

Temporal variability of phosphorus fractions in Irish karst springs

Garrett Kilroy · Catherine Coxon

Abstract Transfer pathways of phosphorus (P) from soil to surface waters are the subject of much current research because of concerns about eutrophication. However, P transfer via groundwater discharge has received little attention. Temporal P changes at eight Carboniferous limestone karst springs from two catchments in western Ireland are examined. The eight springs were sampled fortnightly between June and October 1999 and thereafter monthly until February 2000. Each sample was analysed for total P (TP), total dissolved P (TDP) and dissolved reactive P (DRP). Total P exhibited some hydrological response at all springs (e.g. increase from 45 to 107 $\mu\text{g l}^{-1}$) reflecting significant changes in particulate P (PP) (e.g. increase from 7 to 44 $\mu\text{g l}^{-1}$) and dissolved organic P (DOP) (e.g. increase from 0 to 27 $\mu\text{g l}^{-1}$), with DRP displaying greatest temporal stability. Greatest response to rainfall events occurred after the first major autumnal rains in September 1999, when there appeared to be dislodging of loosely bound PP and DOP, which was transported to groundwater. This response to the first autumnal rains probably reflects the hydrological switch where the catchments change from a soil moisture deficit to a soil moisture surplus situation. Daily autosampling demonstrated TP concentrations of up to 1,814 $\mu\text{g l}^{-1}$ due to local pollution, highlighting the need to adopt storm event driven sampling rather than discrete sampling in karstic springs. Identification and management of

springs in karst areas, with associated point recharge via swallow holes, presents an urgent and demanding challenge.

Keywords Phosphorus · Karst aquifer · Temporal variability · Groundwater

Introduction

Phosphorus (P) is a key nutrient limiting plant growth in surface waters. Several international workshops have taken place in recent years focusing specifically on P loss from soil to water (Tunney and others 1997; Foy and Dils 1998; Haygarth and others 2001). Establishing the relative importance of different pathways of P transport within catchments has been identified as a key research need (Sharpley and others 2000). Many investigators have examined phosphorus losses from land through overland flow (e.g. Turtola and Jaakkola 1995) and drainage waters (e.g. Brookes and others 1997). However, the study of phosphorus transfer to surface waters via groundwater discharge has largely been neglected.

In Irish groundwater studies, P has been overlooked primarily because the maximum admissible concentration for drinking waters under the Directive on water intended for human consumption CEC (1980) (5,000 $\mu\text{g l}^{-1}$ P_2O_5) is rarely approached except in areas of gross localised contamination. The revised Directive on water intended for human consumption (CEC 1998), due to be implemented in 2003, does not contain any limit for P. However, in surface waters the concern with P is at much lower concentrations. Annual mean total P concentrations in excess of only 20 $\mu\text{g l}^{-1}$ may trigger eutrophication in some Irish lakes (Champ 1998). The OECD model suggests thresholds of 35 $\mu\text{g l}^{-1}$ for eutrophic lakes (OECD 1982). The flushing effect in rivers may provide them with greater protection to P loadings; however McGarrigle's (1998) study on national river data for the period 1991–1994 suggests that adverse impacts become apparent once unfiltered molybdate reactive phosphate levels exceed 30 $\mu\text{g l}^{-1}$. The recent regulations on water quality standards for P (DELG 1998) set out a similar suite of target levels for rivers and lakes of varying trophic status in a national strategy to tackle

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G. Kilroy (✉)
Shannon River Basin Project,
Newtown Centre, Annacotty, County Limerick, Ireland
E-mail: kilroygg@tcd.ie
Tel.: +353-61-337927
Fax: +353-61-337920

C. Coxon
Centre for the Environment and Department of Geology,
University of Dublin, Trinity College, Dublin 2, Ireland

surface water eutrophication. Therefore, a dichotomy exists between regulatory levels required for groundwater P in terms of drinking water quality and the level of P required to induce eutrophic conditions in surface waters. In karstic environments, there is a strong interaction between surface water and groundwater. This is particularly the case in lowland karsts where rivers and lakes co-exist with a subterranean drainage system. Such areas include much of central Florida, karst areas of Puerto Rico, Cuba and the Yucatan Peninsula in Mexico, and extensive karsts in China, Vietnam and Malaysia. In Ireland approximately 50% of the country is underlain by karstified or partly karstified limestone of Carboniferous age. In the most highly karstified western part of the limestone lowland, there exist drainage systems with complex interactions between surface water and groundwater (Coxon and Drew 2000).

Soil P may be present in organic or inorganic forms and in dissolved or particulate forms. To enter the aquifer, P must be transported from the surface to the water table. Groundwater recharge by effective precipitation will generally drive this movement but P will encounter several obstacles en route. Soils and subsoils will act to intercept P to varying degrees depending on their intrinsic properties. In a review paper, Sims and others (1998) conclude that loss of P through subsurface drainage is of most concern in areas with high soil P concentration, where soil P sorption capacities are low and where subsurface transport is enhanced by artificial drainage systems. Once P reaches groundwater, soluble forms will travel in groundwater by advection and diffusion, but dispersion and retardation factors (e.g. adsorption and precipitation in the case of P) will dilute and restrict their movement (Fetter 1999). In the case of karst aquifers, point recharge via swallow holes may allow the attenuation properties to be by-passed, while rapid flow through the aquifer in solutionally widened fissures and conduits can also minimize attenuation and provide enough energy to facilitate particulate transport during high stage events.

