NATIONAL UNIVERSITY OF IRELAND GALWAY

MITIGATION TECHNIQUES FOR THE TREATMENT OF NUTRIENT LOSSES FROM AGRICULTURAL SYSTEMS IN IRELAND

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This work is dedicated to my amazing wife Alexandra, to our son Maximilian, who was born on 21st December 2008 with Edwards Syndrome and lived for a precious 35 minutes. I miss him every day. Our second child Marlene was born on the 12th June 2010 and as I finish this work keeps me laughing.

For Maximilian
This is a song for a son
This is a song for a sailor
The son I never had
This is a song for a kid
This is the song for a tailor
Who stitched up my old heart
Who stitched up my old heart

This is a song for a dove
This is a song for a blown up bird
The kind that don't return to the nest
This is a song for a star
This is a song for a space invader
Who flew into the sun
Never to return
Never to return

And I am one of many, many more to come, many more to come
And I am one of many more, many more to come, many more to come

-William Patrick Corgan

ABSTRACT

Agriculture management is a landscape issue impacting on water quality. The Water Framework Directive (WFD) aims to achieve ‘at least good status’ in ground and surface waters by 2015. Good status means both ‘good ecological status’ and ‘good chemical status’. Implementation of mitigation measures called “programmes of measures” (POM) to prevent nutrient loss must be in place by 2012. In Ireland, the Nitrates Directive is the basic POM in place. While the WFD aims to prevent nutrient losses from agricultural activities, it does not account for nutrients already lost in runoff or through leaching to shallow groundwater.

The aim of this study was to investigate P and nitrogen (N) mitigation techniques suitable for Irish conditions. For P mitigation, iron ochre originating from copper-sulphur (Cu - S) mines in Avoca, Co. Wicklow was investigated. This was the first time internationally that a metal mining ochre was fully characterised. A maximum P adsorption capacity of 16 to 21 g P kg-1 was determined. Kinetics experiments showed that P adsorption occurred quickly - 97% within 5 min. To investigate the site-specific maximum P adsorption capacity, samples of ochre were analysed for iron (Fe) mineralogy. X-ray diffraction exhibited an Fe mineralogy consisting of jarosite, minor amounts of ferrihydrite and the end product goethite. Goethite was the dominant Fe mineral present on site. The absence of schwertmannite in the Avoca sample restricted the available surface area for adsorption, thereby reducing the maximum P adsorption capacity. In the Avoca samples, P adsorption to oolites and diatoms was present. Inductively coupled plasma mass spectroscopy (ICP-MS) and bulk energy-dispersive X-ray spectroscopy (EDX) investigations exhibited potentially toxic concentrations of Fe, zinc (Zn), lead (Pb), arsenic (As) and copper (Cu). When added to soil, ochre sequestered enough P to protect a waterbody from P losses, but toxic levels of metal release was problematic**.**

For N mitigation, a permeable reactive barrier (PRB), comprising carbon-rich media such as woodchip, was chosen for investigation. As a nitrate plume migrates through the reactive media, nitrate is transformed to the gaseous phase, thereby protecting a down-gradient sensitive receptor. A 4.2 ha site with known nitrate shallow groundwater pollution from a dirty water irrigator was chosen. Using site and groundwater characterisation techniques and geochemistry data from 17 piezometers over a 2-yr period, the location of a PRB on site was determined. Contaminant mass flux calculations showed attenuation on site, but did not point to any transformational processes. Using this data together with denitrification rates from soil and woodchip and soil samples, the dimensions of the PRB were calculated and a location was identified. On the same site, another approach investigated the spatial distribution of nitrate and chloride on site. This showed that saturated hydraulic conductivity (k_s) and distance from source were significant parameters for shallow groundwater nitrate prediction. For chloride, k_s and elevation (m AOD) were significant. The addition of denitrification parameters to the predictive model identified that parameters such as N_2/Argon (Ar) ratio, redox potential and nitrous oxide (N_2O) agreed best with the nitrate distribution on site. The second methodology enabled large savings as it showed that natural attenuation on site was sufficient to protect a sensitive receptor.

In PRB research, denitrification potential within the reactive media of a PRB changes over time, but methodological constraints make the quantification of this potential unfeasible. A new methodology was developed to address this. Using $\delta^{15}N/\delta^{18}O$ isotopes, eight wells were divided into indicative ‘high denitrification’ and ‘low denitrification’ wells. Two ‘low denitrification’ wells with high nitrate concentration were amended with woodchip to enhance denitrification. Water samples were retrieved from all wells using a low-flow syringe and analysed for N_2/Ar ratio using Membrane Inlet Mass Spectrometry. Results showed that there was good agreement with respect to denitrification identification between stable isotope, chemical (N_2/Ar ratio and dissolved organic C (DOC)) and physio-chemical (dissolved oxygen, temperature, conductivity and pH) parameters. Such techniques were able to pick up on small changes in denitrification potential.

Overall the P control technology chosen was effective at P sequestration but could not be used due to high metal losses. For N remediation a number of knowledge gaps were developed, which allowed a more accurate method of identifying areas of natural attenuation on site. Further research should now focus on pollution swapping using column and field scale denitrification bioreactors.

DECLARATION

This dissertation is the result of my own work, except, where explicit reference is made to the work of others, and has not been submitted for another qualification to this or any other university.

Owen Fenton

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ABBREVIATIONS

A	A constant related to the binding strength of molecules onto the ochre
Ae	**A**ctual **E**vapotranspiration
A_i	**A**rea of ***i*th** plot (m^2)
AIC	**A**kaike's **I**nformation **C**riterion
Al	Aluminium
Alum	**Alum**inium
AMD	**A**cid **M**ine **D**rainage
AOD	Above Ordnance Datum
Ar	Argon
As	Arsenic
b_{ad}	Theoretical amount of P adsorbed to form a complete monolayer on the surface
b_{aq}	**aq**uifer thickness (m)
Bgl	Below Ground Level
BMP	**B**est **M**anagement **P**ractice
BOD	**B**iological **O**xygen **D**emand
Br^-	Bromide
b_{wt}	Distance from the **w**ater**t**able height to the bottom of the well
C	Carbon
CAN	**C**alcium **A**mmonium **N**itrate
Cd	Cadmium
C_e	**C**oncentration of P in solution at **e**quilibrium
CEC	**C**ation **E**xchange **C**apacity
CH_4	Methane
C_i	**C**oncentration of constituent in ***i*th** plot (g L^{-1})
Cl	Chloride
$C_{\max}$	**Max**imum N **c**oncentration expected
COD	**C**hemical **O**xygen **D**emand
Cr	Chromium
$C_{treated}$	Desired N **c**oncentration after **treat**ment/remediation
Cu	Copper
D	Length of the well screen
D	**D**istance from the watertable to the impermeable zone
D	**D**iameter of buffer zone (m)
dh/dx	Hydraulic gradient
DM	**D**ry **M**atter
DOC	**D**issolved **O**rganic **C**arbon
e_a	Actual vapour pressure curves (kPa ºC^{-1}
EDX	**E**nergy **D**ispersive **X**-ray analysis
EEC	**E**uropean **E**conomic **C**ommunity

Eh	Redox Potential
EQS	**E**nvironmental **Q**uality **S**tandard
e_s	Saturation vapour pressure curves (kPa $^{o}C^{-1}$
ET_0	Potential **E**vapo**t**ranspiration
EU	**E**uropean **U**nion
$E(y)$	The magnitude of variance of each measurement as a function of the predicted value
Fe	Iron
FYM	**F**arm**y**ard **M**anure
g^{-1}	Link function (ln)
GC	**G**as **C**hromatography
GHG	**G**reen**h**ouse **G**as
GLMM	**G**eneralised **L**inear **M**ixed **M**odel
HCl	Hydrochloric Acid
HNO_3	Hydrogen Nitrate
h_t	**H**ead in the well at **t**ime $t>t_o$.
IGV	**I**nterim **G**uideline **V**alue
K	Potassium
KH_2PO_4	Potassium Phosphate
k_s	Saturated hydraulic conductivity (m day^{-1})
LR	**L**ime **R**equirement
LTPS	**L**ower **T**enches **P**it **S**tream
LU	**L**ivestock **U**nits
M3P	**M**ehlich **3** **P**hosphorus
MAC	**M**aximum **A**dmissible **C**oncentration
Mg	Magnesium
MIMS	**M**embrane **I**nlet **S**pectroscopy
Mn	Manganese
MRP	**M**olybdate **R**eactive **P**hosphorous
N	**N**itrogen
n	Total porosity
Na	Sodium
NBL	**N**atural **B**ackground **L**evels of Cl^-
n_e	**E**ffective porosity
NH_4-N	Ammonium-N
NH_3	Ammonia
Ni	Nickel
nitrite-N	Nitrite nitrogen
N_{IN}	Up-gradient **N**itrate contaminant mass flux (**in** to the PRB)
NO_3^-	Nitrate
NO_x	Nitrogen Oxide
N_{OUT}	The down-gradient **N**itrate contaminant mass flux (**out** of the PRB)
N_2O	Nitrous Oxide
N_2	Di-nitrogen

O_2	Oxygen
P	**P**hosphorus
P_{added}	**P added** in the batch experiments
PAM	**P**oly**a**cryla**m**ide
Pb	Lead
POM	**P**rogramme **o**f **M**easures
PRB	**P**ermeable **R**eactive **B**arrier
ProportionalP-%	**Proportion** of **P** not adsorbed after P equilibrium
PSD	**P**article **S**ize **D**istribution
P_{soln}	**P** in **sol**utio**n** that has not been adsorbed to the ochre
Q	Discharge (m^3 day^{-1})
q_i	Specific discharge in ***i*th** plot (m day^{-1})
R	Denitrification **r**ate (μg N kg^{-1} d^{-1}
RBD	**R**iver **B**asin **D**istrict
r_c	**R**adius of the unscreened part of the well
RDO	**R**ugged **D**issolved **O**xygen (μg L^{-1})
R_e	Radial distance over which the difference in head
REPS	**R**ural **E**nvironmental **P**rotection **S**cheme
R_n	Net radiation at the crop surface (m^{-2} day^{-1})
RP	**R**eaction **P**rogress
r_w	Horizontal distance (**r**adius) from the **w**ell centre to the undisturbed aquifer
S	Sulphur
SEM	**S**canning **E**lectron **M**icroscope
SMD	**S**oil **M**oisture **D**eficit
SO_4	Sulphate
SS	**S**uspended **S**ediment/**S**olid
STP	**S**oil **T**est **P**hosphorus
T_a	Air temperature at a 2 m height (°C)
T	**T**ransmissivity (m^2 day^{-1})
TDS	**T**onnes **D**ry **S**olids
TOC	**T**otal **O**rganic **C**arbon
TON	**T**otal **O**xidized **N**itrogen
TP	**T**otal **P**hosphorus
T_0	Slug test – **t**ime zero (**0**)
U_2	Wind speed at a 2 m height (m s^{-1}),
w(flux)	Total mass **flux** across a control plane (g m^3 day^{-1})
WFD	**W**ater **F**ramework **D**irective
WTR	**W**astewater **T**reatment **R**esidual
x/m	**M**ass of P adsorbed per unit mass of amendment **x** (ochre)
XRD	**X** –**r**ay **D**iffraction

Zn	Zinc
ZOC	**Z**one **o**f **C**ontribution
$X\beta$	Linear predictor
Γ	Psychrometric constant (kPa ºC^{-1}).
ρ_b	Bulk density (kg m^{-3})
ρ_d	Particle density (kg m^{-3})
W	**W**idth (m)
μ	Distribution mean (*ProportionalP*)

Chapter 1 Introduction

1.1 Overview

The implementation of the Water Framework Directive (WFD; 2000/60/EC; OJEC, 2000) in Ireland under S.I. 722 European Communities (Water Policy) Regulations in 2000 has ensured an integrated water resource management approach to the protection of all waters and the achievement of “good status” for all surface waters and groundwater-dependent terrestrial ecosystems. Good status’ means both ‘good ecological status’ and ‘good chemical status’. The WFD classification scheme for water quality includes five status classes: high, good, moderate, poor and bad. High status’ is defined as the biological, chemical and morphological conditions associated with no or very low human pressure. This is also called the ‘reference condition’ as it is the best status achievable i.e. the benchmark. These reference conditions are type-specific, so they are different for different types of rivers, lakes or coastal waters so as to take into account the broad diversity of ecological regions in Europe.

Assessment of quality is based on the extent of deviation from these reference conditions, following the definitions in the Directive. ‘Good status’ means ‘slight’ deviation, ‘moderate status’ means ‘moderate’ deviation, and so on. The definition of ecological status takes into account specific aspects of the biological quality elements, for example “composition and abundance of aquatic flora” or “composition, abundance and age structure of fish fauna”

Agricultural management has been identified as a landscape pressure impacting on water quality in the European Union (EU), specifically with respect to phosphorus (P) and nitrogen (N) (Stark & Richards, 2008). Such transfers from agriculture to water occur in three different ways: a) *point source losses* from farmyards and excessive rates of soiled water application through the use of rotational irrigators; b) *diffuse losses* from soil; which is related to soil P and N concentrations in excess of crop requirements and c) *incidental losses* from direct losses of fertilizer or manures to water during slurry application, or where a rainfall event occurs immediately after application (Preedy et al., 2001).

Adverse impacts on the quality of waters can originate in many forms such as chemical pollution (pesticides and other priority substances), eutrophication (P and N), microbial contamination (faecal pathogens), hydromorphological (arterial drainage) and water quantity (abstraction for irrigation and drinking water). Other emerging chemicals (pharmaceuticals, hormones, additives of personal care products or detergents) (Musolff, 2009) may also be present in rural aquatic systems, but are mostly below the current analytical detection limits.

In Ireland, two groundwater bodies (south east) have been classified as having poor status due to elevated nitrate (NO_3^-) concentrations in groundwater (Daly & Craig, 2009). This classification is based on a mean annual threshold concentration of 37.5 mg NO_3^- L^{-1}, where there is a sustained upward trend over a period of a year. There is a potential for additional groundwater bodies to be classified as “poor” in time if the environmental quality standard (EQS) is lowered. In the future, the EQS for groundwater nitrate maybe reduced to combat eutrophication in surface and estuarine waters where N limitation to aquatic plant ecology is identified. In Ireland, there is no EQS in place for rivers at the time of writing. The EQS for dissolved inorganic N in estuaries has been set at 2.6 mg N L^{-1} (S.I. 272 of 2009). Furthermore, a large number of groundwater bodies (102 in total) are designated as having “poor status” due to elevated groundwater P. Where this P is being transported to groundwater from diffuse agricultural sources by diffuse recharge, then the recharge principals are similar to nitrate, but there will be greater uncertainty as P can be retarded along its migration pathway due to its non-conservative nature. This uncertainty reflects the accumulation of high levels of P in soils and the sorption/desorption processes that occur along the groundwater recharge pathway. Schulte et al. (2010) showed that it may take many years for elevated soil P concentrations to be reduced to agronomically and environmentally optimum levels (Index 1-3, < 8 mg Morgan’s P L^{-1}) . The extent of these delays is predominantly related to the relative annual P balance (P balance relative to total P reserves). While the onset of reductions in excessive soil P levels may be observed within five years, this reduction is a slow process and may take years-to-decades to be completed.

Across Europe, implementation of agricultural programmes of measures (POM) to achieve the aims of the WFD must be in place by 2012. In Ireland, such measures have been outlined in the Nitrates Directive (European Community, 1991) and are in place since 2009. Mitigation measures to achieve the goals of the WFD that are now in place have, in general, been tested in controlled laboratory and small plot experiments. However, it is necessary to quantify mitigation impacts on water quality under a wider range of environmental and agricultural conditions, and at the catchment scale. In Ireland, this is now being carried out under the Agricultural Catchments Programme (Jordan, 2008). Due to catchment buffering and long transit times (>50 years), it is unlikely that responses to interventions will be observed by 2015 in many waterbodies in Europe (Cherry et al., 2008). This delayed response, which has been highlighted by many researchers (Worrall & Burt, 1999; Bechmann et al., 2008; Iital et al., 2008; Wahlin & Grimvall, 2008), occurs as nitrate leaching pathways between soils, groundwaters and rivers are generally long and complex (Collins & McGonigle, 2008) and such pathways vary depending on soil/subsoil type (Stark & Richards, 2008; van Beek et al., 2009), bedrock geology/hydrogeology and climatic factors such as rainfall. The lag time between introducing protection measures and first improvements in water quality is, therefore, likely to occur at different times in different catchments comprising different soils and geologies, and should be considered by policy makers and catchment managers (Kronvang et al., 2008a).

Lag time presents member states with an opportunity to extend deadlines to achieve “good status” and these must be based on timely improvements being prevented by natural conditions or disproportionate costs (Anon, 2008a). Furthermore, the agricultural sector is faced with increasingly stringent legislation on the emission of acidifying gases such as ammonia (NH_3) and emissions of greenhouse gases (GHG), including nitrous oxide (N_2O), methane (CH_4) and nitrogen oxides (NO_x). When investigating N loss to water, consideration of gaseous reactive N emissions must also be made to prevent pollution swapping (Stark & Richards, 2008).

Lag time dictates that nutrients lost from unregulated farming eras (pre Nitrates Directive) are currently affecting water quality status. If proven effective, the present POM will also take many years or decades before they influence water quality status.

Current EU legislation focuses on prevention of nutrient loss. Nutrients that are already lost from agricultural systems are now migrating towards potential groundwater or surface water receptors. After a certain lag phase, these nutrients will contribute to the water quality status of a receiving waterbody. Innovative technologies need to be investigated, which intercept nutrients lost from point/diffuse sources. There is a place for such technologies within the EU legislative framework under the WFD supplementary measures option.

1.2 Irish agricultural context

Agricultural activity accounts for 61% of the land cover of Ireland, with 90% of the utilised agricultural area devoted to grassland production (grass silage, hay, pasture and rough grazing). The remaining 9% of agricultural land is used for arable crop production with spring barley (3.5%) and winter wheat (1.5%) being the dominant crops grown. Irish grasslands support 6.7 million cattle, including 1.1 million dairy cows and 1.2 million beef cows (CSO, 2009). The number of dairy cows has declined steadily as milk production per cow has increased and national output is limited by the national milk quota of 5.1 million litres (O’Mara, 2009).

Irish dairy farming systems are primarily based on grazed grassland with spring calving and average milk yields of 4700 L^{-1} per cow per year. Irish farms are generally small with an average dairy herd size of about 50 cows. Dairy farming is concentrated in the South West and South East of the country, with dairy represented in other regions, but at lower levels. Ireland’s damp temperate climate is suited to grassland production with annual grass growth on well-drained soils ranging from 280 day $year^{-1}$ in inland areas to 330 days $year^{-1}$ in the south western coasts (Schulte et al., 2005). Brereton (1995) reported that the long Irish growing season enabled farmers to exploit grazed grass on 200 days $year^{-1}$ in the North West to 235 days $year^{-1}$ in the South West; more recent research indicates that these figures are likely to have increased further due to the increased emphasis on grazed grass (Kennedy et al., 2005).

Soiled water is produced on dairy farms as effluent from farmyard areas that is contaminated by contact with livestock faces or urine, silage effluent, chemical fertilizers or farmyard washings (S.I. 101 of 2009). Large volumes of soiled water are generated on dairy farms, in particular, due to the frequent washing down of milking parlours (including dairy and plant) and collecting yards. Soiled water is defined in S.I. 1010 of 2009 as having a biological oxygen demand (BOD) of less than 2500 mg L^{-1} and a dry matter (DM) content of less than 1%. More concentrated effluent is considered to be slurry. Soiled water contains nutrients that are potentially available to plants, but if managed incorrectly pose a potential threat to water quality. However, these nutrients are in far lower concentrations than in slurry and soiled water is not subject to closed periods for spreading, although it is subject to other limitations protecting water quality, such as application rates, soil and weather conditions, slope and proximity to water sources. Given the need to mitigate P and N in runoff the distinction between soiled water and slurry has important implications in terms of required storage capacity and management practices, particularly on dairy farms.

Irish beef farming systems are generally located on the less productive, wetter soils with lower stock carrying capacities. The beef cattle sector is a feature of the great majority of Irish farms. It accounts for 35% of the value of agricultural output and almost 90% of production is exported. There are two components of the breeding herd with stock coming from the dairy and beef herds. Beef cow numbers increased steadily from 1984 onwards, peaked in 1998 (1.2 million suckler cows), and have fallen slightly since then. There are approximately 120,000 farmers involved in beef production in Ireland and it is the major enterprise in some 90,000 holdings. Sheep production accounts for 4% of gross agricultural output, with a quarter of Irish farmers involved in sheep production (O’Mara, 2009).

Systems of animal production and land use in Ireland are quite different to those in other EU countries, especially the extent to which grassland dominates agricultural land use (90%) (O’Mara, 2009). The cool summer temperatures facilitate the maintenance of highly digestible grass swards (low lignin concentrations in the pasture) throughout the grazing season. Most dairy, beef and sheep production systems in Ireland are primarily grass based with less than 10% of total feed inputs coming from non-grassland sources. Consequently, the level of concentrated feedstuffs fed to ruminant livestock tends to be very low compared to other EU countries, which results in lower imports of P and N onto farms.

1.3 Need for integrated P and N research

The loss of nutrients (P and N) from grassland agriculture to water has been highlighted as the main threat to water quality in Ireland due to the effects of eutrophication (Jordan et al., 2005 a). A recently completed study on nutrient loss from three Irish grassland catchments at multiple scales highlighted the challenge that Irish grassland agriculture faces in achieving 0.035 mg molybdate reactive P (MRP) L^{-1} in rivers and 0.025 mg total P (TP) L^{-1} in lakes, to prevent eutrophication (Jordan et al, 2005 b). Richards et al. (2009) summarised the results from three catchments ranging from <1 to 885 km^2 in each catchment – instrumented to measure river discharge and water quality parameters. The three catchments studied were the Dripsey, a tributary of the River Lee in Co. Cork; the Oona Water, a tributary of the Blackwater River in Co. Tyrone; and the Clarianna, a tributary of the Nenagh River in Co. Tipperary. River discharge was monitored using a combination of rated control structures, pre-calibrated flumes or weirs, and water level recorders. River nutrient concentrations (TP, total oxidized N (TON), nitrate (NO_3-N) and ammonium-N (NH_4-N)) were monitored at least weekly by taking daily flow-proportionate samples and grab samples (Jordan et al., 2005 b). Strong positive relationships were observed between the discharge frequency percentile (Q5/Q95 ratio) and both mean TP and NH_4-N concentrations, indicating that the more high infrequent flashy high flows that occur in a catchment, the higher the observed concentrations of both TP and NH_4-N. In contrast, a strong negative correlation between mean river TON-N concentration and Q5/Q95 flow ratio was observed, suggesting that elevated TON is more likely to occur in less flashy catchments dominated by groundwater flow (baseflow). The strong correlations between a measure of catchment hydrology (Q5/Q95 ratio) and TP (R^2=0.82), NH_4-N (R^2=0.93) and TON (R^2=-0.60) highlights the importance of hydrology in contaminant transport at the catchment scale. The catchments investigated above did not include a karst aquifer, but elevated P concentrations in Irish karst springs have been reported (Kilroy & Coxon, 2005). Elevated groundwater P concentrations in karst areas in the west of Ireland have been the main cause for groundwater bodies being classified as “poor status”. The origin of such nutrients is uncertain, but may come from soil, sediments within fractures or flows concentrated in conduits. In karst in Galway, flow rates (~metres/hour) and relatively low electrical conductivity (EC) values of the water suggest short storage periods, most of the water appears to have been underground for very short time periods (days to weeks, rather than months to years). Given the nature of the geology in these catchments, the zone of influence on a well may be practically the entire catchment. As nutrients make their way into a waterbody (surface or groundwater), mitigation technologies for P control and N remediation are needed to mitigate against declining water status. P cannot change form whereas N can be transformed in solution to gaseous forms.

The nutrient loss at the catchment scale is related to grassland agricultural practices in each catchment and catchment hydrology. In hydrologically flashier catchments (high proportion of runoff), there are greater losses of TP and NH_4-N due to the main hydrological pathway being runoff, which transports contaminants quickly over the soil surface. In contrast, the base flow-dominated catchments (low proportion of runoff) have much lower losses of TP and NH_4-N, but higher losses of TON due to the main hydrological pathway being leaching and lateral flow to the river channel. Therefore, an integrated approach for P control and N remediation is needed. Both are investigated at laboratory and field scale in this thesis.

In catchments with similar intensities of grassland agriculture, the effect of hydrology/hydrogeology has an over-riding control on contaminant transport. Improving the drainage capacity of soils through the introduction of subsurface drainage alters hydrology, considerably increases infiltration, and changes the transport pathway from surface overland flow/runoff to leaching and through-flow. Under comparable meteorological conditions in the U.K., Deasy et al. (2009) concluded that artificial drainage increased infiltration by up to 50% of total discharge from large grassland lysimeters and small (30 ha) agricultural catchments. The net effect of this change in hydrology was to decrease TP and suspended sediment (SS) mass loss by up to 52%, although it should be noted that artificial drainage has been associated with increased nitrate losses (Kurz et al., 2005). These hydrological controls must be considered when implementing measures to reduce the loss of nutrients to lakes, rivers, groundwater and estuarine/coastal waters (Tunney et al., 2009). Achieving the very low P standards for rivers in agriculturally-dominated catchments is going to be extremely challenging for the agricultural sector. Of the three catchments studied (Tunney et al., 2009), only the Clarianna, with a low Q5/Q95 ratio, had median reactive P concentrations below the standard of 0.035 mg L^{-1}.

Contaminant transport to groundwater and surface waters is highly dependent on the hydrological pathways in catchments. P, pathogenic micro-organisms and sediment are normally transported via overland flow pathways to surface waters and the associated travel times are short. In contrast, nitrate is normally leached through soil to groundwater and transported to surface waters by interflow, drain flow, shallow groundwater or deeper groundwater flow with longer travel times in comparison to runoff. The hydrological pathway of contaminant transport must be understood to enable measures for improving water quality status to be effective. Locating a mitigation technology on an agricultural landscape will need such an understanding. Furthermore, a mitigation technology cannot add contaminants to the hydrological system.

1.4 Objectives of Thesis

Overall the objectives of the study were:

1. To physically and chemically characterise metal mining ochre, and to investigate its P sequestration capacity, adsorption kinetics and potential adverse side-effects.
2. To investigate how the Fe mineralogy of the ochre influences the site- specific P sequestration capacity.
3. To develop a methodology that can be used to determine ochre amendment rates needed to achieve specific water quality targets.
4. To investigate techniques to track denitrification potential of natural and enhanced subsoil.
5. To use correlations between physical and chemical parameters to help identify areas for the optimal location of a PRB.

1.5 Procedure

After an initial literature review of control and remediation technologies for the treatment of waste and nutrients lost from agricultural systems in Ireland, an option for P control and N remediation was isolated for investigation at laboratory and field scales.

Within the literature review section a paper has been published:

Fenton, O., Healy, M.G. and Schulte, R.O. 2008. A review of remediation and control systems for the treatment of agricultural wastewater to satisfy the requirements of the Water Framework Directive. *Biology and Environment*, **108**(B):69-79.

1.5.1 Summary of P mitigation experiments

Ochre is only available in vast quantities in one location in Ireland. Iron (Fe) ochre samples were collected from Avoca Mines, Co. Wicklow South East Ireland (latitude 52º48'N, longitude 6º 12'W). In the laboratory, experiments enabled the physical and mineralogical characterisation of this iron ochre. For physical characterisation iron ochre was tested for bulk density, aggregate stability, hydraulic conductivity and particle size distribution. For mineralogical characterisation, Avoca ochre samples were sent to the U.K. (Intec laboratories, London) and the U.S.A (XRD laboratories, New York) for mineralogical analysis. The interpretation of results was carried out in Ireland. Stereomicroscopy investigated if organisms indicative of acidic environmental deposition were present in the iron ochre samples. X-ray diffraction (XRD) was used to further investigate the site-specific iron mineralogy of the ochre. Inductively coupled plasma mass spectroscopy (ICP-MS) and bulk energy dispersive X-ray (EDX) investigations allowed the total metal content of the ochre to be established. In batch experiments, P-amended water (50 ml) and dairy dirty water was mixed with iron ochre (2.5 g). Both Freundlich and Langmuir isotherms were investigated. Langmuir was used as the b function can predict maximum P adsorption capacity. Using Langmuir Isotherms, the maximum P adsorption capacity and binding strength of Avoca ochre was determined. This maximum P adsorption value was confirmed by saturation experiments. Kinetic batch experiments were used to investigate the speed of adsorption. To investigate ochre amendment to soil, batch experiments utilising two grassland soils at two depths (topsoil and sub-soil), five ochre amendments (control, 0.15, 1.5, 7.5, 15 g kg^{-1} mass per dry weight of soil) and four P concentration levels (0, 10, 20, 40 mg L^{-1}) were used. A proportional adsorption model, incorporating native P in the soil, synthetic P additions and P found in solution after batch experiments, was used to find optimal ochre amendment rates to prevent dissolved reactive P (DRP) losses above the maximum admissible concentration (MAC) for surface waters of 0.035 mg L^{-1}.

Within the P control section two papers have been published:

Fenton, O., Healy, M.G., Rodgers, M. 2009. Use of ochre from an abandoned acid mine in the SE of Ireland for phosphorus sequestration from dairy dirty water. *Journal Of Environmental Quality*, **38** (2):1120-1125

Fenton, O., Healy, M.G., Rodgers, M, O'hUallachain, D. 2009. Site-specific P adsorbency of ochre from acid mine drainage near an abandoned Cu-S mine in the Avoca-Avonmore catchment, Ireland. *Clay Minerals*, **44** (1):113-123

1.5.2 Summary of N remediation experiments

A general blueprint for locating a permeable reactive barrier (PRB) was developed from the literature. For a site-specific approach, a stepwise regression nitrate predictive function was developed using groundwater chemical and physical data from 17 piezometers. Using membrane inlet spectroscopy (MIMS), areas of dilution and denitrification were determined, thereby identifying areas more clearly where a PRB could be located to protect a nearby waterbody. A direct denitrification investigative method was developed using MIMS and woodchip slugs were installed in wells on a dairy farm. This method can be used to investigate "denitrification hotspots" in natural or enhanced environments, e.g. a PRB or denitrifying bioreactor. The wells were used to mimic a monitoring well inside a PRB.

Within the N remediation section two papers have been published:

Fenton, O., Richards, K.R., Kirwan, L., Khalil, M.I., Healy, M.G. 2009. Factors affecting nitrate distribution in shallow groundwater under a beef farm in South Eastern Ireland. *Journal of Environmental Management*, **90**:3135-3146

Fenton, O., Healy, M.G. and Richards, K. 2008. Methodology for the location of a subsurface permeable reactive barrier for the remediation of point source pollution on an Irish Farm. *Tearmann*, **6**:29-44.

1.6 Structure of dissertation

In Chapter 2, a review summarising the EU water quality legislation, the status of Irish water quality and its link to agriculture is presented. The review identifies several P control and N remediation possibilities for Ireland, to achieve at least "good ecological status" for all waterbodies by 2015. A number of those mentioned in the literature review are then tested at multiple scales.

Chapter 3 presents study site descriptions and schematics, Chapter 4 presents physical and mineralogical characterisation of Avoca ochre and Chapter 5 investigates the P sequestration properties of ochre and ochre amendment to soils in the field. In Chapter 6, two permeable reactive barrier location methodologies are investigated and denitrification potential techniques to identify denitrification hotspots are developed. Finally, conclusions are drawn on all aspects of this work. In the appendix, the published and submitted papers from this work are itemised.

Chapter 2 Mitigation techniques for the treatment of waste and nutrients lost from agricultural systems in Ireland: Literature Review

2.1 Legislative context - Identification of the problem

The Surface Water Directive, 75/440/EEC (European Economic Community, 1975), the Groundwater Directive, 80/68/EEC (European Economic Community, 1980), the Drinking Water Directive, 98/83/EC (European Community, 1998), the Nitrates Directive, 91/676/EEC (European Economic Community, 1991 a) and the Urban Wastewater Directive, 91/271/EEC (European Economic Community, 1991 b), combined with recent proceedings taken against the State by the EU Commission alleging non-implementation of some aspects of the directives, have focused considerable attention on the environmentally safe disposal of agricultural wastewaters in Ireland.

To address these directives, the WFD (2000/60/EC, Official Journal of the European Community, 2000) came into force on 22nd December 2000 and was transposed into Irish legislation by the European Communities (Water Policy) Regulations 2003 on 22nd December 2003. Eight “river basin districts” (RBDs) were established across the island of Ireland, North and South, with the aim of achieving “good status” in all surface, estuarine and ground waters by 2015. The WFD has and will bring about major changes in the regulation and management of Europe's water resources. Major changes include:

- A requirement for the preparation of integrated catchment management plans, with remits extending over point and non-point pollution, water abstraction and land use.
- The introduction of an EU-wide target of "good ecological status" for all surface and groundwater, except where exemptions for "heavily-modified" water bodies are granted. Measures to protect groundwater and surface water must be planned and implemented while being efficient and cost-effective.

POM to achieve “good status” must be implemented by the agricultural sector by 2012. The Nitrates Directive is Ireland’s agricultural POM. Supplementary measures for particular river basin districts may include buffer strip implementation or confining cattle access to streams.

2.2 Status of Irish water quality

The main pollutant threats to the status of waters in Ireland are nutrients (N and P) and pathogenic microbes (Lucey, 2009).

The proportion of river and stream channel length of satisfactory water quality status in 2006 was 71.4% compared to 70% for the 2006 to 2008 period (Lucey, 2007, 2009). The concentration of nutrients in surface waters continues to be of concern with increasing trends of nitrates in rivers (180 river sites tested in 2008 in the South East were of concern) and median MRP concentrations in six of the eleven main rivers being above the surface water quality target of 0.035 mg MRP L^{-1} (Lucey, 2009).

Nutrient enrichment of Irish estuaries and coastal water bodies is of concern with 21.7% of estuaries being classified as euthropic or potentially euthropic due to enrichment by N (35) and P (2) (Lucey, 2009).

In Ireland, the nitrate concentration in groundwater is much lower than in other EU member states, and in 2008, only 2% of Irish groundwater supplies had NO_3^- concentrations in excess of the drinking water MAC of 50 mg L^{-1} (11.3 mg NO_3-N L^{-1}) (Lucey, 2009). The overall challenge for agriculture is that the EQS for estuaries is of 2.6 mg L^{-1}. However, as the resolution of the monitoring network increases over time, the overall percentage of “poor status” waterbodies may increase. From 2010 onwards, a groundwater threshold value of 37.5 mg NO_3^- L^{-1} must be attained. If the mean annual nitrate concentration of groundwater exceeds the threshold value and nitrate values show a significant inter-annual increase, then a waterbody will be categorised as “poor status” and will be subject to additional testing by the WFD competent authority. In such cases, implementation of supplementary measures to the basic POM may be considered; these will only be considered after lag time and cost-effectiveness of potential measures have been taken into account. Any proposal for supplementary measures will be subject to a consultation process with relevant stakeholders, e.g. farming organisations. The interpretation of this trigger value differs in several EU countries. For example, in the Netherlands the trigger value only corresponds to surface waters and not groundwater (Pat Dillon, (Teagasc, Moorepark, Co. Cork) *pers comm*).

In Ireland, four groundwater bodies (two due to unsustainable long term abstraction and two due to abstractions impacting on the supporting water level/flow conditions of wetlands; both in east of the country) have been classified as “poor status” due to quantitative status. There are 111 groundwater bodies (based on chemical status) at poor status (14% of Republic of Ireland’s land area). The main drivers are MRP contributing to surface water eutrophication, metals from historic mining activities and contaminated land. There is a potential for further groundwater bodies to be classified at “poor status”, if the EQS is lowered. In the future, the EQS for groundwater nitrate maybe reduced to combat eutrophication in surface and estuarine waters where N limitation to aquatic plant ecology is identified. In the Interim Guideline Values (IGV) for groundwater in Ireland, the EPA (2003) proposed an IGV for nitrate (as NO_3^-) of 25 mg L^{-1}. The EQS for dissolved inorganic N in estuaries is 2.6 mg N L^{-1} (S.I. 272 of 2009).

A large number of groundwater bodies in the 2007 to 2008 period are designated as having “poor status” due to elevated groundwater P. Only 0.2% of groundwater bodies were of “poor status” due to a breach of nitrate thresholds. Such breaches are prevalent in the south (intensive dairy farming) and South East (tillage farming), but in the west of Ireland breaches have been correlated with karst limestone areas such as Galway, Mayo and Roscommon (Lucey, 2009). Phosphorus in such limestone aquifers may originate from soil, desorption from calcium carbonate, sediment trapped in fractures or native P in groundwater flowing in conduits. Where this P is being transported to groundwater from diffuse agricultural sources by diffuse recharge, the recharge principals are similar to nitrate, but there will be greater uncertainty due to the non-conservative nature of P. This uncertainty reflects the accumulation of high levels of P in soils and the sorption/desorption processes that occur along the groundwater recharge pathway. In the 2007 to 2008 period, 67% of groundwater (wells and springs) tested had at least one sample with faecal coliforms. This was an increase of 10% on the previous reporting period of 2004-2006 (Lucey, 2009).

Interim assessment of the status of lakes in Ireland estimated that 66% of lakes achieved “high/good status” and 2.9% of lakes achieved “poor/bad status” (Anon, 2008b). For Irish coastal and transitional waters, there is a lack of monitoring data available, and this has led to 42% of water bodies not being assigned a status. Of those coastal and transitional waters classified, 70% of the surface area was classified as “high/good status” (Anon, 2008b).

2.3 Drinking water

Local Authorities, group water schemes and private abstractions make up the drinking water distribution in Ireland. 81% of drinking water is sourced from surface water (rivers, lakes and reservoirs), 13% is sourced from groundwater and 6% from springs (Environmental Protection Agency, 2005). However, in some counties groundwater is the main source of drinking water e.g. Roscommon. The main threat to surface and groundwater drinking supplies is contamination by organic matter and poor maintenance of large and small-scale wastewater treatment systems leading to leakage of nutrients (Environmental Protection Agency, 2004 a). The primary receptor of nutrients leached from agriculture is groundwater. Therefore, interception of lost nutrients before reaching a potential receptor, either through natural attenuation or by enhanced means, is important.

Studies of low-yielding wells have also shown that, although nitrate contamination is not widespread, areas of Carlow, Cork, Kerry, Louth and Waterford may be susceptible to eutrophication as a result of nitrate leaching through groundwater (Thorn & Coxon, 1991; Lucey et al., 1999; Environmental Protection Agency, 2003). McGarrigle et al. (2002) recorded drinking water breaches in 15 counties (Carlow, Cavan, Cork, Galway, Kerry, Kildare, Kilkenny, Laois, Louth, Meath, Offaly, Tipperary, Waterford, Wexford and Wicklow). However, overall compliance for public water supplies and group water schemes in 2003 was 96.1% (Environmental Protection Agency, 2003). Background conditions of a groundwater body are needed in order to define clearly the status of that waterbody. Baseline data for groundwater will be of great significance working towards the requirements of the WFD. Other sources of pollution could come from landspreading of non-agricultural waste e.g. biosolids.

2.4 Link to agriculture

In Ireland, farming is an important national industry that involves approximately 270,000 people, 6.191 million cattle, 4.257 million sheep, 1.678 million pigs and 10.7 million poultry (CSO, 2006). Agriculture utilizes 61% of Ireland’s land area (Fingleton and Cushion, 1999), of which 91% is devoted to grass, silage and hay and rough grazing (DAFF, 2003). Grass-based rearing of cattle and sheep dominates the industry (Environmental Protection Agency, 2004 b). Livestock production is associated with external inputs of nutrients. P surpluses accumulate in the soil (Culleton et al., 2000) and contribute to P loss to surface and groundwater (Tunney, 1990; Regan et al., 2010). Elevated soil P status has been identified as one of the dominant P pressures in Ireland (Tunney et al., 2000).

The aquatic agri-environment is vulnerable from nutrient losses to surface and groundwater. Nutrient loss and subsequent transport may lead to nutrient interaction with surface and groundwater and may have an adverse impact on biodiversity and ecology of aquatic ecosystems (Schulte et al., 2006). A survey of 1132 rivers and streams from 2001 to 2003 estimated that the percentage of pollution attributed to agriculture was approximately 32% in the case of rivers and streams, which were slightly or moderately polluted, but only 15% of serious pollution (Toner et al., 2005).

River quality trends have been correlated to population and intensity of agriculture where threshold levels are breached (Environmental Protection Agency, 2004 a). In 2004, 60 million tonnes of agricultural waste were generated, of which 60.6 % was from cattle manure and slurry (Table 2.1) (Environmental Protection Agency, 2004 a). Agricultural nutrient inputs are the most significant nutrient load entering receiving waters in Ireland and have been estimated to comprise 75.3% and 33.4% of the N and P load, respectively (River Basin District, 2005). Diffuse P losses from agriculture may contribute to eutrophication (Clabby et al., 1992; Bowman et al., 1996; Lucey et al., 1999; McCarrigle et al., 2002).

TABLE 2.1 ESTIMATED AGRICULTURAL ORGANIC MANAGED WASTE GENERATION IN 2001 (ENVIRONMENTAL PROTECTION AGENCY, 2004 A).

Waste Category	Waste Generation	
	Tonnes wet weight	%
Cattle manure and slurry	36,443,603	60.6
Water (dairy only)	18,377,550	30.5
Pig slurry	2,431,819	4.0
Silage effluent	1,139,231	1.9
Poultry litter	172,435	0.3
Sheep manure	1,336,336	2.2
Spent mushroom compost	274,050	0.5
Total	60,170,025	

In their review of nutrient loss from agriculture to water, Schulte et al. (2006) correlated reduced river quality to areas where P pressures coincided with transport vectors. The source-pathway-receptor concept was combined with agro-meteorological factors and pressures to account for nutrient loss to water.

Figures from 2010 show slight changes in organic waste amounts with a combined total of cattle manure slurry and dirty water (36,005,848 tonnes), pigs (2,219,407 tonnes), poultry (135,385 tonnes) and sheep (1,014,876 tonnes) (Bernard Hyde (Environmental Protection Agency, Co. Monaghan), *pers comm.*).

2.5 Measures in place to overcome the problem

In Europe, the WFD strategy exists to restore the “good status” of surface and groundwater. It focuses on reducing nutrient pressures to prevent further nutrient loss to surface and groundwater. However, intensification of agriculture poses a challenge to the sustainable management of soils, water resources and biodiversity. N losses from agricultural areas can contribute to surface and groundwater pollution (Stark & Richards, 2008; Humphreys et al., 2008).

