17. Assessing nutrient enrichment risk to groundwater-dependent ecosystems in the border counties of Ireland

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Geological heterogeneity across the border counties of Ireland leads to variable levels of resilience in groundwater-dependent ecosystems (GWDEs). In a review of 26 catchments, with contrasting land-use and geology, we investigated the roles that soil and subsoil geochemistry may play in protecting GWDEs against nutrient enrichment from external sources. While the Tellus soil geochemical data sets provide estimates of soil and subsoil geochemistry at a regional scale, the analysis of field water quality samples revealed highly variable nutrient levels at high-risk sites, indicating influences from diverse hydrological processes. These overprint the geochemical influences on attenuation in source–pathway–receptor (SPR) catchment models. Study findings underscore the value of ground truthing for checking model assumptions and identifying overlooked processes.

Introduction

Protecting the health of groundwater-dependent aquatic and terrestrial ecosystems forms a core element of the EU Water Framework Directive (WFD) and the Habitats Directive (HD) (EC 2015a, 2015b). The WFD recognises that interrelationships of GWDEs and their surroundings can underpin habitat ecological health and that these need to be considered in conservation plans. This requires an integrated approach to land-use management and conservation in areas where certain land-use practices may put GWDEs at risk (Blann *et al.*, 2009). Implementation proves particularly challenging in physically heterogeneous catchments with variable land-use.

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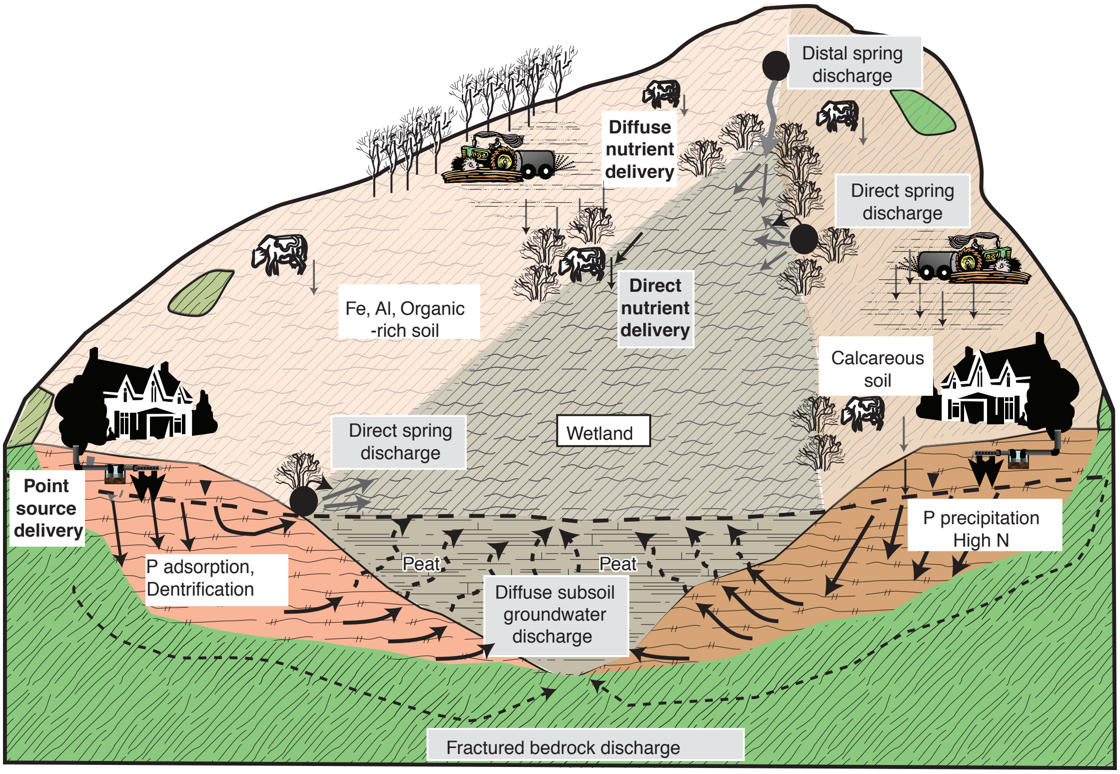


Figure 17.1. Schematic source–pathway–receptor model employed for Border Region GWDEs. Sources in bold type; pathways in shaded text boxes; the wetland is the receptor of concern. P, phosphorus; N, nitrogen.

Land-use intensity in the Tellus Border survey area is highly variable. This is, in part, due to the heterogeneous natural topographical and geological conditions, which result in contrasting levels of drainage and intrinsic soil fertility. Application of fertilisers aims to improve soil fertility but can also lead to loss of excess nutrients to groundwater that may in turn discharge to ecologically sensitive receptors.

Nutrient-enriched water can have detrimental impacts on the functioning of wetland and aquatic ecosystems (Mitsch and Gosselink, 1993), particularly during sustained dry periods when dilution with less enriched water, which may be delivered via other hydrological pathways, is reduced. Moreover, highest dependence on groundwater often occurs during periods of intense biological activity, such as the summer growing season, when demand for water and nutrients is greatest (Neal *et al.*, 2006).

