# Tellus Investigation of Wetland Ecology and Geochemistry (TIWEG)

# Final Report

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## Executive Summary

A variety of groundwater dependant terrestrial and aquatic habitats (groundwater dependant wetlands or GWDWs) occur in the area surveyed by the Tellus and Tellus Border surveys (Tellus Surveys). Studies completed elsewhere have demonstrated heightened ecological sensitivity of many of these environments to anthropogenic disturbance, arising from landuse activities within their catchments. EU legislation, including the Water Framework Directive and the Habitats Directive, aims to protect GWDWs from ecological degradation. This requires an understanding of the hydrological and geological processes that control the delivery of nutrients to ecological receptors. To date, characterisation of geological influences has focused on the physical properties of soils and subsoils found in wetland catchments. However, the role of geochemistry has largely been neglected, due in part to the absence of suitable datasets, despite the demonstrated influence of soil and subsoil geochemistry on nutrient fate and transport.

The TIWEG project, funded under the Tellus Border research programme, aimed to investigate the utility of the soil geochemical datasets generated by the Tellus (Tellus and Tellus Border) surveys, as tools to assess the risk posed by potentially polluting landuse activities that may lead to nutrient enrichment of wetlands. Investigations consisted of two phases. An initial phase involved the development of a geographic information system (GIS) to assess the risk posed by landuse activities to 147 wetland sites, considered representative of GWDWs in the area covered by the Tellus surveys. Compilation of relevant spatial datasets to assess risk of nutrient enrichment in each wetland catchment required merging of vulnerability schemes and landuse datasets employed in Northern Ireland with those from the Republic of Ireland, thereby permitting a common level of risk ranking to be employed. Once completed the risk ranking investigated the potential influence of pollutant source proximity on risk. Sensitivity analysis has suggested that landuse intensity, rather than source proximity play a greater role in influencing risk of nutrient enrichment at the sites considered.

GIS also provided the basis for investigating soil geochemistry variations according to soil type, as represented by soils maps in both Northern Ireland (generated by AFBI) and the Republic of

Ireland (generated by Teagasc). Superimposition of elemental datasets, generated by the Tellus surveys over published soils maps, and subsequently processed using ARCGIS software, permitted the variations in composition, by mapped soil type, across the survey area to be quantified. This in turn permitted the utility of existing soils maps for understanding geochemical influences on nutrient fate and transport to be more confidently defined.

Characterising the role of geochemistry on deeper subsurface nutrient fate and transport required investigation of the elemental composition of subsoil. Although subsoil geochemistry data is currently unavailable for the Tellus Border dataset, comparison of soil and subsoil geochemistry from the Tellus (NI) dataset provided a basis for predicting inorganic subsoil geochemical conditions in the Tellus Border dataset from overlying soil composition. Furthermore, the approach allowed soil geochemical process to be examined. Enrichment and depletion mechanisms for each element relative to subsoil parent material could be defined according to soil type.

The outcome of the GIS investigations permitted shortlisting of sites for further field-based investigation/ground truthing, based on calculated risk of nutrient enrichment, along with organic matter content (as indicated by loss on ignition), calcium content and iron content. Analytical results from soil samples collected during once-off field visits revealed that concentrations of the three parameters investigated in field samples broadly corresponded to those of generated using the data from the Tellus surveys for the soil types investigated.

Analytical results from 55 soil samples and 72 water samples collected from the nineteen sites selected, revealed a complex relationship between risk ranking and nutrient levels in wetlands. When the impacts of point sources were eliminated from datasets, a poor correlation persisted. However, it was noteworthy that the range of nutrient concentrations observed in wetland water samples declined with declining risk of nutrient enrichment. The higher variation observed at higher risk sites is believed to reflect the diversity of attenuation processes influencing nutrient delivery to ecological receptors in wetlands. High risk sites containing water with low levels of nutrients suggest delivery occurred along pathways where geochemical reactions, leading to nutrient attenuation can play a significant role, such as diffuse

groundwater discharge through materials rich in organic matter, leading to reduced nitrate levels. Conversely, where high nutrient levels occurred in water samples delivery was suspected to occur along pathways experiencing little geochemical attenuation, such as spring discharge. Consequently, the risk of nutrient enrichment to wetlands is greater.

Defining the influence of soil geochemistry on nutrient levels proved challenging. Insufficient data are currently available to confidently characterise these processes at most sites studies. Detailed investigations at the Tellus Border wetland site at Rockmarshall, Co. Louth, demonstrated that organic matter content could play a critical role in reducing nitrate concentrations in groundwater. On the other hand relationships between soil calcium and iron levels at all field sites proved more difficult to discern, largely due to significant overlap in the concentration ranges of contrasting soil types. TIWEG researchers are continuing to investigate this topic and the wider utility of the data sets collected in the Tellus Surveys as a means of better evaluating interactions between human activities and the health of groundwater dependent wetland ecosystems.

# 1. Aims and Scope of the Research

## 1.1 Introduction

Nutrient levels play a critical role in controlling the trophic status of wetland ecosystems. Human activities in wetland catchments can lead to changes in the nutrient loads entering the system, potentially leading to eutrophication. Groundwater dependent wetlands (GWDW) are wetlands which rely on groundwater to maintain their ecosystem functioning and represent a significant proportion of wetlands within the UK and Ireland. Like other ecosystems, GWDW catchments experience multiple anthropogenic pressures from activities in the area contributing water to GWDW, including those from intensive agriculture (pasture and tillage), water abstraction/drainage and household sewage disposal, all of which can result in elevated levels of nutrients discharging to wetlands. Many GWDW have been damaged in this way and no longer provide full ecohydrological functions or ecosystem services (Hughes and Heathwaite, 1995).

European Union policy aims to protect GWDWs. The principal policy drivers include the Water Framework Directive (WFD, 2000/60/EC) and the Habitats Directive (92/43/EEC). These directives require physical and ecological characterisation and management of wetland habitats. The WFD provides a framework for a more holistic approach to water management compared to previous legislation, including a focus on interactions between groundwater, surface water and ecological receptors. Implementation of the WFD across Ireland has led to an increased need for decision makers to understand the links between nutrient sources, pollution pathways (water delivery mechanisms), and the ecological health of receptors. In addition, the WFD also requires that conservation objectives for legally protected areas must also be achieved. Understanding geological influences controlling the transport of nutrients to GWDWs provides a scientifically defensible means of developing sustainable land use strategies, which also account for wetland ecosystem conservation.

The influence of soil and subsoil geochemistry on the fate and transport of nutrients to aquatic systems has been recognised from previous studies in the border region of Northern Ireland (NI) and adjacent counties of the Republic of Ireland (RoI)) (Jordan *et al.*, 2005). However,

Irish studies investigating the risk to groundwater quality have largely neglected the influence of geochemistry in controlling nutrient levels. For example recently published EPA guidelines consider subsoil permeability and thickness as important influences on nutrient mobility (Daly *et al.*, 2012). At the same time these approaches apply generic attenuation factors to account for attenuation, regardless of soil geochemistry.

The availability of the Tellus and Tellus Border (Tellus) geochemistry data have provided an opportunity by which the importance of geochemical processes on nutrient fate and transport can be investigated on a regional basis. This will be done in order to assess their utility for establishing risk of impact from various landuse activities.

This project, the Tellus investigation of wetland ecology and geochemistry (TIWEG), investigated the influence of soil (soil and subsoil) geochemistry on nutrient levels in groundwater dependant wetland (GWDW) catchments. The project involved an initial GIS-based regional study of GWDWs in the Border Region, followed by more detailed site-specific investigations at sites with varying geochemical conditions and risk levels. The desk study involved incorporating Tellus geochemical survey results with existing spatial datasets, including those for topography, land use, geology and drainage to refine conceptual models of nutrient fate and transport in wetland catchments. Groundwater dependent wetland catchments were classified according to vulnerability and catchment nutrient loads (pressures). Catchments displaying comparable risk, but contrasting soil geochemistry of those constituents suspected to influence nutrient mobility, such as organic matter content calcium (Ca) and iron (Fe), were selected for further field investigation. Comparison of anticipated analyte levels, determined by estimating concentrations for mapped soil types using Tellus geochemical data, with nutrient levels in wetland water samples provided the basis for:

- Assessing the role of soil geochemistry in influencing the impact of catchment-derived nutrients on the status of GWDWs, and;
- Investigating the utility of Tellus data for evaluating the risk posed by various land use activities to GWDW ecosystems.

The study results provide a basis for better defining the confidence with which the Tellus geochemical dataset may assist in evaluating the impact of nutrient loads associated with different land use practices on GWDW ecosystems across the area surveyed. Knowledge of these impacts is necessary to provide a scientifically defensible basis for the sustainable development and management of agricultural resources in the border area of Ireland, while protecting wetland ecosystems, in line with legislation. Similarly, the field studies permit comparison of nutrient levels in wetland catchments having limited land use pressures, with those where land use is more intensive. This provides for establishing a more rigorous baseline for discriminating between natural and anthropogenic impacts to GWDWs and the ability of GWDWs in the border region to withstand anthropogenic impacts.

## 1.2 Project Objectives

The principal aim of this project was to evaluate the role of soil and subsoil geochemistry in influencing nutrient attenuation and delivery mechanisms to GWDWs. The study investigated the potential for incorporating Tellus soil and subsoil geochemistry data into screening tools to assess the impact of land use practices on wetland systems.

Specifically the project aims to:

- Propose a protocol for characterising anthropogenic risks to GWDWs in the transnational river basin districts making up the Republic of Ireland/Northern Ireland Border Region.
- Identify data gaps in existing datasets that would strengthen the scientific basis for characterising eutrophication risk to wetlands in the area covered by the Tellus and Tellus Border Surveys.
- Improve current understanding of the role of soil and subsoil geochemistry in influencing nutrient attenuation mechanisms and rates, and their role in determining the risk of impacts to GWDW ecosystem function as a consequence of various land use activities;
- Evaluate the utility of Tellus data for improving current understanding of the role played by geological conditions in influencing nutrient loading on GWDW ecosystem functioning;

- Assess the potential of Tellus geochemical datasets to inform risk assessment models aiming to assess the likely impact of land use activities on nutrient loading to wetland ecosystems.

## 2. Background

### 2.1 Groundwater Dependent Wetlands

The term wetland can be used to describe a large number of diverse and often complex habitats that traverse the transitional zone between aquatic and terrestrial environments (Blackwell *et al.*, 2002). Groundwater Dependent Wetlands are wetlands which critically depend on groundwater flows and/or chemistries to maintain the environmental supporting conditions required to sustain that habitat (Schutten *et al.*, 2011). Input of groundwater to the wetland may be either direct, such as in fens and petrifying springs, or indirect, in that the groundwater influences the habitat by maintaining high and stable water levels such as within raised bogs (Kilroy *et al.*, 2009).

In the RoI the National Parks and Wildlife Services (NPWS) have identified 22 types of habitat which are considered to be groundwater dependent (Kimberley & Coxon, 2011). These include cladium fen, petrifying springs, active raised bog and turloughs. Implicit within the requirements of the EU WFD and Habitats Directive is the need to protect wetlands which are connected to groundwater bodies. The WFD focuses principally on the groundwater bodies and associated wetlands, whereas the focus of the Habitats Directive is on the habitat and species within the wetland itself. Nevertheless, there are close linkages between the two approaches, with both having significant overlap in terms of objectives. In order to assess the likely risk of anthropogenic impacts to wetlands it is necessary to identify the key hydrogeological and ecological indicators of significant damage. However, the ecohydrology of various GWDW types remains poorly understood. There is an increasing recognition of the role played by groundwater in many ecological communities. Influxes of groundwater to a wetland can influence whole system physico–chemical properties such as temperature and salinity, but it can also provide more subtle influences on micro environments and their ecological processes (Hancock *et al.*, 2009).

### 2.2 Nutrient Enrichment of Groundwater Dependent Wetlands

In order to meet the requirements of European legislation, a number of Member States have developed source-pathway-receptor models to carry out risk assessments. Groundwater

dependent wetlands are subject to a range of pressures, some of which are likely to become increasingly important in the future, such as the effects of climate change on water quality and quantity and the distribution of species. In addition, increased demand for agricultural land driven by high commodity prices, energy crops and concerns about food security may also place many of these habitats under increasing pressure. Groundwater dependent wetlands in Ireland experience multiple anthropogenic pressures, including those from intensive agriculture (pasture and tillage), water abstraction/drainage and household sewage disposal. Wetlands increasingly act as net receptors (sinks) of nutrients potentially leading to alteration in the structure and functioning of the system (Cherry, 2012).

Evidence suggests that catchments dominated by agricultural land-uses and human settlement have higher aquatic nutrient levels (Houlahan & Findlay, 2004). Excessive input of nutrients such as phosphorus (P) and nitrogen (N) to watercourses can cause nutrient enrichment, a process referred to as eutrophication (Vollenweider, 1971). Several pieces of EU legislation target this problem. However, only two actually provide a definition of the concept. In the Urban Waste-water Treatment Directive (91/271/EEC), eutrophication has been defined as 'the enrichment of water by nutrients, especially compounds of N and/or P, causing an accelerated growth of algae and higher forms of plant life to produce an undesirable disturbance to the balance of organisms present in the water and to the quality of the water concerned.' Nutrient enrichment can cause a range of negative ecological effects, primarily an excessive growth and proliferation of phytoplankton. This can lead to a loss of water clarity as well as a reduction in available oxygen. Reduced oxygen can cause problems for fish and other aquatic organisms, resulting in increased mortality of certain taxa and overall changes in the composition of aquatic communities.

Conventionally, P was considered to be the principal nutrient limiting plant growth in freshwater ecosystems, and as such was seen as the only nutrient of concern for surface water pollution (Mainstone and Parr, 2002;Withers and Haygarth, 2007). However, it is now accepted that nitrogen may also play a role and that it is the ratio of one nutrient to the other which is the major factor determining nutrient limitation. Concentrations of total P as low as

20 μg $L^{-1}$ (Correll, 1998), and orthophosphate in excess of 30 μg $L^{-1}$-P (Lucey *et al.*, 1999) can lead to eutrophication.

Phosphorus and N are both naturally occurring elements which are capable of moving through the environment in a series of physical, chemical and biological processes. Precipitation reactions are principally responsible for P attenuation in soils in which $PO_4^{3-}$ reacts with aluminium ($Al^{3+}$), calcium ($Ca^{2+}$), manganese ($Mn^{2+}$) and iron ($Fe^{3+}$) in the presence of oxygen, to form a range of low solubility minerals such as hydroxylapatite ($Ca_5(PO_4)_3(OH)$), variscite ($AlPO_4.2H_2O$) and vivianite ($Fe_3(PO_4)_2.8H_2O$). Retention of P by precipitation is therefore more likely to occur in an aerobic unsaturated environment (Beal *et al.*, 2005). Furthermore phosphate can adsorb to soil minerals owing to the presence of strongly charged positive surfaces, rendering P unavailable for plant uptake. In addition, adsorbed P has been known to migrate into the interior of the minerals that adsorbed them (absorption), making it even less bioavailable (Troeh and Thompson, 2005). The types of reactions which occur will vary according to subsoil type. This is closely related to pH. In acidic environments, for example, reactions mostly involve adsorption to Al, Fe or Mn, whereas in alkaline or calcareous subsoils, precipitation reactions forming calcium phosphate minerals or adsorption to iron impurities on the surface of carbonate clays will occur (Gill *et al.*, 2004). Phosphate, typically has low mobility in soils and is directly related to the cation exchange capacity of the soil, with transport of P through the subsoil more likely to occur in coarse-textured, non-calcareous soils which are low in clay content and organic matter.