The extent to which phosphate is retained within karst aquifers is expected to vary according to the relative importance of diffuse and conduit flow. An example of phosphate retention is provided by Smith and Schrale (1982) in their study on Mount Gambier in Southern Australia (a young karstic aquifer with predominantly diffuse flow), while Kresic and others (1992) suggest that calcium phosphates (which are a common waste of fertilizer factories in Yugoslavia) are mostly precipitated in karst aquifers when not rapidly transferred by underground streams. Systems dominated by conduit flow are most likely to transport P, especially in particulate form. Imbach (1993) reported concentrations of phosphate ranging from 190–880 $\mu\text{g l}^{-1}$ for karstic springs in the Çekirge-Bursa area of Turkey, while Elhatip (1997) reported concentrations of phosphate ranging from 70–90 $\mu\text{g l}^{-1}$ for the Pamukkale thermal karst springs in Turkey, where municipalities used the main fault zone and swallow holes in the upstream area of the thermal karst springs for their solid waste and wastewater disposal. In British caves, Hardwick (1995) found that phosphate

concentrations in cave recharge were massively greater than natural inputs from rainfall and generally increased following applications of sewage sludge to the overlying field. However, even in a conduit flow situation, phosphate may be retained within the aquifer: Wiersma and others (1986) note that in the Door Peninsula shallow groundwater system in Wisconsin, with travel times from swallow holes of only a few hours, a seasonal pulse in total phosphorus in the recharge waters did not produce a corresponding pulse in the spring discharge.

The temporal variability of phosphorus concentrations in water will vary depending on the hydrological situation. In surface waters, the controls on temporal P variation include both hydrological factors (storm events) and biological factors (P uptake by plants and algae). Heathwaite and Dils (2000) in their study of the Pistern Hill catchment in Leicestershire, UK, conclude that the surface runoff of P is temporally confined to high magnitude, high intensity rainfall events. Groundwater may exhibit hydrologically controlled changes in P concentrations, but these may be dampened by storage in the aquifer. Karst aquifers should exhibit responses closer to surface waters due to their high connectivity with the land and surface water. Mahler and Lynch (1999) in their study of a karst system (Barton Springs) in Texas, US, conclude that sediments can enter from the surface and traverse the aquifer to discharge at a spring, and that virtually all sediment transport occurs immediately following storm events.

Temporal variability of P fractions at springs are examined in two lowland karst catchments in western Ireland. This work forms part of a larger study of phosphorus in Irish groundwater in a range of hydrogeological and landcover situations (Kilroy 2001).

Site locations

Two catchments in the west of Ireland were sampled (see Fig. 1). They have a cool temperate maritime climate, with long term mean annual rainfall of 1,100–1,200 mm and mean annual evapotranspiration losses of the order of 400–500 mm. Four springs from the Robe catchment (RS01, RS03, RS04 and RS06) and four in the Fergus catchment (FS05, FS08, FS13 and FS18) were chosen for systematic monitoring. These springs have been subject to previous hydrogeological studies, thus making them ideal candidates for detailed analysis.

The Robe catchment in Co. Mayo is underlain by highly fractured Carboniferous limestones. In the western half of the catchment where the sampling sites are located, the limestone is a pure bioclastic calcarenite of Visean age, susceptible to karstification; to the east the limestones become less pure and the degree of karstification decreases (Coxon 1986). The topography is gently undulating (altitude 20–60 m above sea level) and the dominant landforms are due to glacial and fluvioglacial deposition with limited karst landforms. Glacially deposited material is thickest in the east of the catchment, thinning to patchy cover at the shores of Lough Mask (Drew and Daly 1993).