Despite the threat posed to GWDEs by contaminant-bearing groundwater, nutrients such as nitrogen (N) and phosphorus (P) may undergo reactions in the subsurface that result in their immobilisation and/or degradation. The mitigating reactions have been demonstrated at the laboratory and field scales and shown to be a function of the interaction of hydrological and geochemical processes, both of which depend strongly on the soil and subsoil properties. These include concentrations of iron oxyhydroxides, calcium carbonate and organic matter (Jordan *et al.*, 2005; Rivett *et al.*, 2008). The presence of these minerals in soil is reflected by concentrations of principal constituent elements (iron, calcium) and loss on ignition (a surrogate for total organic carbon content), respectively.

Kimberley and Coxon (2013) highlighted the importance of catchment geological conditions in influencing Irish wetland hydrological regimes, nutrient delivery via the groundwater pathway and the need for improved characterisation of these processes. SPR models provide a conceptual framework for better characterising nutrient delivery to GWDEs. The model is illustrated schematically in Fig. 17.1. It shows the sources of nutrients routinely encountered in the border counties and the attenuation processes operating on them in GWDE catchments underlain by calcareous and iron-rich soils/subsoils. However, application of these models to protect GWDEs proves challenging in catchments with high degrees of natural heterogeneity. Spatial variations in soil chemical and physical properties, coupled with differences in land-use, and associated nutrient application rates, lead to varying levels of risk (Archbold *et al.*, 2010).

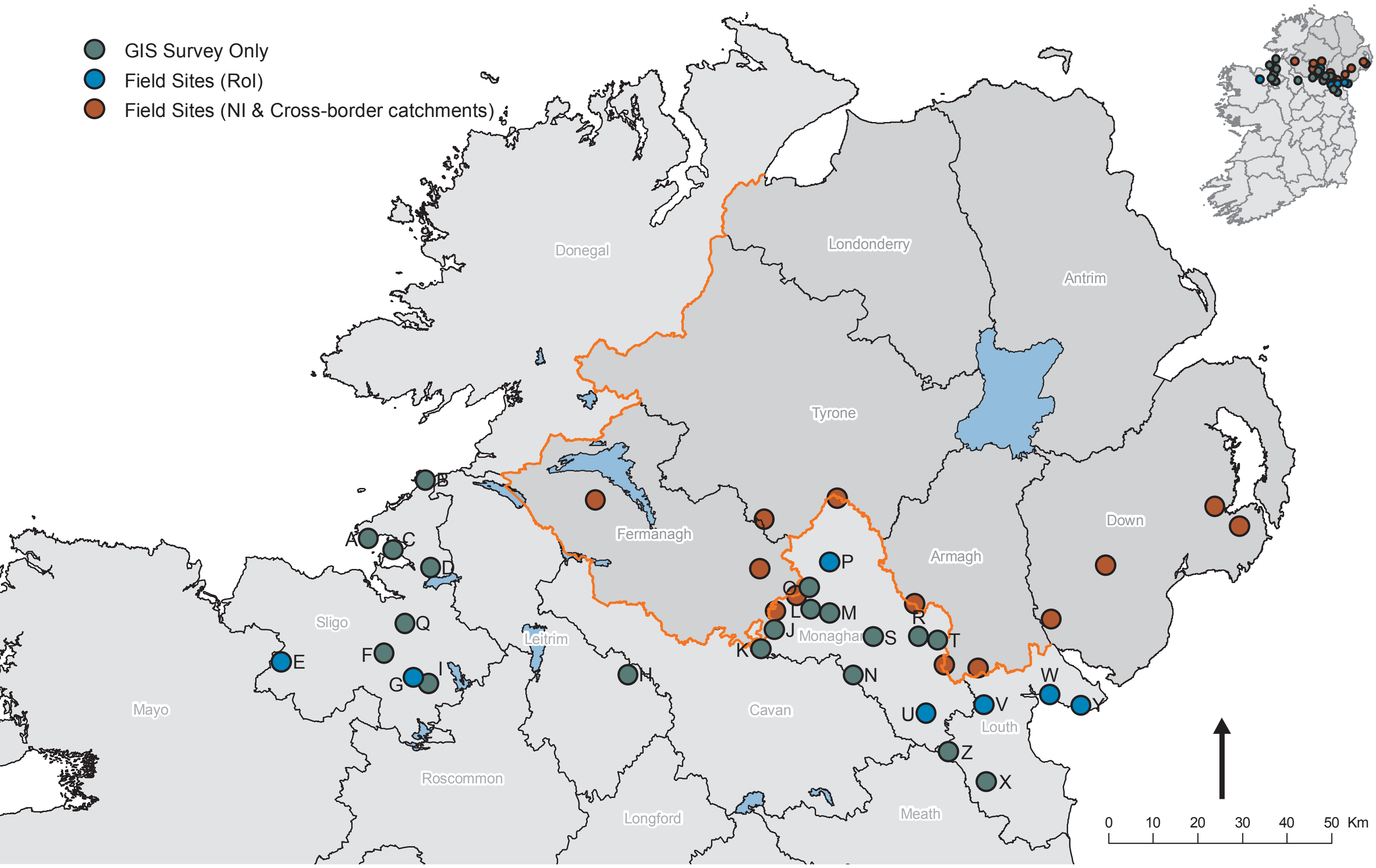
Geographic information systems (GIS) provide a means of assessing differences in spatially variable parameters. However, the confidence with which spatial data may be employed depends on the accuracy of contributing data sets. Over the past 20 years both Northern Ireland and the Republic of Ireland, supported by EU finance, have devoted considerable efforts to creating digital spatial data sets to support environmental and natural resources management. These include digital terrain models (DTMs), subsoil permeability maps, hydrogeological maps and the geochemical data of the Tellus Projects. The data sets generated, when combined with land-use and hydrological data, provide a means of investigating the relative roles played by hydrology and soil geochemistry in determining the risk of excess waterborne nutrients affecting GWDEs via the groundwater pathway. The approach described below provides the basis for developing a screening tool for assessing the risk of anthropogenic nutrient inputs to GWDEs using these data.

