Adsorption of Nutrients to Particles in Urban Stormwater Systems.
Part 2: Nitrate and Ammonium

A Project

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by

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This thesis was prepared for the School of Civil Engineering at the University of Sydney, Australia, and describes the adsorption and desorption of Nitrate and Ammonium from particles in urban stormwater. The opinions, conclusions and recommendations presented herein are those of the author and do not necessarily reflect those of the University of Sydney or any of the sponsoring parties to this project.

ACKNOWLEDGEMENTS

ABSTRACT

Phosphorus (P) and Nitrogen (N) are essential nutrients for the ecological functioning of aquatic ecosystems. However, at excess levels (above that required by plants and micro-organisms), these nutrients can cause the eutrophication of water bodies, which can overstimulate the growth of algae and undermine the ecological functioning of natural ecosystems.

N and P are transported in stormwater as both sediment-bound chemicals through adsorption mechanisms; and as dissolved substances in aqueous solution. Therefore, by removing particles from the flow, a percentage of the available nutrient (which would otherwise travel on to waterways downstream) is also be removed. The aim of this thesis is to quantify what proportion of N and P are adsorbed to solid particles in urban stormwater, and what proportion are dissolved in aqueous solution, in order to better understand the mechanism of nutrient transport to urban waterways.

The process of desorption was replicated in a closed laboratory environment using a beaker and soil solution setup. The developed experimental procedure attempted to simplify what would happen in an urban catchment during a rainfall event.

This part of the thesis (Part 2) focused on nitrates (NO_3^-) and ammonium (NH_4^+). The total NO_3^- and NH_4^+ adsorbed to the solid particles of urban debris was determined by extracting these chemicals into solution and measuring their aqueous concentration using a Water Quality Meter. Subsequently, the exchangeable portion of NO_3^- and NH_4^+ was determined by immersing samples of urban debris in deionised water, and measuring the concentration that desorbed naturally. Statistical analyses of results were carried out using two sample t-tests, analysis of variance (ANOVA), Pearsons r correlation and linear regression analysis.

The results of our experiments found that at least 99.25% of the total NH_4^+ and 94% of the total NO_3^- remain adsorbed to urban debris when immersed in deionised water for 90 minutes, and highly organic debris materials had a larger percentage of these nutrients by mass soil weight than mineral debris. The implications of these findings is that removal of particulate matter is crucial in reducing the NO_3^- and NH_4^+ that travels downstream. Highly organic debris is particularly problematic, and early removal of this material from stormwater runoff is imperative. Furthermore, there was no significant relationship between particle size and total NH_4^+ or NO_3., which suggests a stormwater system does not necessarily have to have the capacity to filter very fine particles to reduce the N which travels into urban waterways.

Results of the experiments can be used not only by policy makers and urban developers, but also the wider scientific community

TABLE OF CONTENTS

CONTENTS

TABLE OF DEFINITIONS

Adsoptive	Adsorbable substance in the fluid phase
Adsorbate	A substance in the adsorbed state
Adsorbent	The solid material on which adsorption occurs
Adsorption	The attachment of chemical species from the aqueous phase onto the surface of a solid
Cl^-	Chloride ion
CV	Coefficient of Variation
Desorption	The release of a chemical species from the surface of a solid into the aqueous phase
DI	Deionised water
DO	Dissolved Oxygen
Fractioned material	Size fractions of the samples 2.36mm-6.0mm, 1.18mm-2.36mm, 600mm-1.18mm, 425mm-600mm, 300mm-425mm, 150mm-300mm, 75mm-150mm, < 75mm
Heterogeneous material	Soil sample fractions which contain a wide range of particle sizes, either <2.36mm or Unsieved
KCl	Potassium chloride extracting solution
M	Molar
$NH4+$	Ammonium
$NO2-$ Nitrite	Nitrite
$NO3-$ Nitrate	Nitrate
pH	A measure of H+ ions in solution
Soil sample 1	Saturated sample taken from the creek basement
Soil sample 2	Partially saturated sample from the edge of the creek
Soil sample 4	Damp soil-like sample from the creek bank
Soil sample 4	Dry organic sample
SDU	Stormwater Decontamination Unit
WQM	Water Quality Meter

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

1.1 Background

It is well documented that Phosphorus (P) and Nitrogen (N) are essential nutrients required for the ecological functioning of aquatic ecosystems (Raven et al., 2005, Conley et al., 2009). However, when N and P are in excess levels (above that required by plants and crops), they become harmful to natural ecosystems as they cause the eutrophication of water bodies, which has been the recent subject of global environmental concern (Anderson et al., 2002).

Typical problems associated with eutrophication include excess growth of macrophytes and the development of algal blooms; which in turn can generate malodours and diminish sunlight penetration to submerged vegetation (Conley et al., 2009, Payne et al., 2013). Furthermore, the eventual microbial decomposition of dead algae or other organic matter (OM) depletes dissolved oxygen and can produce hypoxic or anoxic environments that can have deleterious impacts on aquatic organisms (Carey et al., 2013).

N and P can travel into urban waterways as both sediment-bound contaminants through adsorption mechanisms, and as dissolved substances in aqueous solution (Vaze and Chiew, 2004). Therefore, the filtration and subsequent removal particles from stormwater will reduce the N and P that would otherwise be delivered to urban waterways.

However there is a large scientific debate about what proportion of these nutrients will remain adsorbed to the sediment, and what proportion is labile nutrient and will be released into solution (Aryal et al., 2010, Hongthanat, 2010, Song and Liu, 2013). Understanding the N and P adsorption processes is therefore critical for discerning the mechanisms and tenacity of N and P retention by particles in storm water runoff.

1.2 Research rational

This thesis is being undertaken as a continuation of the thesis by Scott Manning (2013) who looked at the particle removal efficiency of the Stormwater Decontamination Unit (SDU), a proprietary stormwater device. Whilst this product has been proven to sufficiently remove up to 90% of solid particles down to a size of 10 μm (L Crasti, pers.comm., 13 Oct, Manning, 2013), the mesh sediment trap does not prevent dissolved chemicals from passing through.

The aim of this thesis is to quantify the proportion of NO_3^-, NH_4^+ and PO_4^{3-} that remain adsorbed to the particles in stormwater runoff and the exchangeable proportion that is desorbed into aqueous solution.

This was achieved by replicating the process of desorption in a closed laboratory environment, using a beaker and soil solution setup. The process of desorption was replicated in a closed laboratory environment using a beaker and soil solution setup. The developed experimental procedure attempted to simplify what would happen in an urban catchment during a rainfall event.

The total NO_3^-, NH_4^+ and PO_4^{3-} adsorbed to the solid particles was measured by extracting these chemicals into solution and measuring their respective concentrations. Subsequently we measured the exchangeable portion of NO_3^-, NH_4^+ and PO_4^{3-} which unforcedly desorbed into deionised water.

This thesis is documented in two parts. Part 1, written by Jamie Wall, focuses on phosphate (PO_3^{4-}); and this second part of the thesis (Part 2), focuses on nitrite (NO_2^-), nitrate (NO_3^-) and ammonium (NH_4^+).

The motivations for carrying out this topic are part of a global environmental concern, which involves reducing the extent and effects of anthropogenic eutrophication on the natural environment.

1.3 Objectives

The objectives of this thesis are to:

- Determine the total mass of NH_4^+ and NO_3^- carried by soil particles typically present in an urban catchment; and the exchangeable proportion that are desorbed into solution.
- Compare the total and exchangeable NH_4^+ and NO_3^- in urban debris which differ in their material composition, residence time in the urban stormwater system and in-situ moisture state.
- Investigate the relationship between NH_4^+ and NO_3^- desorption and time; to assess whether the desorption of these nutrients is gradual, or whether it is instantaneous.

This thesis intends to bridge the gap in extant literature by clarifying ambiguities in the processes involved in nutrient delivery to downstream waterways. Results of the experiments can be used not only by policy makers and urban developers, but also the wider scientific community.

2 LITERATURE REVIEW

2.1 Introduction

The objective of this review is to synthesize and interpret current knowledge surrounding the sorption and solvation of nutrients (namely N and P) from aquasol particles in urban runoff.

Major contributions to the understanding of adsorption processes are detailed and a critical comparison of both laboratory and field experimentation pertinent to the topic is conducted. Gaps in extant literature and inconsistencies in experimental findings are drawn out, along with areas that require further research.

2.2 Adsorption processes and interactions

Adsorption can be described as the attachment of chemical species from the aqueous phase onto the surface of a solid. The reverse process is desorption, and can occur as a result of changing properties of the aqueous phase such as nutrient concentration, pH and temperature (Figure 2.1).
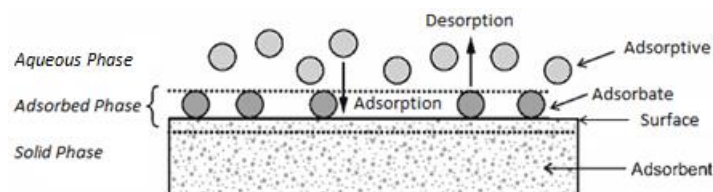
Figure 2.1: The adsorption process and basic nomenclature (Worch, 2012)

Sorption of P mainly occurs when it is in the form of phosphate ion (PO_4^{3-}) and sorption of N generally occurs in the ionic forms of ammonium (NH_4^+), nitrite (NO_2^-) or nitrate (NO_3^-).

Since sorption is a surface process, small particles with a high specific surface area tend to have a high N and P sorption capacity; however additional factors such as particle chemistry also come into play. This will be further discussed in sections 2.3.2 and 2.3.3 below.

2.2.1 Adsorption interactions

The forces governing adsorption are complex and involve both adsorbent[1] and adsorptive[2] interactions. As a molecule in solution approaches a solid surface, a balance is established

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[1] Adsorbent is defined as the solid material on which adsorption occurs
[2] Adsorptive is defined as adsorbable substance in the fluid phase

between the intermolecular attractive and repulsive forces. However, in the case of multicomponent systems where other molecules present and already adsorbed to the solid surface; both adsorbent-adsorbate[3] and adsorbate-adsorbate interactions may influence sorption reactions (Rouquerol et al., 1999). Adsorption can also be categorized into two types:

- Chemical adsorption (chemisorption); a slow (and sometimes irreversible) process where a chemical bond (either ionic or covalent) is formed between the surface of the adsorbent and the adsorbate molecule
- Physical adsorption (physisorption); a rapid process involving van der Waals attraction – dispersion forces and short range repulsion interactions.

Covalent bonds formed in chemisorption are highly dependent on the electron configuration of the adsorbent and the adsorbate, and as a result it is a highly specific process. Conversely, physisorption does not involve the formation of a chemical bonds between the adsorbent and the charged surface of adsorbent, and is therefore non-specific as there is a weak dependence on the solid surface electron configuration. In this case the adsorbate remains in close proximity to adsorbent but is disassociated with the surface (Figure 2.2)
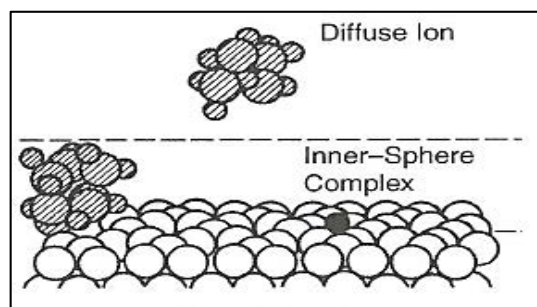
Figure 2.2: Mechanisms of ion adsorption. Chemisorption (left) and Physisorption (right). Source: The chemistry of soils.

2.3 Laboratory experimentation on adsorption

2.3.1 Adsorption isotherm equations

Adsorption isotherms are commonly used to express the equilibrium relationship between the amount of substance adsorbed per unit mass of solid sorbent '*q*' and the amount of the substance present in aqueous solution '*C*', at a constant temperature. The construction of an isotherm, which is specific to the adsorbent and adsorbate in question (for our purpose urban debris and N or P ionic species), allows inferences to be made about the labile N and P content which can be released into solution and travel to downstream waterways.

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[3] Adsorbate is defined as substance in the adsorbed state

At present, a number of theoretically derived isotherm equations exist. The most simplistic equations are the Freundlich (1907) and Langmuir (1918) equations, which are still frequently applied in current literature.

Freundlich was one of the first to believe adsorption did not involve penetration into the solid structure but instead was related to the solid surface. His mathematical relation can be expressed as:

$$q = KC^{1/n} \qquad (3.5)$$

where *K* and *n* are constants for a given adsorbate and adsorbent at a specified temperature, and are substantially empirical parameters.

Langmuir was first to propose that adsorption resulted in formation of a monomolecular layer (known as the '*monolayer*') and that the plateau of the adsorption isotherm indicated monolayer saturation. The Langmuir Isotherm has the form:

$$q = \frac{bCQ}{1 + bC} \qquad (3.6)$$

where *b* is a constant associated with the binding energy with units $\left[\frac{V}{M}\right]$; and *Q* is a constant representing the monolayer adsorption capacity at saturation with units $\left[\frac{M}{M}\right]$.

The parameters for the Langmuir isotherm are usually derived through the linear transformation of the equation, which can be written as:

$$\frac{C}{q} = \frac{C}{Q} + \frac{1}{bQ} \qquad (3.6)$$

Representing a straight line with intercept *1/bQ* and slope *1/Q*.

A desktop review of the Langmuir and Freundlich constants for inorganic particles of varying size (typical of those found in urban roadside runoff) was conducted to determine the range of published values. The Langmuir proved to more accurately describe the adsorption of N and P in scientific literature and as a result formed the focus of the search. Classification of the adsorbent material reported in papers was critiqued and reclassified based on the Unified Soil Classification System (USCS) into broad categories of 'sands' (2mm⁻63μm), 'silts' (63μm⁻ 2μm) and 'clays' (<2μm). Where material of varying size fraction was used for the adsorbent, classification was based on the United States Department of Agriculture textural soil triangle (for example the red clay soils described in Sato and Comerford (2005) were reclassified as sandy-clay-loams). The average and standard deviation of the Langmuir constants were taken

for each broad category, omitting outliers and studies with poor correlation between their data and the Langmuir equation ($r^2 < 0.5$) (refer to Appendix A for the complete set of reported values).

The range of values for of Langmuir constants for NO_3^- and NO_2^-, NH_4^+ and PO_4^{3-} adsorption on different sized fraction sediment is summarized in Table 2.1 a-c below:

Table 2.1 - Mean, standard deviation, coefficient of variation and range of values found in literature for the Langmuir Binding Energy Constant (b) and Monolayer Adsorption Constant (Q) for a) NO_3^- and NO_2^- b) NO_4^+ and c) PO_4^{3-} on sands, silts and clays

a)
NO_3^- and NO_2^-

	b (L/g)						Q (mg/g)					
	mean	sd	CV	Max	Min	Range	mean	sd	CV	Max	Min	Range
Clay (n=19)	11.67	32.85	2.815	136.6	0.060	136.54	5.033	11.24	2.233	42.54	0.567	41.97
Sand (n=14)	0.245	0.173	0.708	0.627	0.073	0.554	2.675	1.791	0.670	5.855	0.140	5.715
Silt (n=11)	0.459	0.461	1.003	1.350	0.121	1.229	1.244	1.104	0.887	4.148	0.226	3.922

b)
NH_4^+

	b (L/g)						Q (mg/g)					
	mean	sd	CV	Max	Min	Range	mean	sd	CV	Max	Min	Range
Clay (n=4)	6.306	0.743	0.118	6.866	5.237	1.629	33.45	14.61	0.437	47.69	13.18	34.52

c)
PO_4^{3-}

	b (L/g)						Q (mg/g)					
	mean	sd	CV	Max	Min	Range	mean	sd	CV	Max	Min	Range
Clay (n=13)	448.0	324.6	0.725	1164.3	130.8	1033.5	19.90	28.96	1.456	91.00	0.360	90.64
Sand (n=39)	9.679	36.70	3.792	181.0	0.021	181.0	0.192	0.171	0.890	0.814	0.014	0.800
Silt (n=12)	293.4	428.2	1.459	1200	0.243	1199.8	0.565	0.502	0.890	1.727	0.061	1.666

As can be seen in Table 2.1, there are large inconsistencies in the Langmuir constants quoted in the literature, with high variation in Q for clay size fraction particles (CV > 1). PO_4^{3-} shows higher variability on sand and silt than NH_4^+ and NO_3^-. Large values of Q for clays support the paradigm that fine particles have a greater adsorption capacity due to their large surface area high cationic exchange capacity.

The large discrepancies in the reported Langmuir constants can be accounted for by several factors. Firstly a limited number of papers were sourced and hence the compiled data set was very small. Secondly, large variations in adsorbent mineral properties and pre-treatments were seen across experiments and many also introduced variables such as pH and temperature changes which influences the equilibrium adsorption capacity. The credibility of experiments should also be questioned as it is presumed that the experimental procedure was carried out correctly and implicit assumptions of the Langmuir equation were obeyed. Sources of

experimental error could include failure to reach thermodynamic equilibrium and not attaining complete solvation of the solute.

Despite these large discrepancies, the above results can be used to determine the order of magnitude of the adsorption constants for each size fraction of sediment. Furthermore due to the statistical empirical rule, it can be concluded that our adsorption experimentation undertaken as part of this thesis should fall within the calculated means plus or minus the calculated standard deviations 68% of the time.

It should also be noted that the Langmuir equation was originally developed for gas adsorption and does not always fit the isotherm data for aqueous solutions (Harter and Baker, 1977, Worch, 2012) which is reflected by the poor correlation in many of the sourced data (Öztürk and Bektaş, 2004, Akosman and Özdemir, 2010, Song and Liu, 2013). Poor correlation is most commonly seen in highly porous and 'engineered' adsorbents such as activated carbons (He et al., 2007, Khani and Mirzaei, 2008), possibly due to the fact that assumptions of the Langmuir equation such as monolayer coverage of the adsorbent surface and energetic homogeneity of adsorption sites are not fulfilled (Worch, 2012). In fact Langmuir himself in his 1916 publication stated *"[on highly porous substances] it is impossible to know definitely the area on which the adsorption takes place".* (Langmuir, 1916).

However despite these uncertainties, the Langmuir equation can generally be used to describe chemical and physical adsorption (Dodor and Oya, 2000, Del Bubba et al., 2003, Bhatnagar and Sillanpää, 2011, Song and Liu, 2013, Zamparas et al., 2013). Nonetheless, using this approach to predict aqueous equilibrium should be exercised with caution.

2.3.2 Relationship between sorption capacity and particle size

Because sorption is a surface process, finer particles (such as clays and silts) are expected to have a greater capacity to adsorb N and P ions due to their large specific surface area. This theoretical statement is supported by many experiments; Sartor et al. (1974) collected urban road surface material from over 40 000 kilometres of streets from 12 cities in the United States, and found that on average silt and clay material made up less than 10% of particulate but contained more than 50% of PO_4^{3-} and 30% of NO_3^- and NO_2^- as sediment bound contaminants. Vaze and Chiew (2004) found between 85% - 95% total P and total N was attached particles less than 300μm (medium grained sands, silts and clays) from material collected in an Urban Street in Melbourne Australia; despite this size fraction making up less than half of the samples. Tai (1991) in Dempsey et al. (1993) found 83% total P was sorbed to particles less than 2mm. One inconsistency identified in Tai's findings is that the smallest particles were not the strongest

sorbents (<74μm sorbed 13.3% of TP whereas the 74-105μm size fraction sorbed 21.4% of TP). Tai postulated that this could be due to a high content of organic matter in the small size fraction which complicates the adsorption process.

2.3.3 Relationship between adsorption capacity and sediment mineralogy

Adsorption of P is recognized to occur as a combination of rapid physisorption on particle surface sites; accompanied by a parallel slow chemisorption where a ligand exchange occurs at hydrous Al and Fe oxide mineral sites. A description of the slow P chemisorption process is presented in Hemwall (1957). By way of comparison, in non-acidic calcareous media Ca causes P to be lost from solution due to precipitation of insoluble $CaHPO_4$ (McGechan and Lewis, 2002). Several equations have been developed to relate sediment mineralogy to Langmuir adsorption capacity of P (Van der Zee and Van Riemsdijk, 1988, Schoumans, 1995, Pierzynski, 2000, Zhang et al., 2005). Such equations are used to provide an indication of the loss of P to fresh water for both agricultural and environmental purposes. The most widely used equation for P sorption was developed by Schoumans (1995), and is given as:

$$Q = \frac{1}{6}(Al_{ox} + Fe_{ox})$$

where 'Al_{ox}' and 'Fe_{ox}' are the Al and Fe content extracted from the soil with ammonium oxalate solution. However, it should be recognized that this equation (among others) only gives an estimate of Q, and no single equation can generically describe the sorption capacity of all media. Despite this, the paradigm that Al and Fe oxide minerals will increase P adsorption is consistent across scientific literature. For example, Edzwald et al. (1976) found the PO_4^{3-} adsorption capacity of the three clay minerals increased in the order of Kaolinite < Montmorillonite < Illite and was closely related to the Fe content of the clays. Sakadevan and Bavor (1998) found the relationship between P and substrate adsorption capacity was strongly correlated to the extractable Al ($r^2=0.890$) and Fe ($r^2=0.736$) content. An even stronger correlation was found when regression analysis was fitted to the combination of these minerals ($r^2=0.901$). Similarly Dodor and Oya (2000) found through multiple regression analysis of 16 soils that P adsorption was accurately described by a combination of clay, organic matter, Fe and Al content ($r^2=0.890$). Fewer studies have been performed on calcareous sediments. Del Bubba et al. (2003) constructed adsorption isotherms for 13 calcareous sands and found P adsorption was significantly related to Ca content, Mg content, grain size and porosity ($p<0.01$). The results of this study support the scientific consensus that Ca promotes precipitation of non-soluble P salts.

The capacity of sediments for PO_4^{3-} sorption is much more frequently reported on than the capacity of sediments ionic species of N, possibly due to the historical focus of P in causing

eutrophication (Conley et al., 2009) . NO_3^- and NO_2^- adsorption is more strongly influenced by the solvent and solute pH rather than mineralogy due to the molecules anionic nature (Tani et al., 2004, Copcia et al., 2010). For example Black and Waring (1979) found NO_3^- adsorption was positively correlated to specific surface area, and negatively correlated to aqueous pH and organic carbon content (0.872, $p<0.01$). This agrees with Bhatnagar and Sillanpää (2011) who conducted a review on the efficiencies of typical adsorbents employed for water treatment purposes and found carbon based adsorbents consistently demonstrated poor adsorption capacity of anionic molecules. They also found clays treated with HCl showed an increased sorption capacity in comparison to those left untreated due to an ionic exchange process occurring between Cl^- and NO_3^-. The adsorbent surface charge can also be enhanced through impregnation with other minerals, Rezaee et al. (2008) found that almond shell activated carbon (an agricultural waste product) modified with ZnO demonstrated increased NO_3^- adsorption by enhancing the positive surface charge of the carbon and affinity for NO_3^- ions.

2.3.4 Other influences on adsorption

Despite strong evidence that nutrients such as N and P are likely to be adsorbed to sediments with particular physio-chemical properties; it must be recognized that adsorbent and adsorptive interactions are complex and there are many other factors (such as temperature, rate of hydraulic loading and pH) which influence sorption processes (Singh and Kanehiro, 1969, Brix et al., 2001, Akosman and Özdemir, 2010).

Increasing temperature is believed to reduce adsorption capacity due to a weakening of attractive forces between the adsorbate and adsorbent. This agrees with the results of Akosman and Özdemir (2010) who studied adsorption of nitrate on three size fractions of sediment and found the amount adsorbed consistently decreased with increasing temperature.

Hydraulic loading can promote desorption in two ways. The first is through effectively 'washing' the particles and overcoming the weak forces binding sorbate molecules on low energy sites. The second is by replenishing the aqueous solution in the vicinity of the sorbed sites, in effect locally reducing the adsorptive concentration and encouraging release. Conversely enriching the solution with exchangeable N or P will push the reaction in the other direction. However whilst sorption on to static soil components is widely reported on, studies to date on sorption capacity in dynamic environments is limited. Current studies incorporating the effect of flow velocity tend to focus on constructed wetlands. In a review of filter materials used in wetlands Vohla et al. (2011) found that the optimal hydraulic loading rate for nutrient retention varies depending on the adsorbent material. However these studies do not consider how adsorption differs between static material and dynamic material which is carried with

surface runoff in overland flow. Only one model of colloid facilitated transport of nutrients is known, which was developed by Jarvis et al. (1999) to describe transport of sorbed pesticides. As a result this area requires further research.

Another significant adsorption factor is pH, which influences the ionic mechanisms of sorption not only for NO_3^- and NO_2^- (as discussed above) but also PO_4^{3-} and NH^+. Increased adsorption can be achieved by impregnating the adsorbent surface with oppositely charged ions; or alternatively increased desorption can be achieved by altering the pH of the aqueous phase in the direction where adsorption strength decreases.

pH is particularly influential on NH_4^+ adsorption and desorption, as NH_4^+ can be exchanged with H^+ molecules in solution. Therefore, low pH is often associated with high NH_4^+ adsorption. This is reflected by the in the work of Copcia et al (2010) who found that clays were only able to efficiently adsorb ammonium ions when the ammonium concentration in aqueous solution was lower than 100mg/L, and above this concentration, adsorption of NH_4^+ was significantly curbed.

2.4 Field Studies

However, the way these processes translate practically in the field is not well understood. Numerous papers have found that the high adsorption capacity of many materials determined through laboratory batch experiments is not representative of the adsorption capacity of that material observed in the field (Drizo et al., 2002, Del Bubba et al., 2003, Àdàm et al., 2006, Bhatnagar and Sillanpää, 2011). In a review of adsorbent materials used for PO_4^{3-} removal in wastewater Vohla et al. (2011) state *"If one uses maximal P retention capacity calculated from the Langmuir equation… it is easy to make overestimations"*

This is because the transportation of nutrients in urban catchments during storm events is multifaceted; as it concerns many media over many temporal and spatial scales (Ahyerre et al., 1998). These process are influenced by a range of factors including (but not limited to) nutrient loading concentration, temperature variations, attenuation factors (such as dilution processes and nutrient transformations) and changes in moisture content of the sorbing material. These complexities do not lend themselves to simplified mathematical models which have been developed and used in past experimentation, and can often lead to large errors (Ahyerre et al., 1998, Irish et al., 1998).

Numerous field experiments of N and P adsorption to sediments in urban runoff have been conducted. Several studies were found to support the contention that nutrients travel as polluting agents by means of adsorption to the particles in urban runoff. Zanoni (1986) looked at the

chemical characteristics of a storm event and reported that nutrient constituents were predominantly bound to the particulate fraction of runoff residuals rather than the soluble fraction of runoff residuals. This agrees with the work of Ball and Abustan (1995), who found that 85% of P and 70-80% of N was associated with particulate matter. Hvitved-Jacobsen et al. (1994) found that 60-80% of P in stormwater and highway runoff was bound to suspended solids. Similarly Vaze and Chiew (2004) found the dissolved component of total N in stormwater ranges from 20-50%, and total P ranges from 20-30%. They also found the majority of nutrient was attached to particles were in the 53-300μm size range.

The second side to this contention is that nutrients travel as polluting agents in the aqueous phase. This argument is supported by Lewis et al. (1999) who studied 31 watershed in the American tropics and found that on average 70% of N is dissolved and only 30% is associated with particles. Similarly Taylor et al. (2005) conducted a study in Melbourne Australia and found 80% of N in stormwater was of the dissolved fraction. Understanding the composition of N and P in urban runoff is necessary to maximize treatment efficiency. Field studies on attenuation factors such as dilution processes and nutrient transformations within the watershed are also limited. This study aims to help bridge the gap in these uncertainties and find break points and sensitivity to time, temperature and nutrient loading concentrations.

2.5   Contemporary stormwater management responses

To put this into the context of this thesis, contemporary stormwater management responses are shifting away from hard engineered structures and towards 'Water Sensitive Urban Design' (WSUD) solutions such as bioretention systems and constructed wetlands. However, the effectiveness of these stormwater systems at removing nutrients is strongly debated. A review of the pollutant removal performance of biofiltration systems conducted by Payne (2013), reports values of plant N assimilation in terrestrial systems and constructed wetlands ranging from 1 to 180 g N/m^2/year, suggesting inconsistencies in literature on the significance of plant uptake. N removal through biofiltration systems is more variable then P, as it is likely to undergo a range of species transformations and NO_3^- is highly prone to leaching (Hatt et al., 2009). In addition vegetation can only remove nutrients in the short term as when plant tissues decompose between 35% to 75% of plant P is released (Good et. al, 1978 in Richardson, 1985).

The efficiency of non-biologic sorbents in constructed wetlands at removing nutrients is also debated. PO_4^{3-} retention capacity in many cases has been seen to diminish over time as adsorbent materials become saturated, and therefore only serves as a short-term sink for N and P (Drizo et al., 2002, Johansson Westholm, 2006, He et al., 2007). In some instances PO_4^{3-} is

actually re⁻released from the sediments of a constructed wetland into solution (Song et al., 2007). Large accumulations of nutrients in constructed wetlands over time are often misinterpreted to imply large retention capacity, however if substrates are not replaced they can have the opposite effect.

It should also be noted that runoff captured by these systems will undergo extended time and temperature changes which will encourage N and P desorption, as described in the sections above. Consideration should be given to these phenomena when designing stormwater treatment systems. In a typical drainage system contact time between the media and runoff water is constrained to a number of minutes and so only the initial desorption of nutrient in this time period is critical. Further research should be directed towards comparisons between stormwater treatment methods; as early removal of the particles from Stormwater before physical changes have time to occur could ultimately reduce the desorption and solvation of nutrients.

2.6   Summary and Conclusions

The processes involved in P and N adsorption are very complex, however it is agreed that finer particles (such as clays and silts) have a greater capacity to adsorb N and P namely due to their large specific surface area and high ionic exchange capacity. The most commonly used equations to represent surface adsorption and equilibrium concentration of solute in media are the Langmuir and Freundlich models. Some limitations of these models exist, including the overestimations of sediment adsorption capacity in laboratory experimentation when compared to the capacity seen in the field. This could be a result of several factors including competition from other adsorptives or absence of hydraulic flow conditions. However, for the most part these models can be used to describe the adsorption isotherm, with the Langmuir model providing a better representation of the adsorption of N and P ionic species in academic literature.

