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Biogeochemical time lags may delay responses of streams to ecological restoration

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SUMMARY

1. Mounting interest in ecological restoration of streams and rivers, including that motivated by the Water Framework Directive, has stimulated examination of whether management and restoration measures in streams and their catchments have yielded measurable improvements in ecological status ('health'). Evidence for the efficacy of diffuse-source pollution reduction (including best management practices on land) has proven elusive.
2. Several hydrological and biogeochemical processes delay the responses of streams and rivers to a decrease in nutrient and sediment inputs, potentially for decades. The implications of such time lags in response to restoration may not be well appreciated by restoration ecologists, regulators, sponsors of restoration work or the broader community.
3. The groundwater time lag results from the long residence time of ground water. This is particularly important with respect to nitrate, but is increasingly important for phosphorus (P) as well. Isotopic tracers and groundwater age dating suggest that stream water often is more than a decade old, and that several decades are required to flush most soluble contaminants from groundwater reservoirs.
4. Sediment movement through river networks can be protracted because of storage and remobilisation processes involving stream beds, impounded reaches and fringing bars and floodplains. In lowland streams and rivers, sediment accretion can be rapid, but its removal is often far slower and can take decades to centuries.
5. Phosphorus availability is subject to time lags because P tends to associate with minerals, resulting in a potentially large yet exchangeable P reserve in upland soils and alluvial and stream-bed sediments. Thus, soils and sediments can remain rich in P for decades after new inputs are reduced, potentially acting as a source of P to surface waters. Phosphorus saturation of soils along ground water percolation pathways can lead to even longer time lags. Restoration measures that inundate previously dry soils or desiccate previously inundated sediments can induce high rates of P release.
6. These hydrological and biogeochemical time lags can obscure the short-term responses of streams and rivers to restoration measures. In many eutrophic waters, large decreases in nutrient availability would be required to return the ecosystem to a natural nutrient-limited state, and this could take decades.

Keywords: catchments, ecological restoration, eutrophication, nutrients, streams

Introduction

Interest in ecological restoration of streams and rivers has been mounting in recent decades (Bernhardt *et al*., 2005), and restoration has increasingly been encouraged by government mandates. A current example that is a focus of this special issue is the Water Framework Directive of the European Union (CEC, 2000). This directive mandates that member countries seek to restore surface and ground waters to 'good ecological status' by 2015, which is defined as 'slightly different' than the 'high status' (i.e. essentially pristine) condition, and emphasises ecological

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indicators of response to restoration (Moss, 2007, 2008). Whilst the desired target condition is itself a matter of some debate (Moss, 2007), the general consensus is that restoration should strive to return impaired ecosystems towards a greater semblance to their pre-impact state, based on comparison with an appropriate reference system considered to be in pristine or near-pristine condition.

Threats to water quality in streams and rivers and their recipient waters often involve excessive loading of nutrients and sediments, altered channel morphology and hydrology and altered water temperature. Nitrogen (N) and phosphorus (P) are the primary drivers of eutrophication (Mainstone & Parr, 2002; Elser *et al*., 2007; Lewis & Wurtsbaugh, 2008; Conley *et al*., 2009), which is often a greater concern in lakes or marine waters to which streams flow than in the streams themselves. In addition, high nitrate concentrations can impair drinking water quality. Sediments can reduce the quality of stream habitat, and contaminants including P and metals as well as xenobiotics (e.g. pesticides) often bind to and move with sediments (Walling *et al*., 2003). Stream channel alterations as well as altered catchment hydrology are often implicated in aquatic habitat deterioration, and channel simplification for flood control can reduce the retention of nutrients and sediments as water moves from catchments into stream channels and as it proceeds through fluvial networks (Walsh *et al*., 2005; Dosskey *et al*., 2010). On the other hand, construction of impoundments can trap sediment and reduce stream nutrient loads, at least until they fill with sediment (Vörösmarty *et al*., 1997; Foster, 2010), or are removed in restoration projects.