Methodology

A desk-based analysis of several GWDEs, followed by field surveys/sampling of soil and water at selected sites (Fig. 17.2), was undertaken during the summer of 2013 to investigate conditions in areas of contrasting risk of aquatic nutrient enrichment. The study focused on the role of nitrogen, which has greater mobility in groundwater, rather than other nutrients of ecological significance to freshwater ecosystems, e.g. phosphorus (Rivett *et al.*, 2008).

GIS screening tool

Figure 17.3 summarises the protocol followed in developing a GIS-based risk ranking of border counties sites. After generating a list of 148 candidate GWDEs, the development of a GIS using ArcGIS™ permitted potentially suitable catchments to be shortlisted based on (a) their lying fully within the Republic of Ireland and (b) whether sites appeared



likely to receive groundwater discharge, based on physical setting. Considerations of site accessibility reduced the number of sites visited to 26.

Figure 17.2. Location of sites considered in GWDE survey. (Letters beside each point correspond to sites listed in Table 1).

The Ordnance Survey of Ireland (OSI) 20 m × 20 m DTM was employed to define the extent of catchments using the ArcGIS-Hydrotool™. Boundaries extended to catchment watersheds up-gradient of GWDE outlets to constrain the area in which groundwater and associated nutrients could reach a site. Determination of recharge rates across catchments were calculated using the GSI National Recharge Coefficient Map and Effective Rainfall Map (Hunter Williams *et al.*, 2013, GSI, 2015); these provided the volume of water with which infiltrating nutrients, reaching groundwater, would be diluted.

Nutrient loads of agricultural origin were calculated from various information sources:

- Agricultural Census results (CSO, 2002) – livestock numbers and arable areas;
- Corine land-use maps – areas of pasture and tillage;
- Packham *et al.* (2015) – nutrient loads for cattle and sheep;
- O'Reilly (2012) – loads for areas under arable agriculture, assuming a barley crop.

Other agricultural nutrient sources were not provided in the CSO database, e.g. from pigs or poultry. To address this uncertainty, arable land was assumed to receive nutrients at maximum application rates, with deficits from synthetic fertiliser application assumed to be met by organic wastes derived from poultry and pig farming (Packham *et al.*, 2014).