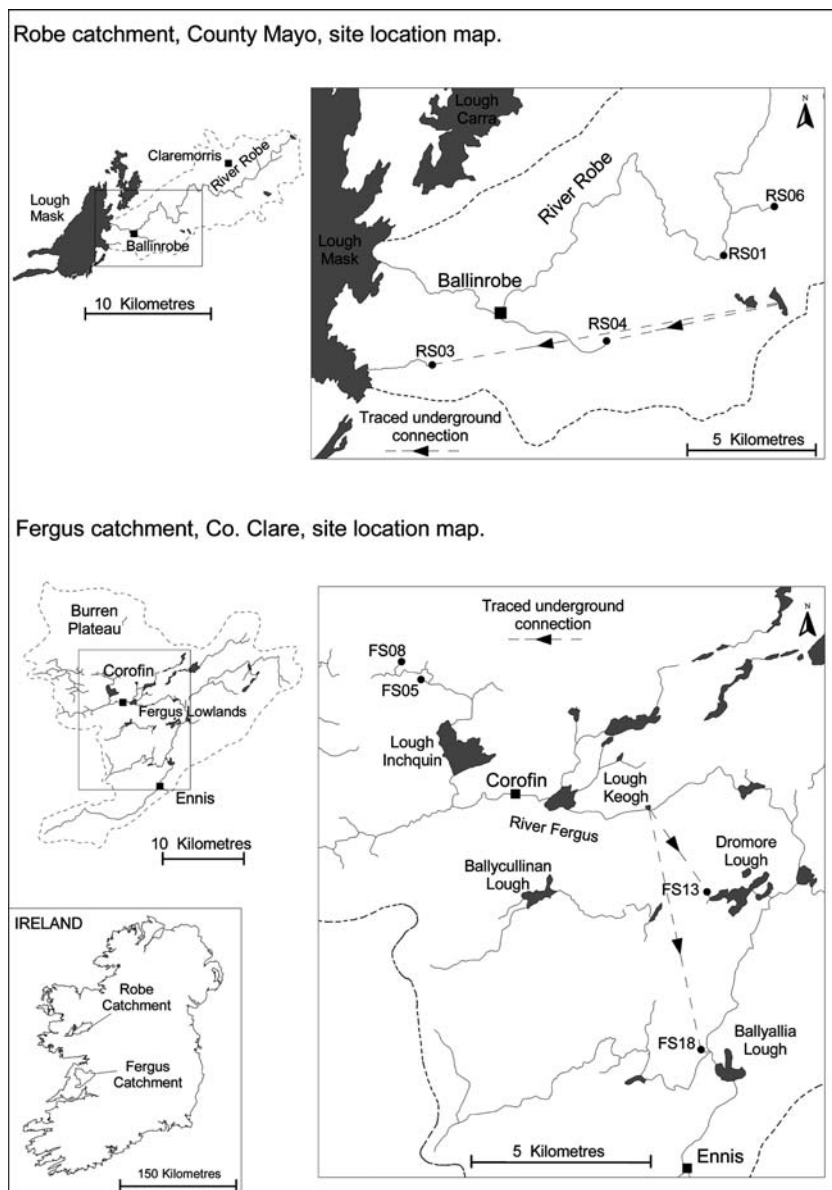


Fig. 1
Catchment and site location maps

Coxon and Drew (1986) have demonstrated the groundwater hydrology as being intermediate in type between a non-karstic diffuse flow aquifer, and the conduit dominated groundwater flow system characteristic of most karstic terrain. The Robe catchment is characterised by autogenic recharge (i.e. arising on limestone), an absence of significant sinking streams, and the presence of turloughs (groundwater-fed seasonal lakes). Whilst carrying out tracing experiments at swallow holes up-gradient of the RS04 spring, Coxon and Drew (1986) measured travel times greater than 100 m hr^{-1} under high flow conditions. The spring flow from the sampling sites reaches Lough Mask either directly or via the Robe River (Fig. 1). This lake is an internationally important game and coarse fishery and also contains a population of rare Arctic Char; its nutrient status is classed as mesotrophic (McGarrigle and others 2002) with total phosphorus levels typically of $10\text{--}12 \mu\text{g l}^{-1}$.

The Fergus catchment in Co. Clare lies in a Carboniferous limestone lowland corridor lying between uplands of Upper Carboniferous shales and sandstones to the west and Devonian sandstones to the east. The limestone contains no primary permeability, but is well bedded and jointed and so has extensive secondary permeability; particularly in the western part of the lowland it is a pure bioclastic calcarenite stratigraphically equivalent to that of the western Robe catchment, and is highly susceptible to karstification (Coxon and Drew 2000). The limestone is overlain by a patchy cover of glacial deposits generally less than 3 m thick, and in places it is absent, with thin rendzina soils developed directly over the limestone bedrock (Coxon 1995). In the Fergus catchment the presence of sinking streams fed by allogenic recharge (i.e. arising on non-limestone rocks) is widespread. North—south underground linkages with velocities of $100\text{--}200 \text{ m hr}^{-1}$ indicate a high degree of karstification, and rapid transfer

potential of contaminants from swallow holes to springs (Coxon and Drew 2000). Groundwater in this area has been identified as particularly vulnerable to agricultural contamination (Drew 1996). FS05 and FS08 are among a group of springs feeding the Fergus River upstream of Lough Inchiquin, a brown trout fishery lake that is of mesotrophic status (McGarrigle and others 2002) and has experienced sporadic algal blooms in recent years. FS05 is the largest and most stable of this group of springs (Drew 1988). FS13 is one of several springs that feed Lough Dromore while FS18 lies upstream of Ballyallia Lough: these lakes are classified as moderately eutrophic and mesotrophic respectively (McGarrigle and others 2002). As shown on Fig. 1, a swallow hole at Lough Keogh has been traced to both of these springs (Coxon 1995)

Materials and methods

Sampling procedures and analytical techniques

From June 1999 until the end of October 1999, a fortnightly sampling programme was undertaken at four representative spring sites in each of the Robe and Fergus catchments to provide detailed temporal data for the summer 1999 period. This sampling programme was extended on a monthly basis from November 1999 to February 2000.

This focussed sampling formed part of a larger project (Kilroy 2001) which included sampling springs, dug wells, boreholes, lakes and rivers for phosphorus in the Fergus catchment (53 sites) and Robe catchment (21 sites) for the period July 1998 to March 2000.

