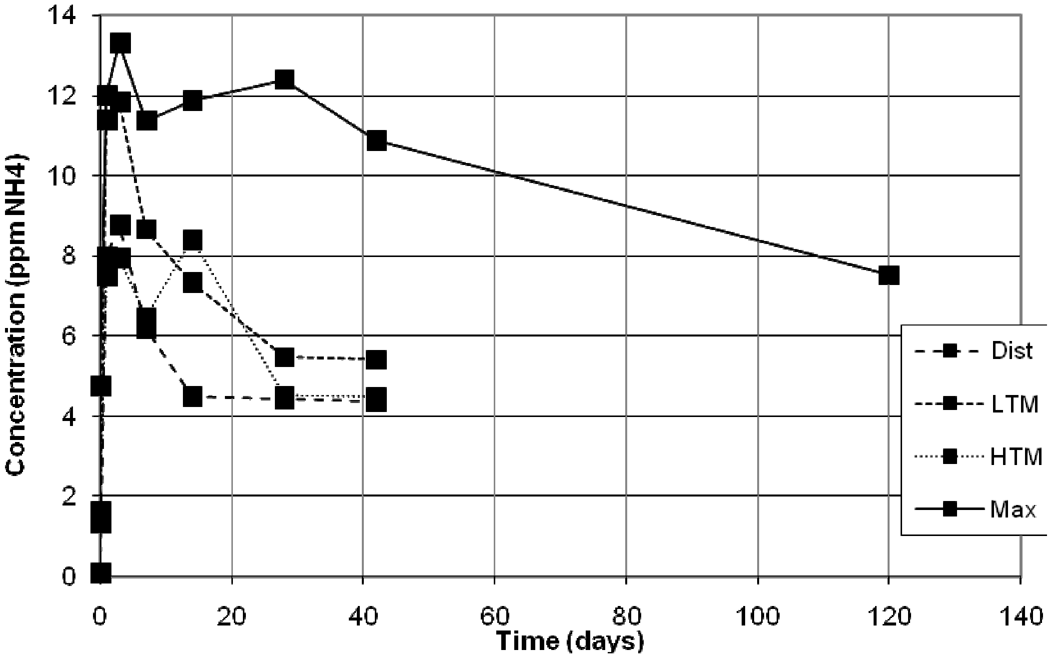


Figure A.16, Ammonium in the IBAA Tank Test

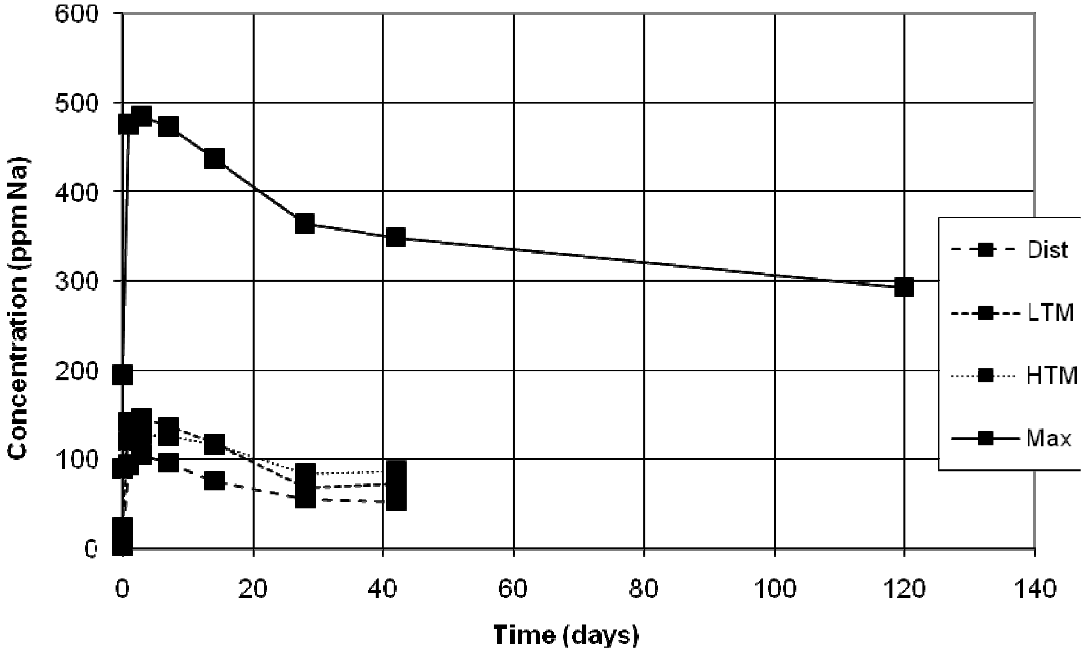
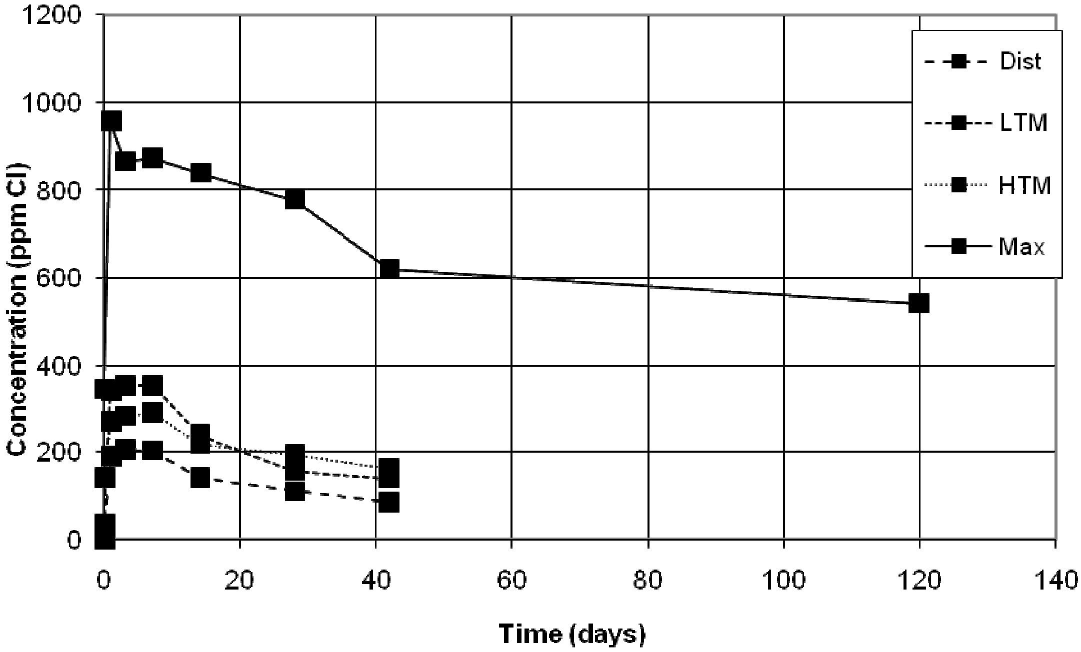


Figure A.17, Sodium in the IBAA Tank Test



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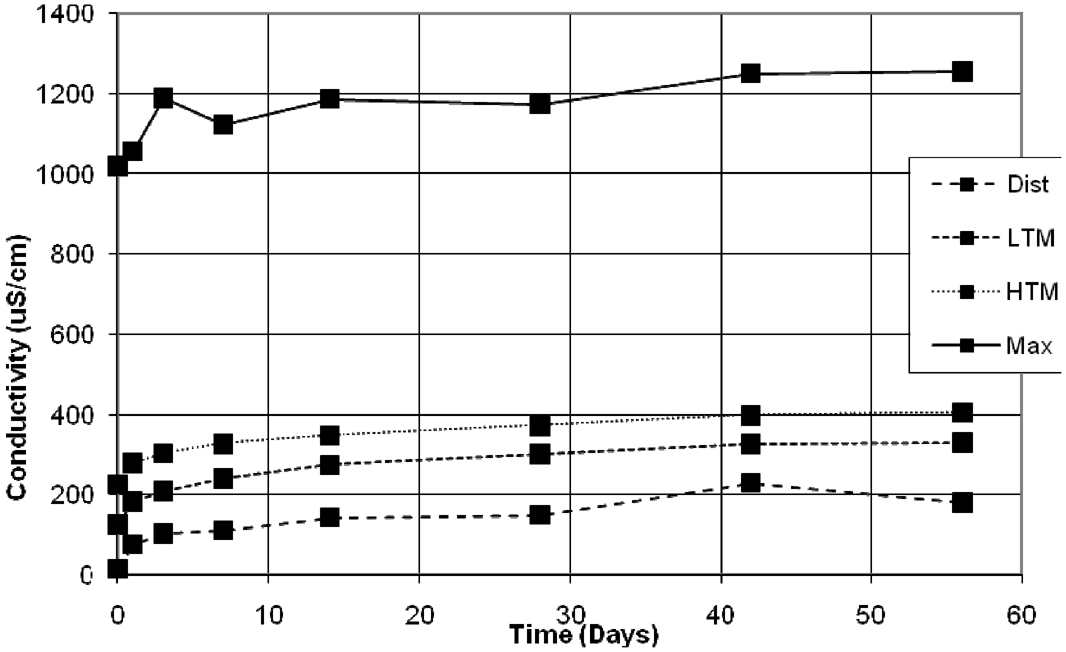


Figure A.19, Conductivity for the Old IBAA Tank Test

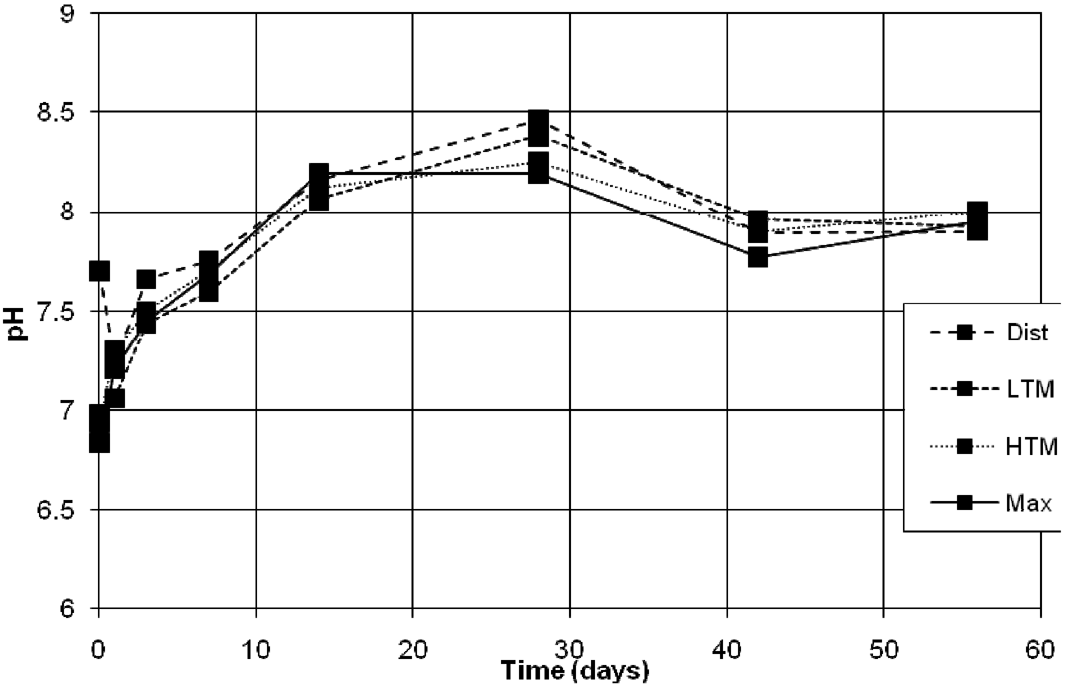


Figure A.20, pH for the Old IBAA Tank Test

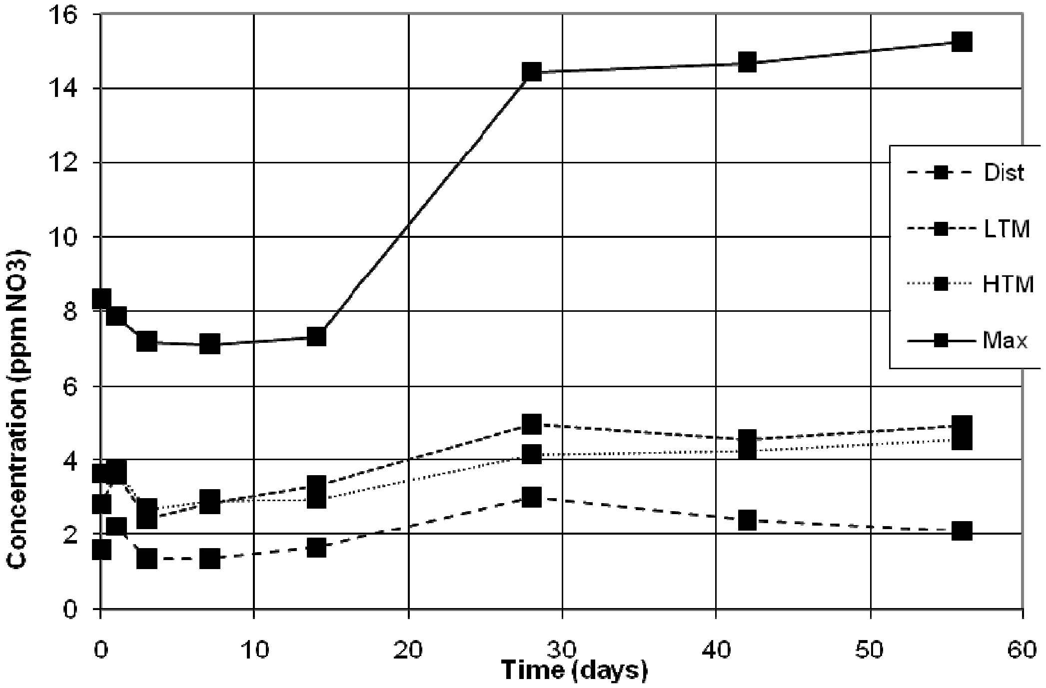


Figure A.21, Nitrate Concentration in the Old IBAA Tank Test

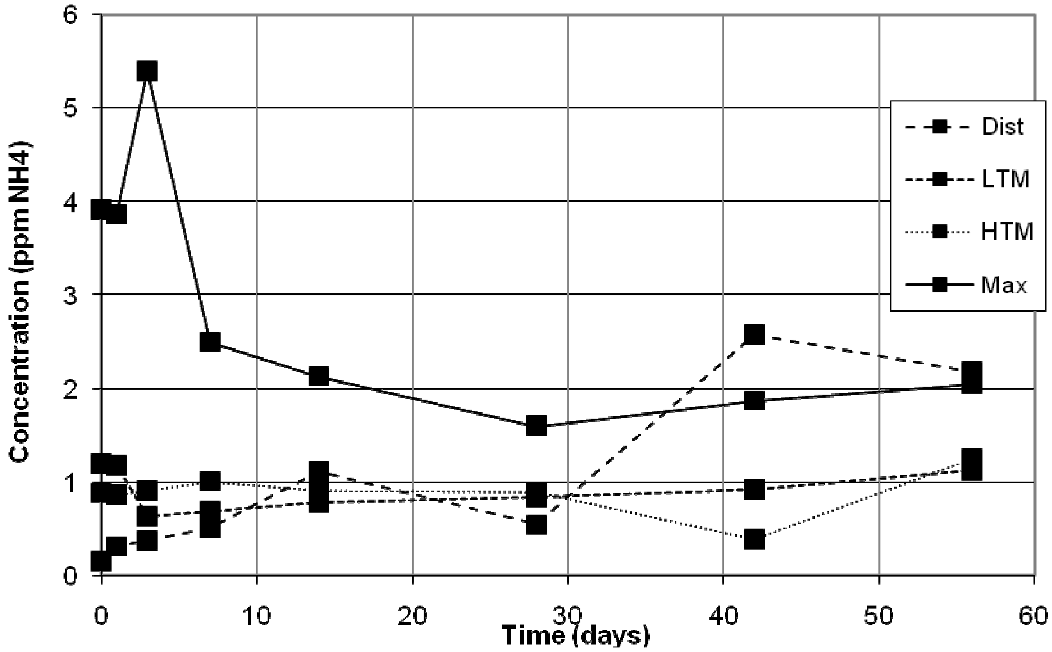


Figure A.22, Ammonium in the Old IBAA Tank Test

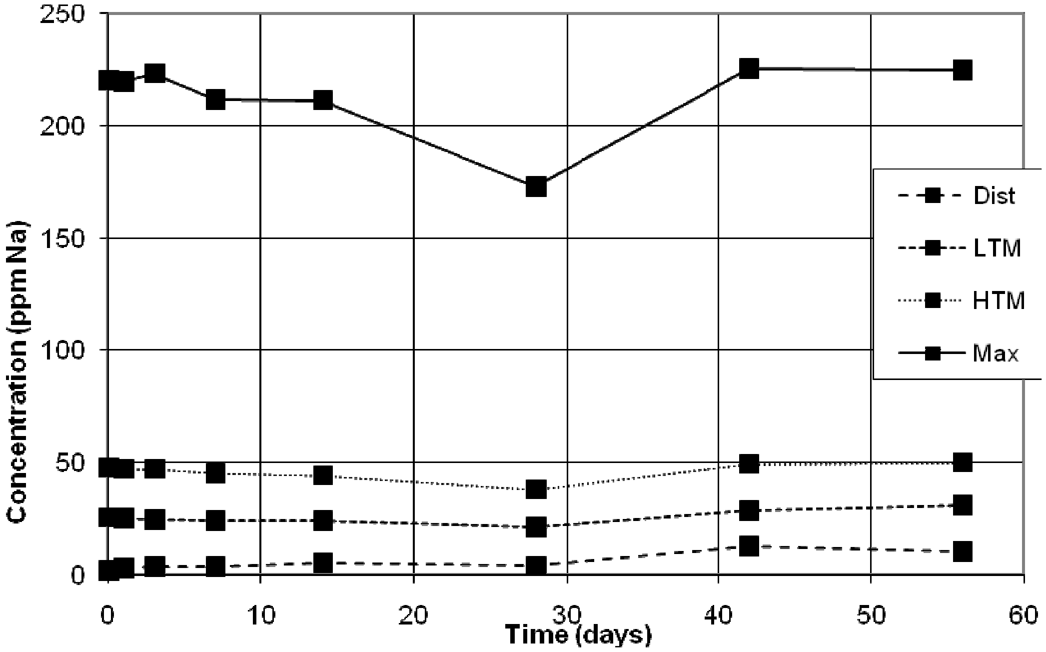
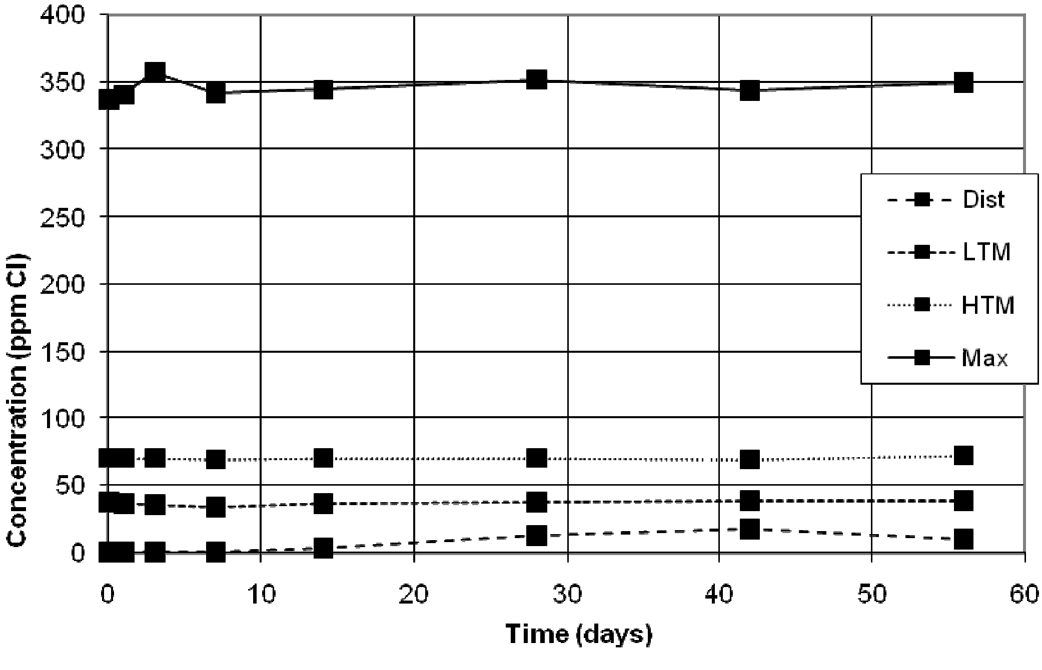


Figure A.23, Sodium in the Old IBAA Tank Test



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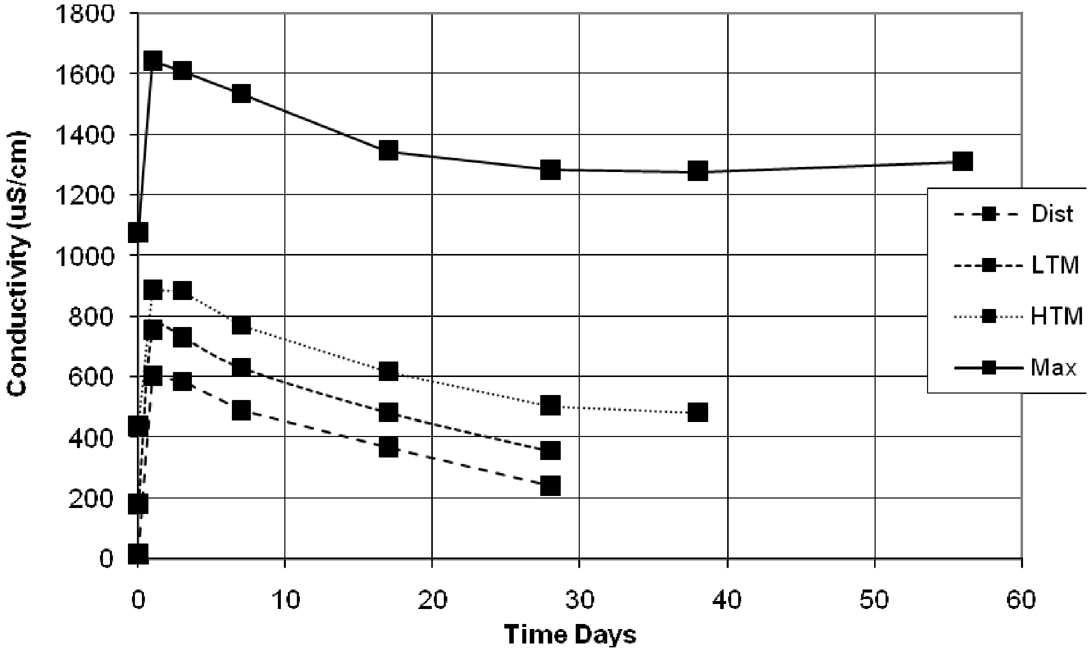


Figure A.25, Conductivity in the RFS Tank Test.

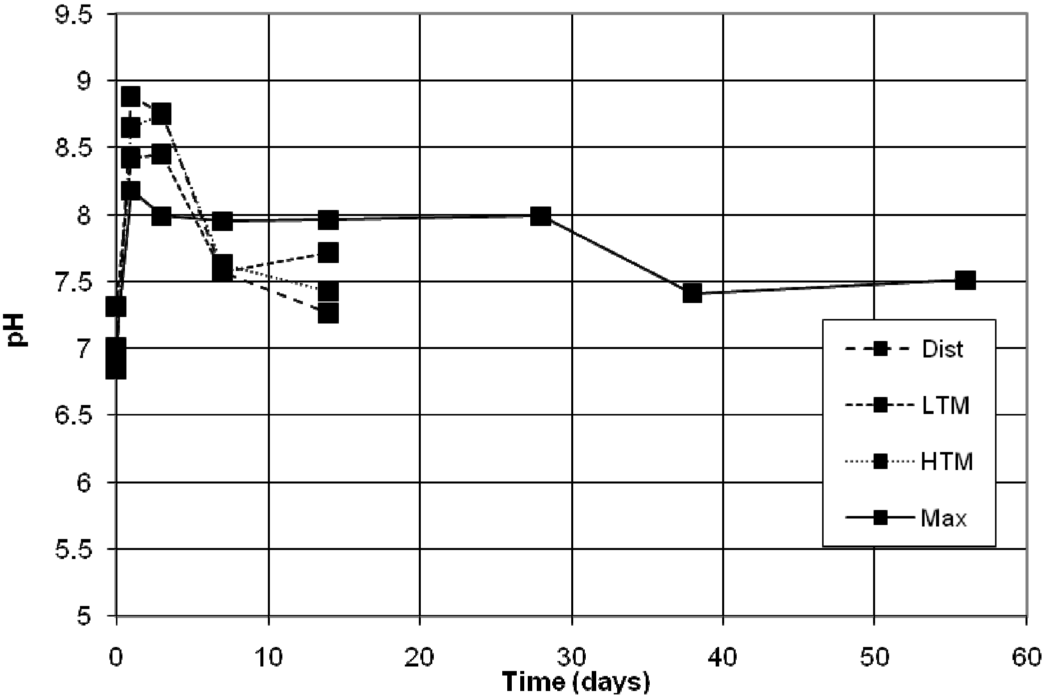


Figure A.26, pH in the RFS Tank Test

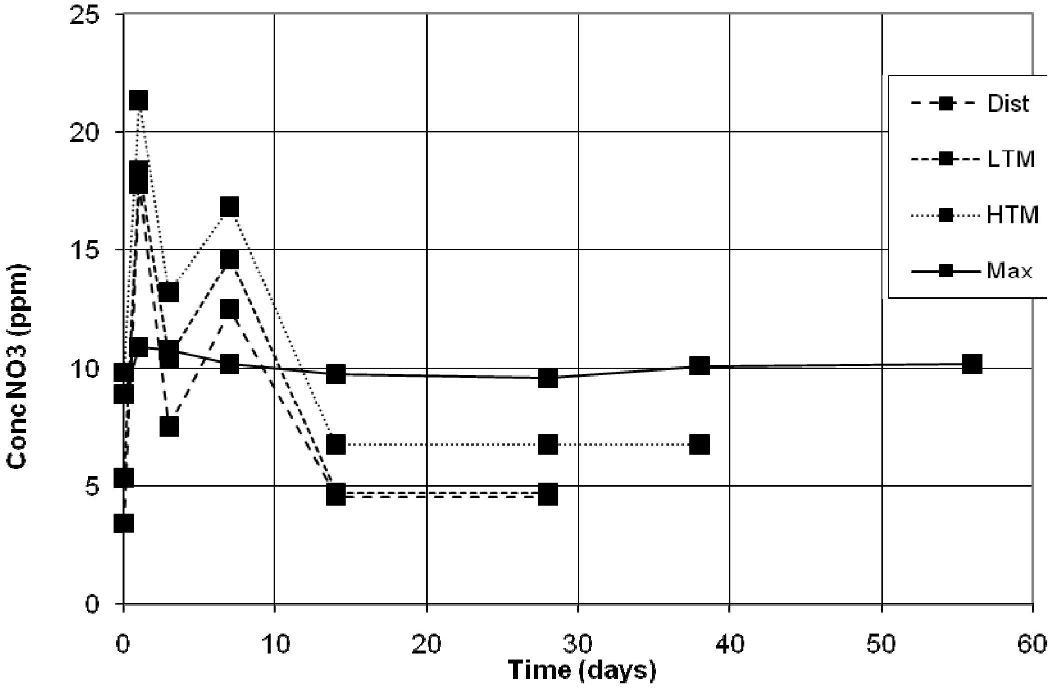


Figure A.27, Nitrate in the RFS Tank Test.

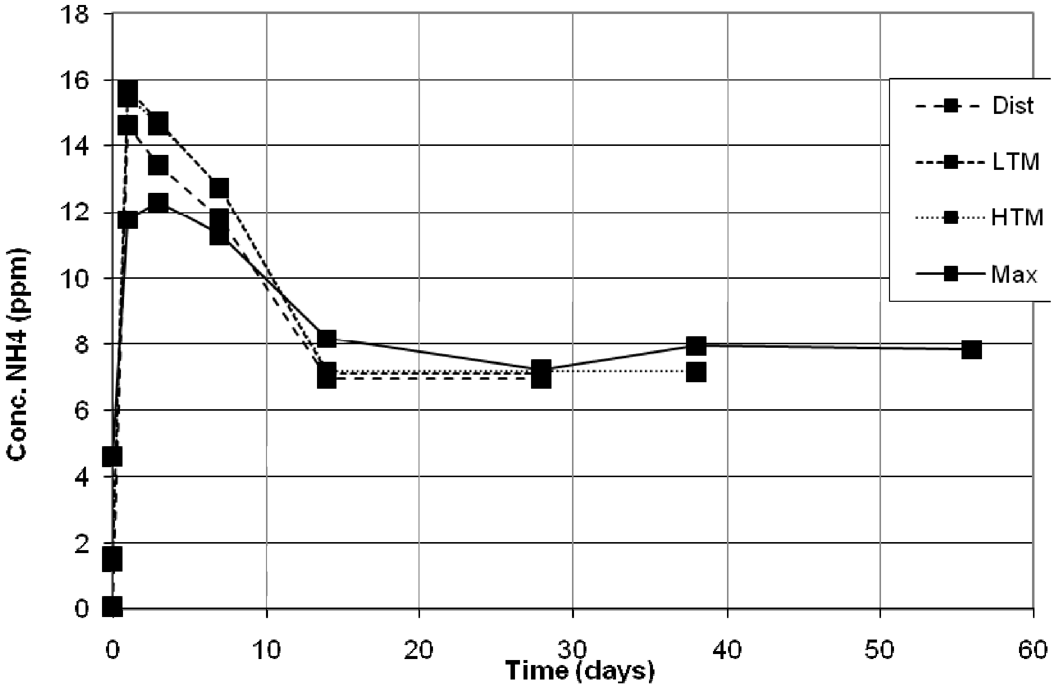


Figure A.28, Ammonium in the RFS Tank Test.

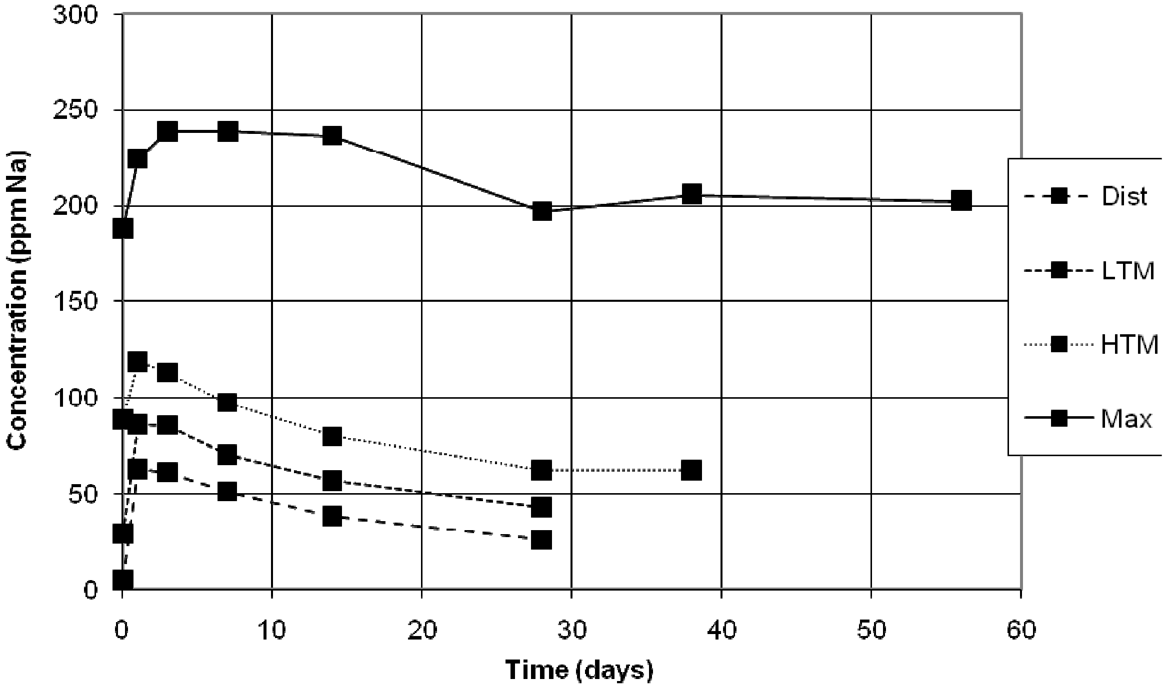


Figure A.29, Sodium in the RFS Tank Test.