Despite adsorption processes and laboratory experimentation being extensively reported; how these processes translate into the field in characterizing stormwater runoff is poorly understood. There is a large scientific debate which is polarized between those who believe N and P are predominantly delivered into receiving water through dissolution; and those who believe N and P are predominantly delivered into receiving waters as adsorbates to particle flocculations. There are also many uncertainties about whether N and P undergo nutrient transformations within a catchment. The mechanisms of nutrient delivery and how this varies spatially and temporally within urban watersheds is identified as an area needing further research.

3   METHODS

3.1   Study site and soil characterisation

Four samples of urban soil debris were collected from Cowan Creek at the Pymble golf course, located approximately 20 km North of Sydney at 33.73ºS 151.15ºE (Figure 3.1) on the 15th of July 2014. This site was selected as it is representative of a typical urban residential catchment. Prior to the date of collection, there had been no significant rainfall ($\geq$5 mm over 24 hours) for 33 days (BOM, 2014) (Appendix B)
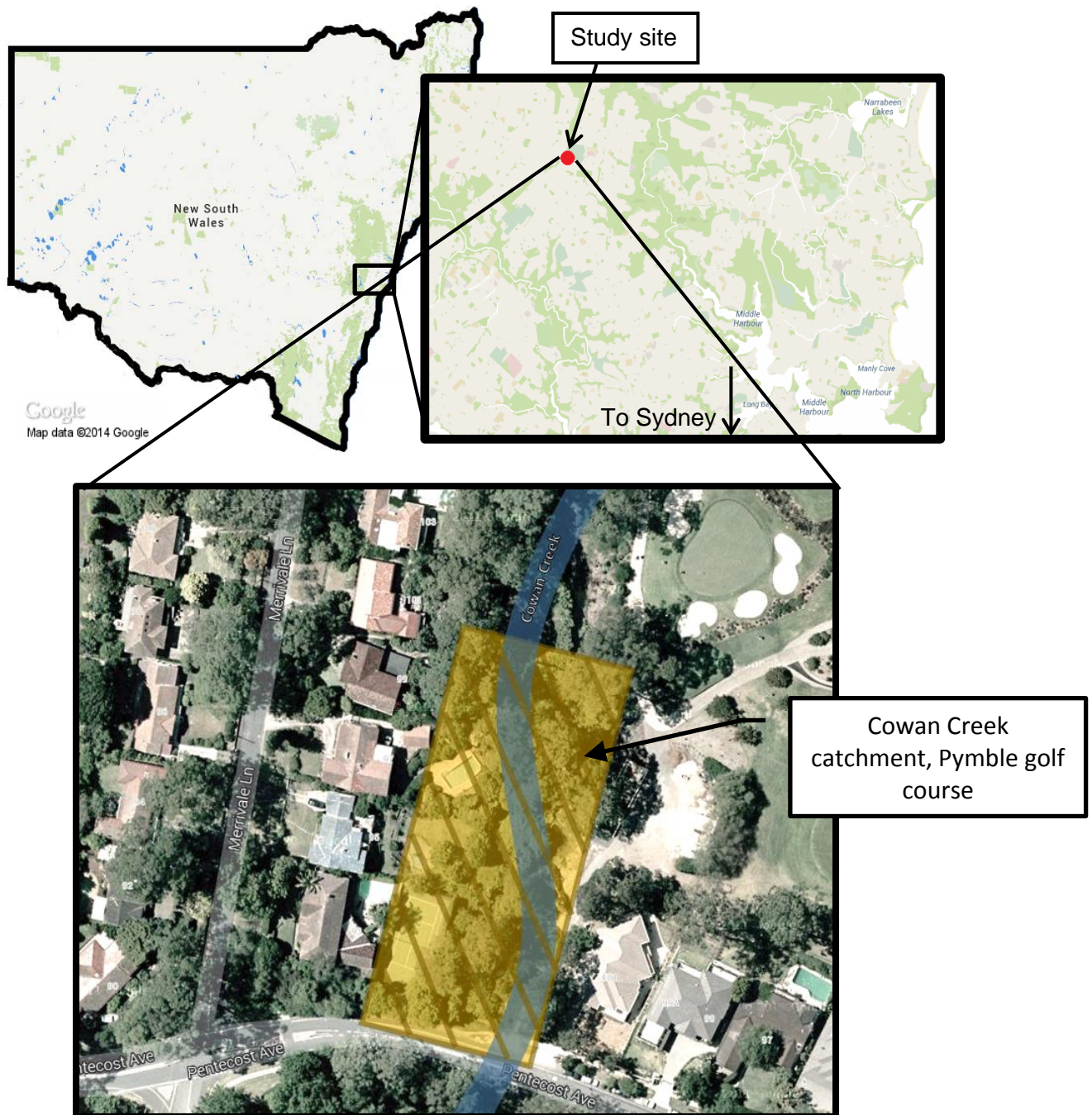
Figure 3.1: Location of study site from which samples were collected (Cowan creek, Pymble golf course). Image source: Google map data 2014.

The four samples were taken from different locations near a stormwater drain outlet to represent the stages of material decomposition in the urban stormwater cycle (Figure 3.2). These samples contained a collection material found near the stormwater drain outlet including pebbles, soil, organic material, leaf litter, animals wastes and pieces of rubbish; however this material will be collectively referred to as 'soil' in this thesis.
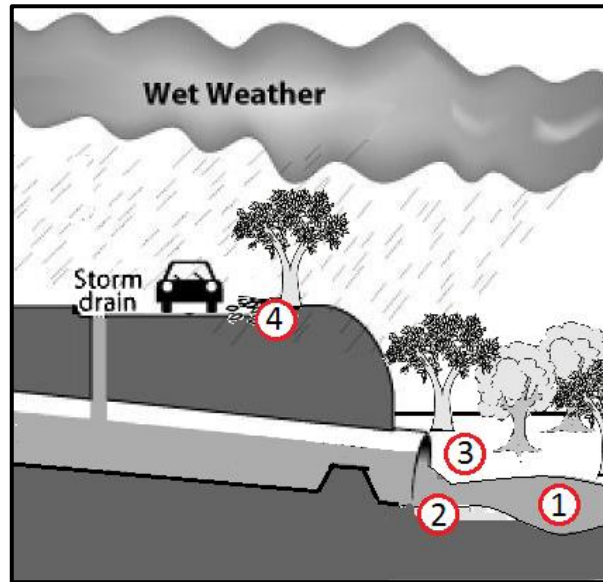
Figure 3.2: Location of four soil samples (labelled 1-4) in a typical urban catchment. Image source: adapted from EPA,2004

Soil samples were recovered from surface material to a maximum depth of 50cm and differed in their mineral and organic composition, as well as their in-situ moisture state.

A summary of the four soils is given in Table 3.1 and a more in depth qualitative description which described differences in their physical characteristics can be found in Appendix C.

Table 3.1: In-situ description of four collected urban debris samples

Soil Sample	Description
Soil 1	Saturated material deposited on the creek basement. Organic decomposition in the latter stages, material has been integrated into the urban stormwater system for a long period of time.
Soil 2	Partially saturated material where the creek was beginning to evaporate due to lack of rain. Similar to Sample 1, organic decomposition is in the latter stages and the material has had a long residence time in the urban stormwater system.
Soil 3	Pre-wetted damp material on creek bank with moderate decomposition and some vegetation cover. Scouring suggested the particulate matter had the potential to wash into the creek with the next onset of rain.
Soil 4	Freshly deposited, dry roadside material. Not yet entered the stormwater cycle but has the potential to wash into creek with the next onset of rain.

Samples were oven dried at 180°C and the mass fraction of water by weight was determined (Appendix D). For the saturated and partially saturated samples, the supernatant water was siphoned and left to evaporate in order to retain the fines suspended in the soil-water slurry.

Particles larger than 6mm (large stones, leaves and pieces of rubbish) were removed from the soils by means of hand sieving. The particle size distribution was then determined for each sample using the conventional dry sieving technique described in AS 1289.3 Method 3.6.1. Samples were thoroughly mixed in order to attain homogeneity, and 300g of each was weighed out. Sieve trays were stacked in order of descending aperture size and the 300g sample was placed in the top sieve tray. The assembled soil sieve column was placed in a mechanical shaker for 15 minutes, after which the mass (M) of soil retained on each sieve was calculated as:

$$M_{soil} = M_{soil+sieve} - M_{sieve}$$

The weight of each size fraction was then divided by the total weight of the sample to give the percentage composition of the soil by fraction. Particle size distribution charts can be found in Appendix E.

The remaining soil from each sample was separated into the following 10 fractions: Unsieved, 2.36mm-6.0mm, 1.18mm-2.36mm, 600μm-1.18mm, 425μm-600μm, 300μm-425μm, 150μm-300 μm, 75μm-150μm, < 75μm and <2.36mm diameter (Figure 3.3).
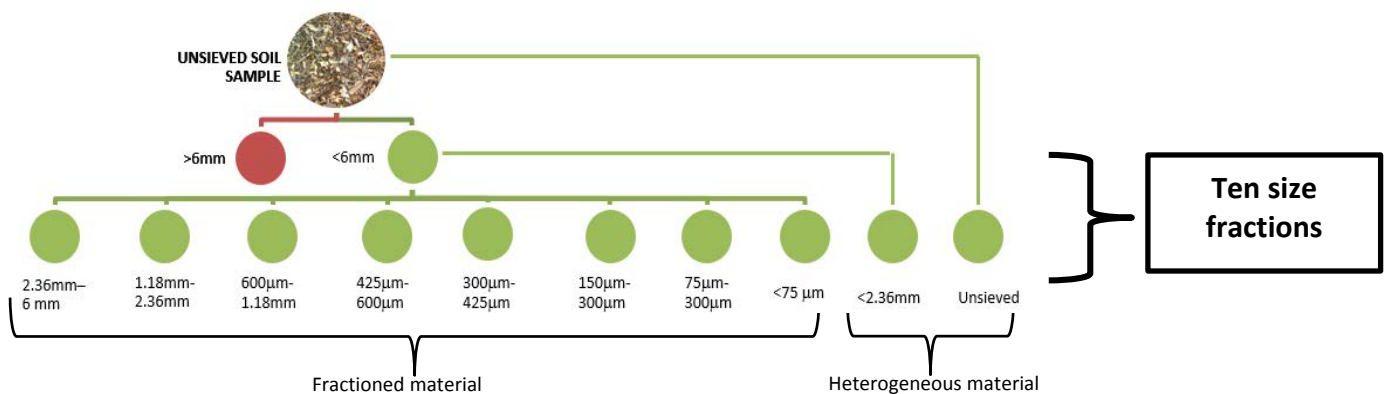
Figure 3.3: Ten fractions used in adsorption experiments

The unsieved and <2.36mm fractions contained a range particle sizes, and will be referred to as the 'heterogeneous material'; whereas the other eight were comprised of one size range of soil particles, and will be referred to as the 'fractioned material'.

The surface characteristics and composition of the 10 fractions were observed using an Otek OT-508 USB Digital microscope. A description and united classification of each soil type is found in Appendix E, and microscope imagery is found in Appendix C.

3.2 Total and exchangeable NH_4^+ and NO_3^-

The total NO_3^- and NH_4^+ were first extracted from the 10 fractions using $2M$ KCl, in order to determine the mass of these nutrients within the material. Concurrent experiments were conducted using an equivalent amount of deionised water in replacement of the KCl extracting

solution, in order to determine the mass of exchangeable NO_3^- and NH_4^+. Details of these procedures are described in Sections 3.2.1 to 3.2.3 below.

In these experiments the 'exchangeable' NO_3^- and NH_4^+ is defined as the nutrient that desorbed into deionised water without being forced. On the other hand, total NO_3^- or NH_4^+ is the absolute mass of these nutrients present in the material, as determined through the chemical extraction.

3.2.1 Equipment calibration

NO_3^- and NH_4^+ were measured in solution using the TOA DKK Water Quality Meter (WQM), Model WQC-24. This device provides $\pm$ 5% accuracy in NH_4^+ and NO_3^- readings, can also measure 5 additional parameters (pH, dissolved oxygen (DO), electrical conductivity, temperature, and chloride ion (Cl^-)). Furthermore, it has the capacity to take continuous measurements that are then stored in the inbuilt data logger.

To calibrate the WQM to measure NO_3^- and NH_4^+, eight standard solutions of NH_4 NO_3^- which ranged in concentration from 1mg/L to 3500 mg/L were prepared. This was achieved by diluting *1M* concentrated NH_4NO_3 with quantified volumes of deionised water. Two standard solutions were used to calibrate the WQM with the calibration range dependent on the experimental sample being measured (Table 3.2).

Table 3.2: Range of concentrations of NH_4^+ and NO_3^- used in the calibration of the WQM. The assigned range was dependent on the sample being measured.

Experimental Sample	Calibration Range	
	NH4	NO3
Soil + deionised water	1.0 mg/L – 29.2mg/L	1.0 mg/L – 10.0mg/L
Soil + KCl extracting solution	100.0 mg/L – 1292.7 mg/L	100.2 mg/L – 1050.62 mg/L

A third known concentration that fell within the measurable range was used to check the calibration.

3.2.2 Total NO_3^- and NH_4^+ in each soil fraction

NO_3^- and NH_4^+ were extracted from each soil fraction using a method adapted from Sparks (1996). *2M* potassium chloride (KCl) solutions were prepared by dissolving reagent grade KCl in deionised water with a ratio of 15g per 100ml. Solutions were sealed in glass jars and immersed in 60°C water for 20 minutes. They were then stirred using a magnetic stirrer until all KCl had dissolved and allowed to cool to room temperature.

10g of oven-dry soil was weighed for each fraction of the four debris (40 samples with 3 replicates of each = 120 samples total). The soil was placed in a glass jar with a screw top lid along with 100ml of the extracting solution. The jars were shaken by hand 30 times at 15 minute intervals over a 90 minute period.

16

Supernatant fluid was then filtered through the 300μm sieve, and samples smaller than the 300μm size fraction were subsequently filtered through Whatman No. 42 filter paper.

To measure NH_4^+ and NO_3^- in the extracting solution filtrate, the WQM was calibrated according to Table 3.2, and deionised water was incrementally added until the concentration was in the measureable range of the WQM using the procedure in Figure 3.4 below.
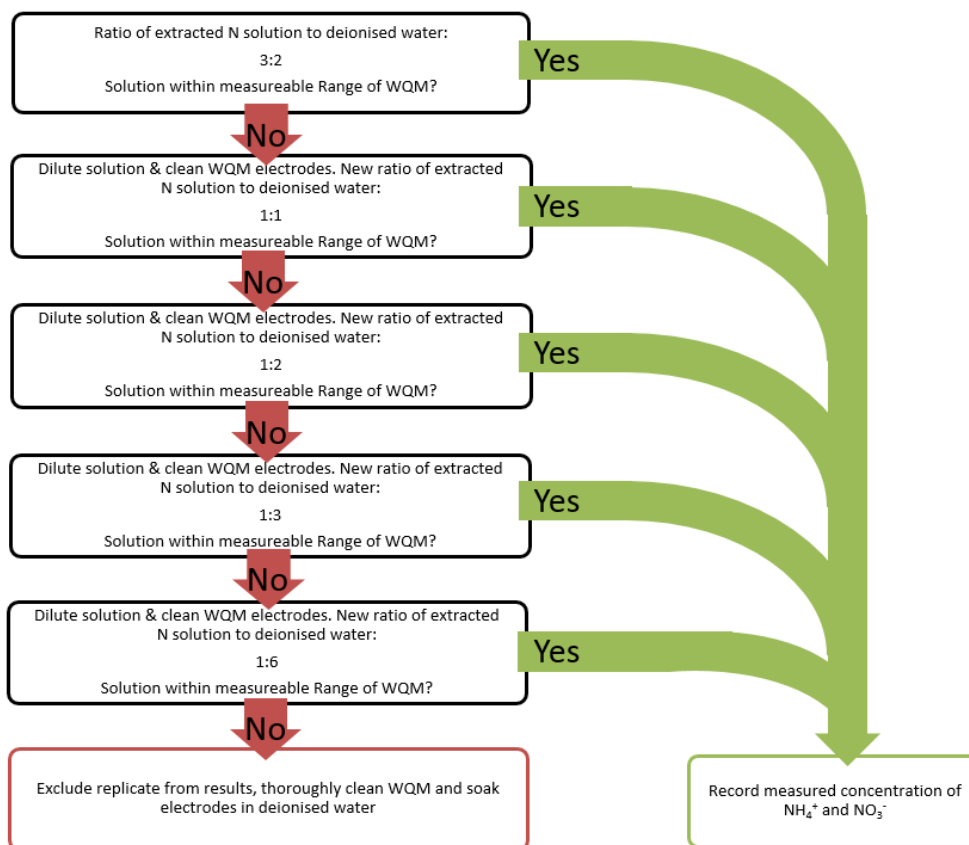
Figure 3.4: Flow chart process to establish measureable range of NH_4^+ and NO_3^- with the WQM.

From the measured aqueous concentration, the total NH_4^+ and NO_3^- content of the soil was then calculated in terms of milligrams per gram of soil.

3.2.3 Exchangeable NO_3^- and NH_4^+ in each soil fraction

The procedure described in Section 3.2.2 was repeated, replacing the 100ml KCl extractant with 100ml of deionised water, in order to determine the mass of exchangeable NO_3^- and NH_4^+ in the four soils. This is the nutrient which would be desorbed in natural environmental conditions (for example in short duration rainfall). The WQM was calibrated according to Table 3.2. It was unnecessary to dilute supernatant fluid, so the aqueous concentration of NH_4^+ and NO_3^- was measured and recorded directly after filtration. The pH, chloride concentration, dissolved oxygen and temperature and electrical conductivity were also recorded. The desorbed NO_3^- and NH_4^+ was then converted to units of μg N per gram of soil

3.3 Time dependent desorption of exchangeable NH_4^+ and NO_3^-

3.3.1 Exchangeable NO_3^- and NH_4^- measured over 24 hours

The time dependent release of NH_4^+ and NO_3^- into deionised water from soils was measured over a 24 hour period. Experiments were conducted on the heterogeneous <2.36mm soil fraction, which was a good representation of the in-situ soil gradation and composition. The unsieved material was not used, as particles >2.36mm were either large pieces of leaf litter or pebbles/stones; both of which were expected to cause spurious adsorption results.

100g of <2.36mm soil was weighed out for each soil, and placed in a large beaker with 2000mL of deionised water. The solution was stirred by hand 50 times to ensure complete saturation of the soil, and the WQM (pre-calibrated in accordance with Table 3.2) was immediately immersed in the solution. Seven parameters (pH, dissolved oxygen, electrical conductivity, temperature, Cl^-, NH_4^+ and NO_3^-) were measured and recorded every minute over a 24 hour period using the WQM built-in data logger. Three replicates were conducted for each of the 4 soils.

Time traces of the exchangeable NO_3^- and NH_4^+ in aqueous solution were deemed to be in equilibrium when there were only small fluctuations in the system. First reach of equilibrium was defined as the time when the 15 minute average aqueous concentration did not differ from the previous 15 minute average by more than 5% for at least 2.5 hours. Following this point if the 15 minute average consistently changed by less than 5% over the next 2.5 hours, the equilibrium value was taken as the average over this time interval (Figure 3.5).
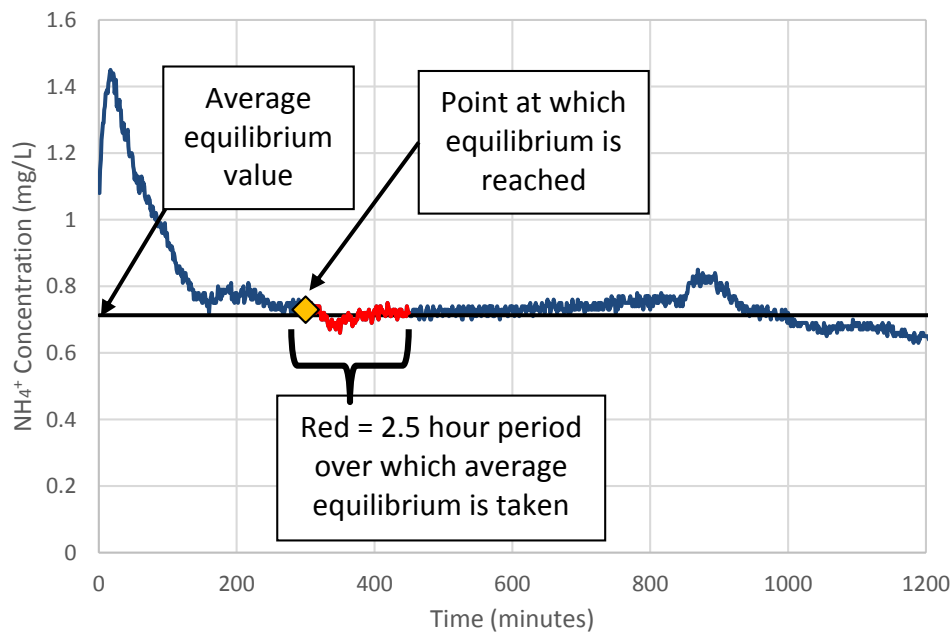
Figure 3.5: Typical time sequence and method of determining equilibrium

3.3.2 Extraction of recoverable NO_3^- and NH_4^+ from the soil used in the time dependent release experiments.

After soaking soils for 24 hours, the supernatant solution was decanted and the remaining soil was placed in an 180^oC oven for 3 days. Once dry, NO_3^- and NH_4^+ were extracted from the soil using the method detailed in Section 3.2.2.

3.4 Data analysis

Statistical analyses were performed using Microsoft Excel and Matlab.

Linear regression analysis was used to analyse the relationship between mass of NO_3^- or NH_4^+ and particle size, and differences in the mass of NO_3^- and NH_4^+ between soils were assessed using an analysis of variance (ANOVA). Post-hoc comparisons used pairwise t-tests to test for differences in the cumulative NO_3^- and NH_4^+ in each soil sample.

Pearsons correlation coefficients (r) were calculated to test for correlation between total NO_3^-/NH_4^+ and e NO_3^-/NH_4^+ in all four soils. Where time series data were collected, the relationship between NH_4^+ and NO_3^- desorption with time was assessed by constructing time sequence plots. Finally other water quality parameters (DO, pH, temperature and Cl^-) were correlated with the concentration of NO_3^- NH_4^+ at the point of equilibrium using Pearsons r correlation. This was achieved by taking the average of the measured NH_4^+ or NO_3^- over the 2.5 hour defined equilibrium period. The average of the variable being correlated was taken at the same time instance where equilibrium occurred for NH_4^+ or NO_3^- (Figure 3.6) A total of 450 data points were used in each average (150 time measurements at equilibrium for three replicates).

All statistical analyses used a statistical significance level of ($p < 0.05$).
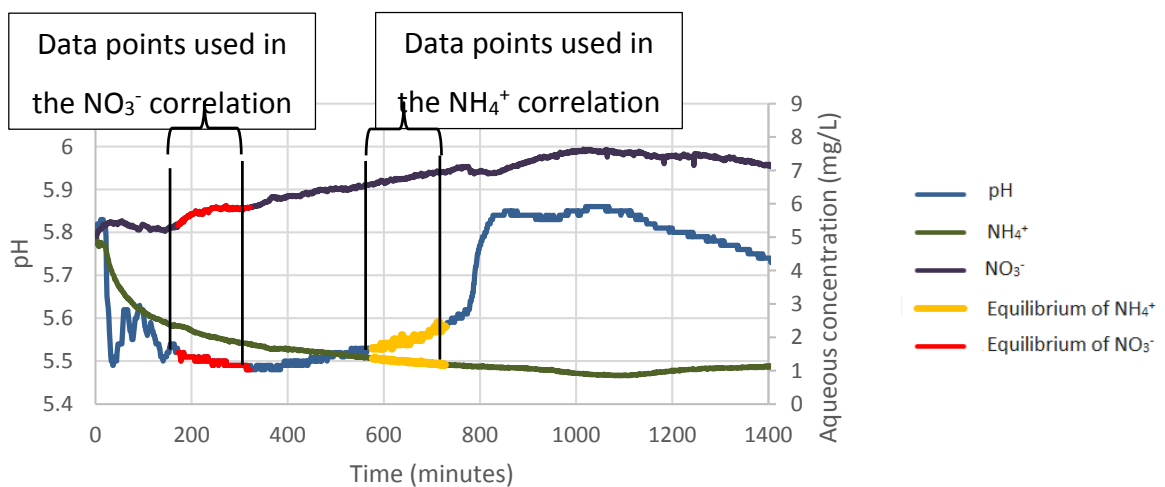
Figure 3.6: Example of the 150 data points used to calculate the average value at equilibrium for one replicate. pH is plotted on the primary axes and NH_4^+ and NO_3^- are plotted on the secondary axis. Note the values of pH (an example of one of the 5 variables) is averaged at a different point in time for the NO_3^- correlation and the NH_4^+ correlation

4 RESULTS

4.1 Extraction and natural desorption

4.1.1 Chemical extraction of total NO_3^- and NH_4^+

The mean and standard deviation (sd) of the total NO_3^- and NH_4^+ in 3 replicates of each fraction of the four soils ranged from 0.002% to 3.8% mass soil weight. Total NH_4^+ was consistently higher than NO_3^- in all four soils (Figure 4.1). Raw data can be found in Appendix F.
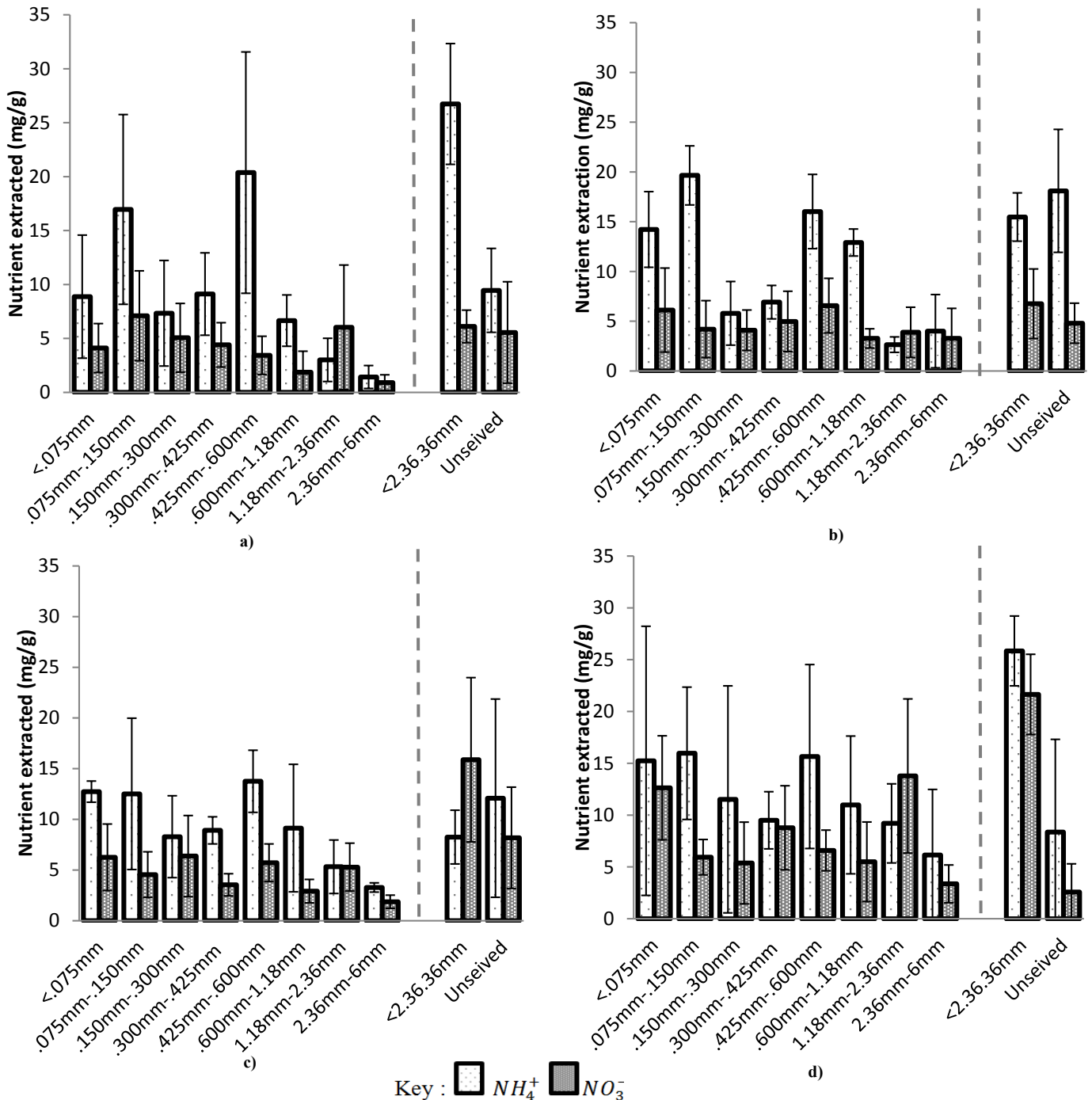
Figure 4.1: Mean (sd) of total NO_3^- and NH_4^+ in a) Soil 1 b) Soil 2 c) Soil 3 and d) Soil 4. Left of the dashed line are the fractioned samples and right of the dashed line are the homogenous samples

20

4.1.1.1 Comparison of size fractions

Linear regression analysis was used to investigate any relationship between total NO_3^-/NH_4^+ and particle size, up to a maximum size of 2.36mm. Size fractions larger than 2.36mm were not included in the regression because they comprised mainly stones and leaf litter. There was a statistically significant decreasing trend between NH_4^+ and increasing particle size for soil 1 (saturated material from the creek basement). There was no significant linear trend for NH_4^+ and particle size for the other 3 soils ($p > 0.05$), and no significant linear trend between NO_3^- and particle size for any of the soils ($p > 0.05$) (Table 4.1).