Results from a Water4all project suggest that regulation alone will not achieve sufficient increase in water quality; the build up of nitrate in soils and the long residence time of groundwater in aquifers needs a more immediate solution (Water4all, 2005). As the WFD is concerned with nutrient loss prevention and lag time between nutrient losses at farm level and improvement in water quality at catchment scale are vast, mitigation technologies will help achieve the targets set down by the WFD within this timescale. Therefore, integrated remediation (N) and control (P) technologies must be an integral part of the process for point and diffuse pollution from historic or future incidental nutrient losses. Such technologies may not be present at the same location on a farm or within a catchment. Two strategies are considered: reduction; and remediation and control.

2.5.1 Strategy 1 - Reduction

The Nitrates Directive (European Council, 1991), enacted in the Republic of Ireland in 2006 under S.I. 101, 2009, is currently the basic POM in place to achieve the goals of the WFD. The Nitrates Directive sets limits on stocking rates on farms in terms of the quantity of N from livestock manure that can be applied mechanically or directly deposited by grazing livestock on agricultural land. A limit of 170 kg N ha^{-1} year^{-1} from livestock manure was set. However, the EU Nitrates Committee approved Ireland’s application for a derogation of this limit to allow grassland-based (mostly dairy) farmers to operate at up to 250 kg N ha^{-1} year^{-1} from livestock manures, with the stipulation that this derogation will not impinge on meeting the requirements of the Nitrates Directive. The current average stocking density on dairy farms is 1.81 livestock units (LU) ha^{-1}. The number of dairy farmers is declining at a rate of between 2% to 3% per year, resulting in more concentrated production on fewer larger farms, which are generally more specialised and intensive.

The “Good Agricultural Practice for the Protection of Waters” regulation, S.I. 378 EC (European Community, 2006), came into effect on August 1st 2006. It regulates farmyard and nutrient management, but also examines prevention of water pollution from fertilizers and certain activities. The linkage between source and pathway can be broken if pollutants remain within farm boundaries and are not discharging to drainage channels, subsurface drainage systems; or entering streams or open waterways within farm boundaries. As of 1st of January 2007, the Nitrates Directive places restrictions on land spreading of agricultural wastes. This strategy looks at present loss and future loss prevention. There are no guidelines in place for the remediation or control of contaminated discharges to surface and/or ground water or future discharges due to incidental losses. Traditionally, agricultural wastes are disposed of by land spreading. In land spreading, the recharge rate, the time of year of application, the hydraulic conductivity of the soil, the depth of soil to the water table and/or bedrock and the concentration of nutrients and SS in the wastewater (soiled water and any discharge containing nutrients) are some of the defining parameters that determine nitrate movement through the soil to the water table. The recommended maximum rate of application is 5 mm per hour and the quantity applied should not exceed 50 m^3 per hectare per application (ADAS, 1985, 1994; DAFF, 1996) and these recommendations are present within best farm management practices. Infiltration depth of irrigated water and rainfall may be estimated when the annual effective drainage, number of effective drainage days, effective porosity, annual precipitation and the hydraulic load of the irrigator are known. This data may then be combined with surficial and bedrock geology as well as groundwater data to examine if excess nutrients recharge to groundwater within a specific time frame.

The Nitrates Directive and rising costs are now forcing better use of nutrients in slurry. Research in the U.K. (Misselbrook et al., 1996; 2002; Smith & Chambers, 1993; Smith et al., 2000) includes improving N recovery from slurry by examining the effect of spreading method and timing, and reducing NH_3 losses from slurry by evaluating splash-plate versus alternative techniques such as trailing shoe or trailing hose slurry application methods. The average abatement of these methods varies and differs when grassland or arable application are considered (Smith & Misselbrook, 2000; Misselbrook et al., 2002). Current research in Ireland follows similar patterns (Ryan, 2005). NH_3 emissions with respect to trailing shoe versus splash-plate and subsequent N uptake by the sward are being investigated in Irish grasslands (Lalor & Schulte, 2008). Farm management strategies aimed at prevention of nutrient loss to water have recently been reviewed by Schulte (2006).

An intermediary between implementation and water quality at a receptor is to investigate the nutrient status leaving the rooting zone. This is the zone commonly investigated in lysimeter studies, and nutrient models, such as NCYCLE_Ireland (Del

Prado et al., 2006), tend to finish at this depth. Such a direct approach is termed ‘nutrient budgeting’, which aims to establish the efficacy of measures in the short-term. It is inferred that, if surplus (leaching) nutrient concentrations are below MAC, the chemical and ecological status of a waterbody will improve. For policy to incorporate such a methodology the following knowledge gaps need to be addressed:

1. There are many different forms of organic N in soils and soil amendments. What is the N uptake for different crops using these different forms? Without such information, how much should the farmer spread and pay? How can we test for N in the soil to answer such questions?
2. Organic and mineral N in fertilizers - these proportions change when added to soil. How much of this mineral part is immobilised or lost, and how much of the organic fraction is mineralised and when? Is this soil-specific?
3. Do we need to consider higher resolution weather data to calculate soil moisture deficits (SMD) and effective drainage? SMD is presently being calculated using daily weather data. Some SMD models do not use actual runoff data (e.g. Schulte et al., 2005). Soil moisture deficit land use specific models need to be calibrated e.g. for tillage areas.
4. Further use of ^{15}N-labelled animal manure studies and labelled studies in general to trace N uptake and loss pathways (Hoekstra et al., 2007; 2009)
5. Numerical modelling needs to integrate surface and subsurface processes and requires high resolution data (*see 3, above*).
6. Combined research of N leaching and gaseous losses is important in order to understand the correlations in N transformation processes. It is important to measure not only potential denitrification, but also actual denitrification to compile the N budget. It is important to switch to a more ‘process driven’ understanding and to find better ways for describing the system’s behaviour in connection with N retention and dissipation. It is important to connect different scales of study (i.e. from soil biology to groundwater at regional scale), and to determine if the hotspots are important for the total budget.
7. There is a need for N gas loss measurements from a variety of scenarios. Two black holes currently exist – denitrification, and N_2O and NH_3 emission and deposition. Emissions from GHG hotspots (gates, tracks, seepage manure

heaps, drains), should be investigated, added to loads and incorporated into balances. These should be identified and quantified. With reduction of N_2O emissions and denitrification, the management of N_2/N_2O ratio should be explored further in connection with soil physics, geo-chemistry and microbial communities.

8. N losses will occur in agricultural systems, as it is inherent in the biological and biophysical processes involved. The use of farm N balances can be improved and expanded by the analysis of N inflows and outflows that are identified by the kind of item and their trophic level.
9. There is often an unexplained surplus from 70 to 100 kg N ha^{-1} in nutrient balances, which at present cannot be accounted for.

2.5.2 Strategy 2 - Remediation and control

Strategy 2 acknowledges that nutrient losses exist now and will exist in the future, due to accidental losses or non-compliance with codes of practice, and seeks to use pre-treatment and *in situ* remediation techniques to satisfy the requirements of the WFD. A solution that seeks remediation of nitrate while controlling P losses at pre-treatment and *in situ* phases is needed.

In Ireland, groundwater quality is under increasing risk from diffuse (agriculture) and point sources (manure, silage storage and septic tank systems). The safe disposal of on-site wastewater is essential for the protection of groundwater. The accumulation of excess soil P in catchments under intensive animal production has been linked to increases in dissolved P concentrations in rivers and streams draining these catchments (Boesch et al., 2001). Concentrations of dissolved and particulate P are related to discharge rates and surface slope, suspended soil material and discharge rate, respectively (Djodjic et al., 2000). P losses occur shortly after fertilizer application during rainfall events or from high P Index soils (> 8 mg L^{-1}). Overland flow and erosion lead to P losses. P leaching can also occur, but is dependent on the soil type. In Ireland, 111 water bodies fail good water quality status; of these, 102 fail due to P concentrations in groundwater (predominantly in the west of Ireland) (Anon, 2008 b).

The sorption capacity and desorption dynamics were examined in Irish grassland soils by Daly et al. (2001). They found that P sorption capacities correlate negatively with organic matter, indicating that the percentage of organic matter may inhibit P sorption from solution to soil. High organic matter-soils have low P sorption capacities and poor P reserves compared to mineral soils. Therefore, organic matter blocks sorption sites in peat soils. This results in P remaining in soil solutions. Heavy applications of manures on these soils may lead to early P saturation and P losses. Herlihy et al. (2004) studied the rate of decline in Morgan's P as a function of time, soil type and P balance, over a four-year period on Irish soils. Their study was part of an extensive field experiment on interactions between soil type, soil test P, P fertilizer rates, P fractionation and herbage P uptake in mineral soils in grasslands. This study was also described by Herlihy et al (2004), Herlihy & McCarthy (2006), Herlihy & McGrath (2007) and Schulte & Herlihy (2007). Results show that a lag time in P release exists and it may take years-to-decades for soils to recover back to levels that are safe for the environment (Soil P Index 3 and below). Soil P fertilisation is recommended on an addition or replacement basis for low and optimum soil P concentrations respectively at rates specific to grassland, arable and horticultural crop requirements. Soil P Index categories of 1 (deficient), 2 (low), 3 (optimum) and 4 (excessive) are used to classify soil P test concentrations. In Ireland, the soil P index is based on the Morgan's extraction and for grasslands is categorised from Index 1 (0 to 3 mg P L^{-1} of soil), 2 (3 to 5 mg L^{-1}), 3 (5 to 8 mg L^{-1}) and 4 (>8 mg L^{-1}). Soils at soil P Index 4 are considered to be excessive in terms of agronomic production (i.e. no yield response to P additions) and are at greater risk of transferring this excess via runoff to water bodies (Tunney, 2000). P transfers from high P soils to water courses can vary from 0.5 kg ha^{-1} yr^{-1} (Ulen et al., 2007) to over 2.5 kg ha^{-1} yr^{-1} at the field scale (Jordan et al., 2005). The measures prohibit P addition to soils of P Index 4; and in the absence of a soil P test, all soils are assumed to have a soil P Index of 3, which limits allowable P fertiliser amendment to rates that only maintain soil P fertility and only following off-take in crops. Farms availing of derogation are required to have soil P tested in all fields (Schulte et al., 2010).

In terms of expectation of reduced agricultural nutrient transfers and improvements in the trophic status of waters, and with the explicit target dates for good water quality status, it is necessary to provide policy makers with guidance on the likely rates of change in both reductions in nutrient source pressures at the soil and field scale and also in terms of realistic travel times from land based sources to water receptors. The abatement of both P and N transfers to water from agricultural point sources has been expedited by grant aided capital investment in slurry storage and soiled water separation, and is also designed to support closed periods for land spreading. This is a measure that should have a rapid mitigating effect on both point and incidental transfers. In terms of N transfers in diffuse sub-surface pathways, however, slow travel and flushing times could possibly hinder the achievement of target concentrations in water receptors such as ground waters (limit of 11.3 mg NO_3-N L^{-1}) or estuaries, where there has been a long history of nitrate leaching in contributing catchments (Fenton et al., 2009). For the abatement of diffuse sources of P, the rate of decline in soil P index from excessive to optimum levels will influence the degree to which water quality targets can be met in the 2015 timeframe. Factors that influence the rate of soil P index decline include the magnitude of the initial available soil P pool (Index 4 does not have an upper bound), soil type and rate of off-take in products; *viz* the P balance. Grassland studies at the catchment scale indicate that particulate P (PP) - as opposed to DRP - is the predominant form exported from agricultural land. Lambert et al. (1985) and Gillingham and Thorrold (2000) found that PP comprised 91% and 62%, respectively, of TP in surface runoff after slurry application. The proportion of PP to DRP in runoff can vary significantly with season. Cooke (1988) found that PP was the dominant form in surface runoff in winter and spring, but that DRP became the dominant fraction in summer and autumn. This proportion also changes with the presence or absence of grazing animals and the altitude of the plot. Besides storm events, baseflow conditions may also contribute significant amounts of DRP in some grassland catchments.

Nitrate has a negative electrostatic charge. As soil also has a negative electrostatic charge, nitrate travels relatively quickly through the soil, leading to increased potential for groundwater contamination (Abu-Ashor et al., 1994; Kung et al., 2000). Nitrate leaching leads to nutrient loss to groundwater and is dependent on the hydraulic loading rate on the irrigated plot, soil water content and soil type (Ryan et al., 1998). Preferential flow in several Irish soil types has been investigated by Kramers (2009).

To reduce N and P losses, pre-treatment and *in situ* technologies for N and P should be commonplace on Irish farms. In order to reduce nitrate below the MAC of 11.3 mg NO_3-N L^{-1}, the N concentration applied in dirty water may be reduced by prior or in-field treatment. Implementation of current legislation (Nitrates Directive) requires separation of faecal matter and water, thereby reducing the nutrient content of soiled water. As the nutrient value of this product is low and as storage costs and water charges become higher, an alternative solution to land spreading is to remediate and recycle this soiled water for yard washing. Farmyard remediation technologies using biofilm reactors and P sequestration aim to remediate and recycle dirty water on farms, cutting storage and water costs. A 1.5 m buffer strip parallel to watercourses, specified by the Rural Environmental Protection Scheme (REPS), could be utilized for subsurface remediation trenches. Unused field corners could be utilised as buffer strips amended with reactive materials to prevent P losses.

Nitrate leaching pathways between soils, groundwaters and rivers are generally long and complex (Collins & McGonigle, 2008) and such pathways vary depending on soil/subsoil type, bedrock geology/hydrogeology and climatic drivers such as rainfall. The lag time (also termed delayed response or time lag) between introducing protection measures and first improvements in water quality is, therefore, likely to occur at different rates in different catchments comprising different soils and geologies, and should be considered by policy makers and catchment managers (Kronvang et al., 2008 a, b). However, current plans for implementation of water quality protection measures under the WFD by 2012 and their first assessment in 2015 may not account for different lag times in different catchments.

The saturated zone beneath the water table or potentiometric surface is technically defined as groundwater, which is a principal receptor of water and leached nutrients from the unsaturated soil/subsoil. This definition applies to groundwater protection schemes. In Ireland, all subsurface materials are classed as aquifers, and aquifers are defined as any stratum or combination of strata that stores or transmits groundwater. Under the WFD the term ‘groundwater’ was introduced and defined as is the management unit that is necessary for the subdivision of large geographical areas of aquifer in order for them to be effectively managed. Groundwater in subsoils, albeit the initial recipient of leached nutrients is not, therefore, considered part of the underlying bedrock aquifer. However, saturated subsoils and an underlying groundwater body may often form a hydraulic continuum, but usually do not share the same hydrogeological characteristics. This defining framework has clear implications for nutrient migration pathways and their management. It is in this zone that environmental technologies may have the most direct impact on water quality. In a recent study investigating groundwater and surface water contributions to stream flow in Ireland, subsurface soil and subsoil water (with the exception of sand and gravel) are termed ‘interflow’, and shallow groundwater is described as ‘shallow bedrock groundwater’, where permeability is higher and fracturing and weathering is more dominant (RPS, 2008).

Saturated subsoils (interflow) and an underlying groundwater body (shallow and deep groundwater) may often form a hydraulic continuum, but usually do not share the same hydrogeological characteristics. This defining framework has clear implications for nutrient migration pathways and their management. Therefore, it is important to investigate all scenarios that could contribute to water quality status. A greater understanding of lag time is needed to allow policy makers to acknowledge the process and allow adequate time to test the efficacy of measures before implementing more stringent legislation on farmers. The time of first occurrence of a nutrient in a waterbody and its flushing completely from an aquifer may take some time (except in the case of karst aquifers). Fenton et al. (2009) showed that hydrological response times can vary greatly from months to years and, thus, they indicate the potentially long total travel time period between farming activities and receptor response. The hydrological lag time of water quality response to the implementation of mitigation measures has been shown to be a function of effective drainage and the hydrogeological properties of soil, subsoil and aquifers. Biogeochemical processes during nutrient transport will further complicate the interpretation of water quality responses. Lag time places a greater need on mitigation technology research in Ireland. Identification of environmental technologies that can aid in the control of P and remediation of nitrate will help to achieve the aims of the WFD.

2.6. Possible P control technologies - Pre treatment and *in situ* amendments

In a farming system, P losses may originate from the soil (P Index 4) and from the fertilizer applied (organic or inorganic). Chemical amendment may occur in situ on the farmyard, i.e. application to slurry directly, or may be applied in the field. Where chemical amendment is added directly to a surface waterbody, the implications for chemical losses to the environment must be appreciated.

2.6.1 Aluminium and polyacrylamide

Aluminium (Al) (alum-used in literature) and polyacrylamide (PAM) are chemical flocculants commonly used in wastewater treatment plants to remove P and sediment, and can be used as pre-treatment and *in situ* amendments. PAM promotes sediment floc formation and alum removes the soluble P by settling processes.

Alum should be applied to water or wastewater with a pH range from 5.5 to 9.0. In this range, aluminium hydroxide is insoluble and its concentration remains below 0.05 mg L^{-1} (Mason et al., 2005). This is a safe upper-limit concentration for the protection of fish (Kennedy & Cooke, 1982).

2.6.2 Alum and PAM for sewage sludge: a review

Sludge from drinking water treatment plants, containing alum, could prevent P loss to waterways. Several water treatment plants in Ireland use an addition of alum to decrease P concentrations in wastewaters to satisfy the Urban Waste Water Treatment Directive, 91/271/EEC (European Economic Community, 1991 b). The waste product of this process is alum sludge and must be re-used whenever appropriate. Various forms of sewage sludge are available. Non-hazardous sludge includes: water, wastewater, industrial and agricultural treatment sludge.

In Ireland, up to 45 tonnes (dry solids) (TDS) of alum sludge are produced daily and this number is set to increase with rising population figures. With the quantity of sewage sludge arising from waste water treatment plants set to increase to 130,000, disposal alternatives need to be examined. Prior to 1999, sludge was disposed of by sea, land application or landfill. Environmental Protection Agency landfill licenses limit or preclude the disposal of sludge to landfill.

Previous research has focused on using sludge or biosolids (sludge that has been treated by composting or anaerobic digestion) as a fertilizer substitute. Studies looking at P loss in runoff from agricultural soils receiving sewage sludge, fertilizer and farmyard manure show that sewage sludge biosolids are a useful source of P for crop growth and for maintaining soil P fertility (Withers et al., 2000; Flynn & Withers, 2001). They do not pose a greater eutrophication risk than other P amendments at similar P application rates (Withers et al., 2000).

A literature review of denitrification behaviour in Biological Excess Phosphorus Removal activated sludge systems notes that P uptake in the presence of nitrate is possible with the addition of acetate under anaerobic conditions (Barker & Dold, 1996; Sponza & Atalay, 2004).

2.6.3 Alum and PAM for farm water treatment

Pre-treatment amendments can be directly applied to the agricultural wastewater and then landspread. In Ireland, 90% of all sludge is produced by agriculture. The addition of alum and PAM to farm wastewater before land application would reduce the risk of nutrient loss to surface waters. Alum has been shown to be effective in immobilizing P, thereby reducing leaching in coarse-grained soils with a long history of waste application (Zvomuya et al., 2006). Moore et al. (1999) showed that alum amendment to poultry litter decreased NH_4 concentrations, reduced the solubility of P in litter and reduced P runoff losses. PAM has also been used to separate solid and liquid components of swine manure (Vanotti & Hunt, 1999). Sims & Luka-McCafferty (2002) used alum as a poultry amendment on a farm-scale study and measured a decrease in the solubility of P from 2.2±0.2 to 2.0±0.2 mg kg^{-1}, inorganic arsenic (As) from 19±4 to 7±3 mg kg^{-1}, copper (Cu) from 272±50 to 172±45 mg kg^{-1} and zinc (Zn) from 29±7 to 15±10 mg kg^{-1}.

Kronvang et al. (2005) examined the effects and uncertainties of targeted mitigation measures in EU agricultural areas where, P loss is commonplace. The application of alum increased the binding potential of P in soils and was used in the immobilisation of P. The impacts of alum-amended soils and subsequent runoff P concentrations were carried out using a rainfall-simulator on a field historically used for dairy effluent application (McFarland et al., 2003). In a 20-year study, Moore & Edwards (2005) applied four alum addition rates of 2.24, 4.49, 6.73, and 8.98 mg ha^{-1} (1, 2, 3, and 4 tons $acre^{-1}$); and NH_4 rates of 65, 130, 195 and 260 kg N ha^{-1} (based on the amount of N applied with alum-treated litter) on 52 small plots at the University of Arkansas. Large decreases in soluble P from runoff and soil extractable P were measured in the alum-amended plots. P in runoff associated with alum amended poultry litter was less soluble in the soil than P derived from non-amended poultry litter. No long-term, replicated studies under natural rainfall conditions were carried out in this study. Addition of alum at 20 mg L^{-1} in irrigation return waters can remove approximately 50% of soluble P (Leytem et al., 2005).

Best management practices (BMP) ‘at source’ aim to reduce the amount of P available in runoff and drainage waters, whereas riparian buffers, such as vegetative buffer strips, limit P movement pathways from the field to a waterbody (Sharpley et al., 2006). Low-cost alum buffer strips have also been used to reduce nutrients in surface runoff (Dayton & Basta, 2005). Other studies using buffer strips have shown reductions in runoff DRP (Peters & Basta, 1996; Basta & Storm, 1997; Gallimore et al., 1999; Haustein et al., 2000; Dayton & Basta, 2003). Razali et al. (2006) demonstrated that alum sludge could successfully be used to remove 47% of SS and 23% chemical oxygen demand (COD) from farmyard wastewater. To date, there has been no large scale application of this technology in Ireland.

In Ireland, on land receiving organic manure, dirty water or inorganic fertilizer as part of an agri-environmental scheme, vegetated buffer zones may be up to 10 m (5 m on each side of the watercourse) in width where the slope towards the watercourse exceeds 10%; 5 m (2.5 m on each side of the watercourse) for any other watercourse, and 3 m (1.5 m on each side of the watercourse) adjacent to open drains, or where the land adjacent to the watercourse is a narrow parcel of land less than 50 m wide and not more than 1 ha in area. Other agri-environmental schemes across Europe have similar stipulations. Vegetative buffer or filter strips have PP removals of 45% (Schmitt et al., 1999) to 90% (Abu-Zreig et al., 2003), but have limited DRP removal (Sharpley et al., 2006; Dorioz et al., 2006). Zhang et al. (2009) reviewed sediment, pesticides, P and N losses through vegetated buffers and performed a meta analysis on results. Buffer width alone explained 37%, 60%, 44% and 35% of the total variance in removal efficacy, respectively. Buffer slope was linearly and positively associated with sediment removal when surface slopes were < 10%, or negatively when slopes were > 10%. They also found that a 30 m buffer, inclined at a slope of 10%, will remove > 80% of all studied pollutants. In Ireland, the buffer strip allowance is only 1.5 m at each side of a stream. Applying P-immobilizing materials (alum, water treatment residuals (WTR), fly ash, gypsum) to such vegetative buffers or filter strips through amendment of edge-of-stream soils is one possible means of reducing soluble P losses to aquatic systems (Penn & Bryant, 2006; Wagner et al., 2008). Fe-rich materials, which have high P adsorption capacities, have been used to sequester P from wastewaters (Moore & Miller, 1994; Gallimore et al., 1999; Elliot et al., 2002; Rhoton & Bigham, 2005; Johansson-Westholm, 2006). Amendment of such substances to soil to prevent edge-of-field losses of DRP has not been investigated.

2.6.4 Alum and PAM for surface waters

In situ application of alum and PAM to surface waters (lakes, streams, tributaries, drainage channels) in conjunction with settlement basins has been considered. Alum may also be used to reduce the SS and nutrient concentration of surface waters. Nutrient-rich agricultural wastewater has caused eutrophication in the Salton Sea, California (Mason et al., 2005). The removal of dissolved P and P-laden sediment from this water using non-ionic PAM (2 mg L^{-1}) and alum (4 mg L^{-1}), added to ditches receiving tributary waters, substantially reduced SS and turbidity, and reduced soluble P by 93%. Best results are obtained when PAM and alum are used in conjunction with settlement basins or low-flow regimes. Chang et al. (2005) investigated the relationship between alum and PAM and concluded that the polyelectrolyte p-DADMAC could be used in conjunction with alum to decrease the dosage needed to improve turbidity in surface waters.

2.7 Iron ochre

The WFD requires each member state to address deficiencies in existing controls governing: wastewater and industrial discharges; landfills, quarries, mines and contaminated lands; wastewater from un-sewered properties; forestry; usage and discharge of dangerous substances; and agriculture. In Ireland, the Good Agricultural Practice for the Protection of Water Regulations 2006 (S.I. No. 378 of 2006) divides the country into three zones (east, midlands and west). Each zone has different rules about the storage capacity of organic fertiliser, as well as specified dates, where the landspreading of organic and chemical fertiliser is prohibited.

Dirty water is generated from dairy parlour water and machine washings, precipitation and water from concreted holding yards. Using a material with a high P adsorption capacity, P could be sequestered from dirty water and made available for farm use. Dobbie et al. (2005) investigated an end use for P-saturated ochre as a slow release fertilizer. P-saturated ochre was added at four rates – 20, 40, 80 and 200 t ha^{-1} – in one application to a soil/sand mixture in 5 L pots planted with either grass or barley. At the end of the four-month study, on average 4% of the measured P in ochre was immediately plant-available and no significant difference was noted in soil total Al, chromium (Cr), nickel (Ni) or Zn between the treatments. Soil Fe and manganese (Mn) increased as the ochre additions to the soil increased, but all metals – with the exception of Ni, which was also high in the study control – were within guideline limits (75/440/EEC, European Economic Community, 1975).

Ochre has site-specific physical and chemical characteristics, which are dependent on: Fe mineralogy, water content of sediments, degree and rate of oxidation, age of deposits, pH, Fe supply and concentrations of alkali and sulphate (SO_4) associated cations (Singh et al., 1999). Saturated ochre from two mine water treatment plants (MWTPs) in the U.K. - Polkemmet, West Lothian and Minto, Central Scotland - showed maximum P retention capacities of 26 g P kg^{-1} and 30.5 g kg^{-1}, respectively (Bozika, 2001; Heal et al., 2003). Comparatively, Heal et al. (2003) gave maximum P adsorption capacities of other materials: Danish sands, 0.02-0.13 g kg^{-1}; blast furnace slag, 0.05-0.65 g kg^{-1}; steel furnace slag, 1.4 g kg^{-1}; zeolite, 2.2 g kg^{-1}, laterite, 0.75 g kg^{-1}; lagoon fly ash, 3.1 g kg^{-1}; iron oxide tailings, 8.6 g kg^{-1}; and precipitator fly ash, 14 g kg^{-1}.

The ability of ochre to adsorb P can be assessed using Freundlich and Langmuir isotherms (Poots et al., 1976; Froelich, 1988); the Langmuir model can be used to provide an estimate of the maximum mass of P adsorbed per mass of the ochre (Sharpley, 2000). One form of the Langmuir isotherm equation is (McBride, 2000):

$$\frac{C_e}{\frac{x}{m}} = \frac{1}{ab} + \frac{C_e}{b} \qquad [2.1]$$

where C_e is the concentration of P in solution at equilibrium (mg L^{-1}), x/m is the mass of P adsorbed per unit mass of ochre (g kg^{-1}) at C_e, *a* is a constant related to the binding strength of molecules onto the ochre and *b* is the theoretical amount of P adsorbed to form a complete monolayer on the surface i.e. the maximum P adsorption capacity of ochre (g kg^{-1}). A more accurate maximum adsorption capacity may be achieved by saturation experiments (Arias et al., 2001). Ochre (a ferric oxyhydroxide precipitate) deposits occur from acid mine drainage (AMD) in specific geological settings. Oxidation occurs as AMD leaves the mine adit resulting in ochre deposition, which is ecologically devastating (Yau & Gray, 2005). The sorption capacity of ochre to sequester P is high, but site-specific i.e. the maximum P adsorption capacity varies from location to location. This characteristic was investigated at numerous sites in the U.K. and ranged from 0.5 g P kg $^{-1}$ to 2 g P kg^{-1} (Bozika, 2001). Maximum P adsorption capacities vary with the media used (Table 2.2).

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TABLE 2.2 MAXIMUM ADSORPTION CAPACITIES OF DIFFERENT MEDIA

Amendment		Maximum adsorption capacity g P kg^{-1}
Danish sands	Mann, 1997	0.02 – 0.13
Gravel	Mann, 1997	0.03 – 0.05
Bottom Ash	Mann, 1997	0.06
Steel furnace slag	Curcarella and Renman, 2009	0.38-1.40
Blast furnace slag	Curcarella and Renman, 2009	0.05 – 0.65
Fly ash	Curcarella and Renman, 2009	0.62
Shale	Drizo, 1999;;;	0.75
Laterite	Drizo, 1999;;;	0.75 – 1.38
Zeolite	Xu et al., 2006	1.00-2.20
Serpentinite	Xu et al., 2006	1.00
EAF steel slag	Xu et al., 2006	2.20
Polkemmet ochre	Heal, 2005	26.00
Minto ochre	Heal, 2005	30.50

The potential for ochre to reduce P from soiled water is high and, if used in conjunction with biofilters, may provide an efficient means of treating soiled water. The vast majority of research in the U.K has focussed on ochre from coal mining areas with no metal contents. Ochre-P pellets, developed by the University of Newcastle in the U.K, allow *in situ* applications of ochre at specific locations (P stripping zones) on a farm without discoloration of water. They absorb P from solution and may be used in the remediation of wastewaters from different sources, such as agricultural runoff (Heal et al., 2005). Exhausted pellets may then be pulverized and applied as fertilizer. As P desorption from saturated ochre is < 1%, it may be used in surface water and replaced when saturated. Constructed wetlands (CW) amended with coarse grained ochre, have removed 90% of P from sewage effluent (Heal et al., 2004)

2.8 Relevance and applicability of alum, PAM and ochre for Ireland

In Ireland, the focus has been on non-hazardous sludge disposal. Numerous legislative constraints regarding sewage sludge applications exist. The EU Directive, 86/278/EEC (European Economic Community, 1986), regulates the use of sewage sludge in agriculture preventing harmful effects on soil, vegetation, animals and humans. It specifies limit values for maximum concentrations of heavy metals in soil and sludge, and limit values for maximum annual quantities of heavy metals introduced to the soil.

A Code of Good Practice for the Use of Biosolids in Agriculture (DEHLG, 1999) set new standards for treatment. These standards are broadly in line with the United States EPA “Class A” standards (USEPA, 2002). This presents new challenges for the optimisation of sludge treatment and final effluent quality. However, not all sludge is suitable for land application. In a study in the South East of Ireland, 21% of soils examined breached the provisions of the EU Sewage Sludge Directive, 86/278/EEC (European Economic Community, 1986), for heavy metals before any sludge application (McGrath & McCormack, 1999). This, coupled with the suitability and availability of tillage lands, poses problems for sludge application.

With 90% of all sludge coming from agriculture, the addition of alum or PAM to farm wastewater before land application would reduce the risk of nutrient loss to surface waters. This could be done in two ways: simultaneous application or prior application to wastewater. Another option is to apply alum and PAM to buffer strips. Direct application to surface waters (lakes, streams, tributaries, drainage channels), in conjunction with settlement basins, could also be considered.

A feasibility study examining the management and remediation of AMD-rich waters in the Avoca-Avonmore river catchment shows, that the capital cost to build a full scale treatment plant would be €3.6 million (ex VAT) with an annual operational cost of €0.5 million (ex VAT), while an annual operational cost of €300,000 would be required for sludge disposal (Anon, 2007). An alternative use for the ochre sludge now needs to be found. If suitable, ochre from such remediation could be used to sequester P from farm yard wastewater or other P solutions. Saturated ochre could then be used as a slow release fertilizer.

2.9 Possible N remediation technologies

Conventional methods for N removal, including monitored natural attenuation (ASTM, 1998), pump-and-treat (USEPA, 1990), wherein treated water is used to irrigate crops, pump-and-waste (USEPA, 1990), wherein contaminated water is evaporated or injected into a saline aquifer or geological unit and phytoremediation (Suresh & Ravishankar, 2004) have been used to remediate nitrate contamination. Pump-and-treat can be expensive and works most effectively in homogeneous media, and pump-and-waste is not sustainable and causes plume migration.

New and emerging pre-treatment remediation technologies, such as continuously moving biofilm reactors (Rodgers & Burke, 2002), sequencing batch biofilm reactors (Rodgers et al., 2004), trickling filters (Kuai et al., 1999), activated sludge systems (Gao et al., 2004), fluidised-bed biofilm reactors (Rabah & Dahab, 2004) and rotating biological contractors (Ayoub & Saikaly, 2004) have shown good potential for biological N removal from domestic and agricultural wastewaters. Technologies presently used for septic tank nutrient removal are now being adapted for the agricultural sector. Biological denitrification systems may be introduced into current or old systems to rejuvenate the nutrient remediation process. Amelioration may be achieved at low cost. Such biological denitrification systems have been tested at the Alternative Septic System Test Centre (MASSTC, Massachusetts) (Sengupta et al., 2006). This technology may be used to remediate dairy parlour washings and soiled water, and may reduce storage volumes and associated costs. As the cost of water is due to rise considerably (IFA, 2009), recycling of water on farms is becoming increasingly important. This could possibly reduce volumes of dirty water on farms. Systems with higher efficiencies for wastewater remediation have been developed using partial nitrification, partial nitrification – denitrification and anaerobic ammonium oxidation in single-stage or two-stage reactors. Partial nitrification, coupled with a reduction of nitrate with an organic carbon (C) source or with ammonium, achieves higher remediation than total microbial nitrification (Paredes, 2007).

2.9.1 Permeable reactive barriers (PRB)

An alternative, medium to high cost (depending on type of PRB envisaged and depth of excavation) *in situ* treatment system may be a PRB, defined as “an emplacement of reactive materials in the subsurface designed to intercept a contaminant plume, provide a flow path through the reactive media, and transform the contaminants into environmentally acceptable forms to attain remediation concentration goals down-gradient of the barrier” (Powell & Powell, 1998). *In situ* subsurface denitrification trenches, wherein wastewater flows through a C-rich mixture to reduce nitrate concentrations, is a PRB adapted for agricultural use (Healy et al., 2006). A PRB or denitrification wall is only one of many denitrifying bioreactor types, i.e. denitrification beds, up-flow bioreactors, stream bed bioreactor or denitrification layers. The limitations of a denitrification wall are that they require site-specific analyses of hydraulic gradient, and the depth and extent of the nitrate plume(s). Removal of nitrate is confined to up-gradient pollution sources and within the upper 2 m of groundwater. Problems may arise if the denitrification wall has a lower saturated hydraulic conductivity than the surrounding sub-soil. If this occurs, nitrate plumes tend to flow around the wall and not through it. However, in cases where nitrate contamination occurs below 2 m, the diameter (parallel to flow path of contaminant) of the trench may be widened. This causes up-welling into the more permeable trench.

Organic C amendments offer low-cost surface and subsurface treatment alternatives for wastewater treatment. C availability is an important factor that affects denitrifying activity in soils. The presence of C provides an energy source, thereby enhancing the potential for denitrification. Denitrification may be increased in soils by the addition of an external C amendment. This amendment may be natural C such as woodchip, wheat straw, corn, vegetable oil, sawdust mulch or other materials, such as treated newspaper or unprocessed cotton (Volokita et al., 1996). *In situ* treatment may involve material being used in isolation, or mixed with soil or sand (Table 2.3). Identification of areas with different denitrification potentials, would aid in the location of shallow groundwater remediation technology. In this sense, areas with high natural attenuation capacity could be avoided.

Many Irish farmers currently grow short rotation coppice willow. A Bioenergy Scheme providing establishment grants to farmers for up to 50% of the costs associated with establishing Miscanthus (Miscanthus sinensis 'Zebrinus') and willow (*Salix* spp.) is now in place. Farmers that plant on set-aside land can receive an EU Premium of €45 per ha^{-1} (2010 prices). €8 million is being allocated over the period 2007 to 2009 for the grant scheme to encourage the planting of willow and Miscanthus for the production of biomass suitable for use as a renewable source of heat and energy. In addition, woodchip is being used on Irish farms for bedding on out-wintering pads as an alternative to keeping animal in slatted sheds throughout the winter months. For energy purposes, 1 tonne of woodchip costs approximately €40 (2010 prices).

Four types of PRB exist: a) *a funnel-and-gate system* used primarily for halogenated hydrocarbons, aromatic compounds and heavy metal remediation; (Figure 1 a, b) an *injection well* configuration, where a reactive wall is generated through injection of a reactive solution; c) *passive collection* with reactor cells, where contaminated water is drained to a reactive zone; and d) *a shallow (< 10 m) continuous trench* used for nitrate remediation (Figure 1 b). Deeper trenches are possible but costs would be prohibitive.

TABLE 2.3 RATES OF NITRATE REMOVAL USING VARIOUS SOLID CARBON REACTIVE MEDIA IN MOST RECENT STUDIES .

Experiment type	**Nitrate input**	**Reactive Media**	**Residence time**	**Nitrate removal rate**	**Reference**
	mg $NO_3^-L^{-1}$	% by volume		mg L N day^{-1}	
Field	63.0	Sawdust (30%)	3.5 to 7 days	15.0	Fahner, 2002
Column	12.0	Sawdust (30%)	0.5 to 7 days	7.1	Fahner, 2002
Column	40.0	Sawdust (30%)	1.5 to 7 days	9.5	Fahner, 2002
Column	70.0	Sawdust (10-20%)	1 day	2.8 to 6.5	Vogan, 1993
Column	50.0 to 87.0	Woodchip (100%)	1.6 days	14.0	Carmichael, 1994
Laboratory microcosm	16.0	Sawdust (30%)	n/a	3.6	Schipper & Vojvodic-Vukovic, 1998, 2000, 2001
Field	50.0	Sawdust (31.5%)	9 days	1.4	Schipper et al., 2005
Field	1.2 to 57.0	Sawdust (15 – 20%)	13 to 30 days	0.7 –to 2.6	Robertson et al., 2000
Field	4.8	Woodchip (100%)	3 to7 days	4.0 to 32.0	Robertson et al., 2000
Field	14.2 to 37.7	Wood by-product material	3 to 5 yr	7.0 to >10.0	Robertson et al., 2005
In stream bio-reactor	4.8	Woodchip (100%)	1.5 yr	0.9 (3ºC), 6.6 (14ºC)	Robertson & Merkley, 2009
Field trench near tile drains	< 0.3 to 35.0 [1]	Woodchip (100%)	5 yr	0.62	Jaynes et al., 2008
Field	11.5	Wood particles	20 mo	2.0 to 7.0	Van Driel et al., 2006
Laboratory – denitrification rates with different flow rates	50	Woodchip (23%)	85 days	2.9 (2.9 cm d^{-1}), 4.1 (6.6 cm d^{-1}), 4.5 (8.7 cm d^{-1}), 4.0 (13.6 cm d^{-1})	Greenan et al., 2009
Column	50, 120, 200	Wood chips (100%)	4 weeks	1.3	Saliling et al., 2007

Schipper et al. (2010) reviews all known field studies giving removal rates.

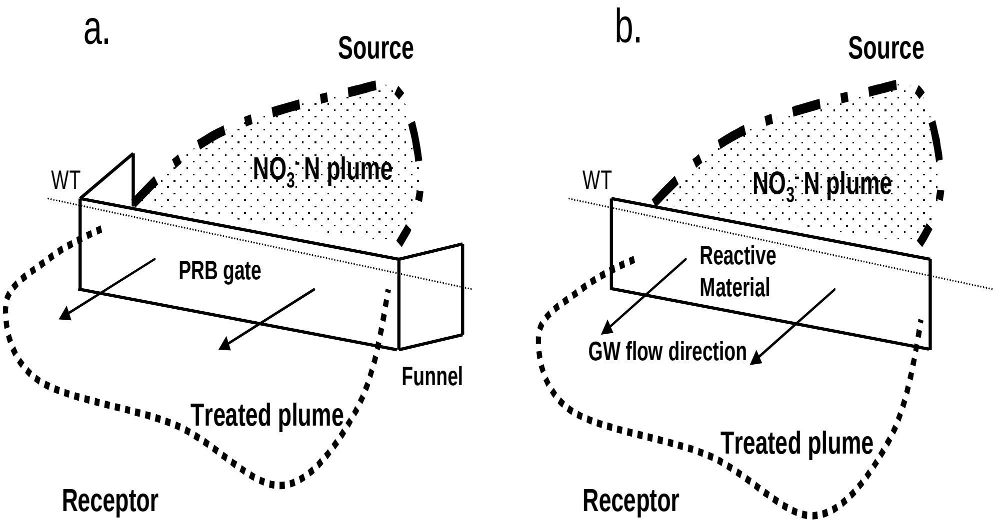

FIGURE 1 A-B FUNNEL AND GATE AND CONTINUOUS TRENCH PRB CONFIGURATIONS.

Microbial denitrification is by far the most important process for converting N back to N_2 (Davidson & Seitzinger, 2006), but, while N inputs to aquatic systems influence denitrification rates, it is hydrology and geomorphology (control retention time) that influence the proportion denitrified (Seitzinger et al., 2006). The reason for denitrification hotspots in part may be due to increased saturated hydraulic conductivity (K_s) or mobile fractions of groundwater, and slow diffusion into the immobile fraction where denitrifiers are active (Schipper et al., 2005). Within a denitrification wall hydraulic properties are likely to change spatially (K_s) and temporally (hydraulic gradient). Denitrification can be differentiated from dilution using chloride (Cl^-) as a tracer (Devito et al., 2000; Hill et al., 2000) as areas with low nitrate concentration and unaffected Cl^- concentration point to denitrification, and low nitrate and low Cl^- point to dilution.

Gurwick et al. (2008) suggested that low K_s areas can also be associated with buried organic matter in riparian soil, which transmits water more slowly. These buried layers, in turn, provide a supply of organic matter for denitrification. In an enhanced denitrification PRB scenario, a solid C source (e.g. woodchip) is mixed with soil, which changes subsurface K_s in the trench. This occurs during construction when compaction or insufficient mixing of soil and C material occurs. The interface between the soil and the denitrification trench may also create preferential flow paths into the reactive media. Other work has shown, that the heterogeneous distribution of denitrification rates in riparian soils is sometimes related to localisation of activity around particles of decaying organic matter (Parkin, 1987; Gold & Jacinthe, 1998; Jacinthe et al., 1998). In these instances, elevated levels of denitrification occurred due to the increased availability of organic C, which would otherwise be limiting.