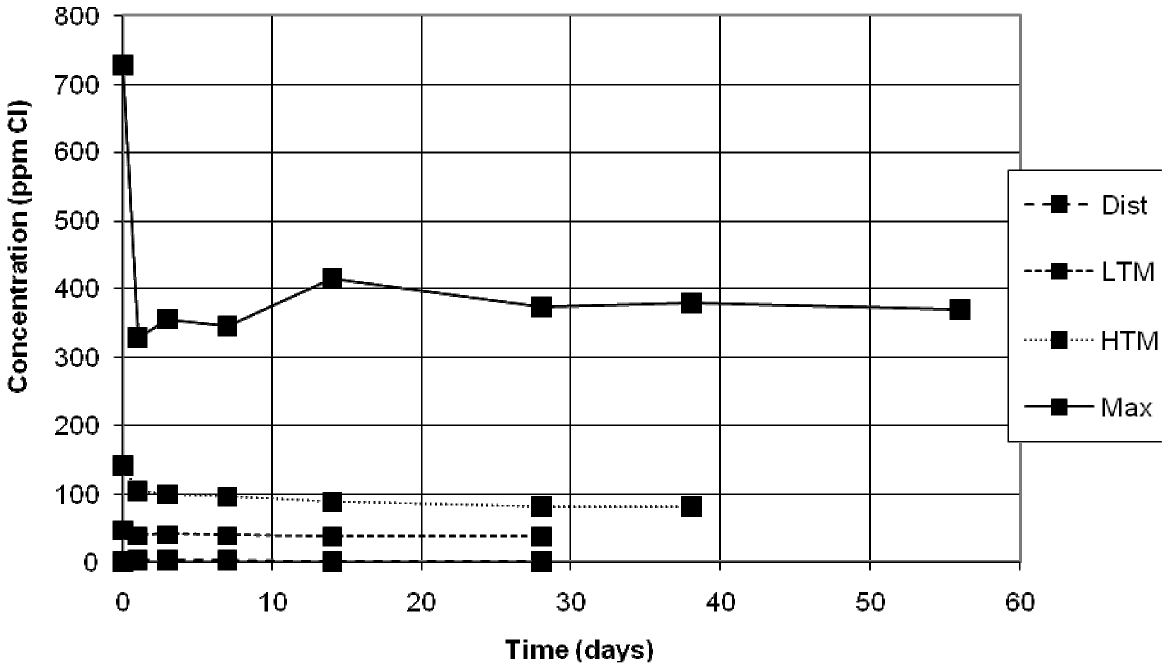


Figure A.30, Chloride in the RFS Tank Test.

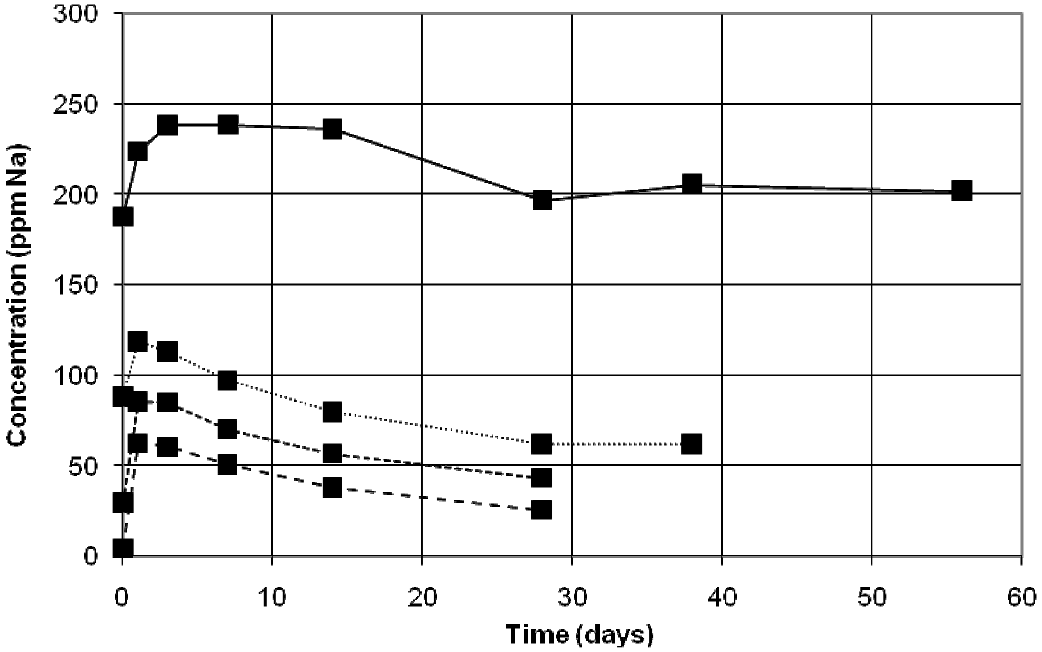


Figure A.31, Conductivity in the Old RFS Tank Test

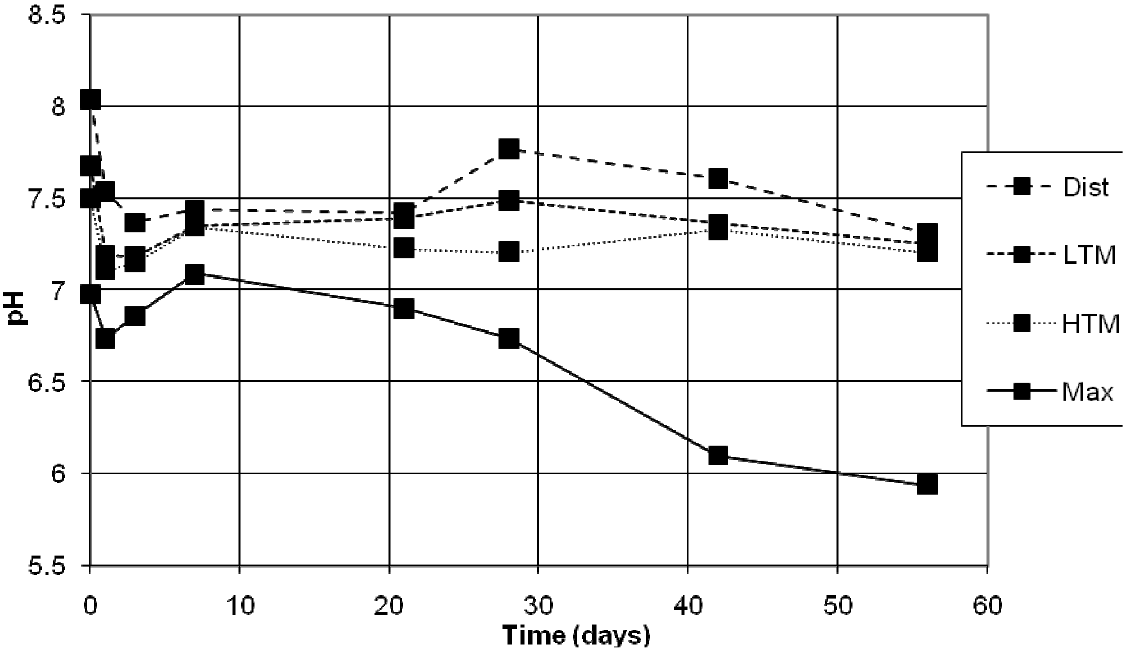
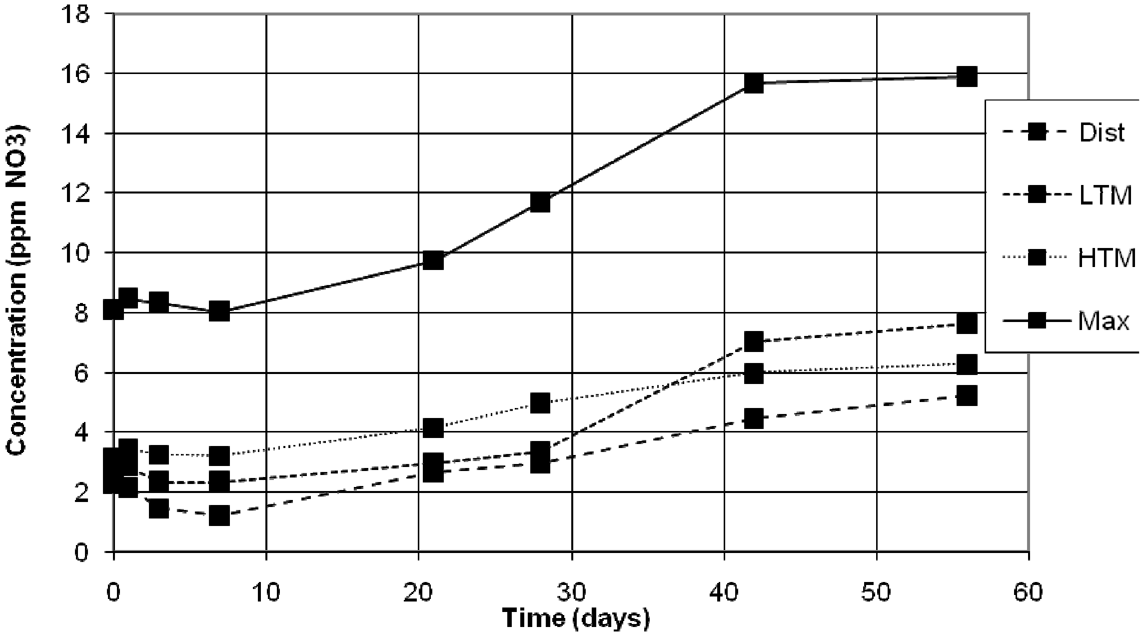


Figure A.32, pH in the Old RFS Tank Test



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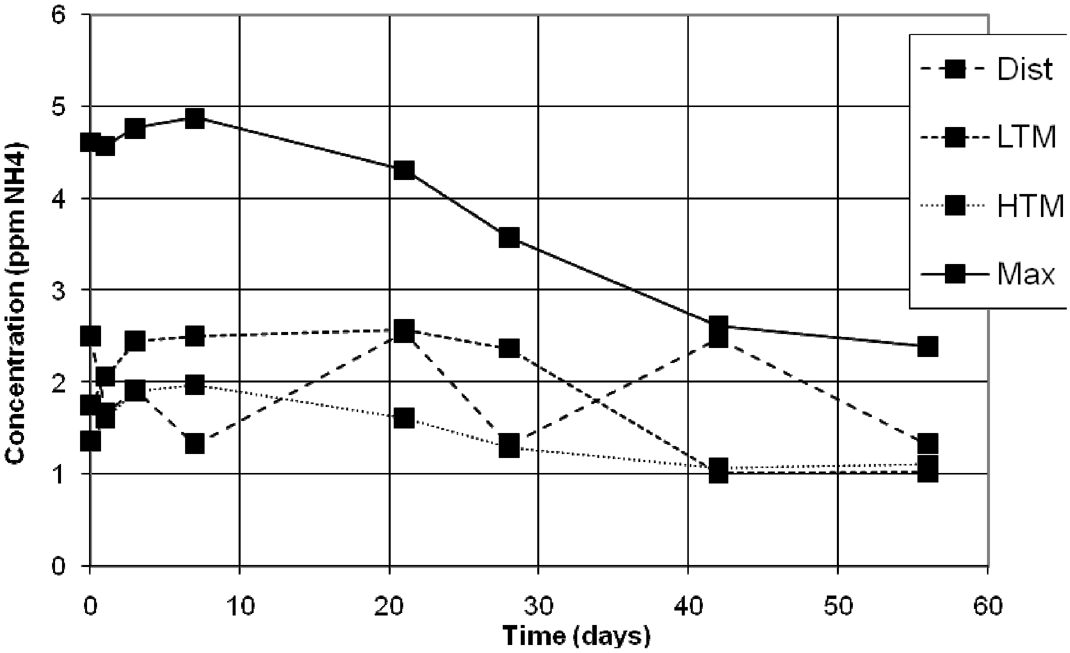
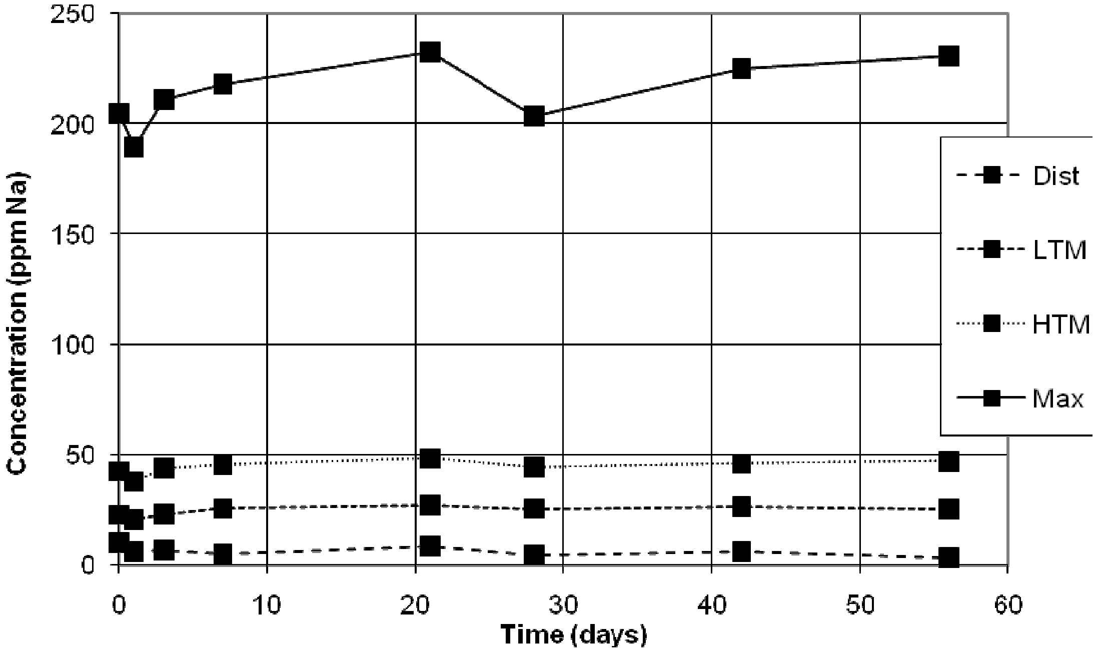


Figure A.34, Ammonium in the Old RFS Tank Test



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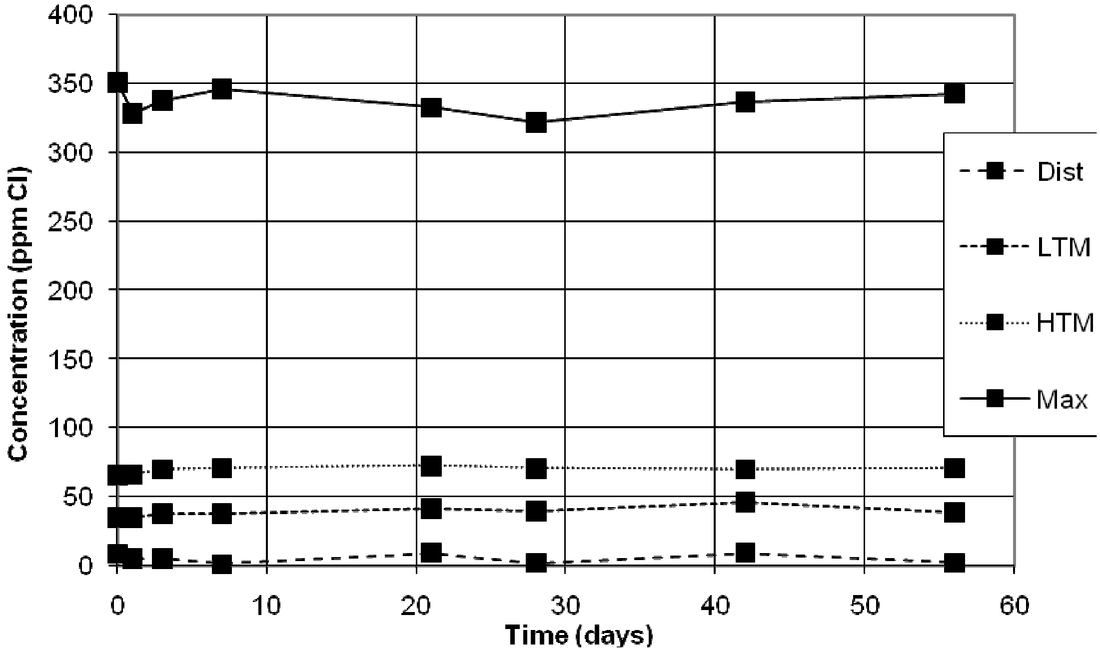

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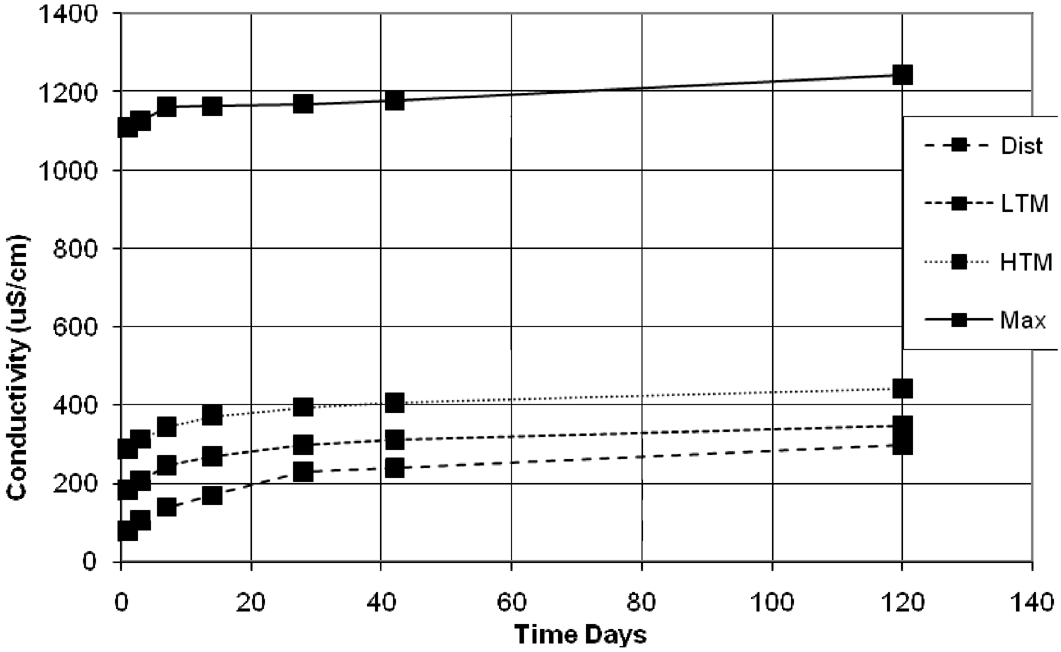
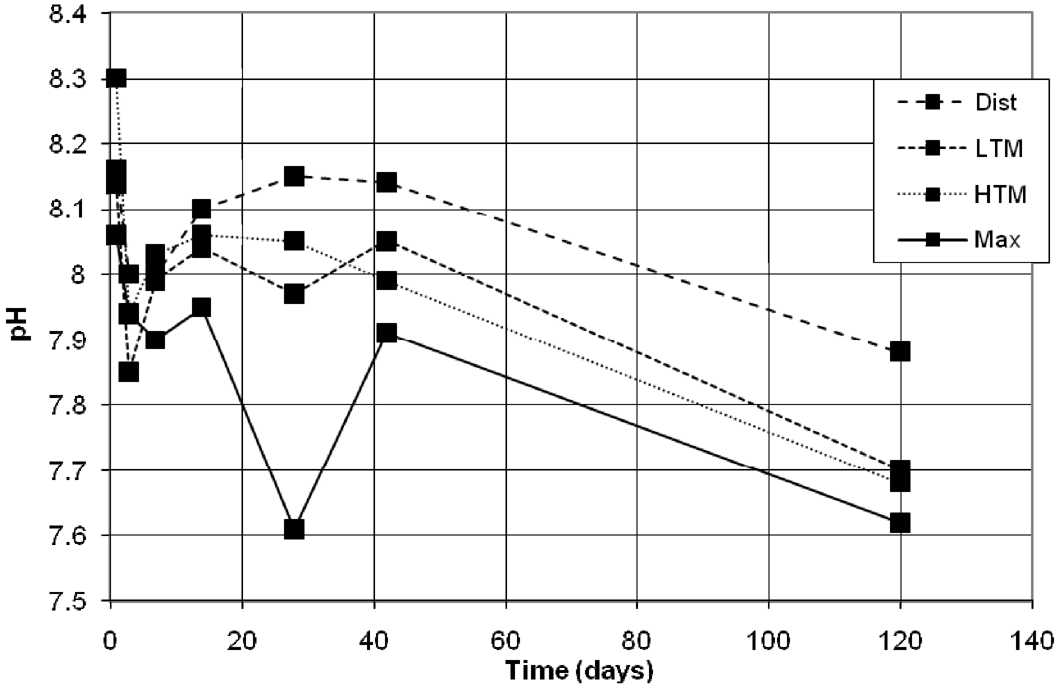


Figure A.37, Conductivity in the BFS Tank Test



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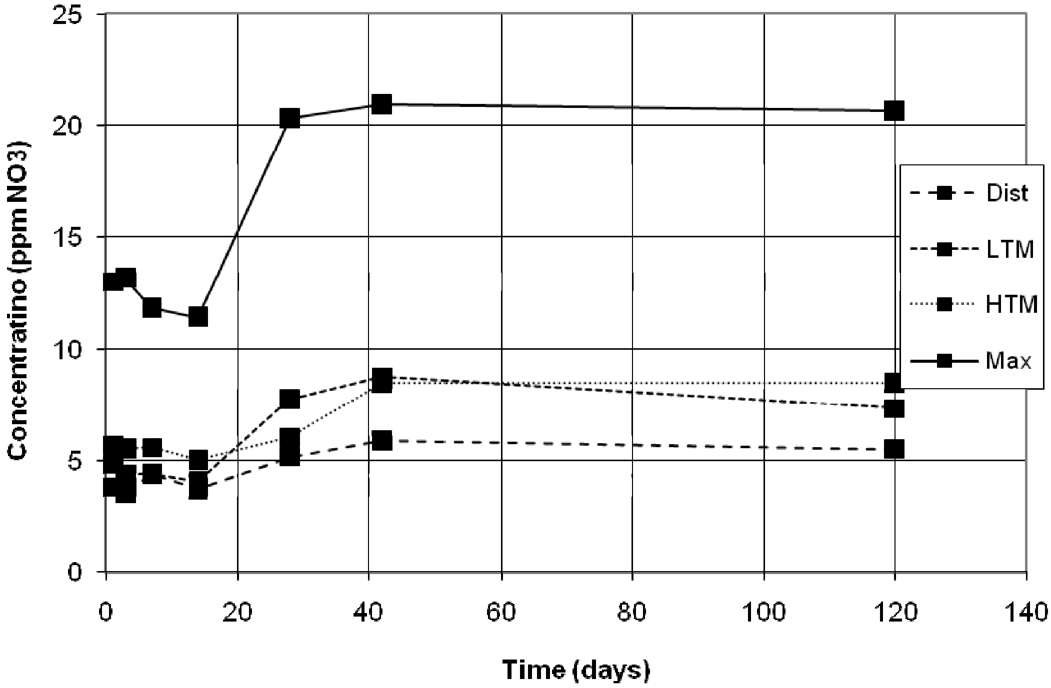

Figure A.39, Nitrate in the BFS Test Tank.

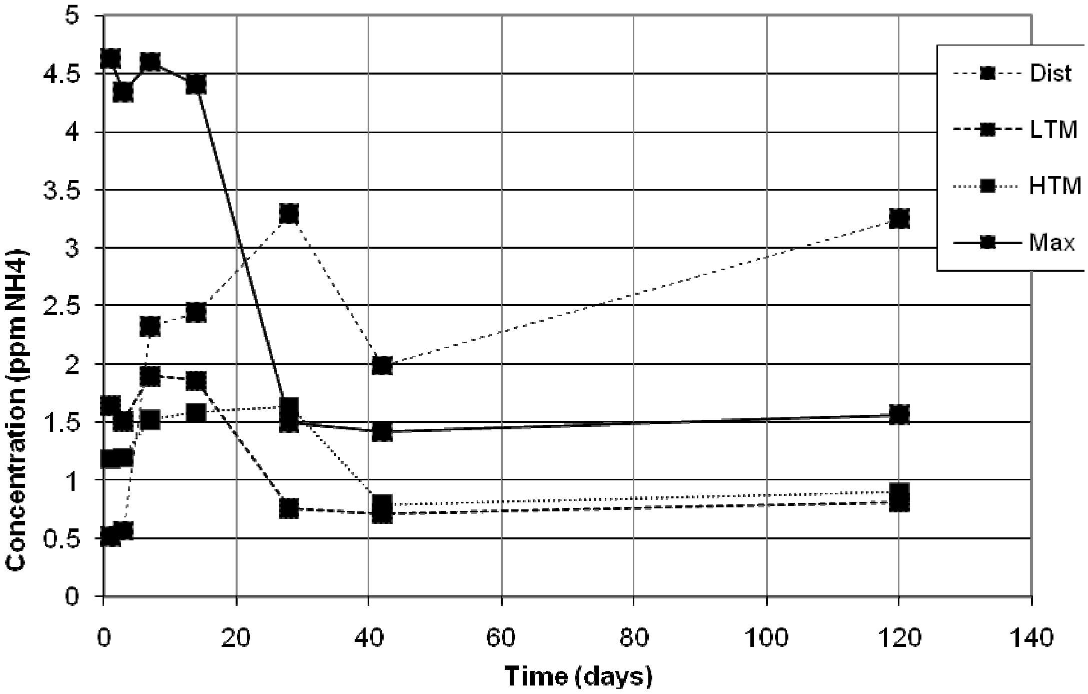

Figure A.40, Ammonium in the BFS Test Tank.

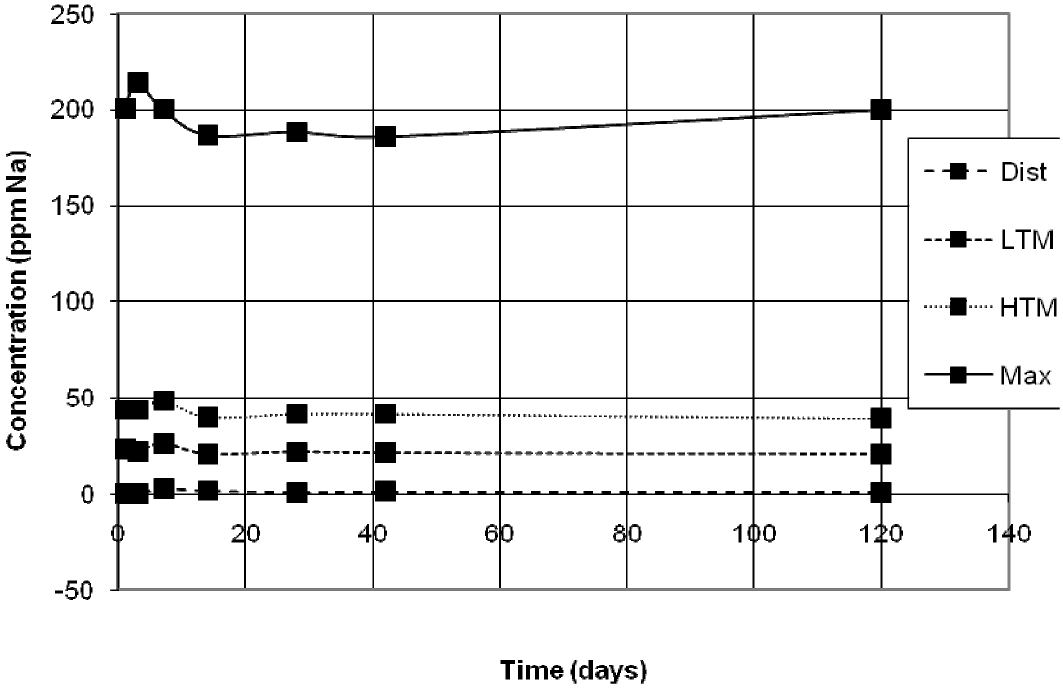

Figure A.41, Sodium in the BFS Tank Test

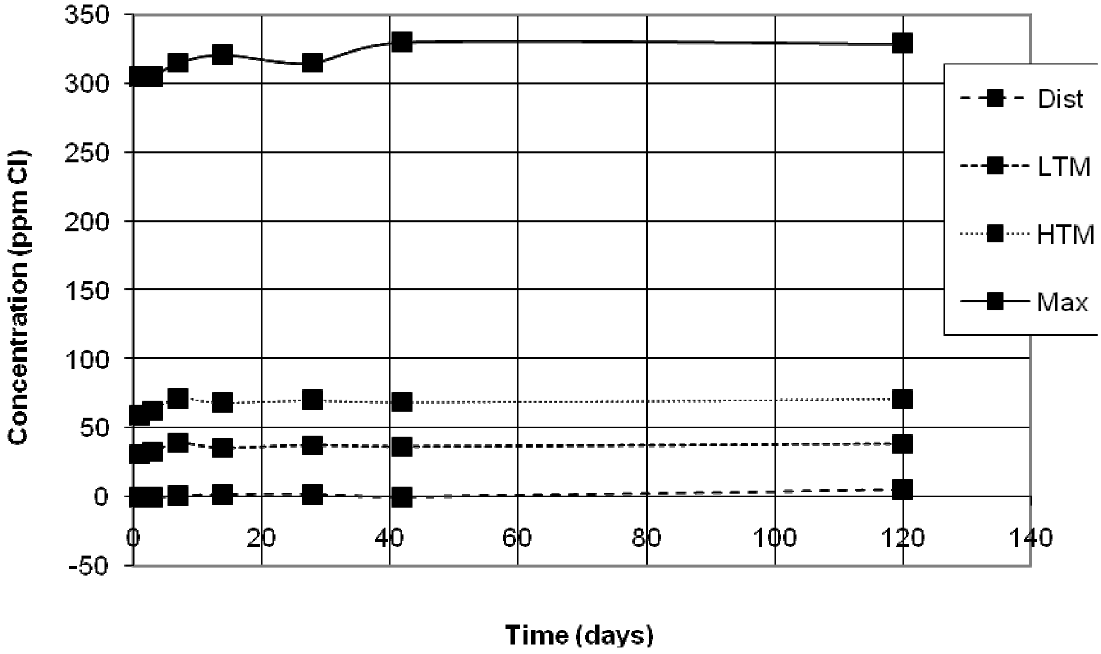

Figure A.42, Chloride in the BFS Tank Test.

APPENDIX B – INFILTRATION TEST RESULTS

Introduction

The following charts present the change in chemical determinands, i.e. conductivity or concentration, across the infiltration test sample. Where there is a positive value this indicates that chemicals have been leached into the water, where there is a negative value this indicates that chemicals have been ad/absorbed by the aggregate.

B.1 Limestone Charts

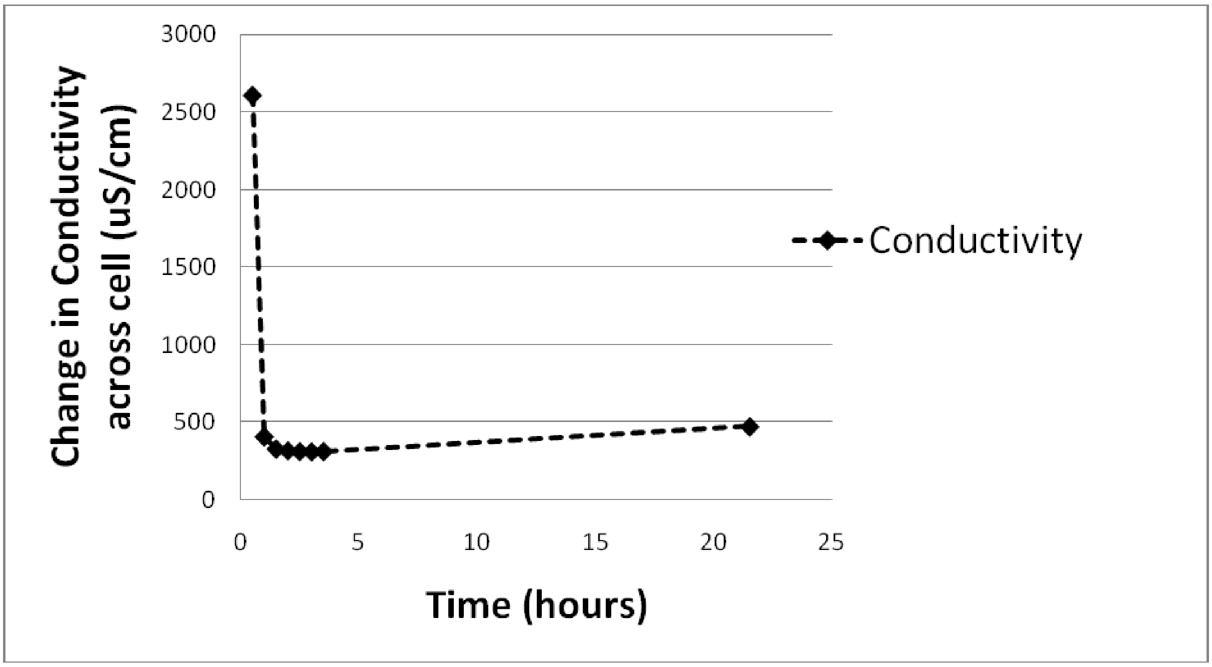

Figure B.1, Limestone infiltration test results for conductivity.