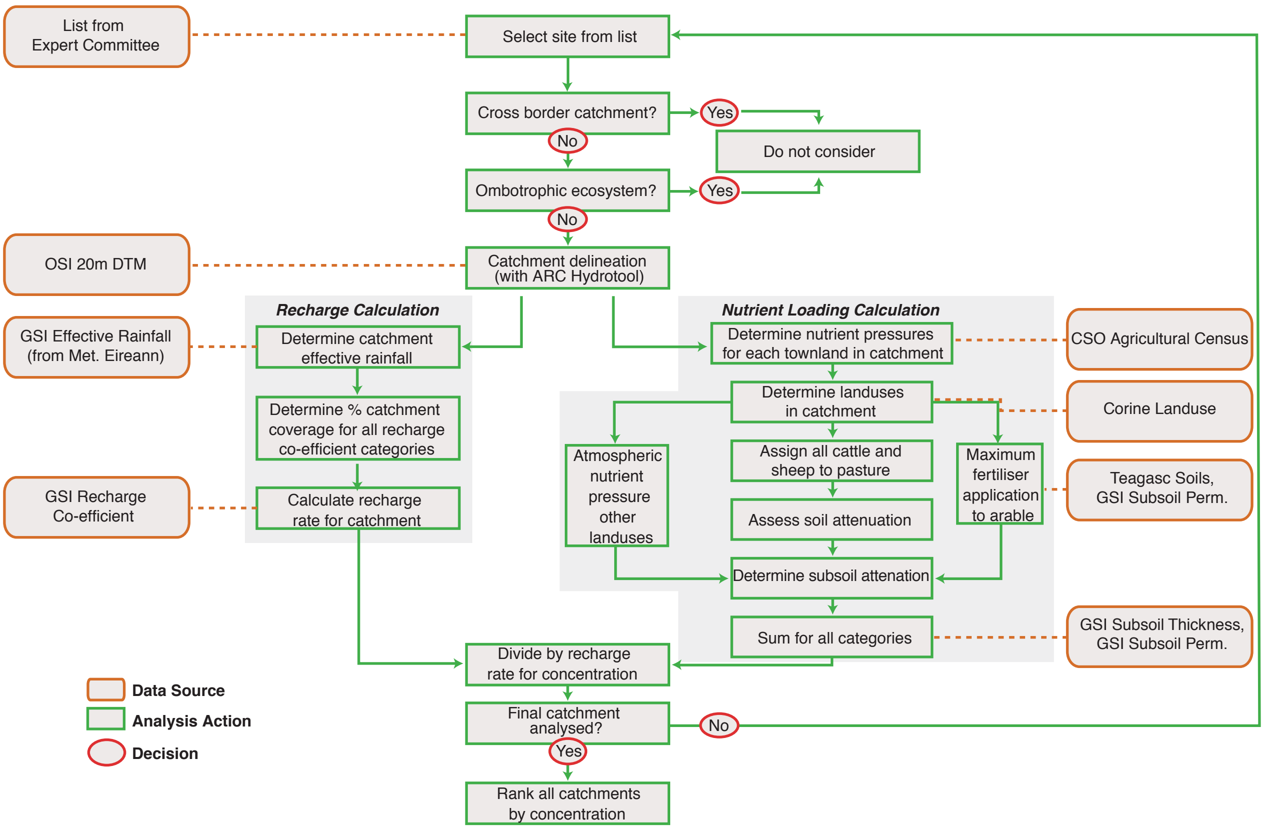


Figure 17.3. Flow chart summarising the protocol and data sets employed in assessing the risk of nutrient-enriched groundwater impacting GWDEs. (Elliptical boxes represent data sources employed in calculations, square boxes represent actions employed in data analyses, circles reflect decisions taken.)

Nutrient loads from onsite wastewater treatment systems (OSWTSs) were estimated from townland populations. The proportion of each townland occupying a GWDE catchment area provided an estimate of the human population contributing nutrients to a site, assuming an averaged population per household. *Per capita* nutrient loadings (from Gill *et al.*, 2009) permitted calculation of nutrient discharges to depth, while attenuation calculations followed the protocol described in Packham *et al.* (2015).

A model, in which attenuation occurred in soil and subsoil immediately below land receiving nutrients, was used to determine loading to groundwater and included the following constraints or assumptions.

- As there are no denitrifying bedrock units in the region, no nutrient attenuation was assumed to occur below the base of the subsoil (Packham *et al.*, 2015).
- Following correction for atmospheric deposition, nutrient attenuation through soil was calculated based on soil permeability and drainage (wet or dry).
- Drainage characteristics were based on Teagasc soil wetness maps.
- Nitrogen attenuation through grassland soil (accounting for volatilisation, nutrient uptake and denitrification) was taken from tabulated NCycle_Irl outputs used in Packham *et al.* (2015), while Anthony *et al.* (1996) provided comparable figures for losses through arable soils.

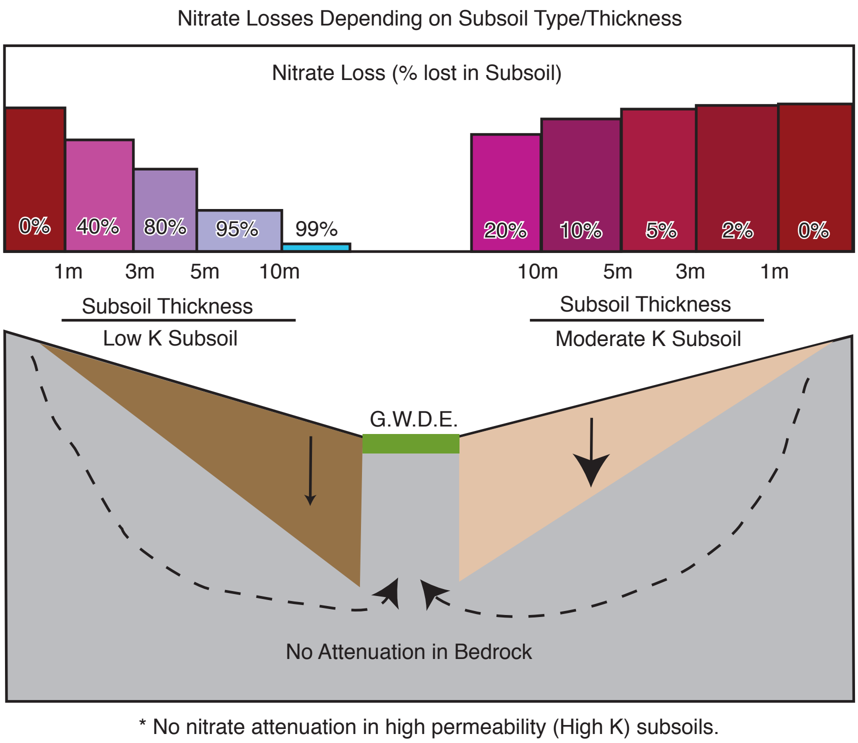


Figure 17.4. Schematic illustration of nitrate attenuation rates through subsoils as a function of their permeability and thickness (Packham *et al.*, 2015).