The P fractions analysed in the fortnightly and monthly sampling programme were total P (TP), total dissolved P (TDP) and dissolved reactive P (DRP). The TP and TDP analytical technique that was employed for this work is derived from Eisenreich and others (1975). The essential ascorbic acid/moybdate colorimetric procedure used to measure DRP is as described by Murphy and Riley (1962). It is acknowledged by the authors that while using a 0.45 µm filter to measure for DRP the filtrate may still contain colloidal material [as indicated by Baldwin (1998) and Haygarth and others (1997)]. Therefore DRP as measured here does not *sensu strictu* represent all dissolved P, but rather P fractions which pass through a 0.45 µm filter.

Total phosphorus (TP) was measured colorimetrically after digestion with potassium persulphate in the unfil-

tered samples. The same digestion method was applied to the filtered samples (0.45 µm), and resulted in total dissolved P (TDP). Particulate P (PP) was determined as the difference between TP and TDP. Dissolved reactive P (DRP) was measured colorimetrically on filtered samples that were not subject to persulphate digestion. Dissolved organic P (DOP) was calculated as the difference between TDP and DRP.

A SIGMA automatic water sampler was installed at the RS06 Spring in the Robe catchment and subsequently at FS05 Spring in the Fergus catchment. This sampler was programmed initially to recover samples every 8 h and subsequently daily to assess temporal changes in more detail at these sites. Dramatic changes in concentration of DRP can occur after collection (Ryden and others 1973; Kotlash and Chessman 1998) and therefore it was felt that TP was the only valid P parameter that could be accurately analysed. Two of the 24 sample bottles were filled with deionised water (to act as a blank) and a QC standard (20 µg l⁻¹ P) to ensure that the sampling procedure did not add or remove P from the sample.

Results and interpretation

Background phosphorus levels in the Robe and Fergus catchments

Background levels of total phosphorus (TP) in the Robe and Fergus catchments for the period July 1998 to March 2000 are presented in Table 1.

In both catchments boreholes had greatest mean TP values. The large standard error values are due to a small number of extremely high TP values (up to 1.3 mg l⁻¹ TP), which skewed the mean value. Both catchments had groundwater mean TP levels in springs and boreholes that are greater than the thresholds for eutrophic conditions in Irish lakes (20 µg l⁻¹; DELG 1998).

Fortnightly and monthly sampling

Robe catchment

Figure 2 presents the P fractions DRP, DOP and PP for each of the four springs sampled intensively in the Robe catchment. Included in the figure are daily rainfall data to pick out individual rainfall events and monthly rainfall/effective rainfall data (based on calculations using rainfall and evapotranspiration data) to compare periods of varying soil moisture deficit. The RS03 and RS04 springs

Table 1

Summary total phosphorus levels (µg l⁻¹) for the Robe and Fergus catchments for period July 1998 to March 2000 (number of sites in parenthesis)*

Catchment	Total P	Spring	Dug well	Borehole	River	Lake
Robe	Mean	42 (6)	18 (2)	111 (11)	46 (2)	N/A
	Standard error	14	15	60	2	N/A
Fergus	Mean	31 (18)	25 (9)	101 (18)	51 (3)	19 (7)
	Standard error	4	9	71	9	3

* The means are calculated from the combined mean values for each site. The sites were each sampled on average five to six times during the study period

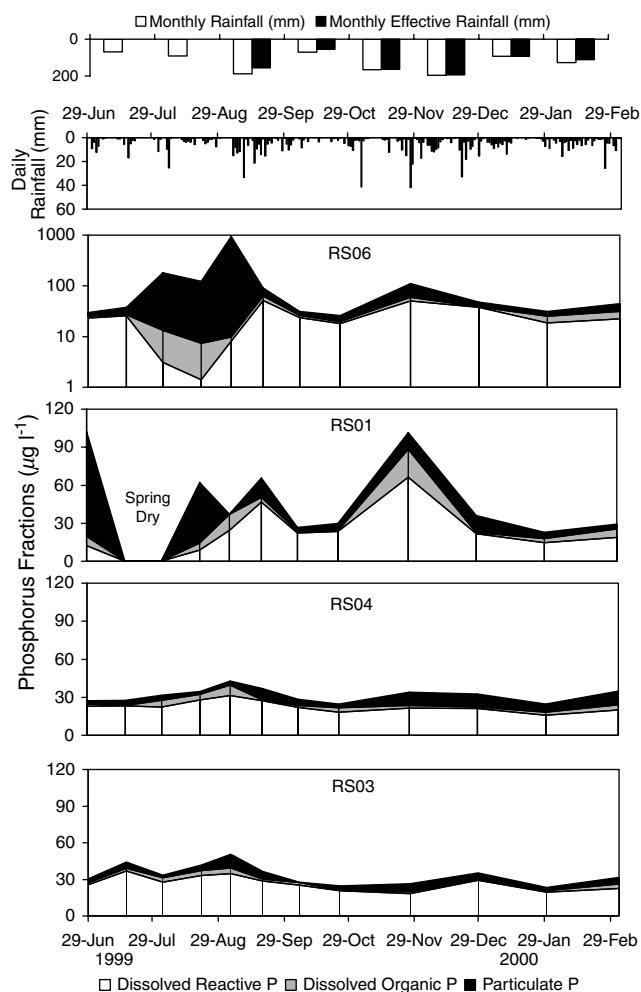


Fig. 2

Phosphorus fractions at four karstic springs in the Robe catchment, County Mayo

are assessed together due to their similarities in P concentration and temporal behaviour. RS06 and RS01 are also taken together for the same reasons. Rainfall data for the Robe catchment at Claremorris are presented in Fig. 3. In 1999 September, November and