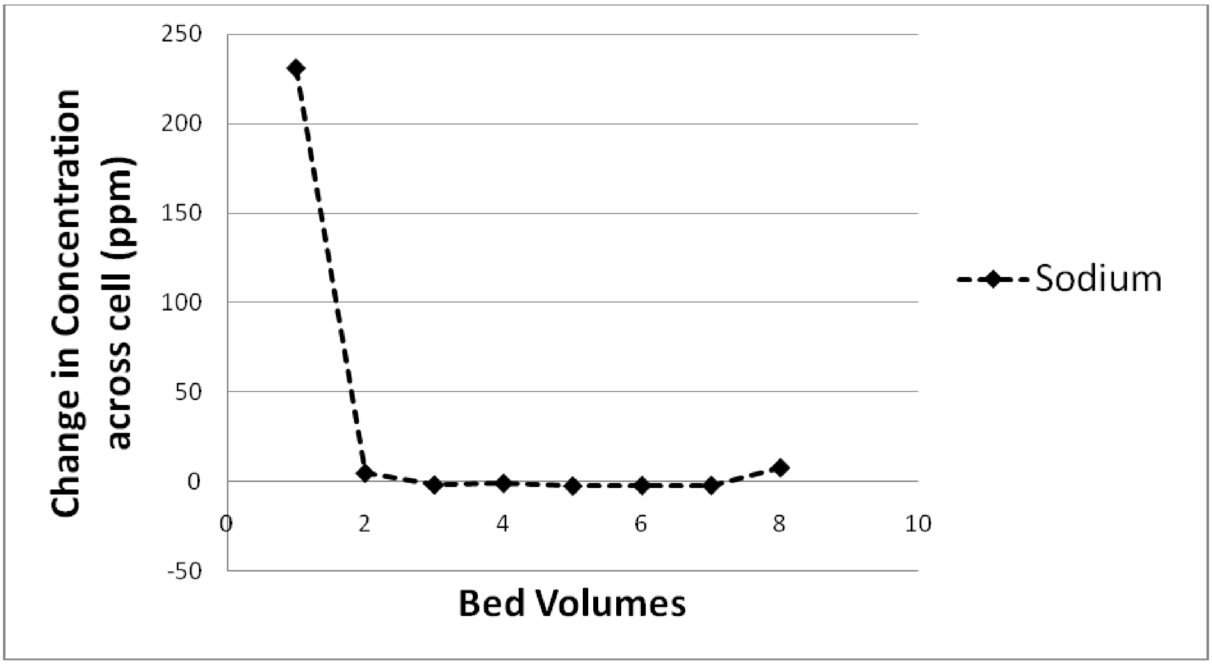

Figure B.2, Limestone infiltration test results for sodium.

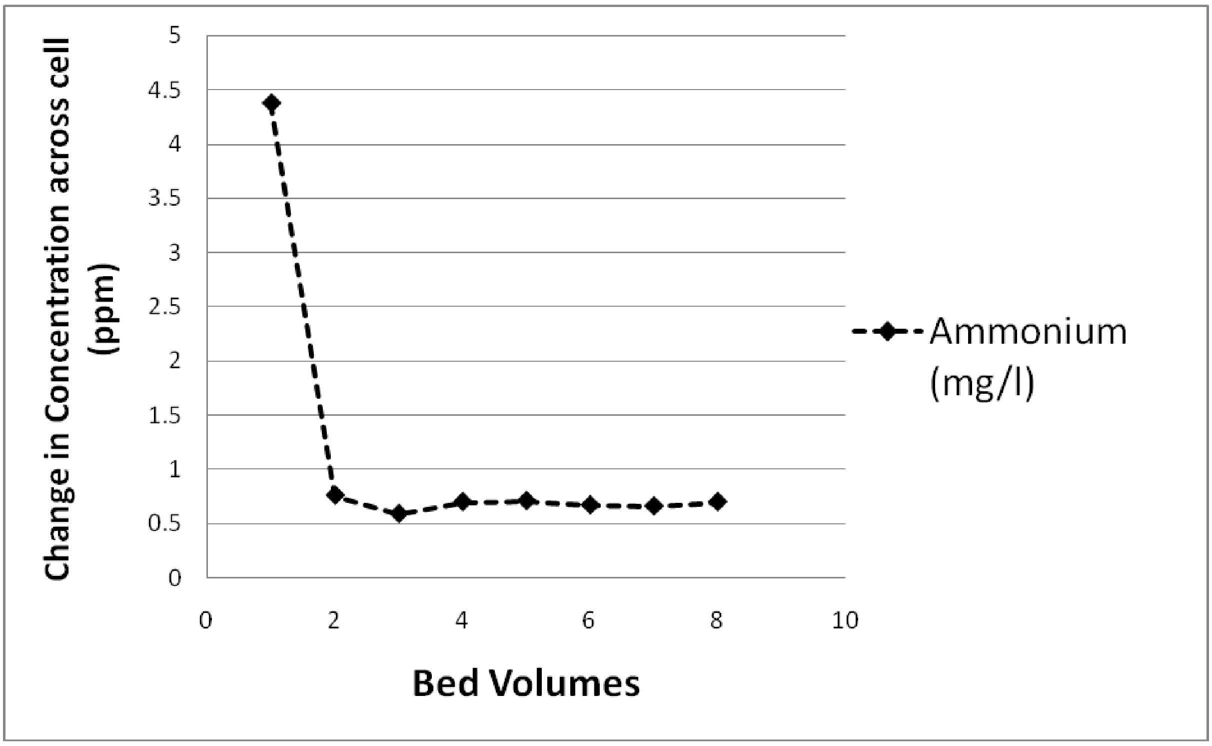

Figure B.3, Limestone infiltration test results for ammonium.

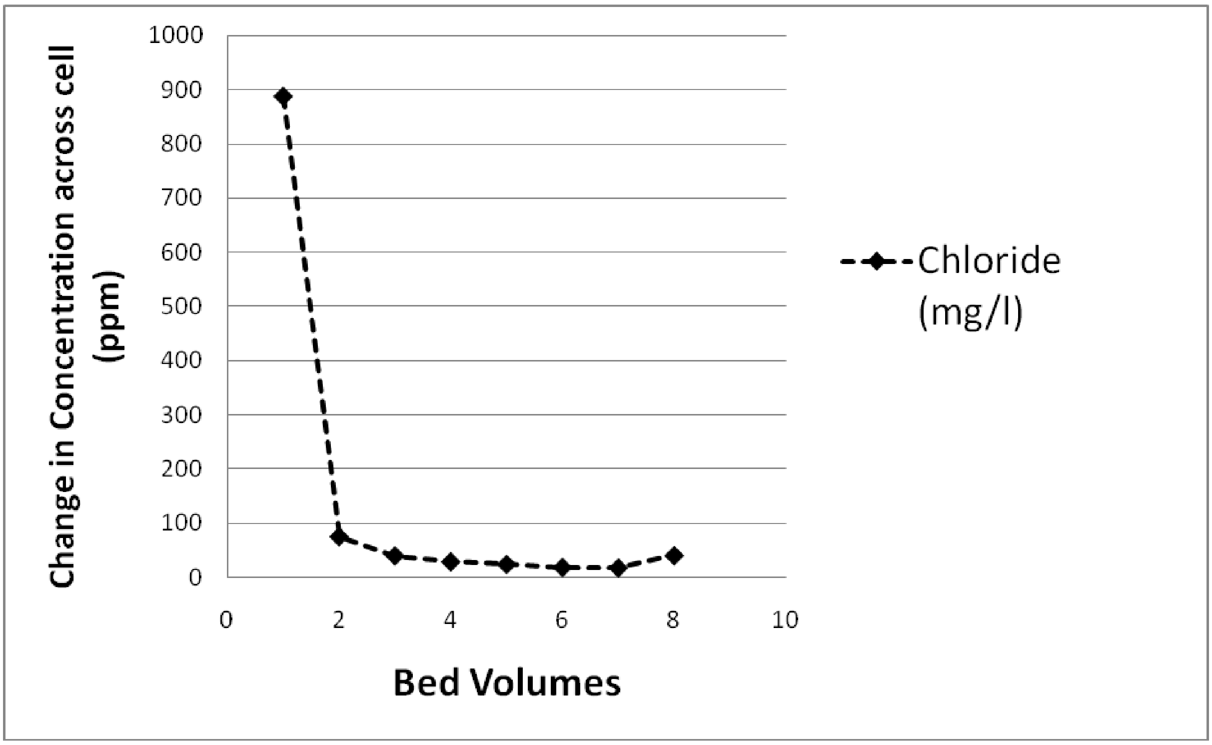

Figure B.4, Limestone infiltration test results for chloride.

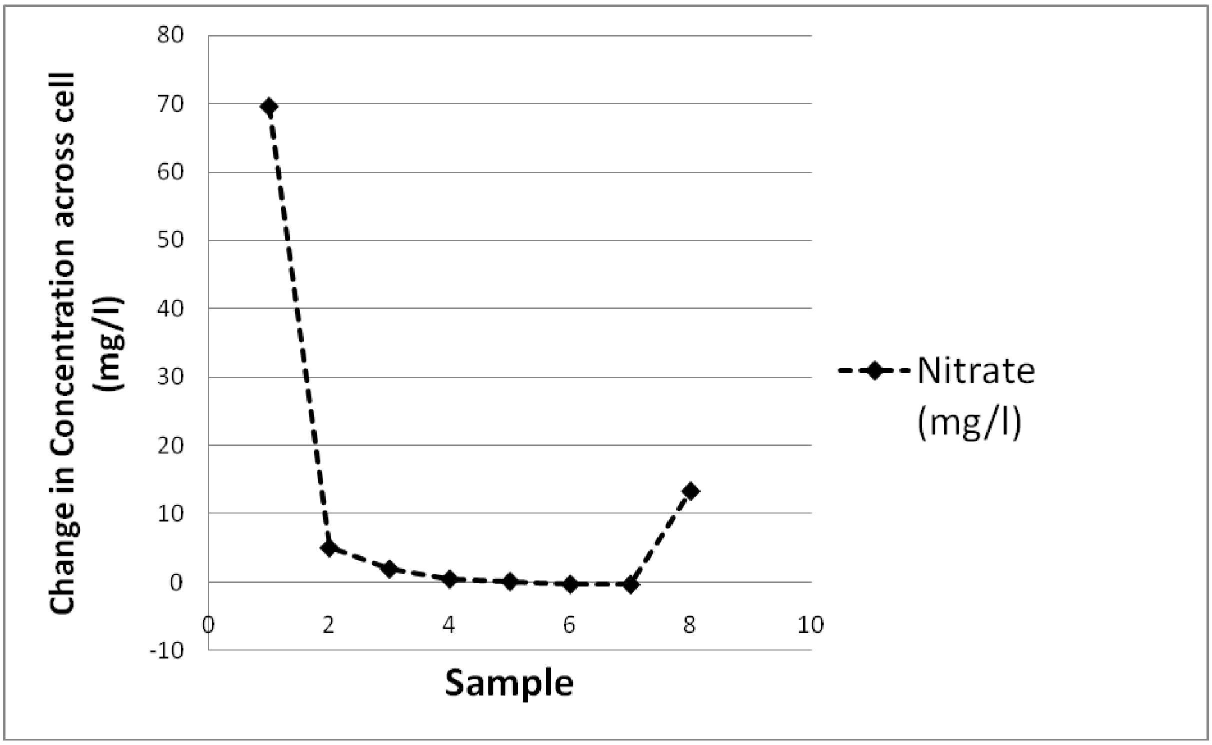

Figure B.5, Limestone infiltration test results for nitrate.

B.2 Old Limestone Charts

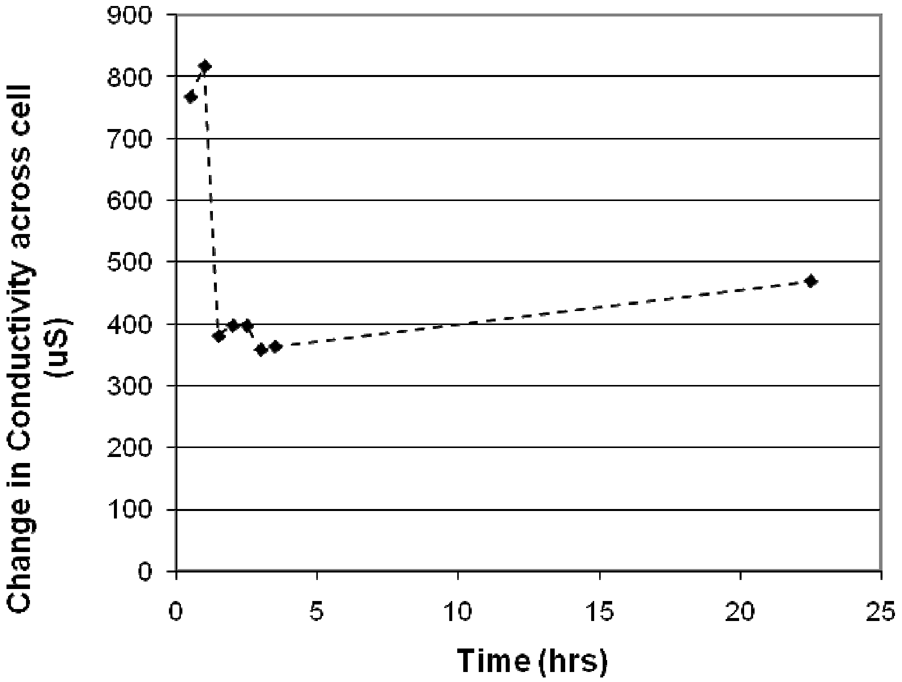

Figure B.6, Old limestone infiltration test results for conductivity.

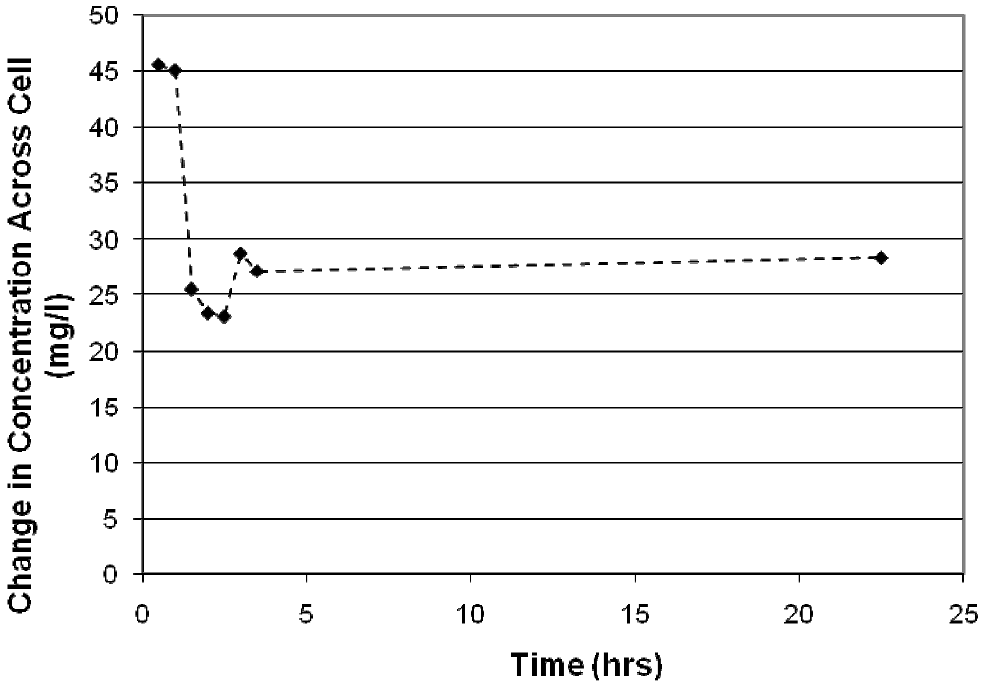

Figure B.7, Old limestone infiltration test results for sodium.

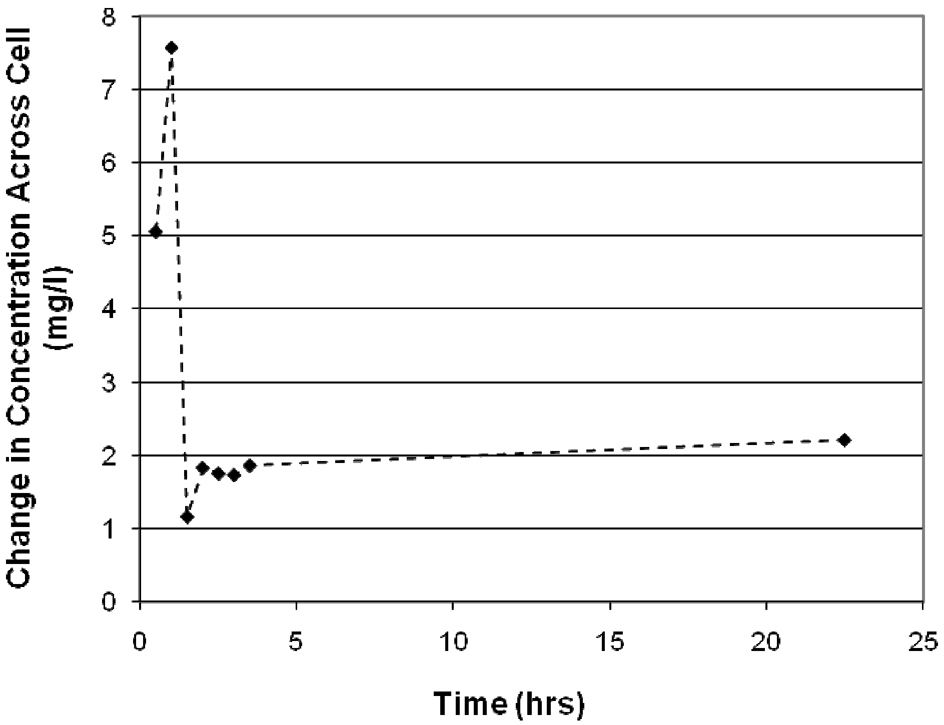

Figure B.8, Old limestone infiltration test results for ammonium.

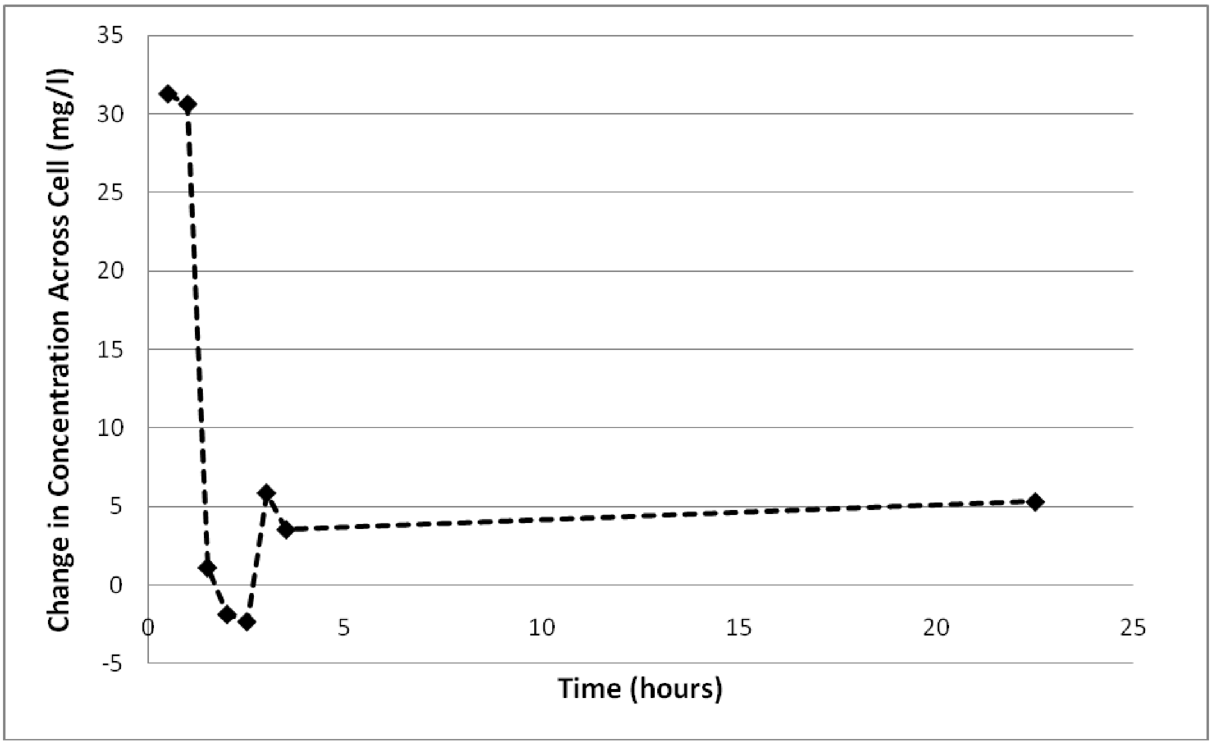

Figure B.9, Old limestone infiltration test results for chloride.

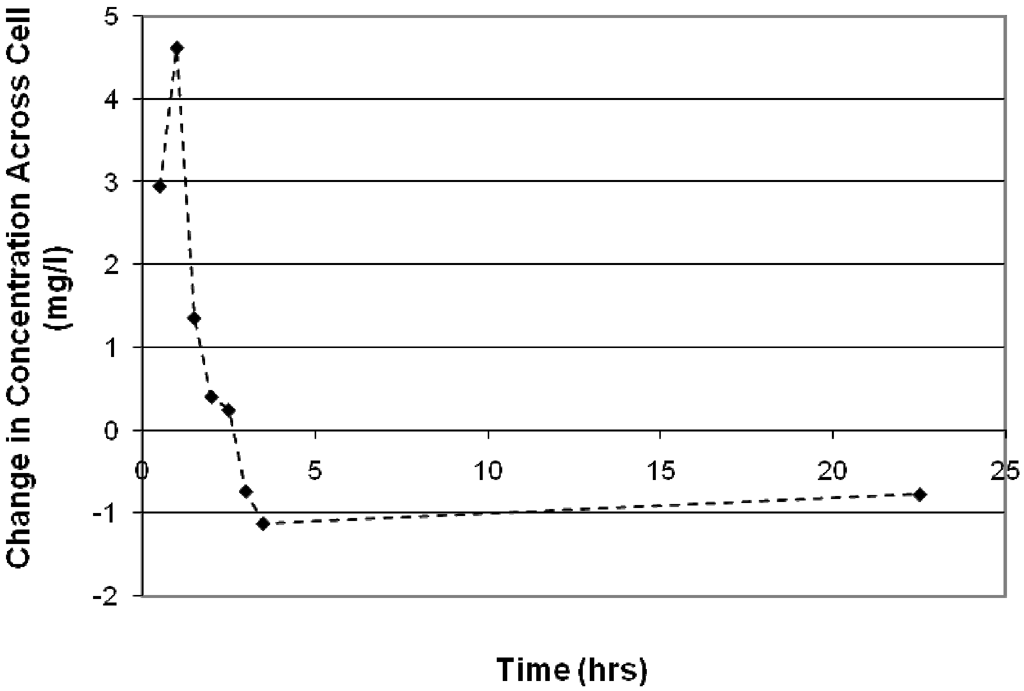

Figure B.10, Old limestone infiltration test results for nitrate.

B.3 IBAA Charts

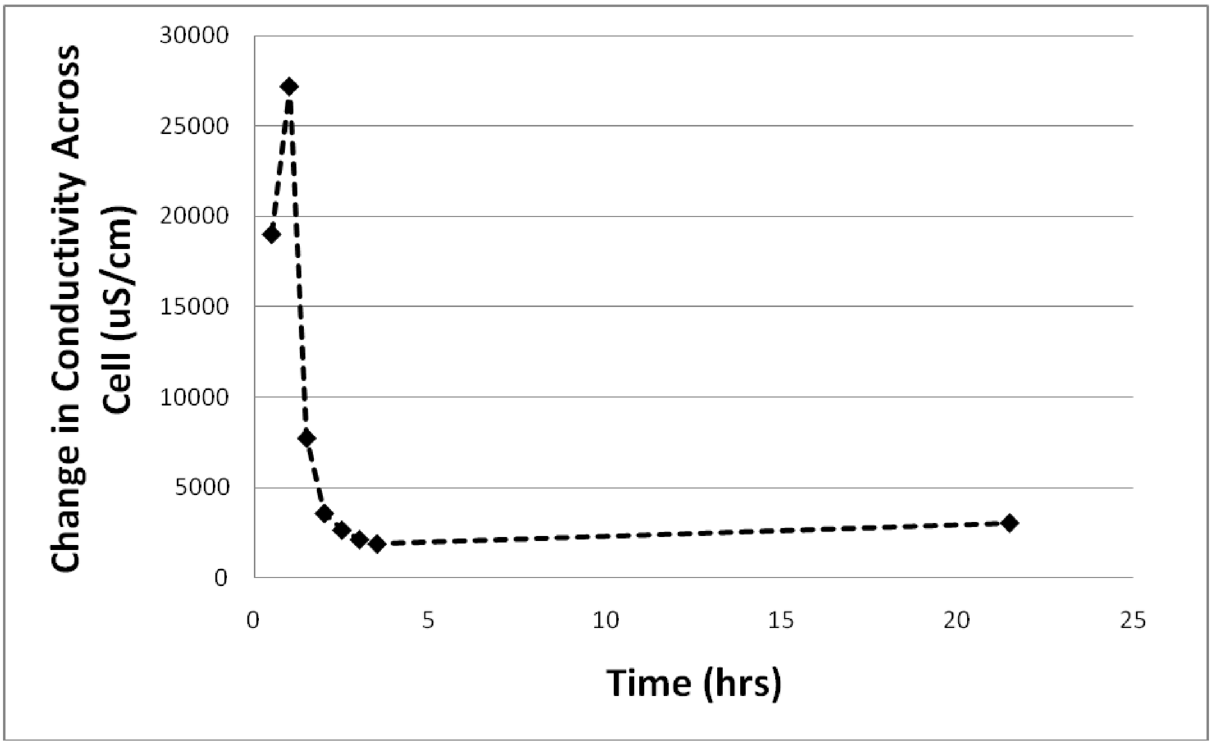

Figure B.11, IBAA infiltration test results for conductivity.

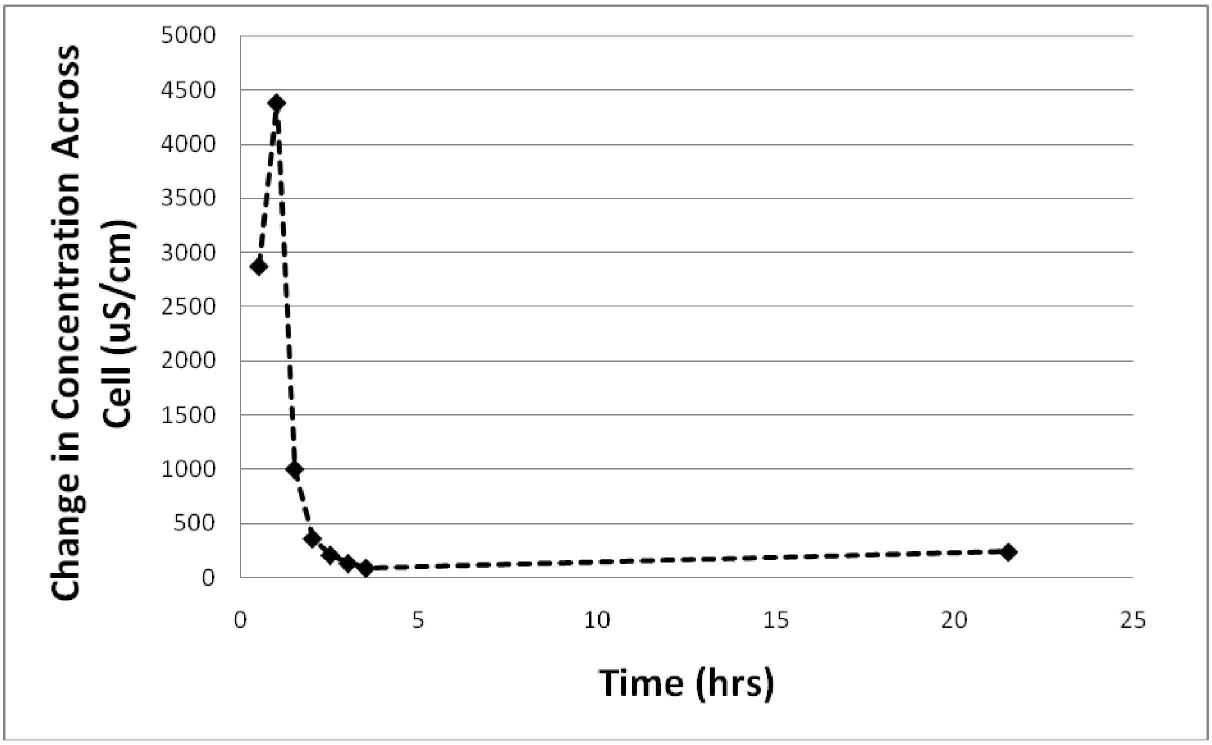

Figure B.12, IBAA infiltration test results for sodium.

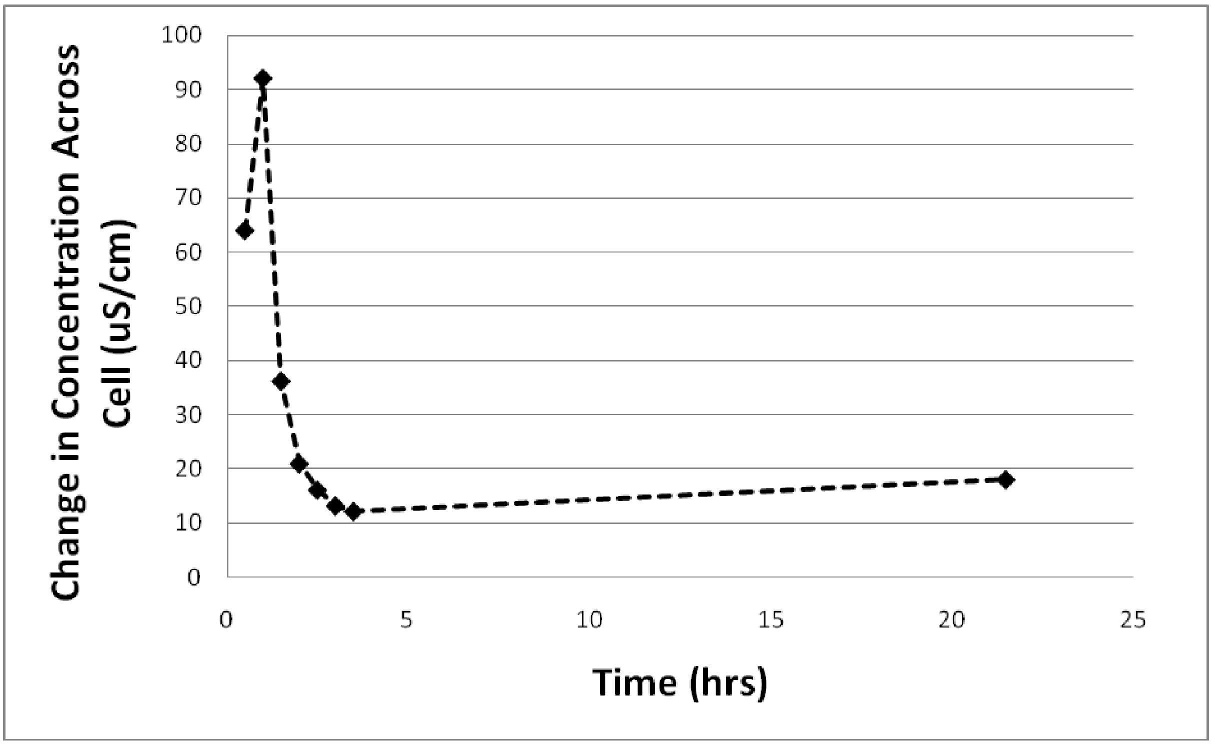

Figure B.13, IBAA infiltration test results for ammonium.

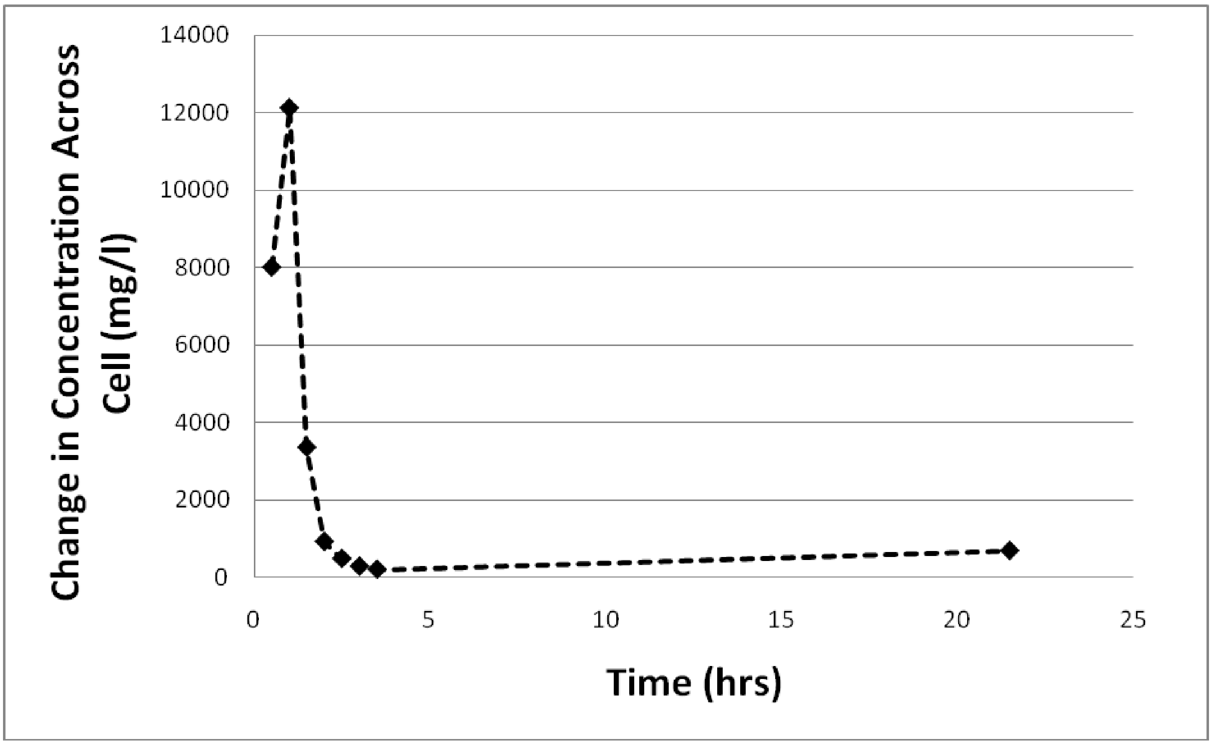

Figure B.14, IBAA infiltration test results for chloride.