Nitrogen (N) fractions that may influence ecosystem health include ammonium ($NH_4^+$), nitrite ($NO_2^-$) and nitrate ($NO_3^-$ ) (Schlesinger, 1997). A number of factors determine how effectively N is assimilated in the soil. These include the redox status of the subsoil, its microbial composition and the composition of organic matter (Wilhelm *et al.*, 1994). Adsorption of $NH_4^+$ in soil can occur under anaerobic conditions. Ordinarily, however, $NH_4^+$ is easily oxidised to $NO_3^-$ by nitrifying bacteria under aerobic conditions (Wilhelm *et al.*, 1994; Barrett *et al.*, 1999). This process, which is known as nitrification, can be limited by lower temperatures, insufficient oxygen or lack of alkalinity (Gill *et al.*, 2004). Nitrification is a two-step process in which $NH_4^+$ is first converted to $NO_2^-$, followed closely by oxidisation to $NO_3^-$. Nitrate is a bioavailable form

of N, and as such it can be taken up by plants and micro-organisms. Nitrate is a highly soluble, stable and mobile in aerobic water (Hatch *et al.*, 2002). Removal of $NO_3^-$ is more efficient in anaerobic conditions as the process of denitrification involves heterotrophic organisms degrading $NO_3^-$ to nitrogen gas ($N_2$, $N_2O$ or NO), when organic carbon is available (Verstraeten *et al.*, 2005).

The capacity of wetlands to remove P is limited in comparison to N as there is no permanent loss mechanism for P, as there is for N (denitrification), other than release downstream. As a result, P tends to accumulate in wetlands at a higher rate than nitrogen does. The majority of P in wetlands exists in its organic form, tied up in either vegetation, plant detritus, macrofauna, microorganisms, soil (soil organic matter or peat) or water (dissolved or particulate).

## 2.3 Pathway Susceptibility

Pathway susceptibility is a measure of the degree of attenuation experienced by a contaminant between its source and receptor (EPA, 2009). It is a measure of the ability of the pathway to reduce the impact of a pressure, in terms of time taken to reach the receptor, pollutant load reaching the receptor, pollutant concentration level in the receptor and duration of the pollution event (EPA, 2009). Typically, this requires the compilation and characterisation of relevant physical influences, such as soil type, subsoil permeability, groundwater vulnerability and aquifer category (EPA, 2009).

In general it can be assumed that only limited attenuation of contaminants occurs in groundwater flowing through bedrock in Ireland, given that groundwater flow occurs almost wholly via fissures. As a result, a greater importance is attached to processes occurring in overlying deposits in mitigating against groundwater contamination. It is the permeability of these materials combined with their thickness that will determine the rates of infiltration and percolation and thus the time taken for nutrients to reach a receptor. A dimension for further consideration is the availability of the unsaturated zone for attenuation. Any reduction to the capillary fringe will impact the attenuation of the groundwater through the restricted transfer of oxygen to contaminated groundwater (Maier *et al.*, 2007).

The term groundwater vulnerability is defined as the intrinsic geological and hydrogeological characteristics determining the ease with which groundwater may be contaminated by human activities (Daly and Warren, 1998). This definition is comparable with that of pathway susceptibility as both are underpinned by a similar set of considerations, and thus it will act as a surrogate for the purposes of this report. Vulnerability is a generic term that does not consider contaminant-specific behavior. Contaminant specific vulnerability depends on the contaminant's time of travel, the quantity which reaches groundwater and the attenuation capacity of geological materials through which the contaminant migrates. These properties are a function of the permeability/porosity of the subsoils overlying the groundwater, the thickness of the unsaturated zone through which the contaminant moves, and the type of recharge. As Fig. 1 suggests, where reaction occurs, they also depend on the chemical properties of the pollutant and the receiving material.

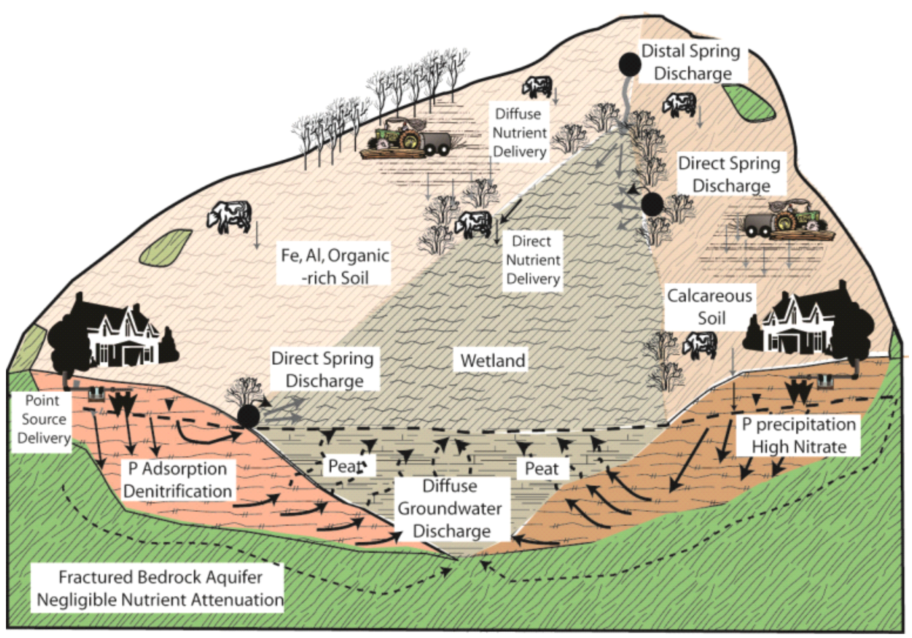



Fig. 1 Schematic illustration of nutrient sources, attenuation processes, and hydrogeological delivery mechanisms to GWDW receptors. Soil and subsoil physical properties determine dominant hydrological pathways and recharge rates. Soil and subsoil geochemistry influence reactive attenuation processes.

Evaluation of the risk to GWDWs requires vulnerability to be considered in conjunction with loading. The degree of attenuation experienced by contaminants will not only depend on soil geochemical and physical properties, but also on the means of application. Loads may be introduced by point or diffuse sources (Fig. 1), although accurate loading (in both space and time) are difficult to define in regional studies. Sources of diffuse nutrients are considered to derive predominantly from arable agriculture and livestock grazing, while point sources include farmyards, intensive livestock rearing units (ILRU) and on-site wastewater treatment systems (OSWWTS). Quantitative estimates of diffuse nutrient loadings can be derived from agricultural census data. Similarly identification of point sources can be achieved using remotely sensed imagery, and published figures for OSWWTS discharge. Relevant data were available to permit estimates of nutrient loads from other point sources, such as farmyards or ILRU in the TIWEG study. The impact of this shortfall is considered less during summer than during the closed winter season when more livestock are kept indoors. Contaminant loads, estimated using these datasets, coupled with vulnerability maps provided a basis for assessing the relative risk of eutrophication to GWDWs across the area encompassed by Tellus surveys.

## 3. GIS-based regional survey of Groundwater Dependent Wetlands

The TIWEG study focused on the areas of Ireland adjacent to the border between NI and the RoI and employed the Tellus and Tellus Border geochemical data sets. These data were made available through the Interreg IV funded Tellus Border project (http://www.tellusborder.eu/) and its predecessor, the Tellus Project, which produced seamless maps of key soil and surface water chemistry parameters across the border area. A range of datasets from a variety of sources were also used through the course of the desk-based regional survey (Table 1).

Table 1. Datasets used throughout desk based risk assessment methodology and field site selection process.

| Data | Source |
|---|---|
| Topographic maps (digital terrain models) | OSI and OSNI |
| Vulnerability maps | GSI, GSNI |
| Topsoil | Teagasc, AFBI |
| CORINE landuse | |
| Total livestock units District Electoral Divisions (DED) | CSO |
| Total livestock units per Ward | Northern Ireland Statistics and Research Agency |
| Percentage of tillage | CSO, Northern Ireland Statistics and Research Agency |
| Annual nutrient application | Teagasc |
| Soil Geochemistry | Tellus and Tellus Border |

### 3.1 Site Selection

Groundwater Dependent Wetlands in this region were identified to generate a shortlist of 147 candidate sites (Fig. 2). Candidate wetland sites were mainly selected from those designated as either Special Area of Conservation (SACs) or National Heritage Areas (NHAs). These sites covered a range of habitat types including wet grassland meadow, raised bogs, woodland bogs, fens, turloughs and transition mires. In addition, a number of wetland sites which remained

undesignated, but for which data is available owing to their involvement in other projects were also included.

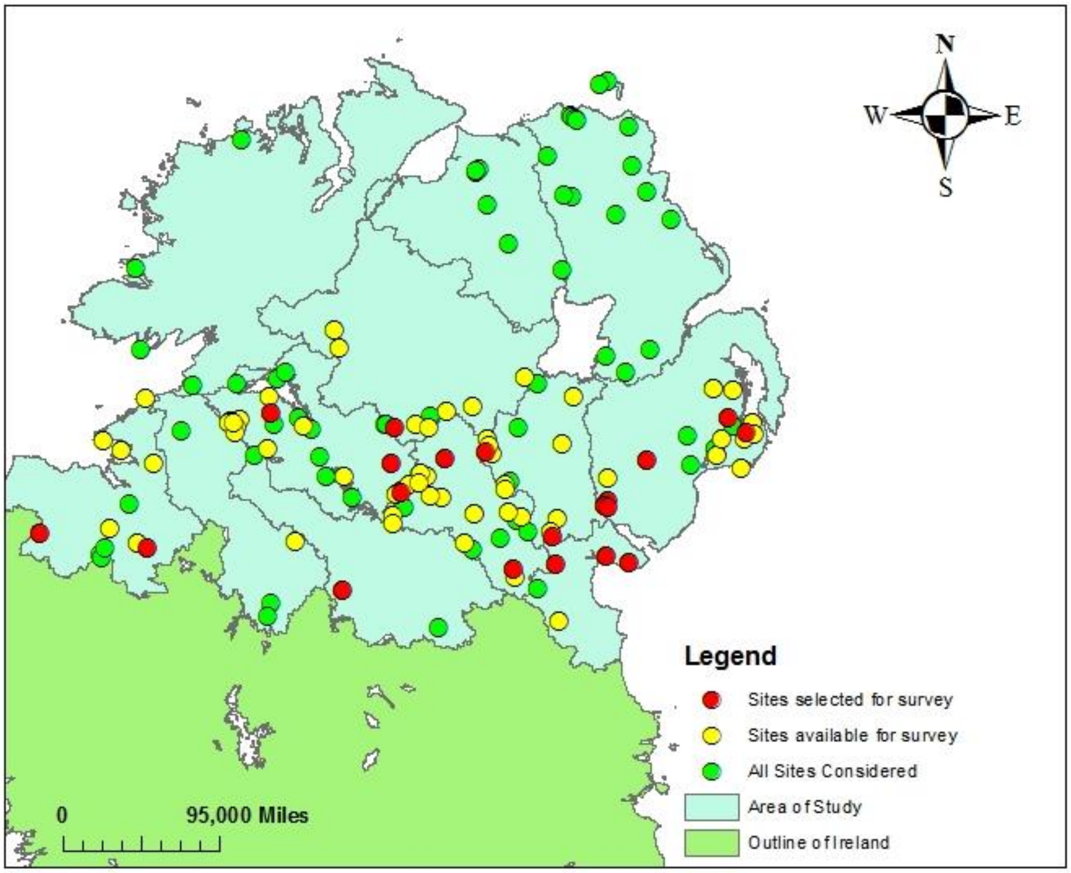



Fig. 2 Candidate Groundwater Dependent Wetland sites for investigation in the border region of Ireland.

The GIS-based review of these sites was carried out to establish the likelihood of groundwater dependency. Topographic maps were used to establish the presence/absence of surface water inflows and outflows. In addition, Geological Survey Ireland (GSI) bedrock geology maps were used to identify sites located at the intersection of a confined aquifer with a slope, stratigraphic change or along a fault, all of which were considered to have a high likelihood of groundwater dependence (Brooks *et al.*, 2007). Sites eliminated at this stage included those with limited indication of receiving discharging groundwater (i.e. sites with significant surface water inflows, raised bogs), turloughs (which are likely dry during the sampling period of this study,

which would preclude water quality sampling), and large lakes which have corresponding large catchment boundaries and poorly definable groundwater dependency.

Following the selection procedure a subset of the 147 shortlisted candidate sites were selected. Ordnance Survey Ireland (OSI) and Ordnance Survey Northern Ireland (OSNI) topographic data (Digital elevation models, DEM), were used to define the catchment boundaries of each site (Maberley *et al.*, 2003; Wade *et. al.* 2006).

## 3.2 Risk Assessment Methodology

Application of a risk assessment methodology, outlined in Fig 3, was based on the source–pathway–receptor model and combined an estimation of pollutant load and vulnerability. The role of geochemisty on nutrient fate and transport was investigated by classifying catchments according to dominant soil type. Estimates of pollutant loads were initially calculated based on the assumption that diffuse pollution originating from landuse activities acted as the dominant pressure to the aquatic receptors in the areas studied.

### 3.2.1 Estimating Pressure

Land use pressure in wetland catchments was determined by estimating diffuse nutrient loading from the surrounding catchment. Livestock density per District Electoral Division (DED) in the RoI (CSO, 2000) and livestock density per electoral Ward in NI (Northern Ireland Statistics and Research Agency) provided an indication of the loads from grazing. The data on livestock units were directly applied to areas of ‘grazing’ identified through CORINE (2000) land use data. To account for the nutrient production rates from these diffuse sources of nutrients, estimates of excretion levels from sheep, beef cattle and dairy cows were obtained from the literature (Teagasc, 2010; Good Agricultural Practice for Protection of Waters, 2010) and multiplied by the total number of cattle and sheep in each DED/Ward. In a similar way estimates of annual nutrient application rates (Teagasc, 2010) to cereal and root crops were multiplied by the total area of arable land identified through CORINE (2000) data.

### 3.2.2 Point Source Analyses

To account for the potential impacts of point sources to ecological receptors, orthographic aerial imagery for each field site was examined in order to locate and count all single dwelling properties in each of the catchment zones. Nutrient loading from domestic properties was then estimated by multiplying the total number of single dwellings by the average annual nutrient emissions of a domestic property. This was estimated based on the average hydraulic loading from a single dwelling in Ireland, which is estimated to be 180 litres per capita per day (EPA, 2009). Based on the typical composition of N and P in domestic wastewater it is possible to estimate the total N (3.29 Kg N/yr) and P (0.66 Kg P/yr) load entering an onsite sewage treatment system each year. A distance weighting system was applied in the sample was as described above. The generation of nutrient loading estimations from point and diffuse sources facilitated a more complete understanding of the relative contributions of nutrient loads from both point and diffuse sources at these wetland sites.

