Science of the Total Environment, Vol.408(8), March 2010, p.1847-1857.

An assessment of the risk to surface water ecosystems of groundwater-P in the UK and Ireland

I.P. Holman[1✉], N.J.K. Howden[1], P. Bellamy[1], N. Willby[2]

M. J. Whelan[1], M. Rivas-Casado[1]

[1] Natural Resources Department, Cranfield University, Cranfield, Bedford, MK43 0AL, UK

[2] School of Biological and Environmental Sciences, University of Stirling, Stirling, FK9 4LA, UK

✉Corresponding author

Tel: +44 (0)1234 750111

Fax: +44 (0) 1234 752970

Email: i.holman@cranfield.ac.uk

Complete correspondence address to which the proofs should be sent:

Building 53, Natural Resources Department, Cranfield University, Cranfield, Bedford Bedfordshire, MK43 0AL, UK

Abstract

A good quantitative understanding of phosphorus (P) delivery is essential in the design of management strategies to prevent eutrophication of terrestrial freshwaters. Most research to date has focussed on surface and near-surface hydrological pathways, under the common assumption that little P leaches to groundwater. Here we present an analysis of national patterns of groundwater phosphate concentrations in England and Wales, Scotland, and the

Republic of Ireland, that shows many groundwater bodies have median P concentrations above ecologically significant thresholds for freshwaters. The potential risk to receptor ecosystems of high observed groundwater P concentrations will depend on (1) whether the observed groundwater P concentrations are above the natural background; (2) the influence of local hydrogeological settings (pathways) on the likelihood of significant P transfers to the receptor; (3) the sensitivity of the receptor to P; and, (4) the relative magnitude of P transfers from groundwater compared to other P sources. Our research suggests that, although there is often a high degree of uncertainty in many of these factors, groundwater has the potential to trigger and/or maintain eutrophication under certain scenarios: the assumption of groundwater contribution to river flows as a ubiquitous source of dilution for P-rich surface runoff must therefore be questioned. Given the regulatory importance of P concentrations in triggering ecological quality thresholds, there is an urgent need for detailed monitoring and research to characterise the extent and magnitude of different groundwater P sources, the likelihood for P transformation and/or storage along aquifer-hyporheic zone flowpaths and to identify the subsequent risk to receptor ecosystems.

Keywords: leaching, eutrophication, baseflow, orthophosphate, phosphorus

Introduction

High concentrations of biologically available phosphorus (P) in freshwater ecosystems are commonly associated with elevated rates of primary productivity and resultant changes in ecosystem composition (Mainstone and Parr, 2002; Withers and Lord, 2002). Major research efforts have been made in attempting to quantify the principal P sources in different catchment systems in an effort to understand and manage eutrophication (Foy, 2005; Withers and Haygarth, 2007; Weatherhead and Howden, 2009). Most work, thus far, has made the distinction between point-sources, such as sewage treatment plants, and diffuse-sources, such as transfers from agricultural soils during storm events (Edwards and Withers, 2007; Howden et al., 2009). The predominant research focus for diffuse-source transfers from land to water has been directed to surface (Heathwaite et al., 2006; Withers and Haygarth, 2007; Burt et al., 2008) and near-surface (Heathwaite and Dils, 2000; Hodgkinson et al., 2002) hydrological pathways. Transport of phosphorus to groundwater and potential P contributions to surface waters via baseflow are generally assumed to be negligible because of the high potential for mobile phosphorus to be retained in the upper soil horizons by adsorption (e.g. to calcite) or metal complex formation (commonly with iron, aluminium or manganese in acidic soils: e.g. Addiscott and Thomas, 2000). Nevertheless, relatively high concentrations of phosphorus have been reported for some groundwater bodies (Kilroy, 2001; Kilroy and Coxon, 2005; Holman et al., 2008) which suggest that groundwater has potential to act as a P source for surface waters, provided it is not removed along the groundwater-surface water pathway (e.g. Griffioen, 2006). In the UK, monitored groundwater P concentrations have historically been compared with the EU drinking water standard (2200 µg P L^{-1}) and have, therefore, not been identified as a concern. If ecologically-based surface water thresholds (Howden et al., 2009) are used as a reference point, however, measured groundwater P concentrations become more significant, particularly since groundwater contributions (as a proportion of total flow) are greatest during low (base-) flow conditions which are often coincident with optimum conditions for primary productivity in spring and summer (Mainstone and Parr, 2002). In some freshwaters and groundwater-dependent wetlands, such as fens (particularly in the absence of point-source discharges), relatively low concentrations of groundwater-P could, therefore, exert a fundamental control on baseline ecosystem function (Neal et al., 2008). Hence, it is important to develop our understanding of groundwater-P source(s) (i.e. anthropogenic or natural) and the potential risks posed by groundwater-P to good ecological quality in surface waters.

This paper presents an overview of groundwater-P concentrations in the UK and Republic of Ireland based on historical data from national routine monitoring. It extends a preliminary overview presented by Holman *et al.* (2008) which focussed on phosphate in groundwater bodies in England and Wales.

Specifically, four questions are considered:

Are there spatial patterns in groundwater-P concentrations in England and Wales, Scotland, Northern Ireland and the Republic of Ireland?

Are there potential links between groundwater-P concentrations and land use?

What are the potential implications of groundwater P concentrations for surface-water quality and ecological management?

What are the implications of the findings for future monitoring requirements in both ground and surface waters, specifically with regard to required limits of detection?

Data and Methods

National datasets

Over 48,000 measurements of groundwater P concentrations were collated from national monitoring datasets for the UK and Ireland (see summary: Table 1). The data originated from almost 3600 groundwater monitoring sites (Figure 1) and were collected between 1968 and 2007. Differences in filtering, analytical methods, P determinands and Limits of Detection (LOD) were evident between countries (Table 1) as follows:

England and Wales (Environment Agency monitoring), Scotland (Scottish Environment Protection Agency monitoring) and Republic of Ireland (Environmental Protection Agency monitoring): Samples are not routinely filtered. Colorimetric analysis is used to give total reactive phosphorus, via the molybdate reaction. This is, however, reported by the agencies as Orthophosphate as P because the majority of the total reactive phosphorus in groundwater samples is expected to be in the form of dissolved orthophosphate, given that concentrations of suspended solids and organic matter in groundwater are normally low.

Northern Ireland (Environment and Heritage Service monitoring): Samples are routinely filtered in the field and analysed using ICP-MS to give total dissolved phosphorus.

The term phosphorus is used within the paper with respect to orthophosphate as P unless otherwise stated.

Limits of detection

In the context of assessing potential risks to surface water receptors from groundwater-P, the treatment of samples below LOD is important because surface water phosphate thresholds for eutrophication can be as low as 10 to 30 µg L^{-1} (Stevenson et al., 2008). Detection limits were inconsistent between: countries; groundwater bodies within the same country; and also within individual datasets. To assess the sensitivity of the analyses to the LOD, the LODs were initially considered by treating samples with concentrations below LOD in four different ways: (1) as zero; (2) as LOD; (3) as half LOD; and (4) removing all samples below LOD.

Temporal analysis of groundwater-P

The groundwater-P data has been analysed with regard to the timing of sample collection, timing of observed high concentrations and national trends. The distribution of samples by month of collection in England and Wales, Scotland and Ireland were examined to assess whether there are temporal biases in sampling. The month of collection of samples with concentrations greater than 5, 10 or 20 times the median concentration for the given groundwater monitoring site were analysed for patterns in the timing of such peak concentrations. Finally, national average median groundwater P concentrations were calculated from all samples collected within the given calendar year to identify any national trends in groundwater P concentration.

Spatial distribution of groundwater-P

National groundwater-P distribution was investigated at the groundwater body scale, by assigning data from groundwater monitoring sites to their respective regionally-defined groundwater bodies using a point-in-polygon procedure within a Geographical Information System. Median groundwater body P-concentrations were calculated from the median concentration values at individual sites for which more than one measurement was available, and single sample concentration values for sites with only one measurement. This normalised the sites for differing sample numbers and prevented sites with large numbers of samples from dominating the median concentration for the groundwater body. The median concentration was used (in preference to the mean) to prevent occasional peaks in concentration from skewing the results.