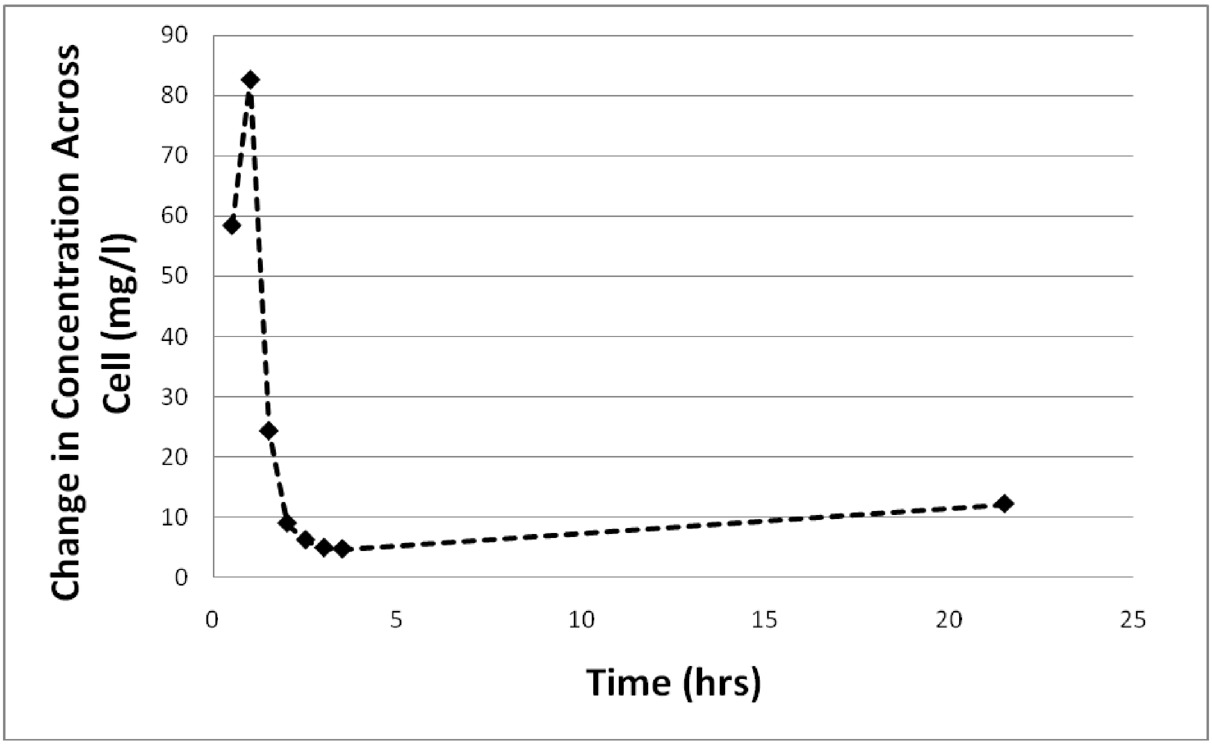

Figure B.15, IBAA infiltration test results for nitrate.

B.4 Old IBAA Charts

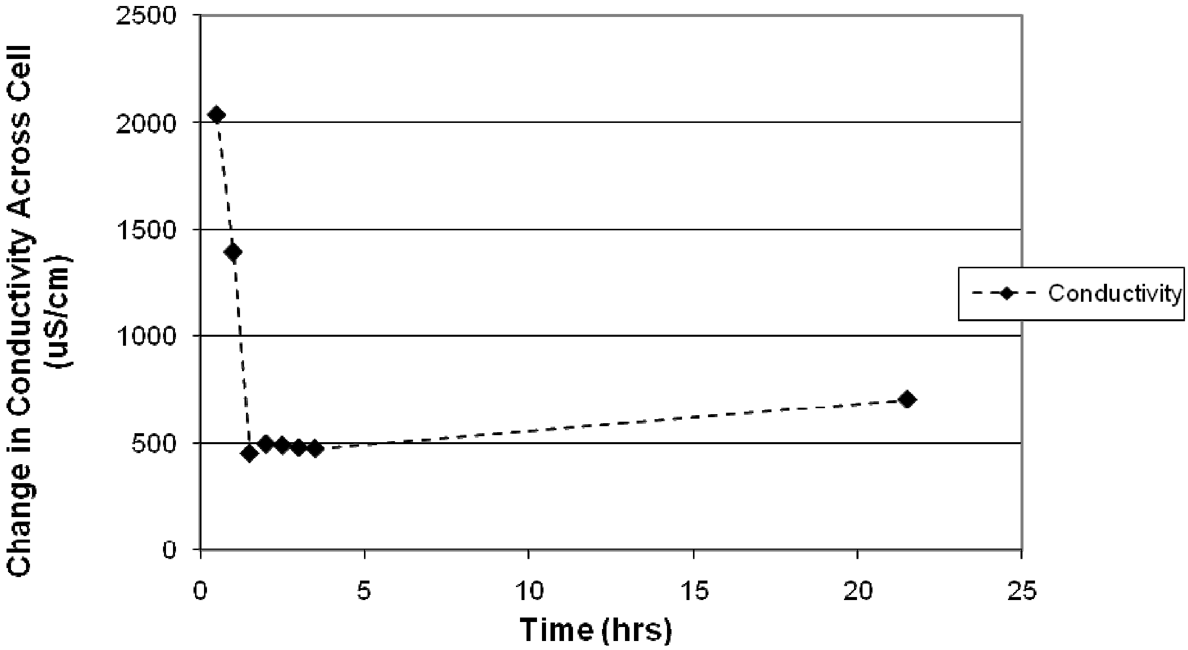

Figure B.16, Old IBAA infiltration test results for conductivity.

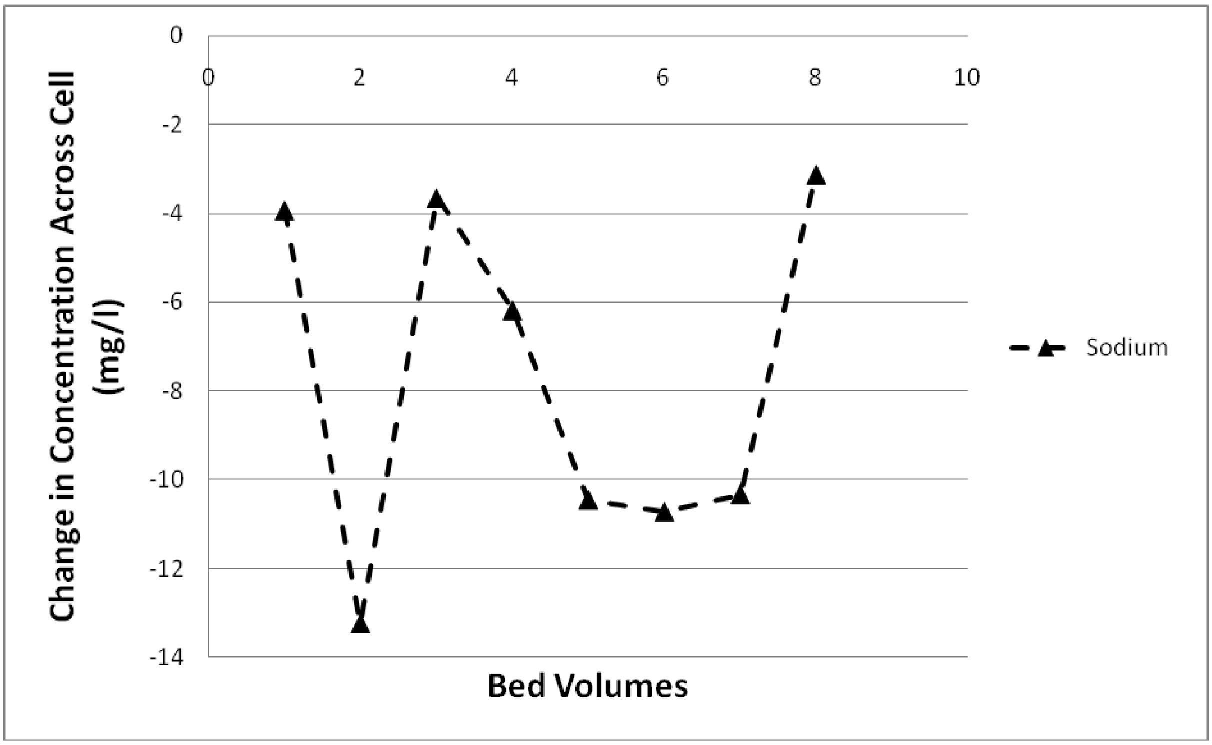

Figure B.17, Old IBAA infiltration test results for sodium.

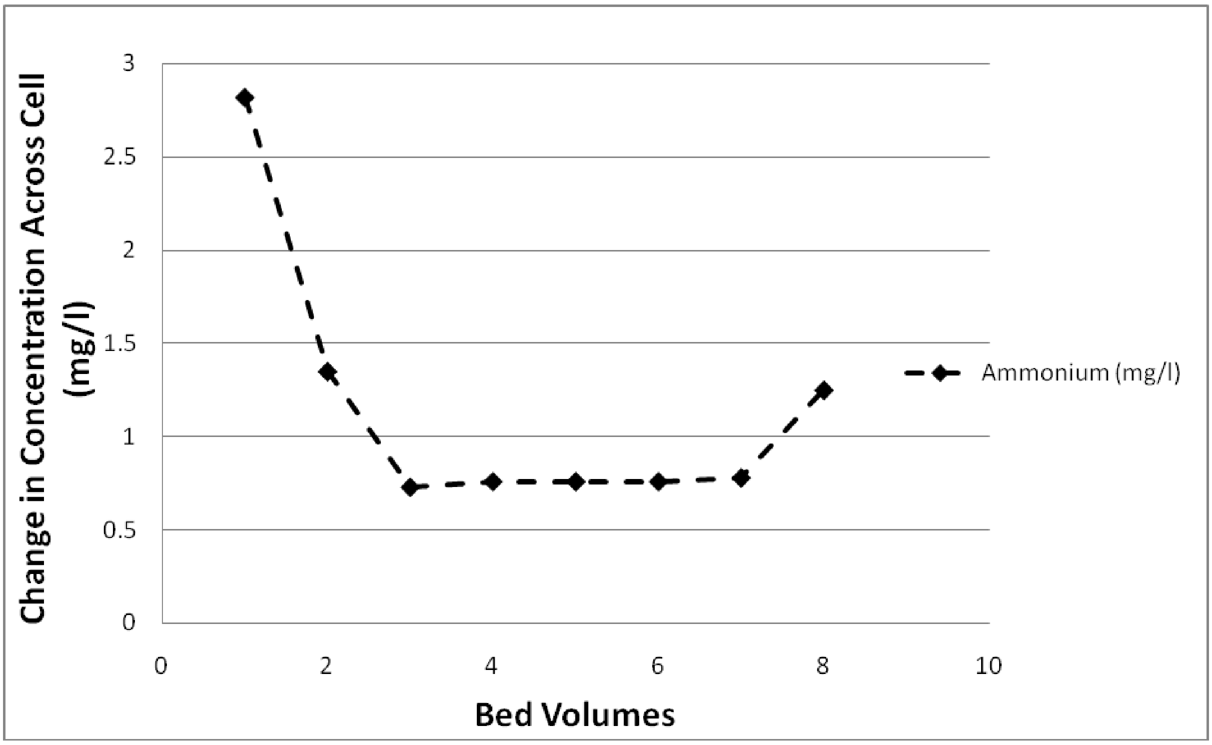

Figure B.18, Old IBAA infiltration test results for ammonium.

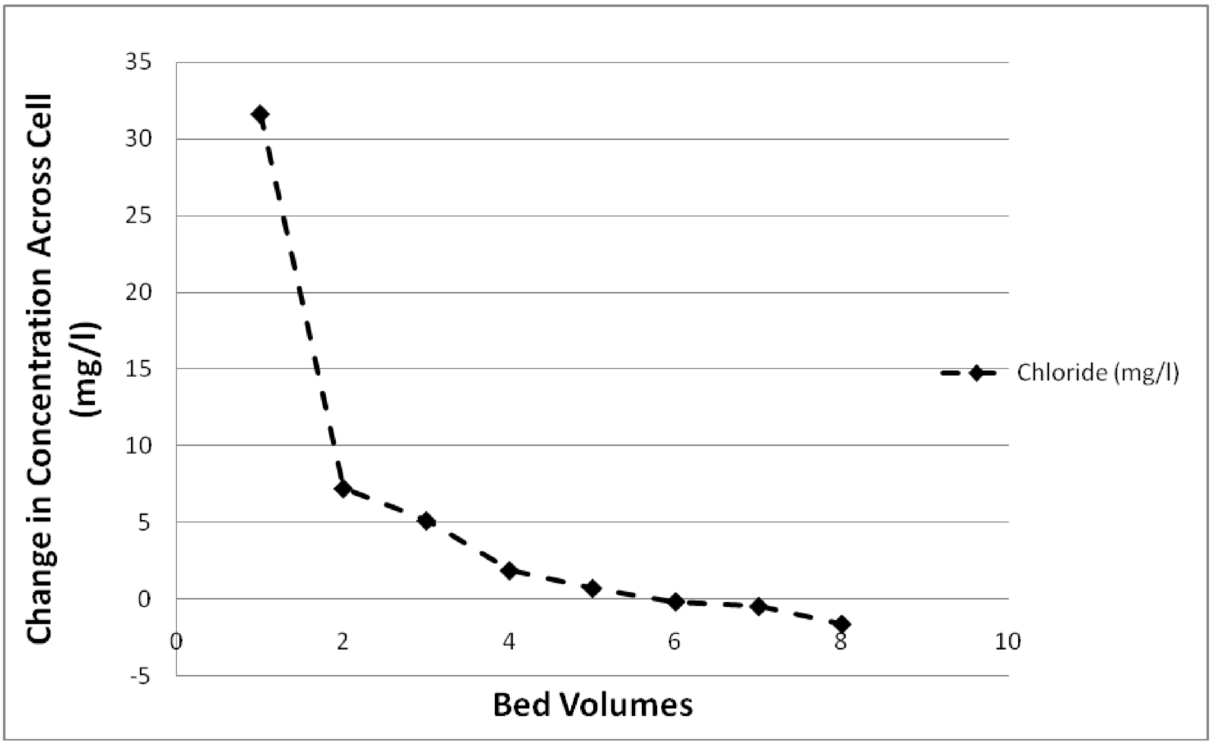

Figure B.19, Old IBAA infiltration test results for chloride.

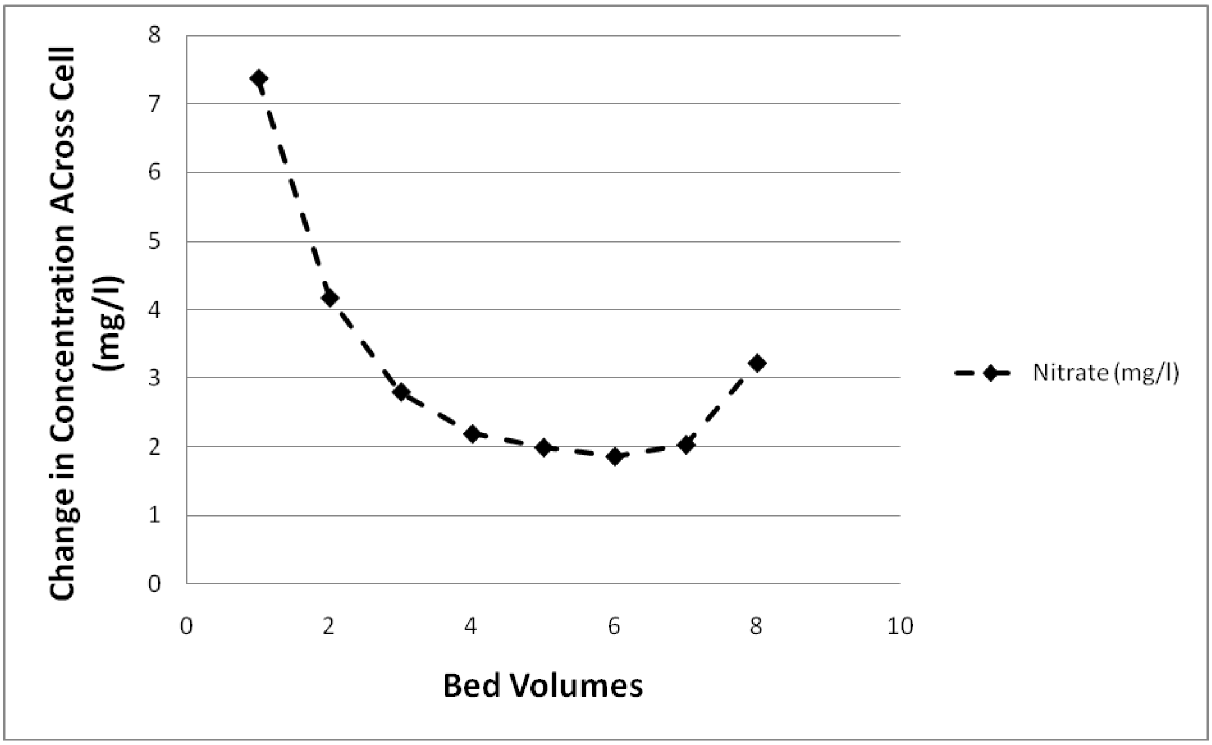

Figure B.20, Old IBAA infiltration test results for nitrate.

B.5 RFS Charts

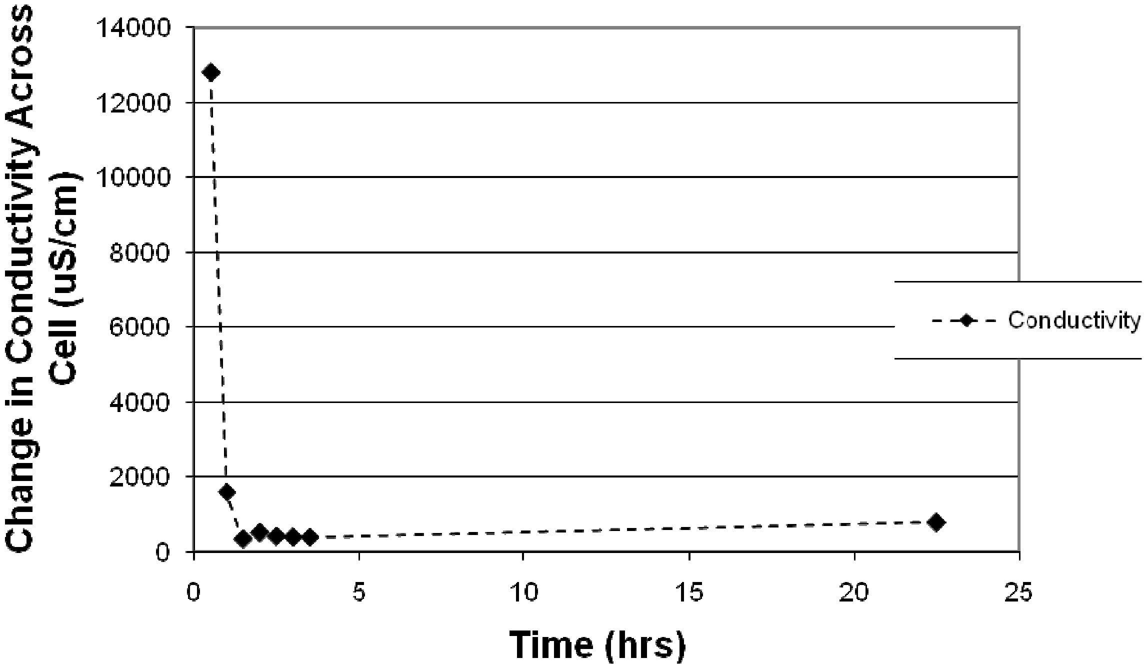

Figure B.21, RFS infiltration test results for conductivity.

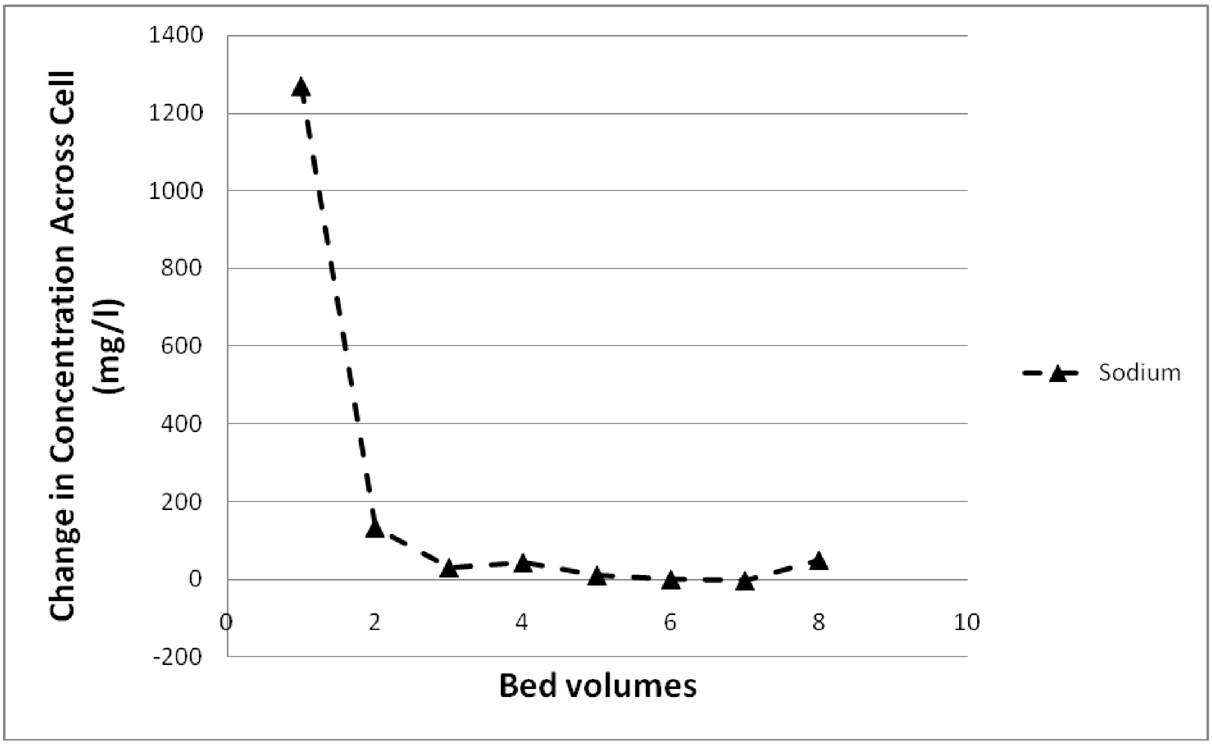

Figure B.22, RFS infiltration test results for sodium.

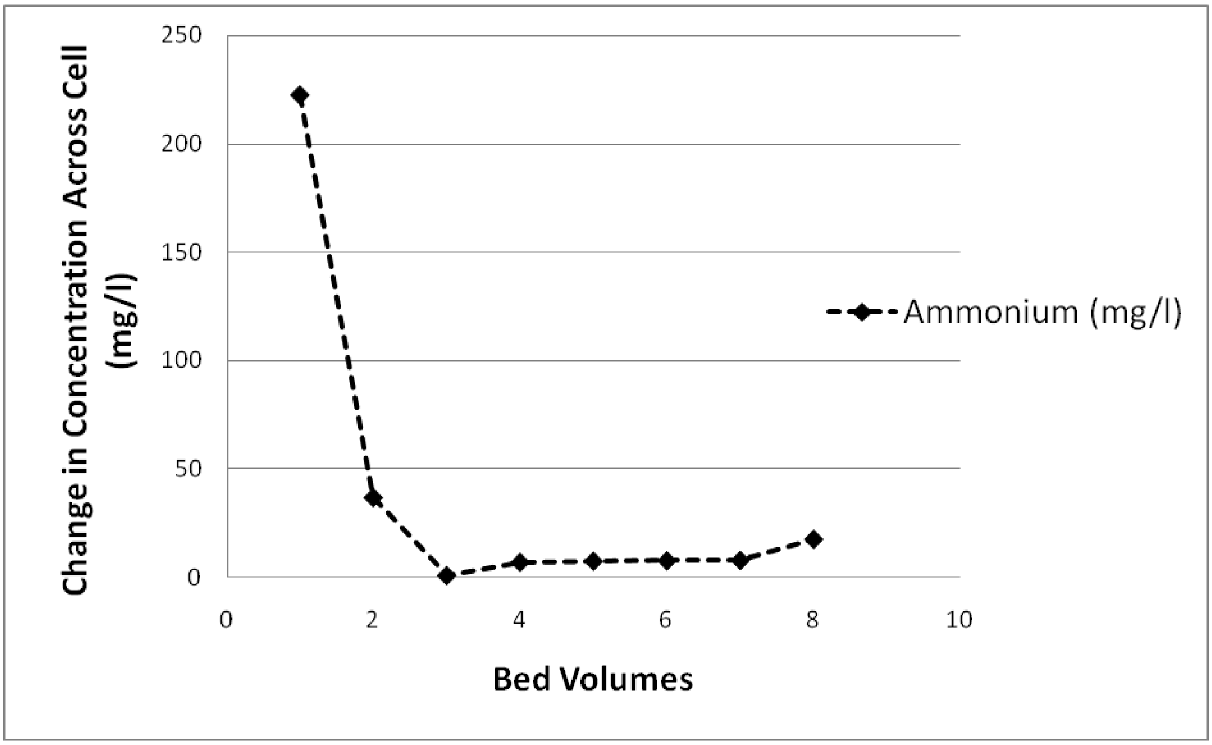

Figure B.23, RFS infiltration test results for ammonium.

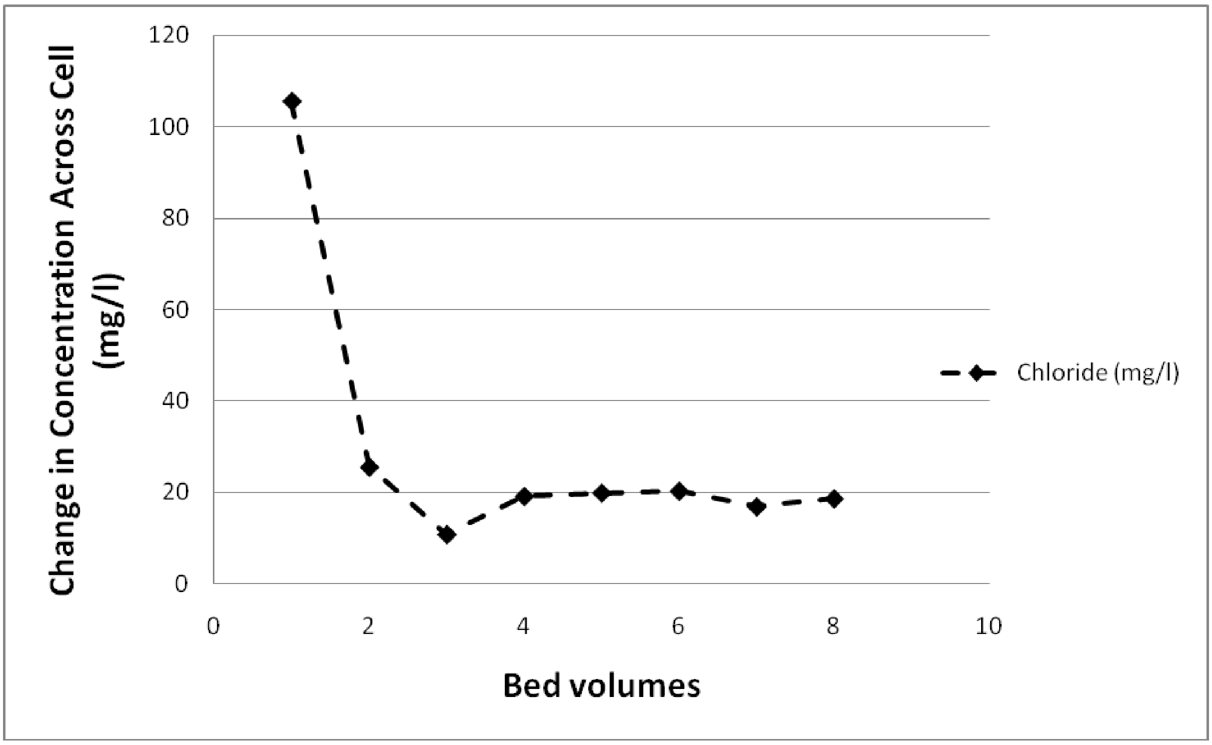

Figure B.24, RFS infiltration test results for chloride.

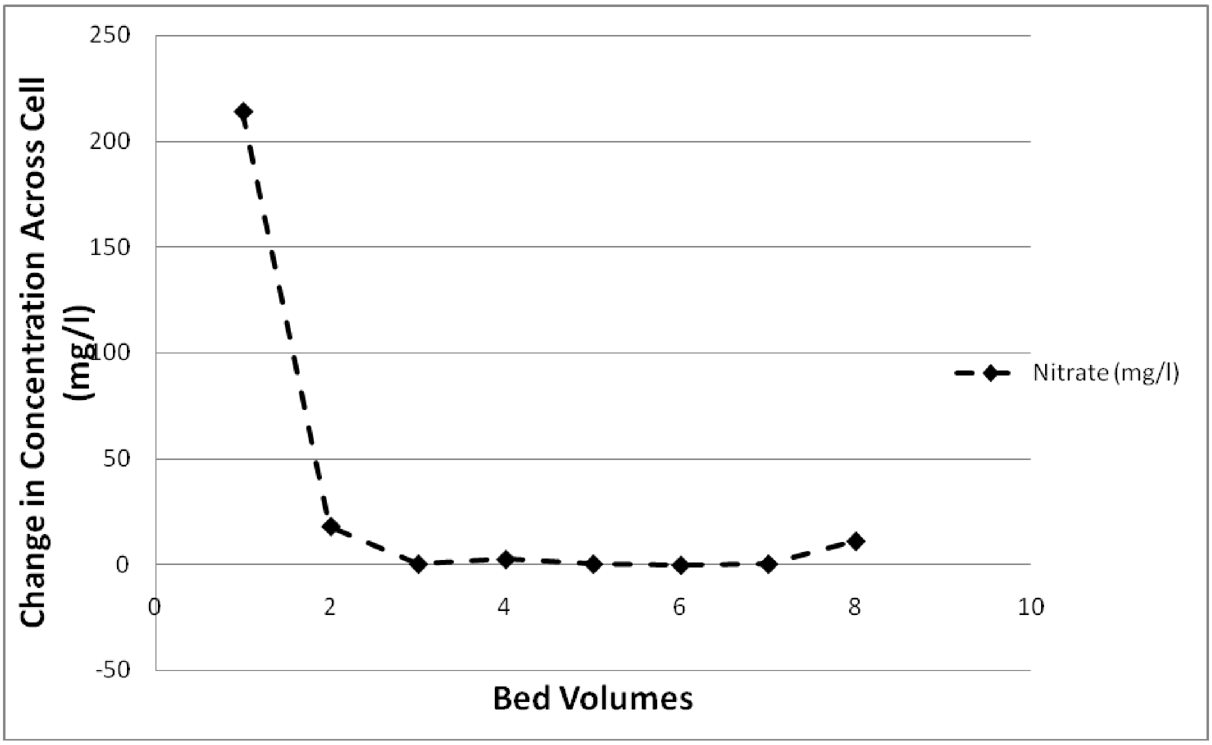

Figure B.25, RFS infiltration test results for nitrate.