Table 4.1: *p* values obtained from linear regression of adsorption capacity vs particle size (bold italicised values are statistically significant using *p* < 0.05 as criteria for significance

Soil sample	NO_3^-	NH_4^+
Soil 1	0.896	***0.003***
Soil 2	0.096	0.797
Soil 3	0.093	1.452
Soil 4	0.245	0.402

A comparison of the coefficient of variation between soils found the unsieved fraction showed significantly more variability than the other 10 fractions (Table 4.2)

Table 4.2: Coefficient of variation (CV) for each soil fraction. Bold italicized values are the three largest for that soil sample

Size fraction	Soil 1	Soil 2	Soil 3	Soil 4	Soil 1	Soil 2	Soil 3	Soil 4
<75µm	0.42	0.35	0.42	0.18	0.22	0.17	0.08	0.63
75µm-150µm	0.4	***0.47***	0.33	0.36	0.56	0.15	***0.6***	0.37
150µm-300µm	0.45	0.34	***0.53***	***0.63***	0.54	***0.55***	0.49	***0.93***
300µm-425µm	0.25	0.32	0.45	***0.49***	0.05	0.16	0.15	0.2
425µm-600µm	0.14	***0.49***	0.44	0.19	0.16	0.23	0.22	0.42
600µm-1.18µm	0.16	0.41	0.11	0.44	***0.95***	0.11	***0.5***	0.58
1.18mm-2.36mm	***0.52***	0.24	***0.52***	***0.48***	0.43	0.23	***0.5***	0.35
2.36mm-6mm	***0.65***	0.12	0.46	0.46	***0.61***	***1.3***	0.14	***1.08***
<2.36mm	0.19	0.20	0.39	0.18	0.22	0.16	0.32	0.09
Unsieved	***0.75***	***0.51***	***0.50***	0.39	***0.59***	***0.32***	***0.81***	***0.93***

Note that in 7 out of 8 cases, the CV of the unseived fraction was in the highest 30% of values for that soil. The <2.36 fraction became the focus of the time dependent experiments because it had lower variability and it still accurately represented the soil sample in its in-situ state.

4.1.1.2 Comparison of four soil samples

A two-way analysis of variance (ANOVA) found the total NO_3^- and NH_4^+ was signficantly influenced by size fraction (NH_4^+ $F_{3,7} = 14.03$, p <0.0001, NO_3^- $F_{3,7} = 6.06$, p <0.0001), the soil sample (NH_4^+ $F_{3,7} = 2.91$, p <0.05; NO_3^- $F_{3,7} = 11.03$, p <0.0001) and the interaction between soil fraction and soil type for NO_3^- ($F_{3,7} = 2.07$, p <0.05) but not for NH_4^+ ($F_{3,7} = 0.89$, $p = 0.60$).

Post hoc comparisons on the differences between soils were conducted, taking into account the soil granulometry. The cumulative nutrient by grain size in 100g of each soil is presented below (Figure 4.2). The highest point on each curve represents the total NO_3^-/NH_4^+ in all particle sizes.
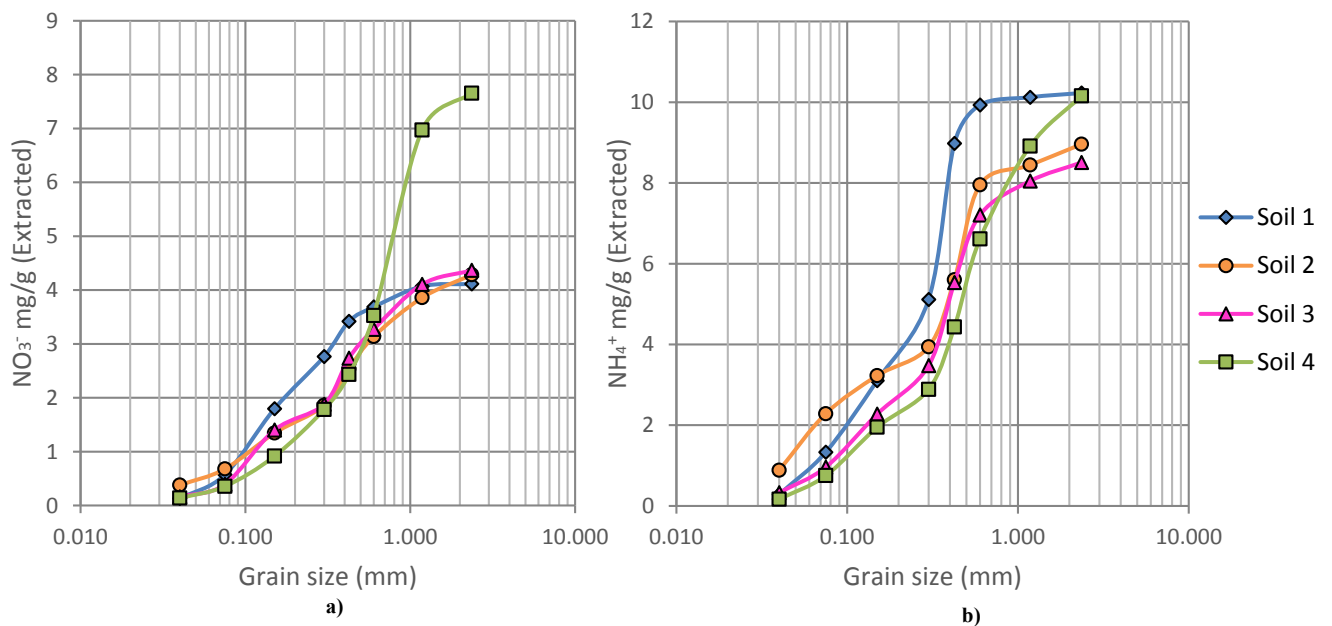
Figure 4.2: Cumulation of a) NO_3^- and b) NH_4^+ in 100g of each of the four soil samples

Pairwise t-tests were used to compare the cumulative NO_3^-/NH_4^+ between soil samples; and it was found soil 4 had a significantly larger NO_3^- content than soil 1 ($p<0.05$), soil 2 ($p<0.001$) and soil 3 ($p<0.05$). There was no significant difference in the NH_4^+ content between the four samples, complete pairwise t-tests can be found in Appendix G

4.1.2 Natural desorption of exchangable NO_3^- and NH_4^+

When the procedure was repeated replacing the 2M KCl extracting solution with deionised water, the exchangeable NO_3^- and NH_4^+ that was desorbed was an order of magnitude lower than the total NO_3^- and NH_4^+ desorbed under forced extraction (Figure 4.3, note the change in the units of desorbed nutrient on the y axis)
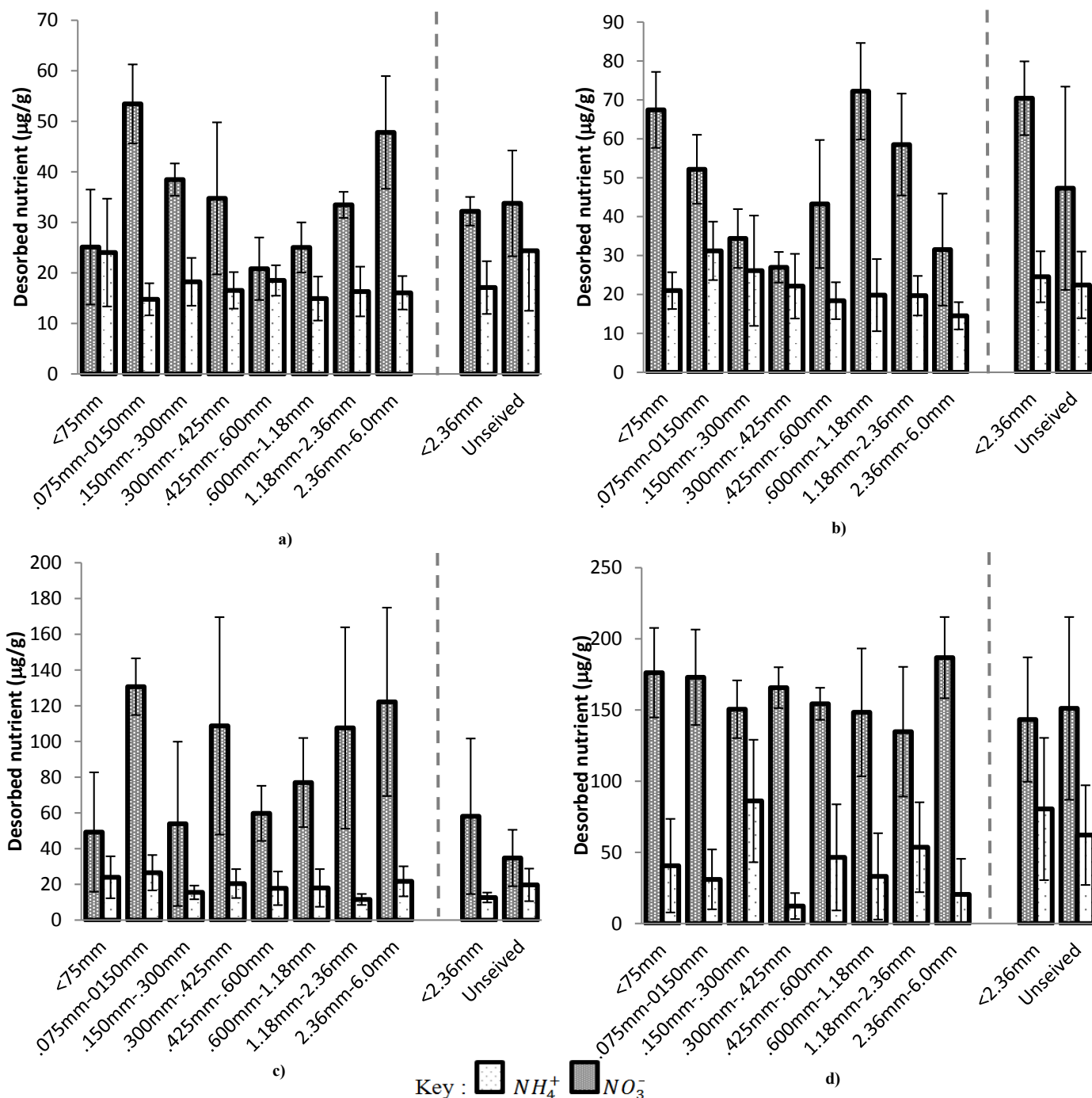
Figure 4.3: Mean (sd) of exchangeable NO₃⁻ and NH₄⁻ desorbed from a) soil 1 b) soil 2 c) soil 3 and d) soil 4 into deionised water.

The exchangeable NO_3^- and NH_4^+ in each fraction of the four soils ranged from 11.6 to 86.1 $\mu g/g$ NH_4^+ and 20.8 to 186.1 $\mu g/g$ NO_3^-. The exchangeable NO_3^- was consistently higher than exchangeable NH_4^+ in all four soil samples. Linear regression analysis found there was no significant trend between NO_3^- desorption and particle size in any of the soils ($p > 0.05$). NH_4^+ desorption had no significant relationship with particle size in soils 1,3, and 4 ($p > 0.05$) yet there was significant decreasing trend with increasing particle size in soil 2 ($p < 0.05$).

A two-factor ANOVA was conducted for both NO_3^- and NH_4^+, on the effect of soil type and fraction size on desorption. For NO_3^- there was a significant effect of soil sample ($p<0.05$),

fraction size ($p<0.0001$), and interaction between soil sample and fraction size ($p<0.02$). However for NH_4^+ the only significant effect was found for sample fraction size ($p<0.0001$) The exchangeable NO_3^- and NH_4^+ raw data can be found in Appendix H.

4.1.3 Correlations between the total and exchangeable NO_3^- and NH_4^+

4.1.3.1 Comparison between NH_4^+ and NO_3^-

The desorption of exchangeable NH_4^+ and NO_3^- was an order of magnitude smaller then the desorption that occurred under forced extraction. Up to 6.0% of the total NO_3^- and 0.75% of the total NH_4^+ was exchangeable nutrient. The percentage of exchangeable NO_3^- as a function of the total NO_3^- was consistantly than the percentage exchangeable NH_4^+ (Figure 4.4).
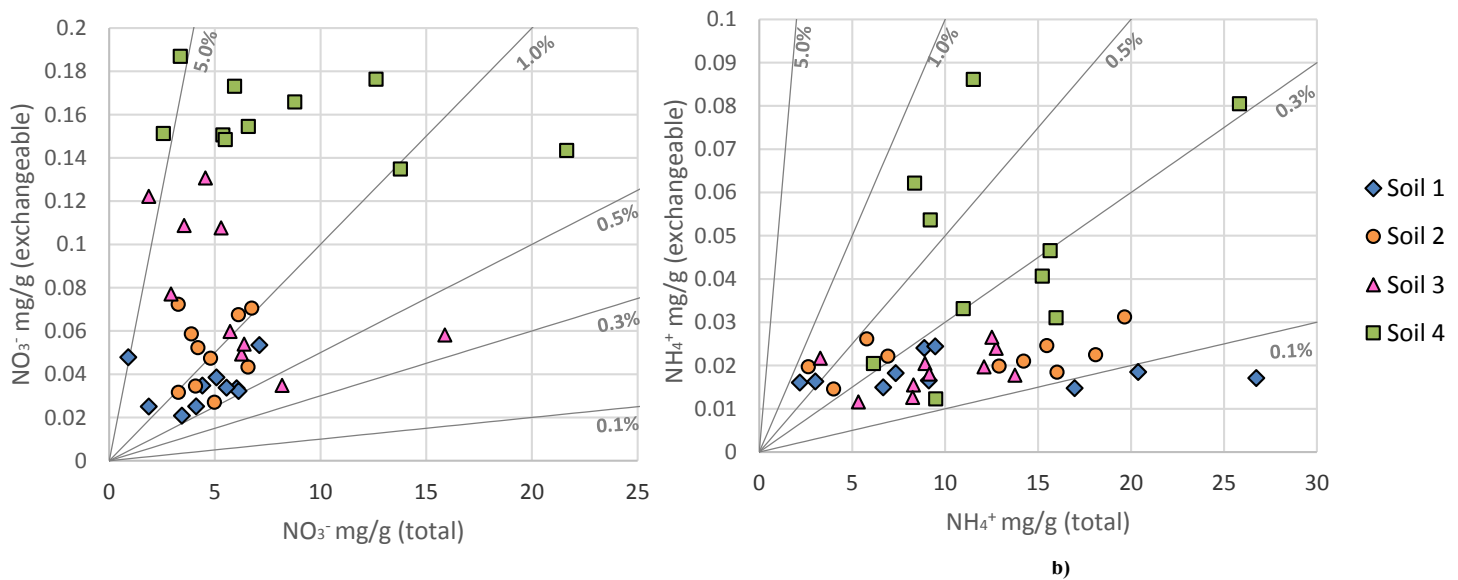
Figure 4.4: Relationship between total nutrient and exchangeable nutrient for a) NO_3^- and b) NH_4^+. The grey lines indicate the percentage nutrient desorbed. Note the majority of NO_3^- desorption was between 0.5-5.0% (the top wedge), whereas NH_4^+ desorption was between 0.1-0.3% (the second last wedge)

There was no correlation between the total NH_4^+ and exchangeable NH_4^+, or total NO_3^- and exchangeable NO_3^- for any of the soils ($|r|<0.8$, $p > 0.05$) (Table 4.3). However, we noticed that soil 4 was more likely to desorb a higher proportion of the available NO_3^- and NH_4^+ than the other 3 soils.

Table 4.3: Pearsons correlation coefficients between total NH_4^+/NO_3^- and exchangeable NH_4^+/NO_3^- (N = 10)

		NO_3^-	NH_4^+
Soil sample 1	Pearson r Correlation	-0.0201	0.0464
	Sig. (2-tailed) p value	0.9561	0.8986
Soil sample 2	Pearson r Correlation	0.3878	0.6085
	Sig. (2-tailed) p value	0.2682	0.0619
Soil sample 3	Pearson r Correlation	-0.4047	0.4130
	Sig. (2-tailed) p value	0.2460	0.2355
Soil sample 4	Pearson r Correlation	-0.3648	0.5197
	Sig. (2-tailed) p value	0.3000	0.1237

4.2 Time dependent experiments

4.2.1 Attainment of equilibrium

Time series of the NO_3^- and NH_4^+ concentration in solution were deemed to be in equilibrium when there were only small fluctuations in the system. Criteria for attainment equilibrium are described in Section 3.4.

The time series of NO_3^- and NH_4^+ for each soil for are seen in Figures 4.5 and 4.6 respectively. The red area highlights the portion considered to be in equilibrium. Note these are raw data and each plot shows the three replicates for one soil. The y axis scale also differs in each plot.
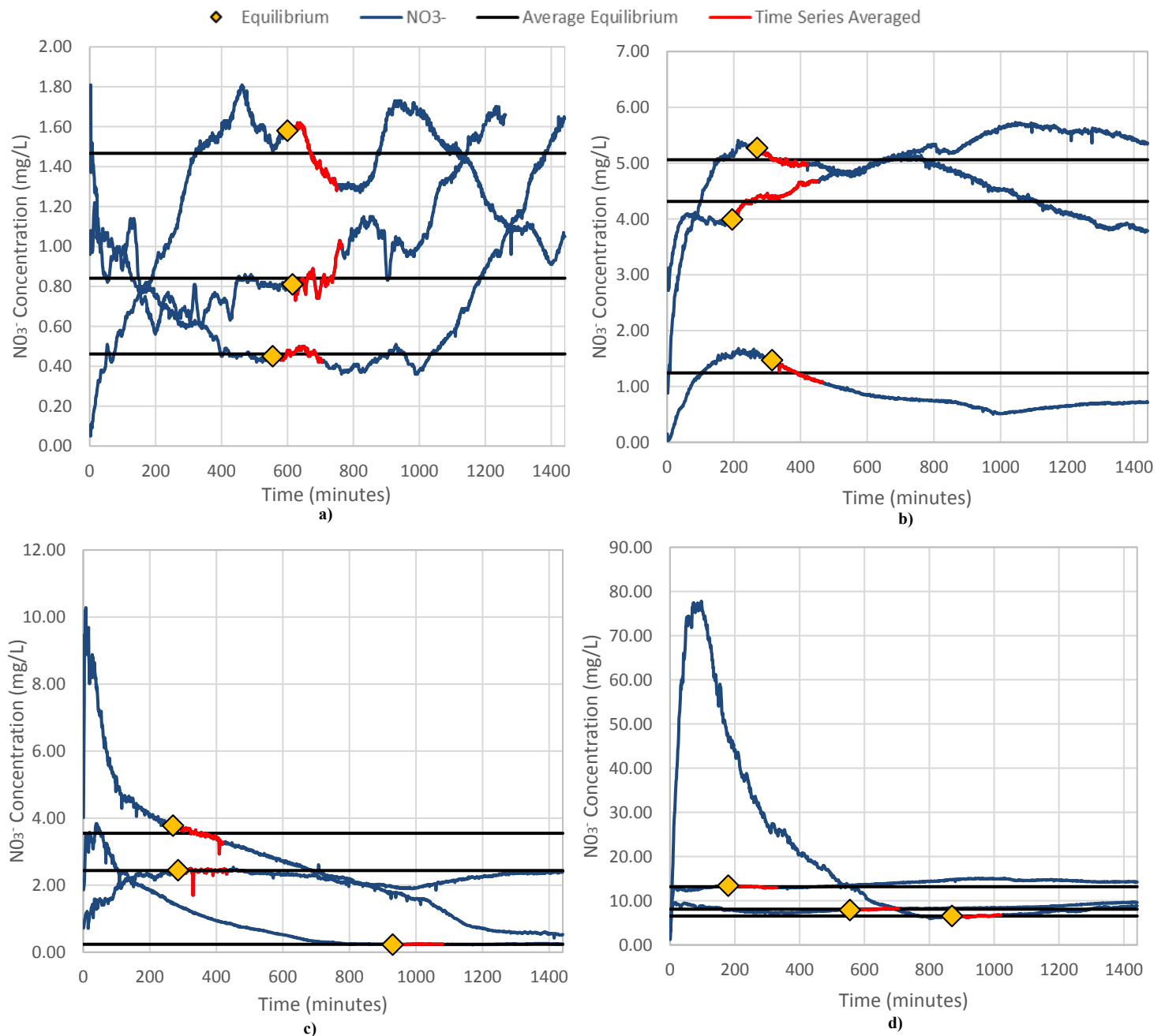
Figure 4.5: Exchangeable NO_3^- desorbed from 100g soil into 2L deionised water for a) soil 1 b) soil 2 c) soil 3 d) soil 4. Each plot shows the three replicates for that soil sample.
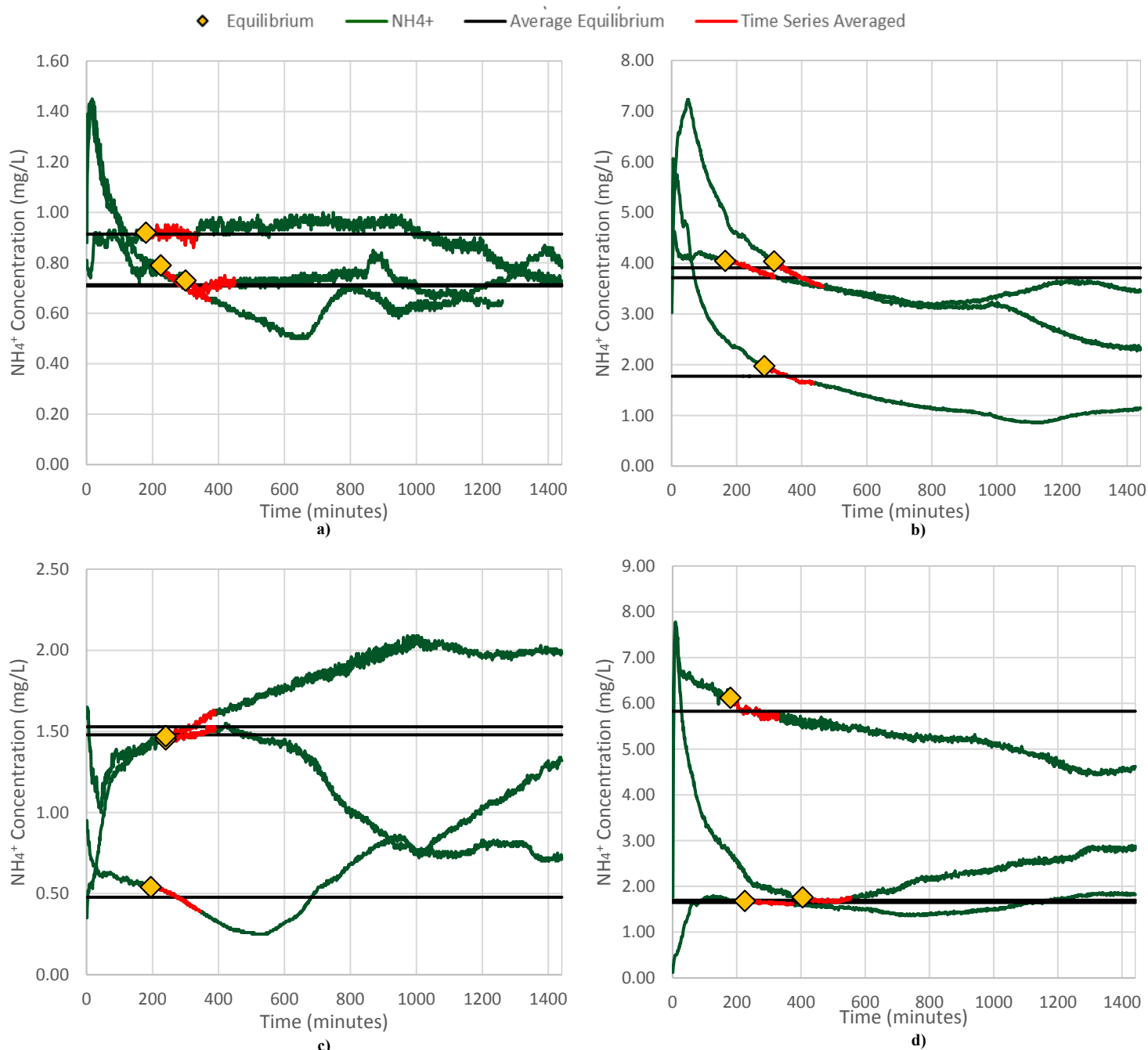
Figure 4.6: Exchangeable NH$_4^+$ - desorbed from 100g soil into 2L deionised water for a) soil 1 b) soil 2 c) soil 3 d) soil 4. Each plot shows the three replicates for that soil sample.

In 20 out of 24 cases there was a measurable concentration of NO$_3^-$/NH$_4^+$ at time=0 in aqueous solution. Replicate 3 of the NO$_3^-$ from soil 4 (Figure 4.5 d.) was excluded from further analysis as this time sequence reached a maximum concentration of 76mg/L (an order of magnitude larger than the other replicates) and was considered to be erroneous.

The mean (sd) equilibrium values of NH4$^+$ and NO3$^-$ concentration from 3 replicates for each of the four soil samples, and mean (sd) time taken to reach equilibrium since experiment setup are given in Table 4.4.

Table 4.4: Mean (sd) equilibrium concentration of NO3- and NH4+ desorbed from 100g of material into 2L of deionised water and mean (sd) time of equilibrium

	NO$_3^-$				NH$_4^+$			
	Equilibrium Value (mg/L). N = 450[1]		Time of first Equilibrium (hours) N = 3[2]		Equilibrium Value (mg/L) N = 450[1]		Time of first Equilibrium (hours) N = 3[2]	
	Mean	sd	Mean	sd	Mean	sd	Mean	sd
Soil 1	0.92	0.07	7.83	3.13	0.78	0.03	3.92	1.02
Soil 2	4.69	0.11	3.88	0.88	3.13	0.11	4.33	1.43
Soil 3	2.07	0.11	8.30	6.30	1.16	0.04	4.25	0.43
Soil 4	9.26	0.14	8.92	5.75	3.07	0.09	4.41	2.08

4.2.2 Comparison between four soils

4.2.2.1 Nitrate

Over a 20 hour period the desorption of NO$_3^-$ from the four soil samples increased in the order of soil 1< soil 3 < soil 2 < soil 4 (Figure 4.7). Soils 3 and 1 converged to a similar value over value over the 20 hour period; however, soil 3 had a greater mean desorption over the time sequence in its entirety. Soil sample 3 initially had higher desorption than soil sample 2, but after 60 minutes the time sequences crossed over, such that NO$_3^-$(AQ) soil 2 > soil 3. The highest variability across the four soils was seen in soil sample 4.
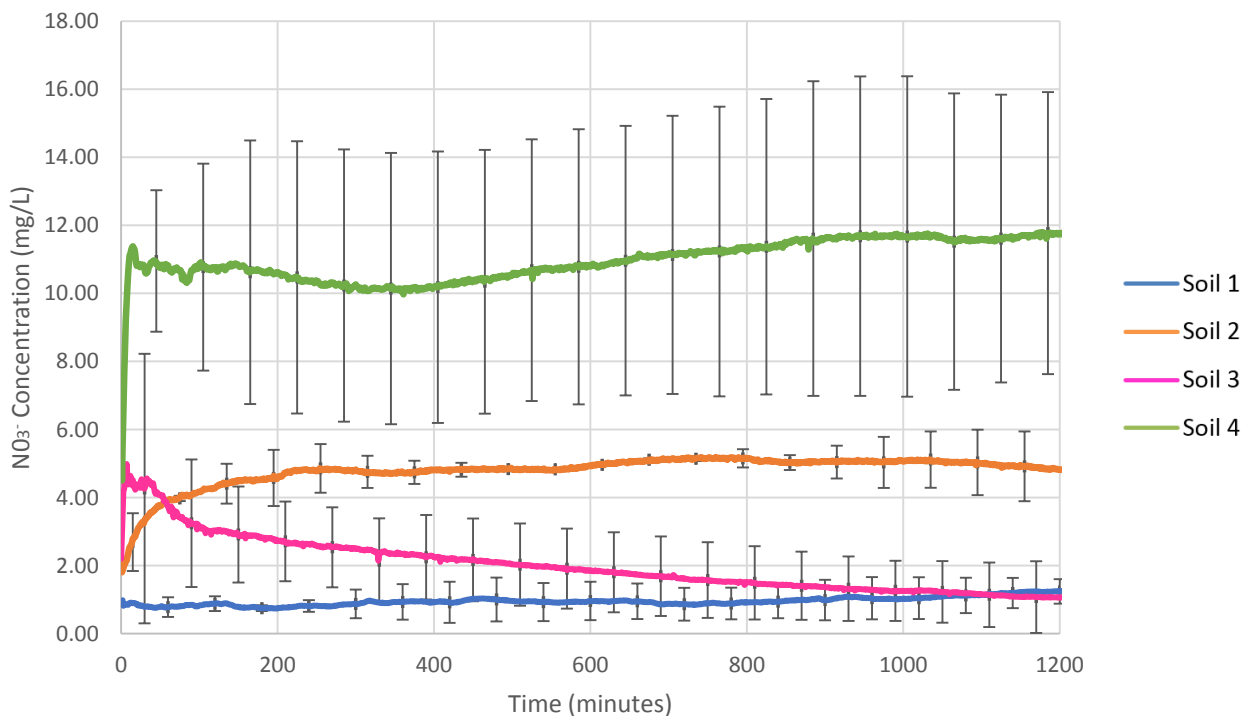
Figure 4.7: Mean (sd) concentration of NO3- desorbed from 100g of soil into 2L of deionised water over 20 hours. Each colour represents a different soil sample which is the average of three replicates

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[1] 3 replicates of 150 time series points at equilibrium (N= 3 x 150 = 450)
[2] 3 replicates of first time instance at which equilibrium is attained