Bromide (Br^-)-to-NO_3^- breakthrough has been used by many to calculate nitrate removal rates (Simmons et al., 1992; Vogeler et al., 2006) using the C/C_o normalisation (Freeze & Cherry, 1979), where C is the nutrient concentration at a certain time and C_o is the nutrient concentration at time zero. Schipper et al. (2005) used a simultaneous injection of nitrate (50 mg NO_3^- L^{-1}) and Br^- (100 mg L^{-1}) in a recharge experiment. Breakthrough in a down-gradient denitrification trench exhibited high nitrate removal rates, calculated using Darcy's discharge Law (section 6.4) of 1.4 g N m^{-3} of wall d^{-1}. Due to a high background of atmospheric N_2, denitrification measurement is generally performed by acetylene block or stable isotope techniques (Bradley et al., 1993; Groffman et al., 2006). Schipper et al. (2005) achieved a lower removal rate of 0.11 g N m^{-3} using such techniques, proving that nitrate availability limited the denitrification process. Other methods include using water chemistry and other parameters measured *in situ* from monitoring wells to imply the presence of denitrification, e.g. low dissolved oxygen, high Fe^{2+} and $Mn^{2+}$with an increase in dissolved organic C.

Another approach is to use monitoring equipment drilled to a specific depth to perform an adapted *in situ* push-pull experiment. In this method, known concentrations and volumes of Br^- and ^{15}N-enriched nitrate are pushed into an aquifer and then, after an incubation period, pulled back again. Groundwater denitrification may be quantified over different time intervals by extracting the headspace of sample bottles and analysing using a gas chromatograph. Mean denitrification rates of 96±19.7 µg N kg^{-1} d^{-1} were found, compared with lower rates found in microcosm experiments from the same site (Addy et al., 2002). Such a method avoids the use of a block, which may also inhibit nitrification and the acetylene may not diffuse into all active denitrification sites in the soil, and may not halt denitrification at N_2O under low nitrate conditions (Addy et al., 2002). Groffman et al. (2006), in a review of denitrification methodologies, points to direct N_2 and N_2/Argon (Ar) measurements in aquatic and marine systems. If a denitrification trench system can remain fully saturated, a closed system may be developed, allowing no gas exchange with the unsaturated zone and, in turn, the atmosphere. MIMS (Kana et al., 1998) can be used to determine N, O_2 and Ar dissolved in groundwater. Ar is used as a conservative tracer to mimic atmospheric N losses. This technique has been used in Irish groundwaters to assess natural denitrification rates (Khalil & Richards, 2008).

2.9.2 Reactive materials for a PRB

At the University of Waterloo, Canada, Carmichael (1994) used a column study, comprising woodchip mulch (100% by volume) to treat dairy parlour washings with an influent nitrate concentration of 50 to 87 mg NO_3-N $L^{-1}$and achieved 87% nitrate removal at 22ºC with a hydraulic retention time of 1.6 days.

Healy et al. (2006) also examined the use of various wood materials (sawdust, sawdust and soil, sawdust and sand, and medium-chip woodchip and sand) as a C source in horizontal flow filters to denitrify nitrate from a synthetic wastewater. Two influent concentrations of 200 mg NO_3-N $L^{-1}$and 60 mg NO_3-N L^{1}, loaded at 2.9 to 19.4 mg NO_3-N kg^{-1} mixture, were used. The horizontal flow filter with a medium-chip woodchip/sand mixture and an influent concentration of 60 mg NO_3-N L^{-1}, which operated over the study duration of 166 days, performed best, yielding a 97% reduction in nitrate at steady-state conditions. Important here is the differential k between the media and the surrounding subsoil. Gomez et al. (2000) investigated process yields, represented as C/NO_3-N ratios of three C sources (sucrose, ethanol and methanol), on submerged filters for the removal of nitrate from contaminated groundwater was examined. Metals such as Al, magnesium (Mg), rhodium, palladium and Cu have been investigated, but are cost-prohibitive (Schrimali and Singh, 2001). Soil texture, soil management, tillage, rainfall events, and rates of microbial respiration and nitrification have all been recognized as variables that regulate denitrification (Hofstra & Bouwman, 2005). Rates of denitrification (µg N g^{-1} dry soil day^{-1}) differed in tests with incubated undisturbed permanent grassland cores of humic cambisol (2.09±0.01 µg N g^{-1} dry soil day^{-1}) and gleyic cambisol (4.34 ±0.10 µg N g^{-1} dry soil day^{-1}) Irish soil groups. The gleyic cambisol soil with woodchip amendment (5:2 g w/w) resulted in a five-fold increase in denitrification rates (Sullivan & McDermot, 2007).

2.9.3 Knowledge gaps in PRB research

Other applications of the woodchip PRB concept have been extended to *in situ* bioreactors, deep drain pipe installations (Greenan et al., 2009), soil reactive layers and effluent beds (Robertson et al., 2000; Robertson et al., 2005; van Driel et al., 2006; Robertson & Merkley, 2009). All such technologies are grouped under ‘denitrifying bioreactors’. Within this body of work ‘denitrification trenches or PRB’ are discussed. The main knowledge gaps associated with denitrification PRB research are (Schipper et al., 2010):

1) Removal rates of nitrate and the controlling factors such as temperature and processes in competition for available C in the sub-soil.
2) The mechanism for nitrate removal. The processes that compete with denitrification are not fully understood. Such processes are reviewed by Rivett et al. (2008).
3) The unknowns of pollution swapping. Complete saturation allows N_2 production, but, as wetting and drying occurs in the soil profile, N_2O emissions could be problematic.

An additional knowledge gap identified by the present review is:

4) There is no method to track denitrification over time in a permeable reactive barrier. An extension of this methodology would be to identify denitrification hotspots within a denitrifying bioreactor.

2.9.4 Implementation of PRB

In a PRB, the reactive material is placed in a trench and sealed to surface level with clay. The reactive zone must have a higher conductivity than the surrounding soil to encourage flow into the reactive zone (Simon & Meggyes, 2000). Gravel should be placed at the edges of the reactive zone to stop small particles washing and clogging the trench. Geotechnical considerations, such as subsurface soil strength and the presence of cobbles, should be considered. A temporary piezometer network, ideally coupled with a ground-penetrating radar survey, should be utilized to identify the location and movement of the migrating contaminate plume on-site. A barrier, orientated adjacent to groundwater flow direction, taking annual deviations into consideration, may be placed at various depths, depending on average watertable heights, and may be placed at strategic positions adjacent to farmyards, soiled water installations, slurry and silage facilities, along shallow groundwater zones adjacent to riparian zones, ditches or open water ways. The identification of the source of nitrate contamination, possible receptors, and the hydraulic connection between these in groundwater is important for barrier location (Jun et al., 2005).

The time frame for site evaluation, hydrogeological study, engineering design and implementation could take from 14 to 30 weeks (Kalin, 2004). Cross compliance focuses the farmer towards management of the land to achieve a higher level of environmental protection. Irish farmers, under the REPS, must leave a 1.5 m wide buffer strip of uncultivated land beside watercourses. Buffer strips may have a positive effect on P and pesticide loss, as low soil P levels and permanent cover “trap” P. A barrier placed at such a location offers receptor protection, as a shallow watertable allows for the entire remediation of the plume and integrates nutrient remediation and control and could potentially cut down on the design and implementation timeframe.

2.10 Focus of this study - potential options for agriculture in Ireland

In addition to the present POM under the WFD, groundwater and surface water remediation and control technologies are required to capture nutrient loss where nutrient management fails or lag time prevents water quality improvements. An integrated remediation and control approach is needed to address multiple simultaneous challenges of N and P losses. Therefore, *in situ* and pre-treatment of farmyard manures should integrate N remediation and P control. A low biofilm technology to achieve organic C, N and SS removal, coupled with P sequestration media such as ochre, are viable options for soiled water recycling. For the purposes of this study, the efficacy and suitability of metal mining ochre P, as opposed to coal mining ochre, was investigated to sequester P from solution, e.g. dairy waste water or surface water. Ochre mineralogy was investigated to unlock the site-specific nature of ochre’s maximum P sequestration potential. The efficacy and suitability of ochre as a soil amendment was investigated to prevent DRP losses in runoff.

Medium-cost, low-management remediation technologies, such as a PRB, have good potential in Ireland, because they can be implemented at farm or catchment level. Research shows that PRBs provide a long-term solution to nitrate remediation in shallow groundwater. The reactive media to achieve denitrification identified in the literature is woodchip, which could be sourced on Irish farms through present grant schemes. The optimal location of a PRB is investigated using hydrogeological parameters and denitrification potential techniques. In the field, a woodchip slug is used to remediate a nitrate plume, which has developed from dirty water irrigation. Direct denitrification techniques are developed, which could later be used on a full-scale PRB.

Chapter 3 Study Sites

3.1 Introduction

Samples for all ochre batch experiments were collected at White Bridge, Avoca, Co. Wicklow. Dirty water samples were collected from the Dairy Farm at Teagasc, Johnstown Castle, Environmental Research Centre, Co. Wexford. For ochre amendment to soil, the ochre was taken from the same Avoca site and the soil was taken from the beef and dairy farms at the Johnstown Castle research site. For the permeable reactive barrier location work, a 4.2 ha site (“Foals House”) was used on the beef farm at Johnstown Castle. For the woodchip slug work, a 20 ha section of the dairy farm at Johnstown Castle was used.

3.2 Study site descriptions

All chemical, metal and MIMS analysis of water, ochre and soil was carried out at Teagasc, Johnstown Castle, Environmental Research Centre, Co. Wexford.

3.2.1 Study Site 1: White Bridge, Avoca, Co. Wicklow

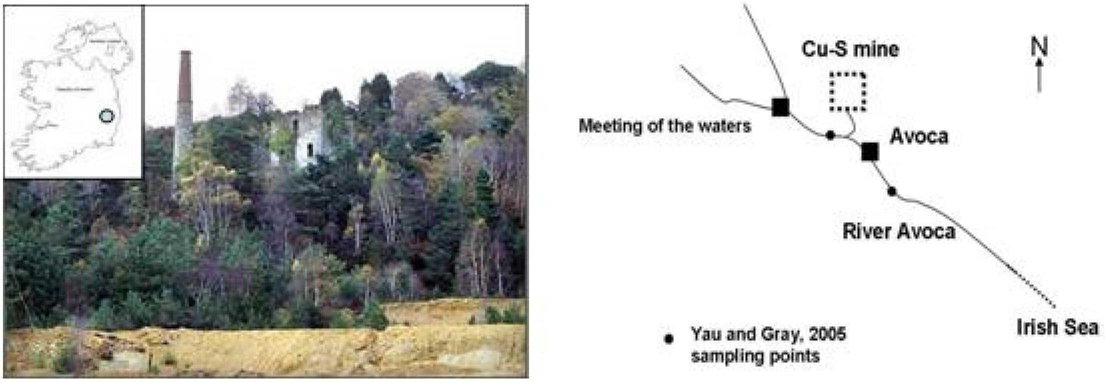

Figure 3.1 The study site location in Avoca, south east Ireland, and Cu-S adit position.

The Cu-sulphur (Copper-Sulphur) drainage adit site is located at White Bridge, Avoca (latitude 52º48’N, longitude 6º 12’W (Figure 3.2 a)). Ochre is deposited for approximately 300 m along a tributary that leads to the Avoca River (Figure 3.1). Sulphide minerals, such as pyrite, chalcopyrite, sphalerite and galena, are present on site. The sulphide mineral deposits, classified as volcanogenic massive sulphide

(VMS), were hosted in the local Ordovician volcanic rocks. Ochre settling pits were used during the mining processes of the 1940’s (Gallagher & O’Connor, 1999). Upstream of the confluence of the Cu-S adit tributary and the Avoca River, Yau & Gray (2005) measured Zn, Cu, Fe and Pb concentrations in the Avoca River sediments of 336±34 µg Zn L^{-1}, 221±101 µg Cu L^{-1}, 5.39±0.17 Fe µg L^{-1} and 334±21 µg Pb L^{-1} (Figure 3.1). Downstream of the confluence, these sediment concentrations were 5640±329 µg Zn L^{-1}, 455±22 µg Cu L^{-1}, 8.08±0.23 µg Fe L^{-1} and 500±194 µg Pb L^{-1}, indicating a contamination source input to the main river between these two sampling points (Figure 3.1).

3.2.2 Study Site 2: Dairy Farm, Co. Wexford

The research area at the Teagasc, Johnstown Castle, Environmental Research Centre (located as in Figure 3.2 a), (latitude 52º 17’N, longitude 6º 29’W) is a 60.5-ha dairy farm situated on undulating slopes with grey-green shale bedrock of low permeability covered by glacial drift (Figure 3.2 b). The contours on this image are groundwater heads (m AOD) Contours are only drawn within the well network. The soil profile consists of fine loam underlain by a loam-to-clay loam subsurface soil (Culleton & Diamond, *pers comm.*).

The landuse on the farm is permanent grassland. Mean precipitation during the 2005 to 2008 period was 1046 mm, of which 553 mm (178 days) was effective drainage (recharge). Several treatments co-exist on the farm since 2004. Treatments are stocked at 2.75 LU ha^{-1}. Other areas - spare areas (poor quality) on the farm operate at 2 LU ha^{-1}. The area north of the farm has < 2 LU ha^{-1}. Spent timber residue (woodchip) from out-wintering pads on site is incorporated into the soil as a fertilizer to some areas for silage production. All dirty water on site is generated from rainwater and milking parlour washings and distributed by splashplate, band spreader or trailing shoe, depending on the treatments involved. Slurry is applied in the same way. The average nutrient N content of slurry was 3.6 kg N per 1000 L of slurry and 0.36 kg N per 1000 L of dirty water. Farmyard manure (FYM) is applied pre-ploughing. In 2007, the area north of the dairy farm received small amounts of slurry, FYM and woodchip in places. In addition, several plots received dirty water from February to October through a ‘Roto-Rainer’ (Briggs, New Zealand) sprinkler irrigation system. The recommended irrigation rates should not exceed 50 mm yr^{-1}. Pre 2007, several areas next to the stream woodland were used as sprinkler locations for soiled water (rainwater, faeces, milk parlour washings with a BOD < 2500 mg L^{-1}). Indicative soiled water concentrations are presented in Ryan et al. (2006). For the denitrification potential experiment in natural and enhanced wells, a 20 ha subsection of the dairy farm (60.8 ha) was taken (Figure 3.2 b). The site comprises mature medium permeability till overburden (k_s, 5 x 10^{-8} m s^{-1} to 5 x 10^{-4} m s^{-1}), which is heterogeneous and morainic in nature. Vertical unsaturated travel times (months to years) on site varies for each well based on unsaturated zone thickness, effective rainfall (600 mm) and effective porosity (n_e from 5 to 30%) (Fenton et al., 2009). The soil is underlain by an unproductive, low conductivity pre-Cambrian greywacke; schist and massive schistose quartzites that have been subjected to low grade metamorphism. Depth to bedrock on site is approximately 12 m. The study site consists of eight wells (Figure 3.2 c) (25 mm LDPE casing; Van Walt Ltd, Surrey, U.K.) installed using rotary drilling (60 mm diameter) – using a Giddings soil excavation rig - to several meters below water strike ensuring that seasonal variations in the water table elevation would be within the well screen zone (mean drilling depth was 6.3 m). Nitrate concentration varies spatially on site, but with little temporal change, indicating N input sources and transformation processes remain constant.

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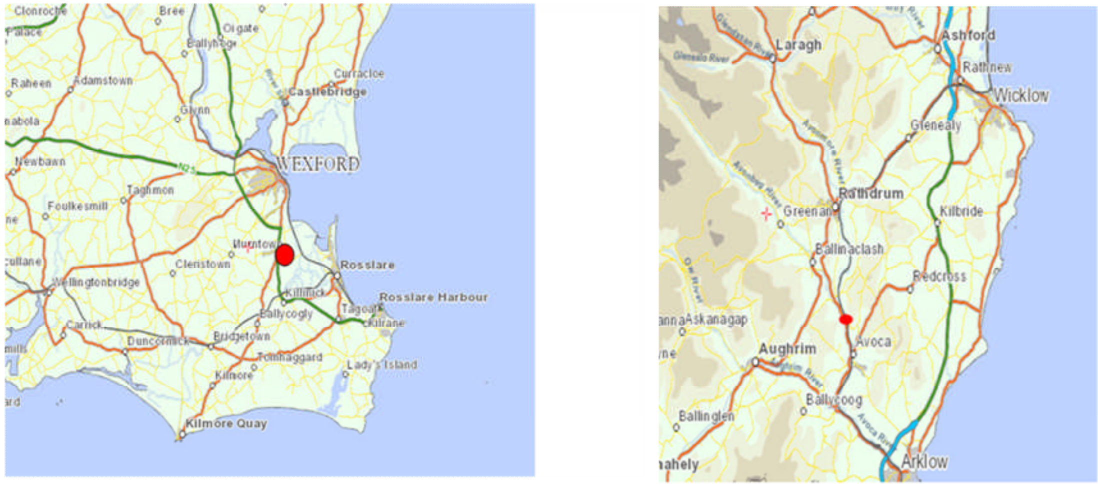
3.2.3 Study Site 3: Beef Farm, Co. Wexford

The site is located on the beef farm, on the Teagasc, Johnstown Castle, Environmental Research Centre (latitude 52º 17’N, longitude 6º 30’W). The site is locally known as “Foals House” a 4.2 ha gently sloping (2%) study site, comprising six study plots (Figure 3.3 a, b). The field site is bound to the north by an elevated 3.2 ha grassland Sandhill area (from 71 to 75 m above ordnance datum (AOD), slope 5%), to the North West by a 2.8 ha grassland site (from 71 to 72 m AOD, slope 2%, and on all other sides by agro-forestry). The dirty water point source was located in this Sandhill area. Possible receptors on site are a narrow contour stream and the larger Kildavin River boarding the site (Figure 3.3 b). The Sandhill and North West areas are up-gradient and hydrologically connected through shallow flow lines to the 4.2 ha study site approximately 200 m away. Groundwater head contours show groundwater flow direction is towards the six isolated plots (Figure 3.3 b). Two shallow, unlined trapezoidal drains, excavated to a depth of 1 m, with bases ranging from 71.08 m AOD to 70.2 m AOD, and from 71.10 m AOD to 70.30 m AOD, respectively, were constructed along the northern edge of the plots. This prevents runoff from entering the plots from the elevated up-gradient area. Runoff from the point source flowed directly into these drains. The plots were also isolated laterally to 1 m bgl to prevent cross flows from one plot to the other.



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1:25000 Source: OSI

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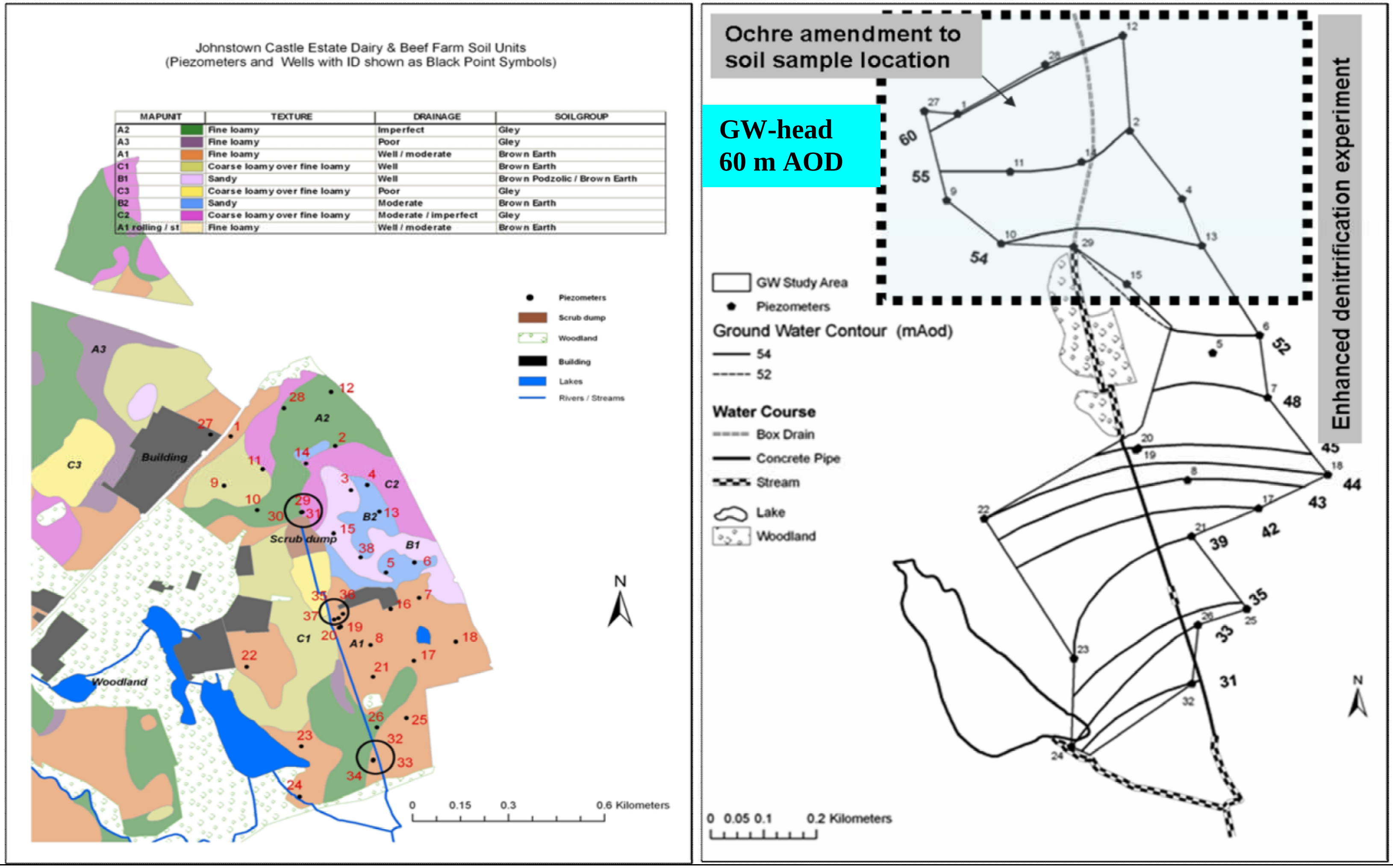
FIGURE 3.2 A SCHEMATIC OF SOUTHEAST IRELAND WITH DAIRY, BEEF FARM SITES AND MINE SITE.



MAPUNIT		TEXTURE	DRAINAGE	SOILGROUP
A2	🟩	Fine loamy	Imperfect	Gley
A3	🟪	Fine loamy	Poor	Gley
A1	🟧	Fine loamy	Well / moderate	Brown Earth
C1	🟨	Coarse loamy over fine loamy	Well	Brown Earth
B1	🟪	Sandy	Well	Brown Podzolic / Brown Earth
C3	🟨	Coarse loamy over fine loamy	Poor	Gley
B2	🟦	Sandy	Moderate	Brown Earth
C2	🟪	Coarse loamy over fine loamy	Moderate / imperfect	Gley
A1 rolling / st	🟨	Fine loamy	Well / moderate	Brown Earth

FIGURE 3.2 B SCHEMATIC OF DAIRY FARM STUDY SITE AT JOHNSTOWN CASTLE, COMPLETE WITH SOIL MAP, GROUNDWATER FLOW MAP, AND WELLS.

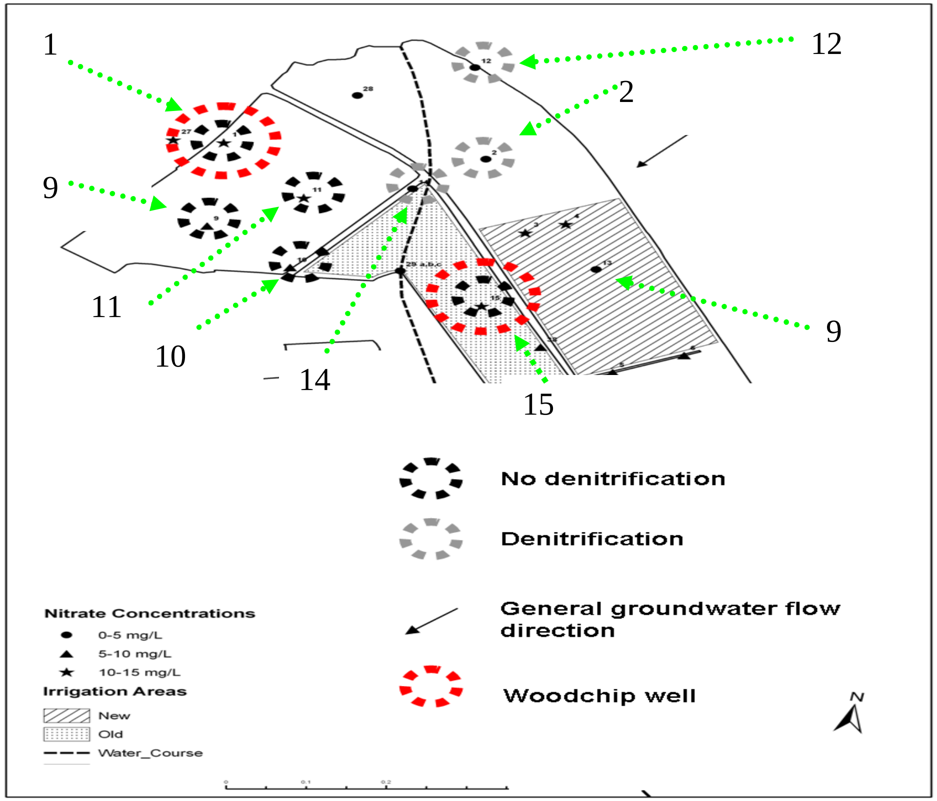


FIGURE 3.2 C SCHEMATIC OF DAIRY FARM STUDY SITE SUB-SECTION FOR WOODCHIP SLUG EXPERIMENT.

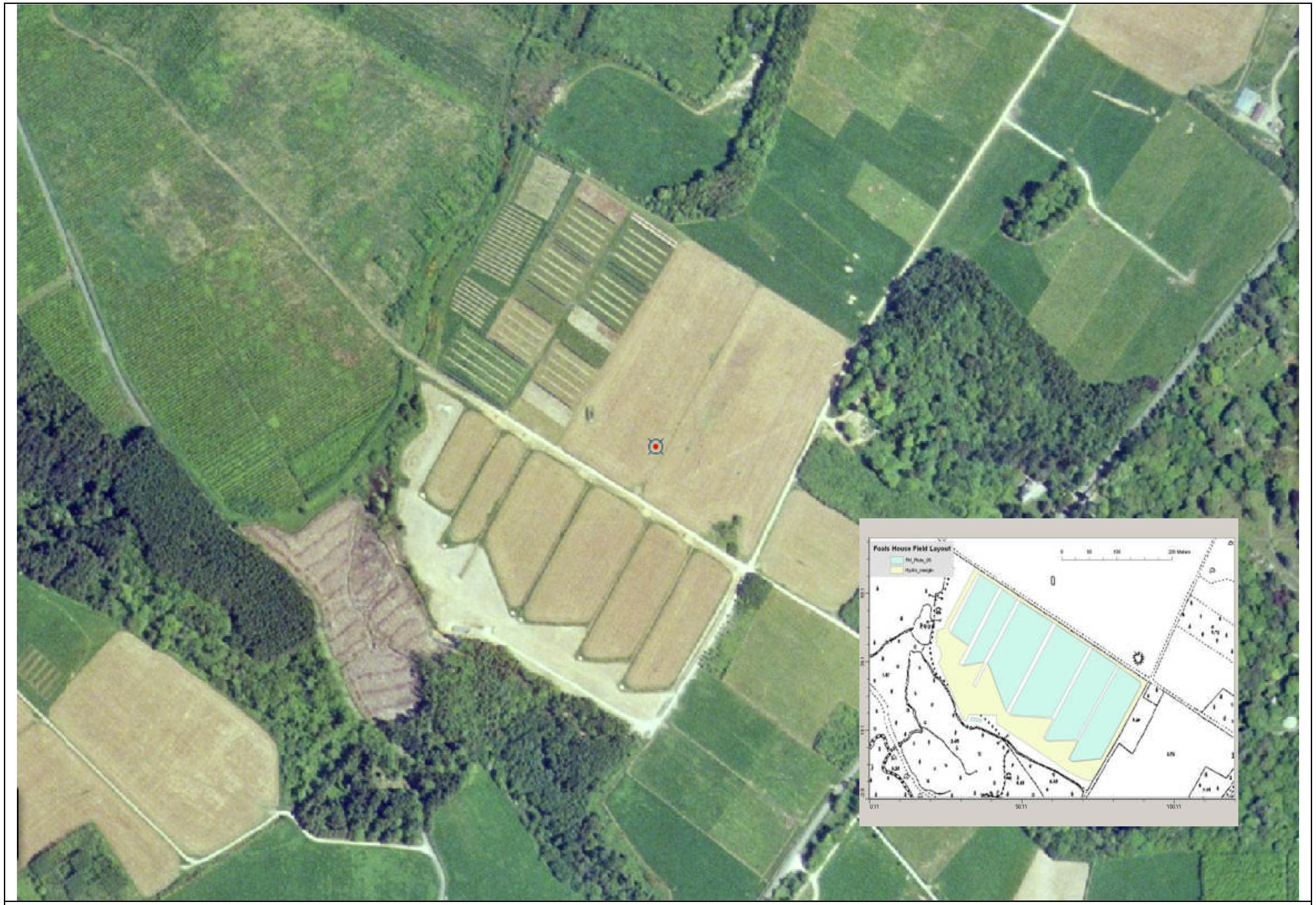


FIGURE 3.3 A AERIAL PHOTOGRAPH OF FOALS HOUSE SITE.

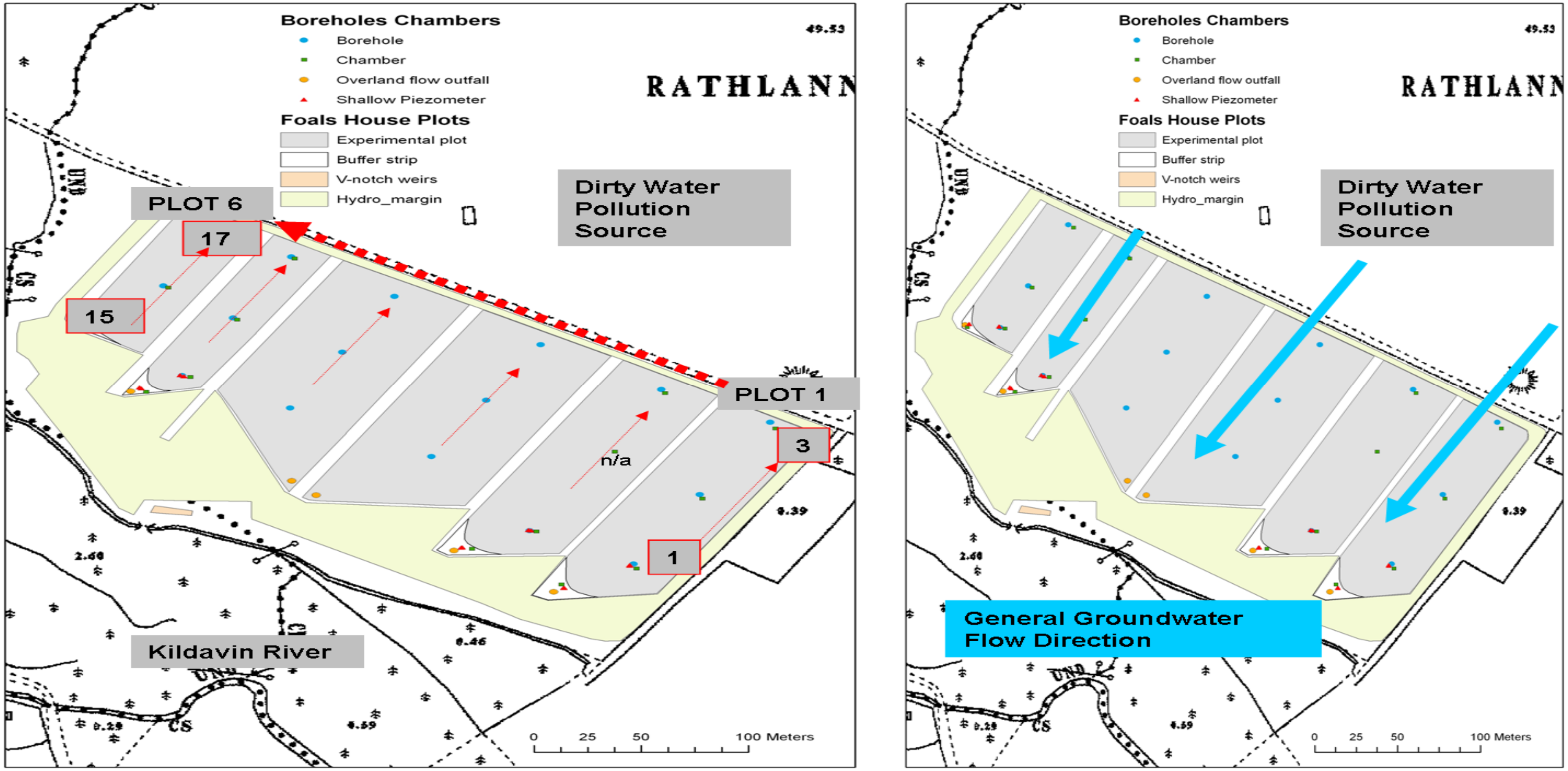


FIGURE 3.3 B SCHEMATIC OF BEEF FARM STUDY SITE AT JOHNSTOWN CASTLE.

Heterogeneous glacial deposits on the farm vary in thickness from 1 to 20 m, which has been confirmed by resistivity geophysical surveys. On site, the glacial deposits are < 10 m, underlain by Pre-Cambrian greywacke, schist and massive schistose quartzite, which have been subjected to low grade metamorphism. The underlying aquifer is generally unproductive (Pl), but of local importance and has moderate vulnerability to nutrient loss. Bedrock outcrops south of the plots indicating the shallow nature of the glacial deposits. This results in a differential K_s at depth. The topography is morainic and, in the area of the point source pollution where the elevation is greater than 71 m AOD, consists of both sand and fine loamy till, and has different topographical form and drift composition. Some of this sand may have been soliflucted downslope, resulting in stratification between sand and underlying fine till. The Sandhill is well- to excessively drained and consists of deep loamy sands (Figure 3.3b). A sandpit of industrial grade sand is in operation in the area. Topsoil samples (0 to 0.4 m) contained 22 ± 3.7 % coarse sand, 26 ± 3.6 % fine sand, 34 ± 5.1 % silt and 18 ± 2 % clay, and subsoil samples (0.4 to 1.0 m) contained 18 ± 5.3 %, 22 ± 4.2 %, 34 ± 4.5 % and 25 ± 4 %, respectively (Diamond, 1988). Clay content increases with depth on site as sand decreases. Silt content remains the same. Textural changes are not due to pedological processes, but to small-scale sorting of glacial till. It is this transition between sand and clay that governs k_s heterogeneity at depth. Subsoils with a high percentage of fines (clay and silt) are classed as having low permeability, poorly sorted subsoils are assigned as having moderate permeability and well-sorted coarse grained subsoils (glaciofluvial sand and gravel) have high permeability (Swartz et al., 1999). In 2005, the first groundwater samples were taken. (The study site was instrumented with piezometers in 2003.) Initially, 30% of all shallow groundwater samples (< 5 m) exceeded nitrate drinking water MAC. A stationary beef dirty water irrigation system, operated on the Sandhill for decades until 2004, was identified as a pollution point source (Figure 3.3 a, b). This small area has been treated uniformly over a long period of time, before and after implementation of the irrigation system. Currently, the site is cut for silage twice-a-year and is being used to monitor natural attenuation (water samples are taken periodically from each well and analysed for nitrate) of the elevated groundwater nitrate plume migration, position and concentration on site.

Chapter 4 Physical and Mineralogical examination of Avoca Ochre

4.1 Materials & Methods

The site-specific nature of Avoca iron ochre was tested in a variety of ways from physical characterisation to maximum P sequestration capacity experiments.

4.1.1 Sample collection and ochre physical parameters

In the field, 81.5 mm-diameter and 60 mm-deep ochre cores were collected from ochre beds and from the adjacent forest floor. Ochre samples were present due to flooding events in the lower reaches of the Avoca–Avonmore catchment. The ochre was examined for dry bulk density and particle density (after Blake & Hartge, 1986), total porosity (after Brady & Weil, 1996), aggregate stability (wet sieving method, BS 1377), undisturbed K_S (falling head method, BS 1377) and particle size distribution (PSD) (sieving and pipette method, BS 1796). Ochre from the forest floor was analysed for total metals, nutrients, mineralogy and was used in all batch experiments. Tributary stream water was also collected and analysed for total metals, nutrients, sulphate (SO_4^+), pH and redox potential (Eh). Stream sediment was also analysed for metals. Water samples were filtered through a 0.45 µm filter membrane. The nutrients were determined using a Thermo Konelab 20 analyser (Technical Laboratory Services, Ontario, Canada) and the metal content was determined using an ICP VISTA-MPX (Varian, California). Total metal determination of ochre sediment and tributary surface water samples were measured by aqua regia digestion using a Gerhard Block digestion system (Cottenie & Kiekens, 1984). To analyse the metals, a 2 g sample of dry sediment material was loaded into a Gerhardt reflux tube and 5 ml of deionised water was added to make up slurry. Then, 16 ml of aqua regia was added (4 ml of hydrogen nitrate (HNO_3) + 12 ml of hydrochloric acid (HCl)). The samples were left to stand overnight and were then placed on a Gerhard reflux system for 2 hrs (40 ºC and left to cool). A 100 ml volume sample was made up with 2 ml of HNO_3. The solution was then filtered and analysed for Cu, Zn, Mn, Fe, Ni, Cr, cadmium (Cd), As, Pb, P, Mg, sodium (Na) and potassium (K) using the ICP VISTA-MPX. For quality control, two reference soil samples of known metal concentration, from the Wageningen International Soil-Exchange Program, were analysed.

4.1.2 Metal and elemental analysis

Thirty mm-deep surface layer ochre samples taken from the forest floor adjacent to the AMD, collected in August 2007 from the same site, were analysed for a complete suite of elements. This area is prone to flooding and ochre is deposited during such events. In this procedure, two 0.5 g sub-samples from an ochre bulk sample, sieved to < 2 mm, were digested using a pressurised microwave digestion with an acid mixture. A trace of material was undigested in the acid. The samples were diluted to volume, including rhodium as the internal standard. The solutions were then analysed by ICP-MS, which was calibrated the same day with acid-matched standards. The results were then corrected for 56.5% loss on drying at 103°C.

4.1.3 X – ray diffraction examination of ochre

Full XRD examination of the mine drainage precipitates was undertaken. An oven-dried sample and an air-dried sample were compared for XRD analysis. The dry sample was prepared as a standard bulk XRD specimen in a side fill holder. The specimen was examined using the Siemens D5000 Diffractometer D6 with Cu $K\alpha$ radiation, a variable divergence of 12 mm, primary sollers, 0.2 mm receiving slit and an energy-dispersive detector. The colour classification of Williams et al. (2002) and Murad & Rojík (2004) was used to confirm the presence of minerals in ochre precipitates.

4.1.4 Stereomicroscopy and bulk X-ray analysis

To determine elemental composition, ochre was subjected to light and electron microscopy. The techniques used included stereomicroscopy (SMZ10-A), polarised light microscopy (Microshot SA) and scanning electron microscope (SEM) with integrated EDX (Hitachi S2700). Stereomicroscopy was used as a technique to prepare samples for SEM/EDX.

4.2 Results & Discussion

The results for all physical and mineralogical work are presented below.

4.2.1 Physical parameters

Physical soil parameters for the *in situ* Avoca ochre from the ochre beds are presented in Table 4.1. The ochre is fine-grained with the following constituency: coarse sand (21.6 % by mass), fine sand (19.5 % by mass), silt (22.3 % by mass) and clay (30.9% by mass). The particle density of the ochre is low at 2.30 g mL^{-1}, which facilitates entrainment and transportation in overland flow during flood events. Avoca ochre has some similar physical characteristics to other ochre found at coal mine sites (Table 4.2).

TABLE 4.1 SELECTED AVOCA OCHRE PARAMETERS FROM THREE SAMPLING LOCATIONS – RIVERINE DEPOSITS, OCHRE BEDS AND ADJACENT FOREST FLOOR.

	Particle density	Total porosity	Air filled pores	Moisture content	MWD
	g mL^{-1}	%	%	%	mm*
Mean	2.30	82.70	65.70	67.20	0.71
Std. deviation	0.53	7.63	7.22	2.48	0.02

*Aggregate stability: wet sieving method - Mean Weight Diameter

TABLE 4.2 COMPARISON OF PHYSICAL PARAMETERS FROM A COPPER SULPHUR MINE (AVOCA OCHRE) AND TWO MINE WATER TREATMENT PLANTS IN THE U.K. (POLKEMMET AND MINTO).

Parameter	Avoca ochre *	Polkemmet ochre**	Minto ochre**
Dry bulk density (g cm^3)	0.80	1.80	0.80
K_s (m d^{-1})	0.90 to 4.80	26.00 to 32.00	0.70-1.70

*Obtained from 3 sampling locations at the study site – riverine deposits, ochre beds and adjacent forest floor, **Adapted from Bozika (2001).

The forest floor ochre collected from Avoca showed higher concentrations of potentially toxic elements such as Pb, Cu and As in comparison with ochre from the Polkemmet site in the U.K. (Table 4.3). Background concentrations and quality objectives for heavy metals in surface sediments (including ochre) of freshwater ecosystems in the Avoca Avonmore catchment are: Pb, 22 mg kg^{-1} and Cu, 23mg kg^{-1}. (Yau & Gray, 2005). These concentrations are considerably higher than the maximum allowable concentrations for contaminated land (86/278/EEC; European Economic Community, 1986). Therefore, Avoca ochre would not be suitable for land application after P saturation. Metal concentrations in the tributary ochre sediment were: Cu, 23 mg kg^{-1}; Fe, 44 g kg^{-1}; Pb, 22 mg kg^{-1}; and Zn, 69 mg kg^{-1}indicating increased metal accumulation in ochre sediment outside the tributary. The elevated metal concentrations in the Avoca River downstream from the adit are directly related to the AMD, as documented by Yau & Gray (2005). In this earlier study, the tributary water had a pH range from 4 to 6 and a positive Eh (450 mV) indicating an oxidising environment. This may yield a rapid precipitation of Fe through oxidation and hydrolysis reactions. During this study, the pH of the AMD ranged from 2.9±0.6 (SO_4^+ - 1108 mg L^{-1}) at the drainage adit to 4.8±0.6 (SO_4^- - 22 mg L^{-1}) upon entering the main river. Redox potential ranged from 415±1.7 mV to 100±4 mV at the same locations.

Avoca ochre physical test results compared well with coal mine ochre tested in the U.K., but its chemical and mineralogical characteristics are site-specific. In particular, Avoca ochre is comparable physically with Minto ochre, appearing as a fine powder ($p< 0.05$), i.e. high surface area due to PSD, similar range of k_s and same dry bulk density. Polkemmet ochre appears more granular, with corresponding differences in dry bulk density, k_s and PSD. The *in situ* k_s of Avoca and Minto ochre is sufficient to indicate that it could be used in P sorption filters, but experiments should be carried out to make sure that the P sorption process does not induce clogging.