Relationship with Land Cover

Historically, samples are collected from a range of monitoring sites (monitoring boreholes, abstraction sites, private boreholes, springs etc), so borehole capture zones were not generally available. Therefore, the predominant land cover for a 1 km radius around each monitoring site, derived from a simplified CORINE2000 (**C**o-**or**dination of **In**formation on the **E**nvironment) land cover class, was used. The CORINE classes were re-categorised into the following broad land cover groups - Urban/industrial; Arable; Managed grassland; Semi-natural vegetation and Woodland. Overall, the distribution of sites by predominant land cover class was 8% urban/industrial; 27% arable; 53% grassland; 3 % semi-natural vegetation and 9% woodland. The distribution of the median groundwater P-data tends to be log-normal so that the data were log-transformed. The relationship between log-transformed median groundwater-P concentration at each site and the predominant local land cover was then assessed, in the four countries, using Analysis of Variance (ANOVA).

Results

Limits of detection

Figure 2 shows the effect of these four LOD treatments on median P concentration for groundwater bodies in England and Wales. The calculated median groundwater concentration changes markedly in a number of groundwater bodies depending on the treatment of samples below LOD. It is apparent, therefore, that the utility of datasets which have a large proportion of samples below LOD will be limited, particularly when the LOD itself is above an ecologically relevant threshold. Since a very high fraction (94%) of the data from Northern Ireland is below LOD, these data have been largely excluded from further analysis. For all subsequent analyses and reporting, samples below LOD were treated as being half the LOD, in line with assumptions made by other workers for statistical analyses (Shand et al., 2007; Reimann et al., 2005).

Data coverage

Significant areas of the countries studied here have no historical groundwater P data. In England and Wales 14% of groundwater bodies by area (or 112 out of 357 groundwater bodies) have no groundwater P observations. In the Republic of Ireland this figure is 37% (or 567 of the country’s 746 groundwater bodies) and in Scotland it is 49% (or 241 out of 343 groundwater bodies).

Figure 3 shows the cumulative frequency distribution of groundwater monitoring sites within those groundwater bodies with some groundwater P data. It is apparent that the number of sites in each groundwater body is generally limited, and a significant proportion of groundwater bodies in all countries have fewer than 3 monitoring sites with groundwater P data.

Temporal results

The sampling times in England and Wales and Scotland are evenly distributed through the year, but there are biases in the sampling in the Republic of Ireland (Figure 4), where less than 2% of samples were collected between April and July, inclusive, which coincides with the period of greatest in-stream biological demand for P. However, taking all of the samples from England and Wales, Scotland and Ireland, there appears to be a uniform distribution in the timing of peak observed concentration (Figure 5) with no evidence, for example, of high observed concentrations at the onset of the recharge period.

The national time series of annual median groundwater-P concentration (Figure 6) show no significant trend for Ireland and Scotland, but the data for England and Wales show an apparent increase in annual median groundwater-P concentration up until 1987 followed by a progressive decrease. However, this reflects the smaller number of samples within the first half of the period (average number of samples per year up to 1987 was 277 compared to 1848 per year after 1987, a significant increase as shown by Students $t=7.2$, $p<0.001$) and the progressively reducing LOD (from usually around 50 to 20 μg P L^{-1}).

Spatial results

Figure 7 shows the spatial distribution of median groundwater P concentration within the sampled groundwater bodies of the four countries (excluding Northern Ireland).

Republic of Ireland

In the Republic of Ireland, the majority of groundwater bodies have median P < 20 μg P L^{-1} (the national background level), which is consistent with the usual extremely low (< 10 μg P L^{-1} SRP) surface water P concentrations due to the widespread dominance of limestone geology and associated co-precipitation of P with calcite. However, in 51 groundwater bodies (covering 22% of the Republic of Ireland - or 36 % of the area of groundwater bodies with data) the median concentration exceeded 20 μg P L^{-1}, suggesting potential anthropogenic impact in these systems. Thirty two groundwater bodies (28 % of the area) in the mid-west, together with more localised groundwater bodies in the east and south (Figure 7) have median concentrations above the national eutrophication threshold of 30 μg P L^{-1}. These results are broadly consistent with the analysis of Kilroy (2001) who reported, using national data from 1995-97, that groundwater P levels were generally low with a national median value of 17 μg

P L^{-1} of unfiltered molybdate reactive P, but that one quarter of the data were higher than 30 μg P L^{-1}. However, Kilroy (2001) suggested that sites with elevated groundwater P concentrations were generally located in the eastern half of the country. This is not apparent in Figure 7.

England and Wales

In England and Wales, median groundwater P concentrations tend to be relatively high compared with the other countries, although large areas have median P concentrations of less than 30 μg P L^{-1}. A number of groundwater bodies have median concentrations > 50 μg P L^{-1} – mainly in the south eastern half of England, but with a notable cluster of high concentrations in the English northwest. Around 9 %, 5% and 1% of area of groundwater bodies with data exceed the three good ecological status river thresholds (UKTAG, 2007) of 40, 50 and 120 μg P L^{-1}, respectively.

Scotland

In Scotland, data on groundwater P concentrations are available for relatively few groundwater bodies. Most of the monitored groundwater bodies have median P concentrations of less than 20 μg P L^{-1}, but a small number have concentrations above 30 μg P L^{-1}. These are generally found in the east of the country, which is drier and has more intensive agriculture than the west and north, although there are clusters in Caithness (in the north east) and in Dumfries and Galloway (in the south west).

Relationships with CORINE2000 Land Cover

The relationship between the predominant CORINE2000 land cover surrounding monitoring sites and mean groundwater-P concentration is shown in Table 2 for England and Wales, Scotland and the Republic of Ireland. There are many more groundwater-P measurements available for England and Wales than for the other monitored areas.

Land-use classes account for only around 15% of the observed variability in groundwater-P concentration across the 4 countries. The ANOVA and Fisher LSD tests showed that:

The observed groundwater-P concentrations are significantly higher in England and Wales, than those in the Republic of Ireland and Scotland, within each of the land-use classes.(Table 2).

Measured groundwater-P concentrations are significantly lower where the predominant land-use class surrounding monitoring boreholes is semi-natural vegetation than those with urban, arable and grassland surrounding the boreholes, for England and Wales and Scotland but not the Republic of Ireland (Table 2 and 3).

Discussion

The quantity and quality of groundwater monitoring data for P is variable both within, and between, countries. The constraints of poorly-designed monitoring schedules, at least for the purposes of evaluating groundwater P levels, inappropriate and variable LODs, and a lack of information about borehole capture zones hinder a more detailed interpretation of the data. Nevertheless, many of the results generated are interesting and challenge previous perceptions. In particular, the data suggest that phosphorus concentrations in many groundwater bodies in Scotland, the Republic of Ireland and, particularly, in England and Wales are relatively high (often > LOD and sometimes > ecological thresholds for surface waters). Further investigation is therefore warranted to answer three key questions:

What is the nature and contribution of anthropogenic sources to high observed groundwater P concentrations?

What pathway and receptor factors influence the eutrophication risks from groundwater P to associated freshwaters and groundwater-dependent terrestrial ecosystems?

How can the sources, behaviour and impacts of groundwater P be better characterised, understood and, if necessary, managed?

Nature and contribution of anthropogenic sources

For the purpose of designing appropriate policy responses, it is necessary to ascertain whether groundwater P concentrations are elevated above natural background levels (i.e. the concentrations which would be expected given undisturbed conditions). However, defining a baseline concentration at any scale (groundwater body, aquifer, or nationally) is not straightforward. One approach is to use a particular percentile concentration from groundwater monitoring data, based on the assumption that only a small fraction of sites will be strongly influenced by anthropogenic activity (Shand et al., 2007). For example, the Natural Background Level for orthophosphate in all Irish groundwaters was set at 20 µg P L^{-1} based on the 90th percentile concentration within confined portions of Irish aquifers, thus excluding samples representative of shallow bedrock flow and “to minimise the risk of influence from anthropogenic inputs” (O’Callaghan Moran & Associates, 2007). In contrast, the 95th percentile concentration was used by Edmunds et al. (1997) and is still used to set background levels for individual groundwater bodies or aquifers in England and Wales (Rob Ward, *pers. comm*).

Although pragmatic, the main problem with such approaches is that they do not identify a natural background concentration if a high proportion of the aquifers being assessed are already polluted by anthropogenic sources. In any case, account should be taken of the number and quality of the monitoring data used, including the consistency of successive measurements, the LODs used, number of samples above and below LODs, and the distribution of concentrations above the LOD. In addition, account should be taken of the hydrogeological context of systems under consideration, including the potential evolution of geochemistry along hydrogeological flow paths.