4.2.2.2 Ammonium

The mass of NH_4^+ desorbed into aqueous solution was greatest in soil sample 2, followed by soil samples 4, 3 and 1 (Figure 4.8) Over the 20 hour period soils 2 and 4 displayed an exponential decay. Soil 2 had a peak value of 5.6 mg/L at t= 1 hour and soil 4 had a peak value of 5.3 at t=1/4 hour. Both converged to a value of 3mg/L ($\pm$ 0.2) over the 20 hour period. Conversely, soils 3 and 1 were relatively steady, with Soil 3 showing a slight increase, and soil 1 showing a slight decrease over time.
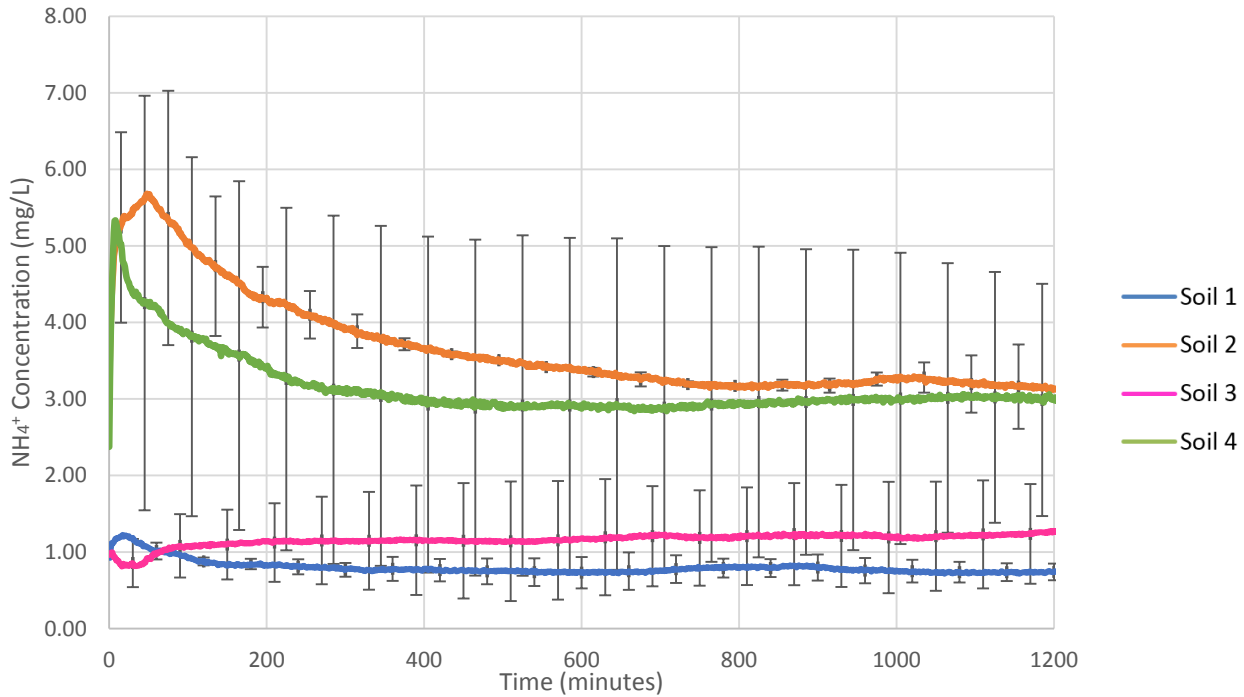
Figure 4.8: Mean (sd) concentration of NH_4^+ desorbed from 100g of soil into 2L of deionised water over 20 hours. Each colour represents a different soil sample which is the average of three replicates

4.2.3 Extraction of recoverable NO_3^- and NH_4^+

The NH_4^+ and NO_3^- remaining in the soils after the 24 hour soaking was extracted (Table 4.5)

Table 4.5: Mean (sd) of recoverable NO_3^- and NH_4^+ in the four soils following the 24 hour period where they were immersed in deionised water. % desorbed is taken as the mass exchangeable/total mass of NO_3^-/NH_4^+

	NO_3^-			NH_4^+		
	μ Desorbed (%)	μ Adsorbed (%)	σ (%)	μ Desorbed (%)	μ Adsorbed (%)	σ (%)
Soil 1	0.04%	99.96%	0.02%	0.75%	99.25%	0.06%
Soil 2	0.12%	99.88%	0.12%	0.97%	99.03%	0.32%
Soil 3	0.74%	99.26%	0.37%	0.54%	99.46%	0.08%
Soil 4	0.63%	99.37%	0.13%	0.20%	99.80%	0.08%

NH_4^+ was in the same range as the extracted results described in Section 4.1; however, the amount of NO_3^- showed a discrepancy with what was previously obtained. Raw data of the extraction can be found in Appendix I

28

4.2.4 Other water quality parameters.

The relationship between the concentration of NO_3^-/NH_4^+ in aqueous solution at equilibrium and other water quality parameters is seen in Figures 4.9 (NO_3^-) and 4.10 (NH_4^+).
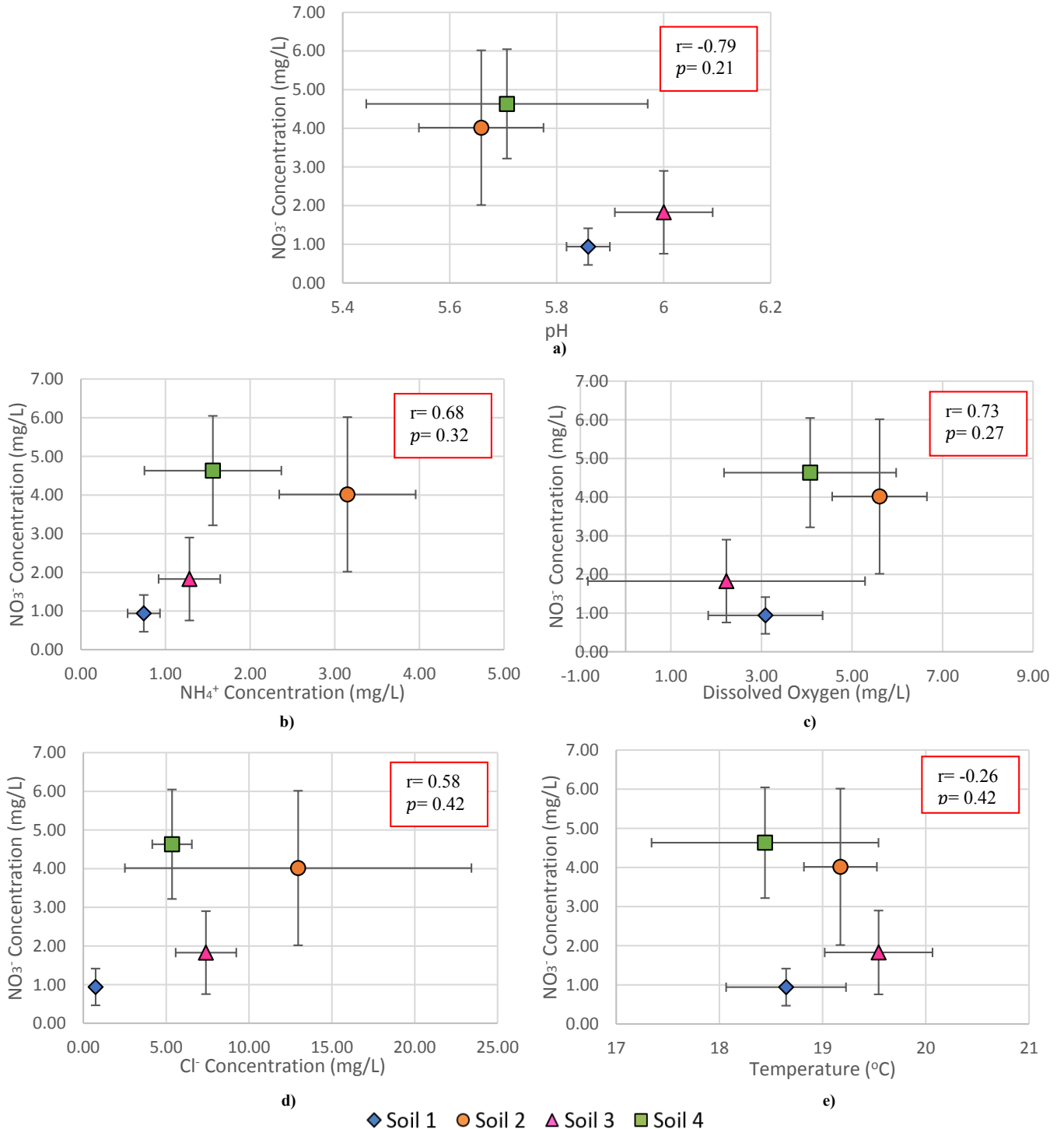
Figure 4.9: Pearsons correlation (r) and significance (p) between NO_3^- and a) pH b) NH_4^+ c) dissolved oxygen d) chloride ion and e) temperature (N=4). Each point on the graph is the mean (sd) of 450 replicates
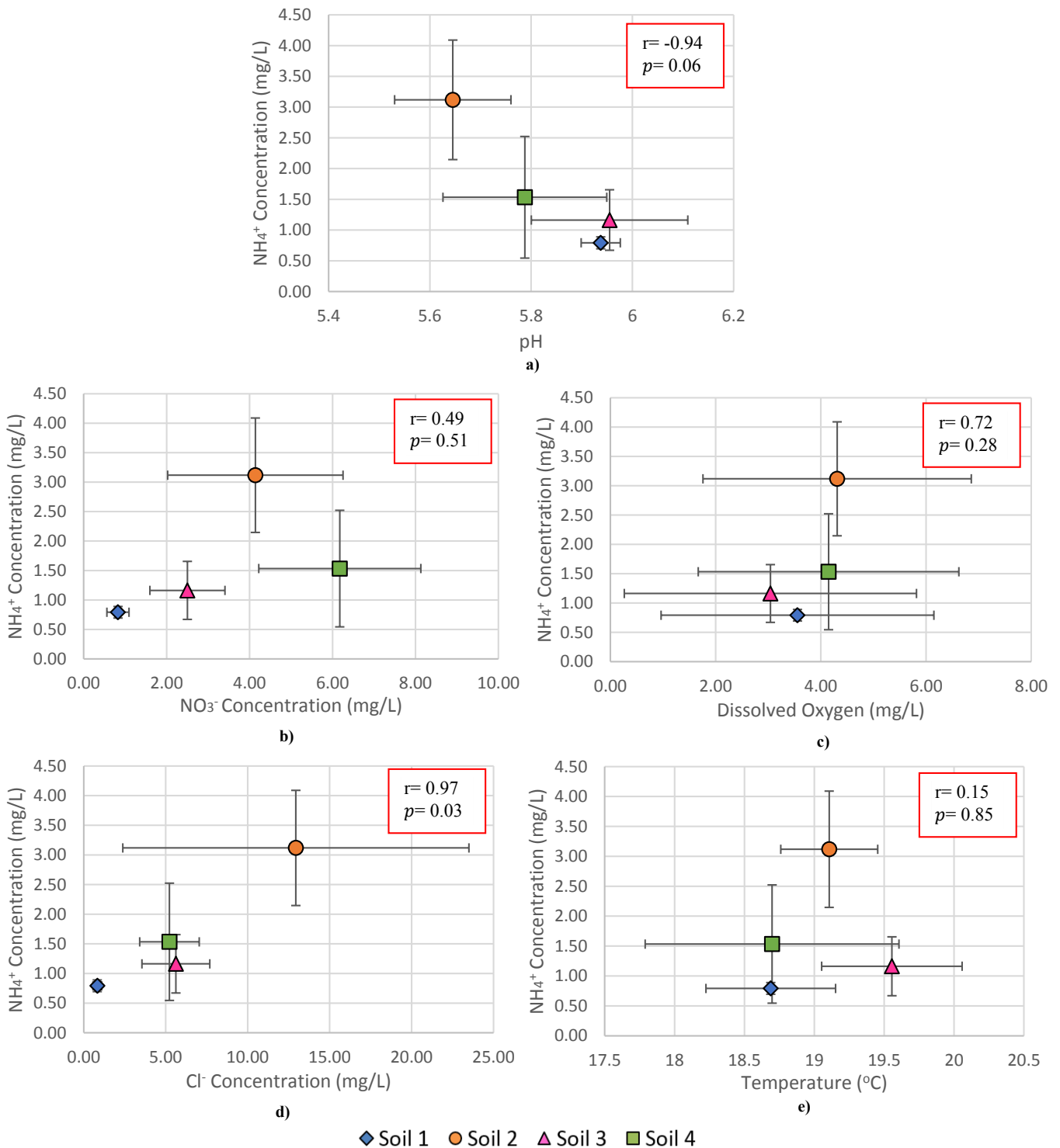
Figure 4.10: Pearsons correlation (r) and significance (p) between NH₄⁺ and a) pH b) NO₃⁻ c) dissolved oxygen d) chloride ion and e) temperature (N=4). Each point on the graph is the mean (sd) of 450 replicates

Although not reaching statistical significance (using a rule of thumb of $r>0.8$ (strong positive correlation) or $r<0.8$ (strong negative correlation)) for pearsons correlation; Figure 4.9 shows that at equilibrium NO_3^- is negatively associated with pH, and positively associated with NH_4^+ and dissolved oxygen.

Similarly, NH_4^+ was negatively associated with pH, and positively associated with NO_3^- (although not statistically significant). NH_4^+ did however, show a strong positive correlation with chloride ($r = 0.97$, $p < 0.05$) (Figure 4.10 d).

5   DISCUSSION

In this section the results obtained in Section 4 of this report are discussed. It is set out in the following 4 sub-sections:

Section 5.1 presents and interprets the results of the chemical extraction which enabled us to quantify the total NO_3^- and NH_4^+ within each of the four soil samples. Firstly, these results are discussed in relation to the existing literature. Secondly, differences between the four soil samples are explored. Finally the relationship between particle size and total NO_3^- or NH_4^+ is investigated.

Section 5.2 compares the exchangeable NO_3^- and NH_4^+ in the four soils and the 10 soil fractions

Section 5.3 explores correlations between the total and exchangeable NO_3^- and NH_4^+; firstly interpreting the differences in NH_4^+ and NO_3^-, and secondly, investigating the differences between the four samples.

Section 5.4 examines desorption trends over time. Firstly, the equilibrium of the system and time of initial desorption of both NO_3^- and NH_4^+ are commented on. Secondly, differences in the time dependent desorption of the four soils is explored. Thirdly the available NO_3^- and NH_4^+ remaining in the samples is discussed.

Sections 5.5 and 5.6 conclude with potential sources of error and areas for further research

5.1   Total NH_4^+ and NO_3^-

5.1.1   Overall results and comparison with existing literature

The chemical extraction experiments showed that the total available nutrient in each fraction of the four debris ranged from 0.90-15.88 mg (NO_3^-) and 1.42-26.73 mg (NH_4^+) per gram of soil. These results are consistent with the existing literature (see review, Section 2), which report the average adsorption capacity of sands, silts and clays are in the range of 5.03 ($\pm$ 11.236) mg/g for NO_3^-, and 33.45 ($\pm$ 14.61) mg/g for NH_4^+.

Whilst most of our experiments fall within this range, there is a wide range of Langmuir constants reported in the literature, as previously mentioned (Section 2). Furthermore the isotherm batch studies used to construct the Langmuir isotherm are indicative of the NH_4^+ and NO_3^- retention potential, but often overestimate field adsorption maxima (Richardson, 1985, Johansson Westholm, 2006, Vohla et al., 2011). For this reason, the obtained results should also be compared with Total Soil Nitrogen (TSN) quantities found in urban environments, which

typically range from 0.2mg/g to 32mg/g in peats (Bremner and Mulvaney, 1982, Wang and Alva, 2000, White and Reddy, 2001). Of this TSN, typically 90% is organic N and 10% is inorganic N (Schepers and Raun, 2008b, Bullock and Gregory, 2009).

Whilst there are large differences in the volume of NO_2^-, NO_3^-, and NH_4^+ found in urban soils, it must be highlighted that the collected samples were not merely 'soils' but a collection of materials found in urban debris. This debris was highly organic in nature, which complicates the adsorption process; as not only does organic matter (OM) have a high adsorption capacity, but OM can also adsorb to clay minerals and modify their surface reactivity (Kang, 2008). By comparison, the majority of literature to date has focused on adsorption to homogenous material of the mineral fraction, so it is difficult to make direct comparisons with the results of this thesis.

Furthermore the collected soils were taken from the upper 50 cm of surface material, and it is well documented that TSN is strongly associated with the accumulation of plant biomass which decreases drastically with depth (Sposito, 1989, Schepers and Raun, 2008b).

These factors may explain why the mass of NH_4^+ and NO_3^- in the debris used in these experiments is at the upper limit of the these nutrients found in typical urban soils.

5.1.2 Comparison of the total NH_4^+ and NO_3^- in the four soil samples

The total NO_3^- within the four samples decreased in the following order: soil sample 4 (the dry, freshly deposited organic roadside material), sample 3 (the moderately organic material collected from the creek bank), sample 1 (the saturated mineral material from the creek basement) and sample 2 (The partially saturated mineral material collected where the creek had evaporated). In comparison the total NH_4^+ content showed no significant difference between the four soil samples.

5.1.2.1 Total NO_3^- in the four samples of urban debris

Differences in the NO_3^- content between the four samples was generally consistent with the existing literature and theory(Maynard and Kalra, 1993).

Soil sample 4[§] which largely comprised of freshly accumulated leaf litter and organic material (Appendix C), had the greatest mass of NO_3^-. This was expected, as organic matter not only acts as a reservoir for N, but also as an energy source for autotrophic microorganisms. The process of nitrification is a result of the breakdown of organic matter by these microorganisms. It therefore follows that the samples whose particles were predominantly organic material

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[§] Soil sample 4 was the dry material collected from the road

would have a greater mass of NO_3^- than the samples comprised of inorganic minerals. In addition sample $4^§$ was almost dry, with a moisture content by mass weight of 8% (Appendix D); whereas soil samples 1^*, $2^†$ and $3^‡$ had moisture contents by mass weight of 100%, 76% and 15% respectively. It is likely that within soil sample 4 the lack of moisture limited the growth of microorganisms; whereas in the other three samples the warm moist conditions provided optimum conditions for bacteria to thrive and consume the inorganic N.

Soil samples 1^* and $2^†$ had a similar mass of NO_3^-. This was expected as both of these samples were predominantly of a mineral makeup and their in-situ locations at the creek basement were in close proximity to one another - approximately 2m apart. However, soil sample $3^‡$ (which contained a moderate amount of organic matter) unexpectedly had the lowest mass of NO_3^- amongst the four soils. This is possibly because this material was largely comprised of well-drained soil from the sloped bank of the creek, and was covered in a small amount of decomposing vegetation. As NO_3^- sharply decreased with depth, it is likely that the sample was very heterogeneous in NO_3^- content directly after collection. The upper layers of the sample were largely comprised of leaf litter/ organic material and would have had a large mass of NO_3; conversely, the bottom layers (down to depths of 50 cm) would have had a very low NO_3^- mass. Once this material was brought back to the laboratory and thoroughly mixed, the overall NO_3^- content throughout the homogenised sample was comparatively low.

5.1.2.2 NH_4^+ content in the four samples of urban debris

A priori we expected the NH_4^+ to be lowest in the mineral soil samples (1 and 2) and highest in the organic soil samples (3 and 4). However, there was no significant difference in the NH_4^+ content of the four samples ($p > 0.05$). This is possibly because soils 1 and 2 were collected from the stagnant oxygen depleted waters of the creek basement, and it is likely that the majority of the inorganic N in these samples was contained as NH_4^+. This is because the nitrification of NH_4^+ into NO_2^- and subsequently NO_3^- requires an oxygen source, however for ammonification this is less critical (Bartholomew, 1965). These samples also contained a slurry of mineral matter, animal waste and other pollutants; and a significant amount of ammoniacal N is contained in animal faecal matter (Masek et al., 2001). Furthermore the literature states that in saturated soils NH_4^+ is the most abundant form of inorganic N, with the opposite being true for non-saturated soils due to rapid biological oxidation of NH_4^+ to NO_3^-.

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§ Soil sample 4 was the dry material collected from the road
* Soil sample 1 was saturated material from the creek basement
† Soil sample 2 was the partially saturated material where the creek had begun to evaporate
‡ Soil sample 3 was damp material from the creek bank

However it is unknown why soil samples $3^{\ddagger}$ and $4^{\S}$, which had in-situ moisture contents by mass weight of 15% and 8% respectively (Appendix D); had larger volumes of NH_4^+ content than NO_3^-, as this disagrees with the statement above. It should be highlighted however, that whilst there is a consensus that nitrification is limited at moisture contents below 3% (Schjønning et al., 2011) the optimum moisture content for nitrification is heavily debated. In comparison, cases of ammonification have been reported to occur in in air dry conditions (Schepers and Raun, 2008a) which provides a potential explanation for the large NH_4^+ content in samples 3 and 4.

5.1.3   Comparisons between the total NO_3^- and NH_4^+ in the 8 particle sizes

A linear regression analysis using a statistical significance level of $p < 0.05$ found there was no significant relationship between particle size and extracted nutrient in 7 of the 8 cases (4 samples and 2 nutrients). This does not agree with scientific literature; which states that the clays and fine particles not only have a larger number of sorbing sites due to their large specific surface area; but clay minerals also have a high ionic exchange capacity due to the abundance of reactive groups on their surfaces (Section 2)(Maynard and Kalra, 1993, Sperry and Peirce, 1999). Inconsistencies with literature may have arisen because no physical abrasive techniques were used to grind particles down into finer fractions after sieving, despite that fact that many of the particles retained on sieves with larger apertures were in fact a flocculation of smaller particles. This would induce a bias into results as particles were considered to be of a coarser size fraction than they were in reality. As a consequence the large particles tested may have been highly porous with large surface areas and hence many sorbing sites.

Another possible explanation for the inconsistency was the large volume of organic material present in the samples, which has a high adsorption capacity and can be either macroscopic or microscopic. Hence organic matter would have been in larger quantities in some of the size fractions, causing large deviations in the obtained results.

The implications of these findings is that it is not necessarily the fine fraction of material that is responsible for NO_3^- and NH_4^+ nutrient loading. In fact, examining Figure 4.2, the cumulation of NO_3^- on Sample 2 is the most unfavourable of the 8 accumulation curves, as this sample carries more nutrient on the finest material fraction than any of the other samples. Therefore, taking this curve (as the worst case scenario) it can be seen that 50% of the nutrient is adsorbed to particles larger than 130µm. Thus, if particles larger than 130µm are removed through

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‡ Sample 3 was moderately organic material collected from the bank of the creek
§ Sample 4 was highly organic material collected from the road

filtration (such as with the SDU) this will reduce the volume of nutrient that would otherwise be polluting waters downstream by 50%.

5.2 Exchangeable NH_4^+ and NO_3^-

A significant difference in the exchangeable NO_3^- was found between the four soil samples ($p<0.05$), but no significant difference was found between the four soils for NH_4^+. NO_3^- decreased in the order of soil 4[§], soil 3[‡] soil 2[†] soil 1[*].

Reasons for soil 4 for having the largest mass of exchangeable NO_3^- could be because this soil sample was collected from the side of the road, where it was accumulating pollutants from car exhaust and other residential wastes. It is likely these pollutants were being dry deposited on the material, and were not becoming chemically adsorbed to the solid surface. Consequently with the addition of aqueous solution, these chemicals had no affiliation to the solid particles and were instantaneously released from the material. Similar arguments can be explained in the differences between the other soil samples, as the exchangeable nutrient decreased in the order of in-situ wetness which suggests evaporation of the aqueous phase may have led to dry deposition of these chemicals.

In comparison, no significant difference in the exchangeable NH_4^+ could be a result of the material having a large number of cationic exchange sites, and a strong affiliation for NH_4^+ molecules. Subsequently, it may have been possible for NH_4^+ to form a strong adsorption interaction with the adsorbent material before it was immersed in solution.

Furthermore, no significant linear relationship was found between particle size and NO_3^- or NH_4^+ ($p>0.05$). A priori we expected the fractioned material would have greater desorption with increasing particle size. The rational for this is that the finer fractions (both silts and clays) have a strong ion exchange capacity and are better able to retain adsorbed molecules (Sperry and Peirce, 1999, Harmand et al., 2010). Despite this, the absence of a linear relationship between desorption and particle sizes is not surprising due to the large presence of organic matter in samples, and agglomerations of fine particles within larger size fractions. These two factors would have strongly influenced the obtained results, as described in Section 5.1.3. Implications of these findings is that is not necessarily the large particles which contribute to

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[§] Soil sample 4 was highly organic and collected from the side of the road
[‡] Soil sample 3 was moderately organic and collected from the creek bank
[†] Soil sample 2 was predominantly made up of minerals and was collected from the edge of the creek
[*] Soil sample 1 was predominantly made up of minerals and was collected from the creek basement

the dissolution of NO_3^-/NH_4^+ and the facilitate nutrification, but the smaller particles also play a role.

5.3 Correlations between the total and exchangeable NO_3^- and NH_4^+

5.3.1 Comparison between NO_3^- and NH_4^+

There was a larger volume of NO_3^- desorbed into deionised water than NH_4^+ in all four soil samples; despite the fact that NH_4^+ made up the majority of total N in the samples. Up to 6.0% of the available NO_3^- was desorbed, but only 0.75% of the available NH_4^+ was desorbed. Reasons for the differences in these molecules could be due to preference of the adsorbent material for NH_4^+ molecules over NO_3^- molecules. This reflects the underlying theory that both the adsorbent and adsorbate interactions influence adsorption reactions (Rouquerol et al., 1999). In particular, certain clay minerals (such as Montmorillonite and Illite) have the ability to hold NH_4^+ using coulomb interactions at cationic exchange sites (Sperry and Peirce, 1999). In comparison, NO_3^- is less frequently held at the surfaces of clay minerals, except in the case where there are positively charged sites on the mineral surface.

However, whilst many clay minerals have the ability to adsorb cationic molecules, when NH_4^+ is compared to other cations such as Mg^{2+} and Ca^{2+}, the preference of the sorbent for particular sorbates is dictated by the ionic valency and degree of ionic hydration. In low ionic concentrations, divalent ions are preferentially adsorbed over monovalent ions; whereas in highly concentrated ionic solutions the opposite holds. Copcia et al. (2010) found that clays were only able to efficiently adsorb ammonium ions when the ammonium concentration in aqueous solution was lower than 100mg/L, and above this concentration, adsorption of NH_4^+ was significantly curbed. In these experiments the aqueous solution and volume of soil was kept constant (using a ratio of 100ml water to 10g soil); further investigation is required into the relationship between PO_4^{3-}, NH_4^+ and NO_3^- desorption using a range of water to soil ratios, as this would significantly change the aqueous concentration of these chemicals and could affect the desorption.

5.3.2 Correlation between exchangeable and total nutrient

No strong correlation was found between the chemically extracted nutrient and the naturally desorbed nutrient for any of the soil samples.

However, as mentioned in Section 5.3.1 only a small proportion of the total inorganic nutrient desorbed into deionised water (6.0% of NO_3^- and < 0.75% of NH_4^+). This was true for all four samples, and presents as a key finding, as it indicates that the majority of these nutrients are

attached to the solid fraction as opposed to dissolved in the aqueous phase. The implication of this is that by removing particles from stormwater, over 94% of the NH_4^+ and NO_3^- would also be removed.

Despite this finding, it should be noted that desorption proceeds in the direction of equilibrium; so in a rain event, the dilution of the NH_4^+ and NO_3^- in aqueous solution would encourage further desorption. In comparison if the concentration of these molecules in solution is increased (for example by excess N travelling to waterways in land runoff) the equilibrium reaction would proceed in the opposite direction.

5.4   Time dependent experiments

5.4.1   Attainment of equilibrium and time of first desorption

There was no consistent trend in the point at which the four samples reached equilibrium. This is possibly a result of how equilibrium was defined in the methodology. Furthermore over the 20 hours fluctuations in the system were relatively small, with amplitude changes in concentration not exceeding 2mg/L (Figures 4.5 and 4.6). Hence some of the fluctuations could be due to the accuracy in WQM measurement or convection of these molecules in solution causing unequal dispersion.

This reflects the chemical equilibrium theory, which acknowledges that a completely steady state will never be ascertained, as NO_3^- and NH_4^+ are very reactive compounds that are continuously undergoing a wide variety of transformations (Stevenson and Cole, 1999).

Furthermore it should be highlighted that in 20 of the 24 time sequences there was a measurable concentration of NO_3^- and NH_4^+ in solution at time = 0. This suggests that desorption of the NO_3^- and NH_4^+ from these samples was very rapid, as the deionised water contained no dissolved molecules prior to being mixed with the soil sample. The implications of this is that the timing of filtration is not a critical variable in reducing the amount of dissolved NO_3^- and NH_4^+. However there are other potential issues associated with delayed filtration and will be discussed further below.

5.4.2   Comparison of the four soils

The differences in the four soil samples reinforces the findings of the desorption experiments which determined the exchangeable NO_3^- and NH_4^+ (Section 5.2). The standard deviation of

the four soil samples increased in the order of sample $2^{\dagger}$ < sample 1^{*} < sample $3^{\ddagger}$ < sample $4^{\S}$. This variability is likely to be a direct reflection of the amount of organic matter present in samples, as organic matter has a very high adsorption capacity and can cause spurious results.

Soil sample 1^{*} (which was collected from the bottom of the creek) was fairly stable over time. This is most likely because only a small volume of NO_3^- and NH_4^+ were released into solution, with maximum measured concentrations of 1.8 mg/L and 1.42 mg/L respectively. Because the desorbed nutrient was within a small range, it appeared fairly stable over time when compared to the other time traces.

Soil sample $2^{\dagger}$ also showed little deviation, and the same reasoning can be used in the NH_4^+ time trace as was used for Sample 1. However, a comparatively large NO_3^- concentration was measured in aqueous solution with only small deviation. This is most likely the result of one of the replicated being excluded from the mean calculation as it appeared to be erroneous (Figure 4.7 b.).

Soil samples $3^{\ddagger}$ and $4^{\S}$ on the other hand showed wide variability amongst replicates. This is likely a result of the large volume of organic matter in these samples which complicates the adsorption process as previously mentioned (Section 5.1.1).

5.4.3 Changes in NH_4^+ and NO_3^- concentration over time

In some cases, the aqueous concentration of NO_3^- and NH_4^+ declined over time, whereas in other cases there was an increase over time.

Reasons for a decreasing trend could be due to the consumption of these nutrients by microorganisms and bacteria. Conversely, an increasing concentration could arise from increased desorption from the sediments, as well as NO_3^- and NH_4^+ being converted from other forms (predominantly though nitrification and ammonification).

It should also be highlighted that many of the samples (particularly Samples 2 and 3) contained a lot of humic acid (Appendix C). Humic substances have been known to react with organic matter and or organo-clay complexes; which defend inorganic N from consumption by microorganisms, and hence a declining trend due to biological consumption is less likely.

[†] Soil sample 2 was collected from the edge of the creek and predominantly mineral makeup
[*] Soil sample 1 was collected from the creek basement and predominantly mineral makeup
[‡] Soil sample 3 was the damp material from the creek bank with moderate organic mater
[§] Soil sample 4 was the highly organic dry material collected from the road
[*] Soil sample 1 was collected from the creek basement and predominantly mineral makeup
[†] Soil sample 2 was collected from the creek edge and predominantly mineral makeup
[‡] Soil sample 3 was collected from the creek bank
[§] Soil sample 4 was collected from the edge of the road

The NH_4^+ time traces demonstrated a decline more often than the NO_3^- time traces. Reasons for this could be that NH_4^+ has two pathways by which it can change forms and exit the system, either through nitrification into NO_3^-, or through volatisation into NH_3 gas. Conversely NO_3^- only has one pathway by which it can exit the system - through immobilisation where it is reconverted into NH_4^+. In the natural environment NO_3^- can be taken up by plants, however this was not possible in the experimental setup. Secondly, these molecules also may form chemical bonds with other molecules in the solution leading to a decline in the measured concentration NH_4^+ is much more reactive than NO_3^-, and is more likely to form bonds with other molecules (for example NH_4^+ bonded to Cl^- and forms NH_4Cl).