4.2.2 Metal and elemental analysis

At low pH, metals are soluble in AMD. As the drainage exits the mine adit, oxidisation occurred, leading to ochre precipitation and resulting in higher concentrations of Ca, Cu, K, Mg, Na and Zn in the ochre than those in the stream sediments. Many concentrations of elements present in the local geology (Na, Sc, V, Ga, Ge, Nb, Sn, Sb, Ce, Ta, W, Hg and Th) were high due to greywaches and rhyolites in the South East of Ireland. Other elements were high due to the mining legacy in the area such as Mg, K, Al, Fe, Pb, As, Cu and Zn. Elements such as Ba (usually 100 mg kg^{-1} in soil), Ti, Cr, Co, Ni, Rb, Mn and Cd were low. Ti is associated with high Cu, Zn and Pb and high Mo is associated with high As and Cu (Fay et al., 2007). Fe accounted for 33% of the sediment. A full table of analysis is presented in Table 4.4 complete with notes of local geology. As is positively correlated with Fe.

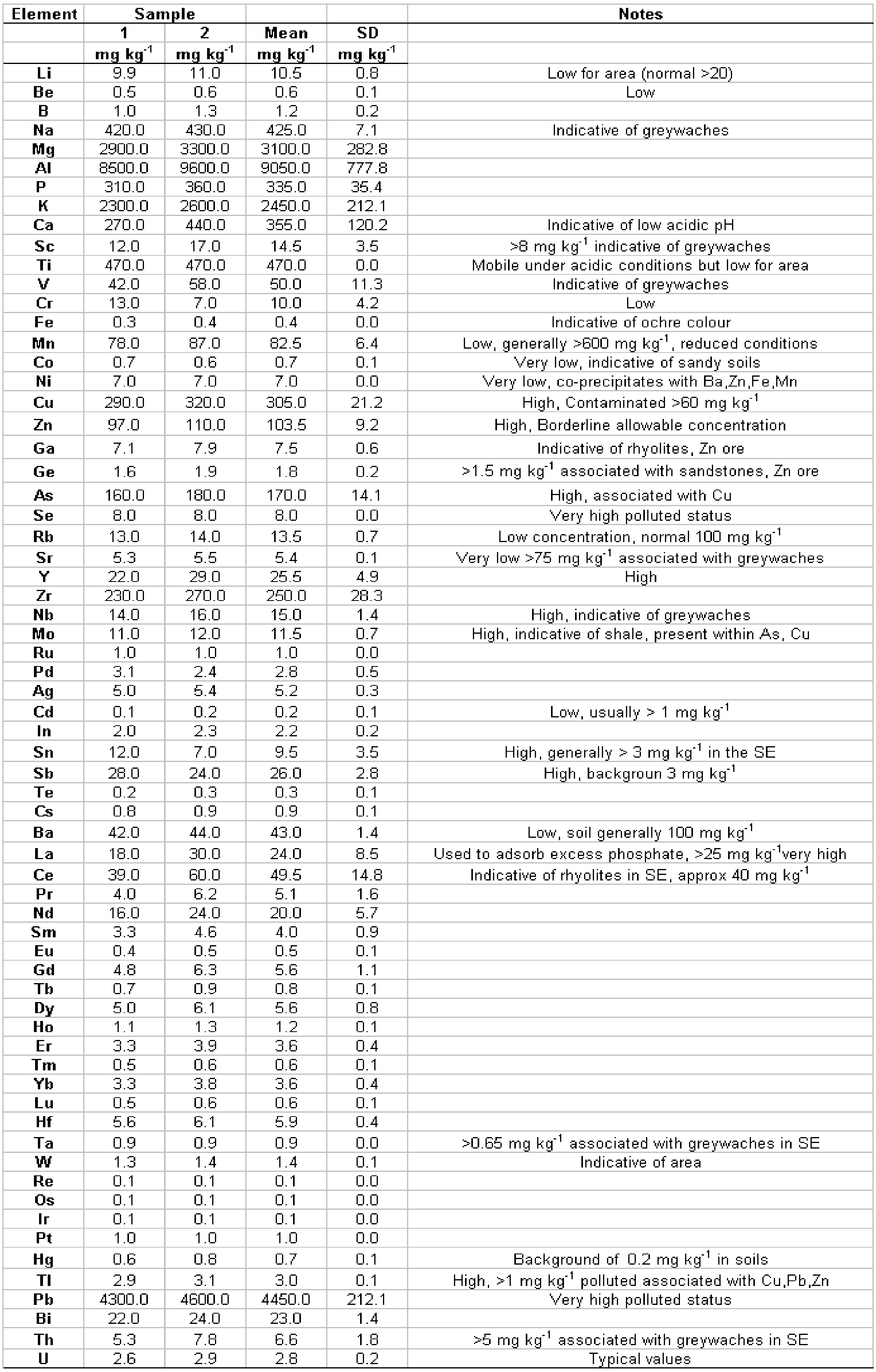
Table 4.3 P and metal concentrations of P saturated forest floor Avoca ochre (metal mine origin) and Polkemmet ochre (coal mine origin).

Parameter	Avoca	Polkemmet*	Limit values**			
pH	3.00	8.70	5.00 to 5.50	5.50 to 6.00	6.00 to 7.00	>7.00
			Concentration (±std.dev.) in ochre g kg^{-1} dry wt.			
Total phosphorus	16.30 (2.30)	22.78 (0.12)				
Available phosphorus	0.91 (0.01)	0.94 (0.07)				
Aluminium	4.80 (0.04)	10.97 (0.38)				
Iron	246.59 (0.02)	271.99 (4.76)				
Manganese	0.53 (0.01)	1.08 (0.01)				
			mg kg^{-1} dry wt.			
Arsenic	162.20 (18.37)	0.10				
Cadmium	3.29 (0.33)	<1.50	3.00			
Chromium	3.19 (1.87)	177.50 (12.70)	400.00			
Copper			80.00	100.00	135.00	200.00
Lead	2087.00 (75.38)	7.50 (1.80)	300.00			
Nickel	1.77 (0.93)	84.00 (7.60)	50.00	60.00	75.00	110.00
Zinc	250.70 (19.88)	99.40 (1.30)	200.00	250.00	300.00	450.00

*After Dobbie et al. (2005).

**Sewage sludge directive 86/278/EEC (European Economic Community, 1986). Values indicate maximum permissible concentrations of heavy metals in soils after application of sewage sludge.

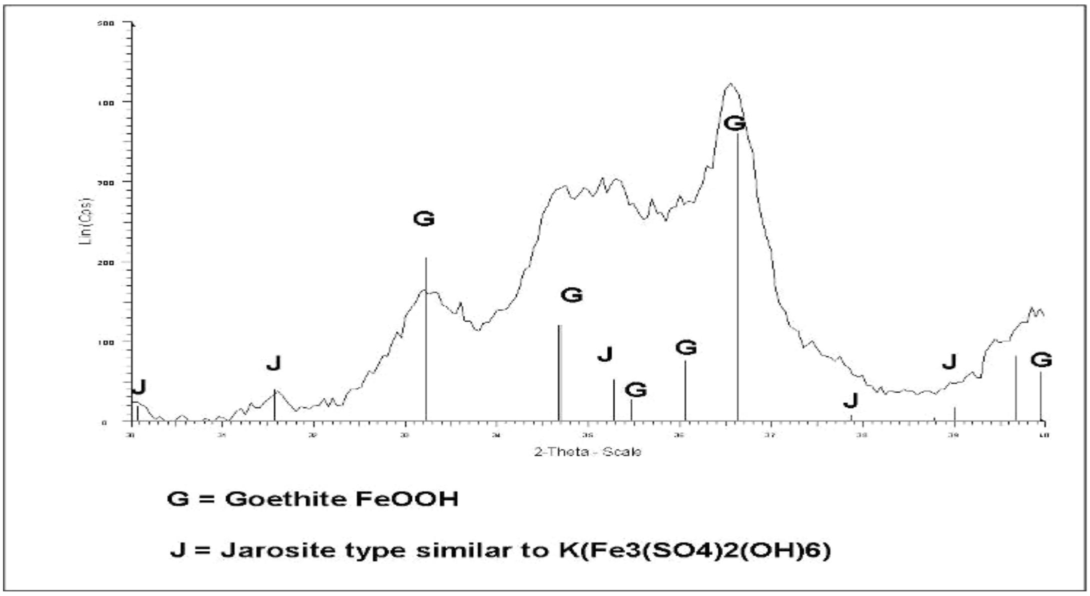
TABLE 4.4 COMPLETE ELEMENTAL ANALYSIS OF OCHRE AND NOTES ON CONCENTRATIONS AND LOCAL GEOLOGY.



Element	Sample				Notes
	1	2	Mean	SD	
	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	
Li	9.9	11.0	10.5	0.8	Low for area (normal >20)
Be	0.5	0.6	0.6	0.1	Low
B	1.0	1.3	1.2	0.2	
Na	420.0	430.0	425.0	7.1	Indicative of greywaches
Mg	2900.0	3300.0	3100.0	282.8	
Al	8500.0	9600.0	9050.0	777.8	
P	310.0	360.0	335.0	35.4	
K	2300.0	2600.0	2450.0	212.1	
Ca	270.0	440.0	355.0	120.2	Indicative of low acidic pH
Sc	12.0	17.0	14.5	3.5	>8 mg kg^{-1} indicative of greywaches
Ti	470.0	470.0	470.0	0.0	Mobile under acidic conditions but low for area
V	42.0	58.0	50.0	11.3	Indicative of greywaches
Cr	13.0	7.0	10.0	4.2	Low
Fe	0.3	0.4	0.4	0.0	Indicative of ochre colour
Mn	78.0	87.0	82.5	6.4	Low, generally >600 mg kg^{-1}, reduced conditions
Co	0.7	0.6	0.7	0.1	Very low, indicative of sandy soils
Ni	7.0	7.0	7.0	0.0	Very low, co-precipitates with Ba,Zn,Fe,Mn
Cu	290.0	320.0	305.0	21.2	High, Contaminated >60 mg kg^{-1}
Zn	97.0	110.0	103.5	9.2	High, Borderline allowable concentration
Ga	7.1	7.9	7.5	0.6	Indicative of rhyolites, Zn ore
Ge	1.6	1.9	1.8	0.2	>1.5 mg kg^{-1} associated with sandstones, Zn ore
As	160.0	180.0	170.0	14.1	High, associated with Cu
Se	8.0	8.0	8.0	0.0	Very high polluted status
Rb	13.0	14.0	13.5	0.7	Low concentration, normal 100 mg kg^{-1}
Sr	5.3	5.5	5.4	0.1	Very low >75 mg kg^{-1} associated with greywaches
Y	22.0	29.0	25.5	4.9	High
Zr	230.0	270.0	250.0	28.3	
Nb	14.0	16.0	15.0	1.4	High, indicative of greywaches
Mo	11.0	12.0	11.5	0.7	High, indicative of shale, present within As, Cu
Ru	1.0	1.0	1.0	0.0	
Pd	3.1	2.4	2.8	0.5	
Ag	5.0	5.4	5.2	0.3	
Cd	0.1	0.2	0.2	0.1	Low, usually > 1 mg kg^{-1}
In	2.0	2.3	2.2	0.2	
Sn	12.0	7.0	9.5	3.5	High, generally > 3 mg kg^{-1} in the SE
Sb	28.0	24.0	26.0	2.8	High, backgroun 3 mg kg^{-1}
Te	0.2	0.3	0.3	0.1	
Cs	0.8	0.9	0.9	0.1	
Ba	42.0	44.0	43.0	1.4	Low, soil generally 100 mg kg^{-1}
La	18.0	30.0	24.0	8.5	Used to adsorb excess phosphate, >25 mg kg^{-1}very high
Ce	39.0	60.0	49.5	14.8	Indicative of rhyolites in SE, approx 40 mg kg^{-1}
Pr	4.0	6.2	5.1	1.6	
Nd	16.0	24.0	20.0	5.7	
Sm	3.3	4.6	4.0	0.9	
Eu	0.4	0.5	0.5	0.1	
Gd	4.8	6.3	5.6	1.1	
Tb	0.7	0.9	0.8	0.1	
Dy	5.0	6.1	5.6	0.8	
Ho	1.1	1.3	1.2	0.1	
Er	3.3	3.9	3.6	0.4	
Tm	0.5	0.6	0.6	0.1	
Yb	3.3	3.8	3.6	0.4	
Lu	0.5	0.6	0.6	0.1	
Hf	5.6	6.1	5.9	0.4	
Ta	0.9	0.9	0.9	0.0	>0.65 mg kg^{-1} associated with greywaches in SE
W	1.3	1.4	1.4	0.1	Indicative of area
Re	0.1	0.1	0.1	0.0	
Os	0.1	0.1	0.1	0.0	
Ir	0.1	0.1	0.1	0.0	
Pt	1.0	1.0	1.0	0.0	
Hg	0.6	0.8	0.7	0.1	Background of 0.2 mg kg^{-1} in soils
Tl	2.9	3.1	3.0	0.1	High, >1 mg kg^{-1} polluted associated with Cu,Pb,Zn
Pb	4300.0	4600.0	4450.0	212.1	Very high polluted status
Bi	22.0	24.0	23.0	1.4	
Th	5.3	7.8	6.6	1.8	>5 mg kg^{-1} associated with greywaches in SE
U	2.6	2.9	2.8	0.2	Typical values

4.2.3 X-ray diffraction examination of ochre

Results from XRD analysis showed no apparent phase changes on drying. The x-ray scatter from the water was reduced and lower intensity peaks became more apparent. The ochre contains amorphous material and the pattern was complex with multiple and overlapping peaks of varying widths (Figure 4.1).



*Background subtracted file with reference pattern scaled to maximum intensity peaks of Goethite and Jarosite.

FIGURE 4.1 XRD PATTERN OF OCHRE.

The XRD patterns of Fe precipitates showed reflections due to goethite and quartz. The major crystalline phase was identified as goethite and iron oxide hydroxide FeO(OH). Goethite present had a poor crystalline structure. Its presence was confirmed by the 7.5YR-10YR colour classification of common Fe^{3+} minerals in mine drainage environments found onsite (Murad & Rojík, 2005). A minor phase of crystalline silicon dioxide, identified as quartz, was present in the diffraction pattern. A minor Fe sulphate jarosite-type phase $K(Fe_3(SO_4)_2(OH)_6)$ was also identified. The minor amounts were reflected in the dark ochre colour with jarosite indicative of a lighter colour (from 2.5Y to 5Y). The presence of jarosite is indicative of sites where sulphide oxidisation is occurring and can be used to track sources of AMD. The jarosite was indicative of younger sediment deposited at the drainage adit where a wet, oxidising and acidic environment is found. In times of flooding, on-site entrainment allowed the ochre to migrate out of the stream and settle on the forest floor. Older ochre sediment on the forest floor was indicative of goethite. There were a number of phases of varying composition with similar diffraction patterns, so the sample phase could not be positively identified, but may be ferrihydrite or schwertmannite (< 10 nm). Due to SO_4^+ concentrations of < 1000 mg L^{-1} and pH range of 4-6 on site, the presence of schwertmannite was doubtful. Broad, but distinct, peaks at 2.5, 2.2, 1.7 and 1.5 A indicate these may possibly be very minor amounts of ferrihydrite.

Bigham et al. (1992) and Schwertmann et al. (1995) established a biogeochemical model where jarosite forms under the most acidic conditions and at the highest sulphate concentrations (pH from 1.5 to 3, $[SO_4^+] > 3000$ mg L^{-1}) followed by schwertmannite (pH from 3 to 4, $[SO_4^+]$ = from 1000 to 3000 mg L^{-1}) and goethite (pH < 6, $[SO_4^+] < 1000$ mg L^{-1}). Ferrihydrite forms under the participation of bacteria that live at near-neutral pH in natural environments. Under such pH conditions the supply and oxidation rate of Fe^{2+} is large and is observed at less acidic (pH > 5) conditions. This is generally in the presence of dissolved silica or organic matter. Ferrihydrite is a precursor of the FeOH groups, hematite and goethite, but no hematite was found on site as in the study of Singh et al. (1999). Trace phases of clay type were tentatively identified: clinochlore (Mg-rich chlorite) type, shown by the ICDD reference diffraction pattern of $(Mg,Al,Fe)_6(SiAl)_4O_{10}(OH)_8$ and muscovite type, shown by the ICDD reference pattern for $KAl_2.9Si_3.1O_{10}(OH)_2$. At the mine site, ochre from different locations becomes mixed due to flooding events, and this may explain the presence of jarosite and ferrihydrite at the same location. Goethite becomes the dominate mineral when the pH value increases and the SO_4^{2-} concentration decreases in the water-ochre deposit system away from the AMD adit.

4.2.4 Stereomicroscopy and bulk EDX

Stereomicroscopy showed the inhomogeneous nature of the deposit (Figure 4.2). Using polarised light microscopy, the ochre formed the main phase of the inhomogeneous mass and particle size varied from single crystallites (< 1 µm) to flocculated agglomerates (2 mm). This supported the PSD results and confirmed a large surface area for adsorption.

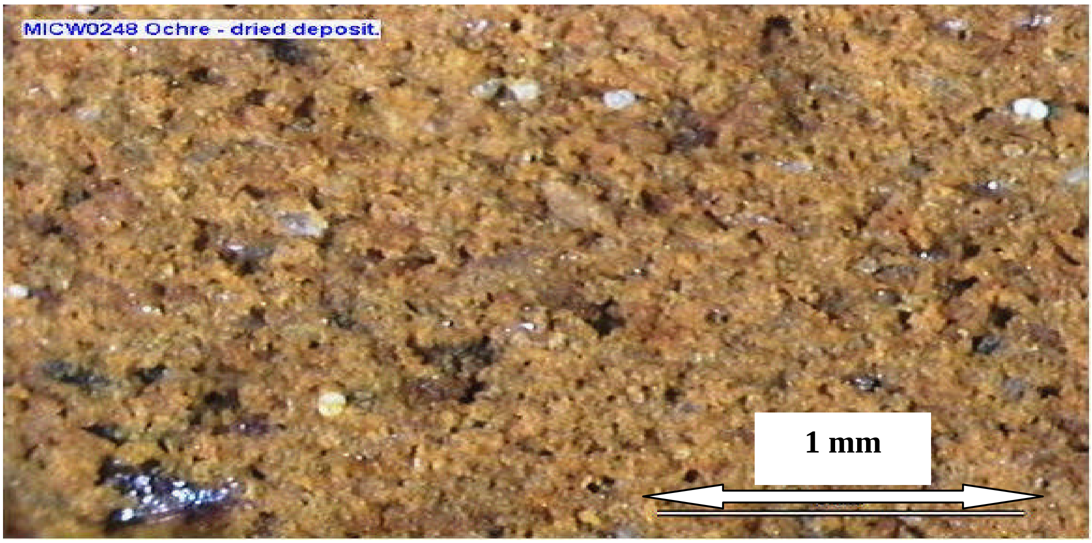


FIGURE 4.2 STEREOPHOTOMETRY

The actual morphology of the ochre crystallites was variable with many single oolithic crystals present. The oolites carry the characteristic colour of the ochre in bright field and form groups of crystals joined together (Figure 4.3 a). Using polarised light microscopy, the radial crystallisation of the oolites became very apparent (Figure 4.3 b). The most common secondary phase was diatoms. Some of these were alive and were highly characteristic of the AMD environment. Two species of diatom dominated the ochre and these were biological indicators of the specific geographic location of the mine (Figure 4.4). The silicon cell wall was coated with ochre and sometimes the cells were hollow and/or filled with chloroplasts.

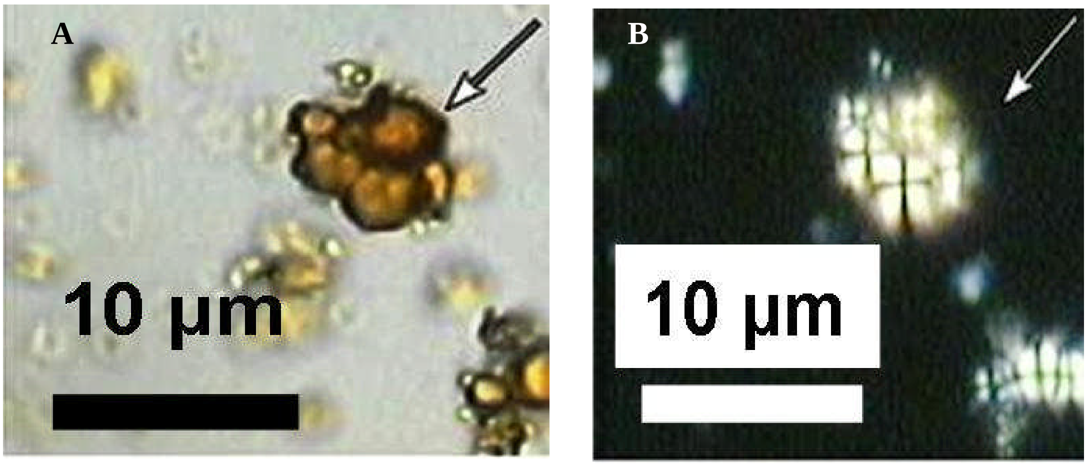


FIGURE 4.3 A) CHARACTERISTIC COLOUR OF OCHRE AS SHOWN BY OOLITIC CRYSTALS IN BRIGHT FIELD AND B) RADIAL CRYSTALLISATION OF THE OOLITE

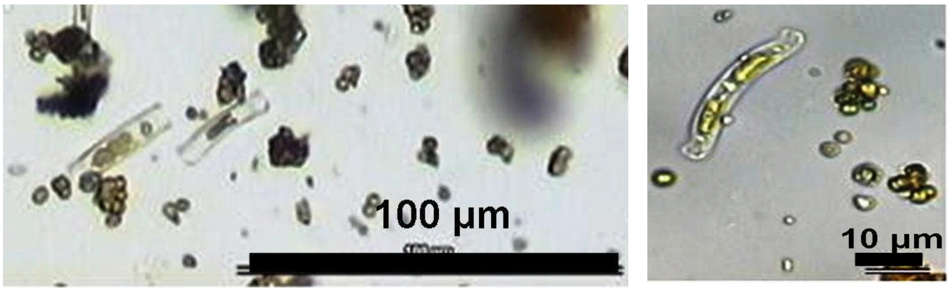
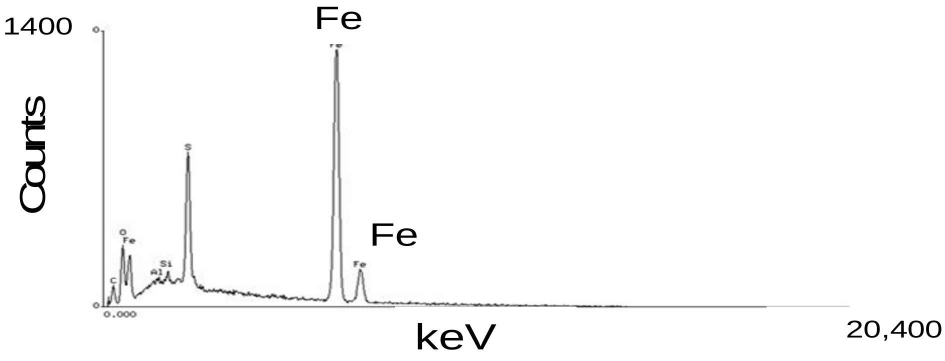


Figure 4.4 The most common secondary phase was diatoms.

There were other lower-level filamentous algae (encrusted and filled with ochre sediment), bacteria and classic unicellular animals also present, which could facilitate ferrihydrite transforming to goethite. Bulk EDX analysis of the ochre revealed C, B, Na, Al, Si, S and Fe. High concentrations of Si were indicative of diatom cell walls and Si in the bulk spectra was associated closely with the Fe compound (Figure 4.5). Goethite, quartz and jarosite have small particle size, large surface area, high defect concentrations, and can adsorb significant amounts of elements that may have been released together with Fe upon the weathering of sulphides. Heavy metals concentration adsorbed to goethite were in the order of Cu>Pb>Zn>Cd>Co>Ni.



Accelerating voltage 20 KeV, take off angle 35º, live time 93 sec and dead time 13.3 sec showing Si and Fe association.

Figure 4.5 Oolite single cell spectra

High porosity, due to the ratio of high particle density relative to low bulk density, allows the ochre in times of flooding to settle on the forest floor. This allows ochre from different locations and distances from the AMD adit to mix, resulting in varied Fe mineralogy. Goethite is found at pH range from 2.5 to 8.0, whereas ferrihydrite is found at ≥ 5.0 and jarosite is found at more acidic sites ≤ 3.0. Goethite, quartz and jarosite can adsorb significant amounts of elements that may have been released together with Fe upon the weathering of sulphides, but have larger particle sizes (lower surface areas) than ferrihydrite (≤ 10 nm). The pH range (from 4.0 to 6.0) on site allows diatoms to exist and such conditions allow for ferrihydrite transformation to goethite.

Avoca ochre has a lower P retention capacity than coal mining ochre. Although physically Avoca ochre is similar to Minto ochre, it differs in its mineralogical consistency. A major controlling factor for a decrease in P retention is the percentage of Fe present. Avoca ochre contains approximately half the Fe percentage as Minto and Polkemmet ochre. The kinetics of sorption may be explained by the dominance of goethite. Maximum phosphate adsorption by Fe oxides may average to approximately 25 µm d m^{-2} (Goldberg & Sposito, 1984). This is the density of one phosphate molecule per 0.66 nm^{-2}, which is approximately the area on a goethite (110) face of two simply co-ordinated Fe-OH groups reacting with one phosphate molecule. Fe immobilisation (Section 4.3) was caused due to P adsorption, only where no agitation occurred, controlling Fe concentration. Yau & Gray (2005) showed that sediment inventories in the Avoca Avonmore catchment provide an assessment of metal contamination. Before the Cu-S adit tributary enters the Avoca River, Yau & Gray (2005) measured Zn, Cu, Fe and Pb concentrations in riverine sediments of 336±34 µg L^{-1}, 221±101 µg L^{-1}, 5.39±0.17 µg L^{-1} and 334±21 µg L^{-1}, respectively. Downstream from the tributary discharge point into the Avoca River, these concentrations were 5640±329 µg Zn L^{-1}, 455±22 µg Cu L^{-1}, 8.08±0.23 µg Fe L^{-1} and 500±194 µg Pb L^{-1}, respectively, indicating a contamination input to the main river between these two sampling points. The Cu-S drainage adit in this study is placed between these two sampling points. The high concentration of metals found in Avoca ochre are higher than those found in metal and coal mine ochre precipitates found in the U.K. Even after natural metal precipitation, tributary water contains toxic levels of metals and can not sustain aquatic life. The binding strength of the P is counteracted by the rapid mobilisation of metals in shaken and unshaken batch experiments. Due to the high initial metal concentrations in the ochre only minor mobilisation of metals to surface water may be toxic. If spread on soils, Avoca ochre could contain problematic levels of trace elements, which could be leached to shallow groundwater. However, metal remobilisation at different soil pH levels should be investigated.

4.3 Summary

Stereomicroscopy identified oolites and diatoms present in the ochre that were indicative of acidic environments. X-ray diffraction exhibited a Fe mineralogy consisting of goethite, jarosite and minor amounts of ferrihydrite. ICP-MS and bulk EDX investigations exhibited potentially toxic concentrations of Fe, Zn, Pb, As and Cu.

Chapter 5 Ochre adsorption capacity, kinetics & amendment to soil

5.1 Materials & Methods

The adsorption capacity of Avoca ochre using isotherms and saturation experiments is investigated. The feasibility of using Avoca ochre in a real-life scenario is then investigated, as amendment to soils has a multi-functional role in P sequestration from high P Index soils, and in runoff after organic or inorganic fertilizer application.

5. 1.1 Batch experiments

All the batch experiments were conducted with ochre from the ochre beds (*see* Section 4.1.1).

5.1.2 P-amended water

In preparation for the P adsorption isotherm tests, the forest floor ochre was air dried, ground and sieved to less than 2 mm. P solutions were made up using dissolved potassium phosphate (KH_2PO_4) in distilled water (pH 6.9). In a set of 104 tests using graduated capped tubes, 2.5 g samples of washed ochre were overlain with 50 ml of PO_4-P solutions ranging in concentration from 24.3 mg PO_4-P L^{-1} to 1137 mg PO_4-P L^{-1}. These samples were not shaken, to establish how agitation affects P adsorption After 24 hrs, the supernatant was extracted, centrifuged for 15 mins, filtered through a 0.45 µm filter membrane and analysed for P on the Thermo Konelab 20 analyser. This experiment was repeated with another set of 104 ochre samples that were shaken for 24 hrs using an end-over-end shaker.

5.1.3 Dirty water

During July and August 2007, 55 dirty water samples were collected from a 120-cow dairy farm and analysed for Cl^-, ortho-phosphate (PO_4-P), TP, total N (TN), TON, NH_4–N and nitrite-N (NO_2-N). Four random samples of dirty water were collected from the dairy yard storage tank and 198 shaken and unshaken experiments were repeated using 2.5 g of ochre overlain with dirty water (50 ml) at three dilutions: 1:20, 1:10 and 1:5. After 24 hrs, the supernatant was analysed for TP.

5.1.4 Ochre saturation and desorption

For the evaluation of the saturation capacity of the ochre, 5 g samples of forest floor ochre, air dried and sieved to less than 2 mm, were placed in five sintered glass funnels and overlain with P-amended water of known concentration (100 mg L^{-1}) and volume (100 ml). The supernatant water was allowed to filter through the ochre sample into a collection flask. Each day, when drainage was complete, a sub-sample of 10 ml was collected from the flask and analysed for PO_4-P. This experiment was repeated until the influent and drainage waters had the same PO_4-P concentration, i.e. until ochre saturation had occurred. This procedure was repeated using dirty water. Desorption of adsorbed P was carried out by taking a 2.5 g sample of the saturated ochre from the sintered funnel experiment. This was shaken with 50 ml of distilled water in an end-over-end shaker for 24 hrs. At the end of this experiment, the supernatant was centrifuged and analysed for PO_4-P.

5.1.5 Kinetic experiments

Four P solutions with concentrations of 26.4, 52.3, 108.7 and 188.5 mg PO_4-P L^{-1} were prepared. Volumes (50 ml) of each solution were poured into 6 graduated tubes with 2.5 g of forest floor ochre – 24 tubes in all. The tubes were shaken in an end-over-end shaker and the supernatant water was sampled, centrifuged, filtered and analysed for PO_4-P after 1, 5, 14, 30, 60 and 120 mins.

5.1.6 Ochre amendment to soil

The P adsorption study was conducted using two permanent grassland soils taken from Johnstown Castle Research Centre (latitude 52º 12’ N, longitude 6º 30’W, mean annual precipitation 1002 mm and temperature 9.6 ºC). Each soil was sampled at two depths:

- Soil A (classified as a humic cambisol after the World Reference Base (WRB); Depth 1, top-soil (0 - 10 cm – standard Irish agronomic sampling depth); Depth 2, sub-soil (11 - 30 cm)
- Soil B (WRB classification- gleyic cambisol); Depth 1, top-soil (0 - 10 cm); Depth 2, sub-soil (11 - 30 cm)

5.1.7 Physical characterisation of the soil and ochre

Samples from both sites and depths were air dried, then sieved to < 2mm, wet sieved into coarse sand (from 0.5 to 2 mm), fine sand (from 0.053 to 0.5 mm) and silt/clay (<0.053 mm) fractions, and then oven dried and weighed. PSD of the silt clay fraction was carried out using the pipette method (BSI, 1989; BS 1796). Physical characterisation of the ochre used in this study was carried out in previous sections. The Avoca ochre used in this research is fine-grained with the following constituency: coarse sand, 21.6% by mass; fine sand, 19.5% by mass; silt, 22.3% by mass; and clay, 30.9% by mass (*see* Chapter 4).

5.1.8 pH, LR, C/N ratio, background nutrient and metal status of soil/ochre

Soil from both sites and depths, ochre samples and ochre-amended soils from both sites and depths used in batch experiments, were first analysed for pH in water using an automated Gilson 215 liquid handler dip system (Middleton, Wisconsin, USA) (n=4). The soil-to-distilled water ratio was 1:2 and samples were allowed to settle for no more than 5 minutes before analysis. For quality control, a laboratory soil of known pH and nutrient status was used (Johnstown reference soil). The control had the following characteristics and no significant difference was found when analysed with the samples from the present study: pH - 5.89; Mg - 205 mg kg^{-1}; K - 72 mg kg^{-1}; and P - 5.3 mg kg^{-1}.

The lime requirement (LR) of all soils (i.e. the lime required to adjust soil to a pH of 6.3) was determined after Pratt and Blair (1963). In this procedure, 10 ml of soil per volume was added to 20 ml of Shoemacher-McLean-Pratt (SMP) buffer (pH 7.5), shaken for 30 min on a G10 gyratory shaker (New Brunswick Scientific, Edison, New Jersey, U.S.A) and poured through a No. 2 Whatman filter (0.2 µm) before analysis on a flow-Gilson 215 liquid handler. Total organic C (TOC) and N of the soils was determined by placing 0.25 g of soil and standard samples in a porcelain combustion boat on a CN2000 analyser (Leco Corporation, U.S.A).

In Ireland, the soil test P (STP) is classified using Morgan’s extraction solution. Depending on the STP of a soil, an Index varying from 1 to 4 is applied to it. The study sites had similar topography and very low-to-low STP. Soil A (Depth 1) had a

STP of 5.5 mg L^{-1} and Depth 2 had a STP of 2.6 mg L^{-1}. Soil B (Depth 1) had a STP of 2.8 mg L^{-1} and Depth 2 had a STP of 2.7 mg L^{-1} (Table 5.2). This minimised native P desorption during the experiments. Optimum growing conditions for grassland would be a STP Index 3 with a soil P range of 3 to 8 mg L^{-1} for mineral soils. STP was measured as Morgan's P (P_m; mg L^{-1}) and converted to Mehlich 3 P (M3P; mg kg^{-1}) for indicative purposes using the following equation from Tunney et al. (1998):

$$M3P = 8.52 * P_m^{\ 0.85} \qquad [5.1]$$

Oven dried soil samples with a grain size < 2mm (6 replicates for each soil type) were analysed for STP, Mg and K as follows: 3 ml of soil by volume were added to 15 ml of Morgan's extracting solution in a round-bottomed flask and shaken on a G10 gyratory shaker for 30 min. The suspension was then filtered through a No. 2 Whatman filter into disposable test tubes and analysed colorimetrically using the chemical reaction between P and ammonium molybdate.

To investigate metal mobilisation and the suitability of metal mining ochre to sequester P from runoff, the supernatant from all batch experiments was analysed for trace metal pseudototals (cadmium (Cd), Cr, Cu, iron (Fe), Mn, Ni, lead (Pb) and Zn) using an ICP-MS. Metal release from ochre over time was carried out in a kinetic test at 1, 5, 10, 15, 30, 60 mins.

5.1.9 Batch experiment with soil and ochre amendment

To achieve a homogenous < 2 mm mix, the soils were saturated with distilled water, manually mixed into a slurry and left to air dry for 60 d. After this time, ochre was mixed to soil aliquots in the following proportions: 0 (the study control), 0.15, 1.5, 7.5 and 15 g ochre kg^{-1} mass per dwt of soil. Such amendment rates were also used in ferrihydrite ($Fe_5HO_8{\cdot}4H_2O$) amendment to soils for P sequestration (Rhoton & Bigham, 2005).

The ochre amendment was applied during continuous mixing of the soil with a spray of distilled water to allow greater incorporation of the ochre into the soil. Next, the soil and ochre mix was air dried, and the bulk dry samples were crushed, rolled and sieved to < 2 mm. All batch experiment protocols were carried out after Cucarella & Renman (2009). In each 100 ml-capacity container, 2.5 g of oven dried-ochre-and-soil mixture – mixed in the ratios described above - and air-dried soil-only mixture was overlain with 50 ml of synthetic P solution (potassium phosphate (KH_2PO_4) with concentrations of 0, 10, 20 or 40 mg P L^{-1} (n=2 per treatment were performed for both soils at two depths, giving a total of 160 tests). Normal runoff losses during baseflow and storm events for tillage and grassland farming are below 10 mg L^{-1}. For example, Withers et al. (2001) shows P concentrations after fertilization by liquid cattle manure (LCS), liquid anaerobically digested sludge (LDS) or dewatered sludge cake (DSC) varies from 0.1 to 0.2 mg L^{-1} on control and sludge-treated plots to 3.8 and 6.5 mg L^{-1} following application of LCS and TSP, respectively, to a cereal crop in spring. For higher concentrations, 100% P sequestration was not expected, nor sequestration to below the MAC for surface waters of 0.035 mg P L^{-1}, above which eutrophication is likely to occur. Instead these concentrations were used to mimic ochre upper thresholds.

Although end-over-end shakers do not simulate overland flow, for consistency with other studies, the samples were sealed and then mixed in an end-over-end shaker for 24 hrs, after which the samples were vortexed for 2 min, centrifuged at 100 rpm for 10 min, filtered and analysed for DRP in a nutrient analyser (Konelab, Ontario, U.S.A.).

5.1.10 Data analysis

A model that could find the optimal rate of any amendment to soil was developed. In the batch experiment, ochre with negligible background P content was added to a soil of known soil test P. This content was based on historic records of inorganic and organic fertilizer application. The model was set up as follows:

$$\mathrm{ProportionalP}\ (\%) = \frac{P_{\mathrm{soln}}}{P_{added} + STP} * 100 \qquad [5.2]$$

The proportion of P not adsorbed by the amendment after P equilibrium (ProportionalP-%) depends on the P in solution (P_{soln}; mg L^{-1}) that has not been adsorbed to the amendment/ochre (this is the P which could be lost to a waterbody in runoff); the Morgan's STP of the soil before any ochre amendment (STP; mg L^{-1}) and the P added in the batch experiments (P_{added} ; mg L^{-1}). In Ireland, soil P fertilisation is matched with crop requirements to avoid P build-up and release of excess P from the soil during rainfall events. Soils at soil P Index 4 (> 8 mg L^{-1} Morgan's P) are considered a risk with respect to nutrient losses to a waterbody. Hence, soils with P Index of 1 to 3 were chosen in the present study.

A high ProportionalP (%) signifies a greater amount of P in solution available to be lost to a waterbody and a low ProportionalP signifies more P has been adsorbed by the ochre. Conversely (1- ProportionalP) is the proportion of P adsorbed to the sediment. This ratio (ProportionalP/1-ProportionalP) increases with increasing ProportionalP, but is not linear. The background pH of the soils before amendments was not the same. To compare results, pH needed to be accounted for in the statistical analysis. The soil variation was accounted for by including pH - determined in SMP buffer - as a random effect. The predictive model was set up as follows:

$$\mathrm{E(y)} = \mu = \mathrm{g}^{-1}(x\beta) \qquad [5.3]$$

where E(y) is the magnitude of variance of each measurement as a function of the predicted value, μ is the distribution mean (ProportionalP), g^{-1} is the link function (ln) and x β is the linear predictor. Statistical analysis was conducted in SAS v 9.1, using a generalised linear mixed model (GLMM) with a logit link and a normal distribution:

$$\mathrm{x}\beta = \ln\left(\frac{\mathrm{ProportionalP}}{1 - \mathrm{ProportionalP}}\right) \qquad [5.4]$$

The effects of ochre additions, P_{added}, soil type and soil depth (topsoil or sub-soil) and their interactions were tested in the model using Type III tests of fixed effects.

After initial analysis was complete, back-calculation within the model enabled P_{soln} to be predicted. This then allowed calculation of the amount of ochre amendment needed per kg of soil to reduce P concentrations in runoff to below thresholds for classification of waters as "good status" in Ireland (mean 0.025 mg L^{-1}).

5.2 Results & Discussion

Synthetic and dairy dirty water batch experiments amended with ochre showed a number of interesting results and exemplified the site-specific nature of Avoca ochre.

5.2.1 Adsorption testing using batch studies and saturation studies

The adsorption experiments showed that shaking in the end-over-end shaker improved the P adsorption capacity of the P-amended water when high initial PO_4-P concentrations were used. For an initial PO_4-P concentration of, say, 200 mg L^{-1} in solution, approximately 4 g kg^{-1} is adsorbed – 39% more than an unshaken sample at the same initial concentration (Figure 5.1 a). Error bars show standard deviation between three samples. However, this difference was less pronounced at lower initial PO_4-P concentrations, e.g. at an initial PO_4-P concentration of 25 mg L^{-1}, 0.50 g kg^{-1} and 0.43 g kg^{-1} were adsorbed for shaken and unshaken batch experiments, respectively. There appeared to be no significant difference between the TP concentrations when the experiment was repeated with shaken and unshaken dirty water samples (Figure 5.1 b). This suggests that shaking may only be necessary in P-amended and dirty water when the initial P concentration is high.