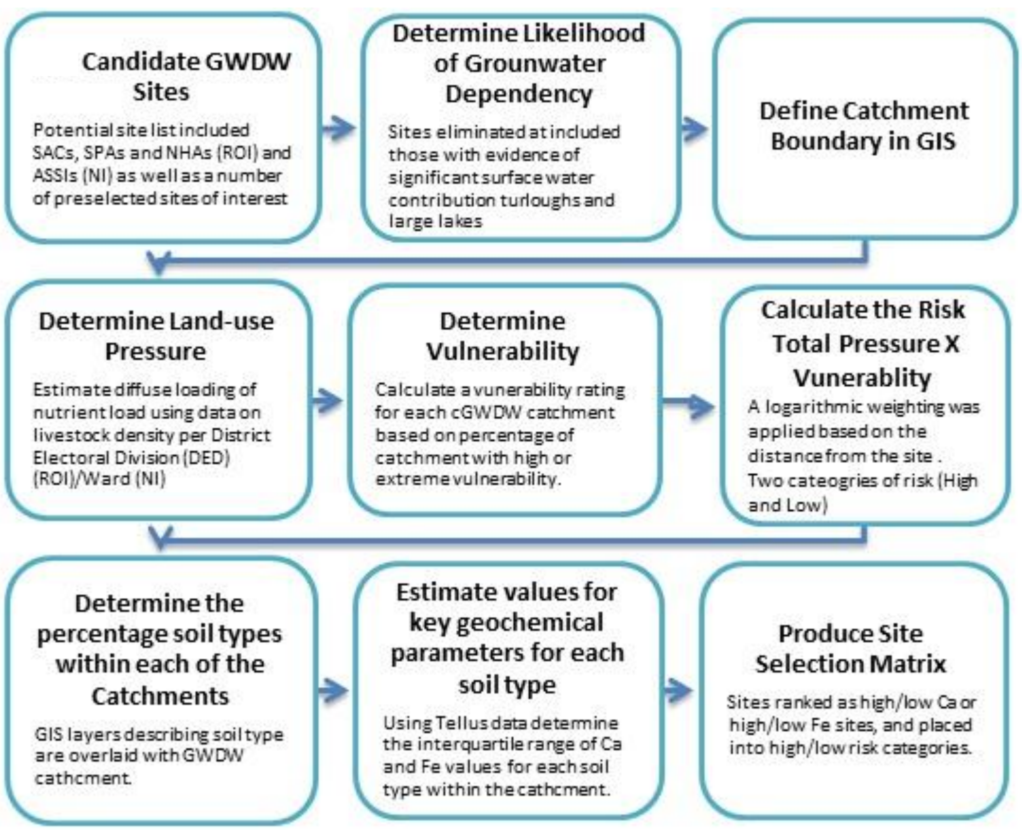



Fig 3. Schematic flow chart showing risk assessment methodology and site selection process utilised during the desk-based phase of the TIWEG project.

### 3.2.3 Estimating Pathway Susceptibility

The geological and hydrogeological characteristics of the deposits influencing processes operating in the pathway between the ground surface and the water table will influence the attenuation of contaminants. The current study investigated groundwater vulnerability, soil geochemistry and distance from the wetland site as the principal influences on nutrient delivery rates to GWDWs.

Establishing a risk ranking system for all GWDW sites considered in the desk-based study required a common scheme for assessing both vulnerability and nutrient loading in both NI and the RoI. Ball *et al.* (2005) viewed groundwater vulnerability as the tendency and likelihood for general contaminants to reach the water table after introduction at the ground surface. Although this generic definition is consistent for the schemes developed in both jurisdictions, the details of the schemes differ. Groundwater vulnerability maps for the RoI have been produced by the GSI, which define five vulnerability classifications depending on depth to bedrock (Table 2). In NI, groundwater vulnerability maps produced by the GSNI also have five vulnerability categories (Table 3). However, these categories are defined using a different depth to bedrock classifications system than those employed by the GSI.

The two vulnerability schemes cannot be compared directly in some cases. Consequently, a new set of categories was proposed and employed in order to allow the two systems to be merged (Table 4).

**Table 2. Groundwater vulnerability classifications of map produced by GSI**

| Hydrological Requirements for Vulnerability Categories | | | | | |
|---|---|---|---|---|---|
| **Depth to rock (m)** | *Diffuse recharge* | | | *Point recharge* | *Unsaturated zone* |
| | High permeability (sand/gravel) | Moderate permeability (sandy subsoil | Low permeability (clayey subsoil, clay, peat) | Karstic environments | Sand and gravel aquifers |
| **0-3** | Extreme | Extreme | Extreme | Extreme (30m radius) | Extreme |
| **3-5** | High | High | High | N/A | High |
| **5-10** | High | High | Moderate | N/A | High |
| **>10** | High | Moderate | Low | N/A | High |

Sourced: (DoELG, 1999)

**Table 3. Groundwater vulnerability classifications of map produced by GSNI**

| Hydrological Requirements for Vulnerability Categories | | | | | |
|---|---|---|---|---|---|
| **Depth to rock (m)** | *Diffuse recharge* | | | *Point recharge* | *Unsaturated zone* |
| | High permeability (sand/gravel) | Moderate permeability (sandy subsoil | Low permeability (clayey subsoil, clay, peat) | Karstic environments | Sand and gravel aquifers |
| **1-3** | 4 | 4 | 4 | 5 | 4 |
| **3-10** | 4 | 3 | 2 | N/A | 4 |
| **10-30** | 3 | 2 | 1 | N/A | 3 |
| **>30** | 2 | 1 | 1 | N/A | 2 |

Source: Ball et al. (2005) table assembled based on a collection of tables

**Table 4: Reclassified Groundwater vulnerability classifications.**

| **Hydrological Requirements for Vulnerability Categories** | | | | | |
|---|---|---|---|---|---|
| **Depth to rock (m)** | *Diffuse recharge* | | | *Point recharge* | *Unsaturated zone* |
| | High permeability (sand/gravel) | Moderate permeability (sandy subsoil | Low permeability (clayey subsoil, clay, peat) | Karstic environments | Sand and gravel aquifers |
| **0-3** | 3 | 3 | 3 | 4 | 3 |
| **3-10** | 3 | 3 | 2 | N/A | 3 |
| **10-30** | 3 | 2 | 1 | N/A | 3 |
| **>30** | 2 | 1 | 1 | N/A | 2 |

It was considered, based on modelling of contaminant transport using analytical solutions, that nutrient loading concentrations can decline logarithmically with distance from source. Model outputs suggest that contamination originating from a source close to a receptor will undergo little or no attenuation compared to those further away. In order to account for the variation in the attenuation of contaminants with distance from a receptor, the wetland catchments were divided in four zones (100 m, 200 m, and > 400 m from the wetland site boundary). Three different scoring systems developed by McKernon (2013) were applied to each vulnerability category, and weighted with distance from a GWDW to investigate the variation in risk closer to a site. A risk ranking sensitivity analysis was then carried which found that the application of different distance weighted systems had limited impact on calculated risk ranking (Fig. 4). The GIS layers for each GWDW catchment permitted the product of loading and vulnerability to be calculated to generate a risk value which ranged from 1 (high risk) – 86 (low risk). Values for all sites investigated were ranked to assess the relative risk of eutrophication for all sites considered.

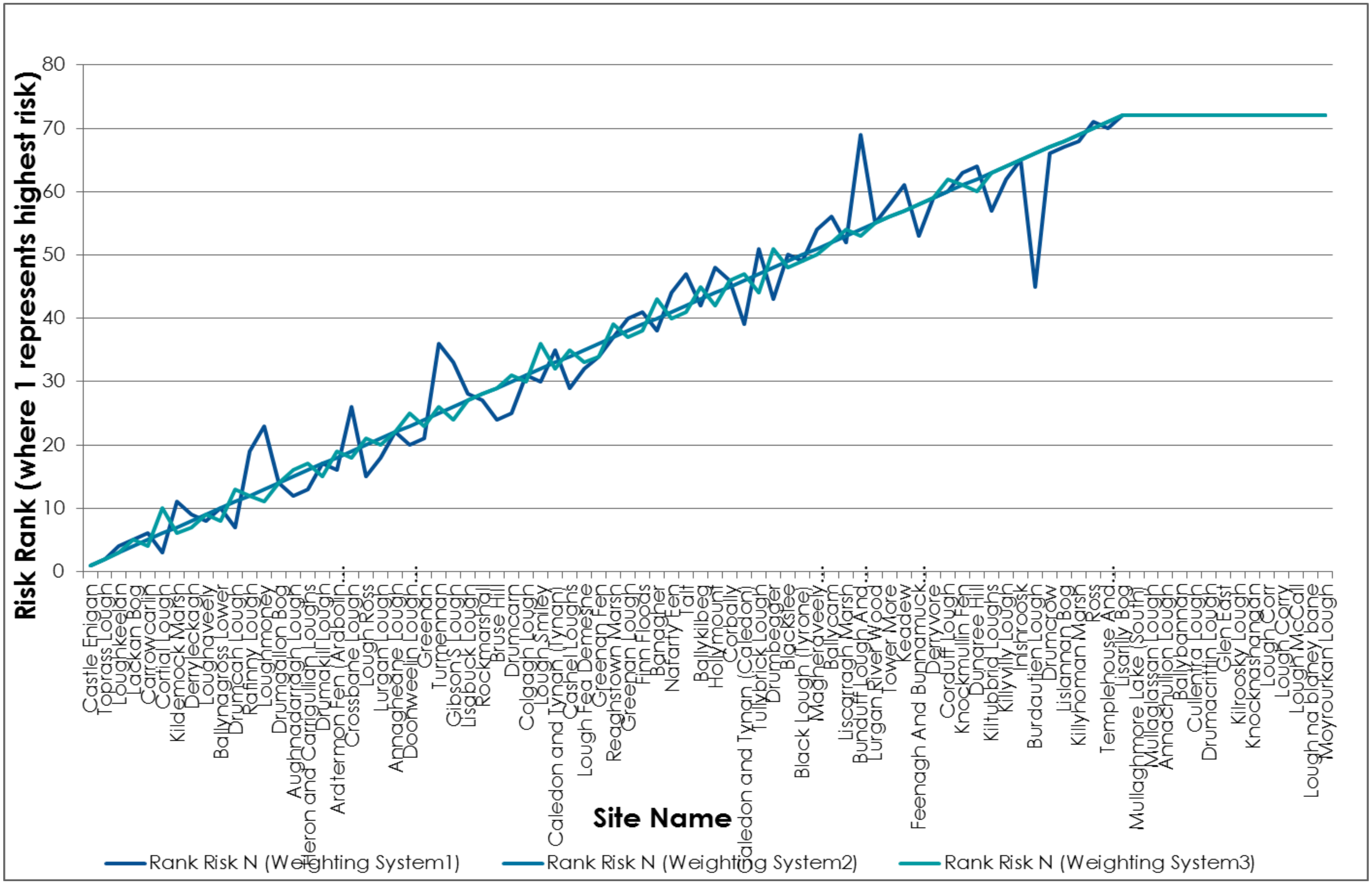



Fig. 4 Assessment of the sensitivity of nitrogen rankings using weighting systems based on proximity to diffuse agricultural loadings to groundwater dependent wetland receptors at candidate sites (From McKernon, 2013).

### 3.2.4 Estimating Impact Potential-Soil Geochemistry

Soil geochemistry was the final factor considered in investigating risk of eutrophication. GIS data layers were applied to catchment boundary maps at each site to identify and calculate the percentage of each soil type within the catchment. Topsoil maps for NI were obtained from the Agri-Food and Biosciences Institute (AFBI), while those for RoI were generated by Teagasc. The approach identified a total of 31 topsoil categories in the catchments of sites in NI and 29 for sites in the RoI (in this instance merger of the datasets was not undertaken owing to the large number of soil types involved and the wide range of variability between each category).

Given the TIWEG project's time constraints, investigations focused on the role of a subset of soil (and subsoil) geochemical parameters that had reported impacts on nutrient fate and transport in the scientific literature. These were Fe and Ca, which have been demonstrated to influence phosphate mobility (Corbett *et al.* 2002; Robertson, 1995; Krom and Berner, 1980), and have been shown to influence phosphate fate and transport in the near surface in studies completed in the border region (Jordan *et al.* 2005). Iron oxides have been demonstrated to have a dramatic effect on limiting phosphate mobility through adsorption, while calcium carbonate can both adsorb and co-precipitate phosphate from solution (House, 1990).

In a similar vein, organic matter was investigated in the Tellus datasets through the loss on ignition (LOI) surrogate. Organic matter has a demonstrated impact on the fate and transport of nitrate in the subsurface, where its presence is conducive to generating the low oxygen/anoxic conditions needed to permit denitrification. Iron, in its reduced form as pyrite, has also demonstrated capacity to cause denitrification, although the media involved are typically in lower permeability units which occur in catchments where nearer surface and surface hydrological pathways play a more important role in delivering nutrients to ecological receptors (Rivett *et al.*, 2008).

Tellus (Tellus Border and Tellus) data on soil geochemistry were used to generate summary statistics to establish the range of Fe, Ca and LOI values for each soil type for both NI and RoI datasets. Tellus sampling points were intersected with the GIS data layers on soil type. The median, $25^{th}$ percentile and $75^{th}$ percentile of each element was calculated for each soil type.

The percentage of each soil type within a catchment was then multiplied by the median Ca and Fe values for that soil type and then catchments were classified as high/low Ca, high/low Fe and high/low LOI sites. This approach permitted catchments to be placed into high/low risk categories by combining results with existing risk ranking and provided an objective measure of pathway susceptibility and nutrient impact potential. This in turn permitted the development of a risk ranking for all sites under consideration, while also allowing for the development of a risk category for each site, based on nutrient loading and soil geochemistry.

This risk ranking was then used to generate a site selection matrix in which a subset of nineteen sites were selected for field investigation. These sites were representative of each of the risk categories as defined during the risk categorisation process (Table 5).

Table 5. Site Selected for further investigation based on risk based categorisation and soil geochemistry characteristics.

<table>
<tr><th rowspan="3">Risk</th><th colspan="4">High Calcium</th><th colspan="4">Low Calcium</th></tr>
<tr><th colspan="2">High Iron</th><th colspan="2">Low Iron</th><th colspan="2">High Iron</th><th colspan="2">Low Iron</th></tr>
<tr><th>High LOI</th><th>Low LOI</th><th>High LOI</th><th>Low LOI</th><th>High LOI</th><th>Low LOI</th><th>High LOI</th><th>Low LOI</th></tr>
<tr><td>High</td><td>Drumcah<br>Nafarty</td><td>Toprass<br>Tullybrick</td><td></td><td>Bruse Hill</td><td>Greenan Lough<br>Rockmarshall</td><td>Loughaveely</td><td>Derryleckagh.<br>Greenan<br>Talt</td><td>Loughmoney<br>Turmennan</td></tr>
<tr><td>Low</td><td>Liscarragh</td><td></td><td>Lackan</td><td>Keadew<br>Kilroosky</td><td></td><td></td><td>Corry</td><td>Mullaghmore</td></tr>
</table>

# 4. Field Site Investigation

Each of the 19 sites selected for further field-based investigation were visited between July and August 2013. At each site surface water grab samples were taken from the wetland inflows, outflows and open water. Consequently, the number of samples varied per site depending on the number of inflows and outflows. Nevertheless, a minimum of three and maximum of five surface water samples were taken at each site. A handheld Garmin Etrex Global Positioning System (GPS) provided coordinates for each sampling location. Water samples were collected in 1 L acid washed, deionised water-rinsed polypropylene containers and transported to the laboratory in cooled insulated boxes and stored at 4°C before analyses within 48 hours of collection. Conductivity, temperature, pH and dissolved oxygen were measured on-site during sampling using a YSI® multiprobe (Model 556 MPS).