- Following passage through the soil zone, nitrate was considered the dominant mobile N phase in deeper units (Rivett *et al.*, 2008).
- Using guidelines provided in the EPA Pathways Report (Packham *et al.*, 2015), which describes protocols for assessing geological influences on nutrient levels in water, losses through subsoil were considered a function of subsoil permeability and thickness. These were determined spatially across GWDE catchments using GSI subsoil permeability maps and subsoil thickness maps (summarised schematically for nitrogen (nitrate) in Fig. 17.4).
- Summing nutrient loads beneath pasture and arable land for each soil–subsoil combination provided estimated nitrate loads to groundwater.
- Division of load by recharge rate for a catchment provided the anticipated concentration expected in a GWDE. These calculations permitted risk ranking of sites based on anticipated nitrate levels.

The risk ranking approach adopted in calculating attenuation rates requires water-borne nutrients to pass through both soils and subsoils with different physical properties, but does not consider the role played by geochemistry. Use of Tellus Border geochemistry data sets, with the soils map, enabled consideration of the role of constituents (iron, calcium and total organic carbon) that might influence nutrient fate and transport for each major soil group. Comparison of median levels in soils with associated subsoils, analysed in the related Tellus programme in Northern Ireland, showed a good relationship for each pairing (McKernon, 2013). The similar nature of the soils in the border counties suggests that a comparable relationship exists and that levels in soil should broadly reflect those in subsoil.

Field investigations

Soils

Field investigations aimed to evaluate whether concentrations of constituents measured by the Tellus Border soil geochemistry, which may influence nutrient mobility, corresponded to levels in soils in the catchments investigated. Catchment selection for further investigation, based on soil type and calculated risk, permitted representative soil types to be sampled under a range of conditions with a minimum of three locations sampled in each catchment. For consistency, sampling protocols followed those employed in the Tellus Border survey.

Water

All GWDE catchment surveys were completed during summer 2013 following periods when no rainfall had occurred for at least three days prior to sampling. This aimed to increase the influence of groundwater in any GWDE surface water samples collected, while reducing the impact of water delivered by other hydrological pathways. Where possible, groundwater samples were also collected from monitoring wells to assess the similarity of results to those sampled at surface. All samples collected were refrigerated at between 4°C and 5°C and analysed in the laboratory within 48 hours of collection.

Results

Table 17.1 summarises the results of nutrient loading calculations and concentrations anticipated in water samples collected from GWDEs. Results show a wide range of estimated nitrogen application rates across the sites surveyed, reflecting the variation in land-use across the region. Similarly, estimates of nitrogen concentrations (as nitrate) in groundwater discharging to wetlands reveal concentrations that vary by over two orders of magnitude. Of the 26 sites investigated, calculated nitrate concentrations in groundwater exceeded 2 mg l^{-1} (as N), sometimes considered to be an upper limit of natural nitrogen levels in water (UKTAG, 2012), in 24 sites. Plotting the ranks of calculated concentrations against loads failed to generate a significant Spearman rank correlation coefficient ($r^2 = 0.38$, $n = 26$, $P = 0.05$). Sensitivity analysis of the model suggested that ranks remain relatively invariant with 10% changes in attenuation parameters.

Nitrate concentrations observed in surface water samples collected from five field verification sites proved consistently lower than those calculated, by approximately an order

Table 17.1. Summary of catchment loadings and anticipated nitrogen levels in GWDEs surveyed (site labels correspond to locations shown in Fig. 17.2)

GWDE	Label on Fig. 17.2	Load kg N ha^{-1} yr^{-1}	Load rank	Calculated N concentration in groundwater (mg l^{-1})	Concentration rank
Annagheane Lough	K	245.96	10	23.43	3
Ardtermon Fen (Ardbolin and Horse Islands)	A	124.18	21	3.71	22
Bunduff Lough and Trawalua/ Mullaghmore	B	172.16	13	5.40	18
Colgagh Lough	D	337.17	5	2.77	24
Corduff Lough	H	598.37	1	11.23	9
Cortial Lough/Drumcah Lough/ Toprass Lough	V	452.77	3	42.40	2
Doonweelin Lough (Cummeen Strand/Drumcliff Bay)	C	166.79	15	5.88	17
Drumakill Lough	T	178.72	12	10.67	10
Drumgallon Bog	S	170.54	14	14.04	6
Feenagh and Bunnamuck Loughs	G	280.72	9	4.98	20
Gibson's Lough	N	157.78	17	12.06	7
Greenan Fen	I	153.42	19	4.00	21
Kildemock Marsh	X	500.77	2	59.56	1
Knockmullin Fen	Q	103.34	24	5.06	19
Lisabuck Lough	J	157.39	18	9.95	11
Lisarilly Bog	L	186.53	11	8.69	13
Liscarragh Marsh	Y	317.57	7	7.86	16
Lough Smiley	R	162.03	16	9.37	12
Mullaghmore Lake (South)	P	151.43	20	0.17	26
Mullaglassan Lough	O	111.02	22	2.95	23
Nafarty Fen/Lough Fea Demesne	U	328.77	6	8.08	15
Rafinny Lough	M	10.55	26	0.74	25
Reaghstown Marsh	Z	282.59	8	19.81	4