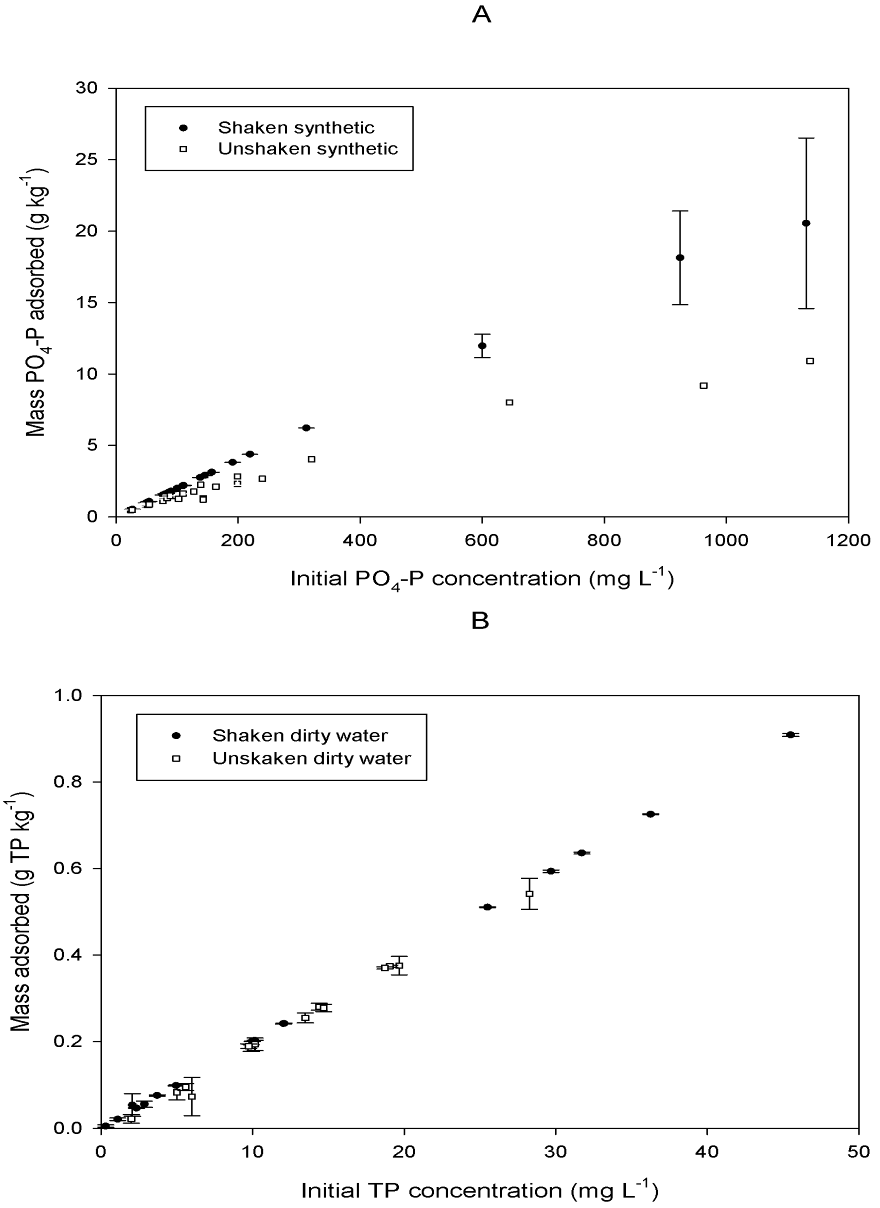


FIGURE 5.1 P REMOVAL IN A) P-AMENDED AND B) DIRTY WATER IN SHAKEN AND UNSHAKEN BATCH EXPERIMENTS

Using a Langmuir isotherm, it was estimated that ochre had a maximum adsorption capacity of approximately 21 g PO_4-P kg^{-1} when mixed with P-amended distilled water (Figure 5.2).

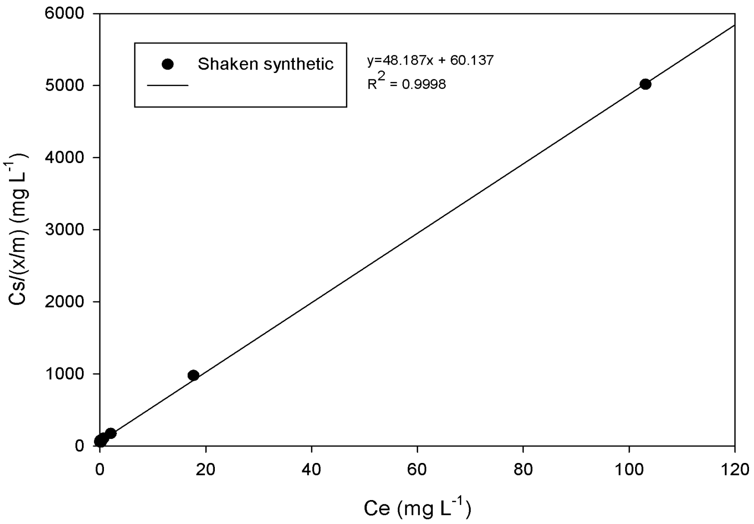


FIGURE 5.2 LANGMUIR ISOTHERM FITTED TO ACTUAL SHAKEN P-AMENDED WATER DATA.

It was not possible to fit a Langmuir isotherm for the dirty water samples as almost all the P was adsorbed by the ochre within the study period. Since the dairy farm produced approximately 9500 L of dirty water daily with a mean TP concentration of 20.1 mg L^{-1} (Table 5.1), it would have taken approximately 9 kg of ochre to sequester all the P in the daily dirty water, based on the Langmuir isotherm maximum P adsorption capacity of the synthetic P solutions. There was agreement between all methods using synthetic solutions.

TABLE 5.1 MEAN *(± STD. DEVIATION)* DAIRY DIRTY WATER (N=55) NUTRIENT CONCENTRATIONS FROM JULY TO AUGUST 2007.

TP	PO_4-P	TN	TON	NH_4-N	NO_2-N
mg L^{-1}					
20.1 (±6.9)	14.0 (±9.2)	170.0 (±33.2)	30.4 (±39.2)	89.7 (±35.3)	18.1 (±27.5)

Ochre in the sintered funnel experiments reached a mean saturation concentration of 16.3±2.3 g PO_4-P kg^{-1}. This compares well with the maximum P-retention capacity of 21 g PO_4-P kg^{-1} estimated by the Langmuir isotherm. Desorption experiments showed < 1% of PO_4-P was released from the ochre within 24 hrs. Using the saturated range for P retention capacity, 10 to 12 kg of ochre would be needed to sequester the daily dirty water on the farm.

5.2.2 Kinetic experiments

P removal by Avoca ochre is rapid. Within 5 minutes of shaking, the supernatant PO_4-P concentration decreased by in excess of 97% (Figure 5.3). This was due to the ochre chemical composition and the large surface area available for P adsorption associated with Avoca ochre mineralogy.

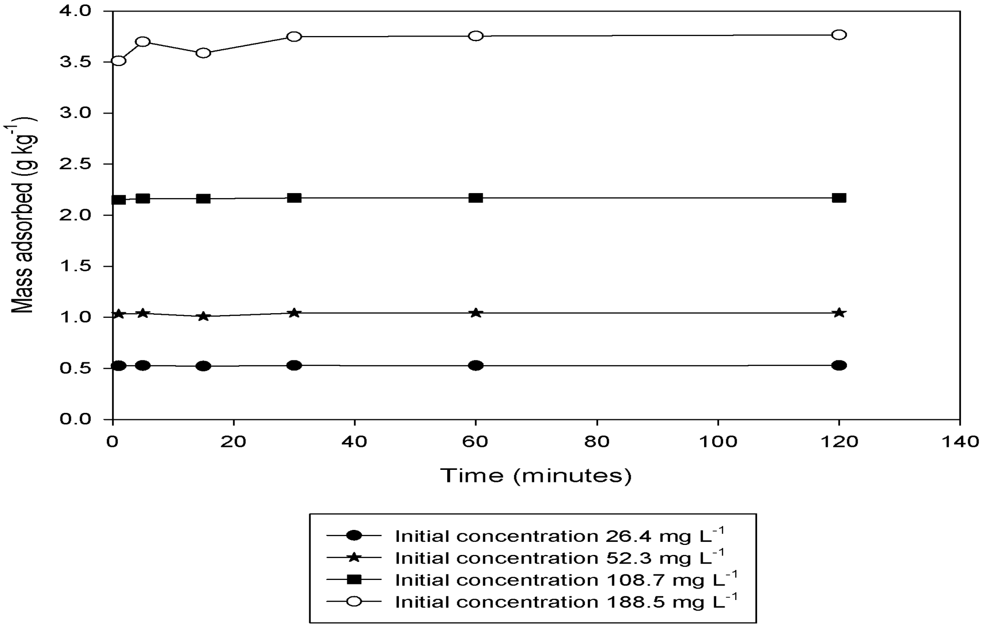


Figure 5.3 Kinetics of P removal showing 97% removal of P within 5 min

5.2.3 Ochre metal mobilisation

Mobilisation of trace metals during batch experiments was evident in all tests and agitation increased mobilisation. The increase in concentration of all metal parameters followed the same trend as the results of Yau & Gray (2005), who found that mobilised metal concentration increased after mixing of the Cu-S adit tributary with the Avoca River. Zn had the highest % increase – greater than 99% in all cases - after mixing with distilled water, dirty water and surface water; this increase was of the same order as the increase measured by Yau & Gray (2005). Of the parameters tested, all the parameters regulated by the EU Directive 75/440/EEC (European Economic

Community, 1975) governing waters intended for the abstraction of drinking water – Fe, Cu, Mg and Zn – were above the mandatory concentrations allowable. Kinetic tests indicated that most of the metal mobilisation occurred within 1 minute of mixing P solutions with the ochre.

5.2.4 Ochre amendment to soil

The PSD of both soils are presented in Table 5.2. Soil A (Depth 1) contains a higher sand fraction and lower silt and clay fractions than Depth 2. There is a slight textural change with depth, but it remains within the sandy-loam textural class. Soil B (Depth 1 and 2) has similar coarse and fine sand fractions, but differ with respect to their silt and clay fractions. Both soil depths also have a sandy-loam textural class. Both soils are well-drained in the field and it was easy to amend the soils with ochre.

Table 5.2 Soil particle size distribution and organic fraction analysis for soil A and B, depth 1 and 2.

Soil (Depth)	Soil P Index	Coarse Sand	Fine Sand	Silt	Clay	C	N	C/N	Pm*	M3P**	Mg	K
		%				mg kg^{-1}			mg kg^{-1}			
Soil A (Depth 1)	3 (3.0-8.0 P_m-mg L^{-1})	43	25	30	2	2.1	0.2	8.8	5.5	36.2	206.2	102.8
Soil B (Depth 1)	1 (0.0-3.0 P_m-mg L^{-1})	26	14	45	15	0.2	-	-	2.6	19.1	202.7	122.1
Soil A (Depth 2)	1 (0.0-3.0 P_m-mg L^{-1})	40	30	17	13	1.5	1.2	12.5	2.8	20.4	256.9	199.8
Soil B (Depth 2)	1 (0.0-3.0 P_m-mg L^{-1})	48	28	6	18	0.7	-	-	2.7	19.8	212.1	132.0

*P_m- Morgan's P, **M3P - Mehlich 3 P

5.2.5 pH, C/N ratio

The mean pH in SMP buffer for each soil amended with 0, 0.15, 1.5, 7.5 and 15 g ochre kg^{-1} soil was 6.2, 6.2, 6.1, 5.9, 5.7 for Soil A (Depth 1), respectively; 7.2, 7.1, 7.1, 7.0, 6.8 for Soil A (Depth 2), respectively; 6.0, 5.9, 6.0, 5.7, 5.6 for Soil B (Depth 1), respectively; and 7.3, 7.3, 7.2, 7.1, 6.9 for Soil B (Depth 2), respectively. The average pH of all soils and soil depths was 6.5±0.6, which is the optimal pH for grass growth. With little ochre amendment, pH remained at, or above, this optimal pH. At higher amendment rates (7.5 to 15 g ochre kg^{-1} mass per dwt of soil), Depth 1-soils become acidic and would need lime correction to maintain grass growth.

The background concentration of Mg in Soil A (Depths 1 and 2) was 0.2 g kg^{-1} and Soil B (Depths 1 and 2) were 0.25 and 0.21 g kg^{-1}, respectively. In an Irish study on low fertilizer-input grassland farms, mean Mg concentrations of 0.2±0.6 g kg^{-1} were found (Leonard et al., 2006). This can be compared to 0.53 g kg^{-1}in the ochre used in this study. Soils in the study sites have generally high background Mg concentrations due to the parent soil material, which is derived from marine till (Fay et al., 2007).

In the same study (Leonard et al., 2006); the mean C/N ratio was 12.0±1.8, compared with 8.8 and 12.5 for Soil A and B, respectively (Table 5.2). Such results match the soil P status of the soils used in the current study – low fertilizer inputs and risk of P loss to surface water.

5.2.6 Batch Experiment with soil and ochre amendment

All factors tested (Soil, ochre, P, ochre*P, ochre*Soil, Soil*P and ochre*Soil*P) had a significant influence on ProportionalP, so no terms were removed from the model.

For Soil (A, B) Depth (1, 2), the regressions of ProportionalP against ochre amendment are displayed in Figure 5.4. The slopes and intercepts of the predicted lines using the ProportionalP model differ depending on the amount of P_{added}. Statistically, differences in background soil pH before any ochre amendment explains variation in ProportionalP between soils. Predicted lines occur at an average pH for that soil and ochre interaction. The P index of the soils ranged from 1 to 3. Soils in Index 1 and 2 are P deficient, indicating an insignificant risk of P loss to water; soils in Index 3 are at target Index, with a low risk of loss to water. Therefore, the observed P losses were likely to originate from P amendments and not from the soil.

For soils with no ochre or P amendment, ProportionalP was < 5%. This is comparable to ProportionalP results (3%) (Table 5.3), where all data across both soils and soil depths are grouped together. However, DRP left in solution after equilibration (P_{soln}) (Figure 5.5) for both soils and soil depths was above the 0.035 mg L^{-1} MAC for surface water. This is also evident in P_{soln} results (0.10 mg L^{-1}) (Table 5.3) where all data across both soils and soil depths are grouped together. In sites with similar topography, STP and soil type, Kurz et al. (2005) measured average flow-weighted DRP concentrations of 0.19 mg L^{-1} in runoff before fertilization, which justifies amendment of soils to protect against accidental losses.

With ochre - but no P – amendment, there was no significant difference for both soil and soil depths until 7.5 g of ochre was added (Figure 5.5). The ProportionalP of both soils and soil depths dropped to low levels (Figure 5.5) and MAC. This decreased further with the 15 g ochre amendment. When the results were averaged across soils, soil depths and pHs, the same pattern emerged. For P concentrations > 0 mg L^{-1} amended with 0.15 and 1.5 g kg^{-1} amendment, more ProportionalP was available to be lost in runoff with increasing P amendment. For this range, results varied and were not consistent with ochre amendment. For amendments of 7.5 g kg^{-1} and 15 g kg^{-1}, the ProportionalP lost increased with increasing P added and decreased with increasing ochre amendments. P added was so high that ProportionalP remaining in solution breached the MAC for surface water (Table 5.3) in all amended batch experiments. These results were consistent when average results were considered in Table 5.3. For the extreme case – 40 mg P L^{-1}, 46% of ProportionalP (Table 5.3) or 19.8 mg L^{-1} of P_{soln} (Table 5.3) only remains after equilibrium with a 15 g kg^{-1} amendment. From these results, it is obvious that lower P concentration ranges would achieve 100% sequestration if tested, with large amounts of P loss reductions during most extreme scenarios.

Therefore, for averaged pH conditions, the model allows an optimal ochre amendment rate to be applied for a given P addition on these two soils. An ochre amendment for soil without any P addition is still needed, i.e. 7.5 g kg^{-1} to maintain losses below the

MAC for surface water. This is of relevance to work carried out by Schulte et al. (2010), where P losses from Index 4 soils can be sustained over long periods of time, even after implementation of Best Management Practices.

5.2.7 Metal mobilisation during batch experiments

The ochre had the following metal content: Al, 4.8 ± 0.0 g kg^{-1}; Cu, 0.3± 0.0 g kg^{-1}, Fe, 246± 0.0 g kg^{-1}; Mg, 0.5±0.0 g kg^{-1}; As, 162±18.3 mg kg^{-1}; Cd, 3.2±0.3 mg kg^{-1}; Cr, 3.1±1.8 mg kg^{-1}; Pb, 2087±75.3 mg kg^{-1}; Ni, 1.7±0.9 mg kg^{-1} and Zn, 250±19.8 mg kg^{-1}. In the present study, the ratio of ochre to solution was 1:20. Average mobilisation of metals into solution after 24 hrs for distilled water amended with ochre was: Cu (14,044±290 µg L^{-1}), Fe (1892±109 µg L^{-1}), K (123±1.6 mg L^{-1}), Mg (1.78±0.2 mg L^{-1}), Mn (323±30.4 µg L^{-1}), Na (2.9±0.2 mg L^{-1}) and Zn (18034±795 µg L^{-1}). The pH of ochre in distilled water was 3, thereby allowing for greater metal release. The soil and ochre combinations decrease much of the metal mobilisation, but not enough in particular instances to prevent breaches of EU limits (Table 5.4 a and b). The control soils without ochre amendment have, in some cases, metal concentrations above the EU limits. Soil A had high Cd, Cr, Fe, Ni and Pb concentrations and Soil B had high Cd, Pb and Zn concentrations.

Kinetic tests indicated that most of the metal mobilization occurred within 1 min of mixing P solutions with the ochre (Table 5.5). For all metals, high concentrations were released in the first minute, decreased and rose again after 1 hr. For P adsorption to ochre the opposite occurs, which involves rapid ligand exchange with surface hydroxide groups at reactive sites and the formation of binuclear bridging complex between a phosphate group and two Fe surface atoms, followed by a weaker ligand exchange.

Table 5.3 Average ProportionalP with different P and ochre amendments. Both soils and soil depths included (n=160).

Ochre amendment	P amendment				P amendment			
g ochre kg^{-1} soil	mg P L^{-1}							
	0	10	20	40	0	10	20	40
	Average ProportionalP (%)				Average P_{soln} (mg L^{-1})			
0	3	39	50	62	0.109	5.2	11.7	26.9
0.15	3.2	38	56	75	0.113	5.1	13.1	32.3
1.5	2.3	33	51	70	0.076	4.5	12.0	30.5
7.5	0.9	22	32	56	0.027*	3.0	7.5	24.5
15	0.6	10	23	46	0.018*	1.4	5.5	19.8

A high ProportionalP (%) signifies a greater amount of P in solution available to be lost to a waterbody and a low ProportionalP signifies more P has been adsorbed by the ochre. Average P_{soln} after equilibrium with different P and ochre amendments. Both soils and soil depths included and all samples used (n=8).

* Below MAC of 0.03 mg DRP L^{-1}

FIGURE 5.4. PROPORTIONALP (PROP ADS-%) RESULTS AND MODEL PREDICTIONS FOR BOTH SOILS, SOIL DEPTHS FOR ALL OCHRE AMENDMENTS AND P CONCENTRATIONS (A AND B).

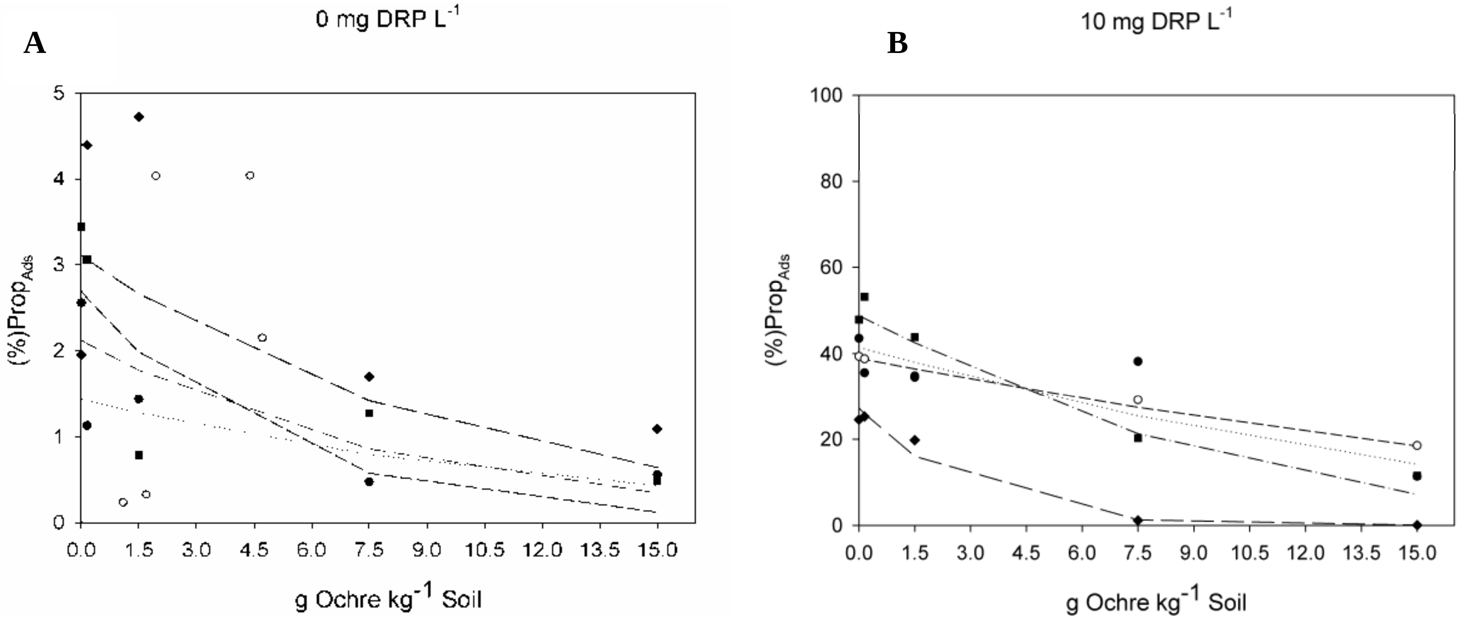


Figure 5.4. ProportionalP (Prop Ads-%) results and model predictions for both soils, soil depths for all ochre amendments and P concentrations (C and D).

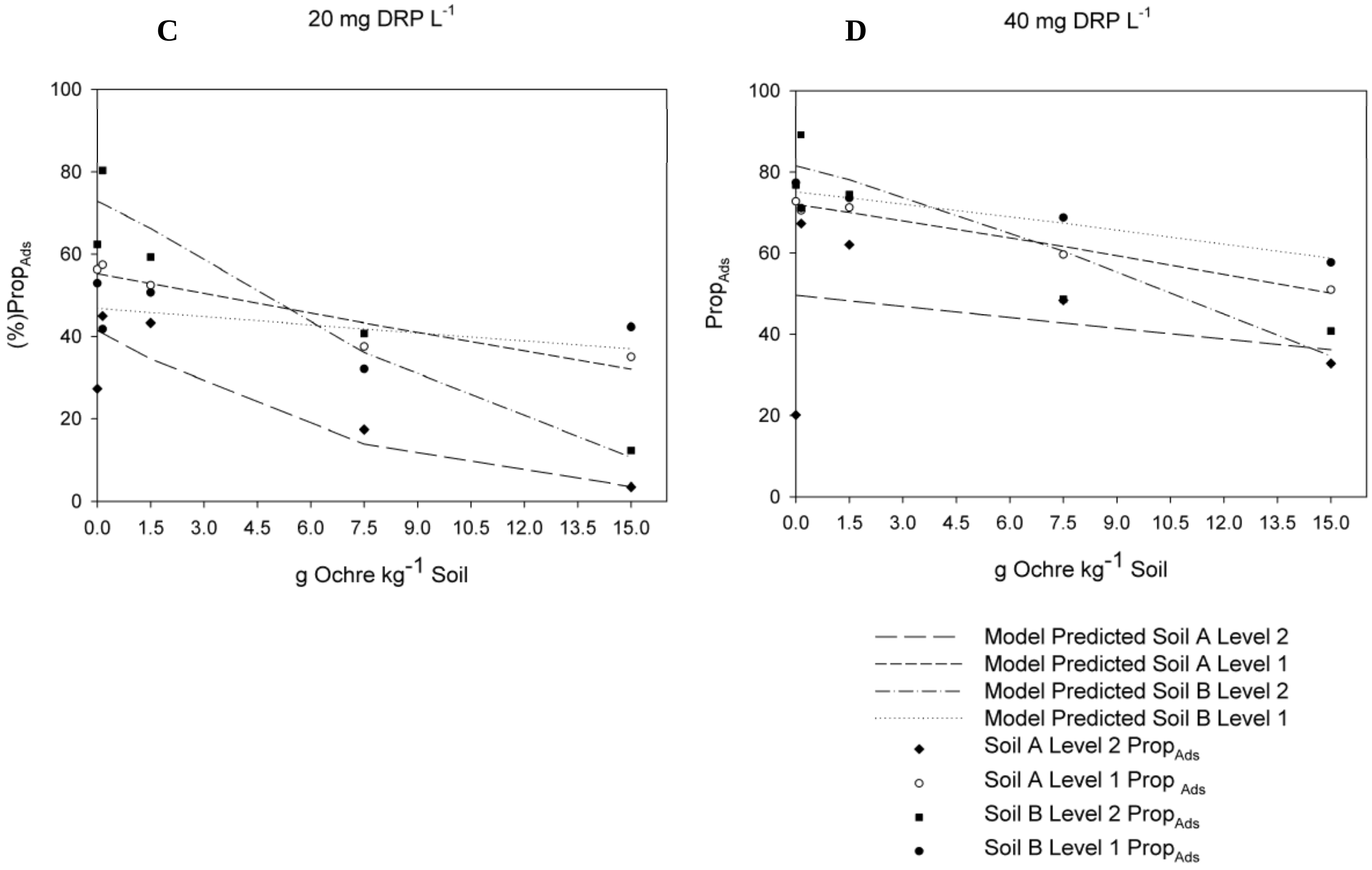


Figure 5.5 Psoln results and model predictions for both soils, soil depths for all ochre amendments, and P concentrations (A and B).

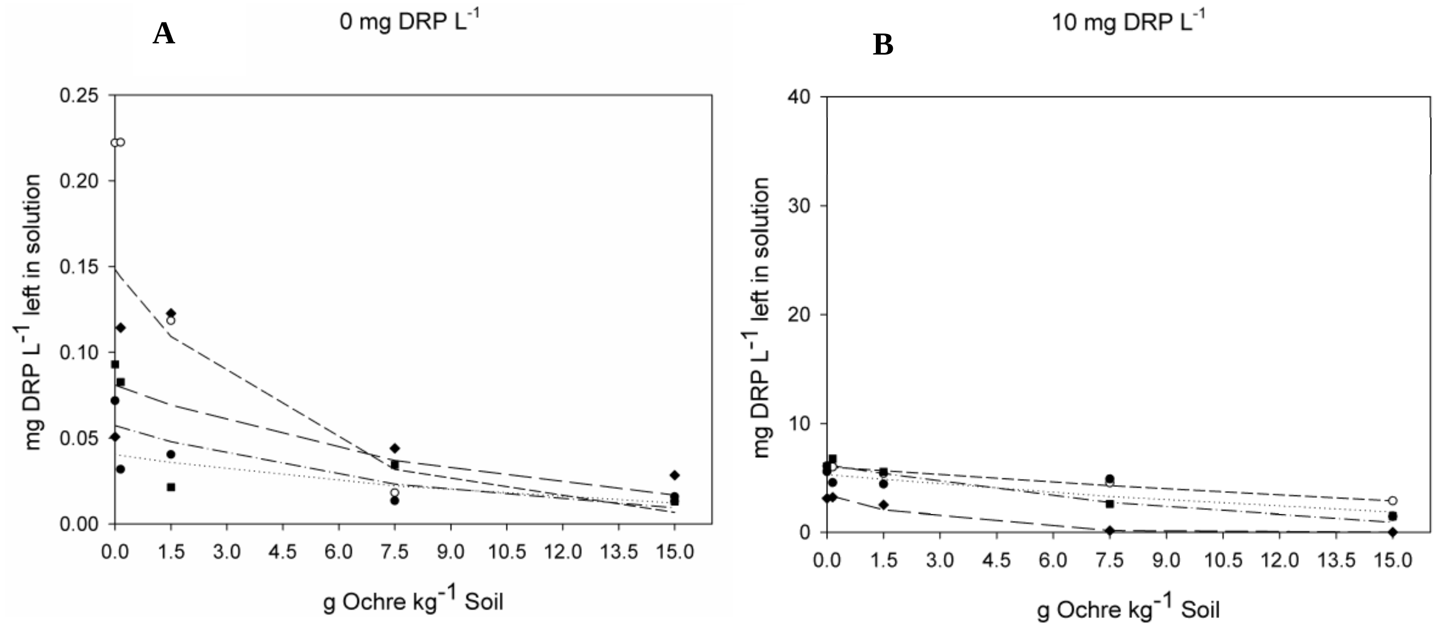


Figure 5.5 Psoln results and model predictions for both soils, soil depths for all ochre amendments and P concentrations (C and D).

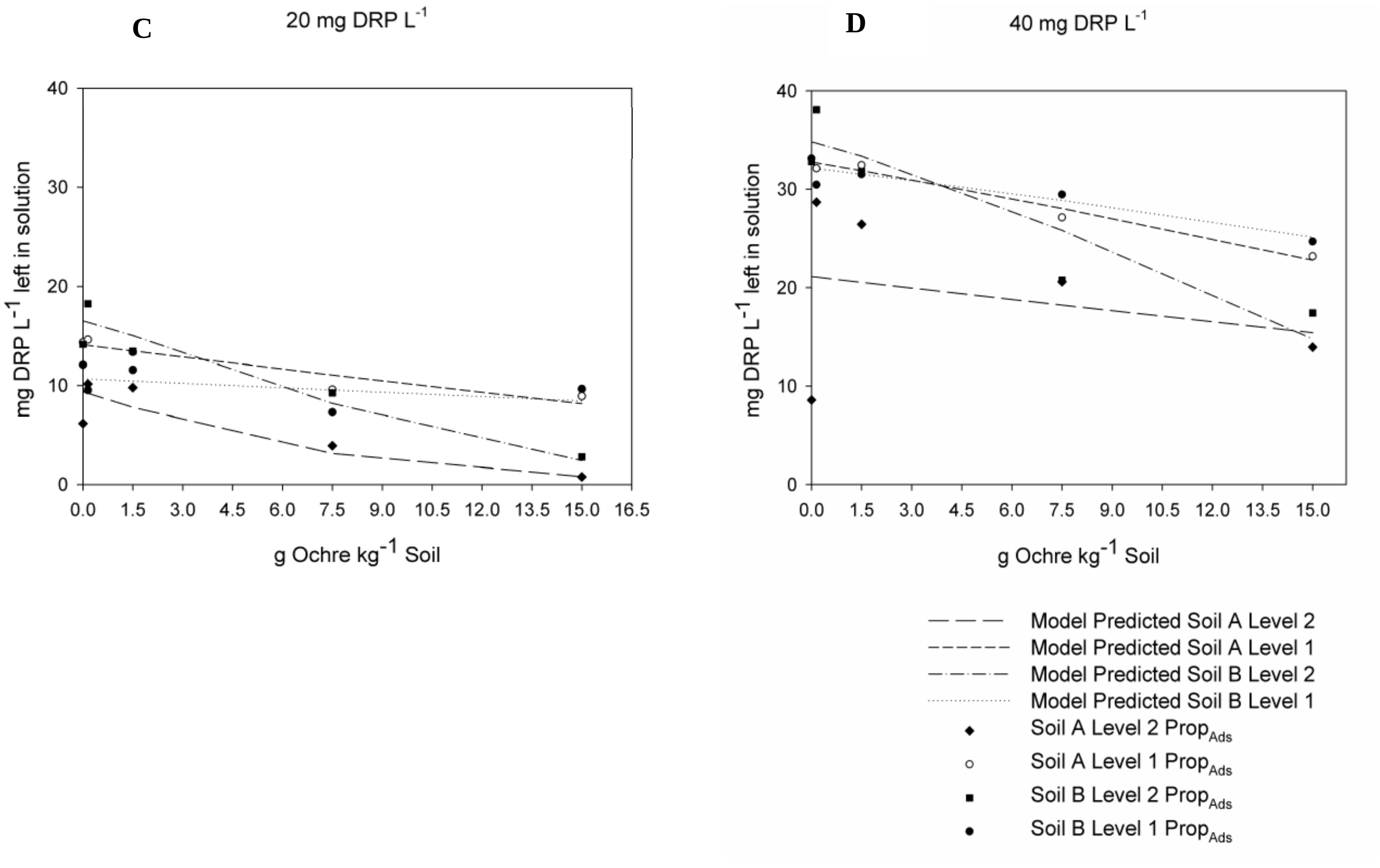


Table 5.4 a. Average mobilisation of metals (n=2) ± (standard deviation) into solution after 24 hrs. Soil A (Depth 1), all P concentrations and ochre amendments.

Ochre	P	pH	Ca	±**	Cd	±	Cr	±	Cu	±	Fe	±	K	±	Mg	±	Mn	±	Na	±	Ni	±	Pb	±	Zn	±
g kg^{-1}	Mg L^{-1}		mg L^{-1}		μg L^{-1}																					
0	0	7.3	4.3	0.2	0.0	0.1	3.3	1.4	47.9	2.7	1500.1	478.0	4.1	0.3	1.5	0.1	2447.2	396.9	1.3	0.1	8.5	1.8	23.5	3.8	13.7	1.5
0	10	7.3	4.4	0.2	0.0	0.0	1.3	1.2	52.5	3.7	1055.4	703.2	10.5	0.2	1.5	0.1	2749.5	157.9	1.3	0.0	11.4	0.9	23.6	8.0	12.6	2.8
0	20	7.3	4.9	0.3	0.0	0.0	0.1	0.3	52.2	6.1	739.9	439.1	18.4	0.2	1.6	0.1	2972.2	209.9	1.3	0.1	10.1	2.2	25.8	5.6	12.6	4.7
0	40	7.3	5.2	0.5	0.0	0.0	1.7	3.3	46.5	15.2	486.5	508.9	36.4	1.1	1.6	0.2	2992.2	392.8	1.3	0.0	11.3	4.3	25.7	4.1	11.0	3.2
0.15	0	6.2	4.7	0.2	0.0	0.0	1.7	1.6	163.8	97.5	1495.0	1173.6	4.2	0.3	1.6	0.3	2900.0	458.0	1.3	0.0	10.1	1.5	36.6	7.9	17.6	4.1
0.15	10	6.2	4.6	0.2	0.0	0.0	0.0	0.2	79.7	3.4	594.9	465.8	10.8	0.0	1.5	0.0	2901.2	237.9	1.3	0.1	9.3	3.1	26.9	14.4	16.8	1.3
0.15	20	6.2	4.9	0.2	0.0	0.0	0.8	1.4	74.1	6.2	307.6	102.9	19.6	0.5	1.5	0.1	3126.8	200.7	1.3	0.1	6.4	4.0	32.9	10.8	13.3	1.2
0.15	40	6.2	6.0	0.4	0.0	0.0	0.5	0.1	81.8	12.6	405.6	101.9	37.1	0.5	1.9	0.1	3736.2	219.5	1.4	0.0	8.8	0.8	31.4	14.3	13.7	1.5
1.5	0	6.1	4.7	1.5	2.0	3.5	6.9	6.2	66.0	22.5	1966.2	2859.0	4.3	1.2	1.8	0.7	2828.9	898.9	1.3	0.4	15.1	8.6	18.3	18.1	21.1	13.2
1.5	20	6.1	5.9	0.5	1.0	1.4	7.1	4.6	85.7	9.4	1150.7	1497.5	11.7	0.6	1.9	0.3	3536.4	277.5	1.5	0.2	7.5	3.6	1.5	2.7	21.0	6.1
1.5	10	6.1	6.2	0.6	0.0	0.0	10.4	3.0	82.7	14.1	3010.4	1001.0	20.1	1.5	2.2	0.8	3770.1	394.6	1.4	0.1	12.5	7.2	5.1	5.0	24.7	15.7
1.5	40	6.1	6.7	0.7	0.0	0.0	4.8	1.4	71.1	12.5	277.5	19.0	37.7	1.5	2.0	0.2	3777.4	430.5	1.5	0.1	5.4	1.7	0.0	0.0	15.3	1.9
7.5	0	5.9	11.8	2.5	0.0	0.2	4.6	1.6	61.4	6.9	340.1	85.7	5.2	0.7	3.2	0.7	6713.2	1360.7	1.4	0.3	11.1	5.0	3.7	6.4	24.2	5.2
7.5	10	5.9	11.6	0.8	0.0	0.2	4.2	2.4	63.5	4.9	368.4	261.1	13.2	0.3	3.1	0.3	6545.3	463.8	1.4	0.1	8.8	5.7	0.0	0.0	27.6	1.0
7.5	20	5.9	11.6	0.6	0.1	0.2	9.1	6.8	76.3	14.6	2050.7	2989.2	22.2	1.1	3.3	0.5	6409.3	105.3	1.4	0.1	13.5	4.0	2.4	2.4	32.1	8.6
7.5	40	5.9	11.2	0.7	0.0	0.1	7.7	5.4	76.4	12.4	2301.0	3175.7	40.8	0.5	3.2	0.5	6201.6	399.6	1.3	0.1	14.9	5.7	4.8	8.3	31.7	9.8
15	0	5.7	17.0	1.1	0.0	0.0	3.6	1.3	76.5	13.2	739.2	356.0	5.8	0.1	4.2	0.2	10366.7	701.8	1.5	0.0	7.4	2.9	0.4	0.6	69.1	13.3
15	10	5.7	15.7	0.2	-0.1	0.1	6.0	1.8	97.9	4.8	655.5	284.0	13.6	1.2	3.9	0.0	9280.6	172.3	1.4	0.1	13.0	8.7	6.0	8.5	66.0	6.8
15	20	5.7	16.1	1.3	4.5	3.4	8.4	3.6	85.3	11.2	400.2	44.8	23.5	0.4	4.0	0.3	9604.4	726.7	1.5	0.2	13.0	5.6	11.9	10.5	72.8	5.2
15	40	5.7	16.0	0.5	0.7	0.3	5.2	5.5	95.0	41.2	1507.3	2105.7	50.8	6.7	4.0	0.5	9546.0	391.8	1.4	0.2	13.2	0.9	4.6	5.0	76.2	8.7
Limit*					0.2		0.6		5.0												20.0		7.2		40.0	

*Annual average EQS for surface waters (other than inland surface waters) (Council of the European Union, 2009) **± (standard deviation)

Table 5.4 b. Metal concentrations in solution after batch experiments (n=2) ± (standard deviation) with Soil B (Depth 1), all P concentrations and ochre amendments.

Ochre	P	pH	Ca	±**	Cd	±	Cr	±	Cu	±	Fe	±	K	±	Mg	±	Mn	±	Na	±	Ni	±	Pb	±	Zn	±
g kg^{-1}	mg L^{-1}		mg L^{-1}		µg L^{-1}																					
0	0	7.0	3.9	0.8	0.3	0.4	6.3	1.8	54.2	9.0	1518.7	707.6	3.4	0.5	1.8	0.4	573.3	181.9	1.4	0.0	4.0	1.1	12.0	6.9	28.8	8.9
0	10	7.0	2.2	0.6	0.1	0.1	5.7	1.0	58.2	5.6	965.0	90.7	9.7	0.4	1.5	0.2	527.6	81.4	1.4	0.2	2.4	1.6	0.0	0.2	32.5	4.9
0	20	7.0	2.8	0.2	0.0	0.2	7.5	1.0	61.4	2.8	1247.9	234.2	18.2	0.2	1.8	0.1	626.8	36.6	1.5	0.1	10.5	3.4	1.3	2.3	39.8	2.8
0	40	7.0	3.1	0.3	0.0	0.1	8.0	1.2	64.1	2.7	1201.7	245.1	41.3	1.1	1.8	0.0	621.8	48.0	1.7	0.3	7.4	2.2	2.6	3.9	39.5	4.3
0.15	0	5.9	3.6	0.7	0.4	0.7	4.9	1.8	37.6	7.5	1391.7	329.3	3.6	0.3	2.2	0.3	749.9	116.1	1.8	0.3	10.7	7.0	8.4	3.9	31.7	5.9
0.15	10	5.9	3.2	0.5	0.2	0.3	6.4	1.6	38.4	2.3	1352.8	147.1	11.1	0.4	2.0	0.1	722.0	74.9	1.7	0.1	8.6	1.9	9.1	15.8	35.1	1.7
0.15	20	5.9	3.7	1.1	0.0	0.1	14.2	2.5	52.5	10.5	2995.6	1450.3	20.6	0.6	2.5	0.5	797.9	194.4	1.9	0.2	12.3	6.5	13.0	9.9	46.4	12.7
0.15	40	5.9	4.5	0.6	3.5	6.0	9.6	4.2	53.8	15.4	1412.1	103.9	43.0	3.4	2.4	0.0	748.6	134.3	1.9	0.1	16.3	4.7	16.3	16.4	45.9	8.4
1.5	0	6.0	5.2	1.4	0.7	1.1	8.8	4.9	47.8	17.4	2098.5	1570.9	3.6	0.4	2.2	0.6	681.9	205.5	1.6	0.0	11.7	2.8	8.9	11.0	36.9	8.6
1.5	10	6.0	4.4	0.1	0.0	0.2	5.9	1.2	47.9	4.3	1481.6	105.7	9.9	0.1	1.7	0.0	596.1	12.0	1.6	0.1	9.9	4.1	17.4	16.6	39.1	2.8
1.5	20	6.0	4.5	0.2	0.0	0.2	3.7	0.4	53.5	2.5	1276.9	486.7	17.6	0.4	1.7	0.1	595.3	26.2	1.5	0.0	10.3	4.1	11.8	14.8	41.2	3.3
1.5	40	6.0	5.1	0.8	0.1	0.1	2.8	2.3	43.1	10.7	1017.3	269.9	39.0	1.9	1.9	0.2	632.7	92.6	1.8	0.3	4.8	5.2	7.9	6.1	39.5	5.4
7.5	0	5.7	9.3	1.0	0.0	0.1	1.3	1.0	61.4	6.4	1165.2	223.4	3.9	0.4	3.3	0.3	1187.2	91.1	1.6	0.1	8.3	1.7	6.5	11.3	53.8	8.6
7.5	10	5.7	7.7	2.2	0.0	0.2	1.4	1.0	63.4	11.4	1049.4	262.0	11.5	0.6	2.8	0.6	943.7	313.2	1.8	0.3	9.4	3.6	17.7	4.5	57.0	14.0
7.5	20	5.7	10.1	3.6	0.2	0.3	4.3	0.9	102.3	14.3	1234.5	66.8	20.3	0.9	3.5	1.2	1236.1	369.8	2.0	0.7	5.6	3.1	22.5	14.7	73.9	5.9
7.5	40	5.7	7.5	0.3	0.2	0.4	2.6	0.4	83.9	5.0	1055.1	256.2	40.8	0.3	2.7	0.1	935.8	33.1	1.6	0.0	9.0	6.0	8.7	11.4	64.9	2.8
15	0	5.6	23.6	2.5	0.0	0.3	8.3	12.5	9.8	9.8	5262.2	5987.8	2.7	1.9	1.6	1.4	128.5	95.8	0.5	0.1	7.6	9.3	7.6	13.2	20.4	14.3
15	10	5.6	27.0	1.7	3.5	3.9	16.0	7.1	22.9	7.1	6366.1	1747.4	12.4	1.0	2.1	0.5	80.0	33.3	0.6	0.1	3.8	4.4	24.8	19.5	23.0	9.8
15	20	5.6	30.7	0.5	0.6	0.2	4.3	1.5	9.7	3.4	1541.1	1320.5	22.7	1.1	1.0	0.3	23.3	12.2	0.5	0.0	2.2	3.8	20.4	7.0	5.4	2.4
15	40	5.6	35.7	0.4	0.3	0.5	1.8	1.7	4.2	1.4	1181.4	52.9	47.1	1.0	1.0	0.1	15.7	1.1	0.5	0.0	0.9	1.1	21.4	7.3	4.5	0.9
Limit*					0.2		0.6		5.0												20.0		7.2		40.0	

*Annual average EQS for surface waters (other than inland surface waters) (Council of the European Union, 2009) **± (standard deviation)

Table 5.5 Kinetic experiment. Metal concentration release over time .