Because there was no consistent increasing or decreasing trend over time, together with the fact that the desorption of nutrient was very rapid (as mentioned above) it is difficult to ascertain whether early removal of debris from stormwater systems is critical in minimising the available NO_3^- and NH_4^+ that would otherwise be desorbed into solution and travel to water bodies downstream.

However, as mentioned in Section 5.3; with a fresh influx of rainwater dilution of the aqueous solution will lead to more desorption as the system re-equilibrates. Others have also noted that fixed NH_4^+ may be slowly desorbed from clay minerals if the NH_4^+ already in solution is being consumed by other reactions (Sowden et al., 1978, Schepers and Raun, 2008b) This suggests that early removal of particulate matter could be beneficial for reasons other than the rate at which desorption occurs; because if the material is left immersed in solution there is the potential for further desorption if the environmental conditions change.

5.4.4 Extraction of recoverable NH_4^+ and NO_3^-

The extracted NH_4^+ was in the range of the extraction performed on the fractioned material (Section 4.1.1). This reaffirms the validity of previously obtained results, and implies that the majority of the NO_3^- and NH_4^+ remained adsorbed to the sediment over the 24 hour soaking period. Whilst in this case the % desorbed decreased in the order of Sample 2[†] < Sample 1[*] < Sample 3[‡] < Sample 4[§] (opposite to the previous extraction), these results should not be misinterpreted as only three replicates were conducted for each, in comparison to the three replicates on the 10 fractions in the previous extraction.

[†] Soil sample 2 was predominantly mineral material material collected from the edge of the creek
[*] Soil sample 1 was predominantly mineral material collected from the creek basement
[‡] Soil sample 3 was moderately organic material collected form the creek bank
[§] Soil sample 4 was highly organic material collected from the road

NO_3^- was considerably out of the range previously measured. However it is likely that this is a result of erroneous readings by the WQM, as suggested by the large standard deviations. Furthermore, the WQM was having difficulties with calibration on that day so it is possible that there was a crystallised NO_3^- molecule on the electrode which would cause measurement errors.

5.4.5 Correlation to other water quality parameters

As part of this study, NO_3^- and NH_4^+ were correlated to both one another, and the other five parameters measured by the WQM (pH, dissolved oxygen, Cl^- ion and temperature) during equilibrium. These water quality parameters differ in their nature and how they affected NO_3^- and NH_4^+ desorption.

pH is a water parameter which gives a measure of the H^+ in solution and can be used to assess environmental quality. For both NH_4^+ and NO_3^-, high desorption was associated with high pH, and low desorption was associated with low pH. The strong influence of pH on desorption has been extensively investigated (Sato and Comerford, 2005, Zhang et al., 2005, Bhatnagar and Sillanpää, 2011). In particular, many soils have the ability to exchange NH_4^+ with H^+ molecules in solution (Copcia et al., 2010). Therefore an increase in aqueous NH_4^+ is often associated with a decrease in the aqueous concentration of H^+, which agrees with our experimental findings. There are also secondary effects of this reaction on the desorption of NO_3^-. As adsorbed H^+ ions are exchanged with NH_4^+ in solution, the aqueous solution becomes positively charged which in turn encourages the desorption of NO_3^- (Copcia et al., 2010). This agrees with our experimental findings, as low pH was associated with a large dissolved concentration of NO_3^-, whereas high pH was associated with low dissolved concentration of NO_3^-. The relationship between pH and the concentration of NH_4^+ in solution exhibited a stronger negative correlation ($r = -0.94$) than pH and NO_3^- concentration ($r = -0.79$). This was expected because the effect of pH on NH_4^+ desorption is primary, whereas the effect of pH on NO_3^- desorption is secondary.

NO_3^- and NH_4^+ were also correlated against each other and found a positive relationship. These results contradict the previous hypothesis that the material was preferentially adsorbing NH_4^+ over NO_3^- (refer to Section 5.4). If this were the case, they would be negatively correlated to one another. It is likely that these results are a secondary effect of the pH, as when pH was low both NO_3^- and NH_4^+ concentration were low, whereas when pH was high both NO_3^- and NH_4^+ concentration was high.

Dissolved oxygen showed a positive correlation with NH_4^+. This was expected, as the nitrification of NH_4^+ into NO_2^- and subsequently NO_3^- by bacteria will reduce the concentration of dissolved oxygen. However, NO_3^- also showed a positive correlation with dissolved oxygen,

which is inconsistent with scientific theory, as the oxidation of NO_3^- should reduce the concentration of dissolved oxygen using the same logic as above. Reasons for this discrepancy could be a result of other processes affecting N cycle, such as the consumption of NO_3^- during oxidation of organic carbon by denitrifies. This would lead to a decrease in both NO_3^- and DO.

Temperature is a thermodynamic parameter, and showed no correlation to the exchangeable NH_4^+ or NO_3^-. However, the temperature was not manipulated and remained within a small range about the average (±1.5 ^{o}C). This increases the validity of the experimental procedures and suggests that erroneous results were unlikely to be induced by temperature variations between replicates.

From a stormwater management perspective, the implication of these findings is that by manipulating some of these variables, a greater mass of the NO_3^- and NH_4^+ could remain adsorbed to particles. For example, it would be beneficial to have an alkaline soil over an acidic soil. However in these experiments the water quality parameters mentioned were not controlled, and further investigation into the effect varying these parameters has on desorption is required.

5.5   Potential sources of error

Several sources of error were present in the experimental procedure which may have impacted the accuracy of obtained results.

Firstly, no abrasive techniques were used to grind particles down into finer fractions after sieving, and it is likely that many of the larger particles were in fact a flocculation of smaller particles. This would introduce bias into the experiments comparing the different size fractions, as it is likely some particles in the larger size fractions would have been made up of many fine particles with large surfaces areas and hence many adsorption sites.

Secondly, the WQM had difficulty calibrating before the recoverable NH_4^+ and NO_3^- was extracted from the debris used in the time dependent experiments. The total NH_4^+ and NO_3^- measured in these debris were significantly larger than the total NH_4^+ and NO_3^- measured in the initial extraction experiments. This suggests there may have been a crystallised NO_3^- molecule on the sensor which would contribute to measurement error.

Thirdly, the WQM terminal had an unexpectedly short battery life and produced erroneous readings if it was unintentionally left on during the 24 hour experiments. For example, soil 4 replicate 3 in Figure 4.5 d reached a maximum concentration of 76mg/L, however the terminal was left on overnight.

Finally the procedure used to extract NH_4^+ and NO_3^- was adapted from Sparks (1996) and we did not have access to a soil shaker or centrifuge as outlined in this method. Furthermore these procedures were developed for colorimetric methods of measuring NH_4^+ and NO_3^- and it is possible the WQM was sensitive to other solutes in the extracting solution leading to overestimation of NH_4^+ and NO_3^- concentration.

5.6 Further research

Further investigation should be conducted into other variables that can influence the desorption of NH_4^+ and NO_3^-. This could include (but not be limited to) temperature variations, dissolved oxygen, presence of other dissolved molecules, pH, dilution processes or increasing the soil to water ratio (thus increasing concentration of dissolved NH_4^+ and NO_3). Water quality parameters that showed a correlation to NH_4^+ and NO_3^- (such as pH) in the time dependent experiments should be a focus.

This is relevant from a stormwater management perspective if certain environmental conditions affecting water quality may reduce the exchangeable NH_4^+ and NO_3^-, and hence be more favourable for minimising nutrient exports to urban waterways.

Finally the effect of water velocity on desorption should be investigated using the SDU prototype, as the experiments described in these experiments overly simplify the processes which occur in stormwater in nature.

6 CONCLUSION

This thesis successfully quantified the proportion of NO_3^- NH_4^+ and PO_4^{3-} that remain adsorbed to particles in a stormwater system, and the proportion that is desorbed into aqueous solution.

This was achieved by simulating the process of desorption in a laboratory environment using a beaker and soil solution arrangement. Part 1 of this thesis (written by Jamie Wall) focused on inorganic PO_4^{3-}, and this part of the thesis (Part 2) focused on inorganic NH_4^+ and NO_3^-

Four key findings (and subsequent implications) which arose from this study were:

1) **At least 99% of NH_4^+ and 94% of NO_3^- remained adsorbed to the sediment when immersed in water.**

This suggests that the mechanism of NO_3^- and NH_4^+ transport in a stormwater system is adsorption to solid particles. This contradicts the previous paradigm that states that N is transported as a dissolved substance in aqueous solution.

The implications of this finding is that the removal of particulate matter is crucial in reducing the inorganic N that travels downstream and would otherwise be available for uptake by aquatic flora and microorganisms.

2) **It is not necessarily the very fine fraction of material that carries the majority of NH_4^+ and NO_3^-.**

No relationship was found between particle size and available NH_4^+ and NO_3^-. Furthermore, when the cumulative NH_4^+ and NO_3^- over all particles sizes within each soil was determined, it was found that 50% of the available nutrient could be taken out of the system by removing particles larger than 130μm in size. The implication of this is that a stormwater system doesn't necessarily need to have the capacity to filter very fine particles to reduce the NH_4^+ or NO_3^- which are transported to waterways downstream.

3) **Freshly deposited, dry material contains the greatest amount of total NH_4^+ and NO_3^-, and a larger percentage of this is exchangeable than any of the other debris tested.**

This suggests that dry, roadside materials that have never been wetted are the critical debris which should be prevented from entering the urban stormwater system in order to reduce NH_4^+ and NO_3^- inputs to receiving waterways.

4) The process of NH_4^+ and NO_3^- desorption begins as soon as the sediment is immersed in water.

In 20 of the 32 time traces, an instantaneous measurement of the NH_4^+/NO_3^- was recorded in solution. The implication of this is that to ensure complete retention of NH_4^+ and NO_3^- by solid particles, wetting of urban debris should be completely avoided. In addition, there was no consistent increasing or decreasing trend in desorption over time, which suggests the timing of removal of debris from stormwater is not a critical factor in reducing the amount of dissolved nutrient. Further investigation into other variables which may affect the N desorption over time (for example temperature or dilution of the aqueous phase) is required.

6.1 Final remarks

The results of this thesis suggest that eutrophication of urban waterways can be reduced (if not prevented) by the removal of urban debris and particulate matter from stormwater. This could be achieved using the Stormwater Decontamination Unit; a stormwater device that is able to filter particles from stormwater (preventing them from travelling into urban waterways), and can be monitored with telemetry and a service regime, leaving water as a safe and healthy resource for flora and fauna.

The results have the potential to inform current stormwater management practises, and find relevance not only to urban developers and policy makers, but the wider scientific community.

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APPENDIX A – LANGMUIR CONSTANTS SURVEYED FROM LITERATURE

Appendix 1: Langmuir binding energy constant (b) and monolayer adsorption capacity (Q) stated in literature for adsorption of ionic species of N and P on clays, silts and sands

<table>
<tr><td>Legend:</td></tr>
<tr><td></td><td>Sand</td></tr>
<tr><td></td><td>Silt</td></tr>
<tr><td></td><td>Clay</td></tr>
<tr><td></td><td>Excluded</td></tr>
</table>

Unified Soil Classification System (USCS)	
sand	<2mm
silt	<63um
clay	<2um

United States Department of Agriculture textural soil triangle

IONIC N							
Particle size (sand silt clay)	Equilibrium adsorbate Concentration b L/g	Maximum adsorbant capacity Q (mg/g)	R^2	Type soil generalised (sorbent)	Type soil stated (sorbent)	sorbate	reference
	6.37	34.48	0.98	Clay	Ri - raw clay	ammonical N	Copcia, V., Hristodor, C., Luchian, C., Bilba, N. & Sandu, I. 2010
	6.87	13.18	1.00	Clay	Ci - natural clay	ammonical N	
	5.24	47.69	0.98	Clay	Rl - Na clay	ammonical N	
	6.75	38.46	1.00	Clay	Cl - Na clay	ammonical N	
	0.0435	0.423	0.28	gravel	gravel	ammonia N	Song, Y. & Liu, H. 2013
	0.4288	0.034	0.17	sand	sand	ammonia N	
	0.4360	0.184	0.46	zeolite	zeolite	ammonia N	
	1.40	42.54	0.98	Clay	Montmorillonite	Nitrate	Cao, Y., Wei, X., Cai, P., Huang, Q., Rong, X., & Liang, W. 2011.
	51.2	2.48	0.98	Clay	Kaolinite	Nitrate	
	137	4.30	0.99	Clay	Geothite	Nitrate	
	0.161	5.855	0.99	Sand	Sand	Nitrate	Selvaraju, N., & Pushpavanam, S. 2009
	0.146	4.225	0.99	Sand	Sand	Nitrate	
	0.073	0.140	0.90	sand	sand	Nitrate	Kinjo, T. & Pratt, P. 1971.
	0.092	0.450	0.89	sand	sand	Nitrate	
	0.121	0.340	0.93	silt loam	silty sand	Nitrate	
	0.169	1.717	0.74	silt loam	HWA	Nitrate	Tani, M., Okuten, T., Koike, M., Kuramochi, K. & Kondo, R. 2004.
	0.285	3.949	0.97	sandy loam	HPA	Nitrate	
	0.240	4.935	0.93	sandy loam	HPA	Nitrate	
	0.356	3.274	0.97	sandy loam	HPA	Nitrate	
	0.203	2.740	0.88	sandy loam	HPA	Nitrate	
	0.147	3.162	0.95	loam	LHA	Nitrate	
	0.627	3.621	0.99	sandy loam	LHA	Nitrate	
	0.497	4.148	0.99	loam	LHA	Nitrate	
	0.597	3.509	0.99	sandy loam	LHA	Nitrate	
	239	38.160	0.68	Clay	Sepiolite activated by HCL	Nitrate	Ozturk, N., Bektas, Ennil, T., 2004
	1059	94.49	1.00	Clay	Activated red mud	Nitrate	Cengeloglu Y, Tor A, Ersoz M, Arslan G, 2006
	27.0	29.99	0.95	Clay	original red mud	Nitrate	
	0.270	1.09	0.80	Silty Clay	Akaka silty clay	Nitrate	Singh, B. R. & Kanehiro, Y. 1969
	0.232	0.89	0.86	Silty Clay	kaolinitic Wahiawa silty clay	Nitrate	
	0.420	0.73	0.88	Silty Clay	Akaka silty clay	Nitrate	
	0.556	0.57	0.97	Silty Clay	kaolinitic Wahiawa silty clay	Nitrate	
	0.203	1.524	0.53	sand	sand (98.2%) silt (0.36%) clay (1.44%)	Nitrate	Akosman, C. & Özdemir, T. 2010.
	0.183	1.372	0.54	sand	sand (98.2%) silt (0.36%) clay (1.44%)	Nitrate	
	0.138	1.035	0.57	sand	sand (98.2%) silt (0.36%) clay (1.44%)	Nitrate	
	0.110	0.823	0.53	sand	sand (98.2%) silt (0.36%) clay (1.44%)	Nitrate	
	0.206	1.544	0.66	loam	sand (52.6%) silt(23.9%) clay (23.5%)	Nitrate	
	0.202	1.512	0.76	loam	sand (52.6%) silt(23.9%) clay (23.5%)	Nitrate	
	0.154	1.157	0.67	loam	sand (52.6%) silt(23.9%) clay (23.5%)	Nitrate	
	0.126	0.946	0.75	loam	sand (52.6%) silt(23.9%) clay (23.5%)	Nitrate	
	0.189	1.417	0.52	Clay	and (8.48%) silt(16.52%) clay (75.0%)	Nitrate	
	0.286	2.148	0.58	Clay	and (8.48%) silt(16.52%) clay (75.0%)	Nitrate	
	0.195	1.460	0.66	Clay	and (8.48%) silt(16.52%) clay (75.0%)	Nitrate	
	0.189	1.417	0.70	Clay	and (8.48%) silt(16.52%) clay (75.0%)	Nitrate	

IONIC N

Particle size (sand silt clay)	Equilibrium adsorbate Concentration b L/g	Maximum adsorbant capacity Q (mg/g)	R^2	Type soil generalised (sorbent)	Type soil stated (sorbent)	sorbate	reference
	N/A	0.933	N/A	Clay	Manly, Clay (76%)	Nitrate	
	N/A	0.773	N/A	Clay	Ormiston, Clay (64%)	Nitrate	
	N/A	0.746	N/A	Clay	Beechmont, Clay (84%)	Nitrate	
	N/A	0.746	N/A	Clay	Buderim, Clay (89%)	Nitrate	
	N/A	0.560	N/A	Clay	Tawoomba, Clay (71%)	Nitrate	
	N/A	0.933	N/A	Clay	Ravensbourne, Clay (75%)	Nitrate	Black, A. & Waring, S. 1979.
	N/A	0.427	N/A	Clay	Tamborine, Clay (81%)	Nitrate	
	N/A	0.400	N/A	Clay	Kumbai, Clay (76%)	Nitrate	
	N/A	0.293	N/A	Clay	Isis, Clay (73%)	Nitrate	
	N/A	0.133	N/A	Clay	Coolabunia, Clay (74%)	Nitrate	
	N/A	0.240	N/A	Clay	Memerambi, Clay (70%)	Nitrate	
	0.060	1.128	0.96	Clay	Clay	Nitrate	
	0.260	1.184	0.98	Clay	Clay	Nitrate	
	0.370	1.143	0.97	Clay	Clay	Nitrate	Harmand, J.-M., Ávila, H.,
	0.380	1.016	0.97	Clay	Clay	Nitrate	Oliver, R., Saint-André, L. &
	0.710	0.873	0.98	Clay	Clay	Nitrate	Dambrine, E. 2010.
	0.780	0.677	0.92	Clay	Clay	Nitrate	
	0.620	0.570	0.92	Clay	Clay	Nitrate	
	0.938	0.226	0.96	Silt	Subsoil	Nitrate	Eick M, J., Brady W, D. &
	1.144	0.285	0.970	Silt	Subsoil	Nitrate	Lynch C, K. 1999
	1.350	0.344	0.98	Silt	Suboil	Nitrate	

IONIC P

Particle size (sand silt clay)	Equilibrium adsorbate Concentration b L/g	Maximum adsorbant capacity Q (mg/g)	R^2	Type soil generalised (sorbent)	Type soil stated (sorbent)	Sorbate	Reference
	0.430	53.659	0.93	mesoporous silicate	activated alumina	phosphate	Shin, E. W., Han, J. S., Jang,
	0.950	81.865	0.95	mesoporous silicate	Al10SBA-15	phosphate	M., Min, S.-H., Park, J. K. &
	0.660	58.787	0.96	mesoporous silicate	Al30SBA-15	phosphate	Rowell, R. M. 2003
	0.043	0.231	0.59	gravel	gravel	phosphate	
	0.044	0.814	0.64	sand	sand	phosphate	Song, Y. & Liu, H. 2013
	0.044	0.302	0.79	zeolite	zeolite	phosphate	
	0.073	0.051	0.97	sand	Birkesig	phosphorus	
	0.765	0.041	0.99	sand	Vestergard	phosphorus	
	0.121	0.104	0.93	sand	Almind	phosphorus	
	0.096	0.049	0.98	sand	Bedsted 1	phosphorus	
	0.147	0.042	0.97	sand	Bedsted 2	phosphorus	
	0.116	0.039	0.99	sand	Bedsted 3	phosphorus	
	0.096	0.266	0.98	sand	Nymolle	phosphorus	Del Bubba, M., Arias, C. A. &
	0.112	0.110	0.97	sand	Aunsogard	phosphorus	Brix, H. 2003.
	0.197	0.035	0.97	sand	Logtved	phosphorus	
	0.068	0.060	0.94	sand	Soro	phosphorus	
	0.021	0.169	0.79	sand	Darup	phosphorus	
	0.042	0.079	0.81	sand	Farum	phosphorus	
	0.140	0.014	0.90	sand	Quartzsand	phosphorus	
	10.4	0.022	N/A	waste material from ste	Slag dust	phosphorus	Vigneswaran, S. Moon, H.
	7.20	0.010	N/A	waste material from ste	Slag Cake	phosphorus	1998
	0.821	0.210	0.78	sand	Birkesig	phosphorus	
	0.919	0.140	0.86	sand	Vestergård	phosphorus	
	0.983	0.300	0.96	sand	Almind	phosphorus	
	1.042	0.350	0.87	sand	Bedsted	phosphorus	
	1.130	0.190	0.67	sand	Bedsted	phosphorus	
	1.327	0.180	0.78	sand	Bedsted	phosphorus	
	0.167	0.280	0.78	sand	Nymølle	phosphorus	Brix, H., Arias, C. & Del Bubba,
	0.983	0.450	0.55	sand	Aunsøgård	phosphorus	M. 2001.
	1.042	0.340	0.67	sand	Løgtved	phosphorus	
	1.130	0.300	0.65	sand	Sorø	phosphorus	
	1.327	0.300	0.62	sand	Darup	phosphorus	
	0.821	0.210	0.87	sand	Farum	phosphorus	
	0.919	0.040	0.56	sand	Quartz	phosphorus	
	349.7	91.000	0.94	clay	kaolinite	phosphorus	Edzwald, J., Toensing, D. &
	1041.0	74.600	0.96	clay	montmorillonite	phosphorus	Leung, M. 1976
	168.0	25.100	0.90	clay	illite	phosphorus	
	590.0	11.600	0.99	Clay	Bentonite	phosphorus	
	430.0	14.450	0.99	Clay	Bentonite	phosphorus	Zamparas, M., Deligiannakis,
	412.0	14.140	0.99	Clay	Bentonite	phosphorus	Y. & Zacharias, I. 2013.
	560.0	11.200	0.99	Clay	Bentonite	phosphorus	

Particle size (sand silt clay)	Equilibrium adsorbate Concentration b L/g	Maximum adsorbant capacity Q (mg/g)	R^2	Type soil generalised (sorbent)	Type soil stated (sorbent)	Sorbate	Reference
	32.2	0.680	0.97	Sand	Clay (S.A = 0.87 m^2.g^-1)	phosphate	Zhang, H., Tian, S., Zhang, M., Wu, L., Kong, J., Chao, Y., Hu, Y. & Li, L. 2012.
	259.3	0.390	0.94	Clay	Montmorillonite	phosphorus	Cao Y, Wei X, Cai P, Huang Q, Rong X, Liang W. 2011
	130.8	0.360	0.94	Clay	Kaolinite	phosphorus	
	1164.3	1.880	0.99	Clay	Geothite	phosphorus	
	0.725	0.084	0.95	sand	PA3	phosphorus	
	0.517	0.904	0.94	sandy clay	LA2	phosphorus	
	0.917	0.178	0.99	sand	EP	phosphorus	
	0.170	0.110	0.96	sandy loam	PL	phosphorus	
	0.243	0.151	0.96	sandy clay loam	PVA	phosphorus	Corrêa, M., Nascimento, D., & Rocha, D,. 2011
	0.431	0.664	0.99	sandy clay	LVA	phosphorus	
	0.296	0.260	0.99	sandy clay loam	PA2	phosphorus	
	0.155	0.103	0.94	Sandy Loam	PA1	phosphorus	
	0.162	0.045	0.71	sand	RQ	phosphorus	
	0.214	0.037	0.85	Sandy Loam	LA1	phosphorus	
	1.270	0.177	0.97	sandy clay loam	sand (66%) clay (25%) silt (9%)	phosphorus	Sato, S. & Comerford, N. B. 2005.
	0.980	0.192	0.99	sandy clay loam	sand (66%) clay (25%) silt (9%)	phosphorus	
	23.5	1.153	0.65	clay	Top soil	phosphorus	
	65.7	1.727	0.92	clay	Subsoil	phosphorus	
	189	0.934	0.96	clay	topsoil	phosphorus	Sakadevan, K. & Bavor, H. 1998.
	180	4.273	0.98	clay	Clayey soil	phosphorus	
	219	5.208	1.00	clay	Clayey soil	phosphorus	
	320	4.484	1.00	clay	Clayey Soil	phosphorus	
	210	0.496	0.94	loam	Loam	phosphate	
	484	0.591	0.95	loam	Evesham clay	Phosphate	
	145	0.314	0.91	sandy loam	Aberford sandy loam	Phosphate	
	181	0.188	0.93	loamy sand	Woburn loamy sand	Phosphate	Holford, R., Wedderburn, M. & Mattingly, G. 1974.
	460	0.183	0.94	clay	Hathaway Black Earth	Phosphate	
	450	0.061	0.92	silty clay	Quast Black Earth sand	Phosphate	
	1060	0.127	0.89	loam	Watts Red Brown Earth	Phosphate	
	1200	0.076	0.90	sandy clay loam	Anderson Red Brown Earth	Phosphate	
	26.207	0.566	0.99	loam	composite sediment sample	phosphorous	Hwang, C. P., Lackie, T. H. & Huang, P. M. 1976.

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APPENDIX B – RAINFALL DATA IN PYMBLE LEADING UP TO THE DATE OF COLLECTION

Daily Rainfall (millimetres)

TURRAMURRA (KISSING POINT ROAD)   (1.9m from study site)

Station Number: 066158 · State: NSW · Opened: 1912 · Status: Open · Latitude: 33.74°S · Longitude: 151.13°E · Elevation: 160 m

2014	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1st	0	0	14.6	0	0	1.2	0	0	0			
2nd	0.4	0	18.6	0	0	1.6	0	0	0			
3rd	1.6	0	4.8	0	1.8	0	0	0	2.0			
4th	0	0	12.6	0.6	5.4	0	0	0	0			
5th	0	6.0	0.4	8.0	0	9.2	0	0	2.2			
6th	0	0.2	0.2	0.2	0	8.4	0	0	6.2			
7th	0	0	0	12.6	0	1.4	0	0	14.0			
8th	2.0	0	0.2	4.4	0	0	0	0	2.0			
9th	0.2	0	0	0	1.0	0	0	0	0			
10th	0	0	0	0	0	10.0	1.0	0	6.8			
11th	0	1.6	0	6.6	1.8	2.8	0	0	0			
12th	0	1.0	0	15.2	0	0	0	7.4	0.4			
13th	0	0	42.6	4.4	5.0	0	0	16.0	4.0			
14th	0	0.4	0	0.4	0	6.0	0	0	0.2			
15th	0	1.6	0	0.2	0	0.6	1.0	0	0			
16th	0	7.0	8.0	18.6	0	0.2	2.3	0	0.6			
17th	0	32.2	17.0	0	0	0	0	26.0	0.6			
18th	0	1.0	0	0	0	0	0	41.0	0			
19th	0	0	0	0	0	0	0	92.0	0			
20th	0	11.6	0	0	0	0	0	6.0	0			
21st	10.2	0	0.4	0	0	1.6	0	4.0	0.6			
22nd	7.6	0	0	0	0	0.2	0	13.6	0			
23rd	1.0	0.4	2.0	0	0	0	0	1.6	0			
24th	0.2	0.8	0.6	0	0	0	0	0.8	0			
25th	4.0	0	20.2	0.6	0	0	0	0	0.2			
26th	0.2	0	0.4	0.6	0	0	11.7	↓	14.6			
27th	0	8.8	12.6	0	0	0	1.2	↓	0			
28th	0	6.6	9.2	5.0	0	0	0	↓	0			
29th	0		34.6	0	0	0	0	↓	0			
30th	0		0.6	4.8	0	0	0	↓	0			
31st	0		7.0		0		0	61.8				
Highest daily	10.2	32.2	42.6	18.6	5.4	10.0	11.7	92.0	14.6	0.4		
Monthly Total	27.4	79.2	206.6	82.2	15.0	43.2	17.2	270.2	54.4			

Annotations: Last significant rainfall event prior to collection of samples (pointing to May 13th, 5.0). Date of collection (pointing to Jun 15th, 0.6).

↓ This day is part of an accumulated total
Quality control: 12.3 Done & acceptable, *12.3* Not completed or unknown

Australian Government
Bureau of Meteorology

Daily Rainfall (millimetres)

TURRAMURRA (KISSING POINT ROAD)

Station Number: 066158 · State: NSW · Opened: 1912 · Status: Open · Latitude: 33.74°S · Longitude: 151.13°E · Elevation: 160 m

Statistics for this station calculated over all years of data

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Mean	143.7	164.6	162.8	123.6	117.6	143.0	71.5	86.8	70.6	96.9	113.0	103.5
Median	115.6	124.8	127.4	88.7	90.3	91.6	51.0	50.0	54.0	72.8	92.1	81.8
Highest daily	200.2	271.8	383.0	194.2	264.9	253.4	178.6	258.6	132.1	156.5	233.6	138.9
Date of highest daily	10th 1949	10th 1956	28th 1942	30th 1988	2nd 1953	11th 1991	6th 1988	6th 1986	2nd 1970	17th 1972	8th 1984	9th 1970

1) Calculation of statistics

Summary statistics, other than the Highest and Lowest values, are only calculated
if there are at least 20 years of data available.

2) Gaps and missing data

Gaps may be caused by a damaged instrument, a temporary change to the site operation, or
due to the absence or illness of an observer.

3) Further information

http://www.bom.gov.au/climate/cdo/about/about-rain-data.shtml.

APPENDIX C – QUALITATIVE DESCRIPTION OF FOUR SOIL SAMPLES

Soil sample 1:

In-situ location	Creek bed
In-situ moisture content	100%
Unified soil classification	SP – poorly graded sand, (4.83% gravel, 91.96% Sand, 3.21% Silts + clay)
Description	High dry bulk density, particles predominantly of the mineral fraction, largely composed of sands and gravel, minerals present include feldspar, quartz, smectite (refer to microscope imagery below), organic matter in the later stages of decomposition (e.g. leaf litter), small amount of bark + twigs present, large pieces of rubbish in sample (plastic, waste paper, cigarette butts).

Figure 1: In situ sample

Figure 2: Location of in-situ soil

Figure 3:Location of sample 1

In-situ location of Soil sample 1

Figure 4: Drying of soil sample in 180°C oven

C2

Figure 5: <2.36 mm homogenous sample

Figure 6: Suspended fines in solution (pre-siphoning)

Figure 7: Fines settled from suspension (pre-siphoning)

Figure 8: Fines collected from suspension

Figure 9: Supernatant water siphoned and evaporated leaving fines.

