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Identifying contrasting influences and surface water signals for specific groundwater phosphorus vulnerability

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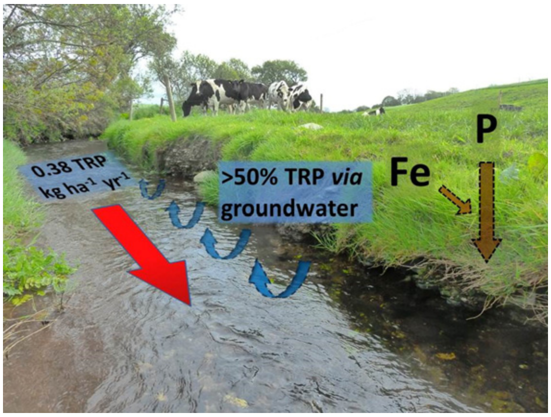
HIGHLIGHTS

- P transfer via groundwater to rivers was investigated in two agricultural catchments.
- Fe-rich soils favour P mobilisation into soluble form and transfer to groundwater.
- P concentrations in near-stream groundwater influence stream P concentrations.
- Groundwater contribution to stream TRP flux was 50% and 59% in winter.
- Susceptibility of P via groundwater should be considered for mitigation.

GRAPHICAL ABSTRACT



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ABSTRACT

Two groundwater dominated catchments with contrasting land use (Grassland and Arable) and soil chemistry were investigated for influences on P transfer below the rooting zone, via the aquifer and into the rivers. The objective was to improve the understanding of hydrochemical process for best management practise and determine the importance of P transfer via groundwater pathways. Despite the catchments having similar inorganic P reserves, the iron-rich soils of the Grassland catchment favoured P mobilisation into soluble form and transfer to groundwater. Sites in that catchment had elevated dissolved reactive P concentrations in groundwater (>0.035 mg l^{-1}) and the river had flow-weighted mean TRP concentrations almost three times that of the aluminium-rich Arable catchment (0.067 mg l^{-1} compared to 0.023 mg l^{-1}). While the average annual TRP flux was low in both catchments (although three times higher in the Grassland catchment; 0.385 kg ha^{-1} compared to 0.128 kg ha^{-1}), 50% and 59% of TRP was lost via groundwater, respectively, during winter periods that were closed for fertiliser application. For policy reviews, slow-flow pathways and associated time-lags between fertiliser application, mobilisation of soil P reserves and delivery to the river should be carefully considered when reviewing mitigating strategies and efficacy of mitigating measures in groundwater fed catchments. For example, while the Grassland catchment indicated a soil-P chemistry susceptibility, the Arable catchment indicated a transient point source control; both resulted in sustained or transient periods of elevated low river-flow P concentrations, respectively.

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1. Introduction

Environmental mitigation measures for phosphorus (P) transfer from land to water must incorporate an understanding of hydrological pathways and chemical mobilisation (Deasy et al., 2009). For example, solubilisation and soil erosion in storm surface runoff pathways are generally proposed to be the main contributors to P flux from agricultural catchments (Sharpley et al., 1992, 2008), which can be amplified by competing land uses (Pacheco et al., 2014; Valle Junior et al., 2014a,b). This is due to a flow dependency where river P concentrations, supported by surface runoff, increase with discharge (Pionke et al., 1999; Doody et al., 2006; Jordan et al., 2007). However, some studies have proposed that P flux may be related to solubilisation mechanisms such as leaching processes due to reductions of soil-P sorption sites (Lookman et al., 1996) and/or transfer mechanisms such as rapid percolation in preferential flow paths (Kilroy and Coxon, 2005); these processes may elevate the concentrations of dissolved P in groundwater (Djodjic et al., 2004; Siemens et al., 2004; Kramers et al., 2012). As a consequence, the contribution of groundwater P to surface water may be significant and cause eutrophication (Holman et al., 2008; Mellander et al., 2012a). To this end, elevated reactive P concentration across groundwater bodies can be used as an *intrinsic* signal to determine if that body is likely to cause a eutrophication risk to adjacent surface waters (Holman et al., 2008). Therefore, in order to reach targeted goals for the aquatic environment, the full range of potential P transfer pathways should be considered, including the groundwater contribution, which may influence P fluxes to adjacent surface waters. For mitigating P loss in groundwater driven catchments this should also include a *specific* understanding of how soil chemistry can influence P mobilisation and transfer to groundwater. Phosphorus dynamics in soil are, for example, often determined by soil properties such as pH, clay content and mineralogy, and the abundance of iron (Fe) and aluminium (Al) oxides (Domagalski and Jonson, 2011; Moody et al., 2013). Other processes that may affect solubilisation and transfer of P to water are temperature, soil drying-rewetting cycles and freezing–thawing cycles (Blackwell et al., 2010; Liu et al., 2013). Mechanisms that drive P uptake and release, such as sorption–desorption, dissolution–precipitation and mineralisation–immobilisation, can often differ between soils depending on soil chemical properties that also influence the lability of soil P reserves (Moody et al., 2013; Daly et al., 2015). Colloidal P forms can also be mobilised from soil through dispersion from the soil matrix, often induced by anoxic (redox) conditions (Henderson et al., 2012) and by P sorption reactions (Siemens et al., 2004). In certain circumstances, these processes may promote vertical P movement to shallow groundwater where subsequent sorption or precipitation may be hindered (Dupas et al., 2015).

