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Delivery and impact bypass in a karst aquifer with high phosphorus source and pathway potential

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ARTICLE INFO

Article history:
Received 15 July 2011
Received in revised form
23 December 2011
Accepted 28 January 2012
Available online 9 February 2012

Keywords:
Agriculture
Diffuse pollution
Nutrients
Groundwater
Conduit flow
Eutrophication

ABSTRACT

Conduit and other karstic flows to aquifers, connecting agricultural soils and farming activities, are considered to be the main hydrological mechanisms that transfer phosphorus from the land surface to the groundwater body of a karstified aquifer. In this study, soil source and pathway components of the phosphorus (P) transfer continuum were defined at a high spatial resolution; field-by-field soil P status and mapping of all surface karst features was undertaken in a > 30 km^2 spring contributing zone. Additionally, P delivery and water discharge was monitored in the emergent spring at a sub-hourly basis for over 12 months. Despite moderate to intensive agriculture, varying soil P status with a high proportion of elevated soil P concentrations and a high karstic connectivity potential, background P concentrations in the emergent groundwater were low and indicative of being insufficient to increase the surface water P status of receiving surface waters. However, episodic P transfers *via* the conduit system increased the P concentrations in the spring during storm events (but not >0.035 mg total reactive P L^{-1}) and this process is similar to other catchments where the predominant transfer is *via* episodic, surface flow pathways; but with high buffering potential over karst due to delayed and attenuated runoff. These data suggest that the current definitions of risk and vulnerability for P delivery to receiving surface waters should be re-evaluated as high source risk need not necessarily result in a water quality impact. Also, inclusion of conduit flows from sparse water quality data in these systems may over-emphasise their influence on the overall status of the groundwater body.

1. Introduction

Defining the chemical and ecological status of water bodies and risks to status are key requirements of the EU Water Framework Directive (WFD; Official Journal of the European Parliament and Council, 2000). Phosphorus (P) and nitrogen (N) transfers from land, for example, have been recognised as one of the major influences on water quality deterioration, causing eutrophication (Schindler et al., 2008; Canfield et al., 2010), and are subject to a series of regulatory mitigation efforts throughout the developed world.

In agricultural landscapes, P mostly reaches surface waters *via* surface runoff pathways during rain events (e.g. Pionke et al., 1997; Gburek et al., 2002). Phosphorus in sub-surface

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doi:10.1016/j.watres.2012.01.048

pathways can also reach surface waters (McDowell and Sharpley, 2001) and has been reported to be elevated in groundwater bodies in England, Wales, Scotland and Ireland (Holman et al., 2008, 2010) and in groundwater pathways in Irish karstified aquifers (Kilroy and Coxon, 2005). While intergranular and fissured aquifer pathways are likely to attenuate P, karstic aquifers under shallow depth glacial deposits are classified as being more vulnerable to P and N inputs from agricultural sources, as water recharges *via* both quick point infiltration and diffuse infiltration. Agricultural soils are therefore quickly connected to the aquifer (Drew, 2008) with dissolved and particulate P fractions at risk of transfer through the aquifer and discharged in emergent springs (Mahler and Lynch, 1999).

The nutrient transfer continuum concept (Haygarth et al., 2005; Wall et al., 2011) describes agricultural nutrient sources that can be mobilised and, *via* hydrological pathways, delivered to streams or other water bodies where a trophic impact may occur. In a karstic spring contributing zone, it is also essential to understand the small-scale heterogeneity of the karstified landscape, and associated risks for nutrient transfer. This enables extrapolation to an entire aquifer, assessment of groundwater resources and protection of the functions of the karst groundwater (Drew, 2008).

In the glaciated karst landscape of Ireland (mainly in the west) the depth to bedrock is often shallow but may contain complex glacial geological features where the subsoil is deeper (Drew and Daly, 1993). Frequently occurring karstic features in Ireland include: epikarst, large springs, swallow holes, enclosed depressions (dolines), caves, losing streams, sparse/intermittent streams and turloughs. The latter occur frequently across the limestone lowlands of western Ireland and are ephemeral groundwater-fed wetlands or lakes that fill and empty *via* swallow holes in karstic aquifers with a relatively small storage capacity.