Significant improvements in water quality have been achieved over the past 40 years by reducing the largest point-source inputs of nutrients and other pollutants to streams, rivers, lakes and coastal waters (Alexander & Smith, 2006). Yet as those large and direct point-source inputs have been diminished to the extent possible under constraints of costs and technologies, diffuse point- and non-point-source pollution has become a larger contributor to widespread and persistent water-quality problems (Carpenter *et al*., 1998; Jarvie *et al*., 2002; Bowes *et al*., 2005; White & Hammond, 2009). Ecological restoration aimed at reducing diffuse-source inputs of excess nutrients and sediments to streams and rivers includes measures such as best management practices on farm land (Robertson *et al*., 2007; Sharpley *et al*., 2009) and naturalisation of stream channels and riparian zones (Bernhardt *et al*., 2005; Dosskey *et al*., 2010).

Stream and catchment restoration has been widely practiced in the U.S.A. and Europe for several decades. Yet, recent analyses of whether management and restoration measures in streams and their catchments have yielded measurable improvements in indicators of ecological status (or 'health') of the streams and their recipient waters have shown equivocal results (Boesch, Brinsfield & Magnien, 2001; Lake, 2001; Duarte *et al*., 2009; Worrall, Spencer & Burt, 2009a; Dubrovsky *et al*., 2010; Meals, Dressing & Davenport, 2010; Palmer, Menninger & Bernhardt, 2010). A number of studies have demonstrated reductions in nutrient export at the field-plot scale in response to best management practices (Robertson *et al*., 2007; Sharpley *et al*., 2009), and Osmond (2010) reviewed recent research in the United States on agricultural best management practices that has shown some evidence of water-quality improvement at catchment scales. However, evidence for positive ecological outcomes as a result of diffuse-source pollution reduction (including best management practices on land) has proven elusive for streams and rivers, to the surprise of many restoration advocates.

The challenge of demonstrating results at the catchment scale is no doubt due in part to the difficulty of quantifying stream ecosystem condition (Boulton, 1999), the tendency for restoration projects to encompass only a portion of the stream or its catchment (Gregory *et al*., 2007; Robertson *et al*., 2007) and the lack of rigour in experimental design with common issues including unrepresentative sites (Gregory *et al*., 2007), poor controls (reference systems; Boulton, 1999) and inadequate monitoring and assessment before and after restoration measures (Bernhardt *et al*., 2005; England, Skinner & Carter, 2007). The importance of long-term monitoring records has been demonstrated in the case of nitrate in rivers, where trends can be obscured by short-term variability (Burt *et al*., 2008; Burt *et al*., 2010; Howden *et al*., 2011; Burt *et al*., 2011a). Identification of responses to restoration can also be complicated because ecosystems subject to restoration efforts typically suffer from multiple stressors (Ormerod *et al*., 2010) and may have experienced fundamental ecological shifts that impede or delay a return to a pre-impact state (Schippers *et al*., 2006; Duarte *et al*., 2009).

Time lags in the responses of streams and rivers to restoration measures also could delay their recovery, potentially for many years. Time lags reflect the sum of delays associated with the time required for restoration practices to produce a desired effect, the time required for the effect to be manifested in a water resource and the time required for a water body to respond to that effect (Meals *et al*., 2010). Several time lags can be ascribed to hydrological and biogeochemical processes that result in long residence times of nutrient and sediment pools in catchments, stream channels and lakes and reservoirs. Such time lags, sometimes referred to as legacies, reflect the fact that the land-cover conversion and nutrient and sediment pollution may have occurred for decades to centuries prior to restoration. The potential for time lags has been recognised in relation to the Water Framework Directive (Cherry *et al.*, 2008), but still may not be widely appreciated by restoration ecologists, regulators, sponsors of restoration work or the broader community.

The purpose of this paper is to review the evidence for and potential importance of biogeochemical time lags in the response of streams and rivers to ecological restoration, drawing on studies from North America as well as Europe. I emphasise nutrient and sediment time lags because ecological time lags, such as the return to natural vegetation and soils and their associated functions, have been the subject of other recent reviews (Harding *et al.*, 1998; Gregory *et al.*, 2007; Dosskey *et al.*, 2010; Meals *et al.*, 2010).