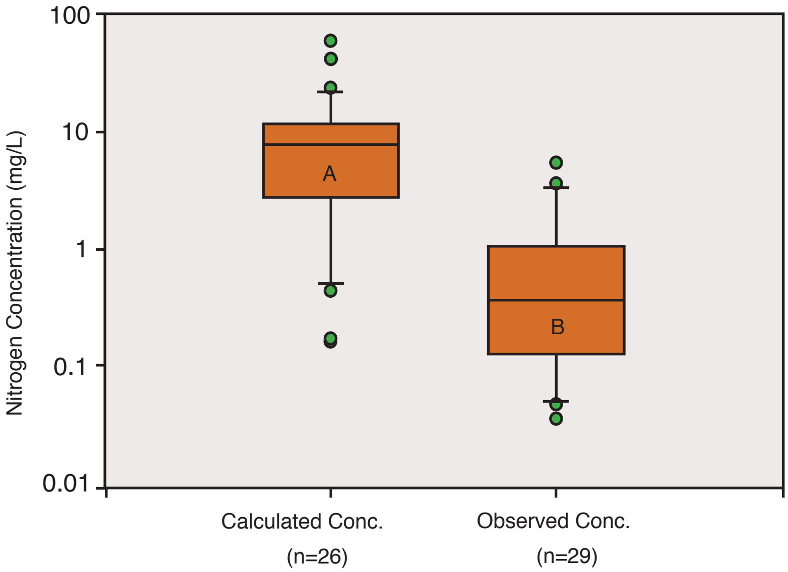


Figure 17.5. Box and whisker plot of (A) calculated and (B) observed nitrate (as N) concentrations in water samples collected in GWDEs.

of magnitude, with all falling below 2 mg l^{-1}; this was considered to be the median background level in groundwater in a survey of Irish aquifers (Baker *et al.*, 2007). The small sample size limited confidence in interpreting findings. However, merging these data with results of a wider field sampling of GWDEs, completed by McKernon (2013), and incorporating Northern Irish and cross-border catchments, revealed that observed nitrogen levels in GWDE water samples lay consistently below those calculated (Fig. 17.5). Significantly, higher risk sites displayed a greater spread in observed concentrations, with minimum concentrations resembling those from low-risk sites, while other samples from the same site could have nitrate levels up to an order of magnitude higher (McKernon *et al.*, 2014).

Findings from a more detailed survey completed at Rockmarshall site, County Louth, where monitoring wells also permitted groundwater sampling, showed nitrate concentrations in groundwater to be considerably greater than in surface water. Figure 17.6 shows that levels of nitrogen in samples from these wells were higher than in overlying surface water, despite comparable electrical conductivities. Similarly, levels in the nearby stream, which infiltrates water to the site, display more elevated concentrations than those in the wetland (Gurren, 2013).

Figure 17.7 (from McKernon, 2013) summarises the results of soil analyses for iron, calcium and loss on ignition in the soil types sampled in the Tellus Border Survey, with the results of field validation samples superimposed. Results show that analyte concentrations extend over a broad range for each soil category, with a significant level of overlap for types investigated. Analyses of samples collected during field validation surveys display a broad level of agreement with ranges determined from the Tellus Border Survey. However, the