Our ANOVA showed that there were significant differences between P concentrations under different land uses, suggesting some role for local land use in controlling groundwater P concentrations. The data presented in Tables 2 and 3 suggest that higher concentrations are generally found under urban, arable and managed grassland areas, particularly in England and Wales. This implies some anthropogenic influence, although interpretation is hampered by the design of the sampling network, the timing of sampling, the length of the data series and by the fact that we only assessed land use in an arbitrary area with a 1 km radius around each monitoring site, in the absence of information on the extent of source protection zones or abstraction rates.

A number of potential anthropogenic point- and diffuse-sources exist, which could lead to enhanced groundwater P loading and explain, in part, the apparent elevation of concentrations under urban and agricultural areas. These include:

Agricultural soils: Phosphorus has been routinely applied to soils for many years, either as mineral fertilizer or as animal feed supplements, in excess of crop requirements in England (e.g. Withers et al., 2001), Northern Ireland (e.g. Foy et al., 1995) and in the Republic of Ireland (e.g. Tunney, 1990). This has led to the accumulation of P in soils and an increased risk of leaching loss (e.g. Foy et al., 1995; Tunney, 1990; Heckrath et al., 1995; Sharpley, 1995).

Septic tanks: Many rural domestic dwellings are served by on-site wastewater treatment systems, such as septic tanks. In Ireland, for example, the domestic wastewater of over 400,000 dwellings (>one-third of the population) is treated by on-site systems (Department of the Environment, 2004). Dissolved P concentrations in septic effluents can be as high as 12 mg P L^{-1} (Weiskel and Howes, 1992; Gill et al., 2007).

Leaking sewers: Raw sewage can have total phosphorus concentrations of 9 to 15 mg P L^{-1}, of which two-thirds is in inorganic forms (Metcalf and Eddy. 2003). If sewers leak, they can generate P-rich plumes which could pollute local groundwater.

Leaking mains water pipes: Around 95% of the UK's public water supplies are dosed with orthophosphate, to reduce plumbosolvency, at concentrations of 0.5 to 1.5 mg P L^{-1}, depending on alkalinity (CIWEM, 2005; Hayes et al., 2008), hence plumes of P-rich water may also originate from leaking water mains.

Slurry lagoons: Studies have shown clear evidence of P leaching and groundwater contamination beneath animal slurry lagoons that lack impervious linings (e.g. Gooddy et al., 1998; Withers et al., 1998). Furness et al. (1991) have estimated that there were an estimated 6150 slurry lagoons on dairy, beef and pig farms in the late 1980s. Nicholson and Brewer

(1997) estimated a total surface area of 7.0 x 10^6 m^2 of livestock slurry and farm yard dirty water stored in such lagoons.

Agricultural manure heaps: Nicholson and Brewer (1997) estimated that the exposed surface area of stored animal manures was 11.9 x 10^6 m^2, whilst Gooddy (2002) reported P leaching from a turkey litter site down to a depth of at least 5 m.

Influence of pathway and receptor type on eutrophication risks in associated freshwater and groundwater-dependent terrestrial ecosystems

The eutrophication risk to receptor systems due to elevated groundwater P concentrations will vary with hydrogeological setting (pathways) and the sensitivity of the receptor system to P. Even if groundwater P concentrations are elevated above natural background levels, adverse impacts will not necessarily be observed in receptor systems because a number of attenuating reactions may occur along the flowpath between monitoring site and receptor. In addition, if groundwater contamination is limited in extent, some dilution would be expected from uncontaminated baseflow. Factors affecting the likelihood of groundwater P transport to receptor systems include:

The sorption potential of the aquifer matrix for P. This will be related to the combined $Fe(OH)_3$ and $CaCO_3$ content. There are a number of potential P sorption and immobilisation processes including relatively rapid adsorption at high-affinity mineral surface sites (Parfitt, 1978, 1989), slower precipitation of metal phosphate complexes (Van Riemsdijk et al., 1984) and slow diffusion into micropores or aggregates (Torrent et al., 1992; Mikutta et al., 2006; Lijklema, 1980; Stollenwerk, 1996). Some of these processes are reversible and some are dependent on redox conditions (e.g. Griffioen, 2006; Loeb et al., 2008);

The degree of contact between groundwater and the aquifer matrix as indicated by the flow type. This is likely to be relatively low in karstic/highly fissured, fissure / fracture and dual porosity systems, where the matrix may be bypassed by most of the flow and higher where a significant fraction of flow is intergranular. Studies considering P movement through groundwater in which P sorption has been shown to be important (e.g Stollenwerk, 1996; Harman et al., 1996; Ptacek, 1998; Corbett et al., 2002) have mostly examined alluvial or intergranular aquifers, whereas groundwater P contamination has more commonly been associated with fractured aquifers (e.g. Withers et al., 1998; Bishop et al., 1998);

The time available for sorption. This will depend upon the likely groundwater residence time, which will depend on aquifer type, transmissivity, hydraulic gradients and typical length of groundwater flow path to the receptor;

The role of the hyporheic zone: Steep gradients in redox potential can exist in the transition zone between groundwater and surface water, with consequences for P mobility (e.g. Griffioen, 2006; Surridge et al., 2006). Under low redox potential iron-associated P may be mobilised, as Fe^{3+} is reduced to Fe^{2+}. When redox potential increases (for example in the hyporheic zone), P may be immobilised. However, the significance of these processes for providing natural attenuation (or otherwise) of nutrients is highly uncertain.

Receptor sensitivity

The sensitivity of a river or wetland receptor to groundwater P inputs will depend on a number of factors associated with the receptor, and the timing and mode of P delivery. These are summarised in Figure 8 and include:

Scale: The variety of potential P sources for surface waters increases as the upstream contributing area increases, as will hydrological damping and the role of in-stream retention (Prairie and Kalff, 1986), hindering the establishment of causal relationships between specific P sources and biological impacts (Edwards and Withers, 2007);

Receptor residence time: The impact of different P inputs on the receptor ecosystem will differ considerably between lentic and lotic systems, because of their differing sensitivity to concentration and load (Edwards et al., 2000). The longer residence times of lentic systems (Johnes et al., 2007), compared with lotic systems, means that a significant fraction of diffuse-source P inputs from winter and spring runoff events will remain (augmented by internal nutrient cycling), thereby contributing to biological P demand in spring and summer and a reduced sensitivity to groundwater P. By contrast, rivers and streams have much shorter residence times (Jarvie et al., 2006) so that baseflow P delivery in spring and summer is likely to be more important, whilst high episodic loads of soil-derived P in the winter are likely to have less direct local significance for the ecosystem;

Flow regime and climate: Groundwater flow is largely independent of individual precipitation events (Edwards and Withers, 2007) and makes its most significant relative contribution during periods of low flow, in both upland and lowland areas. A river with a very high base flow index (such as in a chalk catchment) in a relatively dry climate is likely to have less sediment-derived P inputs because of the fewer runoff and erosion events and a higher groundwater contribution to flow. Depending on the N:P ratio of the groundwater compared with that in the receiving surface water, groundwater discharge can also lead to a shift in the limiting nutrient for primary production, if it constitutes a significant fraction of the total flow (Slomp and Van Cappellen, 2004).

Synchronicity between delivery and biological demand: Groundwater is most important for supporting surface water flows during low-flow periods. These periods (i.e. late spring and summer) are often contemporaneous with high in-stream biological demand for P (Flynn et al., 2002; Foy, 2005). For example, most lowland river macrophytes have committed their biomass by June, having completed their growth and flowered, and generally seek to maintain biomass during the rest of the growing season;

Sensitivity of species: Increases in P supply from groundwater could promote adverse ecological impacts such as the loss of low growing, stress tolerant sedges and herbs in groundwater discharge fens (e.g. in calcareous spring fens) which are highly sensitive to prolonged periods of higher nutrient availability which favour more competitive and productive species. Currently, enhanced P supply is considered to be a far greater risk to the maintenance of endangered plant species in European fens than nitrogen enrichment (Wassen et al., 2005). In rivers, elevated P supply is often associated with increased filamentous algal growth and associated changes in the structure and cover of aquatic vegetation (Hilton et al., 2006). Since rooted macrophytes derive their nutrient supply from both the water column and sediment interstices (Clarke and Wharton, 2001) they may be more sensitive to groundwater P inputs than might be deduced from surface water P concentrations alone, especially in baseflow-dominated systems, such as chalk streams. It is also feasible that, in some situations, high groundwater P concentrations will frustrate attempts to promote ecological recovery in rivers via point-source control, even when these succeed in greatly reducing surface water P loading.