Figure 10: Quartz minerals in <75µm fraction at 390 x magnification
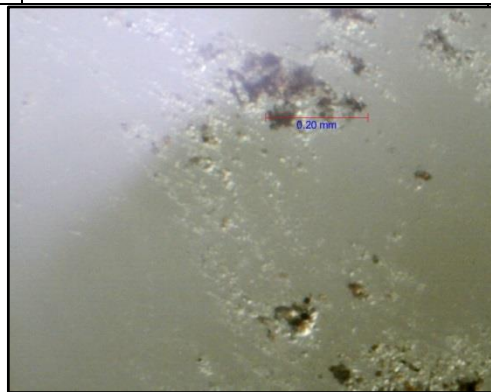
Figure 11: <75µm fraction composed predominantly of minerals at 390 magnification

Figure 12: Feldspar minerals in <75µm fraction at 390 x magnification

C3
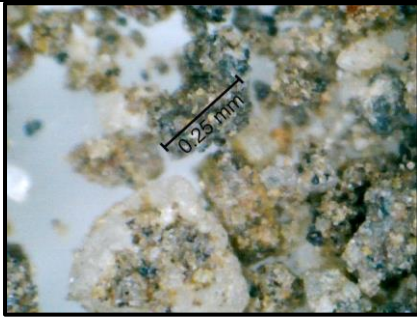
Figure 13: Minerals present in >2.36mm sample. 50 x magnification

Figure 14: Macroscopic minerals present in >2.36 sample at 0 magnification

Soil sample 2:

In-situ location	Creek bed at level of water table (where the creek has just begun to evaporate).
In-situ moisture content	76%
Unified soil classification	SW-SC well graded sand with clay - 12.94% gravel, 80.85% sand, 6.21% fines
Description	Very similar to Soil sample 1 in composition, however the soil has begun to loose some of its moisture. High dry bulk density, particles predominantly of the mineral fraction, largely composed of sands and gravel, also a significant portion of fines making the sample very 'dusty' in comparison to Soil sample 1, minerals present include feldspar, quartz (refer to microscope imagery below), organic matter in the later stages of decomposition (e.g. leaf litter), large pieces of rubbish in sample (plastic, waste paper, cigarette butts). Fine particles predominantly minerals, some organic matter also present in the fine fraction. Large particles (>2.36mm) predominantly organic.

Figure 15: >2.36mm fraction removed from 24 hour time dependant experiments. Note the presence of plant material (dried leaves, twigs, seed pods)

Figure 16: Soil sample 2. Note large presence of fines or "dust".

Figure 17: Composition of soil in-situ

In-sit location of Soil
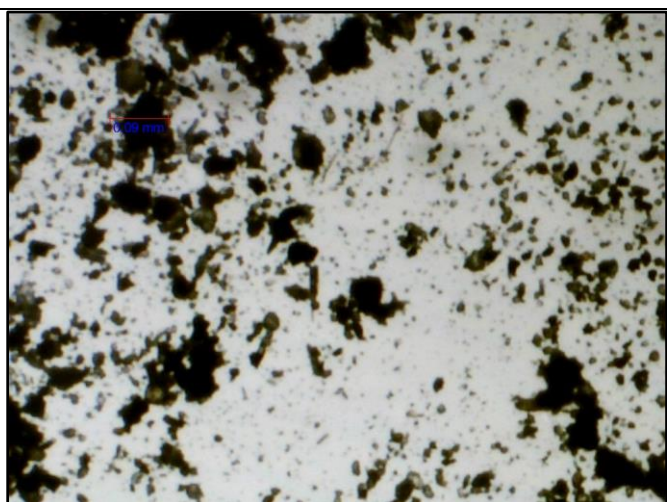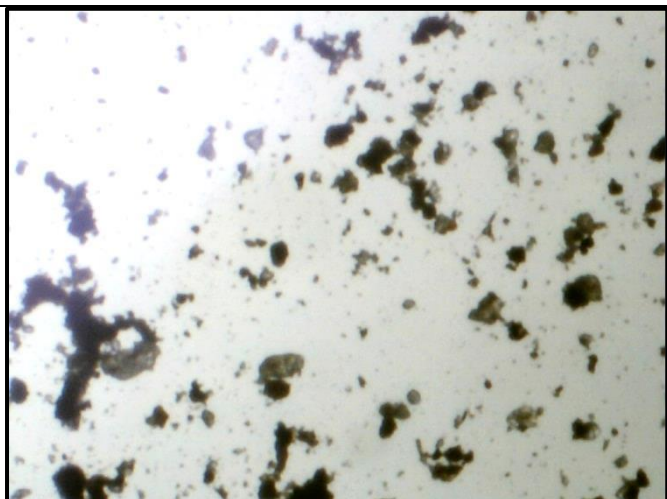
Figure 18: <75 mm fraction. Note the presence of both organic and mineral matter

Soil sample 2 filtrate

Soil sample 3 filtrate

Figure 19: Filtrate from Soil sample 2 and 3. Note Soil sample 2 had a lot of humic acid (indicated by brown color), and Soil sample 3 had even more so.

Soil sample 3:

In-situ location	Creek bank and will be washed into the creek with the next set of rain
In-situ moisture content	15%
Unified soil classification	14.0% gravel 83.4% sand 2.59% fines SP - Poorly graded Sand
Description	Sample very soil like. Moderate dry bulk density, particles predominantly of the organic fraction, some vegetation cover as sample location, living vegetation present in sample small amount of bark + twigs present, large pieces of rubbish in sample (plastic, waste paper, cigarette butts).

Figure 20: Soil sample 3 as in-situ. Red highlights presence of living vegetation in sample.
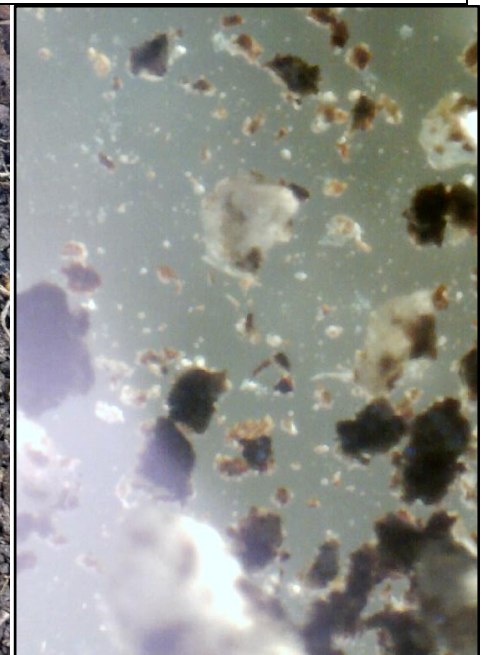
Figure 21: homogenous <2.36mm fraction at 390 x magnification. Note the presence of both minerals and organic matter

In-situ location of Soil sample 3

Figure 22: location of sample 3. Note this is the material that will wash into the creek with the next onset of rain
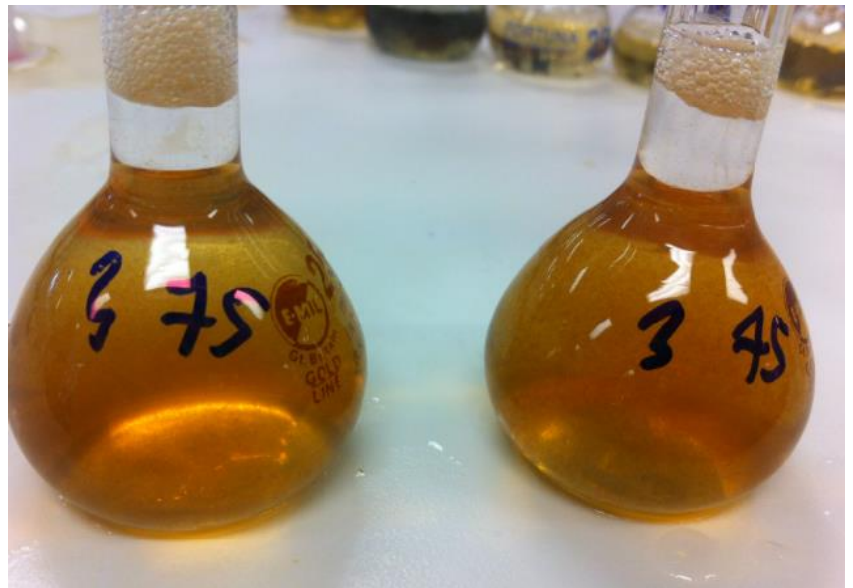
Figure 23: Soil sample 3 had a large volume of humic acid
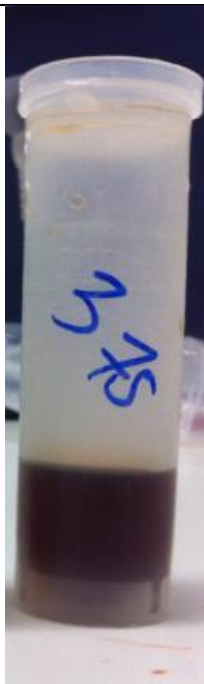
Figure 24: Filtrate from Soil sample 3. Dark brown colour indicates large proportion of humic acid in the sample
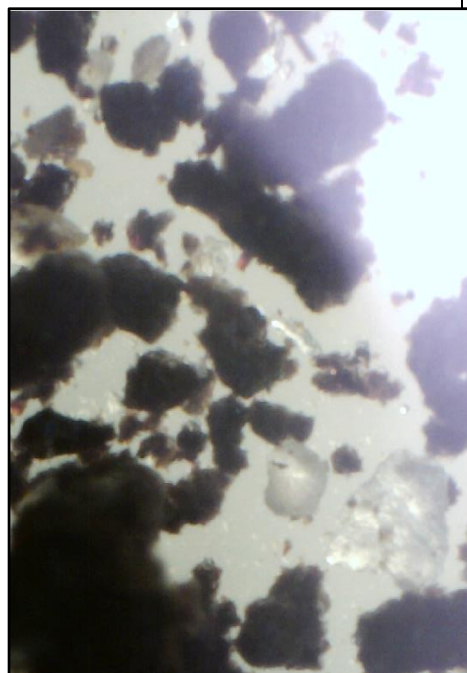
Figure 25: Sample 3 at 390 x magnification
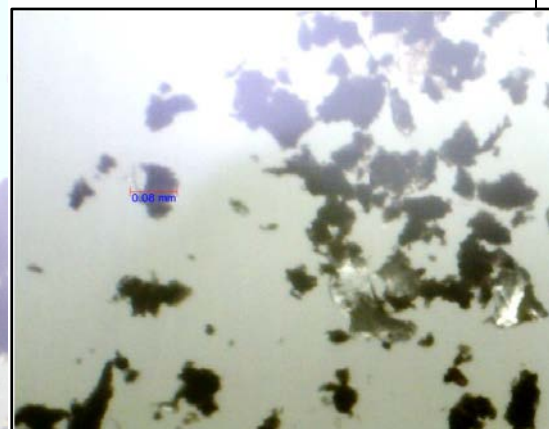
Figure 26: <75mm fraction of sample 3. This size fraction was comprised of both mineral and organic matter

Soil sample 4:

In-situ location	Road side (near a gutter)
In-situ moisture content	8%
Unified soil classification	SW - Well graded sand 0.24% Gravel 78.66% Sand 1.10% fines.
Description	Low dry bulk density, particles almost all of the organic fraction, some vegetation cover as sample location, living vegetation present in sample, many leaves present as well as pieces of bark and seedpods (most of the material had freshly fallen from the surrounding trees, majority of sample volume was >6mm fraction size and was not kept.

Figure 27: Jamie Collecting Soil sample 4

Figure 28: Material in sample four. Note the presence of sticks and some fresh (living) green vegetation

Figure 29: Location of sample 4. Note the presence of live vegetation growingin the material

Figure 30: Oven drying of sample four. Note fresh green vegetation in sample not yet undergone decomposition

Figure 31: Macroscopic (>2.36mm) fraction of Soil sample 4

Figure 32: Large sticks and leaf litter removed from Soil sample 4 prior to experimentation

Figure 33: >2.36 heterogeneous fraction used for 24 hour experiments
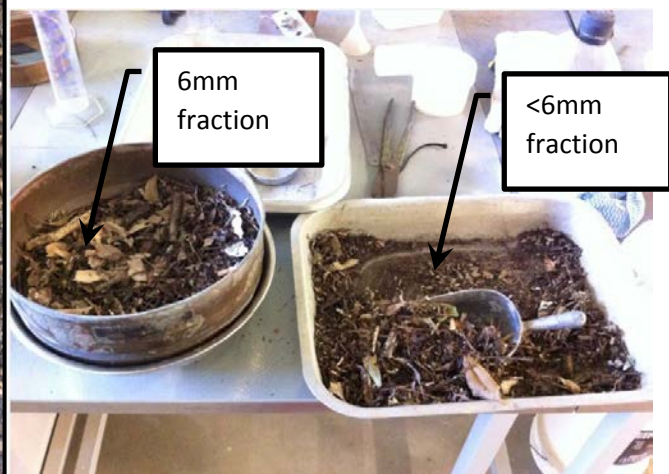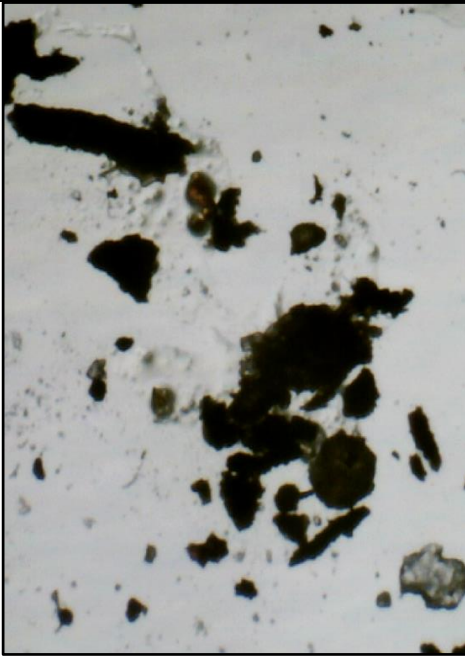
Figure 34: Sample 4 at 390 magnification comprised predominantly of organic matter
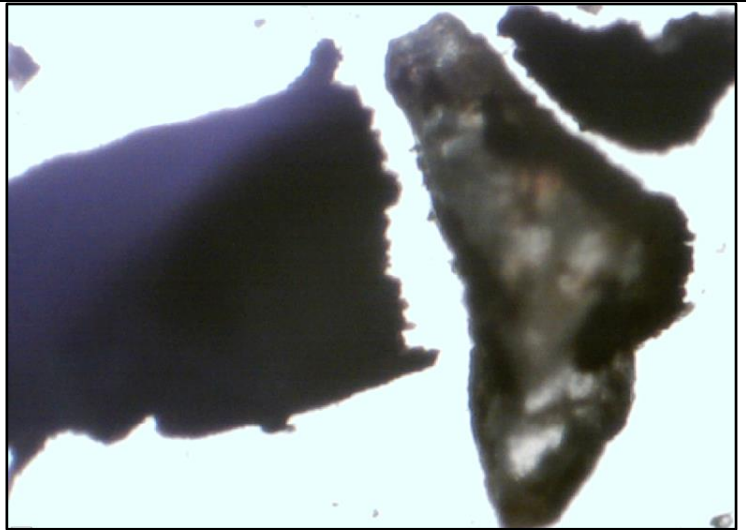
Figure 35: 390x magnification of sample 4 homogenous <2.36mm fraction
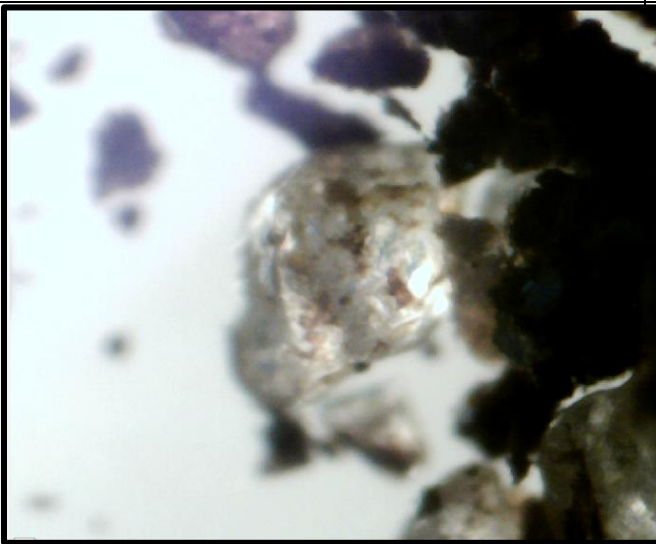
Figure 36: Quartz mineral present in sample 4
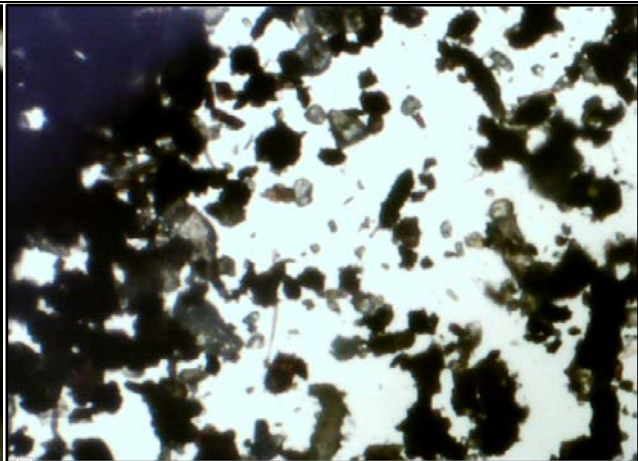
Figure 37:Finest fraction (<75μm) of sample 4 at 390 x magnification. Note the presence of both organic matter and a few minerals in this fraction.

C11

APPENDIX D – MASS FRACTION OF WATER BY WEIGHT

ANALYSIS OF MASS WATER BY WEIGHT

Sample	Replicate	Wet	Dry	Moisture Content	Average
1	i	Saturated	Saturated	100%	100%
1	ii	Saturated	Saturated	100%	
1	iii	Saturated	Saturated	100%	
2	i	57.48	32.8	75%	76%
2	ii	95.16	50.38	89%	
2	iii	75.06	45.64	64%	
3	i	83.39	73.15	14%	15%
3	ii	96.25	82.34	17%	
3	iii	82.02	72.1	14%	
4	i	52.11	48.65	7%	8%
4	ii	36.11	33.29	8%	
4	iii	40.58	37.32	9%	

APPENDIX E – PARTICLE SIZE DISTRIBUTION CHARTS OF THE FOUR SOILS

SIEVE ANALYSIS - SOIL SAMPLE 1

Empty container mass	87.19	g
Container + soil mass	386.78	g
Soil mass	299.59	g

Sieve size (mm)	Mass of Empty Seive (g)	Mass of Seive+Soil Retained (g)	Soil Retained (g)	Percentage Retained	Percentage Passing
2.360	421.25	435.74	14.49	4.83%	95.17%
1.180	378.65	397.75	19.1	6.37%	88.80%
0.600	350.36	393.22	42.86	14.29%	74.51%
0.425	329.13	386.03	56.9	18.97%	55.54%
0.300	323.35	389.35	66	22.00%	33.54%
0.150	304.61	377.04	72.43	24.15%	9.39%
0.075	286.23	304.76	18.53	6.18%	3.21%
Base	271.77	281.41	9.64	3.21%	0%
		Total	299.95	100%	
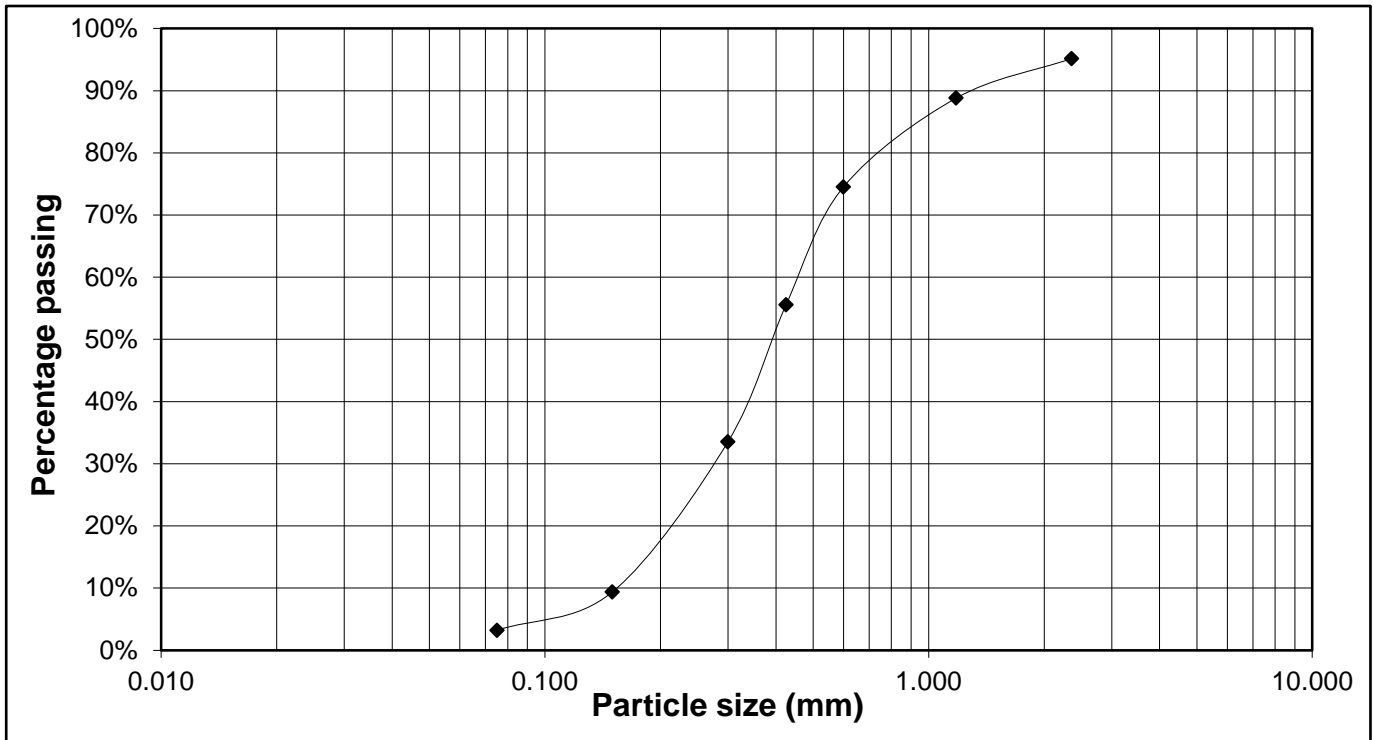
% Gravel =	4.83%	D_{10} =	0.300	mm
% Sand =	91.96%	D_{30} =	0.300	mm
% Fines =	3.21%	D_{60} =	0.600	mm

C_u =	2	C_c =	0.500

Unified clasification of soil	SP - Poorly graded Sand

SIEVE ANALYSIS - SOIL SAMPLE 2

Empty container mass	83.46	g
Container + soil mass	384.25	g
Soil mass	300.79	g

Sieve size (mm)	Mass of Empty Seive (g)	Mass of Seive+Soil Retained (g)	Soil Retained (g)	Percentage Retained	Percentage Passing
2.360	421.33	460.41	39.08	12.94%	87.06%
1.180	378.67	434.73	56.06	18.56%	68.50%
0.600	350.37	405.34	54.97	18.20%	50.30%
0.425	329.13	360.51	31.38	10.39%	39.91%
0.300	323.43	354.49	31.06	10.28%	29.62%
0.150	304.66	353.85	49.19	16.29%	13.34%
0.075	286.28	307.81	21.53	7.13%	6.21%
Base	271.96	290.71	18.75	6.21%	0%
		Total	302.02	100%	
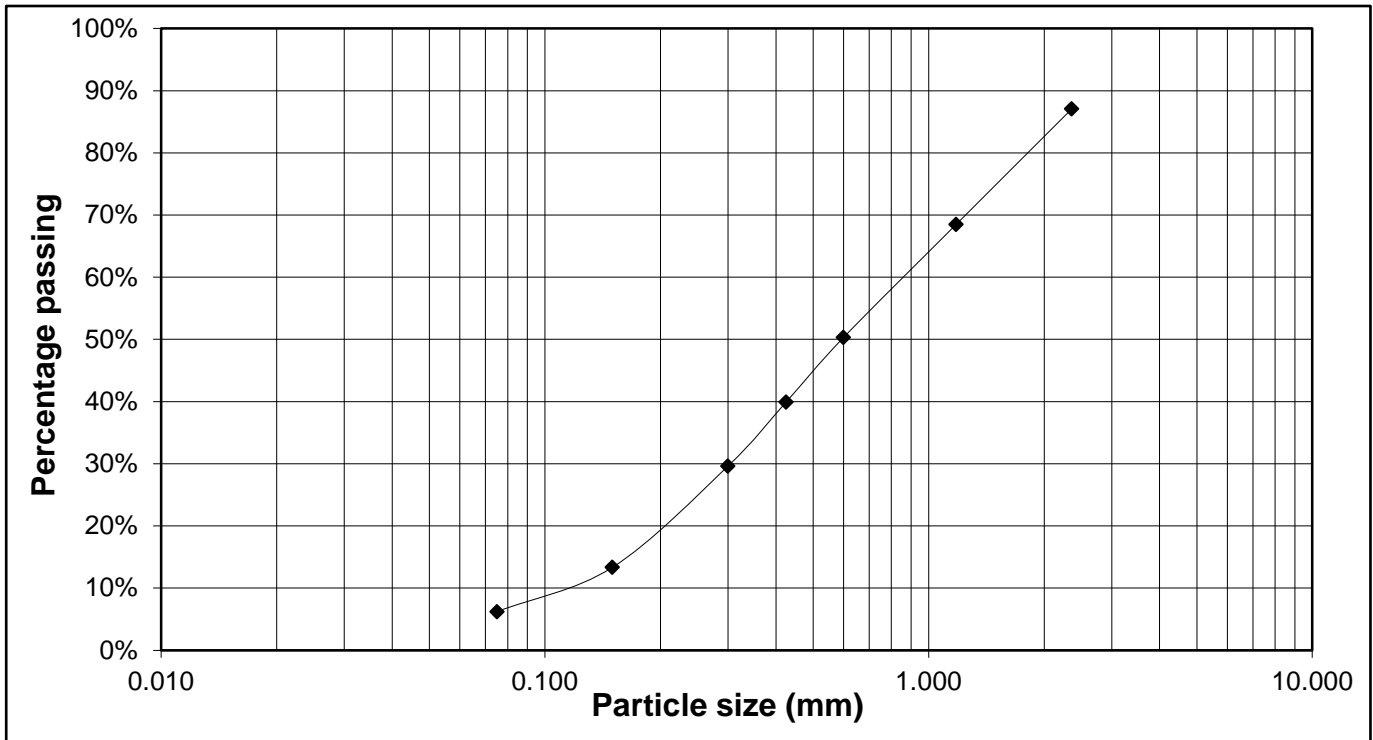
% Gravel =	12.94%	D_{10} =	0.150	mm
% Sand =	80.85%	D_{30} =	0.425	mm
% Fines =	6.21%	D_{60} =	1.180	mm

C_u =	7.867	C_c =	1.020

Unified clasification of soil	SW-SC well graded sand with clay

SIEVE ANALYSIS - SOIL SAMPLE 3

Empty container mass	87.11	g
Container + soil mass	385.62	g
Soil mass	298.51	g

Sieve size (mm)	Mass of Empty Seive (g)	Mass of Seive+Soil Retained (g)	Soil Retained (g)	Percentage Retained	Percentage Passing
2.360	428.47	470.29	41.82	14.00%	86.00%
1.180	379.16	426.20	47.04	15.75%	70.24%
0.600	350.58	405.29	54.71	18.32%	51.92%
0.425	329.30	374.04	44.74	14.98%	36.94%
0.300	317.08	357.28	40.2	13.46%	23.48%
0.150	304.83	352.09	47.26	15.83%	7.65%
0.075	286.35	301.47	15.12	5.06%	2.59%
Base	272.84	280.58	7.74	2.59%	0%
		Total	298.63	100%	
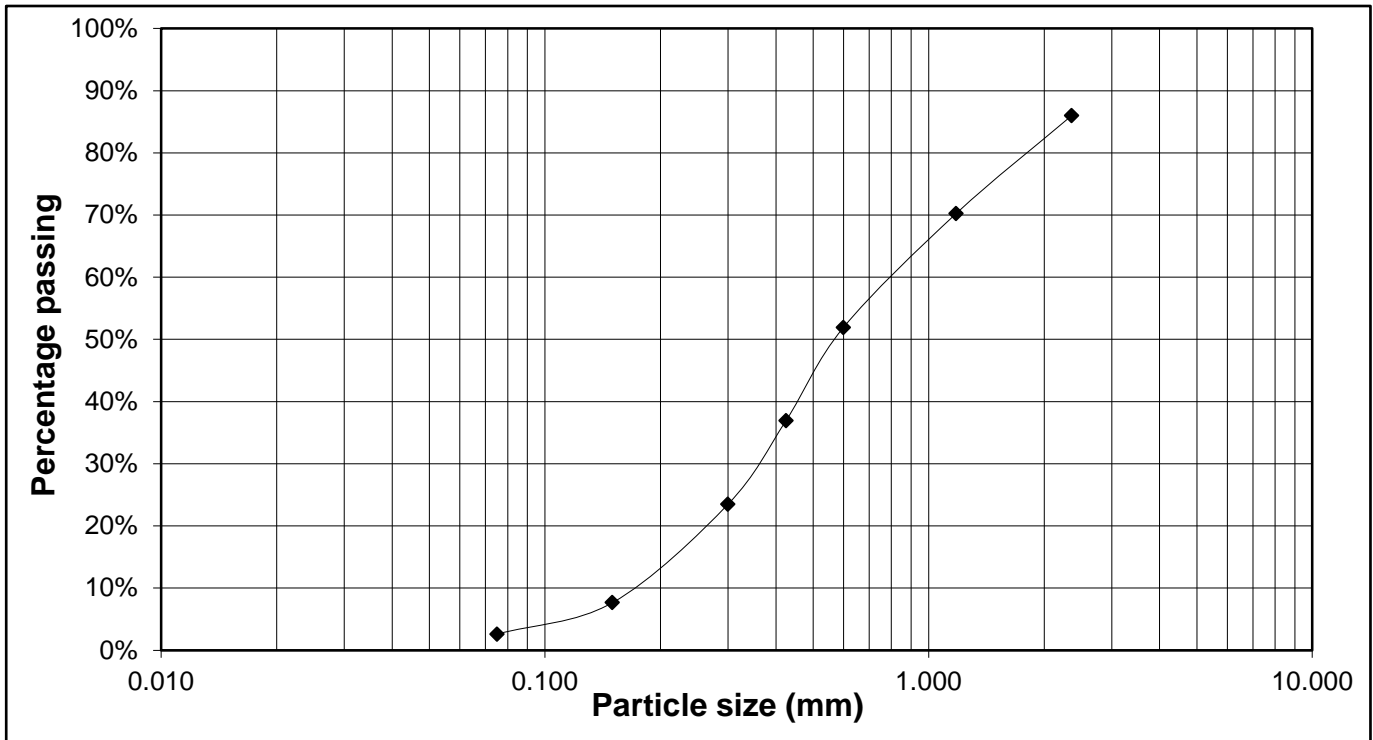
% Gravel =	14.00%	D_{10} =	0.300	mm
% Sand =	83.40%	D_{30} =	0.425	mm
% Fines =	2.59%	D_{60} =	1.180	mm