Time	Ca	±*	Cu	±	Fe	±	K	±	Mg	±	Mn	±	Na	±	Zn	±
Minutes	mg L^{-1}		µg L^{-1}													
1	8.4	0.0	8699	2761	1369	238	134.8	2.4	1.6	0.1	280.2	18.3	2.6	0.0	13045	1163
5	8.1	0.2	12570	121	1358	168	135.8	0.8	1.3	0.0	231.8	8.1	2.2	0.0	15905	308.
10	5.9	2.9	6570	8573	667	441	137.1	3.9	0.6	0.8	187.4	52.9	1.8	0.5	8218	10905
15	4.2	1.9	6180	2491	732	86.0	69.3	27.2	0.6	0.2	118.8	43.4	1.2	0.6	7421	2840
30	3.2	0.0	9014	345	817	28.6	62.5	3.2	0.5	0.0	105.7	8.6	0.8	0.0	10318	842
60	6.1	1.4	14918	4294	973	192.0	109.2	19.5	0.9	0.2	165.6	34.1	1.5	0.3	16564	4295

*± standard deviation

Based on the results of this study – and with caveats discussed below - ochre amendment without any additional P inputs fully protects a waterbody from runoff with concentrations of > 0.035 mg DRP L^{-1}. This is important not only for low Index soils (1 to 3) during storm events, but particularly for Index 4 soils. Schulte et al. (2010) showed that it may take many years for Index 4 soils to be reduced to agronomically and environmentally optimum levels. The extent of these delays was predominantly related to the relative annual P balance (P balance relative to total P reserves). While the onset of reductions in excessive soil P levels may be observed within five years, this reduction is a slow process and may take years to decades, even after fertilization has ceased, to be completed. Additional protection of a waterbody during this delay or lag time phase (Fenton et al., 2009) in Index 4 areas could be achieved by chemical amendment of soils at Critical Source Areas (CSA), identified by risk assessment. A CSA is a district area within a catchment that has a high soil P Index and an associated hydrological pathway that can transport P during storm events to a waterbody.

In the field, a vegetated buffer strip should be designed for such CSA, taking into consideration P loadings from fertiliser and/or animal manures, soil types, STP conditions before or after fertilizer application, rainfall intensity, as well as the required contact time for sequestration of a certain % of P passing through the buffer strip. If the ProportionalP (%) is kept low, a high percentage of P will be sequestered by the amendment mixed in with the soil. The model developed in this paper helps determine if a water quality standard such as MAC 0.025 mg L^{-1} is achievable with a certain ochre amendment to soil. The standard set in this paper has been set for a surface waterbody and not for a runoff concentration. Therefore, the runoff concentrations of this study will be diluted further within a catchment. The P nutrient concentration of such a waterbody will be determined by the mosaic of P pressures across a landuse gradient within a catchment.

5.2.9 Impact on pH

In this study, ochre addition to soils decreased the soil pH, but not to unsustainable levels. The average mineral soil pH for grassland in Ireland, at 5.4, is less than optimal (Tunney & Zhang, 2008). Low pH may slow down the activity of decomposing organisms and the breakdown of organic matter, thereby reducing the release of valuable nutrients. This may limit P, N and S availability, and leaching of acidity to subsoils may be irreversible. Addition of any ochre amendment to vegetated buffer strips may further increase acidity, and metals such as Mg and Mn would become more soluble and could reach toxic levels (Gardiner & Garner, 1953). Therefore, in absence of liming, Mg introduced through natural high levels in the soil and through ochre amendment could be lost at toxic concentrations. However, liming, while improving the availability of P, will increase the solubility of P and therefore risk of P loss.

5.2.10 Impact on metal concentrations

There has been some documentation of hazardous release of metals from coal mining ochre in 5 out of 49 mine-water treatment facilities in the U.K. (Hancock, 2005). The ochre used in this study released toxic concentrations of metals in runoff. Inductively coupled plasma mass spectrometry and bulk energy dispersive spectroscopy showed potentially toxic concentrations of Fe, Zn, Pb, As and Cu (Section 4.2.2.). Remobilisation of heavy metals might occur due to any reduction of iron oxides in the soil and ochre, for example by rising groundwater depths in a perched watertable scenario, e.g. glacial tills or by incorporation into the buffer. Although these concentrations will, to some extent, also be diluted by the main surface waterbody, any release of toxic metal makes Avoca ochre not suitable for use in buffer strips.

The sustained metal release from Avoca ochre over time, makes it unsuitable for use in the open environment at such high concentrations. Such a danger to the environment overrides the high P sequestration capacity of the ochre.

5.3 Summary

In this chapter, P-amended water was mixed with this ochre in batch experiments and a maximum P adsorption capacity, calculated from the Langmuir equation, of between 16 and 21 g P kg^{-1} was calculated. A proportional adsorption predictive model, incorporating ochre amendment, P inputs and native soil test P was developed. Without further P inputs, ochre effectively intercepts P loss from soils and could be used in P Index 4 (soil P range > 8 mg L^{-1}) areas to protect water courses from incidental P losses. With additional P inputs, ochre reduced P concentrations in runoff, but not below the MAC of 0.035 mg L^{-1} for surface water. However, as further dilution of runoff concentration occurs in a catchment, such reductions are significant, especially during storm events. However, very quick and sustained metal release from the ochre tested during P sequestration makes it unsuitable to be used in the environment.

Chapter 6 Nitrate Remediation studies

Denitrifying bioreactor technology, where a solid C reactive media intercepts contaminated groundwater, has been successfully used to convert excess nitrate to N_2. Two methodologies to locate a subsurface “denitrification trench” for nitrate remediation were investigated.

6.1 PRB location method I

The first of two PRB location methods utilises hydrogeological data collected on site, merged with methods reviewed in the literature.

6.1.1 Nitrate Remediation

To account for shallow groundwater contamination, possible point sources and receptors needed to be identified. The 4.2 ha site was located within a beef farm, which generated large volumes of dirty water. From the early 1980’s to 2005, a rotational irrigation system (roto-rainer) was in place up-gradient of this site, to manage agricultural waste on site. The location of the dirty water rotational irrigation infrastructure (subsurface pipes and connectors for irrigator) gave an area in which the roto-rainer was operational. The area was surveyed and the distance from source to receptors was measured. All existing data on the site, such as soil type, thickness, texture, soil profiles, drainage conditions, subsurface geology, subsurface and surface drain location, was collated.

6.1.2 Monitoring on site

Partially penetrating piezometers (n=17) (25 mm LDPE casing; Van Walt Ltd, Surrey, U.K.) were installed in a grid to shallow groundwater of multilevel depths using rotary drilling (60 mm) (Giddings soil excavation rig, Colorado, U.S.A.) to several metres below the watertable. The average piezometer drilling depth was 3.2 m bgl (Table 3.3), with a 1 m screen at the bottom of each well. The screen was covered with a filter sock, surrounded with washed pea gravel and sealed with bentonite to 10 cm below ground surface. Topsoil was then filled on top of the bentonite and reseeded. Two multi-level drilling depths, from 63 m to 67 m AOD and from 67 m to 70 m AOD, respectively, were drilled.

Drilled holes were back-filled with gravel (3 to 6 mm diameter) to 0.5 m above the screen, sealed with bentonite (1 m deep) and then backfilled to the land surface to avoid contamination. All piezometers were surveyed using GPS (X and Y survey only) and the locations of the piezometers were recorded using digital mapping software (ArcGIS^{TM} 9.1, ESRI, Ireland). The site and monitoring network was then digitised using a DGPS antenna, MG-A1 equipment (TOPCON, Ireland) and the site elevations were obtained (Z survey). The depth to the water table in each monitoring well was measured using an electric water-level indicator (Van Walt Ltd, Surrey, U.K.) and groundwater heads were determined using ordnance survey data (Figure 6.1). Data are described using m AOD to allow comparisons of plume position, thus eliminating topographical differences.

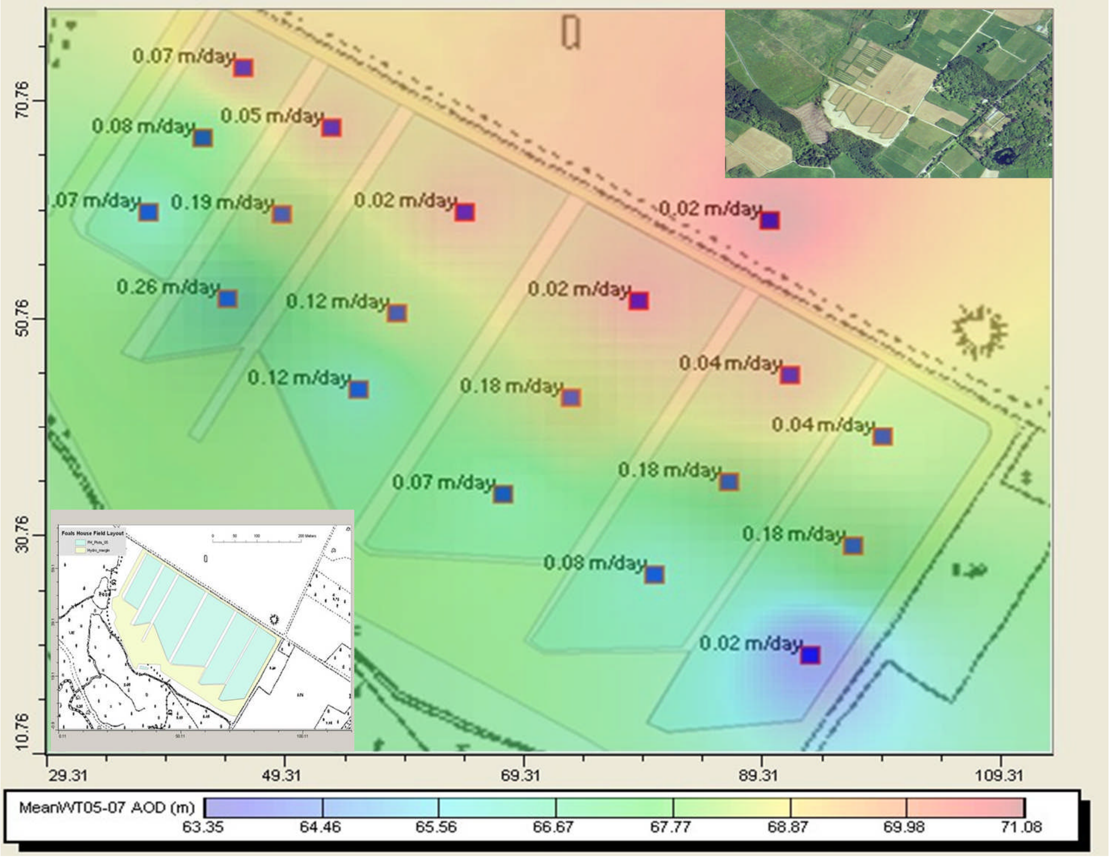


FIGURE 6.1 GROUNDWATER HEADS AND K_S FOR EACH PIEZOMETER.

Surface water features, such as streams, drains and lagoons, were also levelled on the same date. The maps were used to construct groundwater maps and elucidate groundwater flow direction. A topographic base map with a field boundary overlay was generated using ArcGIS^{TM} and merged with well location and groundwater head input files. Two-dimensional groundwater contours were generated using GW-

Contour 1.0 software (Waterloo Hydrogeologic, Canada). Watertable levels were measured weekly, using an electronic dipper (Van Walt Ltd, Surrey, U.K.) and groundwater was sampled in duplicate, using a Waterra hand-held pump (Van Walt Ltd, Surrey, U.K.) Nutrient concentrations were analysed (in duplicate) monthly with a Thermo Konelab 20 (Technical Lab Services, Ontario, Canada) for NO_2-N, TON-N, NH_4-N and Cl^-.

A water balance of the site was used to calculate the travel time from surface level to the watertable in the six isolated plots. Daily weather data, recorded at the Johnstown Castle Weather Station, were used to calculate daily soil moisture deficit (SMD) using a hybrid model for Irish grasslands. Potential evapotranspiration, ET_0 (mm day^{-1}), was calculated using the FAO Penman-Montieth equation (Allen et al., 1998):

$$ET_0 = \frac{0.408\Delta(R_n - G) + \gamma \frac{900}{T_a + 273} u_2 (e_s - e_a)}{\Delta + \gamma(1 + 0.34u_2)} \qquad [6.1]$$

where R_n is the net radiation at the crop surface (m^{-2} day^{-1}), T_a is the air temperature at a 2 m height (ºC), u_2 is the wind speed at a 2 m height (m s^{-1}), e_s and e_a are the saturation and the actual vapour pressure curves (kPa ºC^{-1}) and γ is the psychrometric constant (kPa ºC^{-1}). ET_0 was then converted to actual evapotranspiration (*Ae*) using an Aslyng scale recalibrated for Irish conditions (Schulte et al., 2005). Effective rainfall was calculated by subtracting daily actual evapotranspiration from daily rainfall (assuming no overland flow losses due to the high infiltration capacity of the soil on this site). Higher k_s zones were found in the topsoil, even in the poorly drained plot. SMD on day one (January 1st, 2006 and 2007) was set to zero and effective drainage was estimated for each subsequent day. Modelling the effective drainage enables the infiltration depth of water to be calculated at specific hydraulic loads where the soil effective porosity is known. This infiltration depth may be compared to watertable data to investigate if recharge to groundwater in that particular year affects water quality.

6.1.3 *k_s* determination

The k_s for the open screen area of each piezometer (1 m at the end of each well) was estimated in slug tests using an electronic diver (Eijkelkamp, the Netherlands) set to record heads at 1 sec time intervals in each piezometer. The diver measures the initial head of water in the piezometer before, during and after the test until full recovery occurs in the piezometer. A slug of 1 L of water was placed instantaneously into the piezometer. The start time (t_0) for the test was noted. Data was downloaded and analysed after Bouwer & Rice (1976) slug test for an unconfined aquifer as outlined in ILRI (1990) in steady-state flow conditions:

$$k_s = \frac{\mathrm{r_c^2 \ln(\frac{R_e}{r_w})}}{\mathrm{2d}} \frac{1}{\mathrm{t}} \ln \frac{\mathrm{h_0}}{\mathrm{h_t}} \qquad [6.2]$$

where r_c is radius of the unscreened part of the well where the head is rising, r_w is the horizontal distance from the well centre to the undisturbed aquifer, R_e is the radial distance over which the difference in head, h_o, is dissipated in the flow system of the aquifer, d is the length of the well screen, h_o is the head in the well before the start of the test and h_t is the head in the well at time $t>t_o$.

As the wells on site are partially penetrating, the following equation was used (Bouwer & Rice, 1976):

$$\ln \frac{R_e}{r_w} = \left[\frac{1.1}{\ln(\frac{b}{r_w})} + \frac{A + B \ln\left[\frac{(D-b)}{r_w}\right]}{\frac{d}{r_w}} \right]^{-1} \qquad [6.3]$$

where b is the distance from the watertable height to the bottom of the well, D is the distance from the watertable to the impermeable zone, and A and B are dimensionless parameters, which are function of d/r_w. If $D>>b$, the effective upper limit of ln [(D-b)/r_w] may be set to 6. A spatial k_s map was developed in ArcGIS™ and merged with well location and groundwater head input files. b is measured by an electronic dipper before commencement of the slug test.

6.1.4 Discharge and effective Darcian velocity

The discharge of water from each plot (a known width of aquifer), Q (m ^{3} day $^{-1}$), was determined using (Darcy, 1856):

$$Q = -k_s A \frac{dh}{dx} \qquad [6.4]$$

where $A = bw$, where b is the aquifer thickness (m), w, the width (m) and dh/dx is the hydraulic gradient. w is taken as the combined diameter of the plots.

Prior to the study, soil cores (n = 46) at the piezometer locations and drains were taken at 1m-depths and analysed for bulk density and particle density. Total porosity was calculated from (Brady & Weil, 1996):

$$n = 100\left(1 - \frac{\rho_b}{\rho_d}\right) \qquad [6.5]$$

where n is the total porosity (%), ρ_b the bulk density (kg m^{-3}) and ρ_d is the particle density (kg m^{-3}).

The average effective velocity, v (m day^{-1}), was calculated from:

$$v = -k_s \frac{1}{n_e} \frac{dh}{dx} \qquad [6.6]$$

where v is equal to Q/A and n_e is average effective porosity. A similar approach was used previously in tills by Helmke et al. (2005) to investigate nitrate transport to groundwater in four Iowa till units. It should be noted, that there is a lack of data regarding effective porosity worldwide as this is a difficult parameter to obtain from field experiments.

The transmissivity, T (m^2 day^{-1}), was calculated using the aquifer thickness, b:

$$T = k_s b \qquad [6.7]$$

6.1.5 Trench thickness - bench scale testing

The kinetics of denitrification will depend on C and nitrate availability, pH, temperature, soil texture, soil management, tillage, rainfall events, rates of microbial respiration and nitrification, water filled porosity, soil mineral N content, soil type and redox conditions. A reactive material should be chosen and tested to optimise contaminant residence times in the reactive barrier. On-site soil cores of fine loamy brown earth, fine loamy gley and sandy brown podzolic soils were tested for denitrification rate (µg N lost as NO_3-N g^{-1} dry soil day^{-1}) using soil incubation tests. The denitrification rate of the humic cambisol and gleyic cambisol soils on site amended with lodgepole pine woodchips (5:2 g dry weight of woodchips to soil) was also examined. The retention time, t (days), needed to achieve denitrification was calculated using:

$$t = \frac{c_{treated}}{c_{\max}} / r \qquad [6.8]$$

where $C_{treated}$ is the desired concentration after remediation, $C_{\max}$ is the greatest concentration expected and r is denitrification rate determined from batch experiments. The retention time was then multiplied by the groundwater flow velocity to calculate the thickness of the trench. Based on chemical stoichiometric relations, denitrification of one mole of NO_3^- will require 1.25 moles of C. This equates to a mass balance of 1.07 kg of available C per 1 kg of NO_3-N. With approximately 50% of C availability in woodchip (based on bulk density), the treatment of 1 kg of NO_3-N will be approximately 2 to 2.5 kg of woodchip (Fahner, 2002).

6.2 PRB location method II

The second method uses a more sophisticated approach to divide the site into “denitrification” and “dilution” areas.

6.2.1 Nutrient Management

A detailed account of organic and inorganic application and silage production on the Sandhill, North West and field site was kept from 2006 to 2007. Nutrient records confirm uniform treatment in subsequent years. The N surplus was calculated for each area. These areas are not grazed.

6.2.2 Buffer zone diameter and contaminant mass flux

A land use circular buffer zone around each piezometer was previously used to correlate a landuse area that contributes to groundwater quality (Kaown et al., 2007) where the buffer zone diameter D (m) in the direction of groundwater flow was approximated by:

$$D = \frac{Q}{bv} \qquad [6.9]$$

where Q is calculated using Eqn. 6.4, b is the aquifer thickness as used in Eqn. 6.6 and v is calculated using Eqn. 6.6. The central piezometer in each plot was taken as the centre of the buffer area. In areas where groundwater flow direction is known, the buffer zone method overestimates the groundwater contribution down-hydraulic gradient, while underestimating the area of contribution up-hydraulic gradient, which should extend to a groundwater divide. When groundwater flow direction is known, the buffer zone becomes a true zone of contribution (ZOC). This is then defined as the area surrounding the piezometer that encompasses all areas or features that supply groundwater recharge to the piezometer up-hydraulic gradient to the groundwater divide. In this case, the groundwater divide is represented by the brow of the Sandhill. Over a period of time, determined by effective Darcian velocity, groundwater within the ZOC will flow past the piezometer monitoring point and thus will affect the hydrochemistry at that point. In this study, land use management within the entire ZOC, was assessed.

To evaluate the contaminant mass flux (g m^3 day^{-1}) of a dissolved contaminant, the mass flux was measured across a control plane (a row of piezometers). The total contaminant mass flux across a control plane was determined by summing the mass flux of the individual cells along this plane. Each cell was assigned a unique depth of saturated zone, mean nitrate concentration and groundwater-specific discharge (calculated using mean k_s values at each piezometer and mean hydraulic gradient in each plot). The total mass flux across the plane was determined by summing the mass flux of the individual plots according to (API, 2003):

$$w = \sum_{i=1}^{i=n} C_i q_i A_i \qquad [6.10]$$

where w is total mass flux across a control plane (g m^3 day^{-1}), C_i concentration of constituent in *i*th plot (g L^{-1}), q_i is specific discharge in *i*th plot (m day^{-1}) and A_i is area of *i*th plot (m^2). Within the plots, three control planes were assigned using the top (3, 5, 8, 11, 14, 17), middle (2, 7, 10, 13) and bottom (1, 4, 6, 9, 12 and 15 form the compliance control plane) piezometers. The contaminant mass flux passing through each control plane was calculated and the natural attenuation process assessed.

The overall efficiency of nitrate attenuation/dilution between control planes has been used in riparian studies (Orleans et al., 1994; Dhondt et al., 2006) and may be calculated by the following equation:

$$Efficiency = \frac{N_{IN} - N_{OUT}}{N_{IN}} * 100\% \qquad [6.11]$$

where N_{IN} is the up-gradient nitrate contaminant mass flux and N_{OUT} is the down-gradient contaminant mass flux.

6.2.3 Denitrification determination

Denitrification is considered the most important reaction for nitrate remediation in aquifers. The process of denitrification occurs in O_2-depleted layers with available electron donors and, in agricultural environments with N nutrient losses considerable, nitrate reduction is possible. To further investigate if denitrification is a viable pathway for nitrate reduction, some additional water quality measurements were taken on a random date. Physio-chemical parameters such as pH, redox potential (Eh (mV)), electrical conductivity (cond (µS cm^{-1})), temperature (temp (ºC)) and rugged dissolved oxygen (RDO (µg L^{-1})) were measured in the field using a multi parameter Troll 9500 probe (In-situ, Colorado, U.S.A.) with a flow-through cell.

To elucidate the locations of potential denitrification during groundwater sampling based on dissolved N_2 and the N_2/Ar ratio, three water samples were taken from each piezometer mid-way within the screened interval using a 50 ml syringe and gas impermeable tubing. Samples were transferred from the syringe to a 12 ml Exetainer® (Labco Ltd, U.K.) and sealed to avoid any air entrapment with a butyl rubber septum. Samples were then placed under water in an ice box, transported to laboratory and kept in a cold room at 4°C prior to analysis. Dissolved N_2, O_2 and Ar were analyzed using MIMS at the temperature measured (11°C) during groundwater sampling (Kana et al., 1998). For N_2O concentration, three additional samples were taken in glass bottles for degassing. A sample of 80 ml groundwater was injected into a pre-evacuated 160 ml serum bottle followed by 80 ml pure helium. The bottles were shaken for 5 minutes. Then, using an air-tight syringe, 15 ml equilibrated gas was collected in the headspace. This was transferred into a 12 ml Exetainer for the analysis of dissolved N_2O using a gas chromatograph (GC; Varian 3800, U.S.A.) equipped with electron capture detector. The concentration of dissolved N_2O was calculated using the Henry's law constant, the concentration of the gas in the head space, the bottle volume and the temperature of the sample, but the lowest 14°C was taken due to limitation in gas solubility coefficient to calculate Henry's law constant (Hudson, 2004).

6.2.4 Data processing - Tobit regression

The effects on groundwater nitrate concentration of k_s (m day^{-1}), elevation (m AOD), screen opening elevation (m AOD) and distance from pollution source (m) were assessed using a Tobit regression model (Tobin, 1958). The nitrate concentration was left censored using a background concentration threshold of 2.6 mg NO_3-N L^{-1}. Statistical model selection was performed using a forward selection stepwise procedure. Due to the grid layout of the piezometers, residuals could not be assumed to be independent and their spatial dependence was modeled using an anisotropic power covariance structure. The anisotropic power correlation model depends on two parameters: one that represents the correlation between piezometers in the direction of rows and the other that represents the correlation in the direction of columns. Models were fitted using the MIXED procedure (SAS V9.1, 2003). To separate the effect of groundwater nitrate denitrification from dilution, groundwater nitrate retention is studied by evaluating concurrently groundwater nitrate and Cl^- concentration (Altman et al., 1995). To investigate the effect of dilution on the study area, Cl^- was also inputted into the model. Cl^- is considered a conservative tracer.

6.3 Woodchip slug

The investigation of nitrate removal usually considers a bioreactor as a unit with a designed nitrate removal rate. In nature, denitrification occurs at different rates spatially and temporally in soil, subsoil and groundwater. This is also the case in reactive media within a bioreactor. Several techniques in combination are presented to establish: a) the location where denitrification or dilution occurs on the study site and b) how denitrification potential changes spatially and temporally.

6.3.1 Isotopes

Using a subset of isotopic results from Baily et al. (*pers. comm.*), the occurrence of denitrification in the studied wells was determined. During April (spring), August (summer) and December (autumn) in 2008, isotopic signatures were determined for all the wells used in the present study. Conditions prevalent in a well in which denitrification occurs include: low nitrate, high δ^{15}N and δ^{18}O isotopic values; and high δ^{15}N and δ^{18}O enrichment ratios. δ^{15}N is enriched by between 1.3 and 2.1 times that of δ^{18}O (Böttcher et al., 1990). Source tracking using enrichment ratios can only be definite within a closed system and only indicative under field conditions. In some cases, it is difficult to assign nitrate isotope enrichment factors to the isotope data to quantify the denitrification process, if samples are not collected along discrete groundwater flow paths (Wassenaar et al., 2006). Baily et al. (*pers. comm.*) showed that the spatial pattern of nitrate in shallow groundwater differs, but, as the mild and moist climate present on this site allows biological processes to continue all year round, the temporal pattern is relatively constant. Buss et al. (2005) showed that temperatures above 4ºC are needed for denitrification. The temporal nature of the site allowed the current study to be carried out at any time of the year. To minimise degassing due to higher ambient air temperatures in the early months of the year, the present study was conducted from August to November, 2009. A summary of results from the Baily et al. (*pers. comm.*) study is presented in Table 6.1.

6.3.2 k_s, watertable height and effective rainfall

The k_s of each well was calculated using the Bouwer & Rice slug injection test method (Bouwer & Rice, 1976). A mini-electronic diver (Van Walt, U.K.) set at a 0.5 s resolution, collected drawdown data. The linear part of the response curve was tested, after which the influence of the filter pack had dissipated. Whereas isotopic results differentiated wells into “denitrification” and “no denitrification” categories, k_s divided such wells further into high and low permeability within medium permeability tills. Well water levels were recorded daily using a dipper to ensure the screened intervals of the wells were saturated at all times. Daily meteorological data were collected from the Johnstown Castle Weather Station, which is located on the farm. To estimate daily effective rainfall, temperature, total rainfall, wind speed, solar radiation and humidity were inputted into a hybrid model specifically for grassland in Ireland (Schulte et al., 2005). This was to investigate recharge to shallow groundwater during the experiment and elucidate the effects of dilution on nitrate concentration.

TABLE 6.1 BACKGROUND ISOTOPIC DATA, SOURCE IDENTIFICATION AND PROCESSES IN EACH WELL CHOSEN FOR THE PRESENT STUDY.

Well	NO_3-N Mg L^{-1}	$\delta^{15}N$ ‰	$\delta^{18}O$ ‰	NO_3-N mg L^{-1}	$\delta^{15}N$ ‰	$\delta^{18}O$ ‰	NO_3-N mg L^{-1}	$\delta^{15}N$ ‰	$\delta^{18}O$ ‰	Source of Nitrate	Process
	April 2008			August 2008			December 2008				
1	9.8	6.8	5.3	12.9	7.1	5.7	12.7	8.9	8.7	Manure	Nitrification but no denitrification
9	8.4	7.3	4.6	8.5	6.7	4.1	8.6	7.7	5.6	Manure	Nitrification but no denitrification
15	12.9	6.8	1.4	13.0	6.6	1.4	10.7	7.3	3.7	Low manure signal	Nitrification but no denitrification
11	13.5	7.6	5.4	11.4	7.7	4.8	11.1	8.2	9.6	Manure	Nitrification but no denitrification
10	7.3	9.1	8.1	7.6	7.8	4.4	7.3	8.4	5.7	Manure/sewage	Soil nitrification
2	3.7	9.2	6.1	1.8	11.4	8.1	0.8	11.7	7.9	Manure	Denitrification
12	4.2	11.7	9.6	3.3	13.1	11.6	2.6	16.2	14.7	Manure	Lots of denitrification
14	0.3	7.6	4.6	0.3	16.2	14.2	0.1	16.7	16.1	Manure	High nitrification, volatilisation and denitrification

6.3.3 Water samples

Use of peristaltic or low-flow pumps can be limiting in bioreactor studies due to the inner diameter of wells. Peristaltic pumps can cause degassing of water samples and make them unsuitable for use in groundwater investigations. Instead, in each well, gas-impermeable tubing, with an inner diameter 5 mm, was installed to the centre of the screen interval. At surface level, a three-way stop cock and 50-ml syringe were attached. To elucidate potential denitrification in the screened interval of each well based on dissolved N_2 and the N_2/Ar ratio (Kana et al., 1998; An et al., 2001), triplicate water samples were taken at selected sample dates (24th-25th and 27th-28th August; 1st, 4th, 10th, 17th, 24th, 30th September; 8th, 16th, 28th October; 5th November, 2009). Water samples were transferred from the syringe to a 12-ml Exetainer® (Labco Ltd, U.K.) filled from the base of each container, overfilled, and then sealed to avoid any air entrapment with a butyl rubber septum. Samples were then placed upside-down under water (below the average groundwater temperature of 12ºC) in an ice box, transported to the laboratory, and kept in a cold room at 4°C prior to analysis. Dissolved N_2, O_2 and Ar were analyzed using a MIMS at the temperature measured (11°C) during groundwater sampling (Kana et al. 1998). Nutrient concentrations of water samples were determined using a Thermo Konelab 20 analyser (Technical Laboratory Services, Ontario, Canada) for NO_3-N, TON-N, NH_4-N, Cl^-, total dissolved nitrogen (TDN), TP and calcium (Ca). Water samples were collected in polyethylene screw-top bottles and filtered through 0.45 μm-filter membranes.

N_2 is the final product of the denitrification process. Therefore, assessing how much groundwater N_2 is formed due to denitrification (excess N_2) is important, when comparing denitrification rates in different wells. Measuring excess N_2 is difficult, but can be estimated by taking the measured Ar and N_2 ratios using MIMS and comparing these with Ar and N_2 atmospheric equilibrium, assuming Ar is a stable component. N_2 may be lost during sampling by degassing. Assuming less possibility of degassing due to the water technique employed, excess/denitrified N_2 at mean dissolution of entrapped air (mg L^{-1}) was estimated. Calculation of excess N_2 was after Weymann et al. (2008), using 15ºC water bath temperature, pressure 755 mm HG, based on elevation of site above sea level and a headspace temperature of 15º. In addition, Reaction Progress (RP), representing the extent of nitrate elimination, was calculated after Böhlke et al. (2002) by dividing the denitrification product, N_2-considering N_2O

production was negligible as reported by Khalil & Richards (2010) - by the initial concentration of nitrate and excess N_2.

In addition, other parameters were taken to investigate if denitrification is a viable pathway for NO_3^- reduction. Other parameters, such as pH, conductivity (cond, µS cm^{-1}) and temperature (temp, ºC) were measured in the field using a multi-parameter Troll 9500 probe (In-situ, Colorado, U.S.A.) with a flow-through cell. Dissolved organic C (DOC) and TOC were also measured using a TOC-V Series (Shimadzu, Kyoto, Japan). The metal content (Cu, Fe, Mg, K and Zn) of the water samples were determined by aqua regia digestion using a Gerhard Block digestion system (Cottenie & Kiekens, 1984) and analysed using an ICP VISTA-MPX (Varian, California, U.S.A.).

6.3.4 Solid C enhancement

Washed, untreated woodchip (WC) (10 g, 1-2 mm in length) was packed loosely into a filter sock (Eijelkamp, the Netherlands) approximately 20 cm in length. This was cable-tied and installed in the screened interval of two wells (1 and 15) with high nitrates, a “no denitrification” signal from isotopic analysis and with low (Well 1) and high (Well 15) k_s with moderate permeability tills.

6.3.5 Statistical analysis

To explain the spatial and temporal distribution of nitrate and other parameters on site, the development of predictive models using the available datasets for this field site was examined for NO_3^-, Cl^-, N_2/Ar and DOC. Statistical analysis was undertaken with group variables: WC (Wells 1 and 15) and NWC (Wells 2, 9, 10, 11, 12 and 14) (Figure 3.2 a) were set up as a fixed, treatment effect in the analysis using SAS V.9 (SAS, 2003) software. A factorial model with days and treatment (WC or NWC) and their interaction was developed. As readings within each well were correlated and as the time between sampling events varied, a spatial type covariance structure was fitted across days (14 days in total, between 24th August 2008 and 5th November 2009). Mixed models were used to account for the repeated measures in each well and for heterogeneous variance within treatments.

A number of covariates were available (k_s, O_2 and depth to watertable) and these were tested for inclusion in the model to remove possible bias and for their potential role in a predictive model. As the number of k_s values varied spatially, but not temporally, and the relationship between variables was examined and k_s was statistically significant, apparent non-linearity in the examined relationships was modelled by a nonlinear regression fitted with mixed model equations using Proc Nlmixed (SAS, 2003). Residual checks were made to ensure the approach used, did not violate the assumptions of the analysis. Transformation was used as required for the variable being analysed.

6.4 Results & Discussion: PRB location method I

It was possible to locate a continuous trench PRB on site, but the spatial denitrification capacity of the sub-soil was uncertain. This was ascertained using the second method. In addition, denitrification over time was elucidated using a novel combined isotope and MIMS approach.

6.4.1 Site characterisation

The distribution pattern of the soils is complex; this is a reflection of the intricate nature of the glacial drift deposits from which the soils are derived. The whole farm is underlain by a fine loamy till, which in places is overlain by a stratum of sand of varying thicknesses. On this site, the up-gradient area known as the Sandhill is of course loam overlying the fine loam within the six plots. Across the site, the soil texture comprises a 15 to 40 cm-deep fine loam (Gleyic Cambisol - WRB classification) well-to-moderately drained layer, overlying a loam-to-clay-loam (Humic Gleysol - WRB classification) sub-soil. There is quartzite outcrop along the western side of the site. The textural change across the site was responsible for differential drainage. The study area comprised two well-drained plots (Plots 1 and 2 - brown earth), two imperfectly drained plots (Plots 3 and 4 - gley) and two poorly drained plots (Plots 5 and 6 - gley with higher clay content).

6.4.2 Water balance

Over the study period, the site received mean precipitation of 1046 mm, of which the hybrid model calculated 553 mm effective drainage. Model output showed effective drainage occurred on 178 days, giving an average recharge rate of 3.11 mm d^{-1}. The mean soil total porosity was 32.2±4.9%. The average pore velocity was estimated to be 9.7 mm d^{-1}, giving an approximate mean travel depth of 1.7 m in a moderately drained soil over the study duration. The depth to the median watertable during this period was 1.01 m, which equates with the base of the intersecting drains in Plots 3 and 4. Therefore, the watertable intersects these drains at certain times of the year and infiltrating water upslope (Sandhill) from the drains recharges to groundwater within 1 year. The hydraulic load of the soiled water irrigator, situated on the Sandhill, varied from 10 to 50 mm $year^{-1}$. This would increase the mean depth of travel on the irrigated site when the irrigator was in operation by 10 cm. Therefore, the main receptor was groundwater, but with surface water receptors forming boundaries to the site.

6.4.3 Groundwater investigation

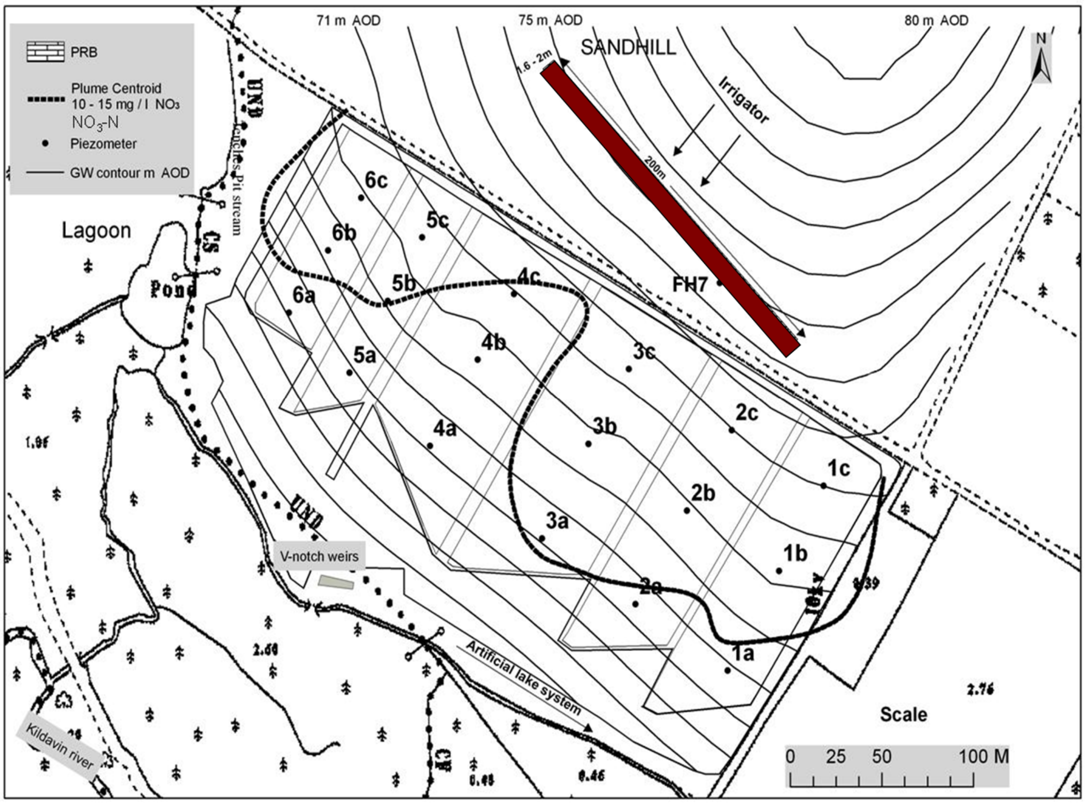
Initial baseline sampling of the piezometers on site showed shallow groundwater nitrate concentrations above the drinking water limit of 11.3 mg NO_3-N L^{-1}. Groundwater temperature on site during the study period ranged from 9.5ºC to 10.5ºC in piezometers 2c (Well 5) and 5c (Well 14), which is suitable for denitrification to occur at depths below 1 m (Rivett et al., 2008). However, this method does not consider the denitrification potential of the sub-soil, but assumes this potential is uniform across the site. Intuitively based on the type of soils and k_s, one can infer a higher or lower potential. It is difficult to differentiate between dilution and denitrification.

The strike and dip of the quartzite outcrop, combined with drilling log data, gave an estimated unconfined aquifer thickness of approximately 10 to 20 m and a saturated thickness, based on mean watertable and depth to the impermeable zone, of approximately 7 m. The piezometer parameters, k_s and groundwater quality parameters are presented in Table 6.2. Hydraulic gradients, calculated using Eqn. 6.4 based on median and maximum watertable heights, showed a hydraulic gradient between the source and potential receptors, i.e. groundwater flow direction in shallow lateral flow-lines exists between source and receptor.

TABLE 6.2 PIEZOMETER AND GROUNDWATER DATA OVER THE STUDY PERIOD .

Plot	I.D	Well number as in Figure 3.3 b	Elevation	Total Depth	Multi level	Watertable depth		Groundwater NO_3-N concentration		Groundwater NH_4-N concentration	
No.			m AOD	m		m		mg L^{-1}			
						Median	Max	Median	Max	Median	Max
1	C	3	71.48	4.35	1	4.35	4.35	4.80	11.85	0.03	1.42
	B	2	69.91	4.13	2	2.85	4.13	12.71	22.56	0.10	2.84
	A	1	67.04	3.64	2	3.73	3.64	6.37	9.54	0.24	0.79
2	C	5	71.83	4.38	1	3.18	4.38	12.80	24.24	0.33	5.63
	B	n/a	69.52	4.13	2	3.00	4.02	12.81	22.30	0.38	5.72
	A	4	67.22	3.14	2	1.01	3.14	1.21	14.77	0.05	2.05
3	C	8	70.87	3.24	1	0.74	2.29	12.31	17.34	0.07	1.38
	B	7	69.47	2.67	1	1.09	2.59	8.99	16.83	0.02	0.31
	A	6	67.90	3.55	2	0.80	2.15	12.26	19.37	0.07	2.18
4	C	11	70.96	2.49	1	1.04	2.24	6.01	10.69	0.05	0.14
	B	10	68.92	2.94	2	0.69	1.41	0.01	6.85	0.08	0.41
	A	9	67.34	2.70	2	0.94	1.75	0.02	6.57	0.04	0.46
5	C	14	71.71	4.33	1	2.18	3.58	14.29	19.94	0.02	0.46
	B	13	68.88	2.87	2	0.67	1.47	9.08	18.92	0.03	0.12
	A	12	67.03	1.55	2	0.53	1.55	9.06	11.35	0.05	2.06
6	C	17	70.68	3.01	1	1.38	2.73	9.61	11.09	0.13	1.02
	B	16	68.09	3.18	2	0.45	1.19	4.19	8.44	0.08	0.71
	A	15	67.24	2.95	2	0.96	1.55	3.12	14.66	0.04	2.23
FH7			72.43	4.14	2	2.97	4.14	6.44	12.66	0.06	0.15

A groundwater flow direction map was constructed using watertable data and surveyed surface water features on July 11th, 2006. As no significant seasonal deviation occurred, a median groundwater map was used to show groundwater flow direction. Groundwater contours (based on groundwater heads) deviated little from topography within the six isolated plots (Figure 6.1).



Flow from high to low hydraulic head contours at right angles to contours. Plume centroid location (from 10 to 15 mg NO_3-N L^{-1}) PRB orientation, location and dimensions.

FIGURE 6.2 GROUNDWATER CONTOURS (BLOCK KRIGING) BASED ON GROUNDWATER HEADS AND TOPOGRAPHY.

Groundwater flow direction was consistent throughout the study period and median groundwater flow contours were used to locate a PRB parallel to watertable contours. If groundwater flow direction changes, the orientation of the PRB should be based on mean conditions. Based on median and maximum hydraulic heads, a barrier containing a 2 m-deep reactive zone is needed (reactive media should fill subsurface from 68 m AOD to 70 m AOD). This would ensure the reactive material was always below the watertable. The extent of the plume migration vertically is unknown; however, it can be assumed that the longitudinal dispersion (in the direction of advective flow) will be significantly greater than transverse dispersion (in the *z* direction) (Fetter, 2002). Lateral plume extent varies from 350 m from 1c (Well 3) to 6c (Well 17) and extends further to 400 m at piezometer 1b (Well 2). As the lateral plume diameter near to the source decreases, the trench needs to be less than 350 m (Figure 6.2) to capture all groundwater flow migrating to Plots 2, 3, 4 and 5 (Figure 6.2).