Saturation thresholds: It is often considered that calcareous systems are protected against the effects of enhanced P concentrations as the co-precipitation of P is an important process for controlling P concentrations. However, a receptor that exceeds or is close to the saturation threshold will be sensitive to additional inputs of P through groundwater. This may be particularly important in chalk systems in which groundwater P enters the surface water body through discrete entry points (e.g. Howden and Burt, 2008, 2009) rather than diffuse inflow.

Requirements to better characterise, understand and manage groundwater P

Despite the many uncertainties, our analysis of existing available data from five countries suggests that more attention should be paid to the potential role of groundwater as a source of P-delivery to surface water ecosystems and that it should not automatically be viewed as a source of dilution. Given the potential significance of elevated groundwater P for the achievement of Good Ecological Status required under the European Water Framework Directive (WFD: 2000/60/EC) in many surface water and wetland receptors, we propose the following:

1. Standardised sampling and analytical techniques to allow comparisons, particularly for transnational water bodies: Present data holdings across the five countries are inconsistent in several ways. The particular form of P determined by water sample analyses differs between countries, regions and, in some cases, sampling events. It is imperative that sampling strategies are applied consistently, such that comparisons may be made robustly;

2. Standardised LODs, at least at a national scale, which are below ecologically-important thresholds: This is a key observation from our analyses. Historically, the LODs for groundwater-P were thought to be unimportant, as samples were being analysed for comparison with drinking water standards and were often relatively high. The progressive changes in LOD in England and Wales over time have also rendered the data unsuitable for trend analyses (Fig. 6);

3. Better-defined and robust sampling strategies (e.g. Burt et al., 2009) which capture the spatial and temporal variability in groundwater P concentration: Past and present sampling strategies are somewhat piece-meal, have limited spatial coverage at the national scale (Fig. 7), and have low sampling frequency in space (Fig. 3) and time;

4. Sampling of the many groundwater bodies with no historical measurements of P concentration is required. This should be prioritised according to estimated risk in associated receptors: Historically, sampling has been focused on aquifers where groundwater was abstracted for public water supply. There are few data from other aquifer systems;

5. An improved knowledge of the locations of point-sources such as slurry lagoons, septic tanks and leaking water and waste water pipes is needed, along with a regulatory means of managing the risks that they may pose to groundwater P concentrations: Source management is key to reducing potential anthropogenic inputs of P to groundwater. The present lack of information about locations of sources should be addressed as a matter of urgency;

6. Further monitoring and research to better characterise the extent and magnitude of anthropogenic influences (relative to potential geological sources of phosphorus) on groundwater P concentrations, the transformation and/or storage of P along the aquifer-hyporheic zone flow path and the subsequent risk to receptors. A more comprehensive understanding of phosphorus attenuation mechanisms along groundwater and hyporheic zone flow pathways is needed.

Conclusions

An analysis of phosphate concentration in groundwater has been presented, based on over 49,000 groundwater samples collected from almost 3600 monitoring sites by the national regulatory agencies for England and Wales, Scotland, Northern Ireland and the Republic of Ireland over the period 1968 to 2007. Notwithstanding the overall size of the dataset, the significance of the interpretations must be viewed in the context of the number of monitoring sites within each groundwater body (often <=3) and the large number of samples (over 24,000) below LOD (which were variable and often at or above ecologically-relevant thresholds). Many groundwater bodies covering extensive areas, especially in the Republic of Ireland and Scotland, have no data on P concentrations. Others have few sampling sites and/or small numbers of samples. That said, significant numbers of groundwater bodies have median groundwater P concentrations which are above ecologically significant thresholds for receiving freshwaters.

The potential ecological risk of high observed groundwater P concentrations for receptor systems will depend on whether concentrations are above the natural background level, the potential for removal along flow pathways, the sensitivity of the receptor to P and the importance of other P sources. Given the important role of phosphorus for achieving Good Ecological Status in surface waters under the WFD, this research suggests that groundwater should not automatically be viewed as a source of dilution, but rather as having the potential to trigger and/or maintain eutrophication. Further research is needed to better characterise the extent and magnitude of anthropogenic P sources (relative to potential geological sources) and the transformation and/or retention of P along the aquifer-hyporheic zone flowpath, in order to quantify any risks posed to receptors.

Acknowledgments

The authors are grateful to the Scotland & Northern Ireland Forum for Environmental Research (SNIFFER Project WFD 85) for funding and to the Environment Agency of England and Wales, SEPA, EHS Northern Ireland and the Irish EPA for the provision of data. We thank the members of the WFD85 Steering Committee for their advice and support.

We are also grateful to two anonymous referees whose insightful comments did much to improve our original manuscript.

References

Addiscott TM, Thomas D. Tillage, mineralisation and leaching: phosphate. Soil Till Res 2000; 53: 255-273.

Bishop PK, Misstear BD, White M, Harding NJ. Impacts of Sewers on Groundwater Quality. Water and Environment Journal 1998; 12(3): 216-223.

Burt TP, Howden NJK, Worrall F, Whelan MJ Importance of long-term monitoring for detecting environmental change: lessons from a lowland river in south-east England, Biogeosciences 2008, 5 (6) 1529-1535.

Burt TP, Howden NJK, Worrall F, Whelan MJ Long-term monitoring of river water nitrate: how much data do we need? J. Environ. Monit. (2010), doi:10.1039/b913003a.

CIWEM (2005). Policies: Lead in drinking water. http://www.ciwem.org/policy/policies/lead.asp. Accessed on 12/10/09

Clarke SJ, Wharton G (2001) Sediment nutrient characteristics and aquatic macrophytes in lowland English rivers. Science of the Total Environment, 266: 103-112

Corbett DR, Dillon K, BurnettW, Schaefer G. The spatial variability of nitrogen and phosphorus concentration in a sand aquifer influenced by onsite sewage treatment and disposal systems: a case study on St., George Island, Florida. Environmental Pollution 2002; 117 (2): 337–345.

Department of the Environment. 2004. Groundwater protection schemes. Department of the Environment and Local Government, Environmental Protection Agency, and Geological Survey of Ireland.

Edmunds WM, Brewerton LJ, Shand P, Smedley PL. The natural (baseline) quality of groundwaters in England and Wales: Part 1: A guide to the natural (baseline) quality study. British Geological Survey Technical Report WD/97/51. British Geological Survey, Keyworth, UK, 1997.

Edwards AC, Withers PJA. Linking phosphorus sources to impacts in different types of water body. Soil Use Manage 2007; 23 (Suppl. 1): 133-143.

Edwards AC, Twist H, Codd GA. Assessing the impact of terrestrially derived phosphorus on flowing water systems. J Environ Qual 2000; 29: 117–124.

Environment Agency (2006). Groundwater body chemical classification. Unpublished document, Environment Agency,

Flynn NJ, Snook DL, Wade AJ, Jarvie HP. Macrophyte and periphyton dynamics in a UK Chalk stream: the River Kennet, a tributary of the Thames. Sci Total Environ 2002; 282-283: 143-157.

Foy RH, Smith RV, Jordan C, Lennox SD. Upward trend in soluble phosphorus loadings to Lough Neagh despite phosphorus reduction at sewage treatment works. Water Res 1995; 29: 1051-1063.

Foy RH. The return of the phosphorus paradigm: agricultural phosphorus and eutrophication. In: Sims JT, Sharpley AN, editors. Phosphorus: agriculture and the environment. American Society of Agronomy Monograph No. 46, Madison, USA, 2005; 911–939

Furness GW, Coleman DR, Webb SF, Hendry K. The status of waste handling facilities on livestock farms in Great Britain . Manchester University Report to MAFF, 1991

Gill LW, O’Súlleabháin C, Misstear BDR, Johnston PJ. The Treatment Performance of Different Subsoils in Ireland Receiving On-Site Wastewater Effluent. J Environ Qual 2007; 36: 1843-1855.

Gooddy DC. Movement of leachate from beneath Turkey litter sited over chalk in southern England. J Environ Sci Heal B 2002; B37(1): 81-91.

Gooddy DC, Withers PJA, McDonald HG, Chilton PJ. Behaviour and impact of cow slurry beneath a storage lagoon: II. Chemical Risk assessment to UK groundwater composition of Chalk porewater after 18 years. Water Air Soil Poll 1998; 107: 51-72.

Griffioen J. Extent of immobilisation of phosphate during aeration of nutrient-rich, anoxic groundwater. J Hydrol 2006; 320: 359-369.

Harman J, Robertson WD, Cherry JA, Zanini L. Impacts on a sand aquifer from an old septic system: nitrate and phosphate. Groundwater 1996; 34: 1105–1114.