A minimum of three and a maximum of five topsoil samples (5 – 20 cm depth) were taken from representative soil types (as indicated by published maps) in the land directly surrounding the wetland site using a Dutch handheld auger. GPS coordinates were also taken at each of these sampling points. Soils were stored in polythene bags and placed in cool boxes prior to preparation and analysis. Soil samples were oven dried at 40 °C prior to analyses. Dried soils were then sieved through a 2 mm mesh, homogenized and ground down using a pestle and mortar. Dried soils were stored in labeled brown paper bags at room temperature.

## 4.1 Laboratory Analyses

### 4.1.1 Surface Water Analyses

Dissolved nutrient analyses (soluble reactive phosphorus (SRP) and dissolved inorganic nitrogen (DIN; nitrate ($NO_3^-$-N) + nitrite ($NO_2^-$-N) + ammonia ($NH_3^+$-N)) were made on water filtered through 0.45 µm Whatman® membrane filters. Phosphorus and nitrogen analyses were carried out colometrically using a flow injection auto-analyser (Lachat Quickchem®, Lachat Instruments, Loveland, Colorado, USA). Nitrate and nitrite, SRP and ammonia were determined following QuickChem® Methods 10-107-04-1-R, 10-115-01-1-V and 10-107-06-2-L, respectively.

Alkalinity was analysed on 50 ml of an unfiltered sample of water by Gram titration according to Mackereth *et al*. (1978). Suspended solids and suspended particulate organic matter were obtained following Allen (1989). Dissolved Organic Carbon (DOC) was analysed on samples filtered through 0.45 µm Whatman® membrane filters and analysed using a UV promoted persulfate oxidation method detected on a TOC analyser (Sievers® 5310C Laboratory TOC Analyzer), using a nondispersive infrared detector following Potter and Wimsatt (2005).

### 4.1.2 Soil Analyses

A weighed aliquot (0.5 g) of dry sediment was placed in a pre-weighed crucible and oven dried over night at 105°C and re-weighed to obtain the dry weight. The samples were then placed in a furnace for 4 hours at 550°C to determine organic matter content by loss on ignition (LOI) according to Heiri (2000).

Approximately 10 g of soil was added to a beaker with 25 ml of deionised water (DI) and the mixture stirred vigorously for one minute, then allowed to settle and the pH was measured using an Orion™ 3-star Plus benchtop pH probe. Each suspension was stirred vigorously using a glass rod immediately pror to pH determination.

A known amount (approx.0.5 g) of dry, homogenized soil was extracted in 10 ml of nitric acid. The acid/sediment mix was placed in fluorocarbon polymer microwave vessels, sealed and heated in a CEM® Mars microwave digester (US EPA 3051A). Following digestion the samples were filtered through Whatman® 42 filter paper and diluted as appropriate. Flame Atomic Absorption Spectrometry (FAAS) was used to determine the concentration of Ca and Fe. Samples were analysed using element specific hollow cathode lamps on a Varian® AA240 spectrometer with an air-acetylene flame (APHA, 1975). Standard curves were developed for each element over the instrument's optimum detection range using the appropriate Reagecon® AA commercial standards. Quality control and instrument blanks were analysed every 15 samples.

At the outlet sampling point at subset of sites considered suitable for macroinvertebrate sampling a 1 mm mesh size pond net was used to collect a representative sample

macroinvertebrates. Samples were stored in 90 % Industrial Methylated Spirits (IMS) in labelled storage bottles. Samples were then sorted in the laboratory and grouped according to their taxonomic Order and used to calculate the EPA Q-value system, which is a biotic index used to assess water quality of streams and rivers and commonly employed in Ireland. The values produced for this study must be viewed with caution given that the Q-value system was not designed for stream beds with mud or sand substrate or sluggish water.

# 5. Results

## 5.1 Use of Tellus and Tellus Border soil data to predict geochemical conditions

Tellus and Tellus Border geochemistry data was utilised in this study in conjunction with groundwater vulnerability to determine pathway susceptibility in the development of a risk assessment to establish risk of impact to GWDWs from various landuse practices. Soil and water samples were then taken and analysed in a set of 19 GWDW sites in order to validate the field methodology.

Understanding geochemical factors influencing nutrient fate and transport along subsurface pathways requires knowledge of subsoil geochemistry. The absence of subsoil Tellus Border geochemical data for the RoI and the lack of availabile subsoil maps for NI prevented a comprehensive investigation of geochemical interactions between specific topsoils and subsoils in this study. Nevertheless, it was possible to investigate the relationship between topsoil and subsoil geochemical content using Tellus (NI) data sets. For the soil types investigated a correlation was observed between topsoil and subsoil Fe concentrations ($r^2$ = 0.93, Fig. 5), and topsoil and subsoil Ca concentrations ($r^2$ =0.86, Fig. 6). More specific investigations of Fe and Ca content for each soil type permitted levels of elemental enrichment or depletion to be estimated (analyses in Mc Kernon, 2013). This suggests that the vertical distribution of elements are broadly similar at different soil depths and demonstrated the utility of using the topsoil data as a surrogate for subsoil data in the Tellus Border data set, for which subsoil geochemistry data was unavailable at the time of this study.

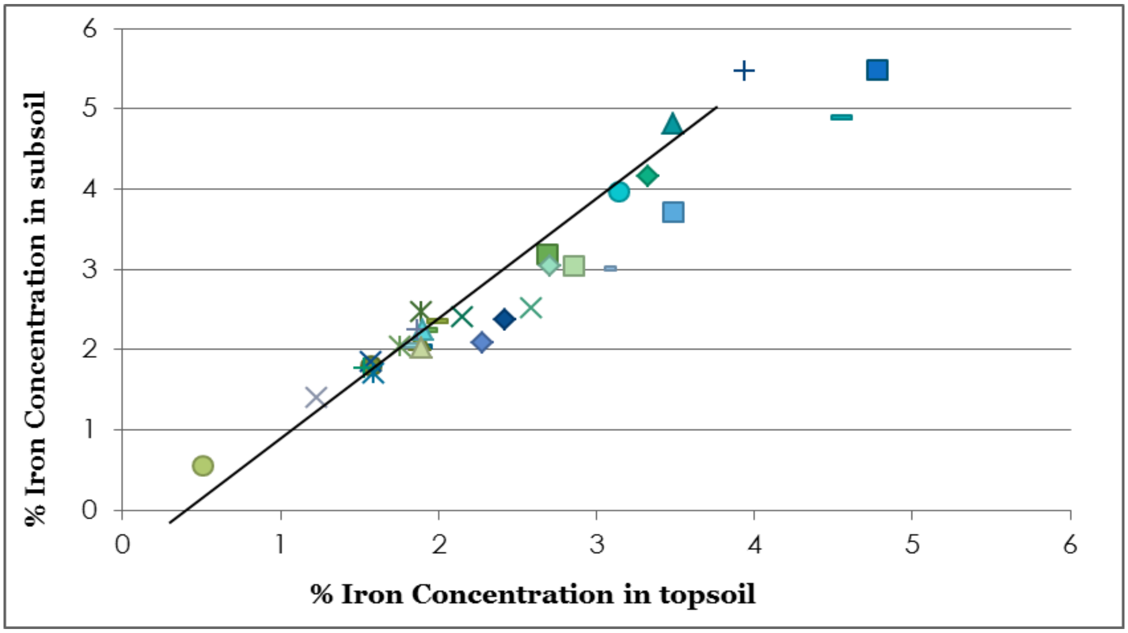



Fig. 5 Relationship between Tellus (NI) topsoil and subsoil iron (Fe) concentrations. Points represent median soil and subsoil concentrations by soil type, as mapped by AFBI.

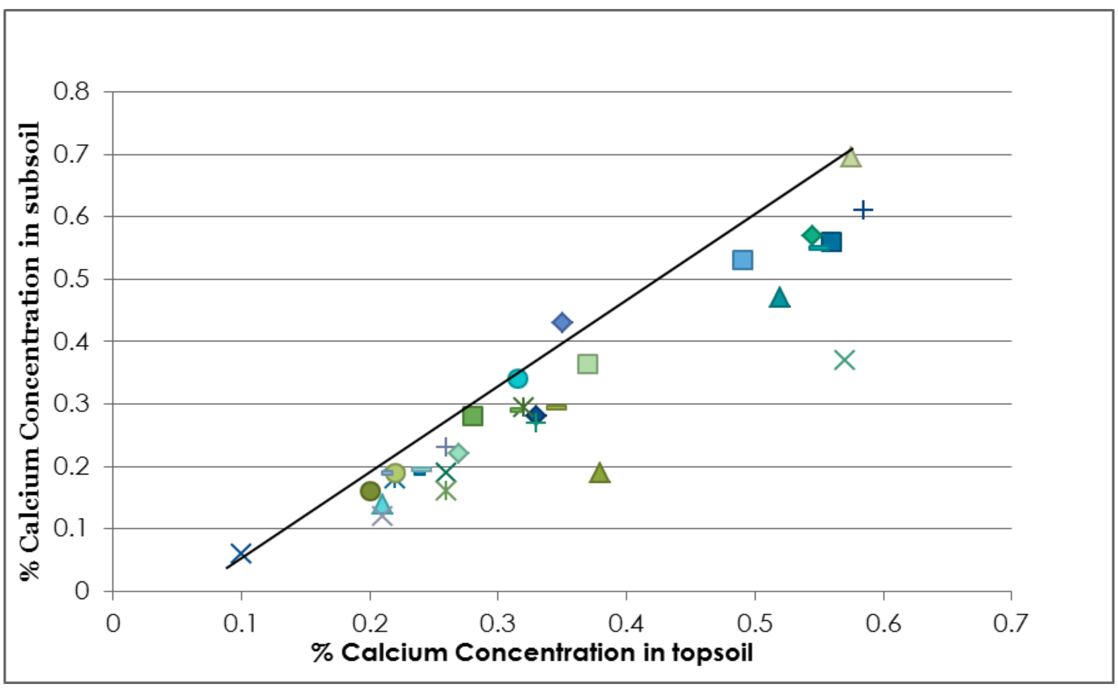
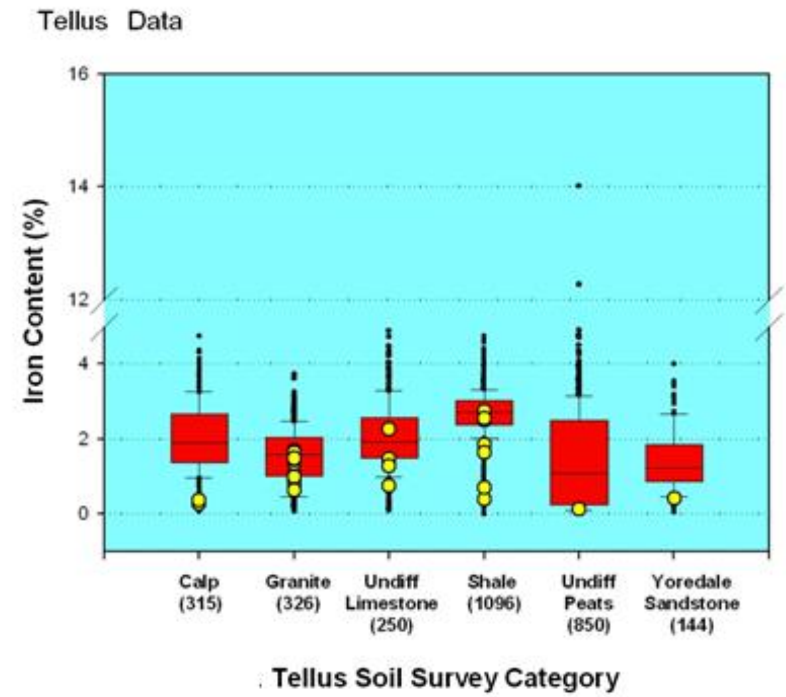



Fig. 6 Relationship between Tellus (NI) topsoil and subsoil calcium (Ca) concentrations. Points represent median soil and subsoil concentrations by soil type, as mapped by AFBI.

The onsite soil samples collected at the field sites were classified into a total of 12 topsoil categories, according to geochemical characteristics ( six in NI and six in the RoI). Levels of Fe (Fig. 7), Ca (Fig. 8) and organic matter as measured as LOI (Fig. 9) in field soil samples compared favourably with those provided in the results of the Tellus and Tellus Border surveys for comparable soil units.

The majority of the topsoils types in both NI and RoI show a small range of Ca content between 0 – 5 %. The exception include calp and carboniferous sandstone-derived topsoils in NI and cutover peat, made ground metamorphic till, blown sand and blown sand in dunes in the RoI. In a similar way the bulk of the topsoil types in NI share a common range of iron concentrations between 0 – 6 %. Highest maximum Fe concentrations in the RoI were observed in blanket and cutover peat, but the majority Fe concentrations in these soil types actually fell below 1.32 % and 2.16 %, respectively. In contrast the values of LOI in both NI and RoI topsoil was highly variable (Fig. 10 and Fig. 11, respectively), with soils such as peats and to a lesser extent chalk-derived soils, felsite-derived soils and organic alluvium containing higher concentrations of organic matter.



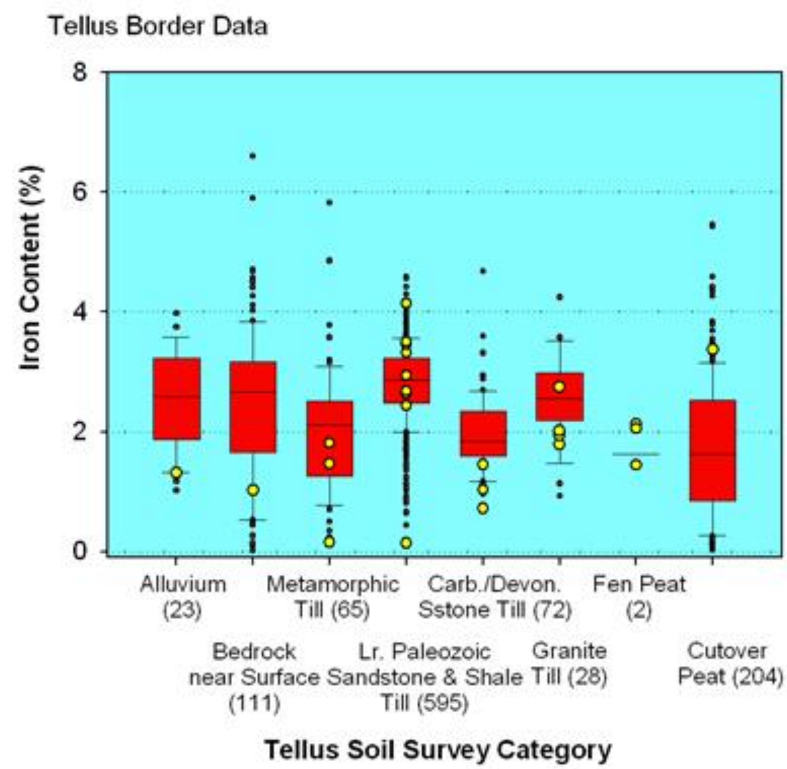




Fig.7 Comparison of iron (Fe) field results against the ranges determined using Tellus and Tellus Border data for selected soil types (sample size in parenthesis), field samples (yellow points).