C_u =	3.933	C_c =	0.510

Unified clasification of soil	SP - Poorly graded Sand

SIEVE ANALYSIS - SOIL SAMPLE 4

Empty container mass	113.8	g
Container + soil mass	413.87	g
Soil mass	300.07	g

Sieve size (mm)	Mass of Empty Seive (g)	Mass of Seive+Soil Retained (g)	Soil Retained (g)	Percentage Retained	Percentage Passing
2.360	428.43	489.16	60.73	20.24%	79.76%
1.180	378.78	453.83	75.05	25.01%	54.75%
0.600	350.41	410.00	59.59	19.86%	34.89%
0.425	329.16	358.74	29.58	9.86%	25.03%
0.300	315.82	345.45	29.63	9.87%	15.16%
0.150	304.68	335.88	31.20	10.40%	4.76%
0.075	286.29	297.27	10.98	3.66%	1.10%
Base	271.91	275.21	3.30	1.10%	0%
		Total	300.05	100%	
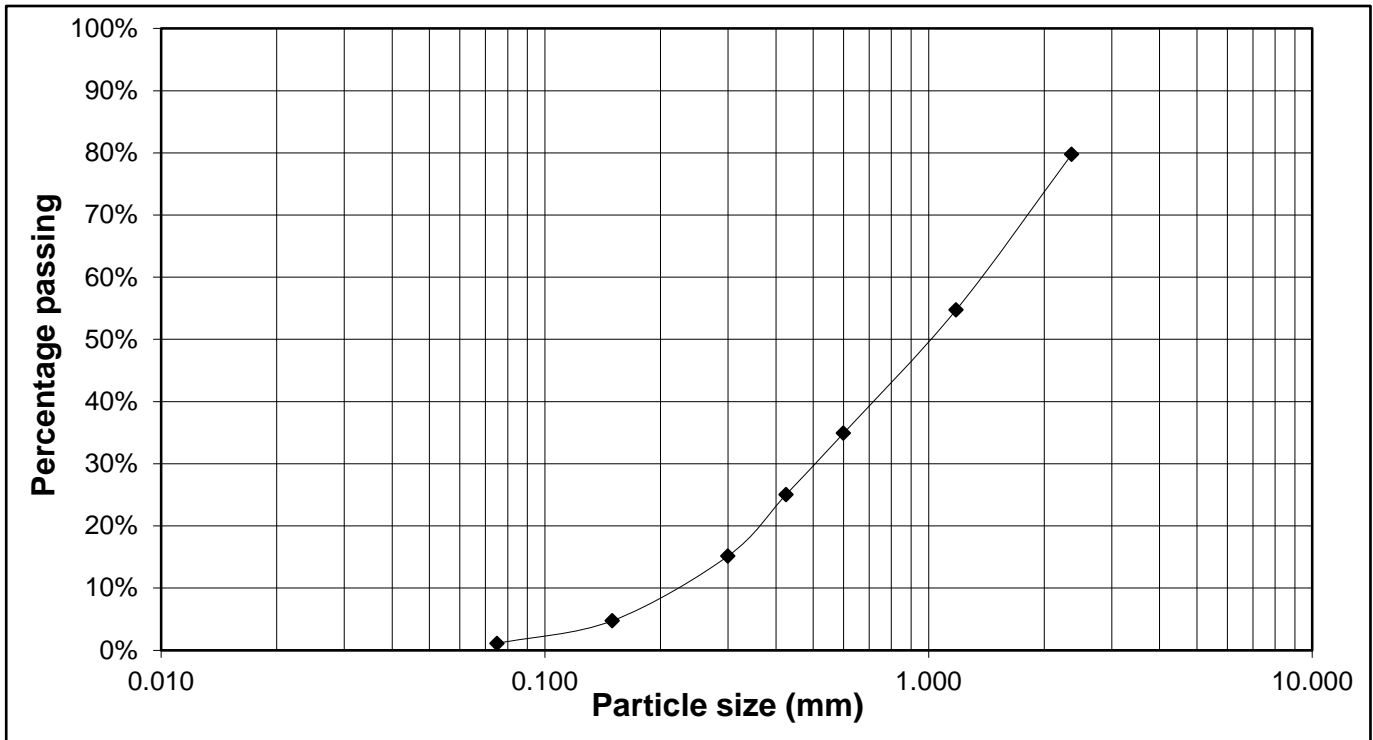
% Gravel =	20.24%	D_{10} =	0.300	mm
% Sand =	78.66%	D_{30} =	0.600	mm
% Fines =	1.10%	D_{60} =	2.360	mm

C_u =	7.867	C_c =	0.508

Unified clasification of soil	SW - Well graded sand

APPENDIX F – RAW DATA: OBTAINED FROM THE EXTRACTION EXPERIMENTS

Repllicate		Sample	Volume of sample (ml)	Volume of water	Water Concentration		Concentration without diluion		Concentration of nutrient in soil		Average + stdev Concentration of nutrient in soil			
					No3 (mg/l) x 1000	NH4+ (mg/L) x 1000	N03 (g/L)	Nh4+ (g/L)	N03 (mg/g)	Nh4+ (mg/g)	μ N03 (mg/g)	σ N03 (mg/g)	Nh4+ (g/L)	σ NH4+ (mg/g)
1	1	<75µm	81	40	0.239	4.900	0.36	7.32	3.563	73.198	4.11	2.27	8.88	5.70
		<75µm	23	72	0.016	0.348	0.06	1.44	0.640	14.353				
	2	<75µm	50	50	0.341	0.465	0.68	0.93	6.815	9.300				
		<75µm	30	120	0.068	0.060	0.34	0.30	3.408	2.975				
	3	<75µm	50	50	0.323	5.400	0.65	10.80	6.455	108.000				
		<75µm	30	120	0.076	1.800	0.38	9.00	3.798	90.000				
	1	75µm-150µm	81	40	0.304	7.726	0.45	11.54	4.541	115.416	7.10	4.16	16.96	8.79
		75µm-150µm	40	60	0.139	4.554	0.35	11.39	3.468	113.855				
	2	75µm-150µm	50	50	0.298	0.400	0.60	0.80	5.967	8.002				
		75µm-150µm	30	119	0.086	0.225	0.43	1.12	4.268	11.181				
	3	75µm-150µm	51	49	0.531	1.130	1.04	2.22	10.402	22.157				
		75µm-150µm	31	120	0.286	0.544	1.39	2.65	13.940	26.511				
	1	150µm-300µm	80	40	0.090	4.700	0.13	7.05	1.343	70.500	5.07	3.19	7.34	4.90
		150µm-300µm	40	60	0.009	2.888	0.02	7.22	0.213	72.200				
	2	150µm-300µm	50	50	0.448	0.055	0.90	0.11	8.958	1.100				
		150µm-300µm	50	50	0.269	0.028	0.54	0.06	5.378	0.560				
	3	150µm-300µm	80	40	0.465	0.516	0.70	0.77	6.969	7.733				
		150µm-300µm	50	50	0.359	0.372	0.72	0.74	7.179	7.447				
		150µm-300µm	30	120	0.109	0.261	0.54	1.31	5.436	13.072				
	1	300µm-425µm	81	40	0.183	4.750	0.27	7.10	2.734	70.957	4.41	2.05	9.12	3.82
		300µm-425µm	40	60	0.143	2.878	0.36	7.20	3.566	71.957				
	2	300µm-425µm	50	50	0.274	0.398	0.55	0.80	5.478	7.963				
		300µm-425µm	80	40	0.209	0.533	0.31	0.80	3.132	7.996				
	3	300µm-425µm	50	50	0.171	0.294	0.34	0.59	3.414	5.876				
		300µm-425µm	29	119	0.159	0.287	0.81	1.47	8.125	14.654				
	1	425µm-600µm	80	20	0.283	3.04	0.35	3.80	3.537	38.000	3.44	1.77	20.38	11.18
		425µm-600µm	21	89	0.096	0.466	0.50	2.44	5.048	24.400				
	2	425µm-600µm	20	80	0.053	0.285	0.27	1.43	2.650	14.253				
	3	425µm-600µm	81	39	0.374	5.600	0.55	8.30	5.544	82.963				
		425µm-600µm	51	49	0.164	0.785	0.32	1.54	3.222	15.392				
		425µm-600µm	28	118	0.012	0.189	0.06	0.98	0.626	9.831				
	1	600µm-1.18mm	81	40	0.278	0.047	0.42	0.07	4.153	0.702	1.87	1.95	6.66	2.38
		600µm-1.18mm	22	88	0.005	0.086	0.02	0.43	0.249	4.277				
		600µm-1.18mm	19	80	0.001	0.096	0.00	0.50	0.037	4.982				
	2	600µm-1.18mm	81	40	0.112	0.006	0.17	0.01	1.666	0.086				
		600µm-1.18mm	52	50	0.244	0.038	0.48	0.07	4.781	0.743				
	3	600µm-1.18mm	81	40	0.140	0.557	0.21	0.83	2.091	8.321				
		600µm-1.18mm	30	120	0.002	0.181	0.01	0.90	0.095	9.044				
	1	1.18mm-2.36mm	79	40	1.095	0.036	1.65	0.05	16.487	0.542	6.03	5.78	3.01	2.01
		1.18mm-2.36mm	30	120	0.100	0.100	0.50	0.50	5.010	5.021				
	2	1.18mm-2.36mm	80	40	0.183	0.057	0.27	0.09	2.748	0.856				
		1.18mm-2.36mm	30	120	0.172	0.031	0.86	0.16	8.618	1.550				
	3	1.18mm-2.36mm	80	40	0.075	0.296	0.11	0.44	1.121	4.434				
		1.18mm-2.36mm	50	50	0.109	0.052	0.22	0.10	2.180	1.039				
	1	2.36mm-6.0mm	80	40	0.116	0.145	0.17	0.22	1.735	2.175	0.90	0.73	1.42	1.06
	2	2.36mm-6.0mm	80	40	0.001	0.001	0.00	0.00	0.015	0.008				
		2.36mm-6.0mm	100	0	0.114	0.007	0.11	0.01	1.140	0.070				
	3	2.36mm-6.0mm	80	40	0.0901	0.001	0.14	0.00	1.352	0.015				
		2.36mm-6.0mm	100	0	0.028	0.067	0.03	0.07	0.280	0.670				
	1	<2.36mm	94	20	0.448	3.513	0.54	4.26	5.433	42.604	6.12	1.51	26.73	5.60
	2	<2.36mm	50	50	0.325	1.175	0.65	2.35	6.500	23.500				
		<2.36mm	30	120	0.077	0.664	0.39	3.32	3.850	33.200				
	3	<2.36mm	80	20	0.604	7.800	0.76	9.75	7.550	97.500				
		<2.36mm	30	120	0.145	0.470	0.73	2.35	7.250	23.500				
	1	Unsevied	80	40	0.143	0.743	0.21	1.11	2.141	11.145	5.55	4.70	9.46	3.89
		Unsevied	50	50	0.262	0.514	0.52	1.03	5.236	10.280				
	2	Unsevied	85	40	0.089	0.624	0.13	0.92	1.301	9.176				
		Unsevied	50	50	0.099	0.678	0.20	1.36	1.981	13.559				
	3	Unsevied	50	50	0.603	0.014	1.21	0.03	12.055	0.285				
		Unsevied	50	50	0.530	0.156	1.06	0.31	10.605	3.125				

	Replicate	Sample	Volume of sample (ml)	Volume of water	Water Concentration		Concentration without diluion		Concentration of nutrient in soil		Average + stdev Concentration of nutrient in soil			
					No3 (mg/l) x 1000	NH4+ (mg/L) x 1000	N03 (g/L)	Nh4+ (g/L)	N03 (mg/g)	Nh4+ (mg/g)	μ N03 (mg/g)	σ N03 (mg/g)	Nh4+ (g/L)	σ NH4+ (mg/g)
2	1	<75μm	84	45	0.078	5.986	0.12	9.19	1.198	91.934	6.12	4.22	14.22	3.80
		<75μm	23	72	0.192	0.246	0.79	1.02	7.930	10.161				
	2	<75μm	85	45	0.183	0.861	0.28	1.32	2.799	13.165				
		<75μm	30	120	0.189	0.285	0.94	1.42	9.429	14.245				
	3	<75μm	50	50	0.175	4.320	0.35	8.64	3.508	86.400				
		<75μm	30	120	0.237	0.386	1.18	1.93	11.848	19.300				
	1	75μm-150μm	89	20	0.128	1.787	0.16	2.19	1.568	21.891	4.20	2.87	19.66	2.97
		75μm-150μm	50	50	0.065	1.143	0.13	2.29	1.306	22.853				
	2	75μm-150μm	50	50	0.338	0.868	0.68	1.74	6.755	17.360				
		75μm-150μm	50	50	0.193	0.794	0.39	1.59	3.859	15.872				
	3	75μm-150μm	29	120	0.146	0.396	0.75	2.03	7.512	20.326				
	1	150μm-300μm	80	40	0.085	3.777	0.13	5.67	1.275	56.655	4.09	2.03	5.79	3.20
		150μm-300μm	50	50	0.142	6.445	0.28	12.89	2.838	128.896				
	2	150μm-300μm	50	50	0.172	0.100	0.34	0.20	3.438	2.002				
		150μm-300μm	50	50	0.290	0.134	0.58	0.27	5.794	2.674				
	3	150μm-300μm	80	40	0.223	0.498	0.33	0.75	3.345	7.470				
		150μm-300μm	50	50	0.225	0.399	0.45	0.80	4.497	7.982				
		150μm-300μm	30	120	0.149	0.176	0.74	0.88	7.447	8.822				
	1	300μm-425μm	81	20	0.239	0.321	0.30	0.40	2.980	4.001	4.98	3.03	6.92	1.68
		300μm-425μm	50	50	0.126	0.293	0.25	0.59	2.527	5.866				
	2	300μm-425μm	50	50	0.192	0.366	0.38	0.73	3.843	7.314				
		300μm-425μm	81	41	0.265	0.521	0.40	0.79	3.991	7.851				
	3	300μm-425μm	50	50	0.290	0.409	0.58	0.82	5.791	8.171				
		300μm-425μm	30	119	0.216	0.167	1.07	0.83	10.726	8.310				
	1	425μm-600μm	80	20	0.168	3.980	0.21	4.98	2.100	49.755	6.57	2.75	16.02	3.73
		425μm-600μm	21	89	0.167	0.420	0.88	2.20	8.756	21.979				
	2	425μm-600μm	20	80	0.199	0.320	0.99	1.60	9.925	16.002				
		425μm-600μm	82	41	0.353	1.086	0.53	1.63	5.289	16.290				
	3	425μm-600μm	49	49	0.329	0.613	0.66	1.23	6.579	12.256				
		425μm-600μm	30	118	0.137	0.275	0.68	1.36	6.751	13.578				
	1	600μm-1.18mm	84	20	0.221	4.45	0.27	0.12	2.736	1.200	3.27	0.96	12.91	1.36
		600μm-1.18mm	21	82	0.084	2.335	0.41	11.45	4.120	114.543				
		600μm-1.18mm	20	80	0.056	2.356	0.28	11.78	2.821	117.823				
	2	600μm-1.18mm	81	40	0.144	0.009	0.22	0.01	2.151	0.137				
		600μm-1.18mm	49	49	0.218	0.020	0.44	0.04	4.365	0.409				
	3	600μm-1.18mm	81	40	0.160	0.800	0.24	1.20	2.390	11.951				
		600μm-1.18mm	30	120	0.087	0.277	0.43	1.39	4.340	13.871				
	1	1.18mm-2.36mm	80	20	0.061	0.302	0.08	0.38	0.763	3.780	3.89	2.52	2.64	0.78
		1.18mm-2.36mm	50	50	0.086	0.157	0.17	0.31	1.723	3.136				
	2	1.18mm-2.36mm	50	50	0.209	0.083	0.42	0.17	4.179	1.665				
		1.18mm-2.36mm	30	120	0.070	0.040	0.35	0.20	3.489	1.985				
	3	1.18mm-2.36mm	51	50	0.275	0.123	0.54	0.24	5.445	2.437				
		1.18mm-2.36mm	30	120	0.154	0.057	0.77	0.29	7.725	2.857				
	1	2.36mm-6.0mm	84	20	0.187	0.534	0.23	0.66	2.315	6.607	3.28	3.01	4.00	3.68
	2	2.36mm-6.0mm	80	40	0.563	0.054	0.84	0.08	8.445	0.812				
		2.36mm-6.0mm	50	50	0.094	0.036	0.19	0.07	1.870	0.717				
	3	2.36mm-6.0mm	80	41	0.046	0.054	0.07	0.08	0.689	0.814				
		2.36mm-6.0mm	50	49	0.155	0.071	0.31	0.14	3.063	1.400				
	1	<2.36mm	80	20	0.401	1.084	0.50	1.35	5.013	13.548	6.75	3.50	15.47	2.42
	2	<2.36mm	30	120	0.181	0.268	0.91	1.34	9.050	13.400				
		<2.36mm	90	450	0.035	1.088	0.21	6.53	2.100	65.280				
	3	<2.36mm	90	450	0.185	0.276	1.11	1.66	11.100	16.560				
		<2.36mm	30	120	0.130	0.368	0.65	1.84	6.500	18.380				
	1	Unsevied	94	20	0.576	1.050	0.70	1.27	6.986	12.734	4.80	2.01	18.10	6.18
		Unsevied	50	50	0.310	0.711	0.62	1.42	6.206	14.219				
	2	Unsevied	85	40	0.186	5.360	0.27	7.88	2.732	78.824				
		Unsevied	50	50	0.232	4.000	0.46	8.00	4.634	80.008				
	3	Unsevied	50	50	0.104	0.949	0.21	1.90	2.078	18.987				
		Unsevied	30	120	0.123	0.529	0.61	2.65	6.138	26.460				

Replicate	Sample	Volume of sample (ml)	Volume of water	No3 (mg/l) x 1000	NH4+ (mg/L) x 1000	N03 (g/L)	Nh4+ (g/L)	N03 (mg/g)	Nh4+ (mg/g)	μ N03 (mg/g)	σ N03 (mg/g)	Nh4+ (mg/g)	σ NH4+ (mg/g)
1	<75μm	50	60	0.170	2.626	0.37	5.78	3.74	57.76	6.26	3.28	12.74	1.04
1	<75μm	20	80	0.210	2.100	1.05	10.50	10.52	105.00				
1	<75μm	50	200	0.044	1.680	0.22	8.40	2.18	84.00				
2	<75μm	40	60	0.205	0.480	0.51	1.20	5.11	12.00				
2	<75μm	30	120	0.087	0.270	0.43	1.35	4.33	13.48				
3	<75μm	50	50	0.381	5.400	0.76	10.80	7.62	108.00				
3	<75μm	30	120	0.206	2.190	1.03	10.95	10.31	109.50				
1	75μm-150μm	40	60	0.145	0.345	0.36	0.86	3.61	8.63	4.55	2.25	12.51	7.47
1	75μm-150μm	50	50	0.161	0.438	0.32	0.88	3.22	8.77				
2	75μm-150μm	50	50	0.141	0.328	0.28	0.66	2.82	6.56				
2	75μm-150μm	31	120	0.182	0.143	0.89	0.70	8.87	6.95				
3	75μm-150μm	50	51	0.184	1.085	0.37	2.19	3.71	21.92				
3	75μm-150μm	29	120	0.099	0.433	0.51	2.23	5.06	22.25				
1	150μm-300μm	40	60	0.057	0.410	0.14	1.03	1.41	10.25	6.38	4.00	8.29	4.04
1	150μm-300μm	50	50	0.180	0.546	0.36	1.09	3.59	10.91				
2	150μm-300μm	50	50	0.555	0.125	1.11	0.25	11.09	2.50				
2	150μm-300μm	50	50	0.570	0.127	1.14	0.25	11.41	2.53				
3	150μm-300μm	80	40	0.174	0.623	0.26	0.93	2.61	9.34				
3	150μm-300μm	50	50	0.381	0.511	0.76	1.02	7.62	10.22				
3	150μm-300μm	30	120	0.139	0.245	0.69	1.22	6.93	12.24				
1	300μm-425μm	81	40	0.267	4.750	0.40	7.10	3.98	70.96	3.54	1.10	8.91	1.34
1	300μm-425μm	50	50	0.248	3.600	0.50	7.20	4.96	72.00				
2	300μm-425μm	40	60	0.174	0.315	0.43	0.79	4.34	7.88				
2	300μm-425μm	81	41	0.151	0.536	0.23	0.81	2.28	8.07				
3	300μm-425μm	50	50	0.115	0.445	0.23	0.89	2.30	8.90				
3	300μm-425μm	30	119	0.068	0.218	0.34	1.08	3.38	10.81				
1	425μm-600μm	40	60	0.210	2.250	0.52	5.63	5.24	56.25	5.72	1.86	13.75	3.06
1	425μm-600μm	30	89	0.059	0.352	0.23	1.39	2.34	13.94				
2	425μm-600μm	80	20	0.550	0.827	0.69	1.03	6.88	10.34				
2	425μm-600μm	50	50	0.382	0.558	0.76	1.12	7.64	11.16				
3	425μm-600μm	49	51	0.317	0.766	0.65	1.56	6.47	15.63				
3	425μm-600μm	31	120	0.118	0.363	0.57	1.77	5.75	17.70				
1	600μm-1.18mm	40	60	0.004	0.400	0.01	1.00	0.10	10.00	2.92	1.16	9.14	6.29
1	600μm-1.18mm	31	89	0.001	0.291	0.00	1.13	0.04	11.28				
1	600μm-1.18mm	80	20	0.305	0.931	0.38	1.16	3.81	11.64				
2	600μm-1.18mm	81	40	0.280	0.0115	0.42	0.02	4.18	0.17				
2	600μm-1.18mm	50	51	0.107	0.029	0.22	0.06	2.17	0.58				
3	600μm-1.18mm	81	40	0.206	1.000	0.31	1.49	3.08	14.94				
3	600μm-1.18mm	30	120	0.027	0.307	0.14	1.53	1.36	15.34				
1	1.18mm-2.36mm	40	60	0.093	0.330	0.23	0.83	2.33	8.25	5.29	2.37	5.33	2.64
1	1.18mm-2.36mm	50	50	0.201	0.449	0.40	0.90	4.01	8.97				
2	1.18mm-2.36mm	40	60	0.355	0.104	0.89	0.26	8.88	2.60				
2	1.18mm-2.36mm	30	120	0.119	0.072	0.59	0.36	5.93	3.60				
3	1.18mm-2.36mm	40	60	0.271	0.154	0.68	0.38	6.77	3.84				
3	1.18mm-2.36mm	31	121	0.078	0.096	0.38	0.47	3.81	4.70				
1	2.36mm-6.0mm	80	40	0.003	0.174	0.00	0.26	0.05	2.61	1.87	0.65	3.28	0.45
2	2.36mm-6.0mm	80	40	0.072	0.209	0.11	0.31	1.08	3.13				
2	2.36mm-6.0mm	50	50	0.123	0.169	0.25	0.34	2.46	3.37				
3	2.36mm-6.0mm	80	40	0.155	0.228	0.23	0.34	2.33	3.43				
3	2.36mm-6.0mm	50	51	0.080	0.191	0.16	0.39	1.62	3.85				
1	<2.36mm	40	60	0.377	0.195	0.94	0.49	9.43	4.88	15.88	8.10	8.25	2.65
1	<2.36mm	30	120	0.440	0.185	2.20	0.93	22.00	9.25				
2	<2.36mm	50	50	0.317	0.306	0.63	0.61	6.34	6.12				
2	<2.36mm	30	120	0.323	0.225	1.62	1.13	16.15	11.25				
3	<2.36mm	5	50	1.055	1.050	11.61	11.55	116.05	115.50				
3	Unsevied	30	120	0.510	0.195	2.55	0.98	25.50	9.75				
1	Unsevied	80	40	0.339	4.600	0.51	6.90	5.09	69.00	8.18	5.00	12.09	9.78
1	Unsevied	30	120	0.231	0.520	1.15	2.60	11.54	26.00				
2	Unsevied	85	40	0.116	0.639	0.17	0.94	1.70	9.40				
2	Unsevied	50	50	0.035	0.494	0.07	0.99	0.70	9.87				
3	Unsevied	50	50	0.416	3.200	0.83	6.40	8.32	64.00				
3	Unsevied	30	120	0.286	0.062	1.43	0.31	14.28	3.08				

Row group header: **3**

Column group headers: Water Concentration (No3 (mg/l) x 1000, NH4+ (mg/L) x 1000) · Concentration without dilution (N03 (g/L), Nh4+ (g/L)) · Concentration of nutrient in soil (N03 (mg/g), Nh4+ (mg/g)) · Average + stdev Concentration of nutrient in soil (μ N03 (mg/g), σ N03 (mg/g), Nh4+ (mg/g), σ NH4+ (mg/g))

Group: 4

				Water Concentration		Concentration without diluion		Concentration of nutrient in soil		Average + stdev Concentration of nutrient in soil			
Replicate	Sample	Volume of sample (ml)	Volume of water	No3 (mg/l) x 1000	NH4+ (mg/L) x 1000	N03 (g/L)	Nh4+ (g/L)	N03 (mg/g)	Nh4+ (mg/g)	μ N03 (mg/g)	σ N03 (mg/g)	Nh4+ (g/L)	σ NH4+ (mg/g)
1	<75μm	40	60	0.591	0.109	1.48	0.27	14.763	2.725	12.63	5.02	15.23	12.99
	<75μm	30	120	0.287	0.112	1.44	0.56	14.350	5.600				
2	<75μm	40	60	0.384	0.956	0.96	2.39	9.588	23.900				
3	<75μm	50	50	0.935	1.436	1.87	2.87	18.7	28.710				
	<75μm	30	120	0.115	1.422	0.58	7.11	5.763	71.090				
1	75μm-150μm	40	60	0.152	0.387	0.38	0.97	3.788	9.675	5.94	1.71	15.97	6.39
	75μm-150μm	50	50	0.279	0.627	0.56	1.25	5.583	12.535				
2	75μm-150μm	51	49	0.276	0.647	0.54	1.27	5.404	12.685				
	75μm-150μm	50	50	0.325	0.982	0.65	1.96	6.503	19.640				
3	75μm-150μm	31	120	0.173	0.520	0.84	2.53	8.445	25.319				
1	150μm-300μm	60	0.3	0.129	2.349	0.13	2.36	1.291	23.607	5.38	3.95	11.52	10.96
	150μm-300μm	50	50	0.059	1.170	0.12	2.34	1.181	23.408				
2	150μm-300μm	50	50	0.410	0.158	0.82	0.32	8.191	3.163				
3	150μm-300μm	80	40	0.435	0.203	0.65	0.30	6.524	3.047				
	150μm-300μm	50	50	0.486	0.219	0.97	0.44	9.714	4.372				
1	300μm-425μm	40	60	0.178	0.208	0.45	0.52	4.450	5.200	8.78	4.06	9.50	2.76
	300μm-425μm	50	50	0.258	0.422	0.52	0.84	5.160	8.430				
2	300μm-425μm	50	50	0.428	0.521	0.86	1.04	8.560	10.423				
3	300μm-425μm	50	50	0.671	0.589	1.34	1.18	13.410	11.783				
	300μm-425μm	50	51	0.610	0.578	1.23	1.17	12.312	11.679				
1	425μm-600μm	40	60	0.2005	0.084	0.50	0.21	5.013	2.100	6.59	1.96	15.65	8.88
	425μm-600μm	21	89	0.185	0.498	0.97	2.61	9.717	26.060				
2	425μm-600μm	50	50	0.256	2.484	0.51	4.97	5.121	49.680				
	425μm-600μm	20	80	0.000	0.407	0.00	2.04	0.010	20.35				
3	425μm-600μm	49	51	0.287	0.719	0.59	1.47	5.853	14.673				
	425μm-600μm	50	51	0.359	0.747	0.72	1.51	7.247	15.083				
1	600μm-1.18mm	40	60	0.07675	0.373	0.19	0.93	1.919	9.325	5.50	3.84	10.98	6.65
	600μm-1.18mm	21	82	0.113	0.089	0.56	0.43	5.566	4.345				
	600μm-1.18mm	49	51	0.233	0.733	0.48	1.50	4.765	14.965				
2	600μm-1.18mm	81	40	0.265	0.200	0.40	0.30	3.951	2.984				
	600μm-1.18mm	48	52	0.200	0.003	0.42	0.01	4.168	0.063				
3	600μm-1.18mm	81	40	0.286	0.943	0.43	1.41	4.272	14.087				
	600μm-1.18mm	30	120	0.277	0.404	1.38	2.02	13.838	20.188				
1	1.18mm-2.36mm	40	60	0.290	0.390	0.72	0.98	7.238	9.750	13.78	7.44	9.20	3.81
	1.18mm-2.36mm	50	50	0.220	0.578	0.44	1.16	4.403	11.565				
2	1.18mm-2.36mm	50	50	0.683	0.018	1.37	0.04	13.663	0.362				
	1.18mm-2.36mm	30	120	0.355	0.237	1.78	1.18	17.758	11.832				
3	1.18mm-2.36mm	51	51	0.722	0.183	1.44	0.37	14.437	3.654				
	1.18mm-2.36mm	30	121	0.5	0.000	2.52	0.00	25.16666667	0.020				
1	2.36mm-6.0mm	40	60	0.080	0.693	0.20	1.73	1.988	17.325	3.37	1.83	6.15	6.33
2	2.36mm-6.0mm	80	40	0.393	0.117	0.59	0.18	5.8875	1.750				
	2.36mm-6.0mm	40	60	0.150	0.138	0.37	0.35	3.738	3.450				
3	2.36mm-6.0mm	80	41	0.082	0.301	0.12	0.46	1.236	4.557				
	2.36mm-6.0mm	40	60	0.160	0.146	0.40	0.37	3.992	3.659				
1	<2.36mm	30	120	0.446	0.519	2.23	2.60	22.300	25.950	21.65	3.87	25.84	3.37
2	<2.36mm	80	41	3.630	1.602	5.49	2.42	54.904	24.224				
	<2.36mm	30	120	0.488	0.432	2.44	2.16	24.400	21.600				
3	<2.36mm	30	120	0.32	0.615	1.60	3.08	16.000	30.750				
	<2.36mm	30	120	0.478	0.534	2.39	2.67	23.900	26.700				
1	Unsevied	40	60	0.008	0.130	0.02	0.33	0.200	3.250	2.57	2.72	8.36	8.95
	Unsevied	50	50	0.010	0.237	0.02	0.47	0.200	4.735				
2	Unsevied	85	40	0.196	6.700	0.29	9.85	2.879	98.529				
	Unsevied	30	120	0.142	4.087	0.71	20.44	7.123	204.350				
3	Unsevied	50	50	0.204	1.088	0.41	2.18	4.082	21.754				
	Unsevied	30	120	0.019	0.074	0.10	0.37	0.950	3.690				