Hayes CR, Incledion S, Balch M. Experience in Wales (UK) of the optimisation of orthophosphate dosing for controlling lead in drinking water. Journal of Water and Health 2008; 6, 177-185.

Heathwaite AL, Burke SP, Bolton L. Field drains as a route of rapid nutrient export from agricultural land receiving biosolids. Sci Total Environ 2006; 365(1-3): 33-46.

Heathwaite AL, Dils RM. Characterising phosphorus loss in surface and subsurface hydrological pathways. Sci Total Environ 2000; 251-252; 523-538.

Heckrath G, Brookes PC, Poulton PR, Goulding KWT. Phosphorus leaching from soils containing different phosphorus concentrations in the Broadbalk experiment. J Environ Qual 1995; 24: 904-910.

Hilton J, O'Hare M, Bowes MJ, Jones JI. 2006. How green is my river? A new paradigm of eutrophication in rivers. Science of the Total Environment 365: 66-83.

Hodgkinson RA, Chambers BJ, Withers PJA, Cross R. Phosphorus losses to surface waters following organic manure applications to a drained clay soil. Agr Water Manage 2002; 57(2): 155-173.

Holman IP, Whelan MJ, Howden NJK, Bellamy PH, Willby NJ, Rivas-Casado M, McConvey P. Phosphorus in groundwater—an overlooked contributor to eutrophication? Hydrol Proc 2008; 22: 5121-5127.

Holman IP, Howden NJK, Whelan MJ, Bellamy PH, Rivas-Casado M, Willby NJ. An Improved Understanding of Phosphorus Origin, Fate and Transport within Groundwater and the Significance for Associated Receptors. SNIFFER Project WFD85 Final Report, 2008, 139pp

Howden NJK, Bowes MJ, Humphries RN, Neal C. Water Quality, nutrients and the European Union's Water Framework Directive in a lowland agricultural region: Suffolk, south-east England. Sci Total Environ 2009; 407: 2966-2979, doi:10.1016/j.scitotenv.2008.12.040.

Howden NJK, Burt TP. Statistical analysis of nitrate concentrations from the Rivers Frome and Piddle (Dorset, UK) for the period 1965-2007. Ecohydrol 2009; 2(1): 55-65, doi:10.1002/eco.39.

Howden NJK, Burt TP. Temporal and spatial analysis of nitrate concentrations from the Frome and Piddle catchments in Dorset (UK) for water years 1978 to 2007: Evidence for nitrate breakthrough? Sci Total Environ 2008; 407(1): 507-526, doi:10.1016/j.scitotenv.2008.08.042.

Jarvie HP, Neal C, Withers PJA. Sewage-effluent phosphorus: a greater risk to river eutrophication than agricultural phosphorus? Sci Total Environ 2006; 360: 246–253.

Johnes PJ, Foy R, Butterfield D, Haygarth PM. Land use scenarios for England and Wales: evaluation of management options to support 'good ecological status' in surface freshwaters. Soil Use Manage 2007; 23 (Suppl. 1): 176-194.

Kilroy G. Phosphorus in Irish Aquifers: implications for input to surface waters. PhD Thesis, Department of Geology, Trinity College Dublin, 2001.

Kilroy G, Coxon C. Temporal variability of phosphorus fractions in Irish karst springs. Environmental Geology 2005; 47: 421–430.

Lijklema L. Interaction of orthophosphate with iron (III) and aluminium hydroxides. Environ Sci Technol 1980; 14(5): 537-541.

Loeb R, Lamers LPM, Roelofs JGM. Effects of winter versus summer flooding and subsequent dessication on soil chemistry in a riverine hay meadow Geoderma 2008; 145: 84-90

Mainstone CP, Parr W. Phosphorus in rivers: Ecology and management. Sci Total Environ 2002; 282: 25-47.

Metcalf and Eddy. 2003. Wastewater engineering: Treatment and reuse. 4th ed. McGraw-Hill, London.

Mikutta C, Lang F, Kaupenjohann M. Citrate impairs the micropore diffusion of phosphate into pure and Ccoated goethite. Geochim Cosmochim Ac 2006; 70(3): 595–607.

Neal C, Jarvie HP, Love A, Neal M, Wickham H, Harman S. Water quality along a river continuum subject to point and diffuse sources. J Hydrol 2008; 350(3-4): 154-165.

Nicholson RJ, Brewer A.J. Estimates of volumes and exposed surface areas of stored animal manures and slurries in England and Wales. J Agric Engin Res 1997; 66: 239–250.

O'Callaghan Moran & Associates (2007) Establishing Natural Background Levels For Groundwater In Ireland. Unpublished report for the The Southeastern River Basin District Project Team

Parfitt RL. Anion adsorption by soils and soil materials. Adv Agron 1978; 30: 1–49.

Parfitt RL. Phosphate reactions with natural allophane, ferrihydrate and goethite. J Soil Sci 1989; 40: 359–369.

Prairie YT, Kalff J. Effect of catchment size on phosphorus export. Water Resour Bull 1986; 22: 465–470.

Ptacek CJ. Geochemistry of a septic-system plume in a coastal barrier bar, Point Pelee, Ontario, Canada. J Contam Hydrol 1998; 33 (3–4): 293–312.

Reimann C, Filzmoser P, Garrett RG. Background and threshold: critical comparison of methods of determination. Sci Total Environ 2005; 346(1-3): 1-16.

Shand P, Edmunds WM, Lawrence AR, Smedley PL, Burke S. The natural (baseline) quality of groundwater in England and Wales. BGS Research Report RR/07/06; Environment Agency Technical Report NC/99/74/24, 2007.

Sharpley AN. Dependence of runoff phosphorus on extractable soil phosphorus J Env Qual 1995; 24: 920-926.

Slomp CP, Van Cappellen P. Nutrient inputs to the coastal ocean through submarine groundwater discharge: controls and potential impact. Journal of Hydrology 2004; 295: 64–86.

Stevenson RJ, Hill BH, Herlihy AT, Yuan LL, Norton SB. 2008. Algae-P relationships, thresholds, and frequency distributions guide nutrient criterion development. Journal of the North American Benthological Society, 27: 783-799.

Stollenwerk KG. Simulation of phosphate transport in sewage-contaminated groundwater, Cape Cod, Massachusetts. Appl Geochem 1996; 11: 317-324.

Surridge BWJ, Heathwaite AL, Baird AJ. Groundwater – surface water interactions and phosphorus biogeochemistry in river floodplains. EGU 2006 Geophysical Research Abstracts, 2006; 8: 05792.

Torrent J, Schwertmann U, Barrón V. Fast and slow phosphate sorption by goethite-rich natural materials. Clay clay miner 1992; 40 (1): 14–21.

Tunney H. A note on the balance sheet approach to estimating the phosphorus fertiliser needs of agriculture. Irish J Ag Research 1990; 29: 149-154.

UKTAG (2007). UK Environmental Standards Aand Conditions (Phase 1). Updated report (November 2007) SR1–2006

Van Riemsdijk WH, Boumans LJM, De Haan FAM. Phosphate sorption by soils: I. A model for phosphate reaction with metal-oxides in soils. Soil Sci Soc Am J 1984; 48 (3): 537–541.

Wassen MJ, Venterink HO, Lapshina ED, Tanneberger F. Endangered plants persist under phosphorus limitation. Nature 2005; 437: 547-550.

Weatherhead EK, Howden NJK The links between land use and surface water resources in the UK, Land Use Policy, 2009, doi:10.1016/j.landusepol.2009.08.007.

Weiskel PK, Howes BL. Differential transport of sewage-derived nitrogen and phosphorus through coastal watershed. Environ Sci Technol 1992; 26: 352–360.

Withers PJA, Haygarth PM. Agriculture, phosphorus and eutrophication: a European perspective. Soil Use Manage 2007; 23 (Suppl. 1): 1–4.

Withers PJA, Lord EI. Agricultural nutrient inputs to rivers and groundwaters in the UK: policy, environmental management and research needs. Sci Total Environ 2002; 282: 9-24.

Withers PJA, McDonald HG, Smith KA, Chumbley CG. Behaviour and impact of cow slurry beneath a storage lagoon: I. Groundwater contamination 1975-1982. Water, Air and Soil Pollution 1998; 107: 35-49.

Withers PJA, Edwards AC, Foy RH. Phosphorus cycling in UK agriculture and implications for phosphorus loss from soil. Soil Use Manage 2001; 17: 139–149.