Karst aquifers in chalk have been conceptualised by the *triple permeability model* (Worthington, 1999) which describes the aquifer with three components; (1) permeability due to conduits (quick flow), (2) permeability produced by fractures and fissures (intermediate to quick flow), and (3) matrix permeability of the bedrock (slow flow). The matrix of Carboniferous limestone, such as that of Irish karst systems, has low primary porosity and permeability (Allen et al., 1997; Ford and Williams, 2007) but with a slow flow *via* small fissures and voids. Most water is however, considered to be transported within the network of secondary solution-enlarged fractures (Allen et al., 1997). In a mature karst aquifer more than 95% of the water transmission is *via* conduits but most of the storage (>99%) lies within the small fissures and voids (Drew, 2010). In Ireland, the total porosity of limestone is only 1–3% (Drew and Daly, 1993). However, due to the high secondary permeability this water has a short travel time through the aquifer (20–300 m h^{-1} and in the lowlands 5–250 m h^{-1} (Drew, 2008) from rapid spring responses to rainfall).

A groundwater protection scheme has been developed in Ireland (DoELG/GSI/EPA, 1999) with a primary aim of maintaining the quantity and quality of groundwater. An important component within the land surface zoning scheme is the mapping of groundwater vulnerability to pollution; influencing components are those affecting travel time, attenuation capacity and quantity of contaminants, such as subsoils, thickness of the unsaturated zone and type of recharge. Point recharge usually implies high groundwater vulnerability. If the recharge is diffuse, subsoil permeability and depth to bedrock become crucial for determining groundwater vulnerability. In such areas dolines may still concentrate recharge as they are vertically connected with the epikarst and conduits.

In Ireland, karstified limestone covers approximately 19% area of the country (Daly, 2009) and a major proportion is located in the west of Ireland. Agricultural use ranges from intensive to extensive and is largely dependent on soil depth. The karstic groundwater bodies' WFD status have been assessed by routine monitoring of discharge and water quality from emergent springs. An assessment is undertaken if an adjacent surface water is at less than "good status", due to diffuse pressures, and the molybdate reactive P (MRP) concentration exceeds 0.035 mg L^{-1} (Environmental Quality Standard, EQS) in any groundwater sample taken from the national groundwater monitoring network in the associated body, during the six year reporting cycle. The groundwater load is calculated using an estimated groundwater contribution to rivers and the aggregated (six year) average concentration from representative groundwater monitoring points. If the load from a groundwater body contributes greater than 50% of the load required to breach the EQS, the groundwater body is at "poor status" and mitigation source management must be undertaken.

With this background, the aim of this study was to apply a high resolution approach to test the assumptions of groundwater risk from moderate to intensive agriculture over a karstic landscape. Specifically, the study objectives were, firstly, to define the soil P source and pathway components of the nutrient transfer continuum at a high spatial resolution, and secondly to evaluate the inferred risk of P transfer using observed P delivery to the primary emergent spring at a high temporal resolution. These objectives were achieved by surveying soil P status in fields as well as mapping of all surface karst features and depth to bedrock within a 46 km^2 area covering a *c.* 30 km^2 spring zone of contribution (ZoC), by sub-hourly monitoring of P concentration and water discharge in the emergent spring and by monitoring meteorology within the zone.

2. Methods

2.1. *Site description*

The 46 km^2 study area is underlain by a karstic aquifer of pure Carboniferous limestone, overlain by glacial deposits (silty till) being thickest (1–5 m) towards the east and which thins out to the west where it is often absent, with exposed patches of limestone pavement (Coxon and Drew, 1986). The landscape is rich in karstic features with the most common topographic feature being dolines. The recharge is autogenic, i.e. it originates from the karst area, with a flow regime characterised by conduit flow, with travel times ranging from 10 to 123 m h^{-1}, draining to the River Robe and Lough Mask in Co. Mayo (Fig. 1).