Combining the hydrogeological characterisation data, plume distance and travel times were calculated (Table 6.3). A steep hydraulic gradient in Plot 4 resulted in groundwater flow to Plots 1 and 6. A significant hydraulic gradient existed between Plots 5 and 6. Average linear velocity was higher in Plots 4 and 5. Therefore, the centroid was able to migrate quickly in two directions. When aquifer thickness was considered, Plot 5 has highest *T* indicating plume migration was quickest from Plots 4 and 5. Therefore, plume migration is greatest (in a given time interval) in Plot 5, migrating to a potential receptor to the west. Migration from Plot 4 eastwards was slower. Travel times from the centroid outwards are also similar with plume migration faster in a westward direction. Therefore, two travel times must be considered in groundwater remediation of the site.

Due to subsurface characteristics, a plume originating from a point source may migrate to several receptors in different timescales. Remediation should concentrate on the most immediate of these pressures, or be located close to the pollution source.

TABLE 6.3 PLUME DISTANCE AND TRAVEL TIMES USING HYDROGEOLOGICAL PARAMETERS

	Plots					
Parameters	1	2	3	4	5	6
area (ha)	0.78	0.75	1.01	0.94	0.41	0.41
Number of Piezometers	3	3	3	3	3	3
piezometer density (piezometer/ha)	0.26	0.25	0.34	0.31	0.14	0.14
Total porosity (%)	0.32	0.32	0.32	0.32	0.32	0.32
Depth to impermeable zone (m)	10.00	10.00	10.00	10.00	10.00	10.00
Depth of saturated zone (m)	7.00	7.00	7.00	7.00	7.00	7.00
Slope (%)	0.02	0.02	0.02	0.02	0.02	0.02
width (m)	50.00	50.00	55.00	55.00	30.00	30.00
Q (m^3 day^{-1}) (mean discharge)	0.11	0.27	0.36	0.65	0.48	0.18
v (m day^{-1}) (average linear velocity) (takes porosity into account)	0.02	0.03	0.07	0.12	0.16	0.05
v (m day^{-1}) (max)	0.02	0.06	0.07	0.13	0.18	0.07
k_s (m day^{-1}) (mean hydraulic conductivity)	0.02	0.08	0.07	0.12	0.19	0.07
T (m^2 day^{-1})	0.14	0.56	0.49	0.84	1.33	0.49
Mean hydraulic head (piezometer c)	67.13	68.65	70.13	69.92	69.53	69.30
Mean hydraulic head (piezometer a)	63.31	66.21	66.80	66.40	66.50	66.28
Hydraulic head (piezometer c) max	67.13	67.45	68.58	68.72	68.13	67.95
Hydraulic head (piezometer a) min	63.40	66.21	65.45	65.59	65.48	65.69
Mean distance (m) between source and piezometer (c)	250.00	250.00	250.00	250.00	250.00	250.00
Mean distance (m) between c and receptor (lower Tenches pit stream) (LTPS)	200.00	200.00	200.00	200.00	200.00	200.00
Plume distance (m) in 1 year (mean)	8.51	11.32	24.99	42.84	57.43	18.04
Plume distance (m) in 1 year (max)	8.71	22.27	26.59	48.18	65.67	24.11
Travel time (year) from proposed PRB to piezometer (a) (120 m)	14.10	10.61	4.80	2.80	2.09	6.65
Travel time (year) from c to receptor (LTPS) (200 m)	23.50	17.68	8.00	4.67	3.48	11.08

6.4.4 Source tracking

Source tracking was used to connect the source, pathway and receptor of the nutrient loss. The median NO_3-N: Cl ratio in drains intersecting groundwater flow between the source and the plots were 0.46 (max 0.84) and 0.38 (max 0.72). Mean watertable depths in piezometers 3c (Well 8) and 2c (Well 5) during the same period were 0.52 m and 2.06 m, respectively. Therefore, the watertable from the up-gradient area (Sandhill Figure 6.1) intersected the drain adjacent to 3c (Well 8) and the flow in the drain was towards 2c (Well 5). Therefore, contaminated groundwater passed into the plots and was then picked up in groundwater samples in the piezometers. To prevent contamination of surface water, the PRB should be located upslope from these drains and attenuate groundwater before any surface water groundwater interactions can take place (Figure 6.1). The NH_4-N concentrations in wells 1c (Well 3), 1b (Well 2), 2c (Well 5), 2b (this well was not operational for Method II)) and 2a (Well 4) suggest an active dirty water contamination source. Even after point source removal, nutrients are being washed from the soil to the perched watertable slowly over time. Interestingly, wells 3a (Well 6), 5a (Well 12) and 6a (Well 15) also have high NH_4-N concentrations. There is no obvious contamination source in these areas.

6.4.5 PRB dimensions

Using the denitrification rates in Table 6.4, Eqn. 6.8 was used to calculate the retention time needed to remediate the highest expected nitrate concentration (24.2 NO_3-N mg L^{-1}) to drinking water standards. The retention time was then multiplied by the groundwater flow velocity to give the barrier thickness.

TABLE 6.4 REACTIVE MEDIA DENITRIFICATION RATE AND PRB THICKNESS.

Reactive media	Denitrification rate* µg L g day^{-1}	Retention time Days	PRB thickness m	
			Mean	Max
Gleyic Cambisol	2.09 ± 0.01	223.04	16.61	19.91
Humic Gleysol	4.34 ± 0.10	107.41	8.00	8.00
Humic Gleysol + Woodchip	21.70	21.48	1.60	1.91

*adapted from Sullivan & McDermot (2007), calculations based on reduction of nitrate concentration from 24.2 mg NO_3^-N L^{-1}(highest concentration) to 11.3 mg L^{-1}(MAC)

For the case study presented, the dimensions, orientation and reactive media chosen for the PRB on this site are presented in Table 6.5. The exact location of the proposed PRB is presented in Figure 6.3.

Table 6.5 PRB orientation, reactive media type and dimensions.

PRB dimensions		
Horizontal (x)	Vertical (y)	Thickness (z)
m	m	m
250	2	1.6 to 1.9
Orientation	Parallel to groundwater contours	
Reactive media	Woodchip and gley soil mix (ratio 5:2)	

The k_s, measured *in situ* provides the retention times needed for denitrification to occur. This value should not be lower than the native soil to prevent ponding. This may be different on other sites where retention times or migration pathways may not make a PRB a viable option for remediation (unconsolidated material or bedrock). On this site, the soils are primarily Humic Gleysols (95%) and the proposed trench location was on this soil type. Denitrification rates found for this soil type would allow natural attenuation in Humic Gleysols within 7.35 years. Potential surface water receptors on site are approximately 200 m from the dirty water irrigator source. The travel time for nitrate already present in shallow groundwater within Plots 3, 4, 5 and 6 would be less than this. However, natural attenuation to the east of the site may be an option as travel times are much higher and the receptors are a greater distance away.

6.4.6 Blueprint for PRB installation

The choice of PRB type will depend on the scale of the project. In this investigation, a continuous trench was chosen over a funnel-and-gate system, as less geotechnical input was needed. Both options, however, would need professional guidance to locate a PRB. A site investigation of this scale may not be viable for individual farmers. Such an undertaking would fall upon a local council if surface water in an area was of “poor status” under the WFD. In such a case, a PRB would need to become a supplementary mitigation measure within the POM structure. As any supplementary measure is likely to be unpopular, another approach would be to include it as an option within buffer areas in an agric-environmental scheme. Such an area usually does not receive fertilization due to machinery constraints, and although not of economic importance, has an impact on biodiversity. In this way, such expertise could be provided by a council engineer or a REPS advisor after appropriate training. A full cost benefit analysis would be required under the WFD and a cost per kg of nitrate removed using a PRB would need to be known.

Construction of a PRB even where shallow groundwater nitrate pollution exists may not be a valid option in some cases. For example, in free draining fluvio-gravels, once the pollution source has been stopped (e.g. removal of point source due to farmyard infrastructure upgrades), contamination residence times may be short due to high permeability. Retention times for denitrification to occur in such cases may be unachievable. Calculation of the contaminant flux at source, or along a control plane away from the source, may be expensive due to drilling costs. Therefore, this methodology is best suited to small point sources or plumes which have already reached shallow watertable interfaces at surface groundwater interaction sites. Further research into less permanent, low-cost monitoring systems is needed.

The nitrate flux relies on Darcian principles and nitrate concentration. If a PRB is located in an area with low nitrate or low groundwater flow rates, the removal rates may be very low.

The following blueprint was used to establish a PRB on the Foal’s House site for point source remediation, but it is applicable to other agricultural sites:

1. All available data relating to the site should be gathered. This should include geological survey maps, ordnance survey maps and aerial photographs. If a digital elevation model of the area is not available, one should be constructed from a high resolution survey of the site.
2. A risk assessment of the site should be carried out and all sources and receptors identified.
3. The contaminant migration pathway should be identified.
4. A non-permanent piezometer or permanent well network should be installed along this migration pathway between the source and a potential receptor. This network needs to be surveyed. The depth of installation should be below

water strike and consider lowest watertable depths during summer months. Borehole logs should be kept and soil samples should be stored and physically characterised. The depth of the watertable is important. Ideally it should be no more than 2 m deep. In Ireland, such a depth is deemed shallow groundwater and is not part of the strict groundwater definition within the WFD. If the watertable is deeper (from 3 m to 5 m) the permeability of the PRB would need to be high and the diameter of the wall extended to create up-welling.

5. A control plane format (rows of wells forming parallel lines between the source and receptor) should be considered to enable contaminant mass flux calculations. Electronic divers should be installed in some of these wells to have high resolution watertable height data. Nutrient probes or composite samplers should also be considered to obtain high resolution nutrient data.
6. The area between the source and receptor should be soil sampled to specific depths. Field visual tools (e.g. VS-Fast system) for soil field assessment may be a useful tool for preliminary studies, which enables *in situ* estimates of soil consistency, soil structure and texture (McGarry & Sharp, 2001). Other systems based on British Standard 5930:1999 (BSI, 1999) are used in groundwater protection schemes to describe sub-soils (Geological Survey Ireland, 1999). Geophysical techniques such as ground penetrating radar and resistivity combined with electromagnetic surveys, can give depth and type of subsoil. This can be confirmed by drilling logs and auger profiles. This will give insight into likely low or high permeability zones.
7. Groundwater samples should be taken at regular intervals, using a low flow pump and flow-through cell. This is to investigate temporal changes in nutrient concentrations. Water samples should be analysed for a range of geochemical parameters. A preliminary dataset should be compiled. The spatial distribution of nutrients on site should also be noted. To avoid nitrate limitations and low removal rates, the level of nitrate contamination needs to be high and the source constant. If the source is removed, the removal rates will decline over time.
8. Physical tests of the piezometer or well network should be carried out, e.g. k_s determination. Calculated parameters can then be used to estimate groundwater travel times, contaminant mass fluxes (k_s and nutrient

concentration) and plume migration. The depth to aquifer can be assessed through drilling or borehole logs in the area. The k_s of the reactive media needs to be > 1 m day^{-1}.

9. Using steps 1 to 8 a conceptual model of the site, should be constructed. For particular dates groundwater flow maps can be constructed. Watertable data (vertical position of reactive barrier) should be compiled. All known water levels should be identified, i.e. perched shallow watertable, deeper groundwater watertable. Geophysics can be used to form a 3D image of the site. Electromagnetic survey composites from 5 m to 6 m depth and gives a good indication of subsoil type. Resistivity profiles offer greater depth penetration. Both of these techniques, together with piezometer or well profile descriptions, create a clearer picture of the subsurface but are expensive.
10. Vertical and horizontal hydraulic gradients should be calculated. In till, vertical hydraulic gradients may be fast due to cracking. Vertical and horizontal travel times should be calculated. For vertical travel times, tracer breakthrough to shallow ceramic cups or shallow piezometers can be useful. Using a soil moisture deficit model (precipitation, effective drainage, amount of recharge days) and effective porosity, depth of infiltration of recharge may be estimated. Where the watertable height is known, an estimation of vertical travel time may be achievable. Horizontal travel time may be calculated using effective Darcian velocity or tracer experiments. This helps define when first breakthrough times at a receptor a certain distance away will occur. It does not estimate how long this flushing of nutrient to below a water quality standard will take.
11. The PRB trench thickness should be designed for specific water quality targets. Batch or column experiments should be carried out to calculate the reaction rate and equilibrium constant of the contaminant with the reactive media. Thicker rather than deeper PRBs are best with high k_s.
12. Identify travel times to potential receptors and locate the PRB up-gradient of the receptor. Compare PRB installation with monitored natural attenuation.
13. Before construction, the site should be evaluated to ensure design depth and width may be achieved. Trial holes should be considered. The ability of emplacing the reactive material without aquifer obstruction should be assessed to avoid clogging of media and smearing soil walls, thus decreasing

permeability. During and after installation, a monitoring network should be installed to investigate if denitrification is occurring in the trench and to investigate groundwater flow alteration due to the barrier construction.

14. The ease of excavating the reactive media for replacement purposes after a period of time should be considered.
15. Monitored natural attenuation or risk assessment on site should also be considered for areas further away from the source. A number of wells should be drilled in such locations. Pump-and-treat and pump-and-reuse would need considerable investment, drilling and discharge licences and would need surface structures and maintenance which could interrupt farming practices. Recycling of water on farms is more likely to stem from soiled water remediation or rainwater harvesting and reuse. Pump-and-waste would also need a disposal licence and would merely export the problem elsewhere. The funnel-and-gate option is cost-prohibitive and would need geotechnical and engineering input in the design phases. However, a more feasible option for gate construction, such as compressed clay or another low-permeability material, should be investigated. A PRB installed south of the investigative plots would not capture all contaminated groundwater and could not achieve surface water quality targets. The current configuration would intercept contaminated groundwater before entering the six plots and before hydraulic gradients at location 4c (Well 11) divide the plume. Explaining the spatial distribution of nitrate on site would identify areas where natural attenuation exists through denitrification. Such areas would not be suitable for PRB location.

6.5 Results & Discussion: PRB location method II

The same study site was differentiated into dilution and denitrification zones.

6.5.1 Site characterisation

In 2006, as in previous years, after the point source was removed, the Sandhill (Figure 6.1) area, the North West area, and the isolated plots received the same N application (Table 6.6). Prior to the removal of the dirty water soiled water application rates above the 50 mm yr^{-1} were applied. These areas were cut for first cut silage at the end of May and for second cut silage in July, but they were not grazed by cattle for the duration of this study. Half of the fertiliser N was applied as urea in late-February and April, and the remaining N was applied in June and August as calcium ammonium nitrate (CAN). Loss of N to the environment from urea would tend to be atmospheric NH_3 losses, as urea tends to be immobile and is retained in the soil by cation exchange capacity (CEC) (Gary Lannigan, *pers comm.*). N applied as CAN is already partially nitrified, and is susceptible to leaching and denitrification.

At a crop uptake rate of 2 kg N $ha^{-1}day^{-1}$ from March to May, a surplus of approximately 75 kg N ha^{-1} remained after first cut silage. The grass needed approximately 80 kg N ha^{-1} before second cut silage at the end of July. Therefore, no N leaching losses would be expected from this surplus. In August 2006, the six isolated plots received a higher application of CAN (83.7 kg N ha^{-1}) for the third cut silage in early October. The grass requirement for third cut silage matched the fertilizer application rate (approximately 90 kg N ha^{-1}).

TABLE 6.6 NUTRIENT MANAGEMENT OF THE SANDHILL, NORTH WEST AND FIELD SITE FOR 2006 AND 2007.

Year	Location	Area	Month	N fertiliser application rate	N fertiliser type
2006		ha		kg N ha^{-1}	
	Sandhill (Figure 6.1)	3.2	Feb	28.5	Urea*
			April	124.1	Urea
			June	102.1	CAN**
			Aug	51.1	CAN
	North West	2.8	Feb	28.5	Urea
			April	124.1	Urea
			June	102.1	CAN
			Aug	51.1	CAN
	Plots	4.2	Feb	28.5	Urea
			April	124.1	Urea
			June	102.1	CAN
			Aug	83.7	CAN
2007					
	Sandhill	3.2	March	56.9	Urea
			April	71.2	Urea
			June	102.1	CAN
			Aug	51.1	CAN
	North West	2.8	March	56.9	Urea
			April	124.1	Urea
			June	102.1	CAN
			Aug	51.1	CAN
	Plots	4.2	March	28.5	Urea
			April	124.1	Urea
			June	102.1	CAN
			Aug	83.7	CAN

*Urea is 46% N

** Calcium Ammonium Nitrate (CAN) is 27% N

In June 2007, in addition to fertilizer application (Table 6.6), the Sandhill (Figure 6.2) and North West area received 118 kg N ha^{-1} as cattle slurry. The Sandhill area was N-deficient by approximately 24 kg N ha^{-1} for first cut silage in May. With the addition of CAN and slurry in June, there was an N-surplus of approximately 70 kg N ha^{-1} after second cut silage. In July and August 2007, there was a large increase in effective drainage. With the time lag between second cut silage and the final application of CAN in the middle of August, there was just enough N available for grass recovery. The same was true for the North West site, but there was a surplus after first-cut silage in May.

6.5.2 Water balance

A water balance for the site showed total precipitation of 992.6 mm and 889.1 mm for 2006 and 2007, respectively. For the two years, the Hybrid model calculated 483 mm and 335 mm drainage through the root zone in a process known as effective drainage. It was assumed that all of this direct recharge reached the watertable, as the rainfall intensity is generally lower than the soil infiltration capacity. Model output showed effective drainage occurred on 87 and 74 days, giving an average recharge rate of 5.5 and 4.5 mm day^{-1}, respectively. Cumulative drainage for both years is presented in Figure 6.3. The mean soil total porosity was 32.2±4.9%. The average pore velocity was estimated to be 17.3 and 14.1 mm day^{-1}, giving an approximate mean travel depth of 1.5 and 1.04 m in a moderately-drained soil for 2006 and 2007. The mean watertable depth for 2006 to 2008 on site was 2.2 m bgl. This is the unsaturated zone vertical travel time (approximately 2 years) achievable due to effective drainage, representative of drainage during the winter period. Lateral migration of the nutrients is with groundwater flow direction under the experimental plots.

Cumulative effective drainage shows differential recharge each year and seasonal differences in recharge led to differential nitrate dilutions over time. Both years had wet winters, but 2006 had a dry summer period (Figure 6.3). Slurry was only spread in times of dry weather. This contributed to higher mean site nitrate concentrations for sampling events in early 2006. The dry summer of 2006 halted significant recharge and nitrate concentrations reached steady-state. As effective drainage increases, overall mean nitrate concentration on site increases. Each piezometer followed the same pattern for mean nitrate concentration, with some piezometers falling below the 11.3 mg NO_3-N L^{-1} threshold for drinking water quality within 1 year. There was no increase in the shallow groundwater nitrate concentration after the slurry application in June 2007, due to a combination of slow groundwater transport (k_s ranges from

0.001 to 0.016 m day^{-1} with subsequent travel distance of 2.9 and 4.5 m yr^{-1}) (Table 6.3) and gaseous losses of NH_3.

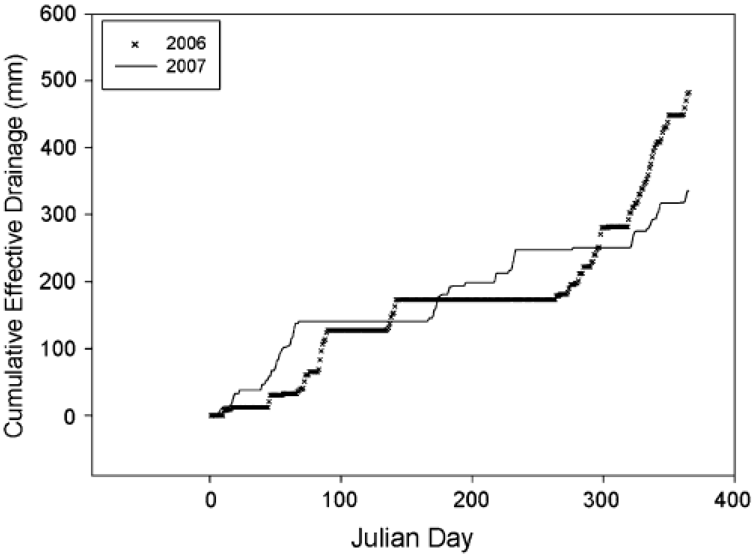


FIGURE 6.3 CALCULATED CUMULATIVE EFFECTIVE DRAINAGE (MM) FROM 2006 TO 2007.

6.5.3 Buffer zone and contaminant mass flux

Buffer zone diameter for Plots 1 to 6, using Eqn. 6.9, was 193, 178, 195, 195, 148 and 120 m, respectively. A mean area of 2.4 ha for the ZOC was calculated. The buffer zones can extend beyond the isolated study site to the groundwater divide in the Sandhill area. Therefore, land management and recharge in the entire ZOC area can contribute to shallow groundwater nitrate contamination within the study site. The historical stationary dirty water point source pollution occurred within this ZOC. The contaminant mass fluxes calculated for three control planes are presented in Table 6.7. Influent contaminant mass flux through the upper control plane cells ranged from 0.0008 to 0.0016 g N m^{3} day^{-1} and the contaminant mass fluxes leaving the site at the compliance plane ranged from 0.00001 to 0.0007 g N m^{3} day^{-1}. The total contaminant mass flux on a plot basis was as follows: Plot 3>1>5>4>6. Total contaminant mass flux decreased from the top plane to the central plane to the compliance plane, demonstrating natural attenuation. Using Eqn. 6.12, a 42 % contaminant mass flux reduction efficiency was calculated from the influent control plane to the central plane. From the central plane to the compliance plane, a 64 % reduction occurred. Plot 3 contributed the greatest contaminant mass flux. The load transfer from the influent control plane to the central control plane showed a reduction of 33.6 %, with a subsequent reduction of 69.5 % at the compliance control plane. Plot 4 showed a 96 % reduction in contaminant mass flux from the influent control plane and the central control plane. Plot 1 doubled its contaminant mass flux from the influent control plane to the central control plane, but then decreased by 51.2 % down-gradient at the compliance control plane. The upper, middle and lower control planes are 18%, 44% and 76% below the compliance control plane threshold (11.3 mg L^{-1} with present flux), respectively (Table 6.7).

TABLE 6.7 CONTAMINANT MASS FLUX CALCULATION FOR SIX ISOLATED PLOTS

Parameters	Plot Number					
	1	2	3	4	5	6
Area (ha)	0.78	0.75	1.01	0.94	0.41	0.41
Width of plot (m)	50	50	55	55	30	30
Mean effective velocity, v (m day^{-1})	0.011	0.006	0.012	0.013	0.012	0.008
Hydraulic conductivity, k_s (m day^{-1})	0.009	0.0083	0.0117	0.0117	0.0123	0.008
Transmissivity, T (m^2 day^{-1})	0.07	0.07	0.09	0.09	0.1	0.06
Mean hydraulic head (Top) (m AOD)	67.13	68.65	70.13	69.92	69.53	69.3
Mean hydraulic head (Bottom) (m AOD)	63.31	66.21	66.8	66.4	66.5	66.28
Mean Travel Distance in 1 year	3.92	2.31	4.44	4.70	4.25	2.76
Q	m^3 day^{-1}					
Top Control Plane Nodes	0.15	0.15	0.15	0.15	0.12	0.09
Middle Control Plane Nodes	0.15	-	0.15	0.20	0.11	0.07
Bottom Control Plane Nodes	0.11	0.01	0.22	0.19	0.04	0.01
Contaminant Mass Flux	g m^3 day^{-1}					
Top Control Plane Nodes	0.0009	0.0017	0.0016	0.0009	0.0015	0.0008
Middle Control Plane Nodes	0.0018	-	0.0011	0.0001	0.0010	0.0004
Bottom Control Plane Nodes	0.00074	0.00001	0.0003	0.0000	0.0004	0.0001

6.5.4 Tobit regression

Selected piezometer parameters are presented in Table 6.8. In each step of the procedure, a series of regressions are fitted (Table 6.9). Each model includes random effects to account for the spatial dependence of model residuals. Type III F-tests for the fixed effects are presented for each model accompanied by Akaike's Information Criterion (AIC). The AIC is a model selection tool that compares the Log Likelihood of models while penalising for the number of parameters in the model. The model with the lowest AIC is the best fitting model. When assessed individually, k_s (p=0.0004) had significant impacts on nitrate concentrations. However, k_s (p=<0.001) and distance from point source (p=0.0014) are significant when k_s is already in the model. The stepwise procedure selected k_s and distance from point source as having more explanatory power than when other parameters are inputted into the model. The final model contains only k_s and distance from point source. The final model is presented in Figure 6.4.

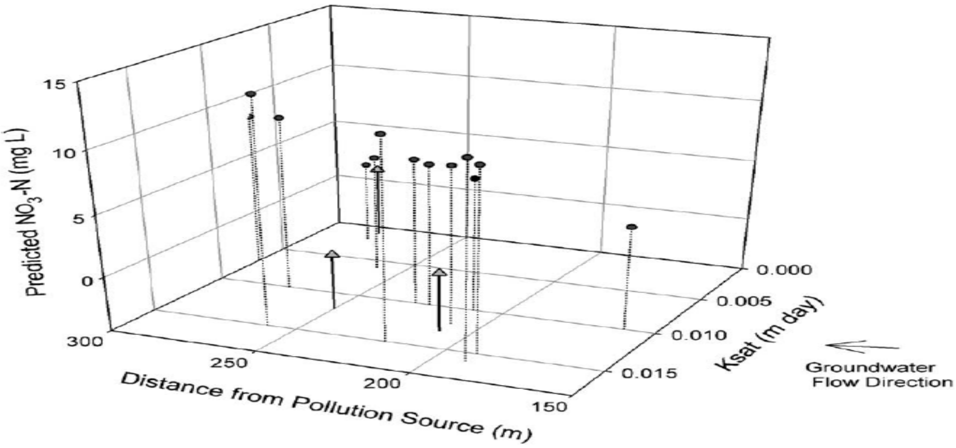


FIGURE 6.4 PREDICTIONS OF MEAN NITRATE FROM FITTED MODEL

Estimated model coefficients for the final model from the Tobit regression are presented in Table 6.10. The model describes the relationship between mean groundwater nitrate concentration and the explanatory variables k_s and distance from pollution source. The percentage variation explained by different factors is presented in Table 6.11. Dilution due to recharge occurred for all piezometers within the contamination plume on site (NO_3-N/Cl^- ratio), but at the same rate for each piezometer. Therefore, dilution did not account for differences in nitrate concentration within the contamination plume. Therefore, diffuse pollution due to fertiliser application within the field site may be discounted. A two-layered conceptual model represents a shallow zone of higher $k_s \geq 0.01$ m day^{-1} with higher nitrate concentrations and a deeper low k_s zone < 0.01 m day^{-1} with lower nitrate concentrations. In the shallow layer, k_s values ranged from 0.01 to 0.016 m day^{-1}, but were not consistent with depth, indicating heterogeneity.

TABLE 6.8 SELECTED PIEZOMETER PARAMETERS FROM 2005 TO 2008.

Piez	Plot	Position	Elevation	TD*	Mean NO_3-N	Stdev±	Mean NO_2-N	Stdev±	Mean Cl^-	Stdev±	Mean NH_4-N	Stdev±	Mean NO_3-N/Cl^- ratio	Stdev±	k_s	WT**
			m AOD	M bgl	mg L^{-1}		mg L^{-1}		mg L^{-1}		mg L^{-1}				m day^{-1}	m AOD
1	1	Bottom	67.80	3.60	6.90	2.70	0.04	0.10	27.10	6.10	0.24	0.30	0.08	0.25	0.007	63.70
2	1	Middle	70.20	4.10	11.60	4.90	0.05	0.20	24.90	7.40	0.25	0.60	0.09	0.48	0.01	66.90
3	1	Top	72.10	4.30	5.60	3.50	0.07	0.10	18.40	4.80	0.34	0.30	0.25	0.30	0.01	67.90
4	2	Bottom	67.60	3.10	1.40	3.50	0.07	0.00	28.80	8.10	1.67	1.10	0.18	0.10	0.001	66.30
5	2	Top	72.00	4.30	11.80	5.70	0.02	0.00	19.00	5.20	0.21	0.50	0.27	0.62	0.015	68.80
6	3	Bottom	68.20	3.50	12.80	3.40	0.09	0.20	32.50	5.50	0.26	0.40	0.09	0.41	0.015	66.60
7	3	Middle	70.00	2.60	7.30	2.60	0.01	0.00	19.00	10.40	0.06	0.10	0.08	0.43	0.01	68.50
8	3	Top	71.70	3.20	11.00	3.40	0.03	0.10	59.00	9.50	0.22	0.40	0.04	0.53	0.01	69.60
9	4	Bottom	67.70	2.70	0.10	1.30	0.01	0.00	9.90	10.60	0.16	0.10	0.06	0.02	0.012	65.10
10	4	Middle	69.50	2.90	0.30	1.50	0.00	0.00	41.40	6.30	0.10	0.10	0.06	0.01	0.013	67.90
11	4	Top	71.80	2.40	5.70	2.70	0.00	0.00	21.90	7.80	0.06	0.20	0.08	0.24	0.01	70.30
12	5	Bottom	67.70	1.50	8.70	2.30	0.01	0.00	32.50	7.20	0.08	0.10	0.07	0.27	0.006	65.60
13	5	Middle	69.40	2.80	9.40	2.70	0.00	0.00	29.10	4.90	0.07	0.10	0.09	0.32	0.015	68.20
14	5	Top	72.00	4.30	12.80	4.10	0.02	0.10	30.20	2.90	0.24	0.40	0.15	0.47	0.016	71.00
15	6	Bottom	67.40	2.90	3.60	2.70	0.02	0.00	33.90	4.10	0.23	0.40	0.08	0.10	0.002	64.00
16	6	Middle	68.40	3.10	5.00	1.70	0.04	0.10	24.50	6.40	0.14	0.20	0.11	0.19	0.01	67.10
17	6	Top	71.10	3.00	9.30	2.00	0.04	0.10	23.20	12.20	0.12	0.50	0.13	0.41	0.012	70.20

*TD total depth of well, **WT mean watertable depth during experiment

TABLE 6.9 STEPWISE PROCEDURE USED TO SELECT THE EXPLANATORY VARIABLES OF IMPORTANCE IN THE RELATIONSHIP BETWEEN MEAN GROUNDWATER NITRATE CONCENTRATION AND HYDROGEOLOGICAL FACTORS. MODEL CONTAINING K_S AND DISTANCE FROM POINT SOURCE IS CHOSEN AS THE FINAL MODEL.

Step 1	Include all variables individually in model	
Effect	F(1,11)	P-value
k_s (m day^{-1})	24.55	0.0004
Elevation (m AOD)	10.23	0.0085
Distance from point source (m)	0.60	0.4562
Screen depth (m AOD)	1.28	0.2826
Result of step 1	k_s chosen as most important	

Step 2	Add other variables to model containing k_s	
Effect	F(1,10)	P-value
k_s (m day^{-1})	13.05	0.0048
Elevation (m AOD)	1.75	0.2156
k_s (m day^{-1})	78.85	<0.0001
Distance from point source (m)	19.10	0.0014
k_s (m day^{-1})	33.75	0.0002
Screen depth (m AOD)	1.47	0.2526
Result of Step 2	Distance is significant when k_s is already in the model	

Step 3	Add other variables to model containing k_s and distance from point source (m)	
Effect	F(1,9)	P-value
k_s (m day^{-1})	53.50	<0.0001
Distance from point source (m)	9.68	0.0125
Elevation (m AOD)	0.08	0.7884
k_s (m day^{-1})	73.45	<0.0001
Distance from point source (m)	15.79	0.0032
Screen depth (m AOD)	1.69	0.2253
Result of step 3	Other variables not significant in a model that contains k_s and distance from point source	

6.5.5 Dilution and denitrification differentiation

In some locations, the Cl^- concentration is representative of natural background levels (NBL). In Ireland, groundwater has a median NBL of 18 mg L^{-1}. Some points were therefore not included in the regression process. Plots 1, 2, 4, 5 and 6 have the highest ratio in the top of the plots nearest the source, but standard deviation shows some change over time (Table 6.10).

TABLE 6.10 ESTIMATED MODEL COEFFICIENTS FOR FINAL NITRATE MODEL BUT ALSO FOR CHLORIDE FROM THE REGRESSION.

Effect	Coefficient	Standard Error	DF*	t-value	P-value
NO_3-N					
Intercept	-13.7328	3.6584	0	-3.75	
k_s	960.98	108.22	10	8.88	<0.001
Distance	0.0506	0.01158	10	4.37	0.0014
Cl^-					
Intercept	212.34	62.22	0	3.41	
k_s	548.59	390.49	12	1.40	0.1854
Elevation	-2.73	0.9294	12	-2.94	0.0123

*degrees of freedom

The model was run a second time to explain Cl^- occurrence using the same parameters as before. Here, k_s and ground elevation have the greatest explanatory power, but k_s is not significant. As shown previously, nitrate occurrence in the same piezometers was explained by k_s and distance from the dirty water point pollution source pollution, while both being significant. Due to the fact that k_s influences nitrate occurrence, but not Cl^- occurrence, denitrification can be inferred. Distances from the dirty water source and ground elevation are linked because of the nature of the sloped site and, therefore, dilution is a factor for Cl^- occurrence. In general, on site:

- Low nitrate concentration and unaffected chloride concentration points to denitrification (Figure 6.5 a)

- Low nitrate concentration and low chloride concentration points to dilution (Figure 6.5 b)
- Overlying Figure 6.5 a and 6.5 b allows areas of denitrification and dilution to be inferred (Figure 6.5 c)

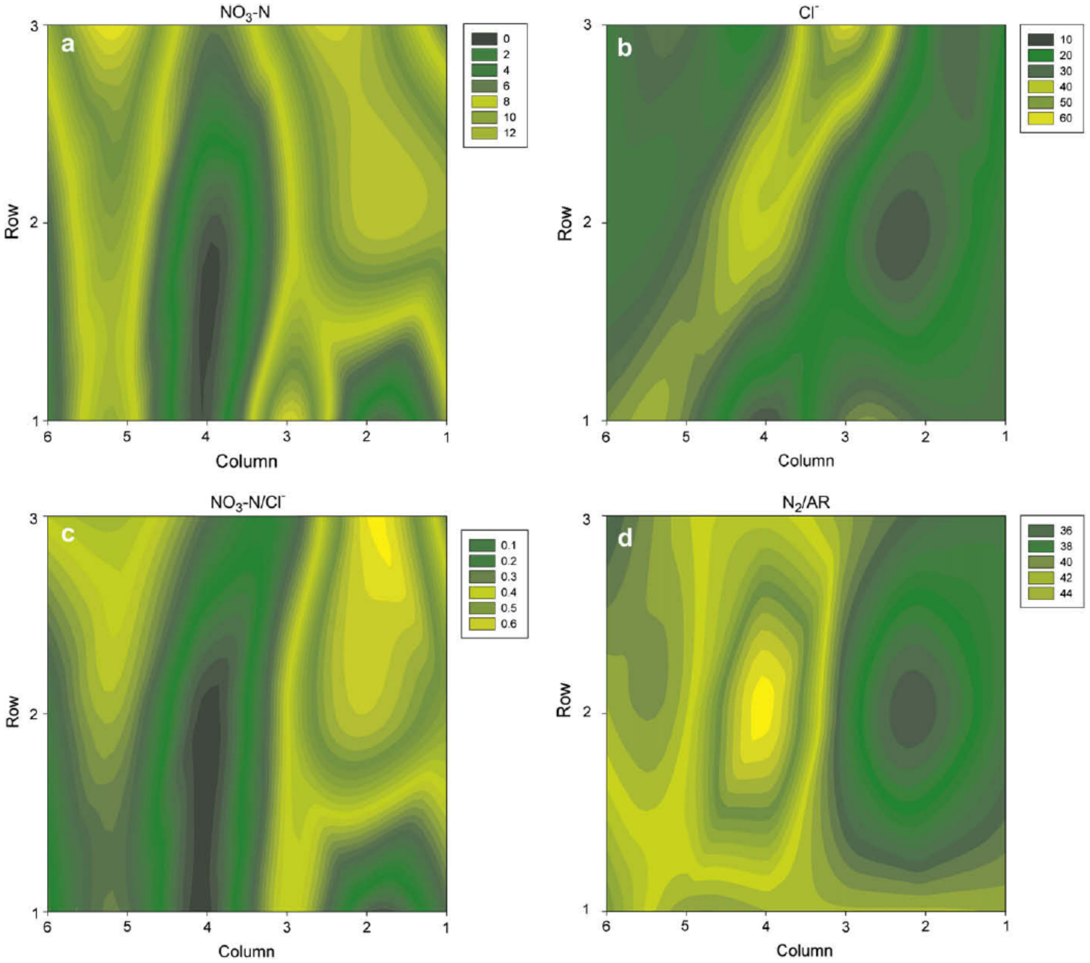


Figure 6.5 Spatial distribution across six plots (x-axis) of groundwater a) Mean NO_3-N concentration b) Mean Cl^- concentration c) Mean NO_3-N/Cl^- ratio and d) N_2/Ar ratio on a random date.

The NO_3^- /Cl^- ratio identifies two zones where the present plume position is evident. This ratio is low in Plot 4 and in the southern part of the site where the plume has not reached. This infers denitrification in the central part of the site (Plot 4) and dilution in other areas.

TABLE 6.11 PERCENTAGE VARIATION EXPLAINED BY DIFFERENT FACTORS

	DF*	SS	% variation
Fixed			
k_s (m day^{-1})	1	63.72	55.50
Distance from point source (m)	1	15.52	13.30
Screen depth (m AOD)	1	5.48	4.80
Elevation (m AOD)	1	0.62	0.50
Random			
Row	1	7.95	6.90
Column	1	4.26	3.70
Residual	5	17.58	15.30
	Total	114.90	

*degrees of freedom

To further elucidate the effect of groundwater denitrification on nitrate occurrence on the site, dissolved gases and physiochemical properties of groundwater collected on a random date were determined and related to the mean groundwater nitrate concentration during the study. Average groundwater nitrate was significantly (P<0.05) related to groundwater N_2/Ar ratio, redox potential (Eh), dissolved O_2 and N_2 and was close to being significant with dissolved N_2O concentration (P=0.08) (Table 6.10). Based on the AIC score, N_2/Ar ratio and redox potential (Eh) were the best fitting models of groundwater nitrate occurrence. The higher ratio of N_2/Ar directly indicates that denitrification is occurring on the site (Figure 6.5 d) and that lower redox potentials and DO are related to lower groundwater nitrate occurrence (Table 6.12).

Documented nutrient management of the study site could not solely account for nitrate distribution, while contributing to the elevated nitrate concentration in shallow groundwater. Surplus nutrients calculated for 2007 in the Sandhill area had not yet reached the shallow groundwater under the plots due to slow travel times. Historic dirty water irrigation occurred on the Sandhill site for decades prior to this study with excessive hydraulic loads leading to elevated infiltration on the Sandhill.

TABLE 6.12 RELATIONSHIPS BETWEEN DISSOLVED GROUNDWATER GASES, REDOX POTENTIAL (EH) AND AVERAGE NITRATE. EACH PARAMETER IS REGRESSED IN TURN AGAINST AVERAGE NITRATE. THE SPATIAL STRUCTURE ON THE VARIANCE COVARIANCE MATRIX IS AS DESCRIBED FOR THE STEPWISE REGRESSION.

Parameter	Estimate	Standard Error	T value $_{13\ DF}$	P>t	AIC
N_2/Ar ratio	-1.33	0.544	-2.45	0.029	81
Redox potential (Eh)	0.040	0.013	3.17	0.0073	86.4
N_2O	0.2247	0.1182	1.9	0.0798	87
RDO	0.0012	0.0003	3.58	0.0034	91.4
O_2	0.0011	0.0004	2.48	0.0275	95
N_2	-0.0012	0.001	-2.17	0.0493	95.5

Vertical unsaturated zone travel time was not within a single drainage season. Saturated shallow groundwater and contamination plume migration time was from 2.92 to 4.50 m yr^{-1} underneath the plots. The travel time from the Sandhill (source) to the plots approximately 200 m away was much quicker due to the sand.

Dilution of the groundwater nitrate concentrations by recharge to the shallow watertable occurred in both study years. A two-layered conceptual model of the site emerged, where higher nitrate concentrations existed in the shallower, high k_s subsurface.

The model describes the relationship between mean groundwater nitrate concentration and the explanatory variables k_s and distance of the piezometers from the point pollution source. To account for bias due to the distance of each piezometer within the grid pattern from the pollution source, the spatial dependence of residuals was modelled using an anisotropic power covariance structure. Higher k_s zones in the subsurface allow faster migration of contaminated groundwater, resulting in shorter retention time. The shorter retention time in the high k_s zone decreases the opportunity for denitrification to occur. Lateral flow in higher k_s layers may result in surface water pollution. The opposite is true of lower k_s zones, where a longer retention time is available for denitrification to occur. This is why low nitrate concentrations may be present at the plume centroid. In elevated areas, the watertable mirrors topography and has a greater hydraulic gradient and higher k_s values.

Groundwater nitrate occurrence was statistically related to topsoil denitrifying enzyme activity, topsoil inorganic N content and depth to water table, and a stronger relationship was observed with vadose zone permeability (McLay et al., 2001). The effect of vadose zone permeability on groundwater nitrate distribution was recognised by Vellidis et al. (1996), who observed low N leaching associated with low subsoil permeability and Hansen et al. (1996) observed high N leaching with high subsoil permeability. Richards et al. (2005) observed lower groundwater nitrate occurrence in deeper wells with clay soils with no cropland nearby, but they could not separate the effect of k_s from landuse or well depth. In Ireland, Ryan et al. (1996) also highlighted the importance of soil type and permeability with lower nitrate losses from soil with the percentage fines (silt and clay) >75%, and estimated mean subsoil travel times of 0.01 m day^{-1} on a site with elevated groundwater nitrate concentrations. The unsaturated vadose zone transport of nitrate is clearly influenced by its permeability. Thus, longer residence time in lower permeability subsoil, favours nitrate reduction through denitrification. The strong relationship observed in this work also clearly identifies the importance of the saturated subsoil zone in favouring nitrate reduction by denitrification in low subsoil permeable zones. Also of importance is the exact location of the point pollution source. The strong correlations between mean groundwater nitrate and denitrification end products (N_2O and N_2) and physiochemical properties favouring denitrification (dissolved O_2 and Eh) further supports that denitrification is the dominant process controlling groundwater nitrate occurrence and transport on the study site. The relationship between subsoil/aquifer k_s and denitrification requires further investigation.