Table 1: Numbers and statistics of groundwater-P samples in England and Wales, Northern Ireland, Scotland and Ireland and details of limits of detection (LOD)

Country	Time period	Number of samples				Detection limits ($\mu g\ l^{-1}$)
		taken	below LOD's	below LOD of >=60 $\mu g\ l^{-1}$)	Above LOD and >= 30 $\mu g\ l^{-1}$	
England and Wales	1968 – 2006*	39 010	20671	0**	13991	1 to 50**
Northern Ireland	2000 - 2006	513	480	322	35	28 to 100
Scotland	1997 – 2007***	3856	1078	0	947	1 to 20
Ireland	1995 - 2006	5057	1692	0	1253	1 to 20

* There are only 12 samples from before 1974

** All data with a LOD > 0.05mg/L were removed by the Environment Agency.

*** There is only 1 sample from before 2000

Country	For all samples with positive detections of P				
	Minimum concentration ($\mu g\ P\ l^{-1}$)	Maximum concentration ($\mu g\ P\ l^{-1}$)	Mean concentration ($\mu g\ P\ l^{-1}$)	Median concentration ($\mu g\ P\ l^{-1}$)	Standard deviation ($\mu g\ P\ l^{-1}$)
England and Wales	2	124 000	145.9	280	1404.9
Northern Ireland	29	1520	268.8	88	408.6
Scotland	2.9	5700	41.1	19	135.2
Ireland	1	10 420	44.4	20	246.6

Table 2 Results of the ANOVA between mean groundwater-P concentrations and predominant surrounding CORINE2000 land cover class

Effect	Sum of Squares	Degr. of Freedom	Mean Square	F-value	probability
Country	630.07	2	315.04	226.13	<0.001
Land cover	67.31	4	16.83	12.08	<0.001
Country*Land cover	48.46	8	6.06	4.35	<0.001
Error	13846.37	9939	1.39		

Table 3 Fisher LSD tests to show significant differences in mean groundwater P between land cover classes, within countries and between countries within the same land cover class

Country	Land cover	Mean P ($\mu g\ l^{-1}$)	Number of sites	Significant differences[1]				Significant differences[2]	
				Arable	Grassland	Semi-natural vegetation	Woodland	Scotland	England
Republic of Ireland	Urban	30.4	385	**	NS	NS	NS	*	***
	Arable	21.1	822		**	NS	***	***	***
	Grassland	28.9	3370			NS	**	***	***
	Semi-natural	23.4	130				NS	***	*
	Woodland	27.7	342					***	***
Scotland	Urban	37.8	172	*	NS	***	**		***
	Arable	26.9	1479		***	***	NS		***
	Grassland	34.6	1533			***	***		***
	Semi-natural	20.1	151				NS		***
	Woodland	16.4	520						***
England and Wales	Urban	103.2	229	**	NS	***	*		
	Arable	74.2	374		NS	**	NS		
	Grassland	98.9	333			***	NS		
	Semi-natural	47.9	49				*		
	Woodland	57.8	65						

[1] Relative to land cover class in the same country

[2] Relative to country in same land cover class

NS Not significant; * p<0.05; ** p<0.01 and *** p<0.001

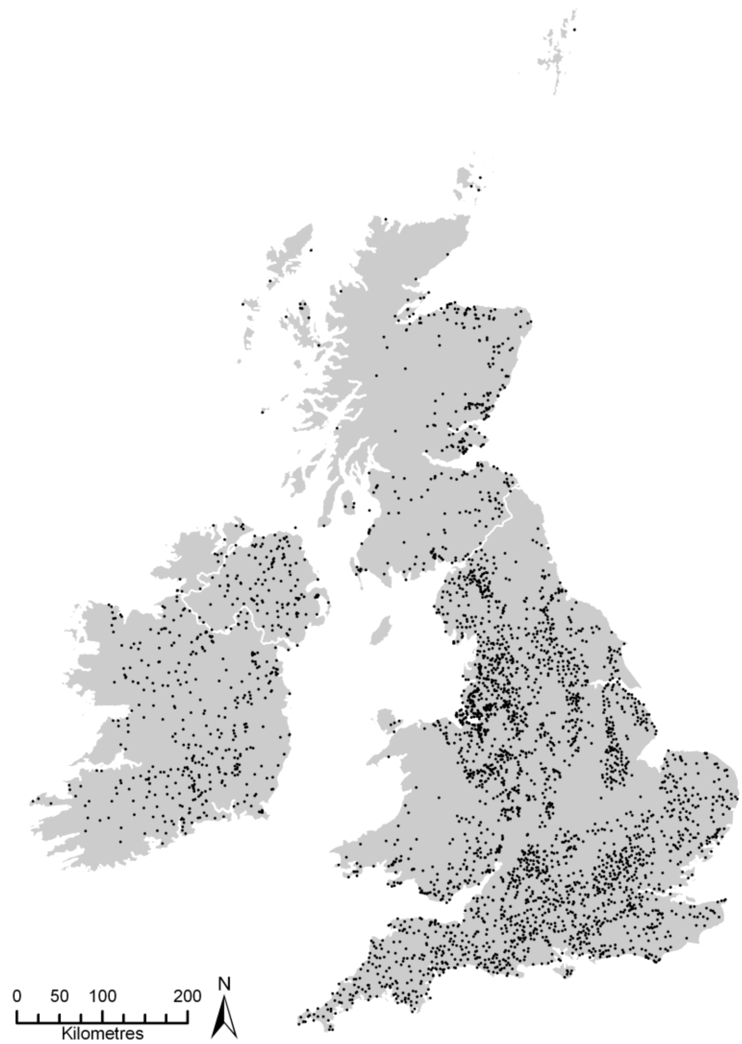

Figure 1 Distribution of groundwater monitoring sites with P data

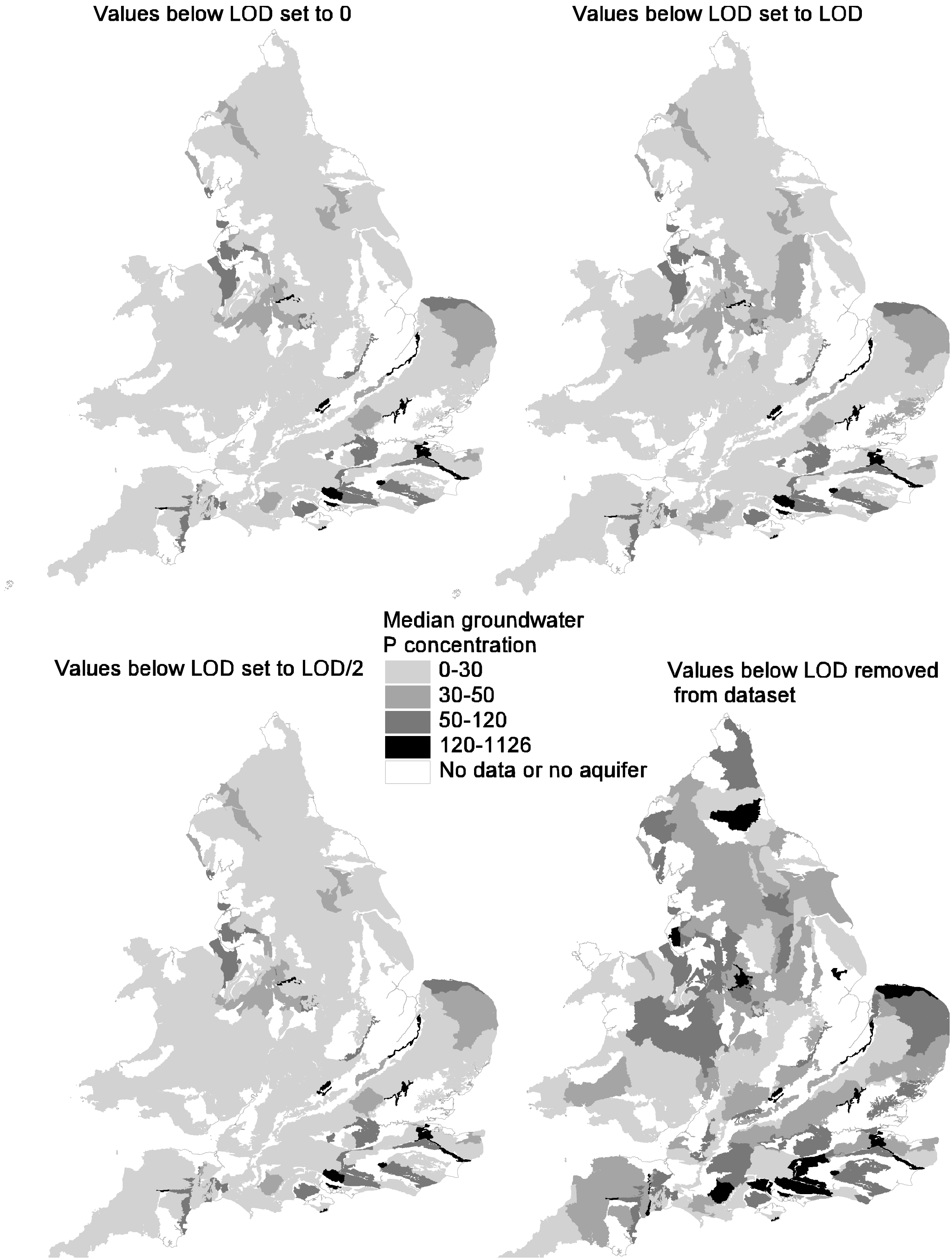

Figure 2 Effects of the treatment of samples below LOD on median groundwater P concentration (µg P l-1) in the groundwater bodies of England and Wales