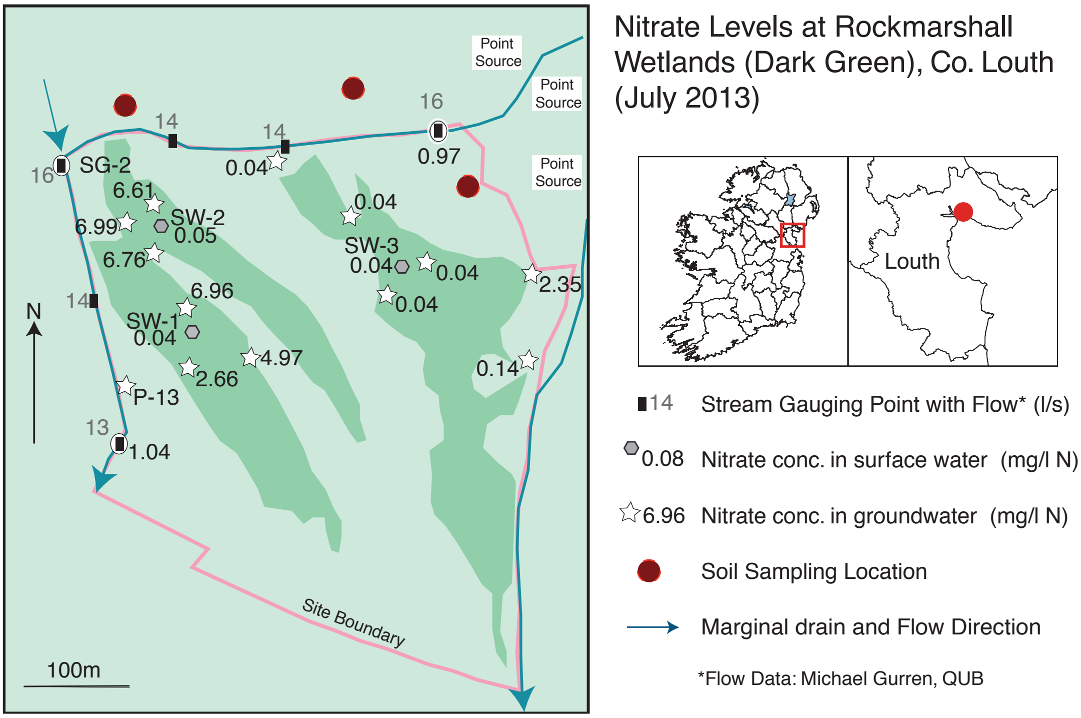


Figure 17.6. Map of the Rockmarshall GWDE test site (from Gurren, 2013).

plots show that no particular inorganic soil type can be considered to have significantly elevated levels of any particular parameter of interest.

Discussion

The SPR model provides a conceptual basis for investigating the potential of anthropogenic nutrients to have an adverse effect on GWDEs across the border counties. Investigation results reveal that GWDEs in this area experience wide variations in nutrient pressures. Calculations suggest that even for catchments where loadings are relatively light, e.g. Lough Talt, nitrogen concentrations in groundwater could exceed the 2 mg l^{-1} threshold. These results contrast with other sites such as Mullaghmore Lake (South) where, even though higher loadings were calculated, anticipated concentrations in groundwater proved lower due to greater protection afforded by thicker subsoil sequences.

Lower than expected nitrogen concentrations observed in water samples collected from the field sites indicate that the current SPR model requires refinement. Source data (and thus loading estimates) particularly need improvement. The failure to explicitly include supplemental nitrogen sources, such as poultry and pig manures, suggests that loads may be underestimated and that the role of soil and subsoil attenuation processes may be greater than assumed using current approaches. Rates of attenuation applied in the GIS were estimated based on results of limited studies of units with comparable texture, but from other