In Ireland, groundwater protection is based on the mapping of vulnerability zones for the protection of groundwater source (wells and springs) and the groundwater resource. Irish aquifers are deemed to have low attenuation potential due to their fractured and karstified nature and thus they are mainly protected by the overlying glacial tills. Vulnerability zones are ranked in four classes from extreme to low vulnerability, based primarily on the thickness and lithology/permeability of the Quaternary subsoil deposits (Daly et al., 1988). Vulnerability decreases with increasing thickness and decreasing permeability of subsoil. The definition of groundwater in Ireland often excludes the shallow groundwater in subsoils (with the exception of sand and gravel aquifers), as it is not valued as a potential source of water for human consumption. Although not sufficient for consumption, shallow subsoil groundwater is environmentally important, as it contributes to through-flow and drain-flow to surface waters bypassing any potential for abatement when transported through deeper aquifers.

In Ireland, groundwater protection for subsoil permeability is not routinely measured in Irish subsoils. Fitzsimons & Misstear (2006) classified Irish till permeability as being highly permeable when $k_s = 10$ m day^{-1}, moderately permeable when k_s ranges from 0.004 to 0.009 m day^{-1} and low permeability (clay content >13%) when k_s ranges from 0.0004 to 0.0009 m day^{-1}. Mean plot k_s values on site range from 0.008 to 0.01 m day^{-1}. This suggests further classification may be needed for moderate to highly permeable classes.

Contaminant mass flux calculations show that the load of nitrate passing through parallel control planes perpendicular to groundwater flow was uneven across the site. A 96% reduction in contaminant mass flux occurred across the control planes in Plot 3. This leads to groundwater nitrate loads of acceptable quality leaving the site. Therefore, there is no need for a PRB on this site. Natural attenuation occurred down-gradient in all plots, except Plot 1.

In this study, subsoil permeability and distance from point source pollution have been clearly identified as significant factors in determining the occurrence of nitrate in groundwater. The subsoil on the study classified as moderate permeability. This study highlights the need to further subdivide this category for risk assessment of nitrate occurrence in groundwater and transport to surface waters via through-flow or artificial drainage. Furthermore, as subsoil k_s is incorporated in the contaminant mass flux calculation, particular hot spot locations may be identified, which contribute significantly more contaminant flux per unit area to potential down-gradient receptors. The identification of hot spots of groundwater contaminants may be used to target areas for locating an environmental remediation technology to reduce contaminant fluxes to sensitive receptors.

6.6 Results & Discussion: Woodchip slug

A methodology to investigate denitrification potential in enhanced and natural denitrification areas was determined.

6.6.1 Isotopes

The k_s on site for each well is presented in Table 6.13. Combining such results with isotopic data from Table 6.1 allowed the wells to be paired, e.g. Wells 1 (WC) and 9 (NWC). Both wells had the same ‘no denitrification’ signal and both have a low k_s of 0.06 m day^{-1}. Similarly, Wells 15 (WC) and 11 (NWC) had a ‘no denitrification’ signal, but had a high k_s of 0.13 m day^{-1}. Wells 2, 12 and 14 were identified by isotope analysis as ‘denitrification’ wells and had a very low k_s allowing enough time for denitrification to occur. The watertable during the experiment was consistently above the screened interval depth, ensuring the woodchip was saturated throughout the experiment (Table 6.13). During most of the experimental period, there was no rainfall (336 mm rainfall, 216 mm effective rainfall), limiting recharge to the watertable. Using the k_s of each well and a uniform hydraulic gradient of 1% and effective porosity of 5%, Darcian velocity ranged from 0.001 to 0.02 m day^{-1}. This is the equivalent of 0.05 to 0.78 years required to travel 5 m down-gradient of the well network. The experiment lasted for 0.24 years and water movement in each well was very slow during this period.

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Table 6.13 Nitrate, chloride and N_2/Ar min, max and mean for each well during the study period .

Well	k_s	Treatment[d]	WT[b]	Screen[c]	NO_3-N	NO_3-N	NO_3-N	Cl^{-a}	Cl^-	Cl^-	N_2/Ar	N_2/Ar	N_2/Ar	DOC	TOC
			Mean		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Mean	Mean
	m day^{-1}		m bgl	m bgl	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	ratio	ratio	ratio	mg L^{-1}	mg L^{-1}
‘No denitrification’ Wells															
1	0.06	WC	2.6	3.4	4.2	11.0	7.1	37.6	45.3	40.2	36.4	43.0	38.8	2.9	30.9
9	0.06	NWC	2.9	5.9	5.4	8.1	6.9	20.0	28.6	23.8	35.7	39.5	37.8	1.2	7.1
15	0.13	WC	2.5	4.9	5.7	8.3	7.1	11.8	18.5	15.8	38.5	40.4	39.3	7.0.	57.1
11	0.13	NWC	1.3	3.0	4.8	8.2	5.9	14.1	19.6	16.3	36.5	39.4	38.0	1.4	6.2
10	0.10	NWC	4.6	7.8	4.1	6.7	5.5	18.7	30.8	21.6	36.8	39.2	38.0	3.2	12.8
‘Denitrification’ Wells															
2	0.03	NWC	7.4	8.1	0.3	1.5	0.8	20.8	24.5	22.3	39.0	42.4	40.4	1.7	5.8
12	0.03	NWC	0.9	2.5	0.2	2.7	1.8	10.3	22.6	16.8	37.5	41.3	39.3	1.4	6.6
14	0.001	NWC	4.0	4.5	0.003	1.0	0.4	21.9	26.5	24.2	41.4	46.5	43.8	1.9	4.7

[a] In Ireland natural background levels of Cl^- in groundwater are 18 mg L^{-1}. Concentrations above this are due to influences from the pollution sources on the farm

[b] Mean Watertable Height

[c] Top of screen, total Well depth + 1m

[d] WC – with woodchip, NWC – no woodchip

6.6.2 Water samples

As expected from the isotopic results, Wells 2, 12 and 14 had low mean Cl^- and NO_3^- concentrations, indicating the occurrence of denitrification (Table 6.13). The isotopic signal of “no denitrification” was changed in Well 1 by woodchip addition. This was associated with high mean Cl^- concentration and a pronounced decrease in nitrate concentration during the experiment, indicating denitrification. Cl^- release from the woodchip was also expected, showing interaction with the contaminated water and the well. Despite the isotopic signal of “no denitrification” in Wells 9, 10, 11 and 15, low mean Cl^- concentration with pronounced decreases in nitrate concentration was observed. This indicated possible dilution in Wells 9, 10, 11 and 15 (Table 6.13). From isotope data from April to August, Wells 1, 2, 12 and 14 isotope composition values are higher in August than in April. For Wells 9, 10 and 11, this decreases and there was no change in Well 15. Therefore, some dilution occurs in Wells 9, 10 and 11. Recharge (105 mm rainfall and 80.4 mm effective rainfall) occurred from Day 5 to 24. N_2/Ar ratios, and NO_3-N and Cl^- concentrations throughout the experiment for all wells are presented in Figure 6.6. Looking at isotopic compositions from Table 6.1, values tend to be higher in the N_2/Ar results for Well 15, with high k_s showing some denitrification activity after solid C addition.

N_2/Ar ratios showed a cut-off point for denitrification of approximately 39. For Wells 2, 12 and 14, the N_2/Ar ratios were consistently near or above 39, indicating the occurrence of denitrification. Between Well 1 (WC) and 9 (NWC), Well 1 consistently demonstrated higher denitrification potential. Again, between Wells 15 (WC) and 11 (NWC), Well 15 consistently demonstrated higher denitrification potential. Both groups have different k_s, but k_s is the same within each group. Among the wells with low k_s Well 1 (WC) showed greatest denitrification potential.

The extent of denitrification in a water sample is the excess N_2, accounting for the solubility and excess air. Conforming to results derived from isotopic signatures, the average NO_3-N, represented as excess N_2, was found to be higher in Wells 2, 12 and 14, compared to the other wells. This demonstrates low levels of denitrification (Table 6.13). Solid C emplacement in Wells 1 and 15 resulted in a small increase in denitrification potential. Denitrification progress reduces the amount of nitrate, but calculated RP mostly produced similar results for the full extent of nitrate elimination

(Table 6.13). In ‘no denitrification wells’, the RP varied from 0 to 0.06 and was highest in the wells containing WC. It increased the most in ‘denitrification wells’, which enhanced reduction of nitrate from 18 (Well 12) to 91% (Well 14).

In Figure 6.7 a, the ‘no denitrification’ wells reached steady-state early in the experiment, with no changes after approximately 10 days. Well 1, however, continued to increase throughout the experiment. For the ‘denitrification’ wells in Figure 6.7 b, Well 14 showed a constant reduction of nitrate throughout the experiment, with Wells 2 and 12 showing reduction at lower rates. Well 10 showed high nitrate reduction and this well is an intermediary between ‘denitrification’ and ‘no denitrification’ wells.

DO in ‘denitrification wells’ is generally below 5 mg L^{-1}, with Well 1 also falling within the low DO group. As a result of low DO, Fe and Mn in these wells can dissolve more readily. Fe and Mn concentration is highest in these wells (> 0.01 mg L^{-1}). In the ‘no denitrification’ wells, DO ranges vary considerably, and Fe and Mn are generally at this 0.01 mg L^{-1} concentration (Table 6.14). The pH for the wells in this study ranged from 5.5 to 7.5. Conductivity and temperature ranged from 200 to 500 µS cm^{-1} and from 10ºC to 15ºC, respectively. Mean concentration of DOC in all wells - except Well 15 - is below 5 mg L^{-1}.

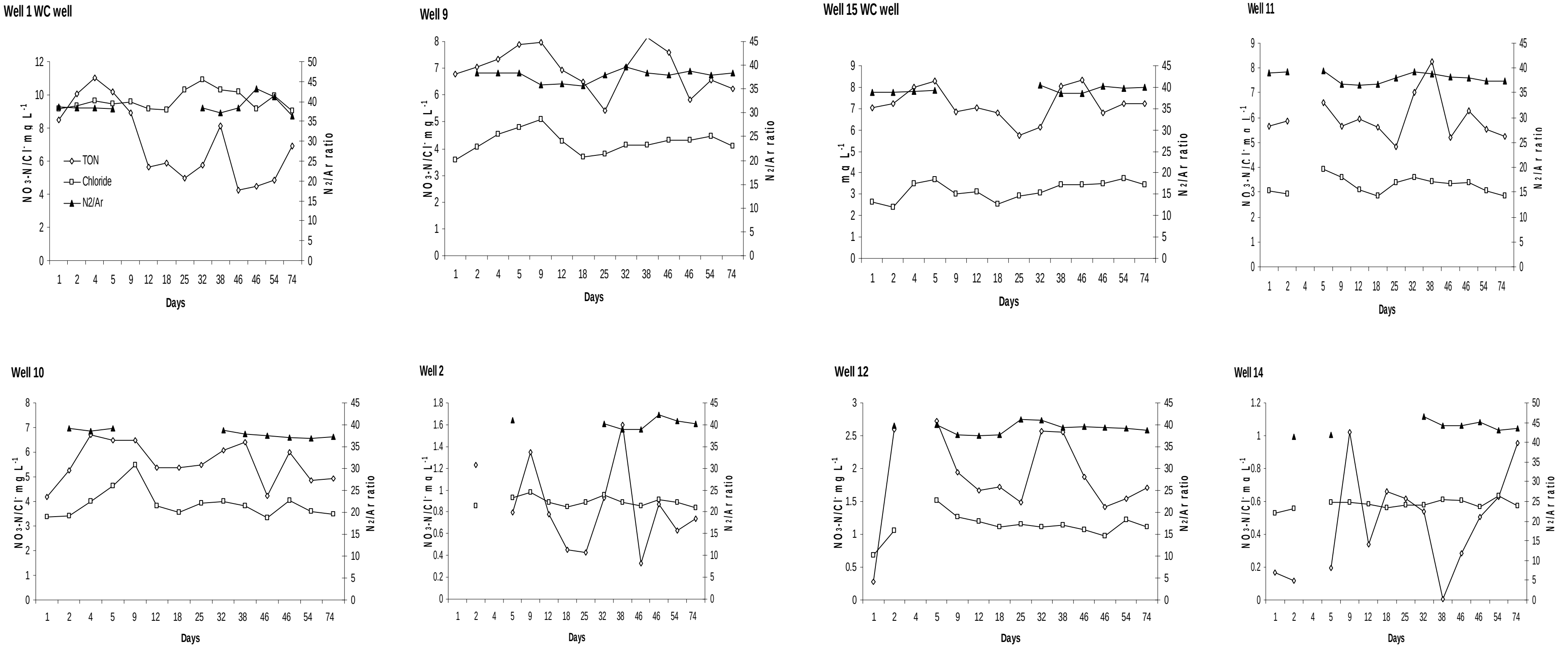


Figure 6.6 N_2/Ar ratios, nitrate (mg L^{-1}) and chloride (mg L^{-1}) concentrations throughout the experiment.

TABLE 6.14 DO, FE, MN, DOC, MEAN EXCESS N2 AND RESACTION PROGRESS FOR ALL WELLS DURING THE STUDY.

Well	DO[a]	Fe[b]	Mn[c]	DOC[d]	DOC[e]	Mean Excess N_2	Reaction Progress
	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	Ratio
				‘No denitrification’ wells			
1 (WC)	0.6	3.4	0.7	1.2	2.9	0.55±0.30	0.05±0.06
9	1.7	10.5	0.0	3.8	1.2	0.02±0.13	0.01±0.03
15 (WC)	0.3	5.2	0.0	1.9	7.3	0.88±0.12	0.06±0.06
11	0.7	8.8	0.0	3.2	1.4	0.00±0.12	0.00±0.02
10	0.5	6.8	0.0	2.5	3.2	0.25±0.18	0.03±0.05
				‘Denitrification’ wells			
2	0.4	0.9	0.0	0.3	1.7	1.29±0.20	0.26±0.26
12	0.3	4.0	0.0	1.4	1.4	0.89±0.13	0.18±0.18
14	0.3	4.8	0.2	1.7	1.9	3.22±0.28	0.90±0.91

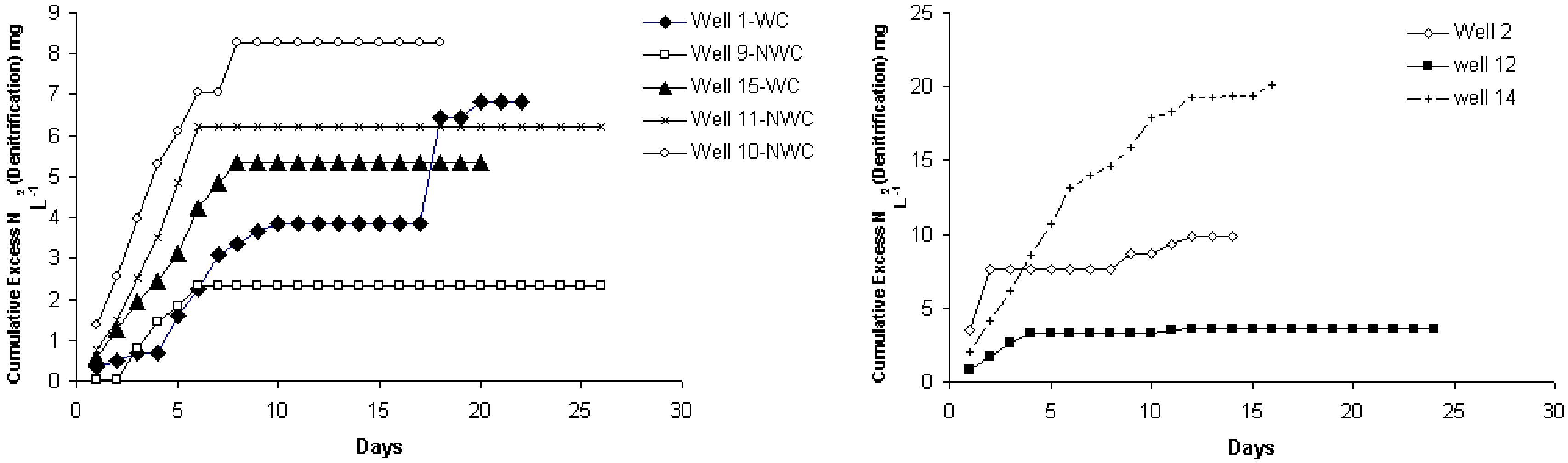
[a]min, [b]max, [c]mean, [d]required for denitrification, [e]available for denitrification.

6.6.3 Predictive models for NO_3-N, Chloride, N_2/Ar and DOC

Initial statistical analysis was directed towards the testing of the effect of woodchip enhancement in Wells 1 and 15. The analysis was formulated as a repeated measures analysis of the factorial structure for treatment and time. As previous work in location method II (Section 6.5.5) identified k_s as an important parameter to explain denitrification, and plotting of the results for some variables indicated a strong relationship, testing it for inclusion as a covariate in any analysis was essential for an unbiased test of the treatment effect. Other covariates were also tested and the water level in the well at time of sampling proved important for some variables. For a test of the treatment effect, an ANOVA-type model was used with those values of k_s that were replicated in the observations fitted as a categorical variable. For NO_3-N, k_s ($p<0.0001$) and a quadratic effect of water level ($p=0.02$) were both statistically significant, but the test for treatment effect resulted in a p value of 0.09. The means for NO_3-N were 4.8 for WC and 4.0 for NWC. Interpretation of the outcome for the treatment is not straightforward as replication of the woodchip addition was limited to two. Given this, the outcome of the test could be regarded as marginally significant.

To examine the relationship between the elements in the analysis model, and in order to use all the k_s information, a nonlinear function for k_s was fitted to the data. Smooth curves proved unsatisfactory because of the small number of k_s values (this parameter does not change over time in saturated conditions and is, therefore, limited to the number of well screens used within an experiment, i.e., eight) relative to the number of parameters required, and, ultimately, a broken straight line fit was used to capture the information. The nonlinear approach also produced a significant fit for a curved (quadratic) relationship between NO_3-N and water level (likelihood ratio test, $p=0.007$). As there is no underlying theoretical relationship in the nonlinear model, its form is not expected to apply generally beyond this experiment, but the model serves to highlight interesting facets of the relationships identified. Figure 6.8 shows a plot of the predicted surface defined by k_s and water level for Day 54 for the WC treatment. A plot for untreated wells or another day would be parallel to this. For Cl^-, the ANOVA-type analysis showed no treatment effect ($p=0.18$) and no effect of the covariates tested. The analysis for N_2/Ar ratio showed no effect of the treatment ($p=0.44$), but a clear quadratic relationship with k_s ($p=0.007$). There was no evidence that water level played a role in explaining the observations for this ratio. The decreasing magnitude of this ratio with increasing k_s (raw data in Figure 6.9) appears to reflect the behaviour of NO_3-N. In this case, a nonlinear fit didn't offer any more information. For the natural logarithm of DOC, there was a significant treatment effect (p=0.04) with both k_s and water level non-significant. The back-transformed, bias-corrected DOC means were 1.85 for NWC and 2.9 for WC.

Agriculture, specifically intensively grazed grassland, receiving high loads of organic and inorganic forms, is prone to elevated nitrate losses. Molecular N_2 is a benign end-product of denitrification, and completes the N cycle in terrestrial and aquatic ecosystems. The interactive effects of C and N sources are important to reduce the knowledge gap associated with denitrification potential in soil, subsoil and groundwater. The identification of how denitrification changes spatially in subsoil will have consequences for groundwater and surface water protection (Hill et al., 2004). Such information allows the identification of areas where natural nitrate reduction in subsoils can actually protect a waterbody and help achieve the objectives of the WFD (Khalil & Richards, 2010).



A) ‘No denitrification’ wells

B) ‘Denitrification’ wells

FIGURE 6.7 A AND B CUMULATIVE EXCESS N_2 IN ALL WELLS

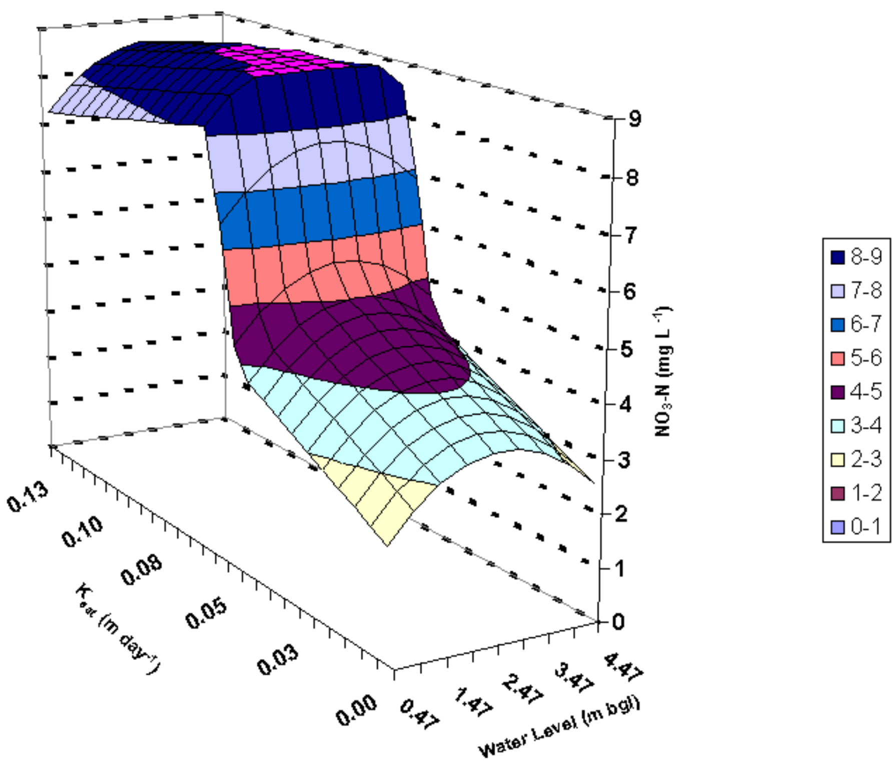


FIGURE 6.8 PREDICTED NO3-N MODEL USING K_S AND WATER LEVEL.

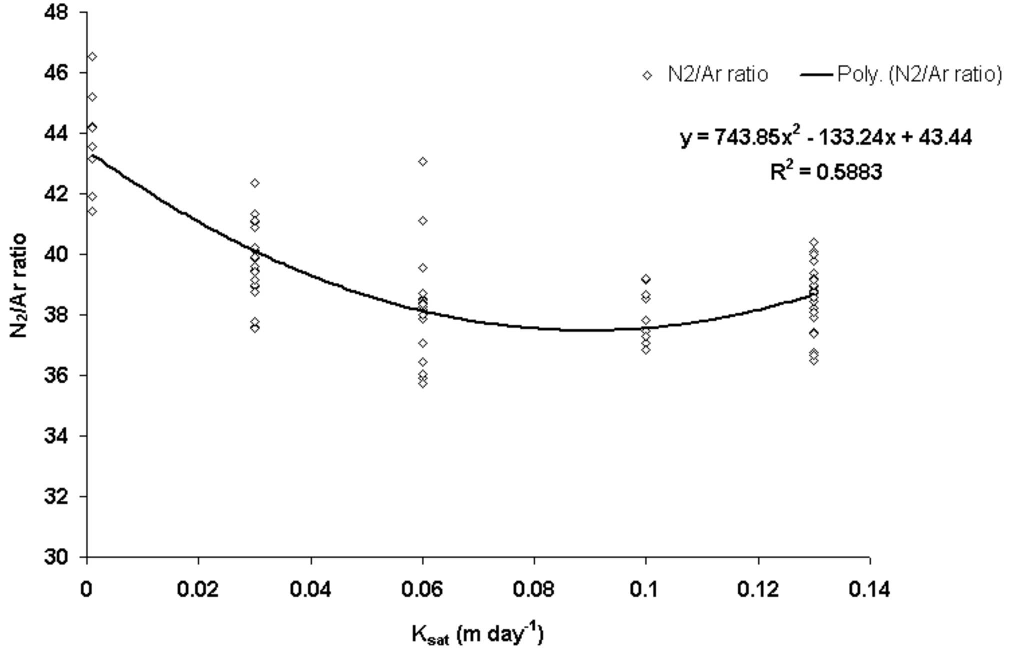


FIGURE 6.9 RELATIONSHIP BETWEEN *K_S* AND N2/AR RATIO.

Based on chemical stoichiometric relationships, denitrification of one mole of nitrate will require 1.25 moles of C. This equates to a mass balance of 1.07 kg of available C per 1 kg of nitrate. With approximately 50% of C availability in woodchip (based on bulk density), the treatment of 1 kg of nitrate will be approximately 2 to 2.5 kg of woodchip (Fahner, 2002). The woodchip amount used in the current study was considerably less at 10 g and, therefore, N_2/Ar ratios with higher peaks could be expected in a bioreactor study. As woodchip amounts used were small, reductions in denitrification potentials towards the end of the experiment were evident. Even at this low amendment rate, the denitrification potential changes were significant. Besides identifying “denitrification hotspots”, such techniques could predict when reactive media needs replenishment in a bioreactor.

Subsoils from the same site as this study - amended with helium-flushed de-ionised water containing ranges of nitrate and glucose, at various soil depths (from 0 to 10 cm, 15 to 25 cm and 60 to 70 cm) under different management regimes (grassed ryegrass and grass clover) - produced N_2/Ar ratios of 40-plus for all treatments (Khalil & Richards, 2010). In this previous study, the N_2/Ar ratio decreased with depth. In the current study, the groundwater depth was 4 m bgl, with N_2/Ar ratios ranging from 35 to 45. C amendment in this study also increased N_2/Ar ratios. Denitrification in the subsurface is controlled by biochemical conditions which vary spatially and temporally. On this site, the glacial till is highly heterogeneous, resulting in variable soil parameters.

Heterotrophic denitrification is controlled by the concentrations of oxygen, nitrate and C in shallow groundwater. Where high nitrate concentrations are present in such a waterbody (e.g. below an agricultural landscape), the availability of degradable C becomes critical for denitrification to occur. Aerobic microorganisms utilise this labile C to consume oxygen. In this study, isotopes identified organic fertilizer as the source of pollution on site from dairy dirty water irrigation (Table 6.1). After removal of such a point pollution source, on site nitrate concentration is maintained though mineralisation in the soil. The application of a denitrifying bioreactor requires an understanding of the hydrological settings and how nitrate differs spatially and temporally within a site (Schipper et al., 2010). While agronomic N inputs are responsible for nitrate concentrations, the proportion of N to be denitrified is controlled by hydrology and geomorphology (Seitzinger et al., 2006). The kinetics of denitrification at N concentrations >1 mg L^{-1} are independent of concentration. This implies that the rate of denitrification is limited by donor availability.

As oxygen and pH levels decrease metals (micronutrients Fe and Mn) dissolve and denitrifying organisms utilise the remaining C as an electron donor. Rivett et al. (2008) found denitrification occurs in aquifers when the DO is 2 mg L^{-1} or less, and heterotrophic denitrifying bacteria prefer a pH range from 5.5 to 8.0. Significant denitrification only occurred in the current study below this DO concentration, which is agreement with many studies dealing with agriculturally derived nitrate plumes (full list in Rivett et al., 2008). The optimum temperature for denitrification to occur is from 25ºC to 30ºC, but studies show a larger range from 2 ºC to 50 ºC. Bailey et al. (*pers comm.*) argued that low temporal variability in nitrate on this site was due to rainfall distribution throughout the year being constant, and a temperate climate allowed microbial process of nitrification and denitrification to continue all year round.

The woodchip used in this study released DOC rapidly, resulting in the significant increase in groundwater DOC. With high nitrate concentrations also present in these wells, the denitrification potential increased, turning such wells from a ‘no denitrification’ signal to a ‘denitrification’ signal. Laboratory column tests have shown that DOC released from aged woodchips of two years can deplete O_2 in DO-saturated water in 1 hour (Robertson, 2010). In preliminary batch experiments on this site, the DOC release in 24 hr reached 50 mg L^{-1} in shaken tests and 40 mg L^{-1} in unshaken tests. In the field, DOC levels of 15 mg L^{-1} and 14 mg L^{-1} were found in Wells 15 and 1, respectively, in the same period. Rivett et al. (2008) found that DOC in most aquifers is < 5 mg L^{-1}. DOC is first oxidised by DO in the system and any remaining DOC can fuel denitrification. It takes 1 mg C L^{-1} to convert 2.7 mg O_2 L^{-1}. Below 2 mg O_2 L^{-1} denitrification can occur. DOC requirements to fuel denitrification in each well are presented in Table 6.14. DOC deficiencies are present in Well 9 (NWC) and 11 (NWC). Before solid C was added, Well 1 and 15 had DOC concentrations of 1.1 and 1.4, respectively, and had a ‘no denitrification’ signal. Wood chip addition to these wells increased DOC sufficiently to stimulate denitrification.

In the saturated zone, k_s remains constant at a particular location but varies spatially, due to the heterogeneity of the aquifer, and between different aquifers and geological units. It may also vary due to anisotropies in the aquifer. However, if the hydraulic gradient in an area changes, the Darcian velocity can change. The k_s of glaciated tills varies considerably e.g. sandy silty tills in Scandanavia range from 5×10^{-9} to 5×10^{-4} m s^{-1} (Lind & Lundin, 1990). Clay tills have very low permeability of $< 10^{-9}$ m s^{-1} or, in some Canadian examples, vary from 10^{-11} to 10^{-12} m s^{-1}. Areas of naturally high or enhanced denitrification potential, referred to as ‘denitrification hotspots’, may, in part, be due to differential k_s, mobile fractions of groundwater and slow diffusion into the immobile fraction where denitrifiers are active (Schipper et al., 2005). The extent to which k_s controls such processes is unknown. Gurwick et al. (2008) reported that low k_s areas can also be associated with buried organic matter in riparian soil, which transmits water more slowly. These buried layers, in turn, provide a supply of organic matter as an energy source for denitrification. In an enhanced denitrification bioreactor scenario, a solid C source is mixed with soil, which decreases subsurface k_s in the trench. This may occur during construction when compaction or insufficient mixing of soil and C material occurs. The interface between the soil and the denitrification trench may also create preferential flow paths into the reactive media. However, lower k_s zones may establish ‘denitrification hotspots’ (Parkin, 1987; Jacinthe et al., 1998; Schipper et al., 2005). Another interesting aspect of k_s related research is how it changes within a denitrification wall over time, due to degradation of reactive material, clogging and/or changes in overburden (Schipper et al., 2010). In a long-term (22 month) barrel experiment, Cameron and Schipper (2010) investigated k_s changes in different reactive media. The k_s ranged from 300 m day^{-1} to 10000 m day^{-1} at the start of the experiment. At the end of the experiment, k_s decreased in larger woodchip diameter bioreactors, whilst remaining constant in finer grained media. The cause of such changes was attributed to gas bubbles, media particle shape and tendency for particle to settle on their flat sides. In the present study, denitrification potential was affected even with small differences in k_s (0.06 m day^{-1} and 0.13 m day^{-1}).

Earlier in the PRB location method II it was shown that mean groundwater nitrate was significantly ($p<0.05$) related to groundwater N_2/Ar ratio, redox potential, DO and N_2, and was close to being significant with N_2O ($p=0.08$). In this study, both spatial and temporal data was utilised for nitrate prediction, k_s and a quadratic effect of water level were both statistically significant. When woodchip-amended and non-amended wells were compared, this was marginally significant. Other good relationship were found between denitrification potential (N_2/Ar ratio) and k_s. A suitable method to calculate in situ k_s such as those examined by Pedescol et al. (2010), in a full size bioreactor will be important for model development.

6.7 Summary

Two methodologies to locate a subsurface "denitrification trench" for nitrate remediation were investigated. A small area associated with soiled water irrigation on a 4.27 ha study site where groundwater NO_3-N concentration exceeds allowable drinking water concentrations of 11.3 mg NO_3-N L^{-1}, was identified. The first methodology was based on site and groundwater characterisation, and successfully located a site for the locations of a permeable reactive barrier. The second more robust method combined shallow groundwater geochemistry data from 17 piezometers over a 2 yr period in the context of a statistical framework and hydrogeological techniques. Results showed natural attenuation occurs on site, although the method does not directly differentiate between dilution and denitrification. It was then investigated if shallow groundwater nitrate concentrations could be predicted from k_s measurements, ground elevation, elevation of groundwater sampling and distance from a dirty water point pollution source. Tobit regression, using a background concentration threshold of 2.6 mg NO_3-N L^{-1} showed, when assessed individually in a step wise procedure, k_s was significantly related to groundwater nitrate concentration. Distance of the point dirty water pollution source becomes significant when included with k_s in the model. The model relationships show areas with higher k_s values have less time for denitrification to occur, whereas lower k_s values allow denitrification to occur. Areas with higher permeability transport greater nitrate fluxes to ground and surface waters. When the distribution of Cl^- was examined by the model, k_s and ground elevation had the most explanatory power but k_s was not significant, indicating that dilution had an effect. Areas with low nitrate concentration and unaffected Cl^- concentration indicated the occurrence of denitrification; low nitrate concentration and low Cl^- chloride concentration indicated dilution. Combining these findings allows areas of denitrification and dilution to be inferred. The effect of denitrification was further supported as mean groundwater nitrate was significantly ($p<0.05$) related to groundwater N_2/Ar ratio, Eh, dissolved O_2 and N_2, and was close to being significant with N_2O ($p=0.08$). Calculating contaminant mass flux across more than one control plane is a useful tool to monitor natural attenuation. This tool allows the identification of areas where intervention other than natural attenuation may be needed to protect receptors.

One of the challenges of groundwater remediation research is how to track denitrification potential spatially and temporally within reactive media. First, using $\delta^{15}N/\delta^{18}O$ isotopes, eight wells were divided into indicative ‘denitrification’ and ‘no denitrification’ wells. Secondly, the k_s in each well was measured, creating two groups of ‘slow’ (0.06 m day^{-1}) and ‘fast’ (0.13 m day^{-1}) groundwater. Thirdly, two ‘no denitrification’ wells (one fast and one slow) with high nitrate concentration were amended with woodchip to enhance denitrification. Results showed that there was good agreement with respect to denitrification identification between stable isotope, chemical (N_2/Ar ratio and DOC) and physio-chemical (DO, temperature, conductivity and pH) parameters. Predictive models were developed using available datasets to explain the spatial and temporal distribution of groundwater nitrate, Cl^-, N_2/Ar and DOC. Initial statistical analysis was directed towards the testing of the effect of woodchip amendment. The analysis was formulated as a repeated measures analysis of the factorial structure for treatment and time. For nitrate, k_s ($p<0.0001$) and a quadratic effect of water level ($p=0.02$) were both statistically significant, but the test for treatment effect resulted in a p value of 0.09. This showed that enhanced wells changed to a ‘denitrification’ signal during the experiment, with more denitrification in the slow k_s well. This non-destructive technique allows elucidation of denitrification potential over time and could be used in denitrifying bioreactor technology to assess denitrification “hotspots” in reactive media, while developing a nitrate spatial and temporal predictive model for bioreactor site-specific conditions.

Chapter 7 Conclusions & Recommendations

7.1 Literature review conclusions

Current legislation such as the WFD is focused on prevention of nutrient losses from agricultural sources. Mitigation technologies suitable for Irish conditions are recommended to control and remediate nutrients already lost from the farming system. They are also needed to mitigate against incidental nutrient losses after land application of nutrients. Sustainable waste products, such as alum from wastewater, could be used for P control in surface water and dirty water. They mitigate against nutrient loss while allowing the crop to utilise other nutrients. In Ireland, ochre from the abandoned mines at Avoca has never been tested for its maximum P sequestration capacity. Options for shallow groundwater nitrate removal include *in situ* denitrification bioreactors or permeable reactive barriers.

7.2 Ochre study conclusions

Different methods should be used to investigate the maximum P sequestration capacity of ochre. Methods such as batch experiments, isotherms and saturation experiments all gave similar results for synthetic solutions - maximum sorption capacity of approximately 21 g P kg^{-1}. For dirty water experiments due to the low nutrient content present the Langmuir isotherm method failed as all P was adsorbed to the ochre. For dirty water, saturation experiments gave a maximum sorption capacity of 16 g P kg^{-1}. Therefore, the saturation method gave best results. After agitation, less than 1% P desorption occurs, which reflects the binding strength of a = 1.Kinetic experiments showed that equilibrium occurred quickly. In the shaken batch experiments, the ochre absorbed up to 97% of the P in the first 5 minutes of the experiment. The ochre examined contained high concentrations of trace metals and Fe (33%) mineralogy of goethite, jarosite and minor amounts of ferrihydrite. The presence of different mineralogy at different sites creates a different surface area for adsorption. Such differences control the maximum P adsorption capacity. Some adsorption also occurred to oolites and diatom in the sample. Rapid remobilisation of heavy metals to toxic levels occurred in synthetic and surface water samples, which limits its potential use as an amendment for P sequestration. This may hinder its use in

P sequestration technologies. The use of ochre from metal mine origin as a P sequestration amendment in conjunction with another environmental technology (e.g. wetland) should be examined.

7.3 Conclusion for soil ochre amendment

It is important to include P sources and P losses in any model, which attempts to predict P losses in runoff. The model developed satisfactorily predicted the amount of P left in solution after ochre amendment to soil and can be used for other chemical amendments to soil. The inclusion of soil test P in the model is vital. Without further P inputs, ochre can intercept P loss from soils. This could be essential in areas with Index 4 soils, which may continue to release P for many years, even after fertilizer inputs have ceased. After P inputs, ochre reduced P concentrations in runoff, but could not bring P concentrations to below the MAC of 0.035 mg DRP L^{-1}. However, further dilution of runoff P concentrations may occur at catchment level. Therefore, the efficacy of ochre to reduce P concentration in surface waters has yet to be quantified. Although metal mining ochre has a high maximum P adsorption capacity it is not a suitable option for Ireland. Importantly, very quick and sustained metal release from the ochre tested during P sequestration makes it unsuitable for use as a soil amendment to control P release to a waterbody.

7.4 Conclusions from PRB location study method I

A continuous, shallow denitrification trench may be suitable for Irish conditions to remediate point sources of nitrate. Each site will have site-specific conditions, but the methodology developed for this 4.2 ha study site, based on site and groundwater characterisation, can successfully site a trench, and calculate the dimensions and orientation of the barrier. The costs of a PRB in heterogeneous glacial tills could be higher than expected due to watertable fluctuations and depth of excavations. Further research should be carried out on the denitrification rates of different reactive media when combined with different soil groups. Higher nitrate removal rates will necessitate lower residence times and increased remediation. The longevity of the reactive media needs to be investigated and a cost-benefit analysis for the remediation of contaminated groundwater undertaken. A broader methodology, which takes into account other site characteristics, such as unconsolidated material, fractured bedrock and a deep watertable should be investigated. Nitrate spatial distribution should be investigated, and differentiation between dilution and differentiation should be made. Identifying areas with low natural attenuation but with connectivity to a waterbody should be investigated. This methodology will always attempt to mitigate the entire nitrate plume on site and will cost more. A more refined approach is needed to pinpoint areas where installation of a PRB is justified.

7.5 Conclusions for PRB location method II

The spatial distribution of nitrate on the same 4.2 ha site was ascertained through data collection and development of statistical relationships between physical and chemical parameters. In the current study k_s and distance from point source are important when assessing the spatial distribution of nitrate in shallow groundwater. For spatial Cl^- distribution, k_s and elevation are important factors. Such site specific relationships allowed the identification of areas of denitrification and dilution to be inferred. Denitrifcation parameters such as N_2O and N_2/Ar were in agreement with areas identified as “denitrification”. Using contaminant mass flux calculations alone does not indicate transformational processes on a site. Many sites such as the one in this study may not need remediation, as the natural attenuation on site (denitrification potential) is adequate to protect any sensitive sensitive receptors in the area.

7.6 Conclusions for woodchip slug

Natural abundance can be used to select indicative “denitrification” and “low denitrification” groundwater areas on a site. Saturated hydraulic conductivity (k_s) can divide these wells further into different classes. Next, groundwater samples retrieved from these wells using impermeable tubing and a syringe can be analysed quickly for N_2/Ar ratios (denitrification potential) using MIMS. These techniques can be used to investigate natural or enhanced attenuation on a site. Within a denitrification bioreactor such techniques could be used to investigate how the reactive media performs spatially and temporally and how remediation within the reactive zone differs (i.e. denitrification hotspot identification). Data generated can then be used to develop site-specific relationships and predictive models for nitrate, chloride, DOC and N_2/Ar ratios.

7.7 Recommendations

Future research should focus on:

If mitigation techniques are to be employed within the WFD as supplementary measures such techniques need to be tested at catchment scale. Also The estimation of vertical and aquifer flushing lag times within various hydrological scenarios e.g. free draining thin soil overlying limestone or thin free draining soil overlying a sand and gravel aquifer. This should be carried out with Irish-specific data together with a robust uncertainty analysis. This would manage the expectations of stakeholders for “good status” achievement and set a more realistic target for accomplishing the goals of the WFD. This time scale would also exemplify the need for remediation and control technologies during this lag time phase.

2. Investigation of chemical amendment to agricultural organic wastes at many scales should be carried out e.g. aluminium chloride amendment to dairy slurry at micro- (agitator), meso- (flume) and macro- (field) scales. The cost and feasibility of using these amendments on a farm should be addressed. Other amendments should be investigated that could be applied directly to soil or emplaced in gabion-like structures in open waterways. The concept of pollution swapping should be investigated within denitrification bioreactors (nitrate remediation) and chemical amendment (P control) research. In PRB research, partial denitrification with production of N_2O should be investigated and CH_4 release due to saturation in the system. Also within the reactive media the transformational processes should be investigated further e.g. DNRA. In amendment research, the alteration of the gaseous phase e.g. increases in NH_4 emissions during land application of amended slurry, should be investigated.

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Appendix I

Published papers

From literature review

Fenton, O., Healy, M.G. and Schulte, R.O. 2008. A review of remediation and control systems for the treatment of agricultural wastewater to satisfy the requirements of the Water Framework Directive. *Biology and Environment*, **108**(B):69-79.

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Submitted Papers

From P control

Fenton, O., Healy, M.G., Rodgers, M., Kirwan,L. P. The suitability of using Avoca ochre as a soil amendment to sequester phosphorus. Biology and Environment. Submitted August 2010. September – accepted with corrections

From N remediation

Fenton, O., Healy, M.G., Henry, T., Khalil, M.I., Grant, G., Baily, A., Richards, K.G. Investigating denitrification potential in groundwater over time using δ15N/δ18O Isotopes and Membrane Inlet Mass Spectroscopy. Ecological Engineering. Submitted September 2010.