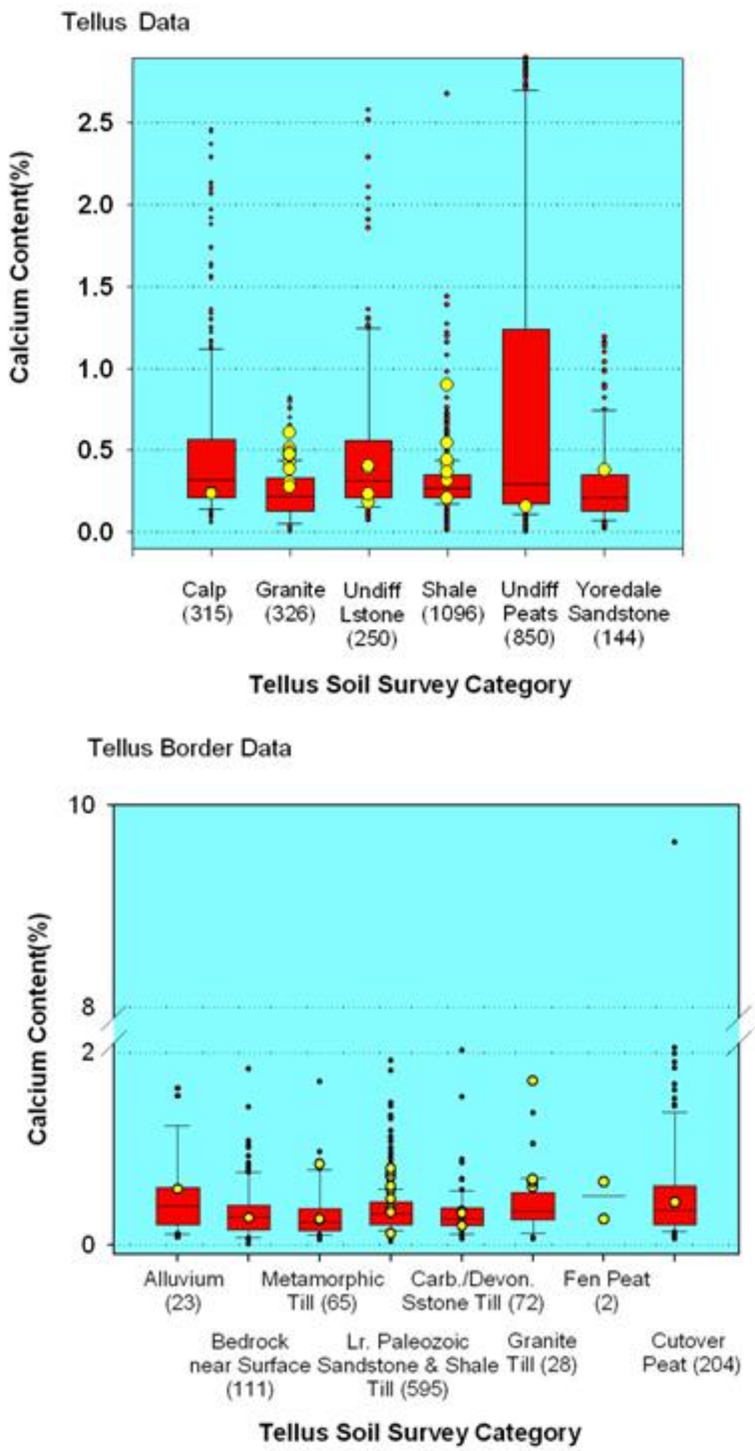



Fig. 8 Comparison of calcium (Ca) field results against the ranges determined using Tellus and Tellus Border data for selected soil types (sample size in parenthesis), field samples (yellow points).

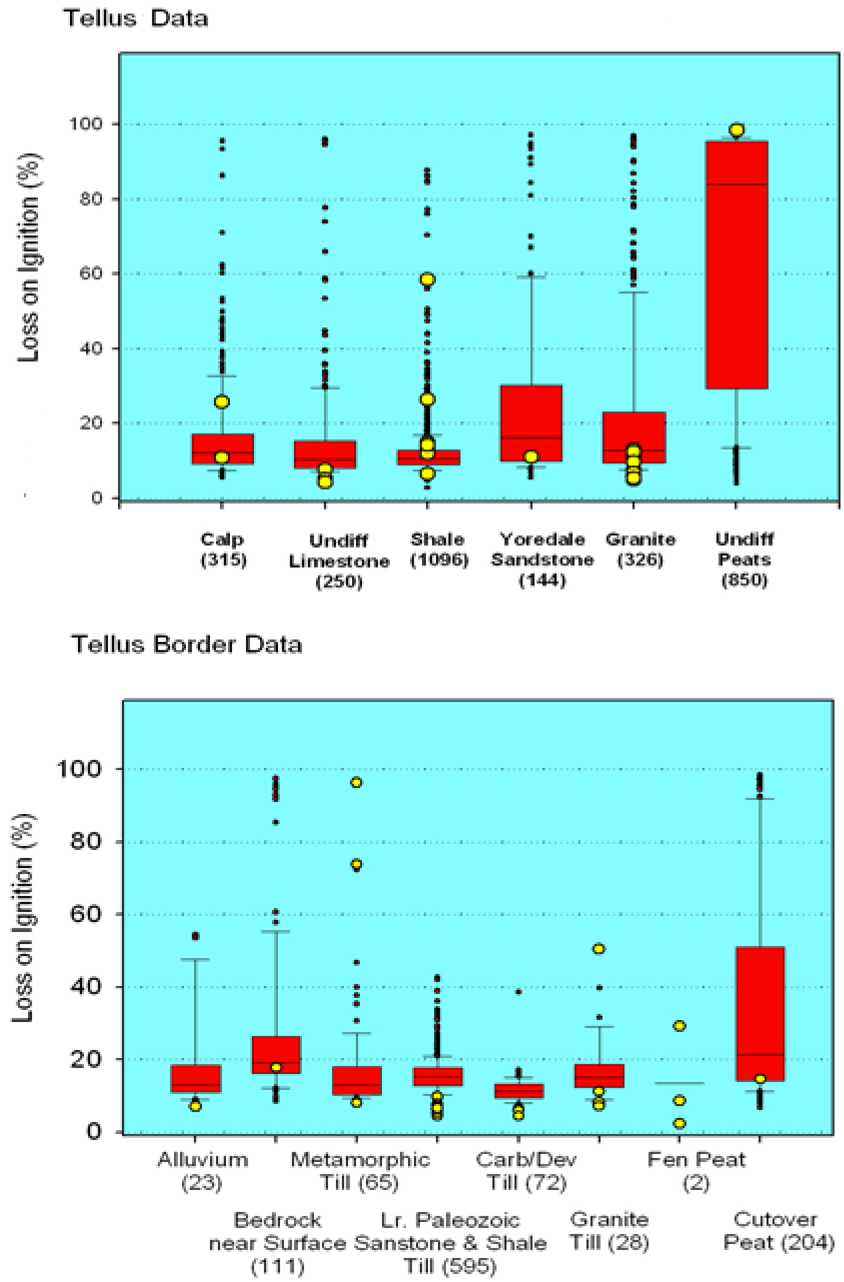



Fig. 9 Comparison of Loss on Ignition (LOI) field results against the ranges determined using Tellus and Tellus Border data for selected soil types (sample size in parenthesis), field samples (yellow points).

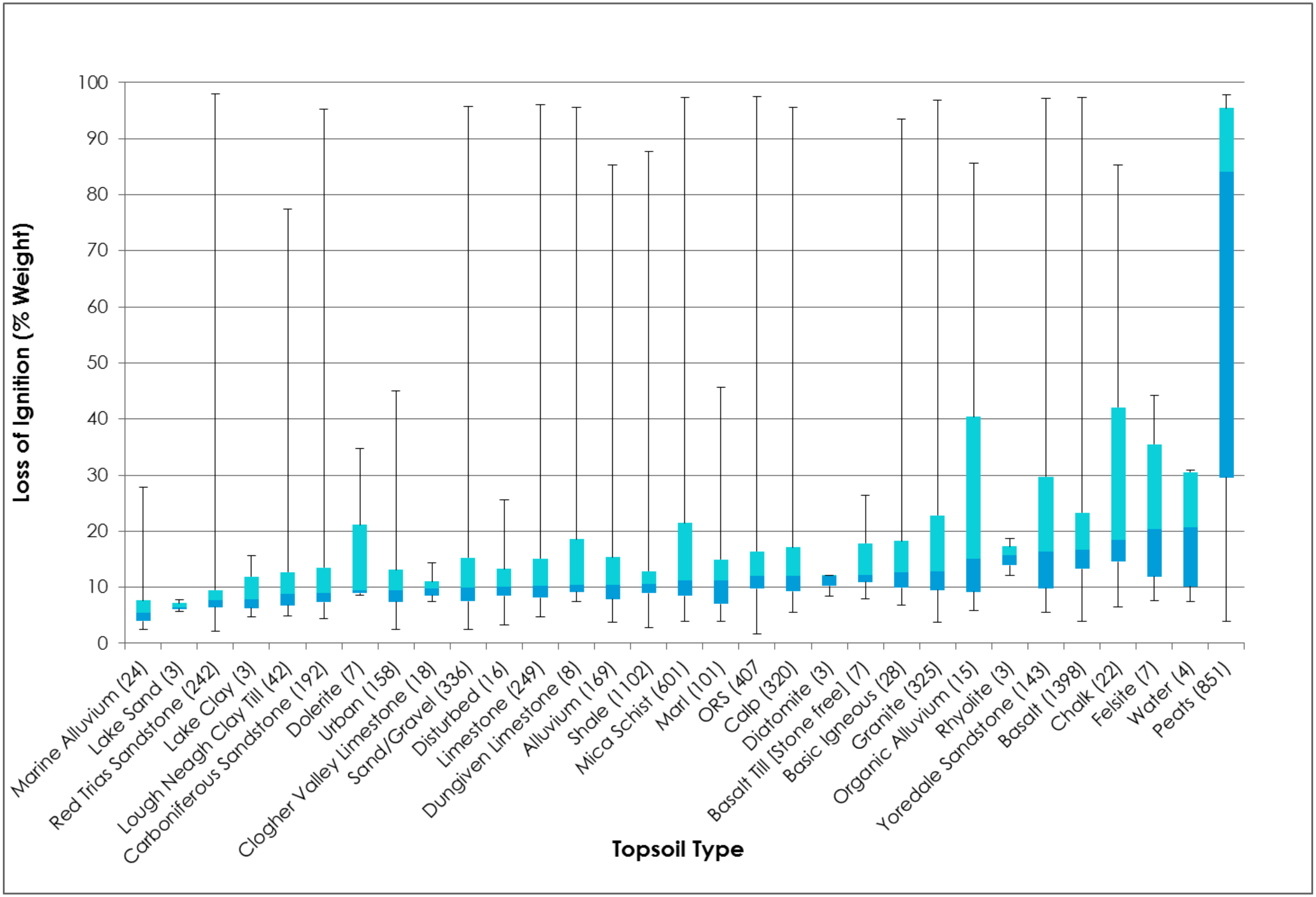


Fig 10. Distribution of Loss on Ignition (LOI) values for all top soil types in the Northern Ireland Tellus survey.

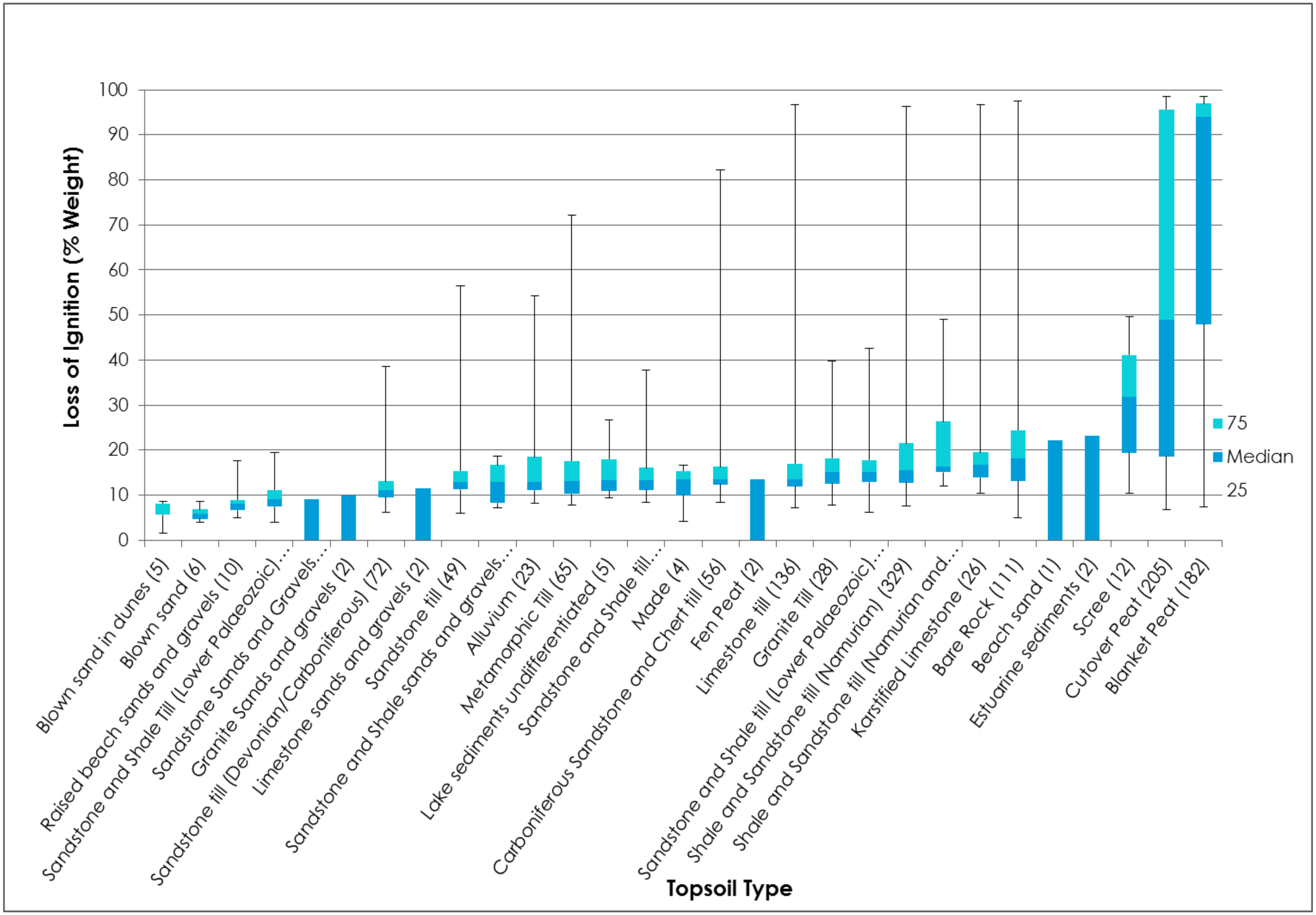



Fig 11. Distribution of Loss on Ignition (LOI) values for all topsoil types in the Republic of Ireland Tellus Border survey.