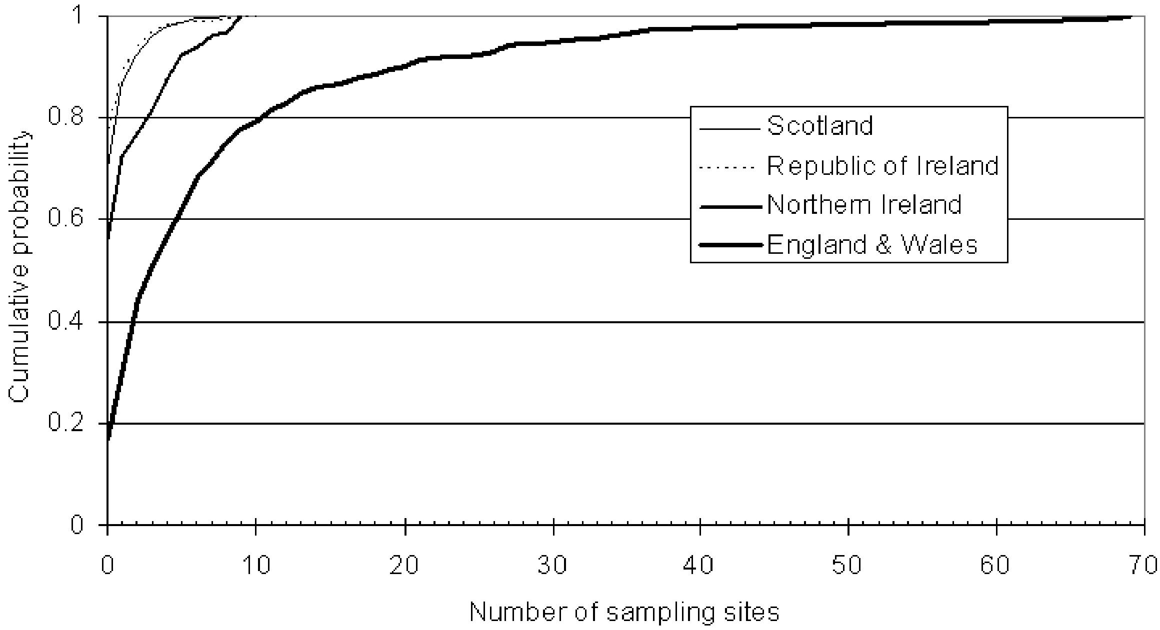

Figure 3 Cumulative frequency distribution of number of national groundwater monitoring sites in all groundwater bodies

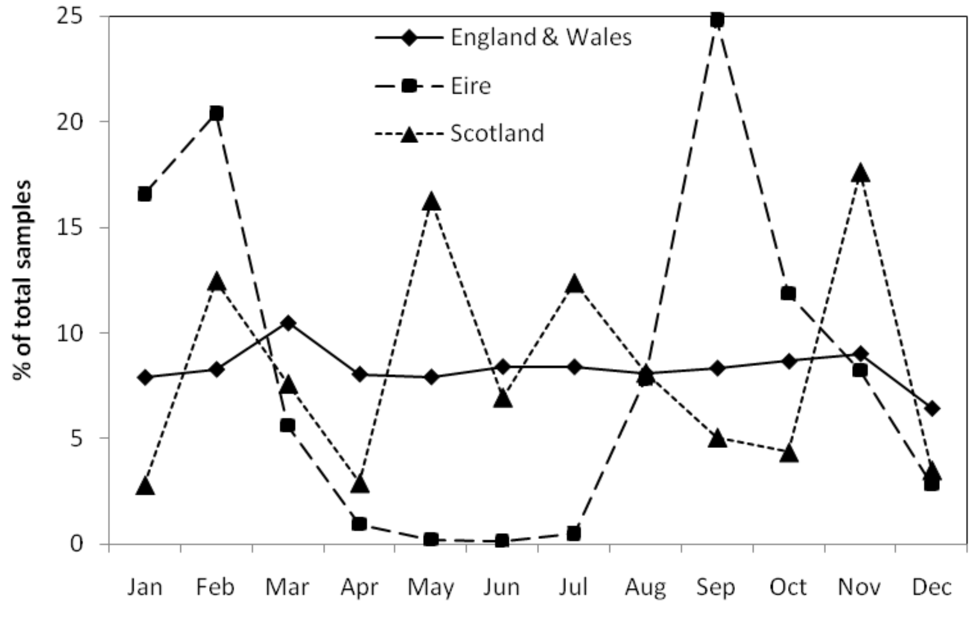

Figure 4 National distributions of samples by month of collection

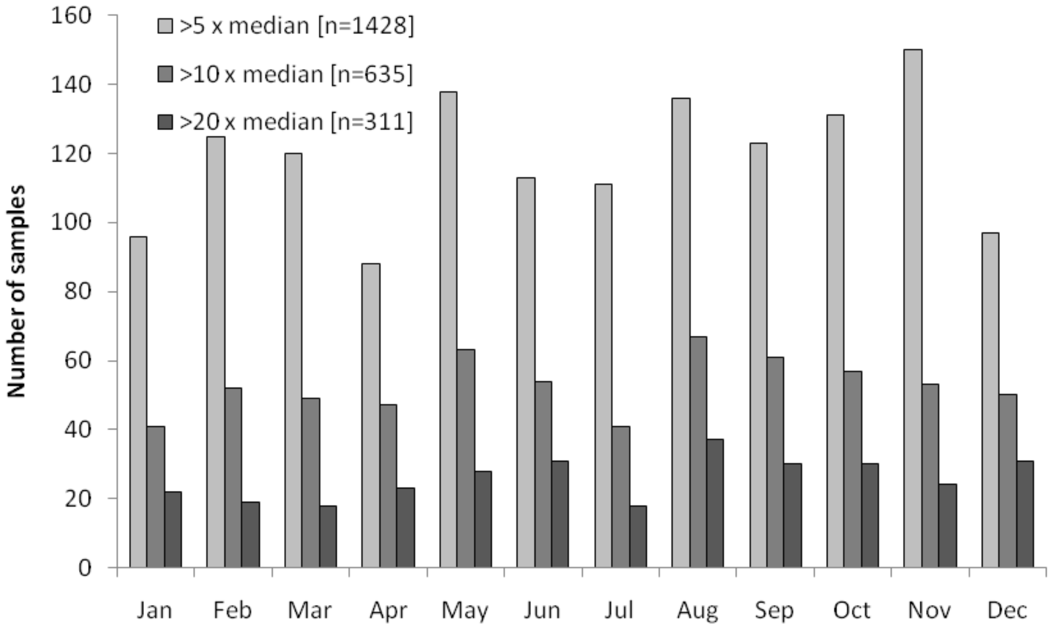

Figure 5 Distribution in the timing of elevated groundwater-P observations (expressed as multiples of the median concentration at a given monitoring site)