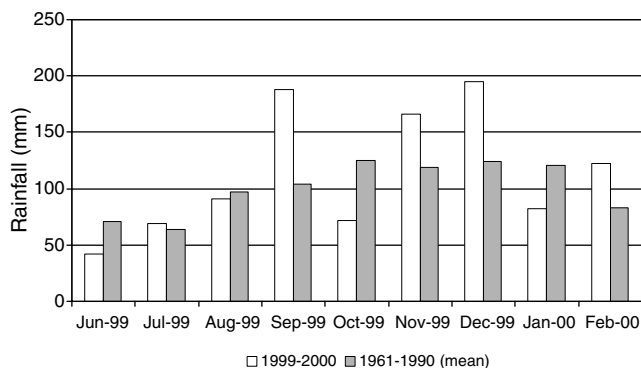


Fig. 3

Rainfall data and 30 year monthly average rainfall data (1961–1990) for the Robe catchment at Claremorris

December were all substantially higher in rainfall than the long-term monthly average. September 1999 was a particularly wet month (188 mm) compared to the long-term average (83 mm).

The two largest springs sampled in the Robe catchment were the RS03 and RS04 springs. Both springs exhibit similar trends in P changes over the sample period. The data from the fortnightly sampling period between June and October 1999 (Fig. 2) illustrates some hydrological control on spring P levels. The first effective rainfall in September which ends the soil moisture deficit coincide with phosphorus peaks at both RS03 and RS04. The monthly sampling period between November and March shows stable P levels despite heavy rains. The two springs also compare when examining the different P fractions. DRP is the dominant fraction in both with marginally more PP in RS03. It is not unexpected that RS03 and RS04 should exhibit such similarities, since water has been traced to both springs from a swallow hole in an up-gradient turlough (Coxon 1986); see Fig. 1.

The springs at RS06 and RS01 are also comparable since it is likely that similar contributing areas feed both. RS06 was subject to a pollution event somewhere between the sampling dates 17th and 26th July when the TP concentration jumped from a background level of $38 \mu\text{g l}^{-1}$ to $122 \mu\text{g l}^{-1}$ (this event is discussed in detail later in this paper). It is likely that RS01 was also impacted by this event. It should be noted that the Y-axis in Fig. 2 for RS06 is plotted on a logarithmic scale to account for the large magnitude of TP values after the pollution event.

Trends at RS01 are not clear. For a period of approximately 7 weeks, between July 17th and August 21st, the spring was either not flowing (a stagnant pool) or dry. Before this dry period there is a particulate P rich peak that may be attributed to nearby livestock (the spring is not fenced off). Thus, as the flow in the spring falls off the impact of the livestock may be accentuated due to a reduced dilution effect. Once the flow is restored in the spring there is a similar particulate P rich peak. This again may be due to stock or it may be associated to the pollution event at RS06, which is 2.5 km up-gradient of RS01. Like RS06, RS01 exhibits a peak in all P forms on the 27th November, which follows the increase in rainfall. This is followed by a decrease in P after December as rainfall decreases.

Fergus catchment

Figure 4 presents the P fractions DRP, DOP and PP for each of the four springs sampled intensively in the Fergus catchment. As for Fig. 2, daily rainfall data are included to pick out individual rainfall events and monthly rainfall/effective rainfall data allow comparison between periods of varying soil moisture deficit.

Rainfall data for the Fergus catchment at Corofin are presented in Fig. 5. In 1999 September, November and December were all substantially higher in rainfall than the long-term monthly average. As in the Robe catchment, September 1999 was a particularly wet month (220 mm) representing a 100% increase on the long term average (110 mm). December was an exceptionally wet month