## 5.2 Nutrient loading

Nutrient loads varied between field sites (Table 6), with highest calculated loads of both N and P estimated at Toprass and Tullybrick and lowest loads at Lough Talt and Lough Corry, both of which were located in catchments dominated by peatlands.

Table 6. Estimated loadings of nitrogen and phosphorus and each of the groundwater dependent wetland sites and estimated risk ranking (1 (high risk) - 86 (low risk)).

| Site Name | Nitrogen Loading Kg/Ha | Phosphorus Loading Kg/Ha | Nitrogen Risk Ranking | Phosphorus Risk Rank |
|---|---|---|---|---|
| **Drumcah** | 348.9 | 54.2 | 11 | 11 |
| **Greenan** | 246.6 | 39.9 | 24 | 23 |
| **Greenan Lough** | 317.5 | 52.0 | 38 | 38 |
| **Keadew** | 176.8 | 27.6 | 57 | 57 |
| **Kilroosky** | 259.6 | 40.2 | 72 | 72 |
| **Lackan Bog** | 382.2 | 60.9 | 4 | 3 |
| **Lough Corry** | 0.0 | 0.0 | 72 | 72 |
| **Lough Talt** | 85.8 | 14.2 | 43 | 43 |
| **Loughaveeley** | 365.5 | 56.4 | 9 | 10 |
| **Loughmoney** | 357.8 | 55.8 | 13 | 13 |
| **Mullaghmore** | 285.0 | 43.7 | 72 | 72 |
| **Rockmarshall** | 213.8 | 37.9 | 28 | 24 |
| **Toprass** | 409.7 | 101.5 | 2 | 2 |
| **Tullybrick** | 409.3 | 90.3 | 42 | 41 |
| **Turmennan** | 252.4 | 39.8 | 25 | 25 |

The contribution of point sources to the overall nutrient loading from anthropogenic sources was estimated as marginal at the majority of sites and rarely exceeded 1 % of the overall nutrient load (Fig. 12 and 13). The percentages of nutrients from point sources was greatest in Rockmarshall and Nafarty Fen (up to 3 %). Lough Corry was the only site at which no point or diffuse sources of nutrient loading could be applied. This

catchment is dominated by forestry and peatlands and it is likely that it received little nutrient input from anthropogenic activities, following planting of trees.

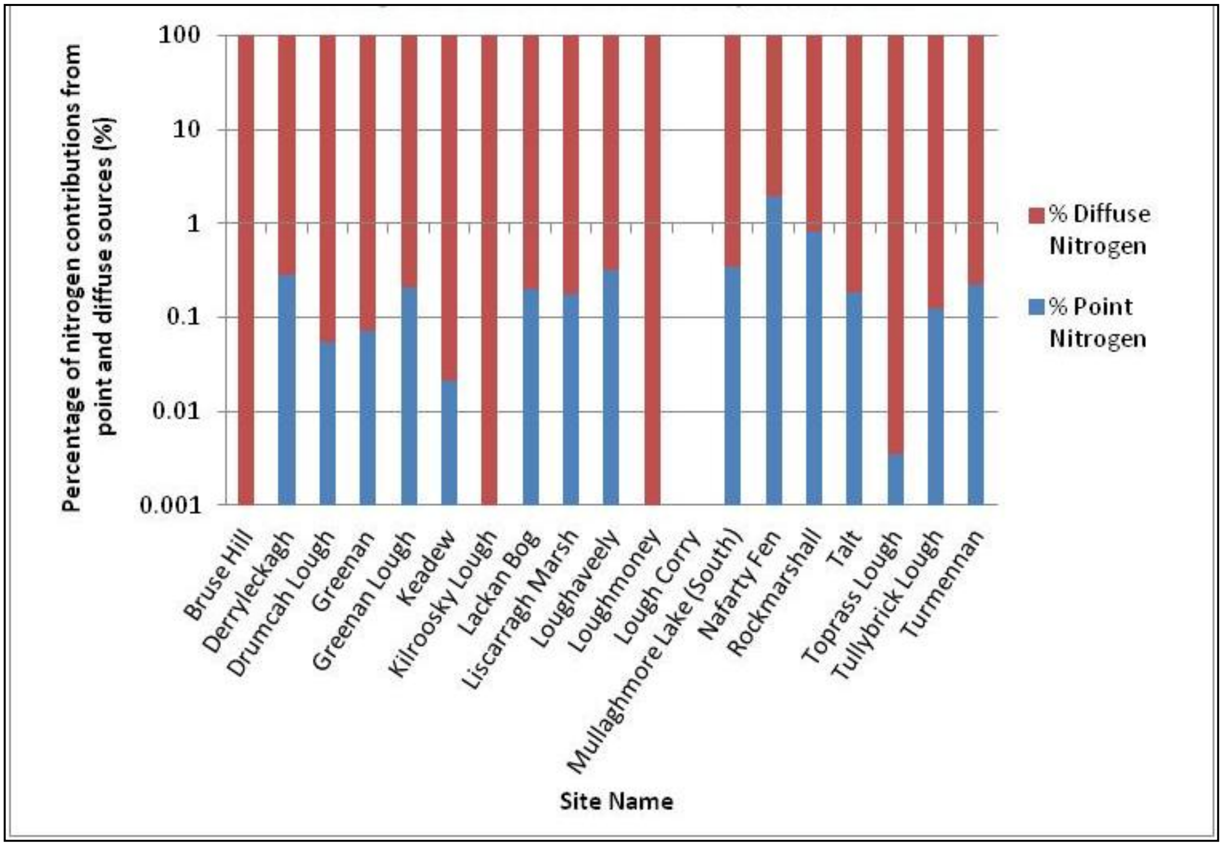



Fig. 12 Percentage relative contribution of diffuse and point source nitrogen loading within each groundwater dependent wetland catchment calculated for sites sampled during TIWEG field-based investigation. Note the use of the logarithmic scale on the y axis.

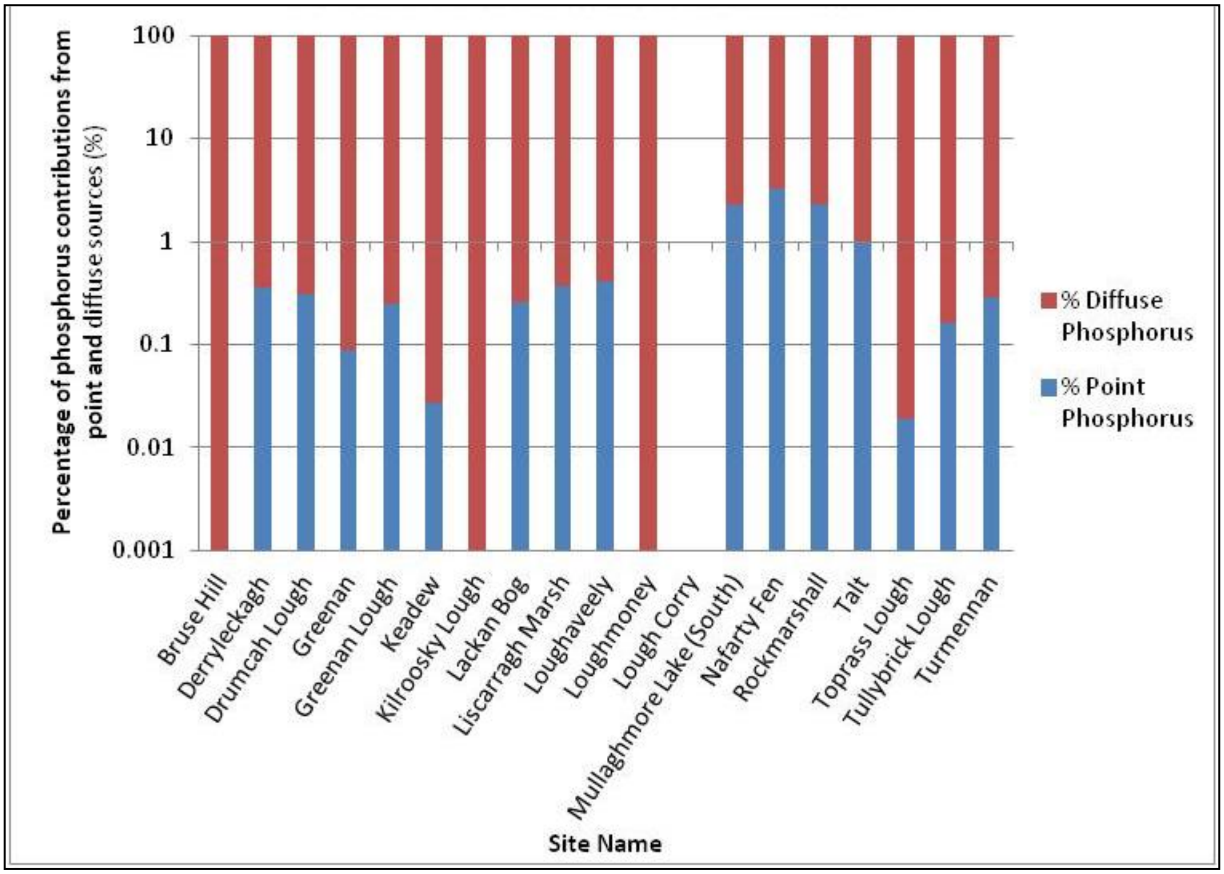



Fig.13 Percentage relative contribution of diffuse and point source nitrogen loading within each groundwater dependent wetland catchment calculated for sites sampled during TIWEG field-based investigation. Note the use of the logarithmic scale on the y axis.

## 5.3 Surface water nutrient concentrations at GWDW sites

Low nutrient concentrations in surface water samples were recorded at the majority of sites, both within the wetland, and at the outflow of the site, with values of orthophosphate generally falling below values considered to lead to eutrophication (0.03 mg $L^{-1}$-P; Lucey *et al.*, 1999). Highest aqueous nutrient concentrations of dissolved inorganic nitrogen (DIN) within the wetland site were recorded at Derryleckagh in addition to Liscarragh and Naferty, both of which were found to have the high point source nutrient contributions following the desk based risk assessment. High

concentrations of orthophosphate were recorded at Rockmarshall, with Turmennan and Greenan also recording high total P values with a mean ± SE of 1.16 ± 0.96 mg $L^{-1}$ and 1.10 ± 0.56 mg $L^{-1}$, respectively recorded at these sites (Table 7). The mean ± SE total phosphorus concentrations for all sites was 0.51 ± 0.15 mg $L^{-1}$ with the lowest concentrations recorded in Lough Talt and Toprass (0.01 mg $L^{-1}$ and 0.02 mg $L^{-1}$, respectively). However, apart from these two sites, the majority of sites had a mean value above the threshold value of 0.06 mg $L^{-1}$-P considered to be indicative of eutrophication (EPA, 2001). In addition, Macroinvertebrates community structure at those sites analysed showed that the majority of sites sampled were moderately polluted based on the EPA Q-value system (Q 3 or Q 3-4). Lower Q-values of Q 2-3 were recorded at Loughaveely and Greenan Lough which is indicative of serious pollution. These values must be treated with caution, however, as the Q-value system was designed for rivers and streams with fast flowing water. Further analyses is ongoing at these sites to assess more detailed macroinvertebrate community structure and seasonal change.

Some differences were observed between N and P values recorded within GWDWs and those at the outflow at some sites. For example, very high concentrations of DIN were recorded at the outflows of Greenan Lough, Kilroosky and Mullaghmore compared to the wetland site itself, and high concentrations of orthophosphate at the outflows of Kilroosky and Toprass were recorded compared to those within the wetland.

Table 7. Surface water dissolved inorganic nitrogen (DIN) and orthophosphate concentrations recorded within each of the groundwater dependent wetland sites and at the outflow of each site.

| Site Name | DIN (mg/l N) | | Orthophosphate (mg/l P) | |
|---|---|---|---|---|
| | **Onsite** | **Outflow** | **Onsite** | **Outflow** |
| **Drumcah** | 0.05 | 0.09 | 0.01 | 0.23 |
| **Greenan** | 0.32 | | 0.02 | |
| **Greenan Lough** | 0.07 | 1.41 | 0.05 | 0.07 |
| **Keadew** | 0.17 | 0.65 | 0.01 | 0.02 |
| **Kilroosky** | 0.08 | 1.83 | 0.02 | 0.25 |
| **Lackan Bog** | 0.30 | 0.39 | 0.08 | 0.04 |
| **Lough Corry** | 0.16 | 0.24 | 0.003 | 0.01 |
| **Lough Talt** | 0.05 | 0.05 | 0.01 | 0.01 |
| **Loughaveeley** | 0.09 | 0.37 | 0.01 | 0.02 |
| **Loughmoney** | 0.17 | | 0.04 | |
| **Mullaghmore** | 0.04 | 1.08 | 0.01 | 0.02 |
| **Rockmarshall** | 0.56 | 1.84 | 0.09 | 0.05 |
| **Toprass** | 0.06 | 0.50 | 0.01 | 0.07 |
| **Tullybrick** | 0.20 | 0.50 | 0.02 | 0.01 |
| **Turmennan** | 0.06 | | 0.01 | |
| **Bruse Hill** | 1.20 | | 0.02 | |
| **Derryleckagah** | 3.57 | 0.43 | 0.04 | 0.03 |
| **Liscarragh Marsh** | | 2.32 | | 0.08 |
| **Naferty** | 1.60 | 2.46 | 0.02 | 0.01 |

## 5.4 Relationship between risk score and nutrients at GWDW Field sites

The risk ranking used in this study provided an estimate the likelihood of impact to GWDW from potentially polluting landuse practices in GWDW catchments. Comparison with nutrient concentrations at the 19 field sites selected for investigation was used to assess the usefulness of this risk scoring. In order to do this, those sites with high percentage contribution from point sources such as Nafarty Fen and Liscarragh Marsh, were removed from the analyses in order to better reflect the impact of diffuse source of pollution, as was the outflows of Drumcah Lough and Tullybrick Lough, which were adversely impacted by evident point source pollution. There was a poor relationship observed between both values of dissolved inorganic nitrogen (DIN) and orthophosphate and risk score across all sites (Fig. 14), with high risk sites demonstrating considerable fluctuation, with high risk wetland sites recording both high and low onsite nutrient concentrations. This indicates that the impact of attenuation processes such as adsorption, precipitation, denitrification, soil storage and plant storage on nutrient availability is highly variable.