In previous work, Mellander et al. (2012b, 2013) showed that specific P susceptibility was a more appropriate risk assessment compared to indicative high intrinsic vulnerability classified for a karst landscape. This is complimented here by using the same principles but in (non-karst) areas of indicative low intrinsic vulnerability. The aim was to increase process understanding for best management practise and determine the importance of P transfer via groundwater pathways in river catchments with well-drained soils but with contrasting soil chemistry and agricultural land uses. The specific objectives were to i) determine the magnitudes of water discharge and P flux between the catchments, ii) investigate the spatiotemporal variability of P concentration in groundwater as influenced by soil chemistry and agricultural management and iii) with regard to groundwater pathways, identify and quantify P transfer during periods when transfer risk of recently applied P was lowest and residual soil P transfer was highest. The results from five years of sub-hourly P flux measurements from the river outlets, together with measurements of collected shallow and intermediate groundwater from 36 piezometers on a monthly basis, was used for the analysis.

2. Study area

This investigation took place in two intensively farmed catchments, one dominated by grassland and the other by arable crop production, in the Republic of Ireland (Fealy et al., 2010; Wall et al., 2011; 2012) (Fig. 1). The Grassland catchment (7.6 km^2) is located in south-west Ireland and uses ca. 90% of land total for agriculture, dominated by grassland used for dairy production. The average livestock density is 1.94 livestock units ha^{-1} (equivalent to 165 kg organic N ha^{-1}) (Murphy et al., 2015) with an average plant available P loading (12% chemical and 88% organic manure and/or cattle slurry) of 30 kg ha^{-1} during growing seasons (predominantly applied during March to April). The catchment has 87% loamy, well-drained brown earths (Cambisols), 10% poorly drained gley soils, and 3% alluvial and peat soils. The catchment lies within the western part of the Devonian South Munster Basin (MacCarthy, 2007) and consists of old red sandstone and mudstone of the *Castlehaven* formation (Sleeman and Pracht, 1995) with a 55° dip to the south. Geological models have been built from onsite geophysical surveys (Mellander et al., 2014) and have indicated a three-dimensional pattern of variably highly weathered to strong mudstone and sandstone at a depth of ca. 4–20 m. Above the bedrock are permeable layers of gravelly clay and lenses of gravel. Belowground flow paths are likely concentrated in the high permeability layers and along the contacts of different layer types and in possible fractures or faults. The aquifer is unconfined and classified as productive with a secondary permeability flow. The mean annual rainfall is 1228 mm (1981–2010) at the nearest synoptic station (Met Éireann). As reference to the importance of subsurface storm hydrology pathways, the groundwater contribution to stream discharge was ca. 88% during a major summer flow event (Mellander et al., 2012a) and the annual average over four years was 75%.

The Arable catchment (11.2 km^2) is located in south-east Ireland and uses ca. 54% of its land for intensive and continuous crop production (mostly spring barley) with a plant available N loading (97% chemical and 3% organic manure and/or cattle slurry) of 136 kg ha^{-1} and plant available P loading (88% chemical and 12% organic manure and/or cattle slurry) of 26 kg ha^{-1} during growing seasons (predominantly applied during March to April). The catchment has 80% well drained acid brown earth soils (Cambisols), 16% poorly drained gley soils and 4% alluvial soils. The catchment lies within the Leinster Terrane and consists of Ordovician green and red-purple buff slate and silt-stone of the Oakland formation (Tietzsch-Tyler et al., 1994). Onsite geophysical surveys indicated stratified layers of highly weathered to strong slate at depths of ca. 2–20 m. Above the bedrock are highly permeable layers of gravelly clay and lenses of gravel (Mellander et al., 2014). The aquifer is unconfined with a poor production. Groundwater, however, forms a shallow aquifer and flow occurs largely within the permeable subsoil and layers of highly weathered bedrock overlying the bedrock. The mean annual rainfall is 1060 mm (1981–2010) at the nearest synoptic station (Met Èireann). Similarly, for reference to the importance of subsurface storm hydrology, the groundwater contribution to stream discharge was ca. 96% during a major spring flow event (Mellander et al., 2012a) and the annual average over four years was 75%.

3. Methodology

3.1. Field data collection

Onsite standard weather parameters were recorded on a 10-min basis by a weather station (BWS200, Campbell Scientific) located in the central lowlands of each catchment. An additional rain gauge was located on the higher grounds (ARG-100 and Solinst rainlogger). Water level was recorded in the catchments' outlet rivers on a 10-min basis with vented-pressure instruments (OTT Orpheus Mini) installed in stilling wells adjacent to Corbett flat-v non-standard weirs. River discharge was calculated via rating curves developed from area-velocity