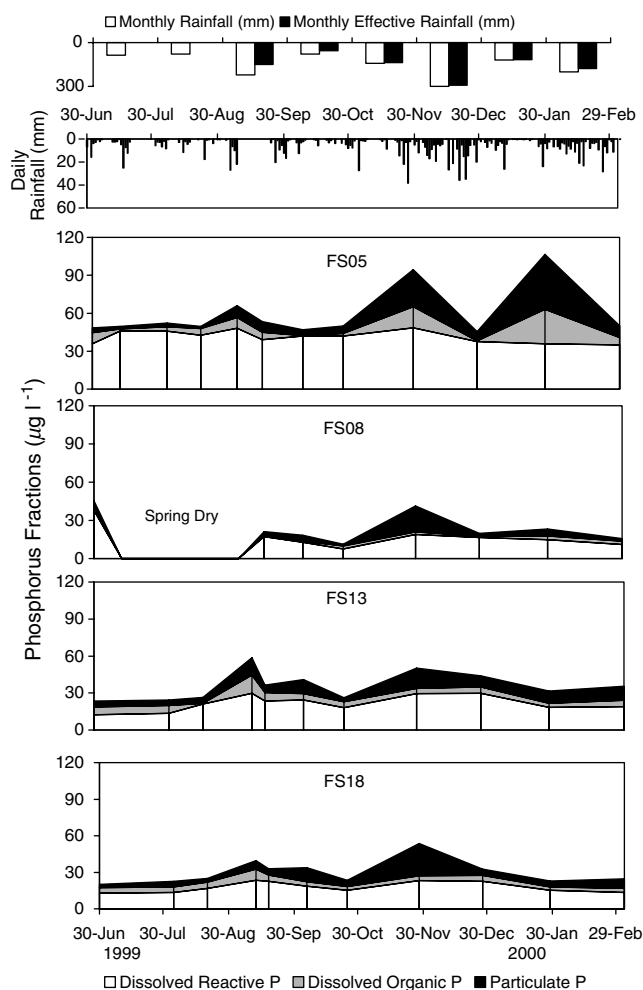


Fig. 4

Phosphorus fractions at four karstic springs in the Fergus catchment, Co. Clare

(300 mm) representing a 122% increase on the long-term average (135 mm).

In the Fergus catchment FS05 and FS08 are the two largest springs sampled in terms of maximum flow (Drew 1988).

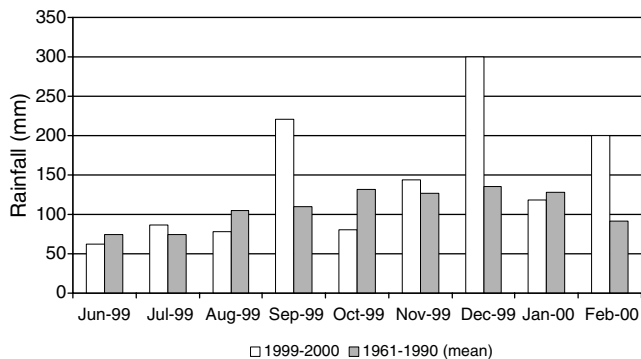


Fig. 5

Rainfall data and 30 year monthly average rainfall data (1961–1990) for the Fergus catchment at Corofin

However, FS08 is very flashy and, like the RS01 spring in the Robe catchment, was dry for a period. FS05 in contrast, is reasonably stable in terms of flow. FS05 exhibits similar responses to recharge to those described for the Robe springs but perhaps more clearly. There is an increase in P concentrations with increasing recharge, predominantly particulate P, but also DOP. Thus, recharge increases the load and relative proportion of particulate P to the spring. The three peaks coincide with three storm events and also match the three greatest effective rainfall months. Otherwise, the P levels are stable with inorganic P being the dominant fraction, background levels averaging $50 \mu\text{g l}^{-1}$ DRP. After each rainfall peak, P levels at FS05 decrease to background levels with DRP once again constituting the major component. FS08, like the RS01 spring in the Robe catchment, presents a more complicated pattern. Prior to FS08 going dry there was a peak in P, which, like RS01, may be due to nearby livestock and reduced dilution effect. Similar to FS05, particulate P increases during intense rainfall periods, especially during the November 28th storm event. DRP is once again the stable parameter. FS13 and FS18 again exhibit the hydrological controls discussed for FS05 and FS08. Both springs increase in DOP and PP in response to storm events, particularly at November 28th. DRP also responds but is more muted. Overall the general P trend appears to be a relatively stable DRP component combined with hydrologically controlled peaks of particulate P. Overall FS13 and FS18 have similar trends in TP temporal trends. This is expected given that a common swallow hole at Lough Keogh (see Fig. 1) feeds both springs (Coxon 1995).

Detailed response to rainfall events

The response to short term temporal events, is illustrated by spring RS06 in the Robe catchment and FS05 in the Fergus catchment.

RS06 Spring – Robe catchment

This site demonstrates marked short term variations in P concentrations. As mentioned above, it was subject to a pollution event commencing around the 20th July. Anecdotal evidence suggests that the source of the pollution was a leaking silage clamp (concrete bund for ensiling grass) located up-gradient of the spring. Results from the auto-sampling corroborate this suggested source. Figure 6 presents the data obtained using the autosampler at RS06 spring.

A background TP value of $38 \mu\text{g l}^{-1}$ was recorded on July 17th, and when the autosampler was installed on July 26th a TP value of $122 \mu\text{g l}^{-1}$ was reported. Therefore, whilst the pollution event could have occurred before July 17th, its arrival at the spring was after this date. For the first two weeks, as indicated on the graph, samples were recovered every 8 h, and thereafter on a daily basis. Once the pulse of contamination was recorded at the spring (26th July), a sustained level of TP was maintained around $170 \mu\text{g l}^{-1}$ for about two weeks. The extreme peaks in TP appear to follow extreme rainfall events. This is particularly true of the TP peak of $878 \mu\text{g l}^{-1}$ on 7/8/99 which was preceded