B.6 Old RFS Charts

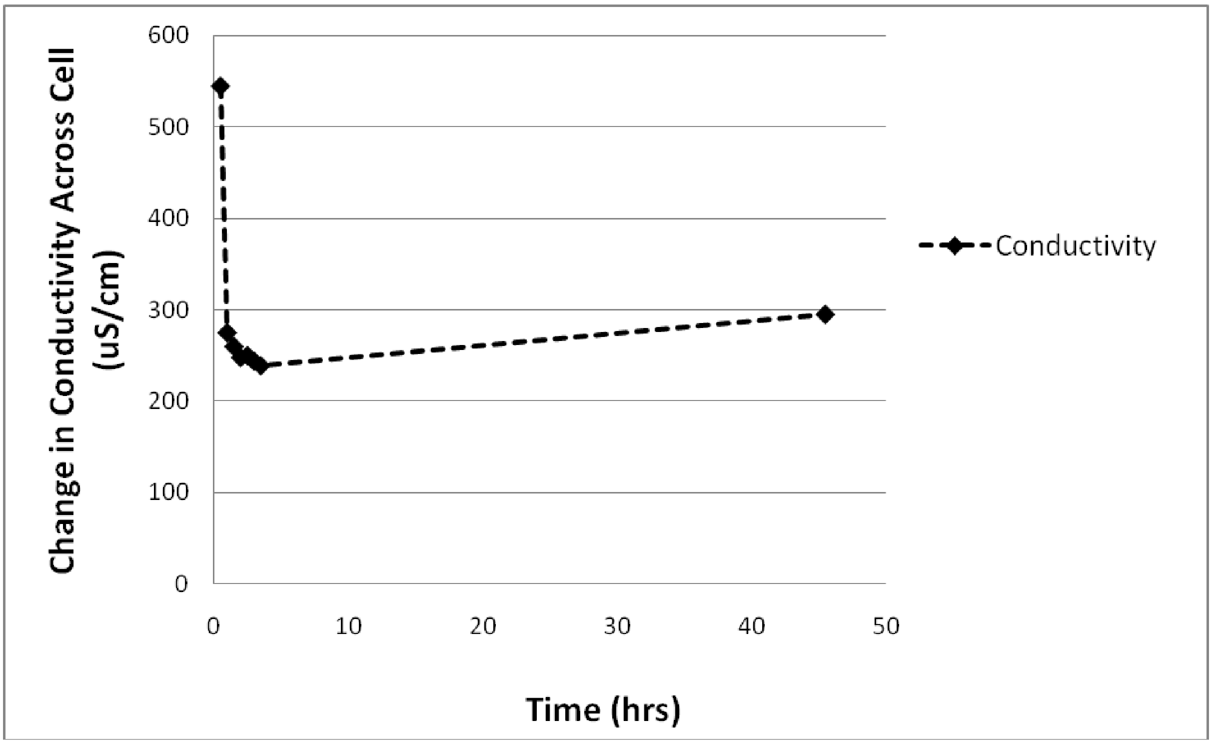

Figure B.26, Old RFS infiltration test results for conductivity.

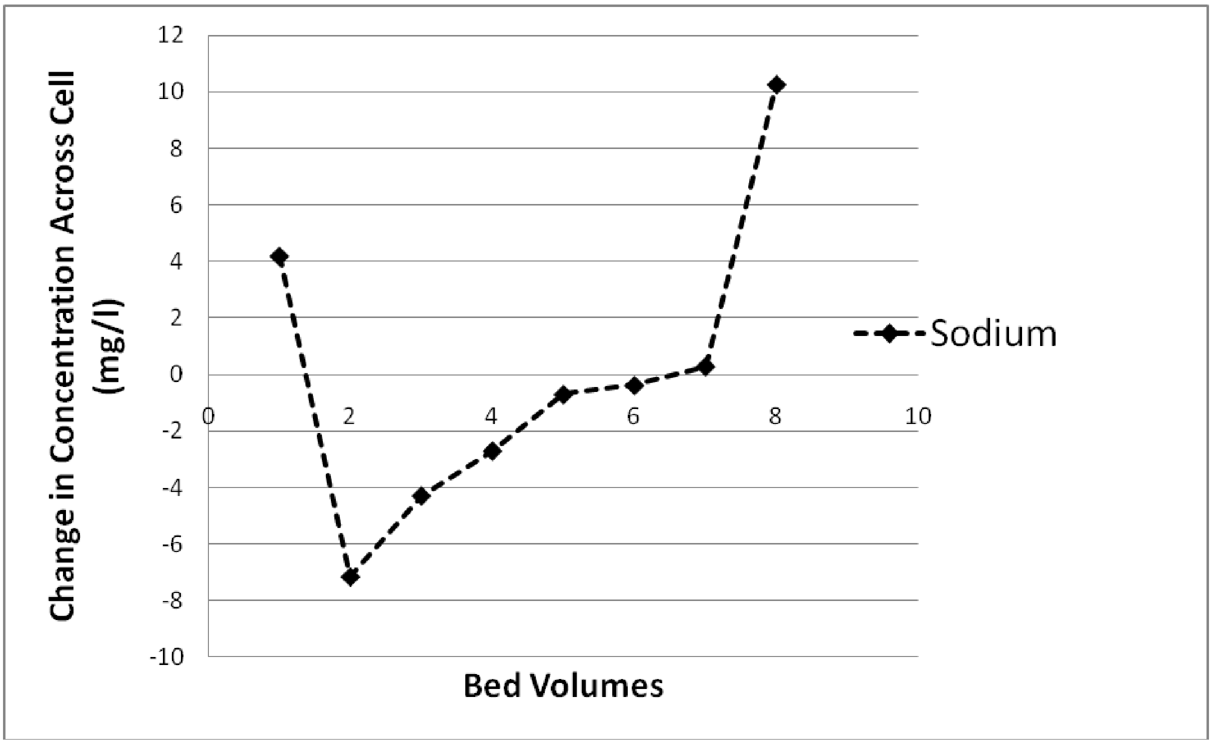

Figure B.27, Old RFS infiltration test results for sodium.

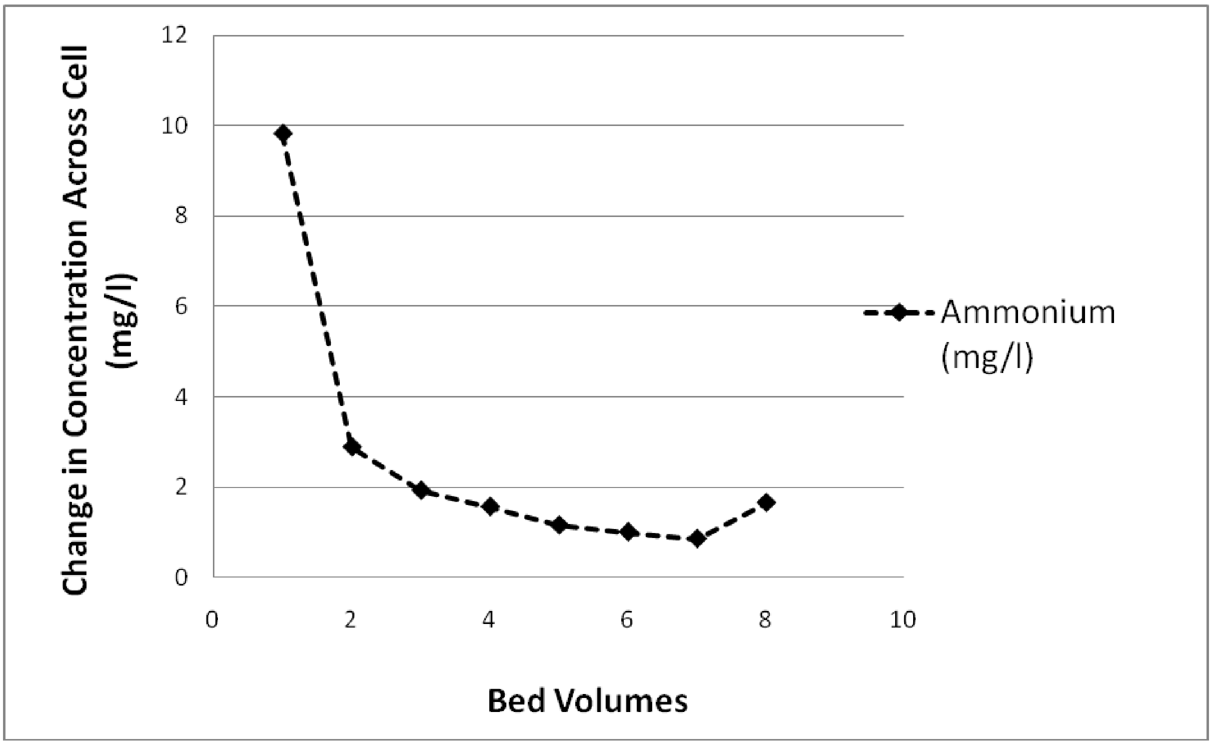

Figure B.28, Old RFS infiltration test results for ammonium.

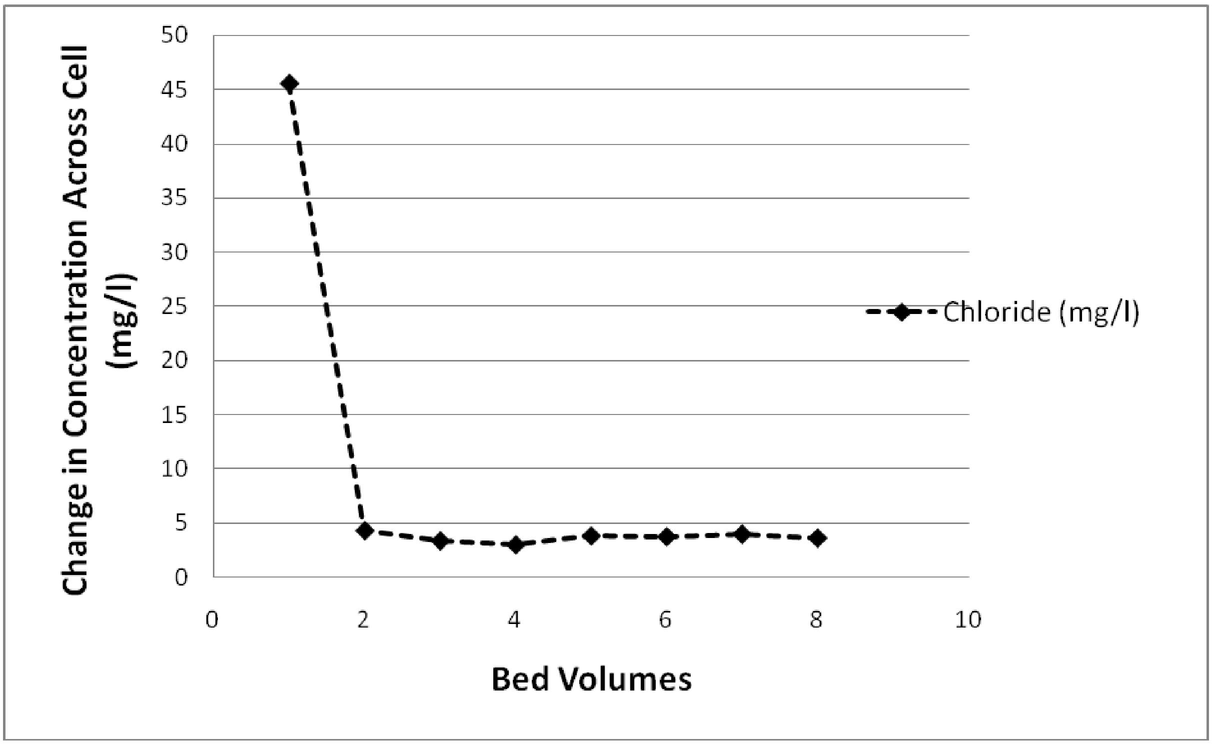

Figure B.29, Old RFS infiltration test results for chloride.

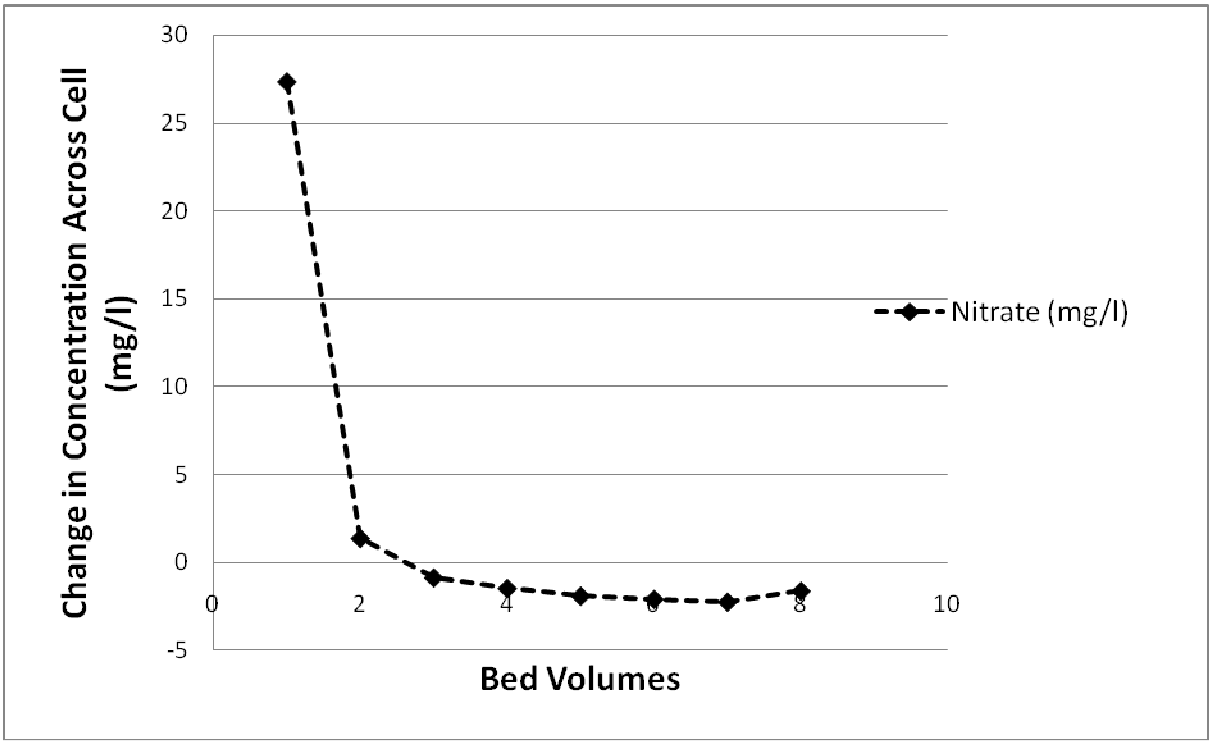

Figure B.30, Old RFS infiltration test results for nitrate.

B.7 BFS Charts

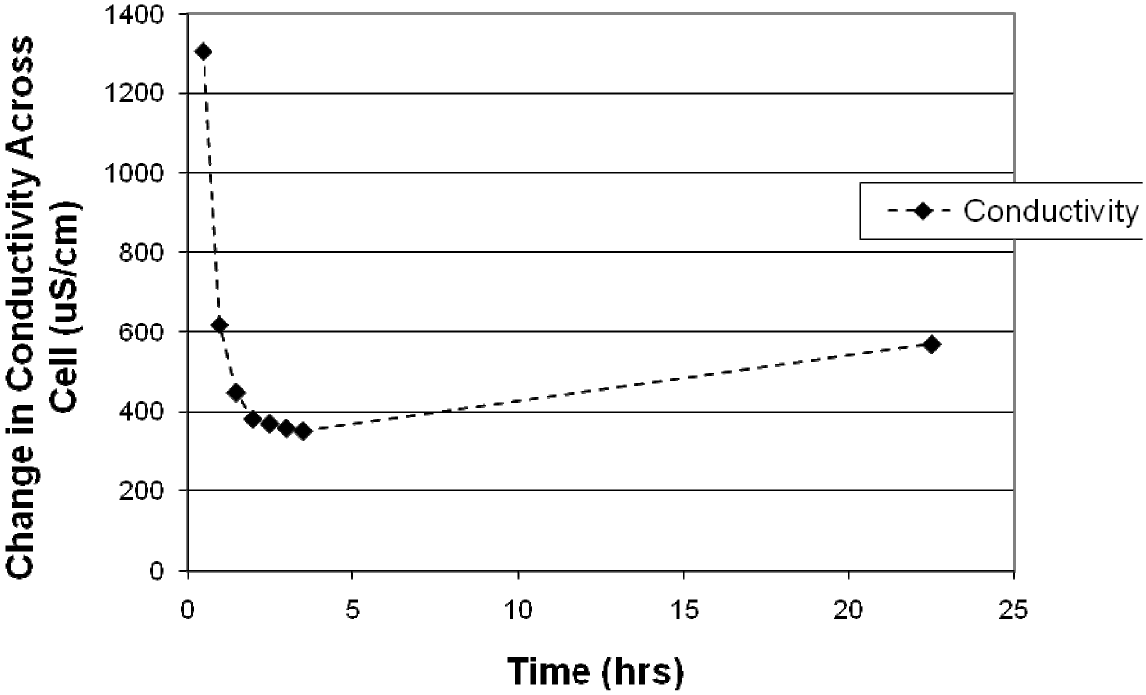

Figure B.31, BFS infiltration test results for conductivity.

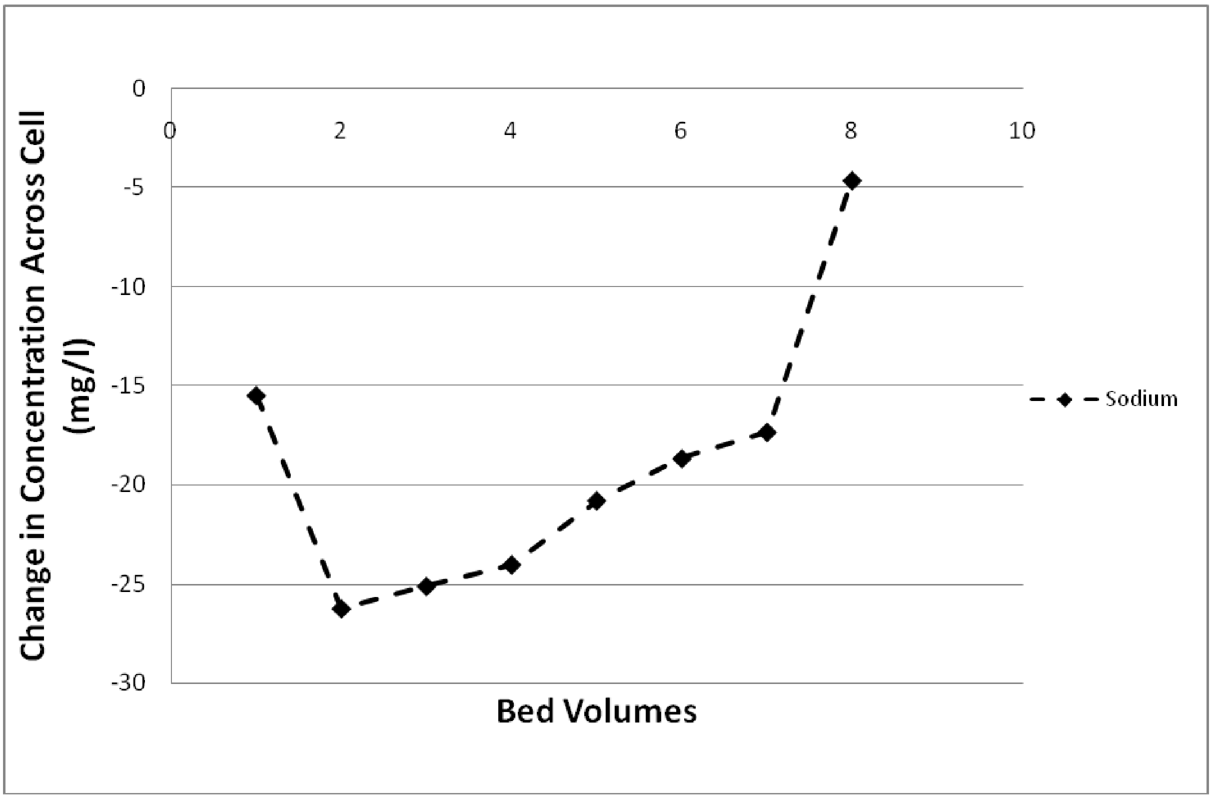

Figure B.32, BFS infiltration test results for sodium.

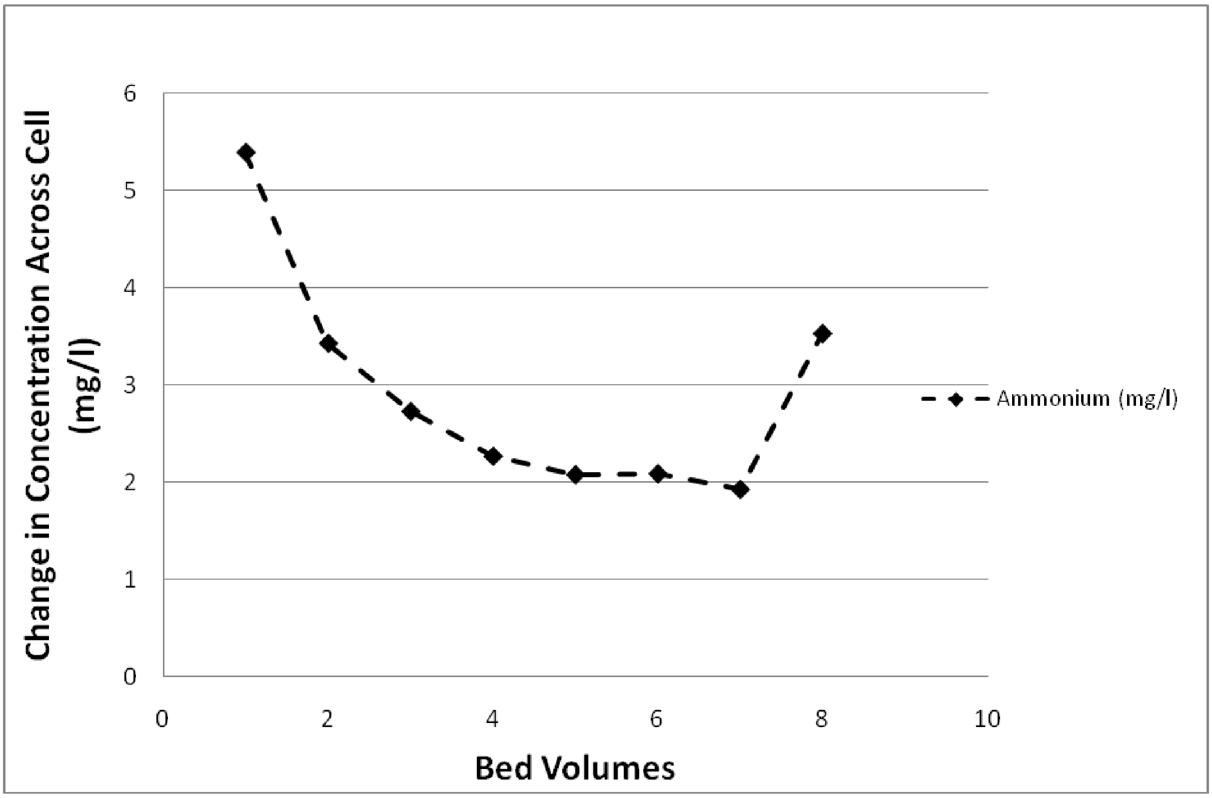

Figure B.33, BFS infiltration test results for ammonium.

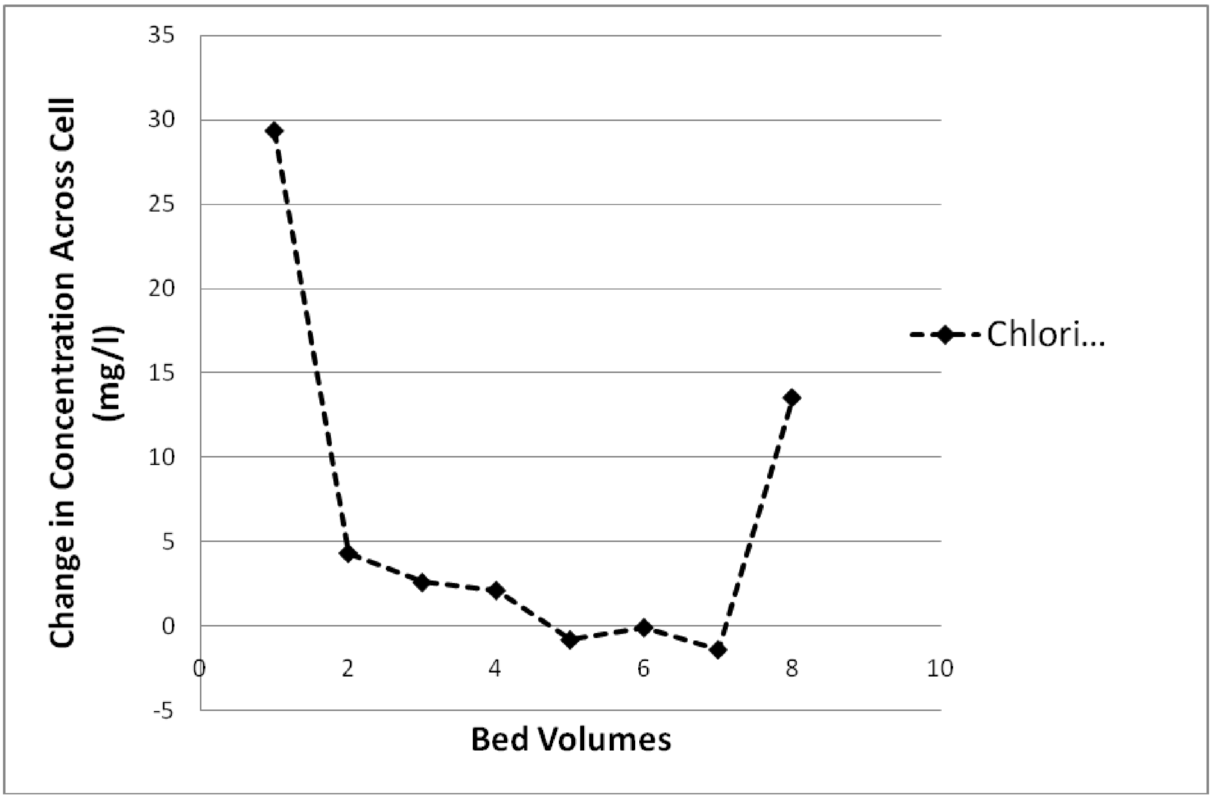

Figure B.34, BFS infiltration test results for chloride.

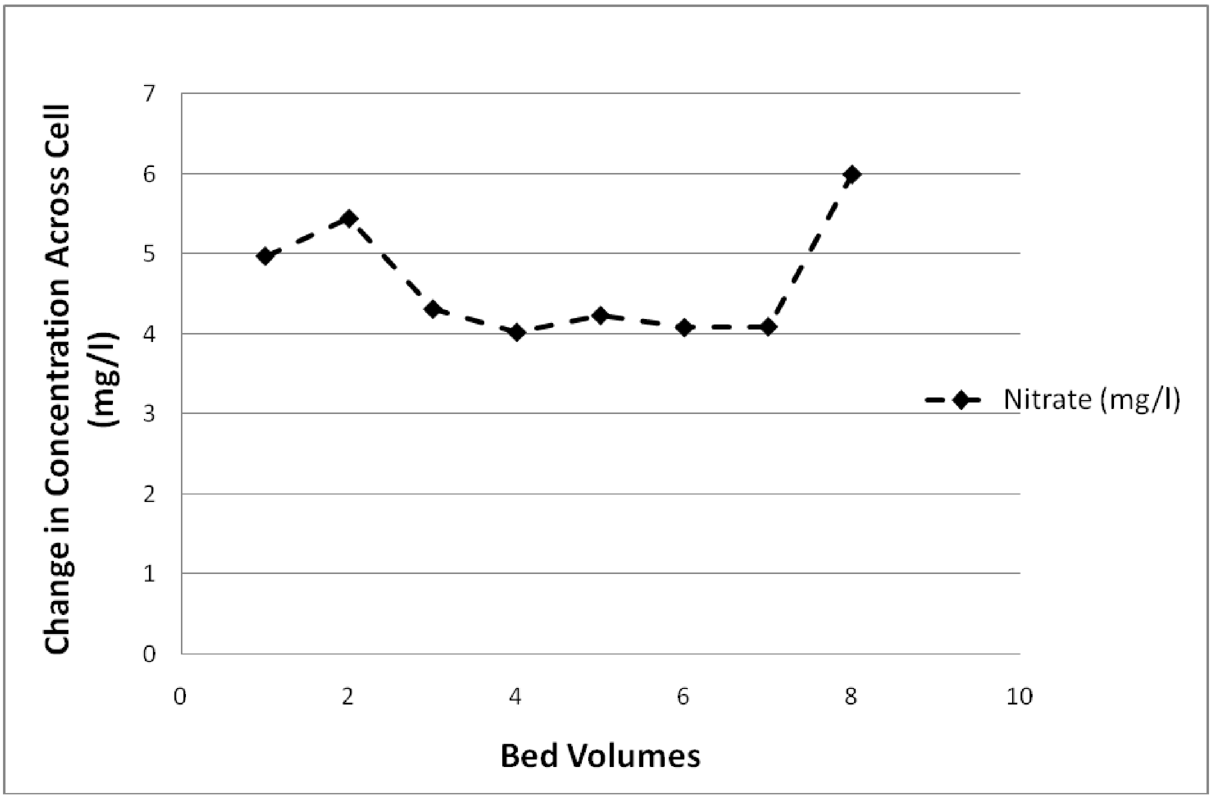

Figure B.35, BFS infiltration test results for nitrate.

APPENDIX C – TANK TEST ANALYSIS PLOTS

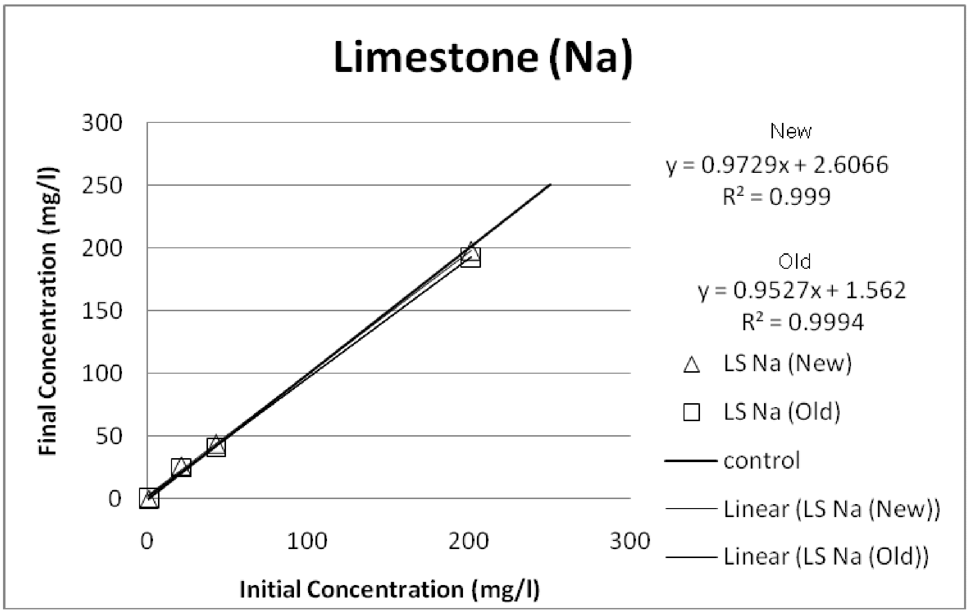

Figure C.1, Analysis chart of sodium results for limestone.

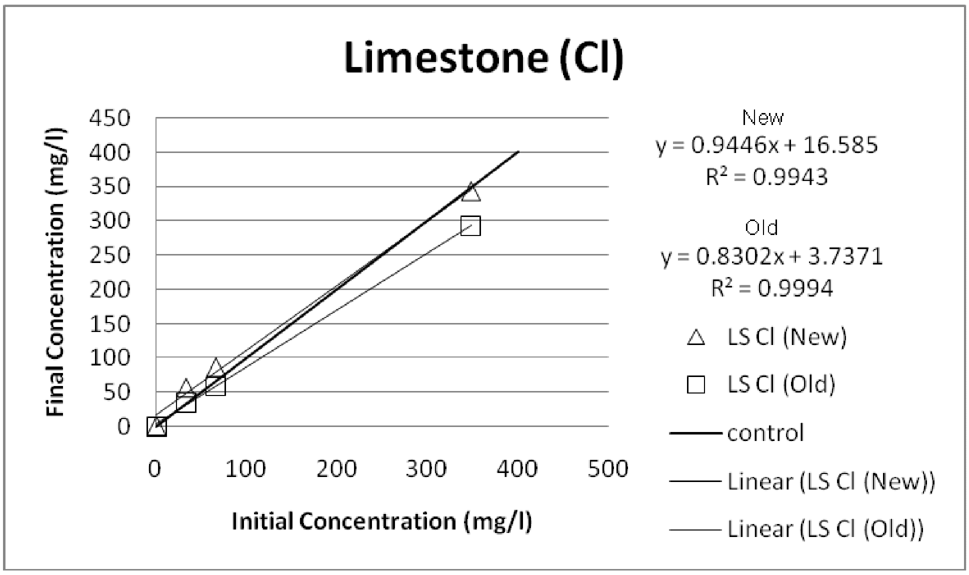

Figure C.2, Analysis chart of chloride results for limestone.