APPENDIX G – PAIRWISE T-TESTS ON THE CUMULATIVE NUTRIENT WITHIN THE FOUR SOIL SAMPLES

NH$_4^+$ Pairwise t-tests

P(x>y)		x		
	Soil 1	Soil 2	Soil 3	Soil 4
Soil 1		0.679	0.665	0.8057
Soil 2	0.321		0.8898	0.9452
Soil 3	0.335	0.1102		0.2677
Soil 4	0.1943	0.0548	0.7323	

(y indicates the row variable)

NO$_3^-$ Pairwise t-tests

P(x>y)		x		
	Soil 1	Soil 2	Soil 3	Soil 4
Soil 1		0.4412	0.374	0.0106
Soil 2	0.5588		0.4052	0.0095
Soil 3	0.626	0.5948		0.0147
Soil 4	0.9894	0.9905	0.9853	

(y indicates the row variable)

No statistical significant ($p>0.05$)

Statistical significance ($p<.05$)

APPENDIX H – RAW DATA: EXCHANGEABLE NH_4^+ AND NO_3^-

10g soil   150ml water

Sample 1 — Water Concentration & Soil Concentration

Sample	Sub-sample	NH4+ (mg/L)	NO3- (mg/l)	Cl- (mg/L)	pH	NH4+ (mg/g)	NO3- (mg/g)	Cl- (mg/g)
1	<75µm	1.01	2.39	6.41	6.82	0.015	0.036	0.096
	<75µm	2.39	0.88	1.80	6.46	0.036	0.013	0.027
	<75µm	1.41	1.75	4.11	7.10	0.021	0.026	0.062
	75µm-150µm	0.81	4.16	7.22	7.27	0.012	0.062	0.108
	75µm-150µm	0.92	3.32	4.23	7.28	0.014	0.050	0.063
	75µm-150µm	1.22	3.20	5.15	6.41	0.018	0.048	0.077
	150µm-300µm	1.03	2.81	1.56	6.63	0.015	0.042	0.023
	150µm-300µm	1.04	2.44	1.76	6.94	0.016	0.037	0.026
	150µm-300µm	1.58	2.44	1.44	6.81	0.024	0.037	0.022
	300µm-425µm	1.28	3.08	2.52	7.52	0.019	0.046	0.038
	300µm-425µm	1.20	1.18	1.23	6.53	0.018	0.018	0.018
	300µm-425µm	0.83	2.69	3.19	6.44	0.012	0.040	0.048
	425µm-600µm	1.01	1.09	1.26	6.50	0.015	0.016	0.019
	425µm-600µm	1.40	1.86	2.42	6.43	0.021	0.028	0.036
	425µm-600µm	1.30	1.22	2.71	7.30	0.019	0.018	0.041
	600µm-1.18mm	0.76	1.29	1.64	7.07	0.011	0.019	0.025
	600µm-1.18mm	0.91	1.90	2.29	6.62	0.014	0.028	0.034
	600µm-1.18mm	1.32	1.82	2.02	6.37	0.020	0.027	0.030
	1.18mm-2.36mm	0.89	2.42	5.57	6.28	0.013	0.036	0.084
	1.18mm-2.36mm	0.91	2.19	4.36	6.62	0.014	0.033	0.065
	1.18mm-2.36mm	1.47	2.08	4.42	6.53	0.022	0.031	0.066
	2.36mm-6.0mm	0.84	4.03	3.68	7.76	0.013	0.060	0.055
	2.36mm-6.0mm	1.28	2.63	4.27	7.59	0.019	0.039	0.064
	2.36mm-6.0mm	1.09	2.90	4.30	7.39	0.016	0.044	0.064
	<2.36mm	0.96	2.18	1.78	6.05	0.014	0.033	0.027
	<2.36mm	1.54	1.94	2.79	6.34	0.023	0.029	0.042
	<2.36mm	0.92	2.32	1.82	7.16	0.014	0.035	0.027
	Unseived	1.11	3.05	3.33	7.05	0.017	0.046	0.050
	Unseived	2.54	1.80	2.65	7.21	0.038	0.027	0.040
	Unseived	1.23	1.90	3.17	6.96	0.018	0.028	0.048
						0.011	0.013	

Sample 1 — Soil Nutrient Concentration (mg/g)

Sample	Sub sumple	µ NH4+ (mg/g)	µ NO3- (mg/g)	µ Cl- (mg/g)	σ NH4+ (mg/g)	σ NO3- (mg/g)	σ Cl- (mg/g)
1	<75µm	0.024	0.025	0.062	0.011	0.011	0.035
	75µm-150µm	0.015	0.053	0.083	0.003	0.008	0.023
	150µm-300µm	0.018	0.038	0.024	0.005	0.003	0.002
	300µm-425µm	0.017	0.035	0.035	0.004	0.015	0.015
	425µm-600µm	0.019	0.021	0.032	0.003	0.006	0.011
	600µm-1.18mm	0.015	0.025	0.030	0.004	0.005	0.005
	1.18mm-2.36mm	0.016	0.033	0.072	0.005	0.003	0.010
	2.36mm-6.0mm	0.016	0.048	0.061	0.003	0.011	0.005
	<2.36mm	0.017	0.032	0.032	0.005	0.003	0.009
	Unseived	0.024	0.034	0.046	0.012	0.010	0.005

Sample 1 — Soil Nutrient Concentration (µg/g)

Sample	Sub sumple	µ NH4+ (µg/g)	µ NO3- (µg/g)	µ Cl- (µg/g)	σ NH4+ (µg/g)	σ NO3- (µg/g)	σ Cl- (µg/g)
1	<75mm	24.027	25.117	61.575	10.660	11.371	34.575
	75mm-150mm	14.773	53.443	83.000	3.173	7.809	22.971
	150mm-300mm	18.233	38.462	23.775	4.735	3.194	2.385
	300mm-425mm	16.545	34.748	34.700	3.610	15.052	14.943
	425mm-600mm	18.510	20.830	31.925	3.007	6.191	11.481
	600mm-1.18mm	14.932	25.032	29.700	4.349	4.956	4.859
	1.18mm-2.36mm	16.315	33.468	71.725	4.916	2.583	10.252
	2.36mm-6.0mm	16.070	47.793	61.225	3.317	11.156	5.221
	<2.36mm	17.105	32.198	31.950	5.218	2.836	8.579
	Unseived	24.398	33.763	45.750	11.903	10.463	5.333

Figure 1: Bar chart (µg/g) of NO3- and NH4+ by sub-sample fraction for Sample 1; accompanying scatter plot of NO3 and NH4+.

Sample 2 — Water Concentration & Soil Concentration

Sample	Sub-sample	NH4+ (mg/L)	NO3- (mg/l)	Cl- (mg/L)	pH	NH4+ (mg/g)	NO3- (mg/g)	Cl- (mg/g)
2	<75µm	1.04	3.75	2.01	7.66	0.016	0.056	0.030
	<75µm	1.53	4.95	2.96	7.11	0.023	0.074	0.044
	<75µm	1.63	4.78	1.89	7.29	0.024	0.072	0.028
	75µm-150µm	1.56	2.99	2.11	7.25	0.023	0.045	0.032
	75µm-150µm	2.12	3.31	2.01	7.79	0.032	0.050	0.030
	75µm-150µm	2.56	4.13	2.93	7.50	0.038	0.062	0.044
	150µm-300µm	1.25	2.14	2.16	6.82	0.019	0.032	0.032
	150µm-300µm	1.14	1.88	3.32	6.78	0.017	0.028	0.050
	150µm-300µm	2.83	2.85	3.33	7.05	0.042	0.043	0.050
	300µm-425µm	2.11	1.60	2.08	7.21	0.032	0.024	0.031
	300µm-425µm	1.23	1.70	3.17	6.96	0.018	0.025	0.048
	300µm-425µm	1.08	2.10	2.78	6.64	0.016	0.031	0.042
	425µm-600µm	0.92	1.68	2.15	6.66	0.014	0.025	0.032
	425µm-600µm	1.55	3.83	2.58	7.12	0.023	0.057	0.039
	425µm-600µm	1.21	3.14	2.63	7.72	0.018	0.047	0.039
	600µm-1.18mm	1.14	5.60	3.77	7.73	0.017	0.084	0.057
	600µm-1.18mm	0.82	3.95	3.31	7.47	0.012	0.059	0.050
	600µm-1.18mm	2.01	4.89	3.33	6.52	0.030	0.073	0.050
	1.18mm-2.36mm	0.94	4.79	2.29	6.71	0.014	0.072	0.034
	1.18mm-2.36mm	1.40	3.87	1.97	6.82	0.021	0.058	0.029
	1.18mm-2.36mm	1.60	3.04	3.09	7.76	0.024	0.046	0.046
	2.36mm-6.0mm	0.70	1.00	3.03	7.49	0.011	0.015	0.045
	2.36mm-6.0mm	1.12	2.75	3.03	6.78	0.017	0.041	0.045
	2.36mm-6.0mm	1.09	2.55	2.26	7.23	0.016	0.038	0.034
	<2.36mm	2.14	4.22	2.93	7.71	0.032	0.063	0.044
	<2.36mm	1.40	4.45	3.64	7.18	0.021	0.067	0.055
	<2.36mm	1.37	5.41	2.38	6.63	0.020	0.081	0.036
	Unseived	0.95	1.19	2.09	7.71	0.014	0.018	0.031
	Unseived	2.09	3.76	1.67	7.18	0.031	0.056	0.025
	Unseived	1.45	4.51	2.18	6.63	0.022	0.068	0.033

Sample 2 — Soil Nutrient Concentration (mg/g)

Sample	Sub sumple	µ NH4+ (mg/g)	µ NO3- (mg/g)	µ Cl- (mg/g)	σ NH4+ (mg/g)	σ NO3- (mg/g)	σ Cl- (mg/g)
2	<75µm	0.021	0.067	0.034	0.005	0.010	0.009
	75µm-150µm	0.031	0.052	0.035	0.008	0.009	0.008
	150µm-300µm	0.026	0.034	0.044	0.014	0.008	0.010
	300µm-425µm	0.022	0.027	0.040	0.008	0.004	0.008
	425µm-600µm	0.018	0.043	0.037	0.005	0.016	0.004
	600µm-1.18mm	0.020	0.072	0.052	0.009	0.012	0.004
	1.18mm-2.36mm	0.020	0.059	0.037	0.005	0.013	0.009
	2.36mm-6.0mm	0.015	0.032	0.042	0.003	0.014	0.007
	<2.36mm	0.025	0.070	0.045	0.007	0.009	0.009
	Unseived	0.022	0.047	0.030	0.009	0.026	0.004

Sample 2 — Soil Nutrient Concentration (µg/g)

Sample	Sub sumple	µ NH4+ (µg/g)	µ NO3- (µg/g)	µ Cl- (µg/g)	σ NH4+ (µg/g)	σ NO3- (µg/g)	σ Cl- (µg/g)
2	<75mm	20.990	67.420	34.275	4.733	9.760	8.818
	75mm-150mm	31.200	52.160	35.225	7.518	8.864	7.597
	150mm-300mm	26.103	34.382	44.050	14.180	7.555	10.089
	300mm-425mm	22.137	26.972	40.125	8.313	3.939	8.278
	425mm-600mm	18.407	43.248	36.750	4.746	16.448	3.915
	600mm-1.18mm	19.830	72.220	52.025	9.262	12.409	3.923
	1.18mm-2.36mm	19.692	58.520	36.725	5.084	13.113	8.685
	2.36mm-6.0mm	14.522	31.527	41.575	3.492	14.394	6.712
	<2.36mm	24.547	70.417	44.750	6.547	9.470	9.475
	Unseived	22.450	47.300	29.700	8.571	26.117	4.083

Figure 2: Bar chart (µg/g) of NO3- and NH4+ by sub-sample fraction for Sample 2; accompanying scatter plot of NH4+ and NO3-.

Sample 3

Sample	Sub-sample	NH₄⁺ (mg/L)	NO₃⁻ (mg/l)	Cl⁻ (mg/L)	pH
	<75µm	1.09	0.83	3.31	7.80
	<75µm	1.21	3.84	9.83	7.91
	<75µm	2.50	5.18	5.72	7.37
	75µm-150µm	1.95	9.27	3.24	7.16
	75µm-150µm	1.04	9.37	2.58	7.55
	75µm-150µm	2.32	7.49	2.84	7.22
	150µm-300µm	1.03	1.88	1.84	7.32
	150µm-300µm	1.29	7.13	2.65	7.91
	150µm-300µm	0.78	1.77	1.69	7.16
	300µm-425µm	1.76	4.38	1.63	7.27
	300µm-425µm	0.75	13.05	1.29	7.91
	300µm-425µm	1.58	10.12	0.49	7.43
	425µm-600µm	0.97	2.80	1.00	7.92
3	425µm-600µm	1.89	4.48	2.34	7.95
	425µm-600µm	0.69	4.67	2.24	7.47
	600µm-1.18mm	2.01	3.54	0.86	7.72
	600µm-1.18mm	0.77	5.00	1.09	7.09
	600µm-1.18mm	0.82	6.86	1.96	7.50
	1.18mm-2.36mm	0.56	11.50	0.91	7.94
	1.18mm-2.36mm	0.97	5.24	1.58	7.07
	1.18mm-2.36mm	0.78	4.77	0.86	7.51
	2.36mm-6.0mm	1.67	12.20	0.79	7.50
	2.36mm-6.0mm	0.81	5.94	0.53	7.62
	2.36mm-6.0mm	1.86	6.29	1.41	5.90
	<2.36mm	1.05	2.85	0.52	7.16
	<2.36mm	0.78	1.62	0.39	7.60
	<2.36mm	0.70	7.15	1.42	7.20
	Unseived	0.65	1.56	3.21	7.74
	Unseived	1.85	3.52	2.05	7.03
	Unseived	1.43	1.87	2.71	7.24

NH₄⁺ (mg/g)	NO₃⁻ (mg/g)	Cl⁻ (mg/g)
0.016	0.012	0.050
0.018	0.058	0.147
0.038	0.078	0.086
0.029	0.139	0.049
0.016	0.141	0.039
0.035	0.112	0.043
0.015	0.028	0.028
0.019	0.107	0.040
0.012	0.026	0.025
0.026	0.066	0.024
0.011	0.20	0.019
0.024	0.15	0.007
0.015	0.04	0.015
0.028	0.07	0.035
0.010	0.07	0.034
0.030	0.05	0.013
0.012	0.07	0.016
0.012	0.10	0.029
0.008	0.17	0.014
0.015	0.08	0.024
0.012	0.07	0.013
0.025	0.18	0.012
0.012	0.09	0.008
0.028	0.09	0.021
0.016	0.04	0.008
0.012	0.02	0.006
0.011	0.11	0.021
0.010	0.02	0.048
0.028	0.05	0.031
0.021	0.03	0.041

Soil Nutrient Concentration (mg/g)

Sample	Sub sumple	µ NH₄⁺ (mg/g)	µ NO₃⁻ (mg/g)	µ Cl⁻ (mg/g)	σ NH₄⁺ (mg/g)	σ NO₃⁻ (mg/g)	σ Cl⁻ (mg/g)
	<75µm	0.024	0.049	0.094	0.012	0.033	0.049
	75µm-150µm	0.027	0.131	0.043	0.010	0.016	0.005
	150µm-300µm	0.016	0.054	0.031	0.004	0.046	0.008
	300µm-425µm	0.020	0.109	0.017	0.008	0.061	0.009
3	425µm-600µm	0.018	0.060	0.028	0.009	0.015	0.011
	600µm-1.18mm	0.018	0.077	0.020	0.011	0.025	0.009
	1.18mm-2.36mm	0.012	0.108	0.017	0.003	0.056	0.006
	2.36mm-6.0mm	0.022	0.122	0.014	0.008	0.053	0.007
	<2.36mm	0.013	0.058	0.012	0.003	0.044	0.008
	Unseived	0.020	0.035	0.040	0.009	0.016	0.009

Soil Nutrient Concentration (µg/g)

Sample	Sub sumple	µ NH₄⁺ (µg/g)	µ NO₃⁻ (µg/g)	µ Cl⁻ (µg/g)	σ NH₄⁺ (µg/g)	σ NO₃⁻ (µg/g)	σ Cl⁻ (µg/g)
	<75mm	23.988	49.252	94.275	11.738	33.437	49.457
	75mm-150mm	26.537	130.640	43.250	9.903	15.883	5.027
	150mm-300mm	15.500	53.885	30.900	3.825	45.985	7.746
	300mm-425mm	20.442	108.725	17.050	8.076	60.847	8.779
3	425mm-600mm	17.767	59.745	27.875	9.397	15.438	11.173
	600mm-1.18mm	18.012	76.998	19.550	10.519	24.972	8.703
	1.18mm-2.36mm	11.560	107.562	16.750	3.092	56.348	6.031
	2.36mm-6.0mm	21.690	122.160	13.625	8.409	52.752	6.813
	<2.36mm	12.627	58.120	11.625	2.763	43.559	8.371
	Unseived	19.683	34.753	39.800	9.116	15.766	8.763

Chart 3 — bar chart (µg/g) of NO₃⁻ and NH₄⁺ by sub-sample size (<75mm, 75mm-150mm, 150mm-300mm, 300mm-425mm, 425mm-600mm, 600mm-1.18mm, 1.18mm-2.36mm, 2.36mm-6.0mm, <2.36mm, Unseived)

Scatter plots (Sample 3): NH4+ and NO3-

Sample 4

Sample	Sub-sample	NH₄⁺ (mg/L)	NO₃⁻ (mg/l)	Cl⁻ (mg/L)	pH
	<75µm	5.00	9.56	5.46	6.43
	<75µm	0.63	13.74	5.46	6.11
	<75µm	2.50	11.94	4.96	6.05
	75µm-150µm	0.50	11.10	5.72	6.83
	75µm-150µm	3.20	13.95	5.72	6.08
	75µm-150µm	2.50	9.54	4.49	6.19
	150µm-300µm	9.00	9.77	2.72	6.38
	150µm-300µm	3.60	11.50	4.32	6.54
	150µm-300µm	4.62	8.84	3.52	6.04
	300µm-425µm	0.62	11.30	4.66	6.24
	300µm-425µm	1.50	9.99	4.49	6.30
	300µm-425µm	0.33	11.85	3.87	6.57
	425µm-600µm	5.63	10.50	3.40	6.11
4	425µm-600µm	0.66	10.92	1.89	6.30
	425µm-600µm	3.02	9.46	2.00	6.27
	600µm-1.18mm	4.55	6.50	1.58	6.60
	600µm-1.18mm	0.99	12.17	6.91	6.27
	600µm-1.18mm	1.09	11.01	4.67	6.60
	1.18mm-2.36mm	5.22	5.48	5.72	6.03
	1.18mm-2.36mm	4.30	10.84	5.58	6.53
	1.18mm-2.36mm	1.20	10.63	3.96	6.45
	2.36mm-6.0mm	3.29	11.50	6.91	6.73
	2.36mm-6.0mm	0.37	11.22	3.25	6.20
	2.36mm-6.0mm	0.43	14.65	4.34	6.51
	<2.36mm	2.45	6.540	2.54	6.97
	<2.36mm	9.00	9.77	2.31	6.71
	<2.36mm	4.64	12.36	2.27	6.84
	Unseived	1.88	14.22	2.54	6.97
	Unseived	6.54	5.67	2.31	6.71
	Unseived	4.01	10.34	2.27	6.84

NH₄⁺ (mg/g)	NO₃⁻ (mg/g)	Cl⁻ (mg/g)
0.075	0.143	0.082
0.009	0.206	0.082
0.038	0.179	0.074
0.008	0.167	0.086
0.048	0.209	0.086
0.038	0.143	0.067
0.135	0.147	0.041
0.054	0.173	0.065
0.069	0.133	0.053
0.009	0.170	0.070
0.023	0.150	0.067
0.005	0.178	0.058
0.084	0.158	0.051
0.010	0.164	0.028
0.045	0.142	0.030
0.068	0.098	0.024
0.015	0.182	0.104
0.016	0.165	0.070
0.078	0.082	0.086
0.065	0.163	0.084
0.018	0.159	0.059
0.049	0.173	0.104
0.006	0.168	0.049
0.006	0.220	0.065
0.037	0.098	0.038
0.135	0.147	0.035
0.070	0.185	0.034
0.028	0.213	0.038
0.098	0.085	0.035
0.060	0.155	0.034

Soil Nutrient Concentration (mg/g)

Sample	Sub sumple	µ NH₄⁺ (mg/g)	µ NO₃⁻ (mg/g)	µ Cl⁻ (mg/g)	σ NH₄⁺ (mg/g)	σ NO₃⁻ (mg/g)	σ Cl⁻ (mg/g)
	<75µm	0.041	0.176	0.079	0.033	0.031	0.004
	75µm-150µm	0.031	0.173	0.080	0.021	0.034	0.011
	150µm-300µm	0.086	0.151	0.053	0.043	0.020	0.012
	300µm-425µm	0.012	0.166	0.065	0.009	0.014	0.006
4	425µm-600µm	0.046	0.154	0.036	0.037	0.011	0.013
	600µm-1.18mm	0.033	0.148	0.066	0.030	0.045	0.040
	1.18mm-2.36mm	0.054	0.135	0.076	0.032	0.046	0.015
	2.36mm-6.0mm	0.020	0.187	0.072	0.025	0.029	0.028
	<2.36mm	0.080	0.143	0.036	0.050	0.044	0.002
	Unseived	0.062	0.151	0.036	0.035	0.064	0.002

Soil Nutrient Concentration (µg/g)

Sample	Sub sumple	µ NH₄⁺ (µg/g)	µ NO₃⁻ (µg/g)	µ Cl⁻ (µg/g)	σ NH₄⁺ (µg/g)	σ NO₃⁻ (µg/g)	σ Cl⁻ (µg/g)
	<75mm	40.603	176.220	79.400	32.880	31.473	4.330
	75mm-150mm	31.000	172.993	79.650	21.018	33.555	10.652
	150mm-300mm	86.083	150.530	52.800	43.044	20.275	12.000
	300mm-425mm	12.243	165.710	65.100	9.147	14.370	6.237
4	425mm-600mm	46.493	154.397	36.408	37.283	11.265	12.664
	600mm-1.18mm	33.125	148.383	65.800	30.363	44.908	40.144
	1.18mm-2.36mm	53.600	134.772	76.275	31.593	45.557	14.655
	2.36mm-6.0mm	20.431	186.814	72.450	24.984	28.550	28.230
	<2.36mm	80.465	143.325	35.600	50.011	43.702	2.186
	Unseived	62.125	151.150	35.600	34.995	64.216	2.186

Chart 4 — bar chart (µg/g) of NO₃⁻ and NH₄⁺ by sub-sample size

Scatter plots (Sample 4): NO3- and NH4+

APPENDIX I - RAW DATA:RECOVERABLE NH$_4^+$ AND NO$_3^-$

Soil	10	g
Extractant	100	ml

Legend: Outside of WQM range (pink) · Within WQM range (green)

Sample	Replicate	#	Volume Sample (ml)	Volume DI (ml)	Water Conc NO₃ (mg/l) x1000	Water Conc NH₄⁺ (mg/L) x1000	Pre-dilution NO₃ (g/L)	Pre-dilution NH₄⁺ (g/L)	Soil NO₃ (mg/g)	Soil NH₄⁺ (mg/g)	Soil NO₃ (mg/g)	Soil NH₄⁺ (mg/g)	μ NO₃ (mg/g)	σ NO₃ (mg/g)	NH₄⁺ (mg/g)	σ NH₄⁺ (mg/g)	NO₃ Natural Release (mg/g)	NO₃ % Released	NO₃ % Adsorbed	NH₄⁺ Natural Release (mg/g)	NH₄⁺ % Released	NH₄⁺ % Adsorbed
4	1	1	50	100	144	0.980	432.00	2.94	4320.00	29.40	24.96	23.21	23.88	1.53	17.84	7.58	0.1618	0.673%	99.327%	0.0583	0.326%	99.674%
		1	50	100	0.832	0.567	2.50	1.70	24.96	17.01												
		2	60	60	99	0.570	198.00	1.14	1980.00	11.40	22.80	12.48										
		2	50	100	0.760	0.452	2.28	1.36	22.80	13.56												
	2	1	60	60	2.600	0.550	5.20	1.10	52.00	11.00	52.00	11.00	101.90	70.57	11.00	0.00	0.2633	0.258%	99.742%	0.0165	0.150%	99.850%
		2	50	100	99	0.034	297.00	0.10	2970.00	1.02	151.80	11.00										
		2	50	200	49	0.220	245.00	1.10	2450.00	11.00												
		2	50	500	1.380	0.070	15.18	0.77	151.80	7.70												
	3	1	50	100	0.500	0.370	1.50	1.11	15.00	11.10	15.00	11.10	13.65	1.91	15.45	6.15	0.1307	0.948%	99.052%	0.0170	0.110%	99.890%
		2	50	100	0.410	0.660	1.23	1.98	12.30	19.80	12.30	19.80										
3	2	1	60	60	99	0.120	198.00	0.24	1980.00	2.40	49.20	2.40	28.58	29.17	2.21	0.27	0.0048	0.017%	99.983%	0.0096	0.431%	99.569%
		1	50	100	33	0.023	99.00	0.07	990.00	0.69												
		1	50	150	1.230	0.013	4.92	0.05	49.20	0.52												
		2	60	60	0.420	0.101	0.84	0.20	8.40	2.02	7.95	2.02										
		2	50	100	0.250	0.006	0.75	0.02	7.50	0.17												
	3	1	50	75	0.360	0.510	0.90	1.28	3.58	5.07	3.58	5.07	4.79	1.720563	4.57	0.705656	0.0710	1.458%	98.542%	0.0296	0.643%	99.357%
		2	50	150	0.378	0.256	1.51	1.02	6.01	4.07	6.01	4.07										
2	1	1	50	50	5.485	0.117	10.97	0.23	109.69	2.34	69.61	2.34	44.69	35.23925	9.70	10.3971	0.0863	0.193%	99.807%	0.0355	0.364%	99.636%
		1	50	100	2.320	0.037	6.96	0.11	69.61	1.12												
		2	50	50	104	0.852	208.84	1.70	2088.36	17.05	19.78	17.05										
		2	50	50	11	0.006	21.09	0.01	210.95	0.11												
		2	50	75	0.791	0.012	1.98	0.03	19.78	0.31												
	2	1	60	60	7.716	0.576	15.43	1.15	154.32	11.52	97.93	11.52	71.22	37.77175	8.55	4.19755	0.1012	0.142%	99.858%	0.0782	0.906%	99.094%
		1	50	100	3.264	0.012	9.79	0.04	97.93	0.37												
		2	60	60	147	0.279	293.80	0.56	2937.95	5.58	44.51	5.58										
		2	50	100	15	0.002	44.51	0.01	445.14	0.05												
		2	50	150	1.113	0.004	4.45	0.02	44.51	0.16												
	3	1	50	50	41	0.057	82.12	0.11	821.15	1.14	84.00	1.14	84.00	N/A	4.70	5.04	0.0248	0.030%	99.970%	0.0743	1.555%	98.445%
		1	50	300	1.2	0.018	8.40	0.13	84.00	1.27												
		2	50	50	782	0.413	1563.35	0.83	15633.52	8.27		8.27										
		2	50	150	79	0.003	315.83	0.01	3158.29	0.11												
1	1	1	50	50	1.474	0.001	2.95	0.00	29.48	0.02	27.94	12.30	89.43	86.96	9.14	4.48	0.0092	0.010%	99.990%	0.1828	1.962%	98.038%
		1	90	50	2.187	0.518	3.40	0.81	34.02	8.06												
		1	90	150	0.761	0.621	2.03	1.65	20.30	16.55												
		2	50	100	160	0.270	481.14	0.81	4811.40	8.10	150.92	5.97										
		2	50	200	12	0.077	57.51	0.38	575.10	3.83												
		2	50	300	2.156	0.058	15.09	0.40	150.92	4.04												
	2	1	50	50	1.511	0.001	3.02	0.00	30.21	0.02	28.63	10.96	24.72	5.53	10.97	0.01	0.0168	0.068%	99.932%	0.0143	0.130%	99.870%
		1	90	50	2.241	0.462	3.49	0.72	34.86	7.18												
		2	90	150	0.780	0.553	2.08	1.47	20.81	14.73	20.81	10.97										
		2	50	100	164	0.241	493.02	0.72	4930.20	7.22												
	3	1	50	50	0.937	0.001	1.87	0.00	18.75	0.02	17.76	13.65	94.23	108.14	9.82	5.42	0.0293	0.031%	99.969%	0.0142	0.144%	99.856%
		1	90	50	1.391	0.575	2.16	0.89	21.63	8.95												
		1	90	150	0.484	0.689	1.29	1.84	12.91	18.36												
		2	60	60	102	0.300	203.94	0.60	2039.40	5.99	170.70	5.99										
		2	50	100	7.313	0.085	21.94	0.26	219.39	2.55												
		2	50	200	3.414	0.064	17.07	0.32	170.70	3.20												