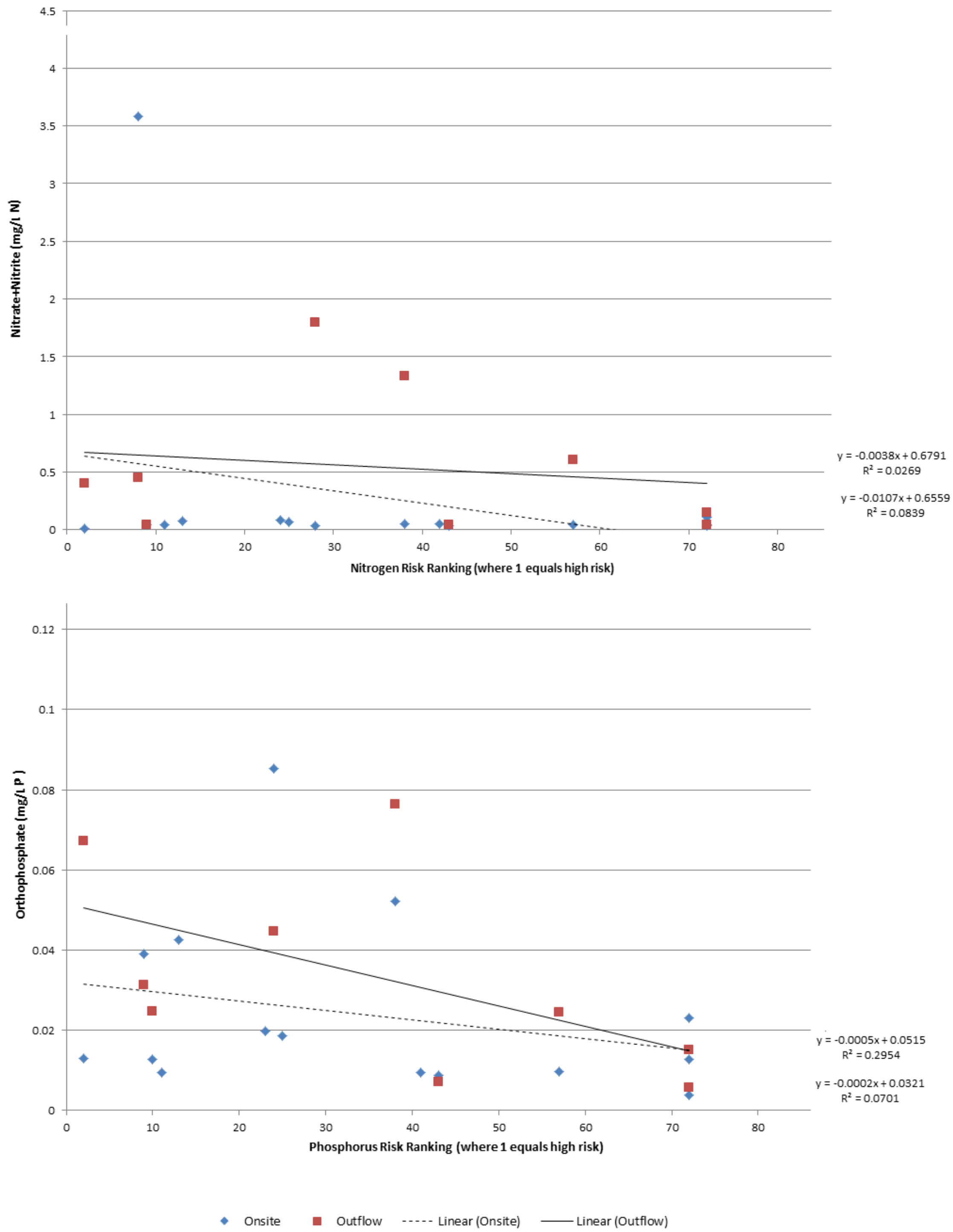



Fig. 14 Plots of nutrient concentration with risk ranking for groundwater dependant wetlands sampled during the TIWEG project.

# 6. Discussion

The results of the GIS-based element of the TIWEG investigation suggest that the risk to GWDWs from diffuse pollution across the area covered by the Tellus surveys varies significantly. This ranges from catchments with no visible pressures (e.g. Lough Corry, Co. Fermanagh) to sites surrounded by areas of intense agriculture (e.g. Tullybrick Lough, Co. Armagh). This variation arises partially from contrasts in nutrient loading, but also due to site physical setting and geological conditions.

The geochemical and physical properties of the soils and subsoils underlying GWDW catchments, coupled with the relative contribution of various hydrological pathways to their water balance, influence how landuse may impact receptors. Combining human and natural influences on water borne nutrient mobility constitutes a necessary step for understanding risk of impacts to ecological receptors in aquatic and wetland environments in this study. Combining vulnerability and landuse data provided a means of spatially assessing this issue. Moreover, calculation of a common metric allows relative risk (and associated risk ranking) to be established to facilitate comparison between sites.

The development of a common vulnerability scheme for NI and the RoI provided a means of assessing the influence of physical conditions in GWDW catchments. Similarly, nutrient loadings calculated for both jurisdictions, using DED data (RoI) and Electoral Ward census data (NI), provided a means for assessing the human element of risk posed to GWDWs (i.e. variations in diffuse nutrient applications between sites). Risk factors, calculated by combining vulnerability and nutrient loading data, thus permitted a common ranking system for assessing the impacts of landuse on GWDWs to be developed. Furthermore, refinement of risk ranking, using distance weighting factors, provided a method of investigating the relative influence of nutrient application distribution occurring in close proximity to a candidate sites, relative to catchment-wide loading.

The findings of investigations on the effect of nutrient application proximity on risk ranking, suggested that contrasting weighting factors had little impact on site rank. This in turn suggested that total nutrient application rates across wetland catchments played a more important role than the distance of application from ecological receptors in influencing the risk ranking for the sites considered.

It should be remembered that the influence of biogeochemical reaction is not considered in the conventional process for assessing the risk for groundwater pollution (combining vulnerability and loading) as described above. Geochemical conditions influence types and rates of chemical reaction. Incorporating geochemistry thus provides a potential means of taking into account a range of reactive processes. Combining maps of soils types, as mapped by AFBI and Teagasc in NI and RoI, respectively, with Tellus soil analyses provided a scientific basis for considering geochemical reactions that may influence nutrient fate and transport as water infiltrates through the soil. Fig. 10 and Fig. 11 summarise the range of LOI levels for the soil types encountered in the area surveyed in NI and RoI, respectively. McKernon (2013) presents comparable plots for iron and calcium. The results show that each soil type displays a considerable degree of spread in concentration. On the other hand, some levels in some soil types are distinct from those in others, e.g. Lough Neagh Clay vs Peats.

Merging the results of Tellus and Tellus Border surveys into a continuous dataset permitted maps of the entire survey area to be generated and soil geochemical results to be related to units on published AFBI and Teagasc maps (Fig. 15). Using the dominant soil types in each GWDW catchment permitted sites with soils containing high and low levels of LOI, Ca and Fe to be identified. Combining these parameters with risk ranking allowed selection of sites with comparable geochemical conditions but contrasting risk ranking. The 19 sites selected for further investigation following this protocol aimed to encompass the range of conditions encountered in GWDW catchments within the area covered by the Tellus surveys. Characterising nutrient fate and transport at depth in the

GWDW catchments proved more challenging, due to the lack of available subsoil analyses for the Tellus Border dataset. Plots of soil and subsoil elemental concentrations, generated from the Tellus NI soil and subsoil data sets, display a good correlation between Fe content and Ca content in soil and in subsoil for the soil types encountered. The results suggest that soil geochemical data may be used with a reasonable degree of confidence to assess subsoil levels of inorganic constituents in subsoil for samples collected during the Tellus Border survey. Moreover, further examination of the data by McKernon (2013) suggested that comparison of levels for mapped soil types permits elemental enrichment and depletion processes for particular soil/subsoil types to be identified.

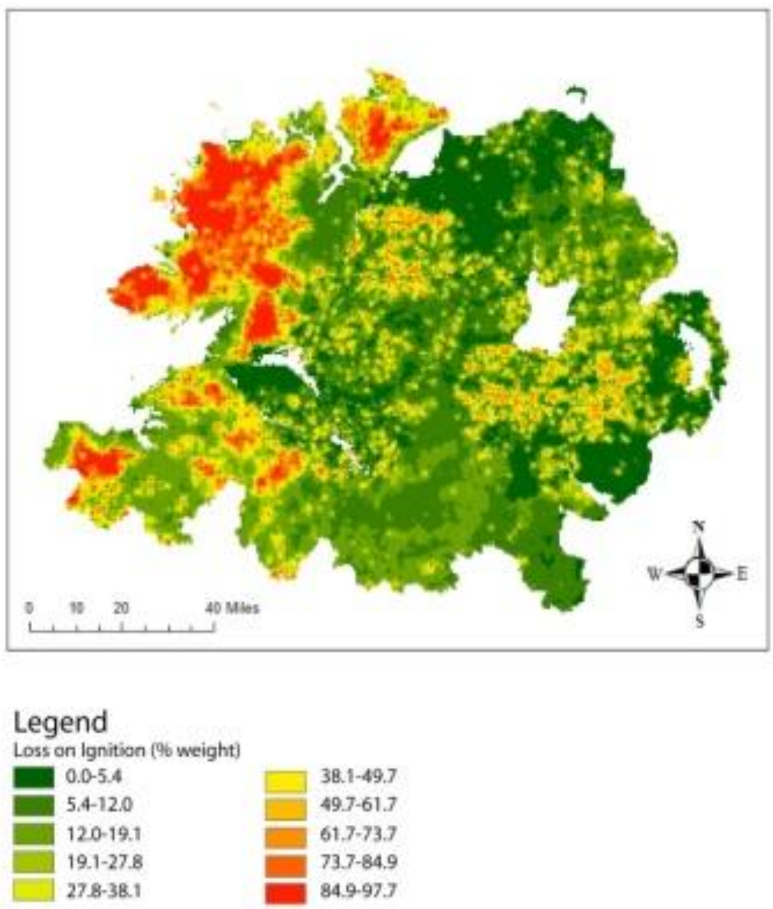



Fig. 15 Map showing of loss on ignition in soil samples for the area covered by the Tellus (NI) and Tellus Border (RoI) Surveys. Similar maps merging datasets from both surveys, have been generated for calcium and Iron (Mc Kernon, 2013)

The results of analyses of soil samples collected during the field-based aspect of the TIWEG report revealed that levels of Ca, Fe and organic matter (using LoI as a surrogate) compared favourably with those encountered in the Tellus survey for comparable soil units. This suggested that data collected during the Tellus surveys may be used as a screening tool for assessing soil geochemistry in the absence of site-specific data. On the other hand the high levels of overlap observed in the soil samples for the elements investigated suggest that employing data from individual analytes to investigate nutrient mobility may be insufficient and that consideration of composite geochemical datasets and/or complementary mineralogical analyses may be more appropriate.

Nutrient levels observed in surface water samples collected at the 19 field sites must be considered with caution, given that water quality at a sampling location may change with time and that concentrations observed at the time of sampling may not necessarily be representative of conditions at other times of the year. Nonetheless, the levels show a significant range of variation in both N and P concentration across the study sites. Poor relationships exist between the concentrations of dissolved inorganic nitrogen measured at wetland sites with the nitrogen loadings estimated during the risk assessment methodology. Similarly poor correlations were observed in plots of phosphate concentration with risk ranking. Further scrutiny of the dataset revealed some sites to be atypical, notably Nafarty Fen, impacted by urbanisation and Liscarragh Lough, which has a disproportionately high area of arable land in its catchment. Removal of these sites did little to improve overall correlation. However, it is noteworthy that onsite and outflow concentration data indicate that the range of variation in both nitrate and phosphate levels declines as the risk of enrichment goes down (reflected by increasing rank in the scoring system employed). The reason for variation in concentration with risk remains to be defined. Many high risk sites display concentrations comparable to sites with much lower risk levels. Examination of nitrogen to phosphate levels at each site suggest that although N/P ratios in catchments remain relatively stable at $6 \pm 0.5$,

(with two outliers at 4.2 ± 0.3,) N/P ratios observed in samples collected on-site from GWDWs range by over two orders of magnitude. Landuse data suggest that agricultural activity and loadings differ little between the sites considered, suggesting that the influence of differential uptake arising from different landuses may not be a significant factor leading to the contrasting nutrient ratios observed at each site. This in turn suggests that the contrast between nutrient levels applied and those observed at the GWDWs receptors may reflect differential degrees of attenuation by natural processes operating along subsurface pathways at sites investigated. This may be attributed, at least in part to (bio)geochemical reactions (if there were no attenuation apart from dilution, ratios of both nutrients would remain equal to those at source).

Identification of the reaction(s) responsible for contrasting nutrient levels remains unclear. High degrees of elemental overlap in contrasting soil types complicate interpretation. However, more detailed investigations at the Tellus wetland sites at Rockmarshall, Co. Louth revealed elevated nutrient levels in groundwater samples collected from points immediately adjacent to GWDW receptors. By contrast, water samples collected from the wetlands contained significantly lower levels. These findings suggest that *in-situ* processes acting in wetlands play an important, and possibly dominant, role in controlling nutrient levels delivered to an ecosystem. In the case of the Tellus study site at Rockmarshall, Co. Louth, nitrate levels in the wetland were over an order of magnitude lower than concentrations in groundwater (Fig. 16). Biogeochemical processes operating as groundwater discharges to the wetland are believed to be responsible for the reduction in concentration. Distinguishing between these processes, and those operating elsewhere in the subsurface has proved challenging and forms the basis on an on-going research collaboration between DkIT and QUB.