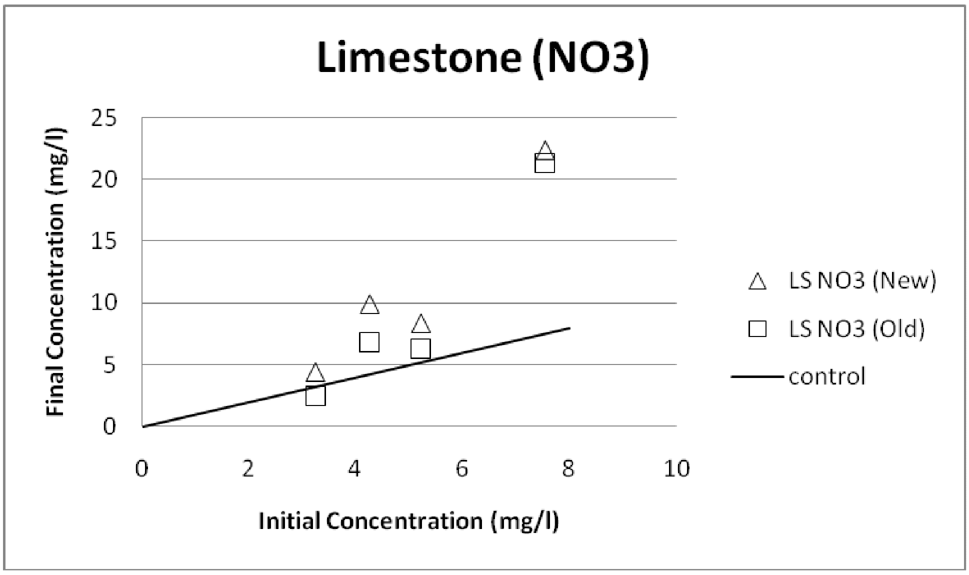

Figure C.3, Analysis chart of nitrate results for limestone.

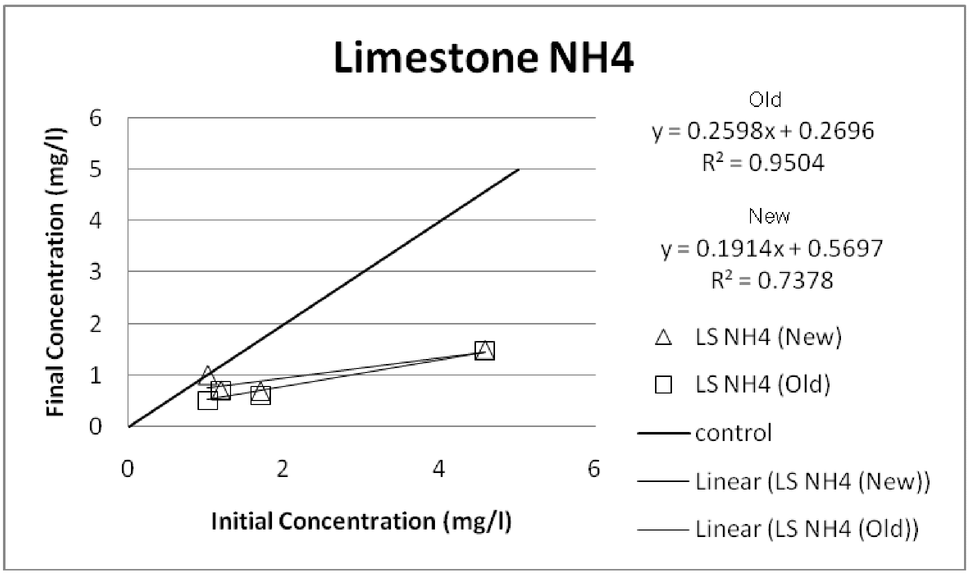

Figure C.4, Analysis chart of ammonium results for limestone.

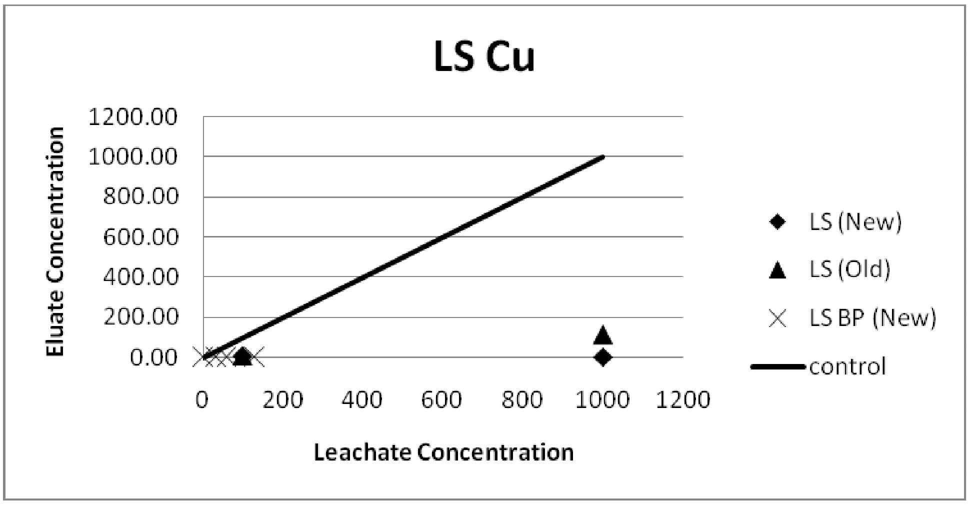

Figure C.5, Analysis chart of copper results for limestone.

LS (New) and LS (Old) in mg/l, LS BP (New) in µg/l.

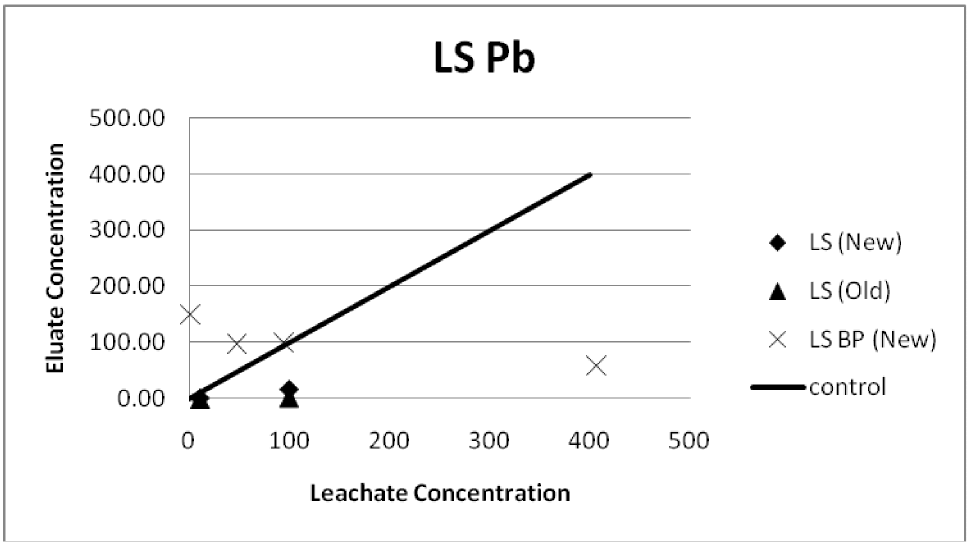

Figure C.6, Analysis chart of lead results for limestone.

LS (New) and LS (Old) in mg/l, LS BP (New) in µg/l.

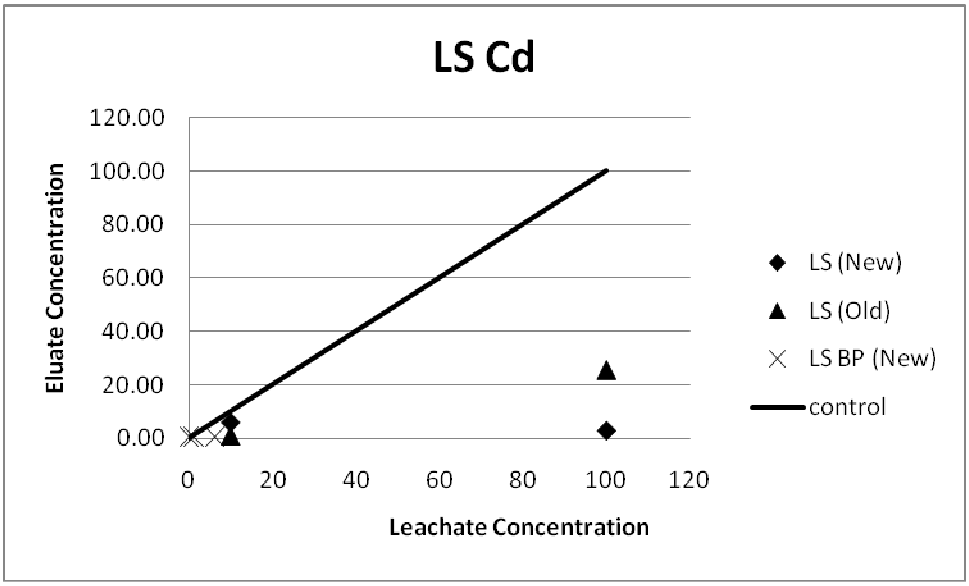

Figure C.7, Analysis chart of cadmium results for limestone.

LS (New) and LS (Old) in mg/l, LS BP (New) in µg/l.

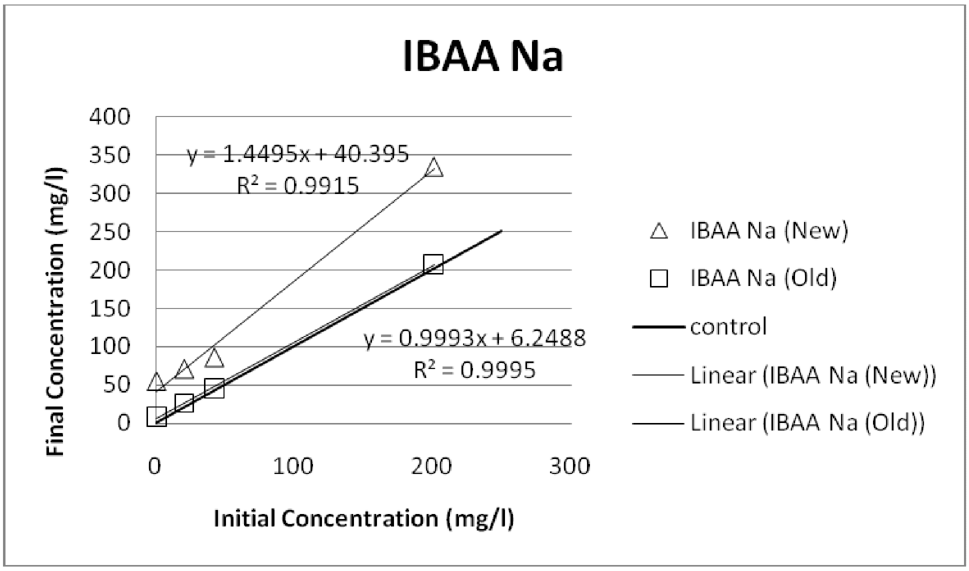

Figure C.8, Analysis chart of sodium results for IBAA.

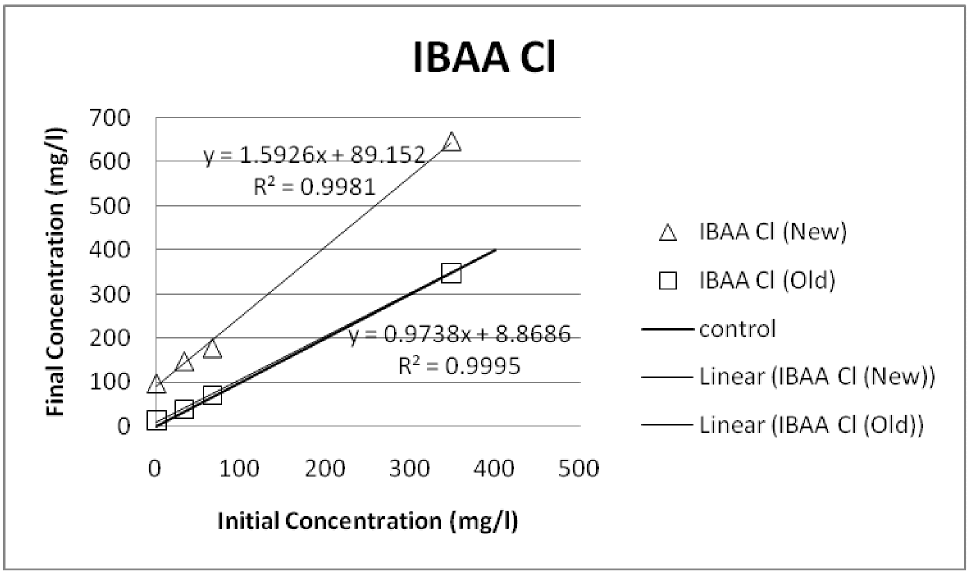

Figure C.9, Analysis chart of chloride results for IBAA.

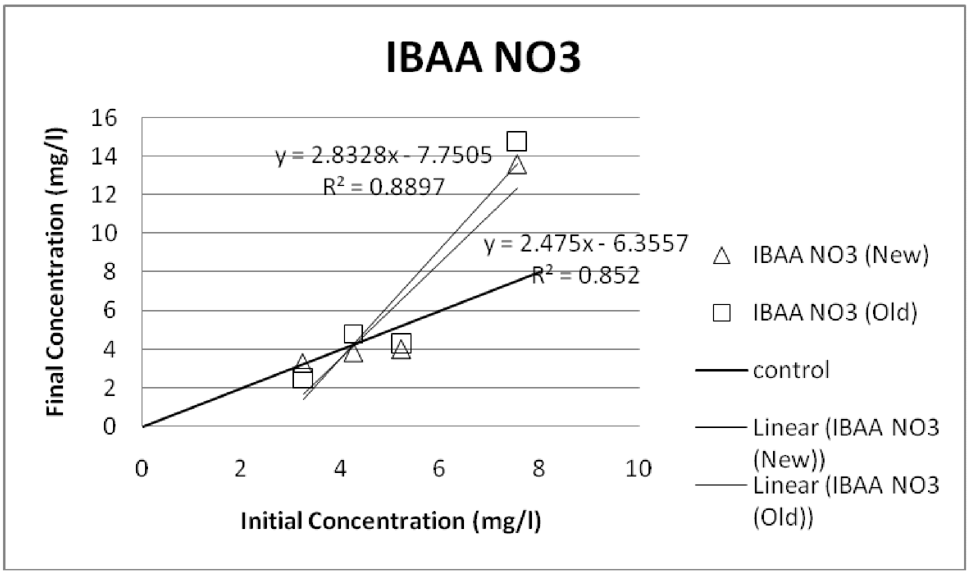

Figure C.10, Analysis chart of nitrate results for IBAA.

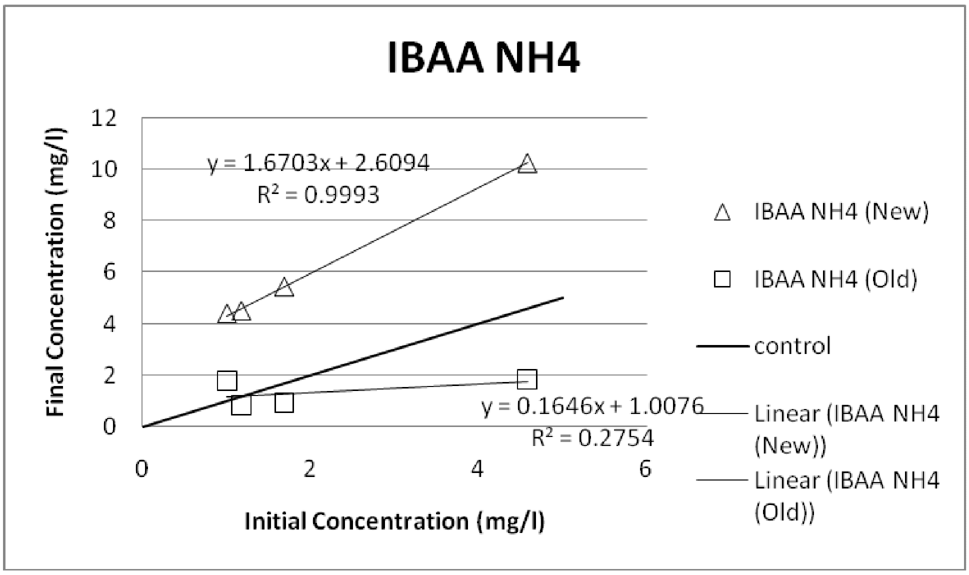

Figure C.11, Analysis chart of ammonium results for IBAA.

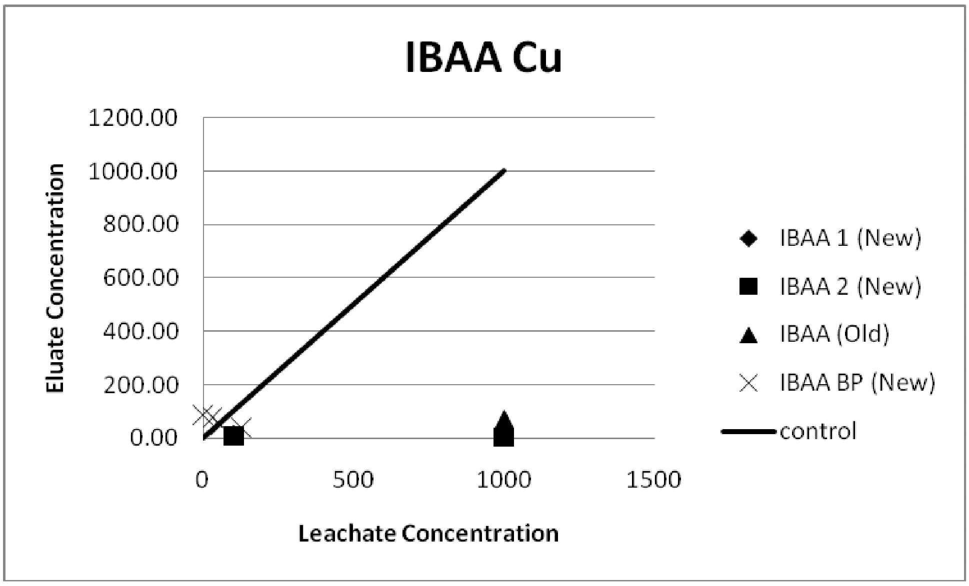

Figure C.12, Analysis chart of copper results for IBAA.

IBAA 1 (New), IBAA 2 (New) and IBAA (Old) in mg/l, IBAA BP (New) in µg/l.

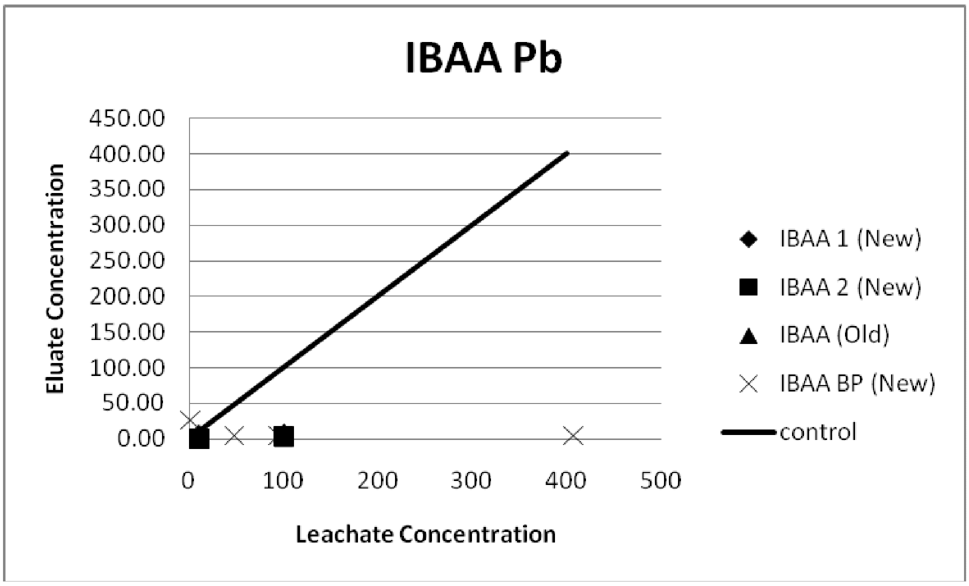

Figure C.13, Analysis chart of lead results for IBAA.

IBAA 1 (New), IBAA 2 (New) and IBAA (Old) in mg/l, IBAA BP (New) in µg/l.

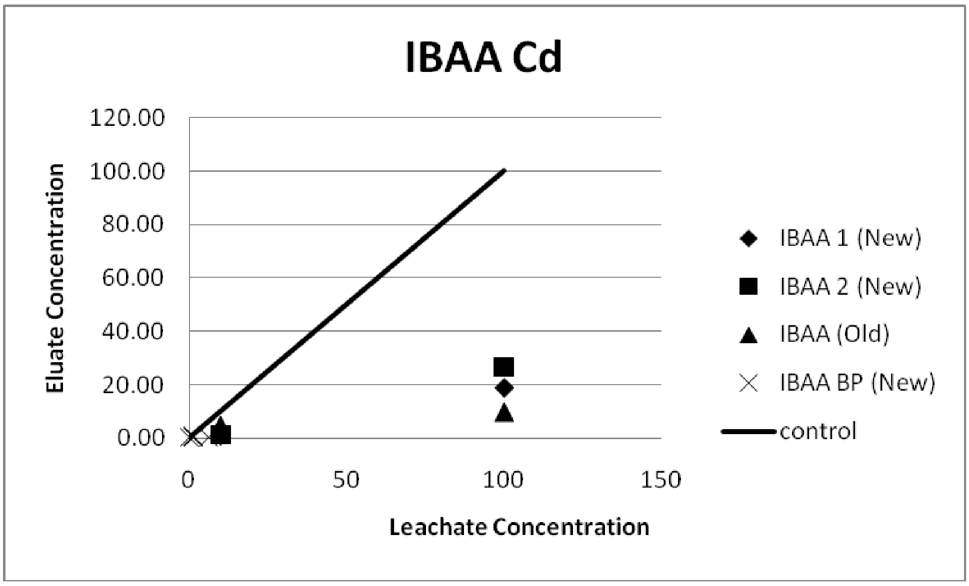

Figure C.14, Analysis chart of cadmium results for IBAA.

IBAA 1 (New), IBAA 2 (New) and IBAA (Old) in mg/l, IBAA BP (New) in µg/l.

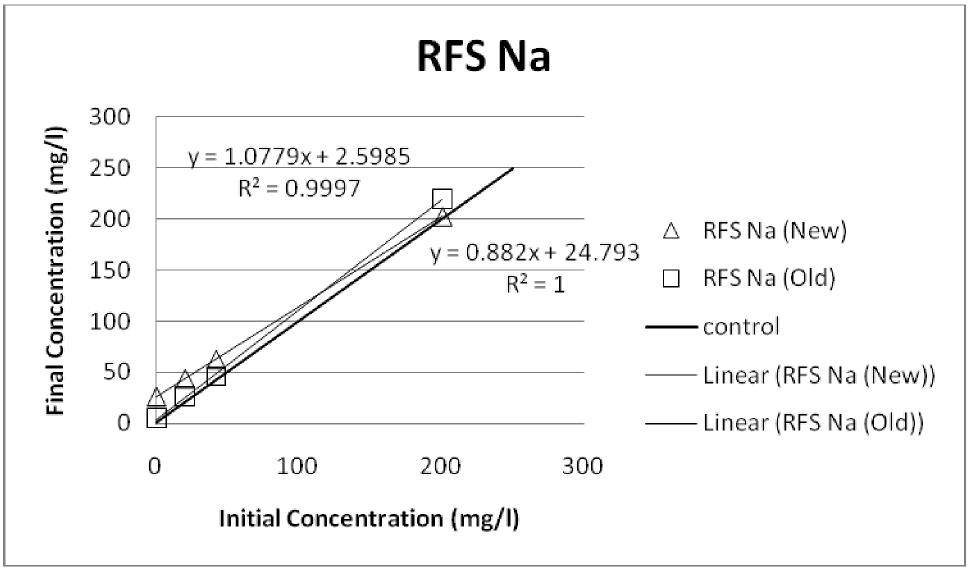

Figure C.15, Analysis chart of sodium results for RFS.

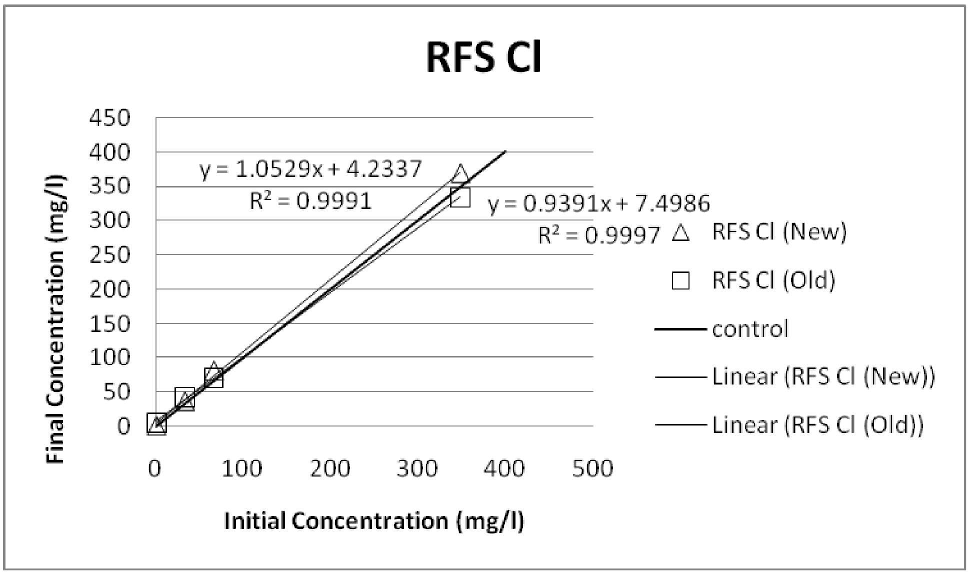

Figure C.16, Analysis chart of chloride results for RFS.

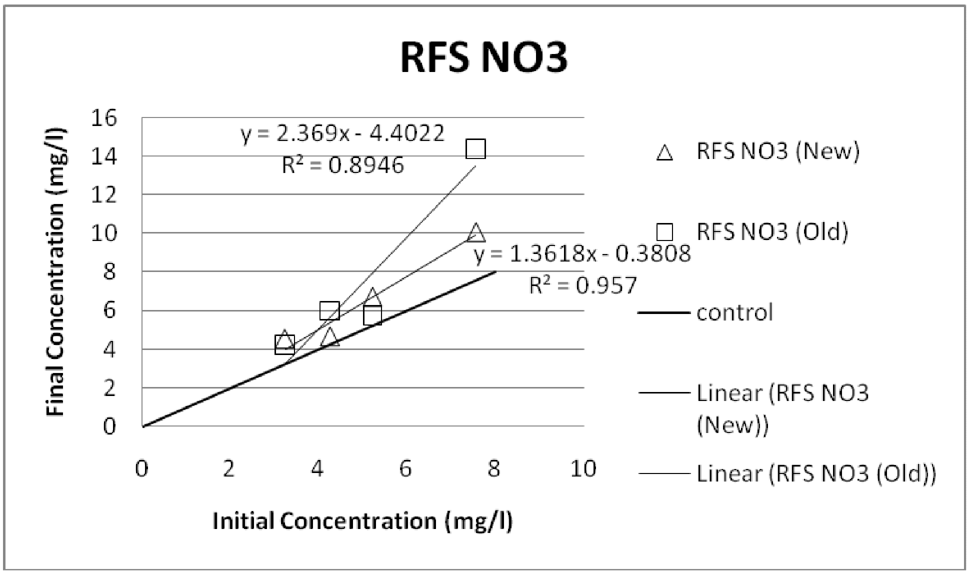

Figure C.17, Analysis chart of nitrate results for RFS.

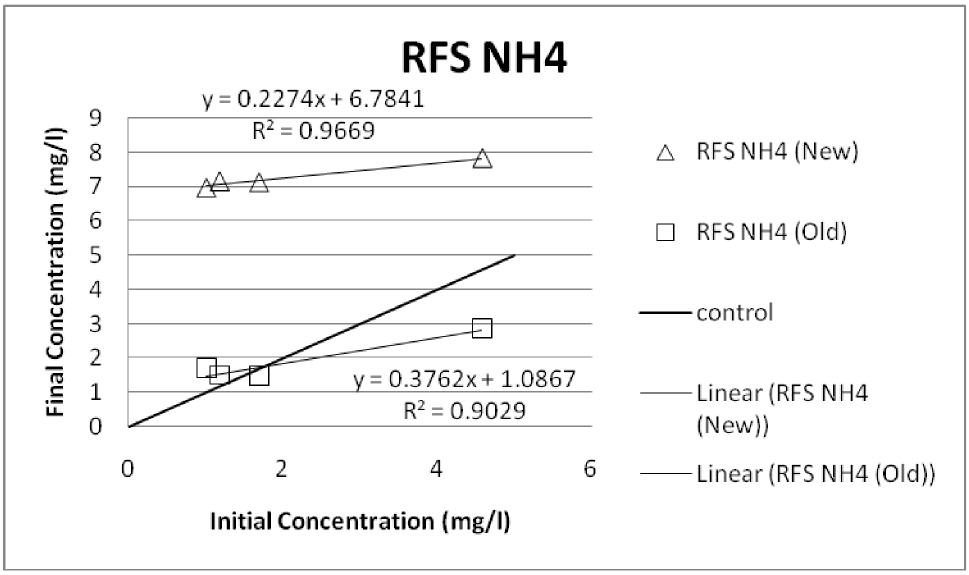

Figure C.18, Analysis chart of ammonium results for RFS.

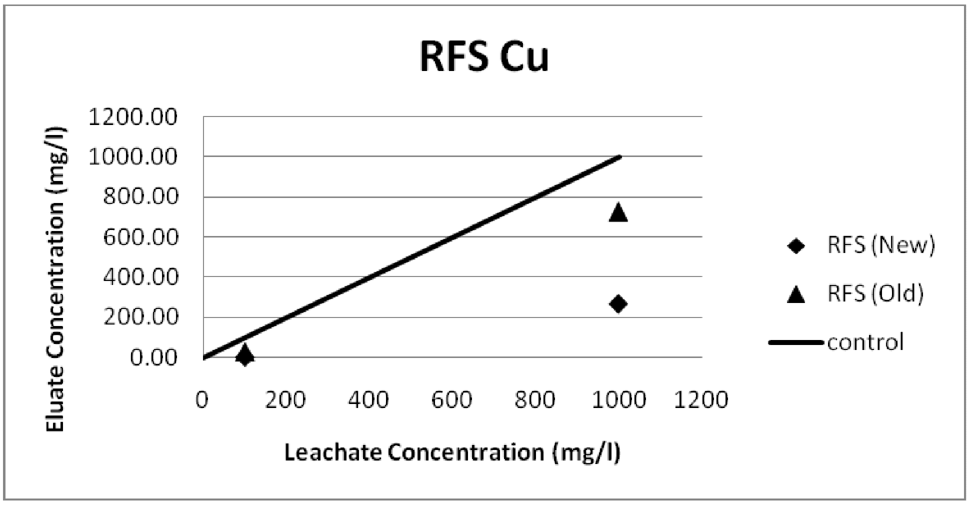

Figure C.19, Analysis chart of copper results for RFS.

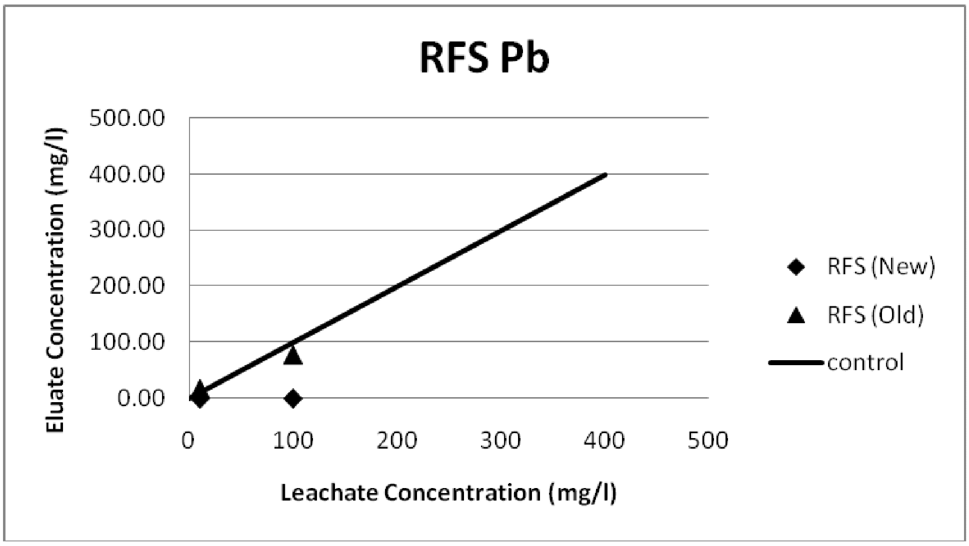

Figure C.20, Analysis chart of lead results for RFS.