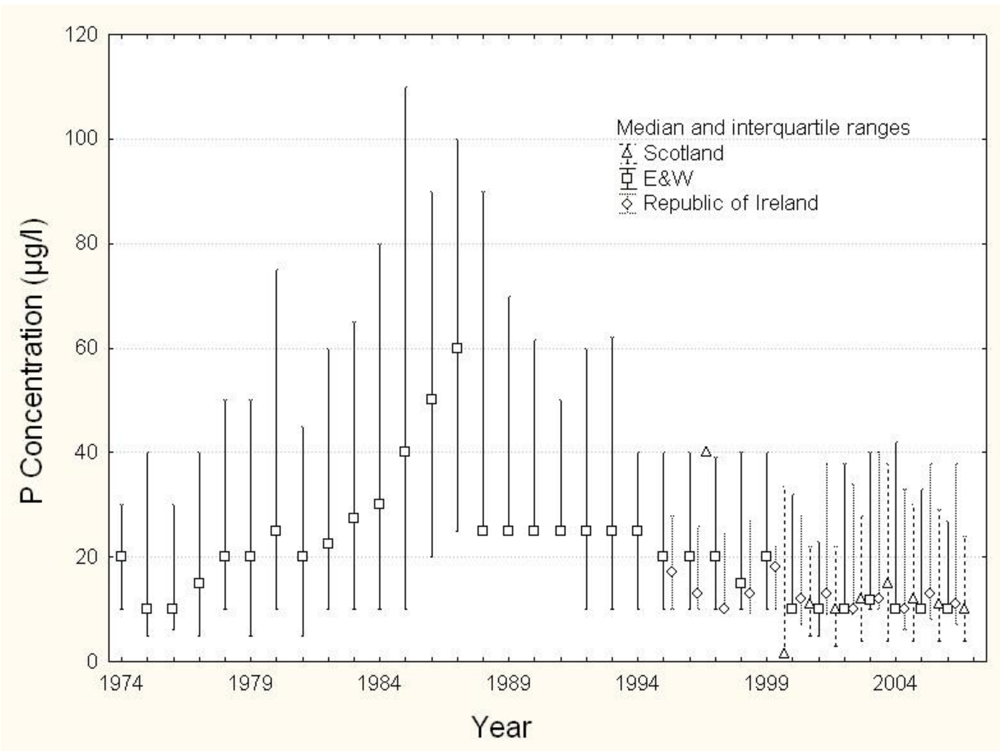

Figure 6 National time series of annual median groundwater-P concentrations

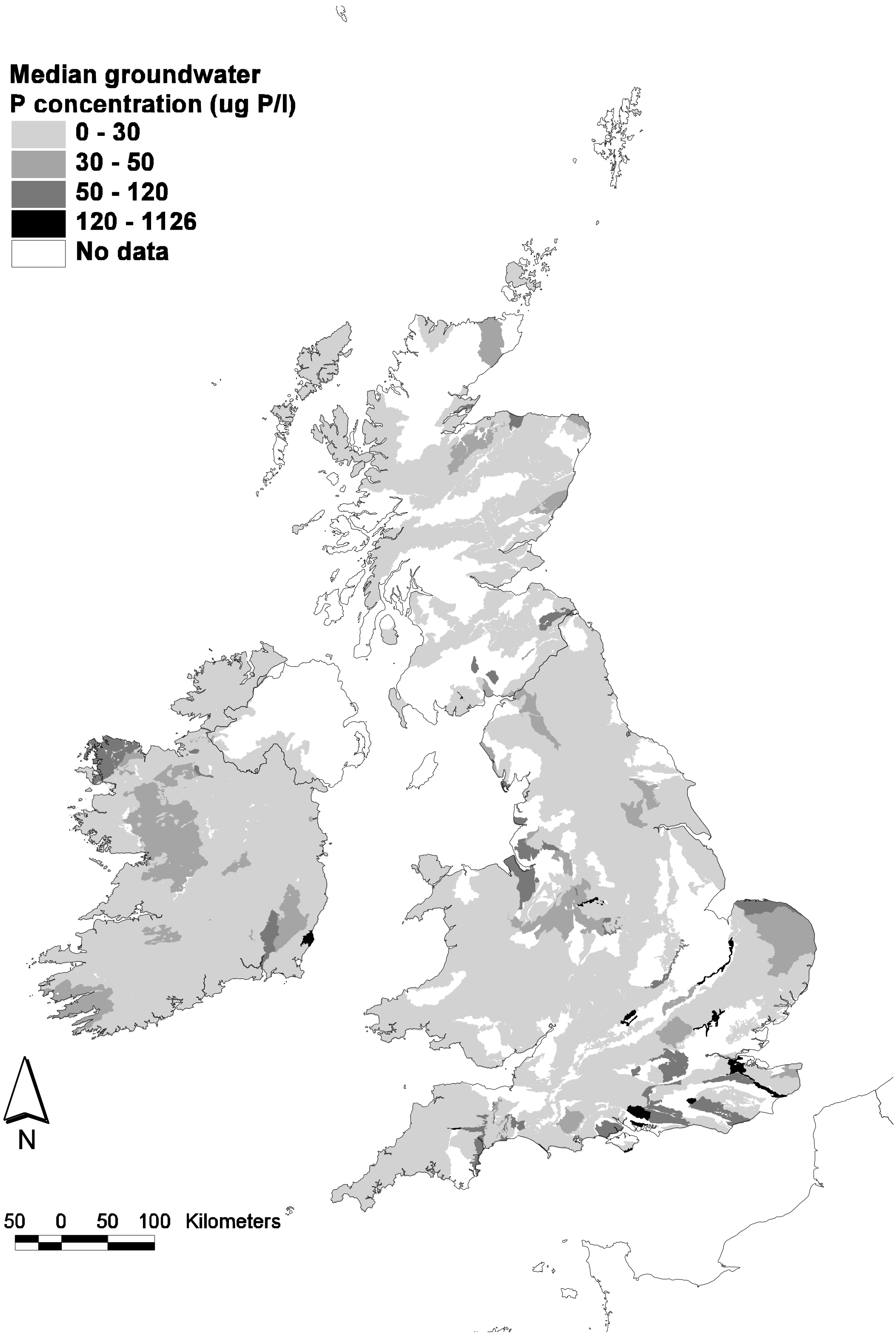

Figure 7 Median groundwater-P concentrations in the groundwater bodies of England, Wales, Scotland and the Republic of Ireland

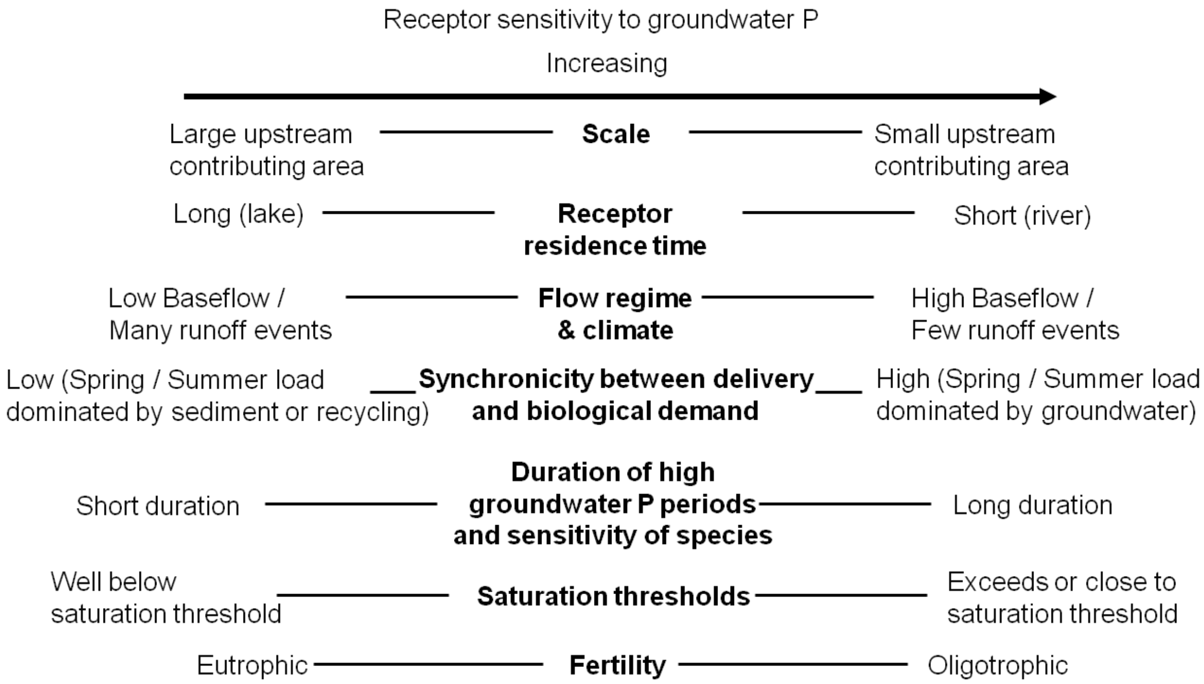

Figure 8 Factors affecting receptor sensitivity to groundwater P.