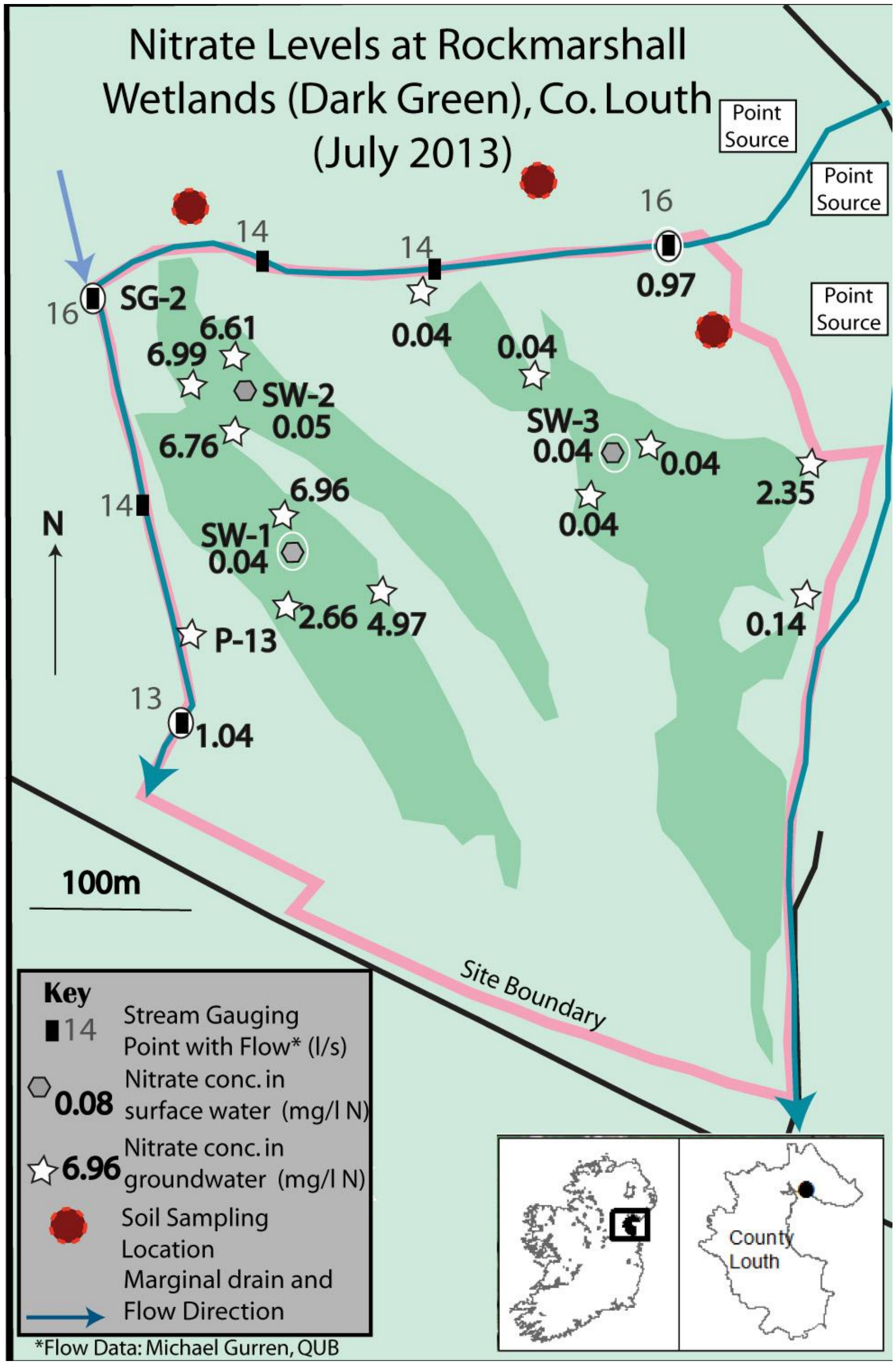



Fig. 16 Location and concentrations of nitrate in groundwater and surface water samples collected from the Tellus Test Site at Rockmarshall.

## 7. Summary of Activities

The results of the six month TIWEG study has developed current understanding of the risks posed to wetland ecosystems by anthropogenic activities and the potential utility of the datasets generated by the Tellus Surveys when coupled with existing spatial datasets. The study has achieved the following:

- A unified vulnerability scheme has been developed reconciling approaches employed in both Northern Ireland and the Republic of Ireland.
- A unified scheme integrating land use data from Northern Ireland and the Republic of Ireland into a common rubric has been developed.
- A scheme for assessing risk of nutrient enrichment from diffuse pollution to GWDWs, which may be applied over the full area covered by the Tellus surveys has been devised and applied.
- Sensitivity analyses of the risk scheme suggests that land use intensity rather than source proximity plays a more critical role in risk of nutrient enrichment of the sites surveyed.
- Comparison of soil and subsoil concentrations for AFBI-mapped subsoil categories using the Tellus (NI) dataset demonstrated a strong relationship between median soil and subsoil concentrations.
- Soil/subsoil comparisons show that the Tellus NI survey results permitted elemental enrichment /leaching in soil to be identified relative to parent material.
- The results of the soil/subsoil comparison, using Tellus NI data, indicate that, in the absence of subsoils analyses for the Tellus Border dataset, the results for soils analyses may be used for estimating elemental concentrations in subsoil.
- Tellus data have been used to generate concentration ranges for organic matter content, iron and calcium that may be anticipated for mapped soil types, based on AFBI and Teagasc soils classifications, for the Northern Ireland and the Republic of Ireland, respectively.
- Application of the risk ranking permitted a subset of 19 representative wetland sites to be selected from a population of 147 GWDWs. More detailed maps of

drainage, landuse, bedrock geology, subsoil geology and vulnerability, including soil and water sampling locations, were generated for all 19 sites, with 100m, 200m, 400m and 800m buffer strips around each site defined.

- Completion of 1 day field visits to all shortlisted field sites, where a total of 70 water samples and 72 soil samples permitted collection and analyses for iron, calcium and loss on ignition content.
- Comparison of soil samples collected during field surveys revealed that elemental concentrations fall into the ranges for (Teagasc and AFBI) mapped soil types, determined from Tellus data sets. This suggests that Tellus data may be used as a screening tool for estimating elemental concentrations in soils prior to field-based investigations.
- A poor correlation was found between estimated risk of wetland eutrophication and nutrient concentrations determined for grab samples of wetland water. Although exclusion of sites impacted by proximal point sources did little to improve overall correlation, plots of nitrate levels with risk reveals an envelope of maximum concentrations, which is highest in high risk categories.
- The increasing variation with risk is believed to reflect contrasting nutrient delivery mechanisms. Sites with lower nutrient levels for comparable risk are suspected to reflect conditions where wetlands receive groundwater which has undergone greater attenuation by geochemical processes.
- The above hypothesis is consistent with the results of more detailed studies at the Rockmarshall Tellus wetland research site, where nitrate concentrations in wetlands can be over an order of magnitude lower than those in groundwater in the underlying aquifer, due to the presence of organic matter.
- Defining the role of calcium and iron levels on nutrient attenuation remains more complex due to the high degrees of overlap between the elements of interest in contrasting soil types.
- Distinguishing between geochemical processes operating in the subsurface of a GWDW catchment from those operating within the GWDW remains an

outstanding challenge. This will be addressed in on-going research initiated by the TIWEG programme.

## 8. Issues arising and relevance for policy implementation

The Water Framework aims to protect GWDWs from anthropogenic damage. Implementation of the WFD rests with Member States, leading to a range of mechanisms for characterising status and assessing impacts, with characterisation and monitoring protocols aiming to provide for conditions within different jurisdictions. However, development of approaches to protect GWDWs in transnational river basin districts (RBDs) proves more problematic. The TIWEG project aimed to provide a coherent approach for assessing the risk to GWDWs on an all Ireland basis. As such the project has highlighted a number of issues that should be considered for the implementation of WFD legislation relating to GWDWs in both NI and the RoI. This would permit comparison of eutrophication risk to sites on either side of the border. This is particularly salient to those sites within the same RBD, but in different jurisdictions, where a common barometer of status is needed to determined the overall WFD status of an RBD. Although the scheme developed as part of this project allowed relative risk of enrichment to be assessed across the region, the datasets available hindered quantifiable application, particularly in areas where individual sites lay within transnational RBDs. This occurred largely due to the absence of consistent dataset. More specifically, consistent data were not available for the following topics:

- Soil and subsoil maps: Soil and subsoil maps in NI and the RoI employ contrasting classification systems. This prevented the assessment of their geochemical properties using a common approach. Use of a consistent system would not only facilitate the generation of systematic subsoil permeability maps, but allow geochemical influences on nutrient mobility to be compared to for sites on either side of the border.
- Subsoil Thickness: Consistent subsoil thickness maps were not available at the time of writing. Although these maps have been generated for both sides of the

border, the resolution of those available in NI are lower than those available for the RoI (Peter McConvey, *pers. comm.*). This leads to inconsistency in data quality (and conclusions that may be drawn) for sites in NI compared to the RoI.

- Subsoil Permeability: Contrasting systems for classifying subsoil permeability are employed in NI and the RoI. A system reconciling both approaches is needed for cross border comparisons.
- Nutrient loading: Calculations of nutrient loads to catchments proved one of the most challenging tasks of the TIWEG project. Estimates on both sides of the border relied on published agricultural census data, on a townland (RoI) and electoral ward basis (NI). Moreover, not all nutrient sources could be incorporated. The absence of figures for pigs and poultry limited the degree of confidence that could be placed in loads derived from livestock, while a lack of information about crop types raised levels of uncertainly about loads derived from arable agriculture. More precise information concerning location, timing and intensity of nutrient loads in wetland catchments would assist greatly in quantifying reliable landuse pressure (and thus risk). Moreover the (low) spatial resolution of datasets proved inconsistent and hindered more confident quantification of the effects of proximity on wetland ecological health (improved spatial and temporal resolution are available from the LPIS data set in the RoI, but are not currently available to the public).

Overall, generation of systematic datasets, particularly in transnational RBDs, is essential if WFD legislation is to be effectively implemented and coherent risk assessment protocols are to be applied.

Provision of data sets in a consistent format will permit more confident quantification of eutrophication risk. Significant advances have been made in generating tools that can help achieve this goal, particularly in the RoI. A catchment management tool (CMT) currently being completed under the EPA-sponsored STRIVE-Pathways programme is due for release in mid-2014. This tool provides a basis for assessing impacts of land use to nutrient loads reaching surface water bodies in the RoI. The CMTs architecture

provides considerable scope for modification to assess risks to GWDWs, including definition of the level of site specific groundwater dependency and associated nutrient fluxes.

The conceptual basis underpinning the CMT views subsoil permeability and thickness to be fundamental controls influencing nutrient delivery and mobility in groundwater systems. However, the role of inorganic subsoil geochemistry is not considered. The inconsistency and lack of availability of fundamental datasets encountered during TIWEG resulted in the use of a derived parameter (vulnerability) to investigate this topic, which was not considered ideal but was viewed as a best approximation using available data. Use of the CMT could strengthen the science underpinning the functioning and classification of wetland ecosystems.

Application of the CMT, employing fundamental datasets, provides a mechanism for more confidently quantifying nutrient fluxes (and the hydrological pathways delivering them to wetlands). This in turn offers the potential for Tellus geochemical data to be employed to systematically investigate GWDW eutrophication risk, particularly if consistent data sets are available on an all Ireland basis. This approach would employ the same overall protocol as utilised in the TIWEG project. Model outputs could be used to predict anticipated nutrient loads delivered to wetlands and anticipated nutrient concentrations. Comparison of observed and anticipated levels would, in turn, permit development of appropriate risk classification, incorporating geochemistry where relevant.

Verification of model predictions requires field data. To date, protocols for GWDW monitoring of chemical water quality and ecological conditions in wetlands remain poorly constrained. Little work has been carried out on this area in most Irish GWDWs. This is in part a consequence of the difficulty of selecting sampling points for monitoring biotic and abiotic conditions. Water quality sampling completed as part of the TIWEG programme has shown high levels of hydrochemical variability across individual sites

suggesting impacts in some parts and pristine conditions elsewhere in the same site. Similarly, detailed ecological and hydrochemical surveys completed at selected sites, as part of the Tellus Border Wetland Project, have shown high levels of spatial and temporal variability. The processes underpinning these variations require further characterisation for confident definition of links between threshold nutrient levels and wetland ecosystem health.

Understanding the significance of wetland ecological indicators in terms of anthropogenic impacts requires an understanding of the relationship between biotic and abiotic conditions. Critically, selection of appropriate monitoring points within GWDWs to examine these relationships will prove fundamental. The TIWEG study suggests that processes operating within some wetlands attenuate nutrients, depending on the delivery mechanism. Once again the CMT offers considerable scope for deepening current understanding of this issue.

In a similar vein the resilience of some plant species in GWDW communities to eutrophication needs characterisation if their significance for reflecting anthropogenic inputs is to be established and used to define WFD status. Once again the variety of conditions encountered during the TIWEG study suggests that selection of appropriate monitoring points needs justification (based on scientific findings).

Identification of appropriate parameters and monitoring locations provides a protocol for refining the CMT to allow the impacts of anthropogenic activities to GWDWs be confidently identified. This may include scope for improving the quantification of wetland ecological services, which in turn will allow pragmatic, yet scientifically defensible land use policies to be implemented. The quality of the Tellus data, coupled with the recommendations in Section 9 provide an important means of furthering current understanding of the role played by soil and subsoil geochemistry in catchment scale nutrient attenuation. These elements have the potential to provide valuable contributions in the approach to adapting land use practice to meet both economic and legislative requirements.

## 9. Recommendations and Future Work

The Water Framework Directive requires coherent implementation by Member States across RBDs irrespective of the international borders. This project's aim of assessing the risk of pollutant impacts on wetland ecosystems in the border region of Ireland was completed in this spirit. To the best of the authors' knowledge, this is the first cross border study of this kind carried out in Ireland. In order to implement the research methodology required to short list sites for further investigation, it was necessary to develop schemes for assessing eutrophication risk in wetland catchments, common to both NI and RoI. The schemes developed provided a mechanism for assessing the relative risk of enrichment to be assessed across the region. However, the available data restricted the confidence with which the approach could be employed and tested. This occurred largely due to contrasting datasets on both sides of the border, in addition to the application of a risk scheme utilising derived parameters, i.e. vulnerability.

Aside from issues relating the availability of certain datasets, the results of this brief study have highlighted the need for further information on the role of soil and subsoil geochemistry in controlling nutrient delivery to wetland receptors. As more detailed data from the Rockmarshall site have demonstrated, geochemistry can play a significant role in nutrient delivery to wetlands. However, the large overlap in concentrations of selected parameters in soil types has prevented identification of the role played by soil and subsoil geochemistry using the Tellus data sets. This arises in part from the fact that different minerals contain common elements. Relating soil and subsoil geochemistry to mineralogical content could assist considerably in further constraining geochemical conditions in wetland catchment. This could be achieved in part by a programme of X-ray diffraction analyses on existing Tellus soil and subsoil datasets.

The results of the field sampling programme have assisted considerably in improving knowledge of wetland ecosystems in the border region. However, it must be borne in mind that data collected from site visits provide a snap shot of conditions at sites. As

more detailed studies, completed both in the border region and further afield, have shown hydrological and water quality conditions in wetlands can vary with time. A programme of repeated sampling, ideally coupled with high resolution monitoring would contribute significantly to characterising the degree of variation experienced in these wetlands. This in turn would provide improved information about nutrient delivery and attenuation mechanisms and fluxes. This approach is currently being piloted by QUB/DkIT at the Rockmarshall Test Site, with a view to quantifying geo-ecosystems services provided by wetlands. This in turn will proved further justification, beyond legislative requirements for wetland conservation (in the case of Rockmarshall the reduction in elevated nitrate levels in groundwater, which would otherwise discharge to Dundalk Bay, can be assigned a cash value equivalent to the costs of treating the same volume of water in a wastewater treatment plant).

As a corollary to the above point, if nutrient attenuation processes are affected in a wetland ecosystem by human activities, this may give rise to ecological impacts due to water borne nutrients entering from surrounding areas. According to WFD legislation if a groundwater dependent terrestrial ecosystem status degrades, a corrective programme of measures (POMs) needs to be implemented. In order to meet WFD requirements and define appropriate restoration targets, an understanding of hydrological processes and nutrient delivery mechanisms is necessary. Monitoring data provides essential information for characterising the condition a GWDW, identifying conditions and trends in concentrations that may give rise to ecological impacts, and defining appropriate water quality targets for POMs, if needed. The TIWEG study has highlighted the significant degrees of spatial variation that may exist in individual wetlands. Further investigations are necessary if a scientifically defensible approach to water quality monitoring of wetlands is to be developed. Once again, higher resolution spatial and temporal monitoring of sites investigated in the TIWEG project would assist considerably in meeting this goal.

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