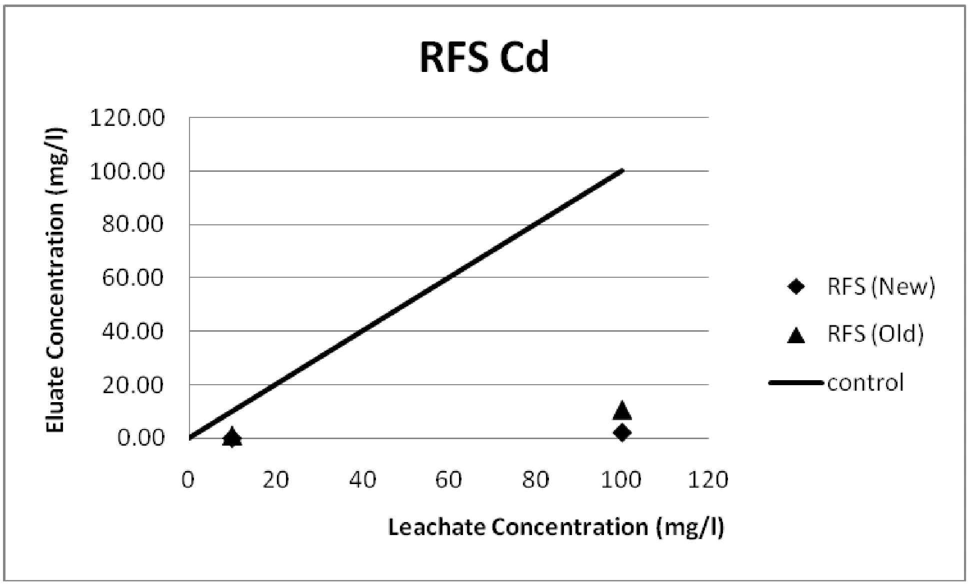

Figure C.21, Analysis chart of cadmium results for RFS.

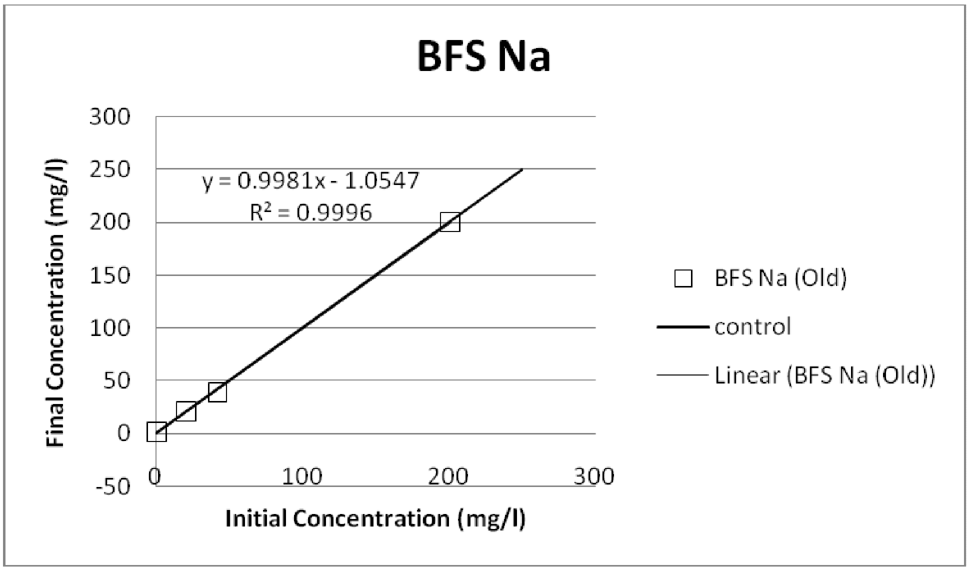

Figure C.22, Analysis chart of sodium results for BFS.

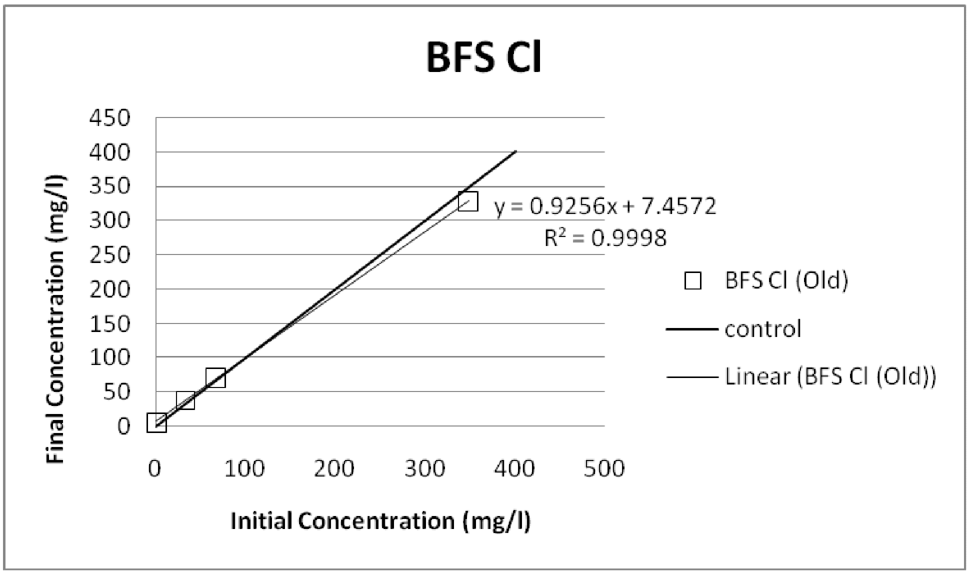

Figure C.23, Analysis chart of chloride results for BFS.

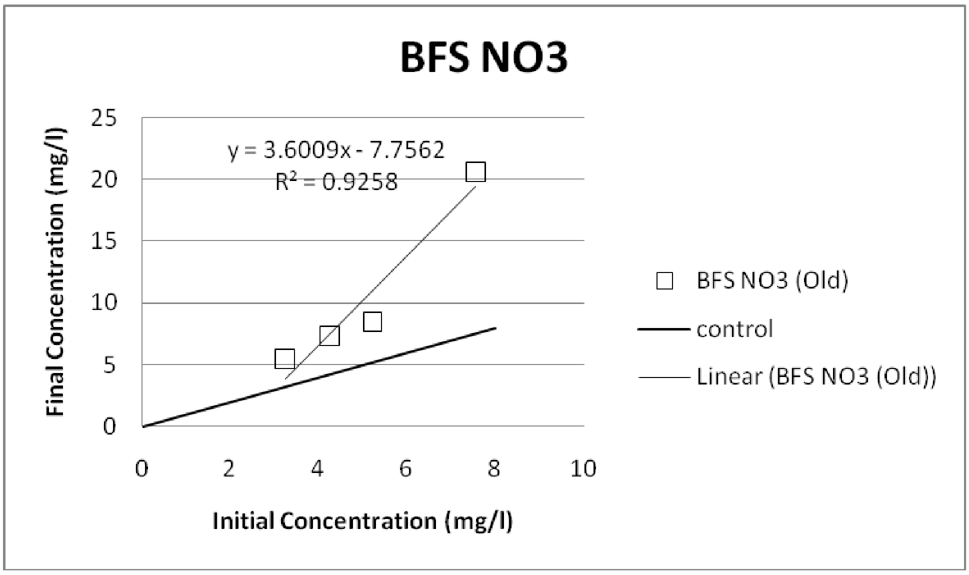

Figure C.24, Analysis chart of nitrate results for BFS.

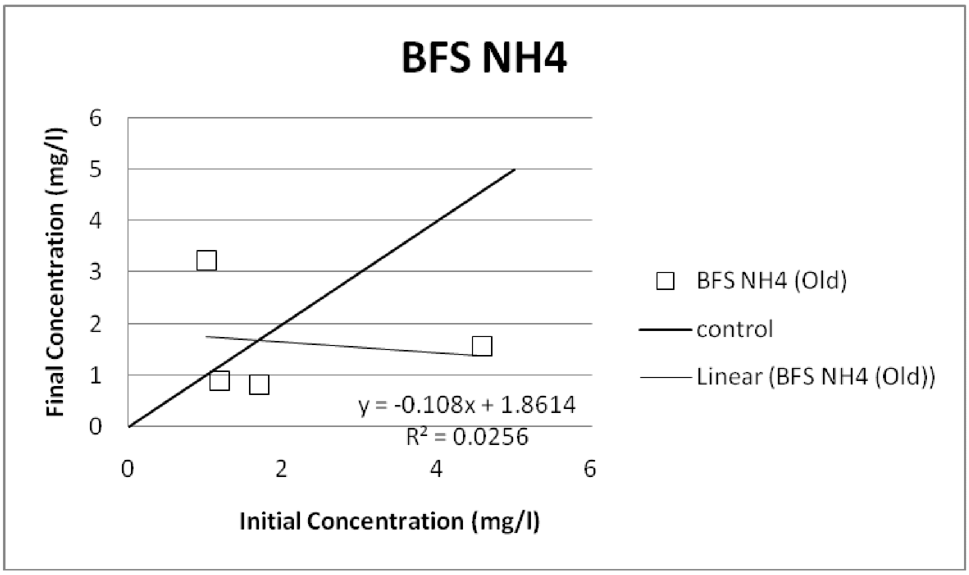

Figure C.25, Analysis chart of ammonium results for BFS.

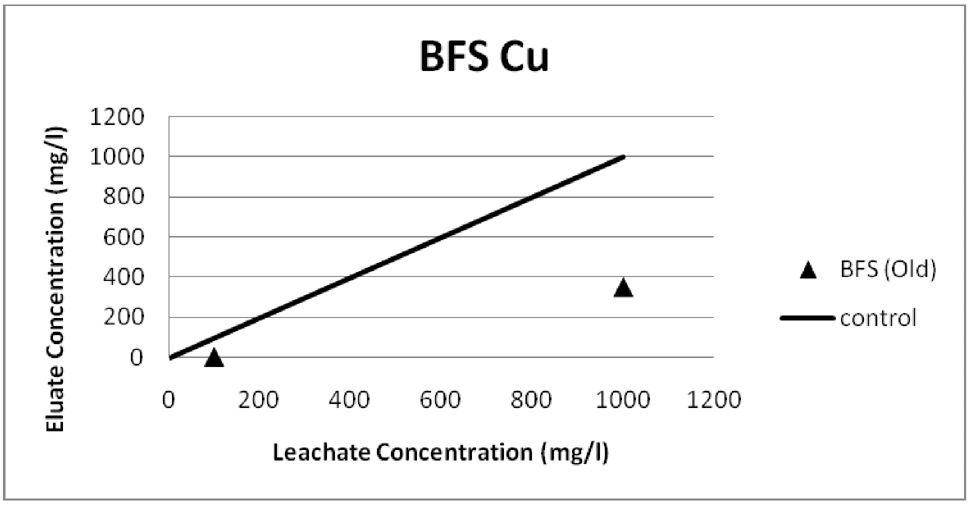

Figure C.26, Analysis chart of copper results for BFS.

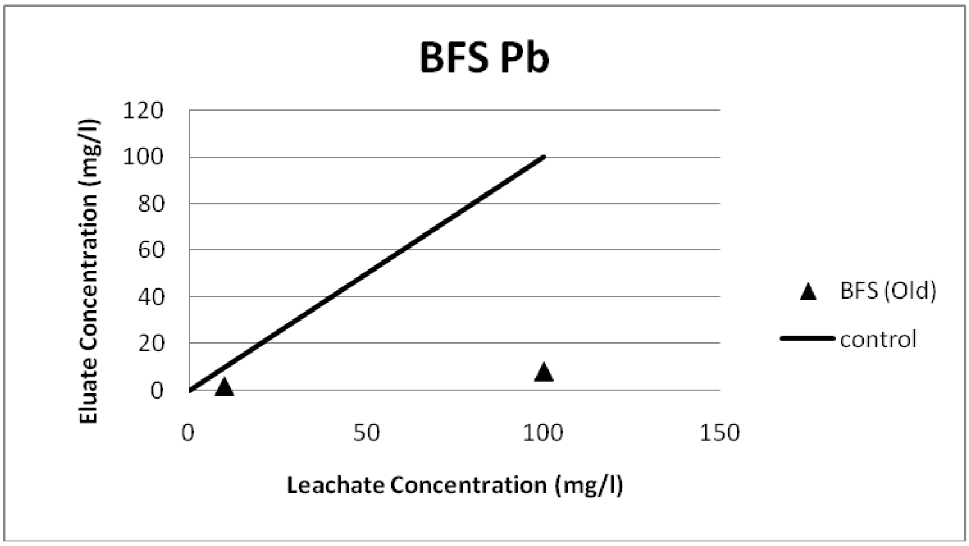

Figure C.27, Analysis of lead results for BFS.

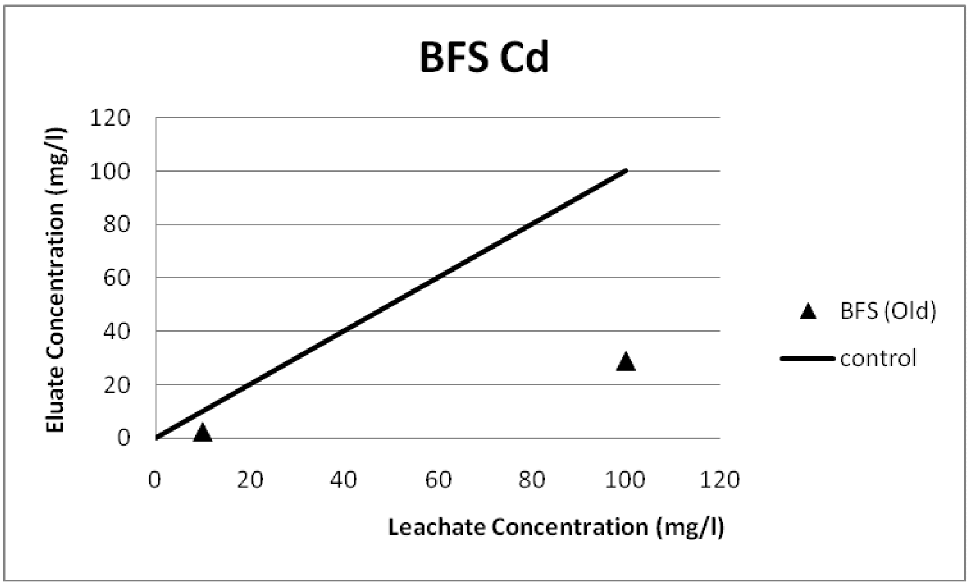

Figure C.28, Analysis chart of cadmium results for BFS.