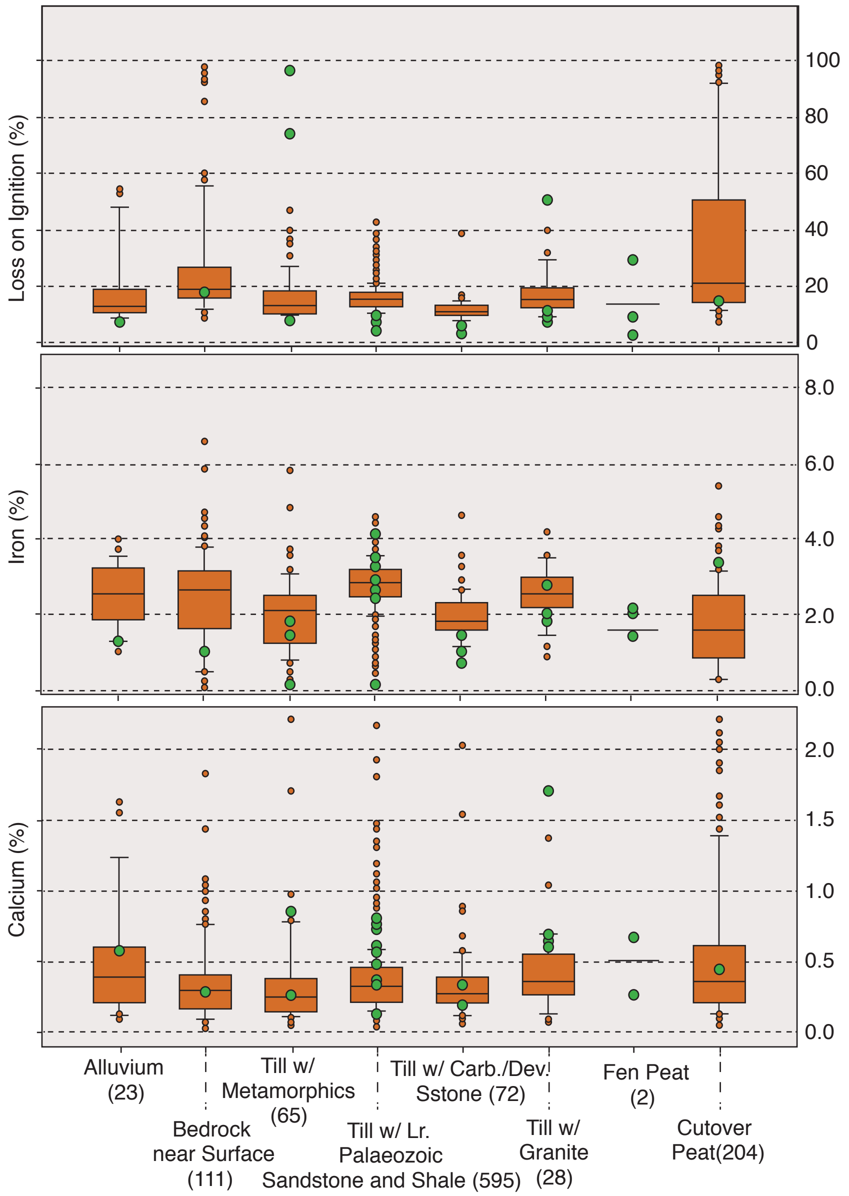


Figure 17.7. Results of Tellus Border soils analyses for loss on ignition, iron and calcium for principal soil units encountered in GWDE catchments surveyed. (Sample sizes in parentheses; yellow circles show analyses of field samples.)

regions of Ireland. Contrasts in concentration may arise due to different geochemistry. However, consistently higher levels of nitrate calculated, compared with those observed, indicate that there are further influences that require incorporation into the model. More detailed site-specific data point to possible mechanisms. These include processes operating within wetlands, such as the passage of nutrient-bearing water through layers of organic-rich material, which further reduce nutrient loads before they become available to plant communities.

Findings at Rockmarshall, County Louth, where significant differences in nitrate content were observed between samples collected from the GWDE and groundwater discharging from underlying gravels, emphasise the importance of considering processes along the entire groundwater flow path, and not just in recharge zones. The high rates of attenuation experienced in the silts underscore the need to view geochemical processes in an integrated manner with hydrology. The model employed in this investigation provided a simplified basis for investigating risk of nutrient enrichment, yet highlights the need to incorporate processes operating in groundwater discharge zones and within GWDEs for better understanding the risks posed to ecosystem health.

The greater variations in water quality encountered in samples from higher risk wetlands further underscore the importance of considering diverse aquatic nutrient delivery pathways and the contrasting attenuation processes that may operate along them (Fig. 17.1). Spatially and temporally variable levels of nutrient attenuation occur along different pathways. This further complicates interpretation of the role played by geochemistry. The findings point to the need for further investigation of this topic.

The broad correspondence between the content of soils sampled in the Tellus Border programme and those analysed during field verification imply that the Tellus data can act as a screening tool to provide initial estimates of elemental soil (and subsoil) chemistry. On the other hand, high levels of overlap in content for the different soil classes examined imply that linking single element data sets to existing soil categories is insufficient for identifying units in which geochemical processes may have a greater or lesser influence on nutrient attenuation.

Perspectives

Applying measures to address the impacts of anthropogenic activities on GWDEs under EU law is challenging in catchments displaying high levels of geological heterogeneity. Application of SPR models to sites across the border counties has provided a screening tool for assessing risks of impacts. However, as the results of this study have shown, the method requires further development if risk assessment and the role of geochemistry are to be defined with greater confidence.

Findings at Rockmarshall, County Louth have demonstrated how a more integrated understanding of pathways provides valuable insights into natural processes influencing GWDE health. At the same time, improved characterisation of nutrient loading using higher resolution spatial data sets, e.g. Land Parcel Information System (LPIS) data, could better constrain model inputs. Similarly, further characterisation of threshold values can improve understanding of nutrient impacts on ecological receptors (Kimberley and Coxon, 2013). The influence of geochemistry on nutrient fate and transport requires additional scrutiny, including a reappraisal of whether existing categories of soil and subsoil maps can be used to define nutrient attenuation rates.

These issues can be expected to become more pressing with the implementation of proposed Food Harvest 2020 measures aimed at intensification of agriculture across the country (Farrelly *et al.*, 2014). Identification of nutrient-vulnerable zones (areas of elevated contamination risk) in GWDE catchments will prove particularly critical if these measures are to be implemented, while also satisfying the requirements of EU environmental legislation. Understanding of natural geo-ecological services provided by soils and subsoils, and how these contribute to ecosystem resilience, is essential in achieving this goal.

Controlled studies completed to date have demonstrated that geochemistry plays an important role in aquatic nutrient fate and transport. In their current form the Tellus Border data sets require further integration with hydrological models to permit more confident use in quantification of geochemical processes that operate not only in groundwater, but also along shallower pathways. Hydrologically integrated catchment management tools, such as that generated by the EPA (Packham *et al.*, 2015), provide a basis for investigating this topic further. At the same time study results have highlighted the need for ground truthing to check model assumptions and to identify further issues that may influence aqueous nutrient fate and transport, and which can be considered in future model development.

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