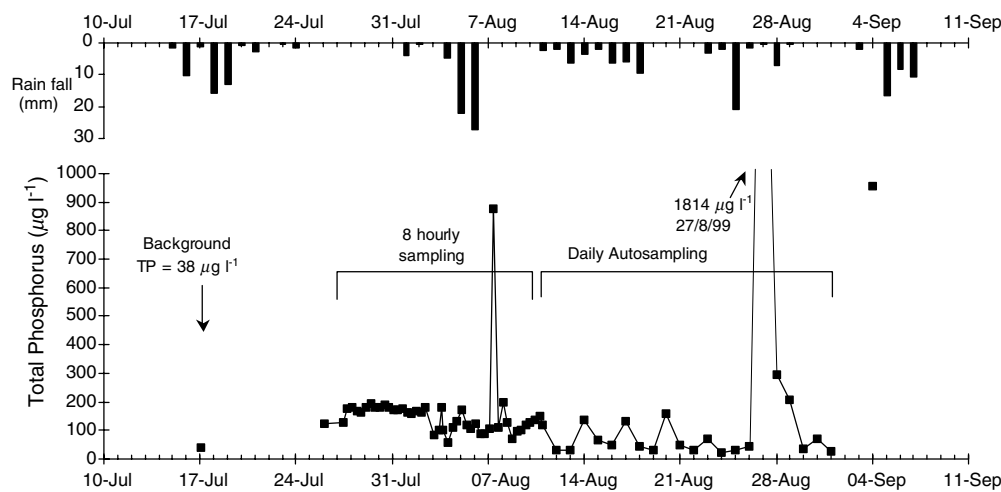


Fig. 6
Autosampler total phosphorus data and daily rainfall for RS06 spring, Robe catchment

with 22 and 27 mm of daily rainfall on the 5/8/99 and 6/8/99 respectively. Similarly, the TP peak of $1,814 \mu\text{g l}^{-1}$ on 27/8/99 was preceded by 21 mm of daily rainfall on the 25/8/99. These timings would indicate a 24 to 48 h response at the spring to rainfall events. Local climatic variations may dictate a slightly shorter or longer response time. July and August 1999 were both months with nil monthly effective rainfall. Therefore the spring is responding to rainfall and producing contamination even when calculations suggest that there is a soil moisture deficit.

Between August 12th and August 26th TP follows a saw tooth effect. Between these dates there are also a series of rainfall events. Whilst these TP peaks do not coincide consistently with the storm events, their regularity suggest some hydrological control. An explanation of this pattern could be that some effluent in the initial two week pulse did not come through to the spring but got caught up in some dead-end karstic fissures: these trapped pockets of effluent only rejoined the main flow path to the spring during storm events which acted to flush them out. The timing of this pollution event and the sustained pulse for the first two weeks strongly indicate that silage effluent was the cause. Several authors have reported that most of the effluent from a silage clamp is produced within the first two weeks of ensiling (e.g. Bastiman 1976). July and August are common months for silage production and a similar contamination event happened at RS06 the following year in August 2000. All this evidence points towards silage effluent contamination. However, this could only be verified through detailed site-specific assessment of potential sources.

The significance of this pollution event can be put into context when the TP loading from the spring to the River Robe is compared with typical in river P load values. The load during the contamination event was estimated at 14.3 mg s^{-1} TP from stream gauging at RS06 on 4 September 1999 (Kilroy 2001). In comparison during the low flow period of 11 June 1999 a TP load of 27.3 mg s^{-1} was measured in the River Robe upstream of RS06. Therefore, contamination events such as that experienced at RS06

could potentially contribute a 50% increase in the total in river TP load during summer low flows.

FS05 spring – Fergus catchment

The FS05 spring was sampled between 8th and 25th of October 1999. Due to an initial mechanical failure, only daily samples were taken between these dates. Figure 7 presents the TP data and daily rainfall data for this period at FS05.

FS05 is the largest spring sampled in the Fergus catchment and unlike many of the other flashier springs has quite a stable flow, reflecting the more diffuse nature of its recharge. Drew (1988) reported that 39 mm of rain falling over a 72 h period caused a tenfold increase in discharge in most springs of the upper Fergus catchment, but FS05 only experienced a twofold increase. This stability in terms of flow is paralleled with stability in TP concentration during this two and half week period. Rainfall events do not appear to influence TP levels at FS05, which hover around $40 \mu\text{g l}^{-1}$ during the auto-sampling period and the maximum was only 5.9 mm on October 16th, of which only 3.3 mm was calculated as effective rainfall. As is evident from Fig. 4, this spring

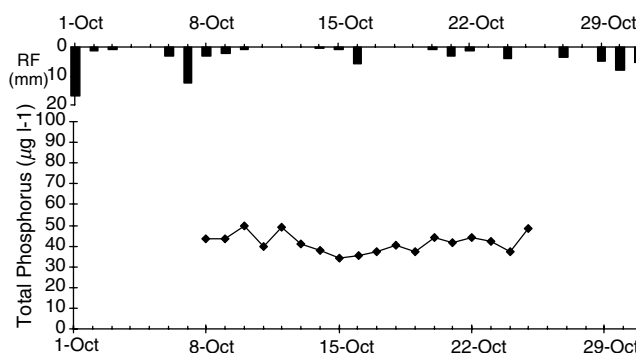


Fig. 7
Autosampler total phosphorus data and daily rainfall for FS05 Spring

experienced significant increases in particulate P in November 1999 and January 2000. During these periods rainfall was of greater intensity and frequency than during the autosampling period in October 1999. Thus it appears that this large spring with its stable flow, generally exhibits stable P concentrations, except during extended periods of effective rainfall where particulate P levels can increase accordingly.