APPENDIX D – CONTAMINANT FRONT CHARTS FOR CASE STUDY ANALYSIS

Limestone Figures

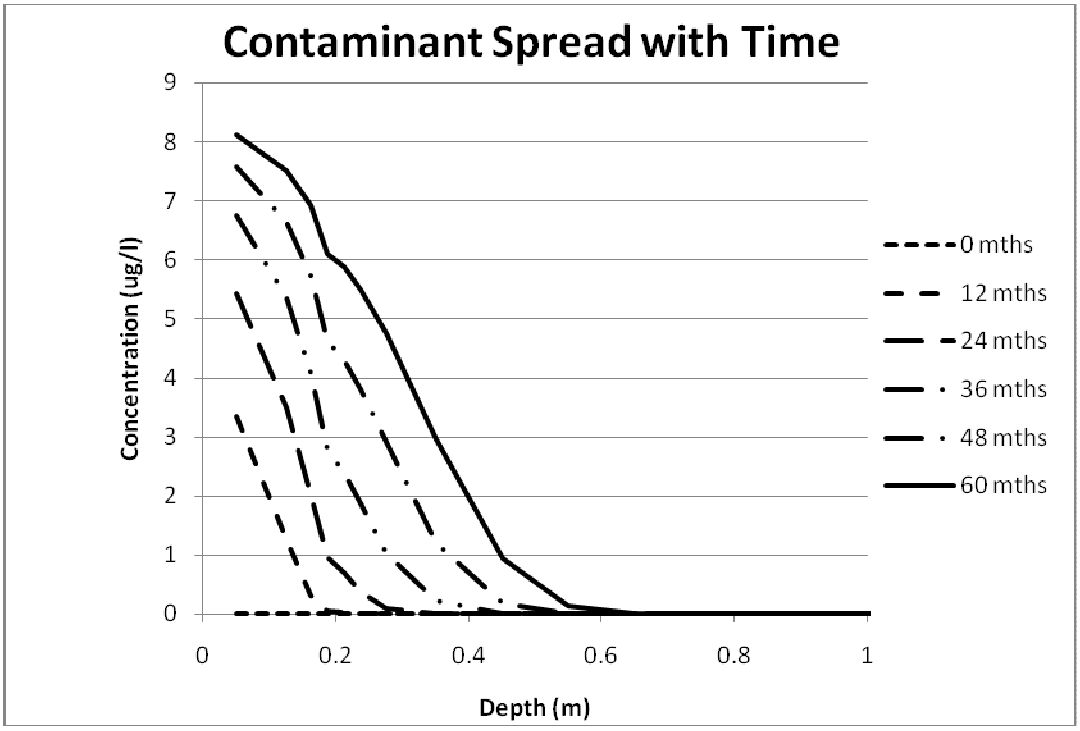

Figure D.1, Cadmium analysis with Limestone and MAX runoff

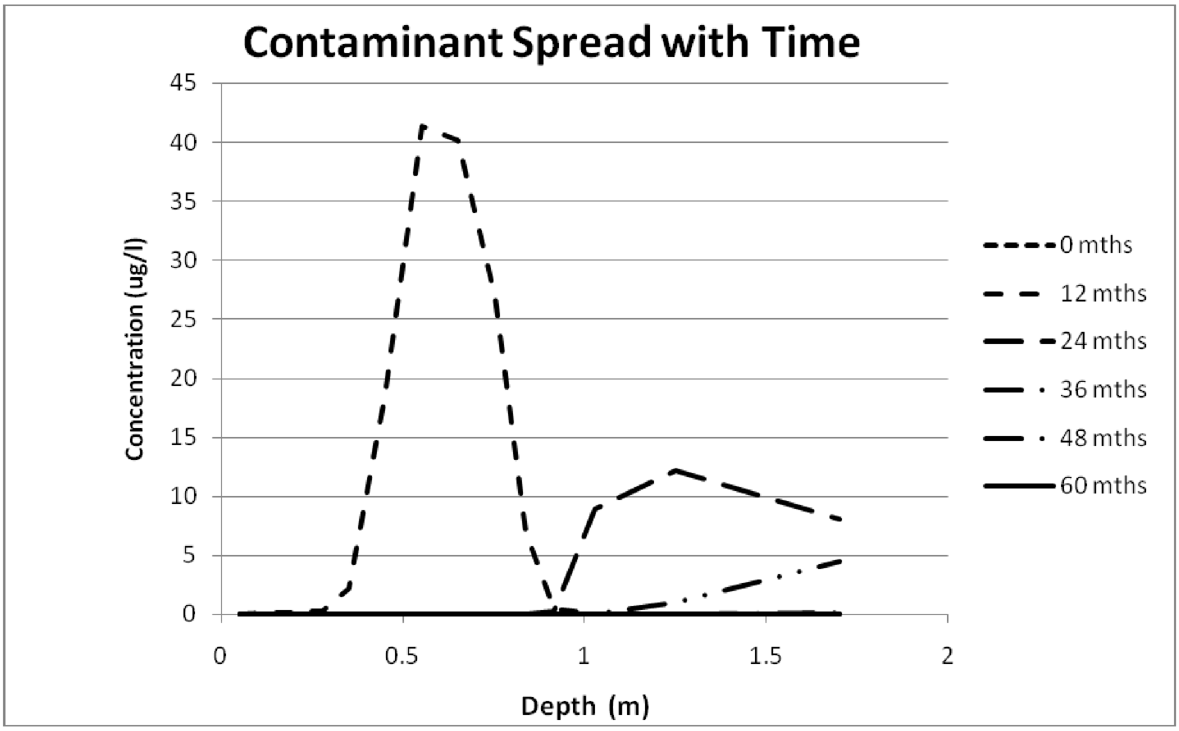

Figure D.2, Sodium analysis with Limestone and DEI runoff

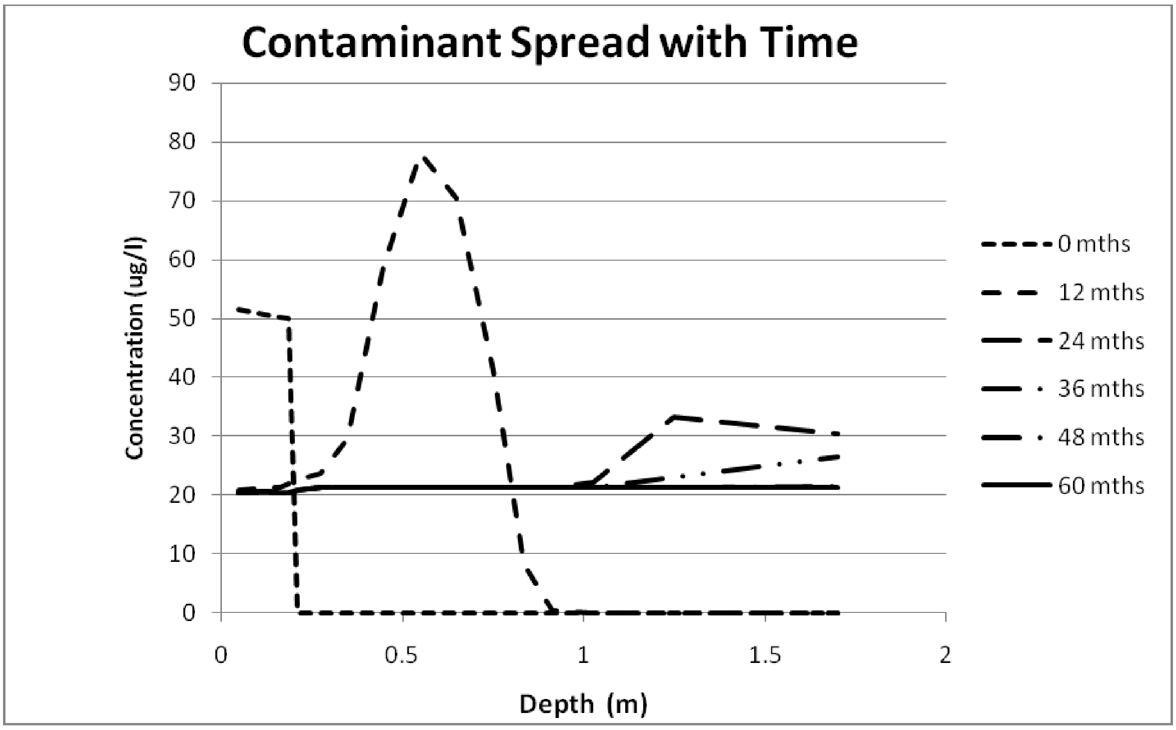

Figure D.3, Sodium analysis with Limestone and LTM runoff

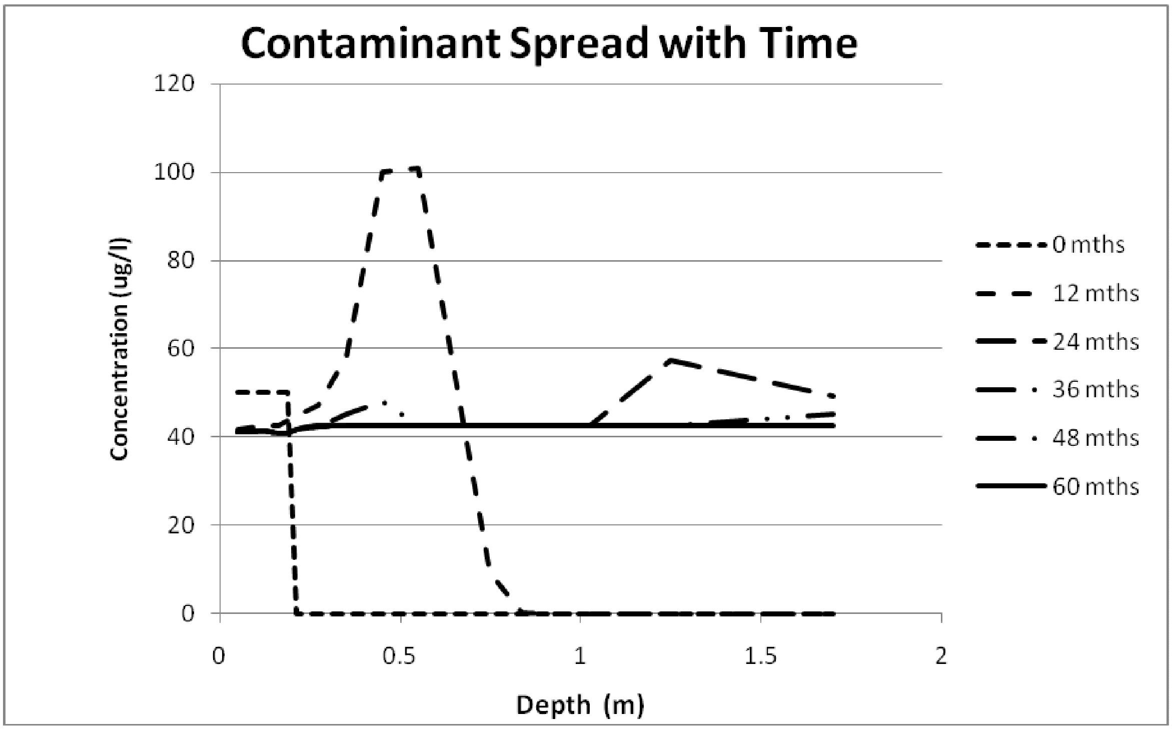

Figure D.4, Sodium analysis with Limestone and HTM runoff

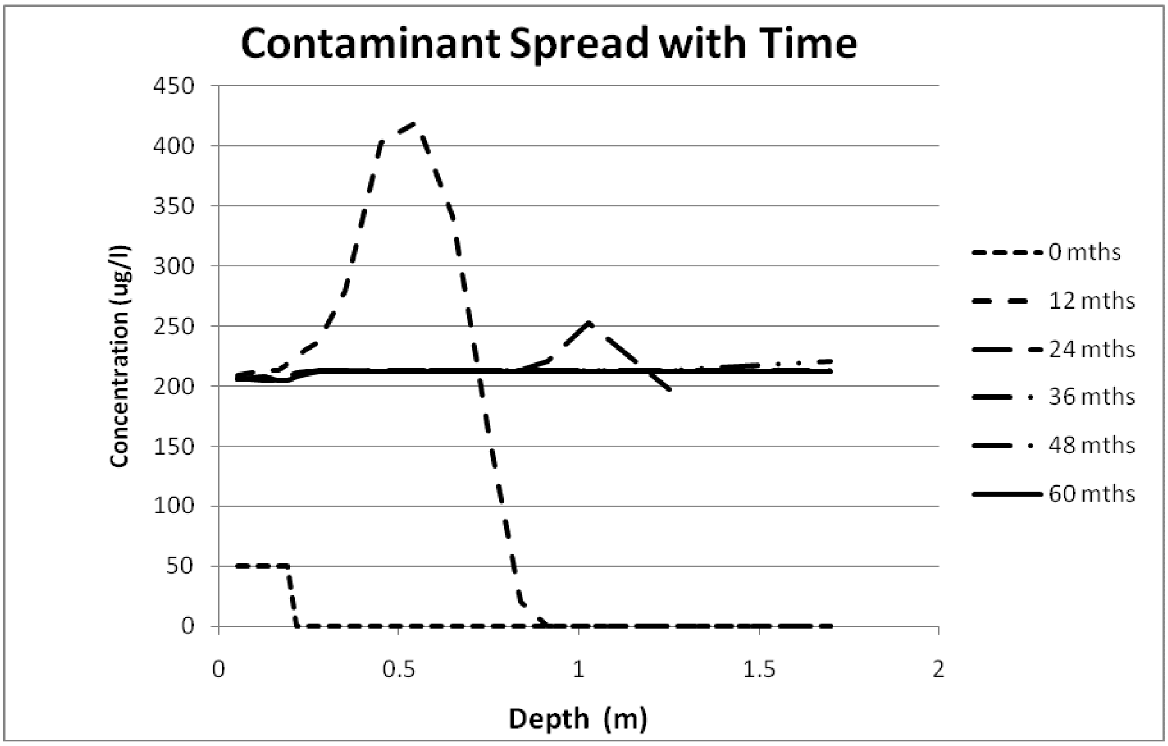

Figure D.5, Sodium analysis with Limestone and MAX runoff

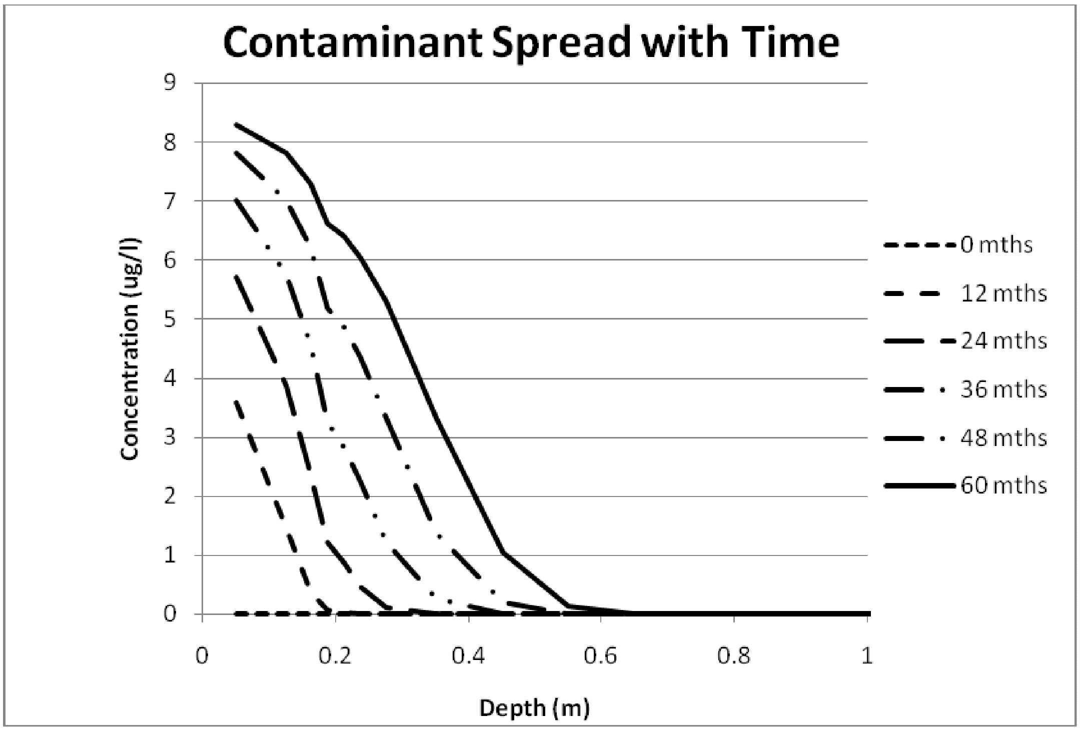

Figure D.6, Cadmium analysis with IBAA and MAX runoff

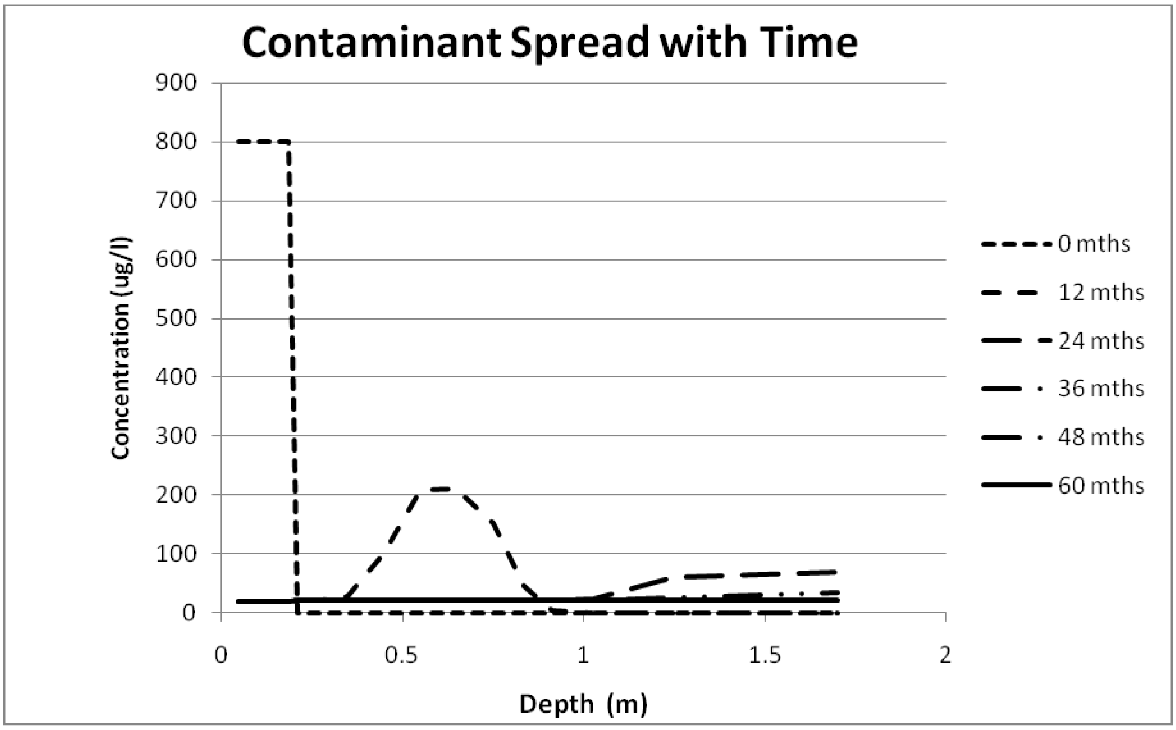

Figure D.7, Sodium analysis with IBAA and DEI runoff

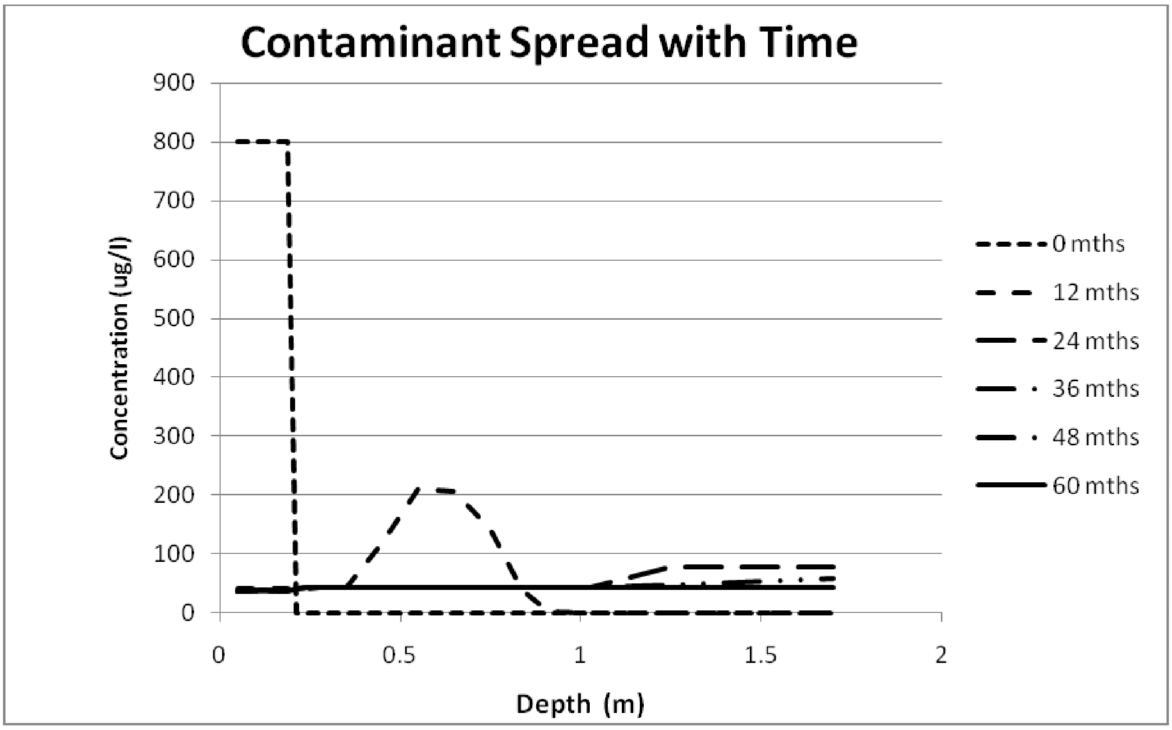

Figure D.8, Sodium analysis with IBAA and LTM runoff

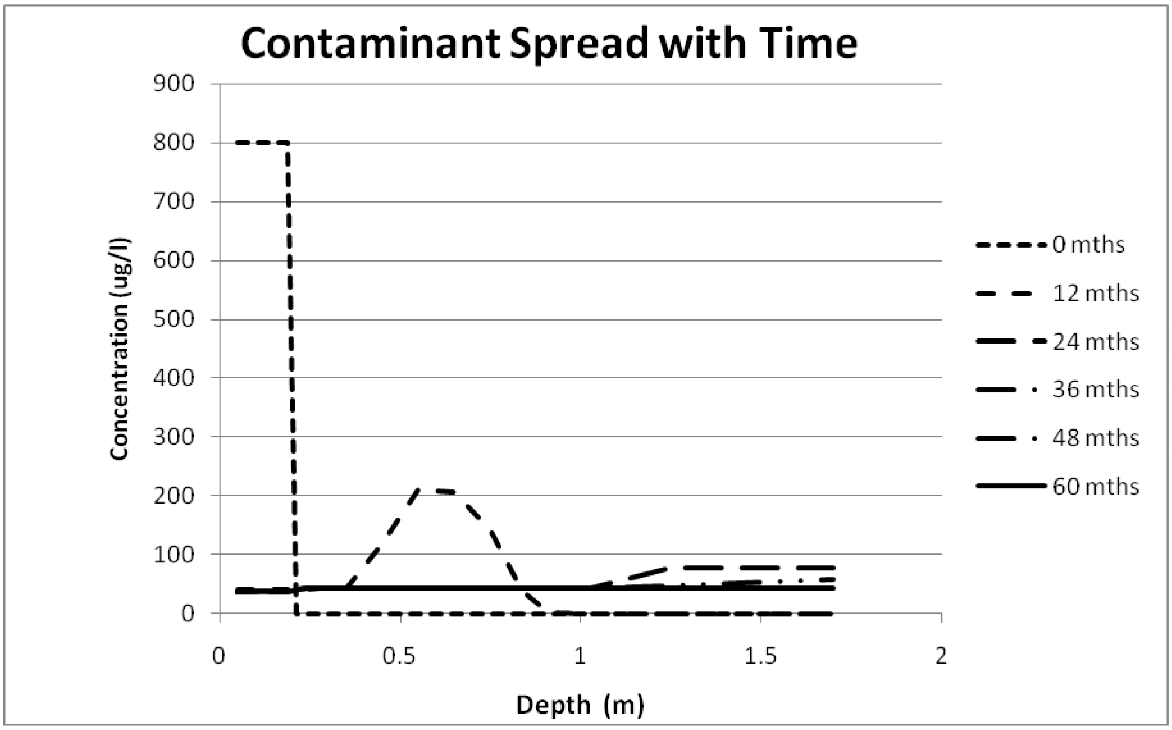

Figure D.9, Sodium analysis with IBAA and HTM runoff

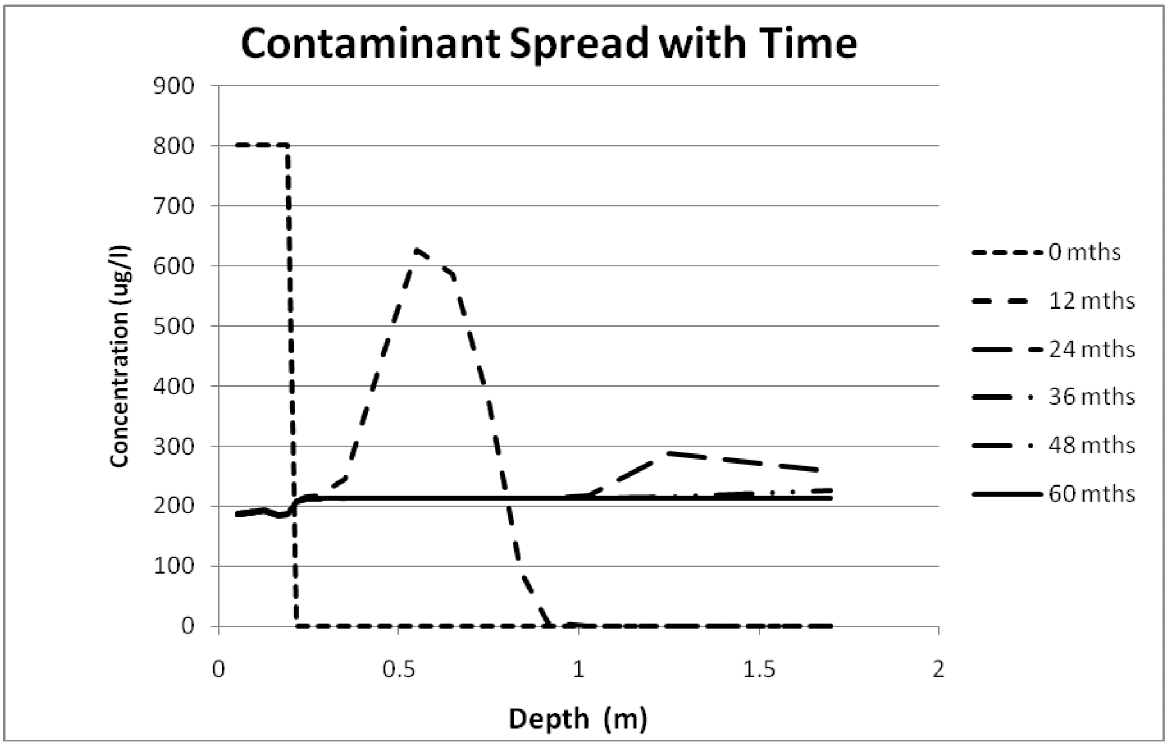

Figure D.10, Sodium analysis with IBAA and MAX runoff

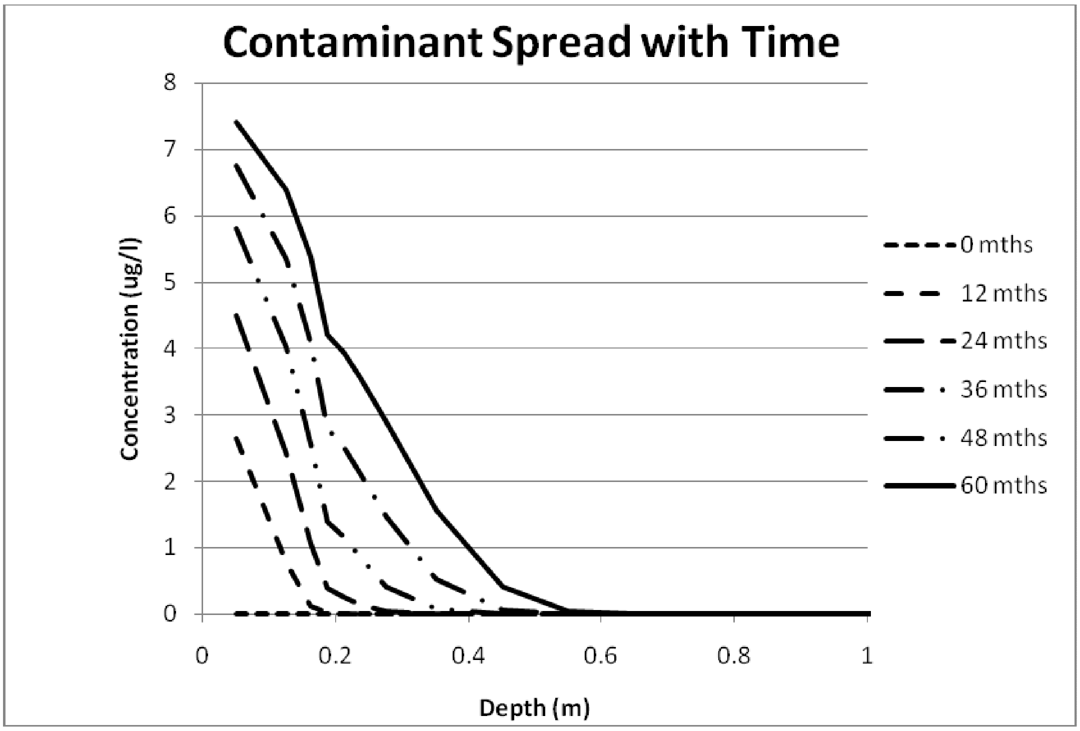

Figure D.11, Cadmium analysis with RFS and MAX runoff

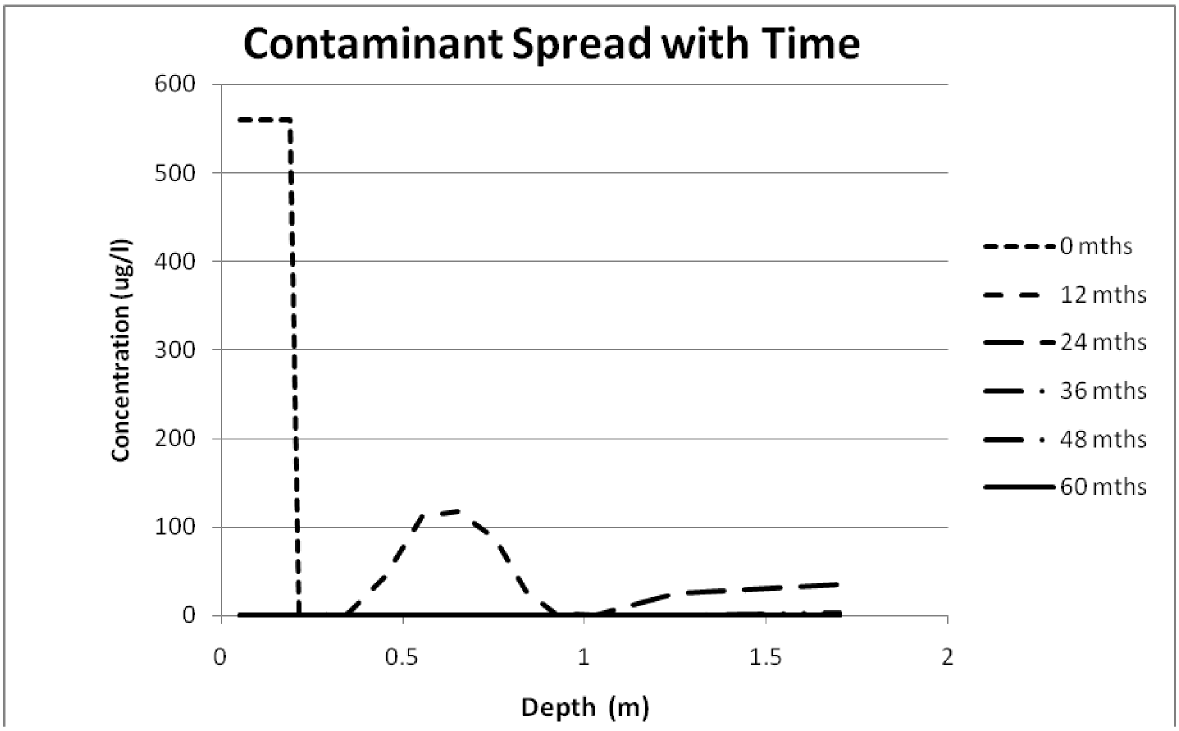

Figure D.12, Sodium analysis with RFS and DEI runoff

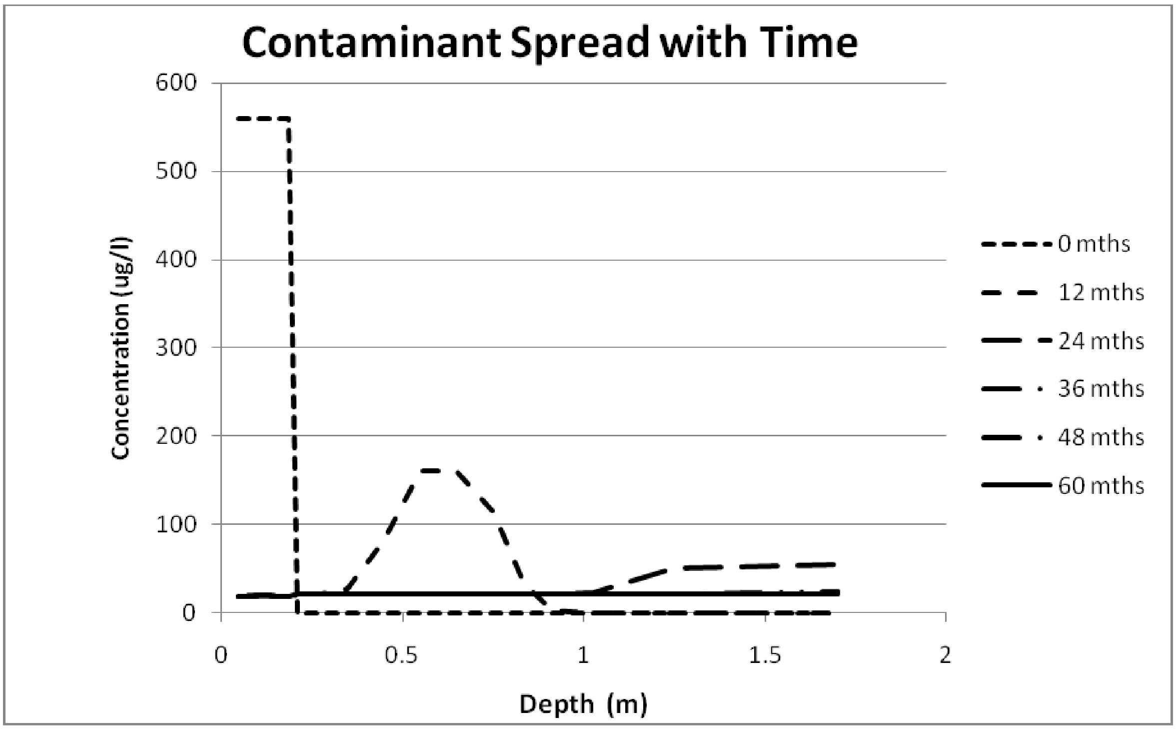

Figure D.13, Sodium analysis with RFS and LTM runoff

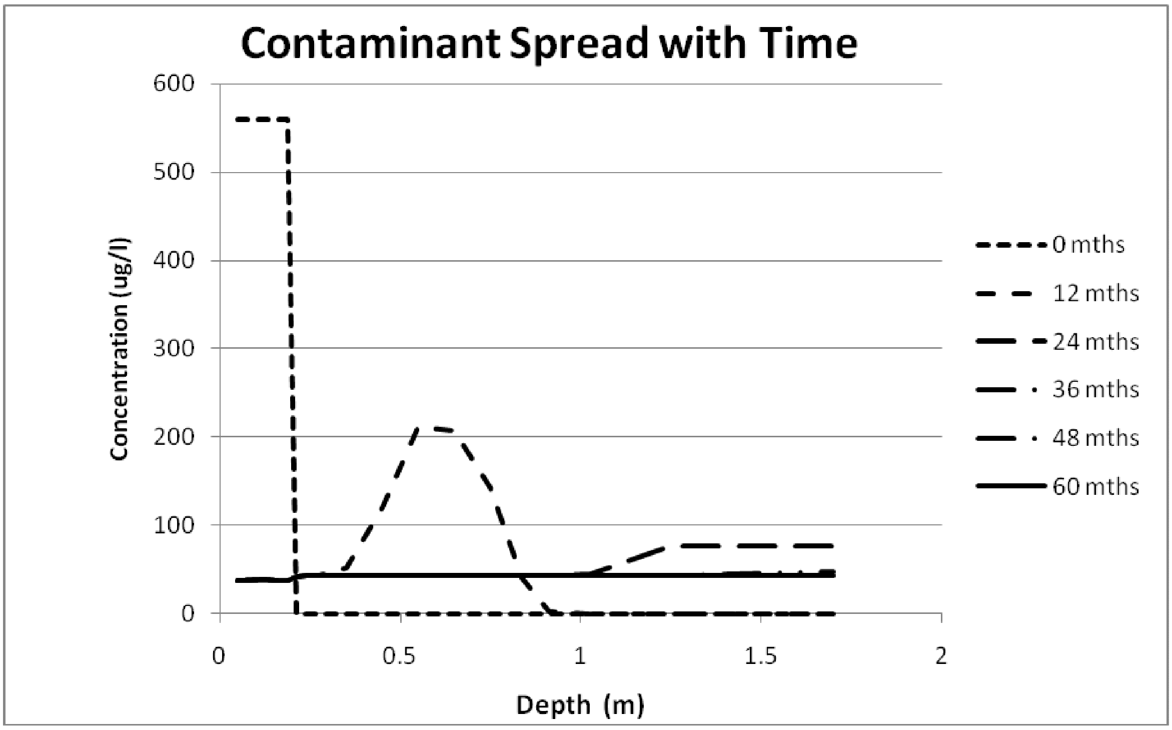

Figure D.14, Sodium analysis with RFS and HTM runoff

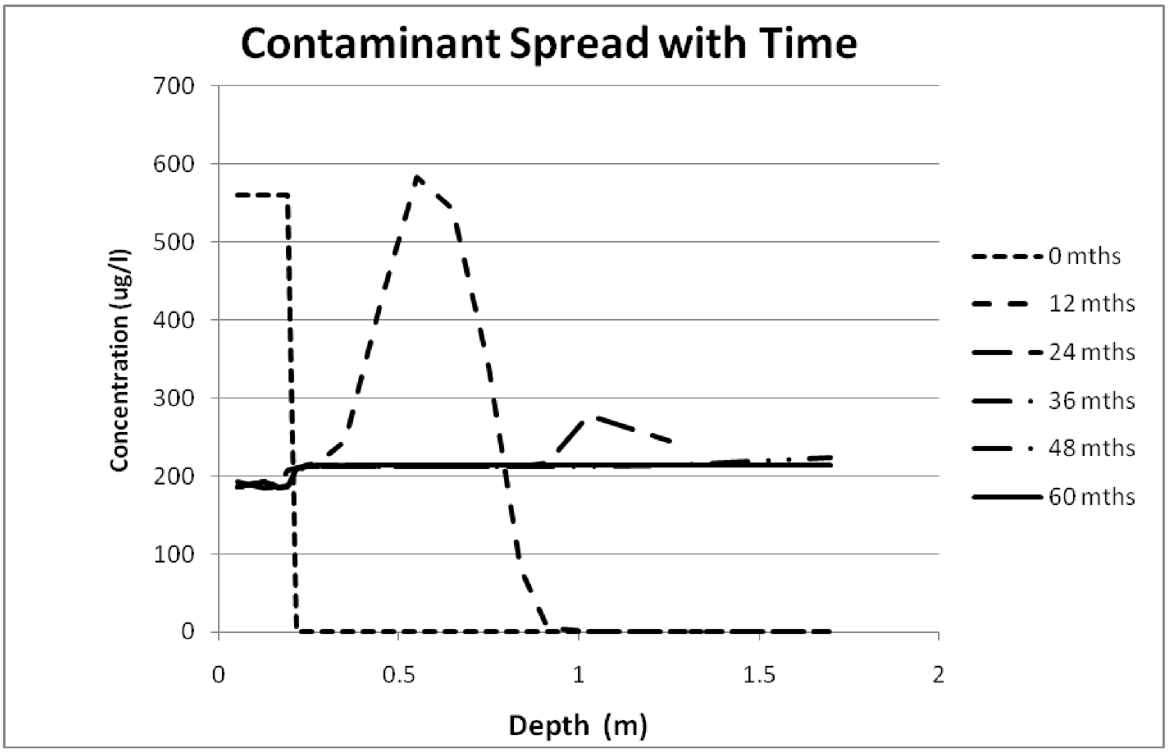

Figure D.15, Sodium analysis with RFS and MAX runoff

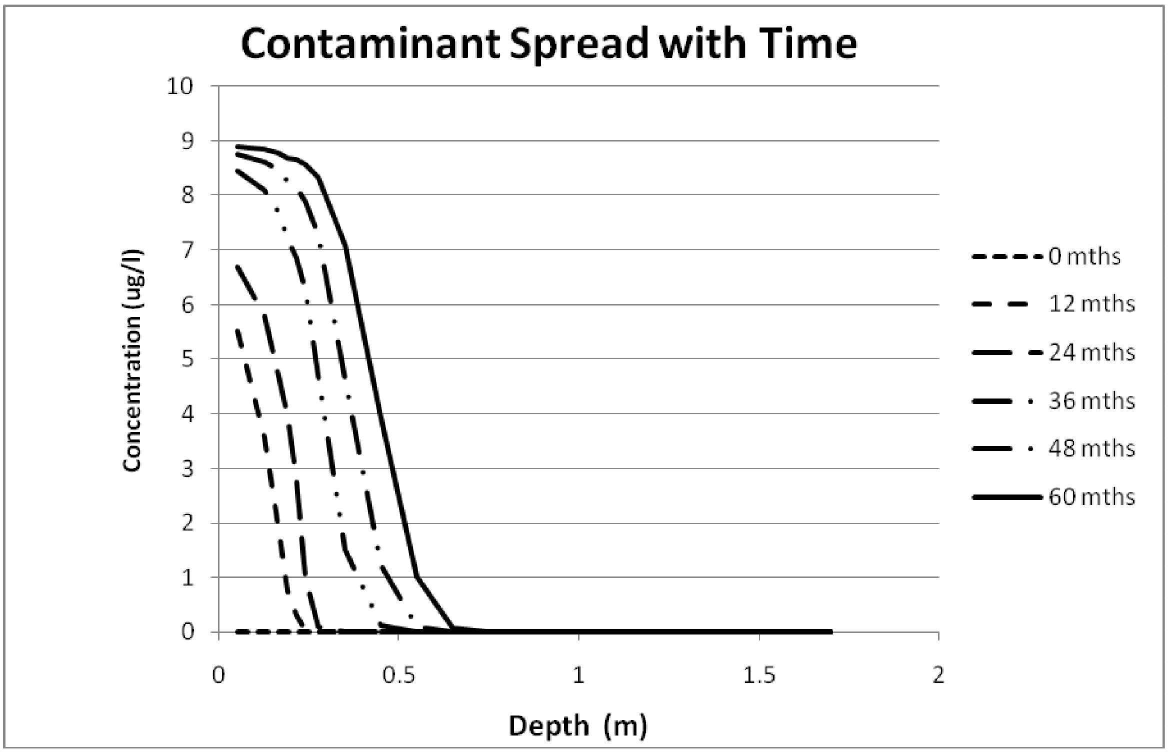

Figure D.16, Cadmium analysis with BFS and MAX runoff

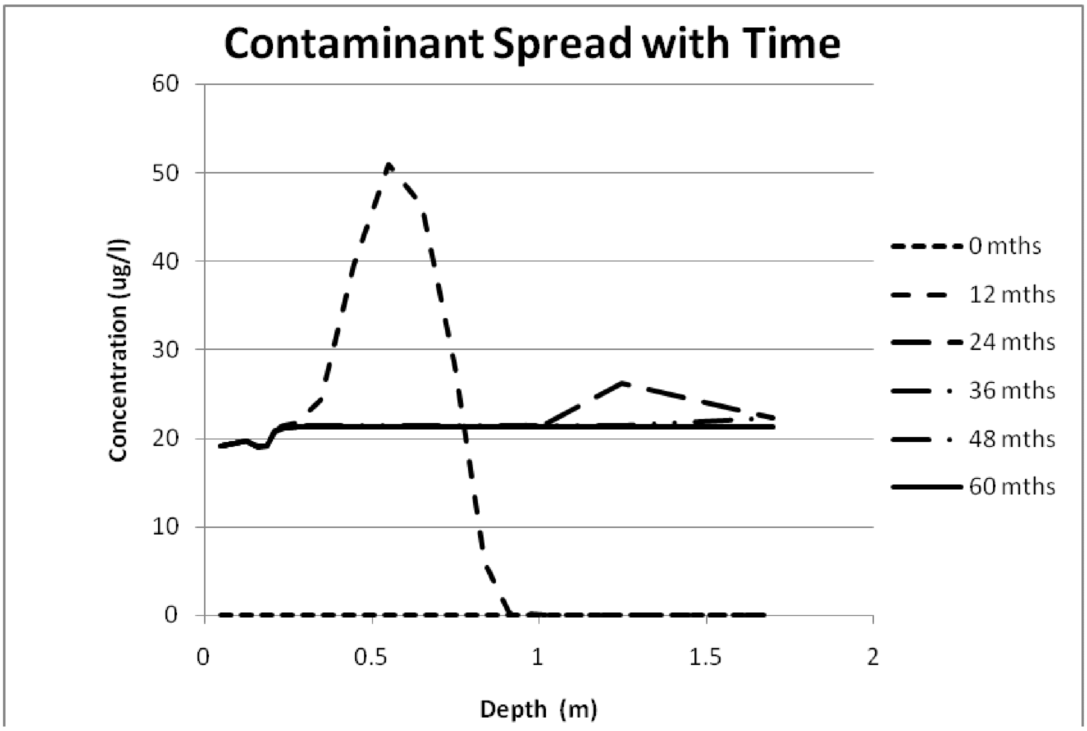

Figure D.17, Sodium analysis with BFS and LTM runoff

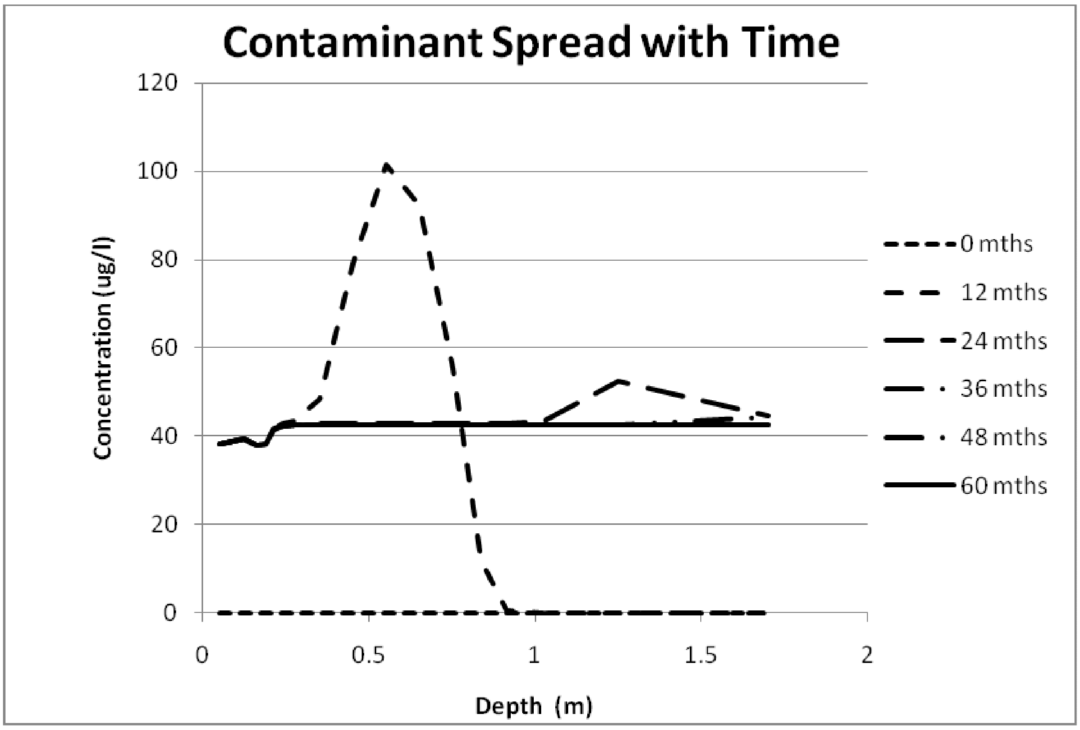

Figure D.18, Sodium analysis with BFS and HTM runoff

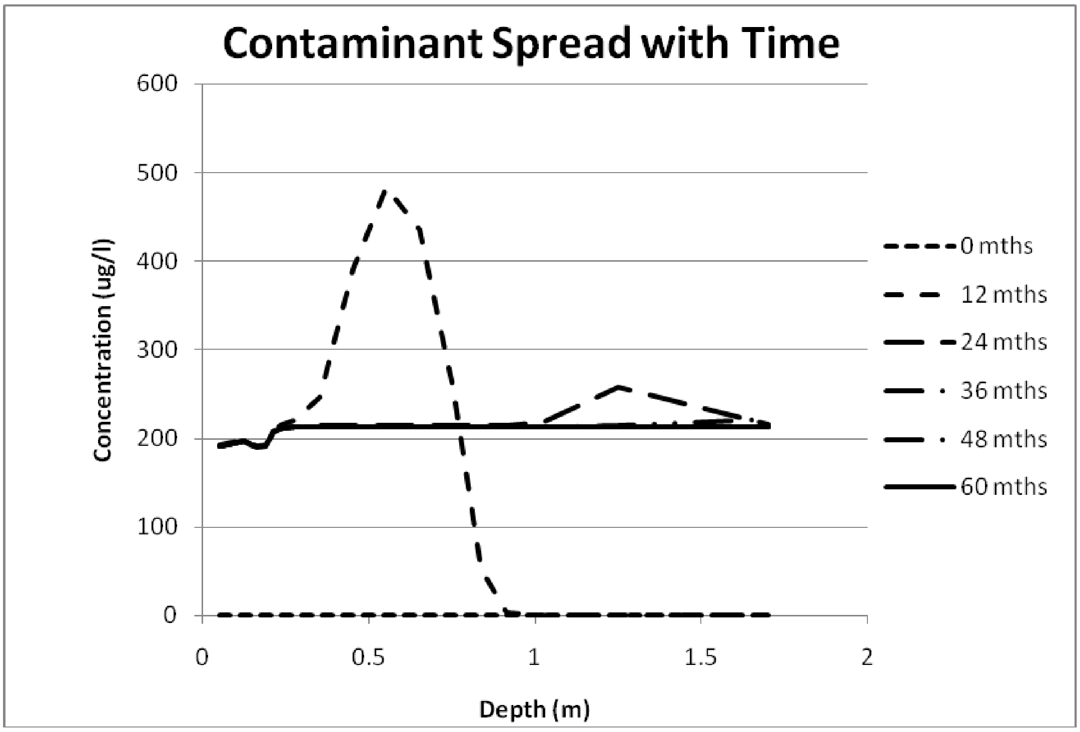

Figure D.19, Sodium analysis with BFS and MAX runoff