General discussion

Groundwater quality is often considered more stable than that of surface waters primarily due to greater residence times. Temporal trends will therefore tend to evolve far quicker in surface waters than in groundwater (Loftis 1996). There are exceptions, karstic aquifers being an example, as illustrated by the Fergus and Robe catchments. In karstic springs with travel times of the order of 100 m hr^{-1} , point recharge and conduit flow can result in rapid responses at springs to rainfall events.

Groundwater sampled at springs and boreholes in both catchments had mean TP levels greater than the eutrophication thresholds for rivers and lakes discussed in the introduction.

The Robe and Fergus catchment springs exhibited some hydrological control of P fraction levels. All eight springs particularly responded to the first major autumnal rains in September 1999. All but RS03 and RS04 springs also responded to rainfall events at the end of November/early December. Dils' (1997) study of a grassland catchment in Leicestershire reported greatest TP concentrations during storm events, particularly in response to the first autumnal rains. Similarly, Kurz's (2000) study of overland flow in a high soil P plot in Co. Wexford reported highest P loadings during August 1997, the first major rains after the summer in that year. In the Robe and Fergus catchments, it is likely that P accumulated in the soil during the summer (e.g. from landspreading of fertilizers and effluents) was released to the groundwater in the autumn, following the heavy rains of September meeting the soil moisture deficit. All P fractions tended to increase to varying degrees after periods of heavy effective rainfall. However, whilst DRP remained the dominant and most stable fraction in all cases, PP and DOP tended to increase to a far greater degree than DRP during periods of high rainfall. This would indicate that during these periods a greater proportion of DOP and PP are being transported through the aquifer to the springs. Kronvang (1992) found strong positive relationships between particulate P concentrations and discharge in the Lyngbygaard's River in Denmark. Grant and others (1996) also reported high PP concentrations in subsurface drains during storm events from arable catchments in Denmark. In the Fergus and Robe springs, the increased volume and speed of water travelling along flow paths to the springs is providing sufficient energy to transport particles either flushed through the

soil or present in the aquifer, which under normal stage conditions would not be mobilised.

RS06 spring in the Robe catchment offered a unique example to examine the behaviour of a spring in terms of TP during extreme pollution stress. The spring appeared to respond to rainfall and produced contamination even where calculations suggested that there was a soil moisture deficit. The fact that the likely source of the pollution at RS06 was close to a swallow hole would mean that there is a direct link to the spring. Therefore, even a high soil moisture deficit will have no effect, the soil being bypassed. The benefit of high frequency autosampling was demonstrated. The load from RS06 spring potentially increased 50% of the total P load in the receiving River Robe. The more stable daily TP levels experienced at FS05 spring reflect the more diffuse recharge and large catchment area of the spring. In such instances, TP remains relatively stable except in the case of extended periods of effective rainfall, where particulate levels are prone to increase.

The pollution event at RS06 highlights the notoriously effective ability of karst aquifers to transmit rather than treat pollutants (Ford and Williams 1989). It is only because the spring was supplying drinking water that the event was noted. The vast majority of the effluent had passed through the spring in almost ten weeks, so quarterly sampling for P might have missed the event entirely, while even weekly sampling could have missed short-term events with P increasing from $42 \mu\text{g l}^{-1}$ to $1,814 \mu\text{g l}^{-1}$ within 24 hours. Short-lived pollutant pulses are characteristics of karst springs: marked changes in calcium and faecal coliforms over a period of a month as a result of changing flow conditions at another Irish karst spring are documented in Coxon and Thorn (1989), and the need to adopt storm event driven sampling in karst springs has been recognised by several authors (e.g. Quinlan and Alexander 1987).

These events are particularly important when considering their contribution to surface water quality. Short-term pollution events will be of particular concern during the summer months, during low stage conditions when in-river P concentrations are typically low due to plant uptake. Even small volumes of P rich contamination being transmitted via springs could have a dramatic effect on surface water productivity and ecology. Therefore, it is important that point recharge locations feeding karst springs should be identified and managed responsibly.

Conclusions

The detailed examination of phosphorus concentrations over time in these eight karstic springs yielded some important findings.

- Total P concentrations at each spring exhibited some increase with rainfall events.
- These increases reflect significant changes in PP and DOP, with DRP displaying greater temporal stability.

- Greatest response to rainfall events occurred after the first major autumnal rains in September 1999. This response to the first autumnal rains probably reflects a hydrological switch where the catchments change from a soil moisture deficit to a soil moisture surplus situation. In addition, there appears to be an initial dislodging of loosely bound PP and DOP during these first rains, which are transported to groundwater.
- Daily autosampling results at the Robe spring (RS06) highlighted the need to adopt storm event driven sampling rather than discrete sampling in karstic springs. Such short term pollution events will be of particular concern during the summer months, during low stage conditions when in-river P concentrations are typically low due to plant uptake and when overland flow will be low due to soil moisture deficit build up. Phosphorus rich contamination being transmitted via springs could have an adverse effect on surface water ecology through excessive plant productivity.
- High-risk land use activities involving phosphorus and the timing of such activities pose a particular threat to surface water quality in karst environments. Identification and management of swallow holes and springs in karstic areas presents a demanding challenge.

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