Examples of time lags

The groundwater flow time lag

One potential time lag results from the slow movement and long residence time of groundwater reservoirs in many catchments. With regard to stream water quality, this is a particular issue for nitrogen because of the high solubility and mobility of nitrate in subsurface flow paths (e.g. Jarvie *et al.*, 2008). The high mobility of nitrate implies that it would be more readily flushed out of catchments than a contaminant that tends to bind with soils and sediments (e.g. P: see below). However, the time scale of flushing depends on groundwater flow paths and residence times of storage reservoirs.

Large groundwater reservoirs that contribute substantially to surface water bodies present a 'natural risk factor' that predisposes a particular catchment to a long groundwater time lag (Fig. 1). Loading of contaminants in the recharge zone because of human actions, as for example by agricultural land use, leads to contamination of the groundwater reservoir. Transport of contaminants from the land surface to ground water is facilitated by rapid infiltration and percolation, and in the case of nitrate, by low rates of denitrification in the subsurface.

In drier climates and particularly where there are thick unsaturated zones, water and solute movement through the unsaturated zone can also be protracted, resulting in time lags between contamination at the land surface and the appearance of the contaminant in underlying ground waters. Such time lags can be on the order of decades to even a few centuries (McMahon *et al.*, 2006), and contamination of this flow path is often associated with irrigation and cultivation in drylands.

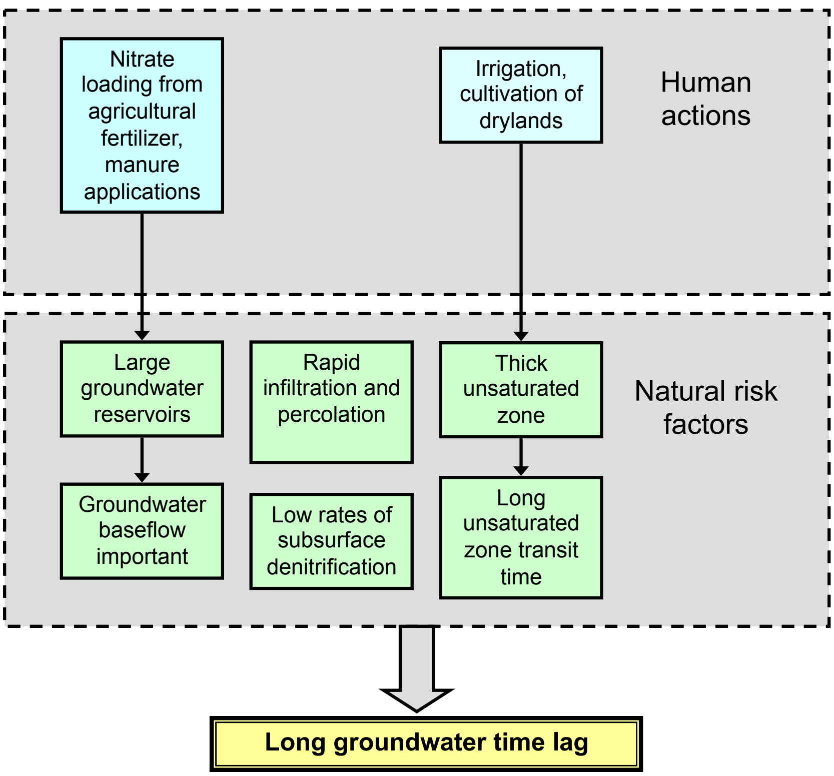

Fig. 1 Human actions and natural risk factors likely to lead to protracted time lags for the response of stream groundwater inputs to changes in catchment nutrient loading. Natural risk factors predispose a catchment to longer time lags, and human actions introduce the contaminant into the system (and can sometimes increase the risk factors). Arrows connect boxes where there are clear linkages. See text for sources of information.

The mean transit time of water through catchments and the distribution of water transit times that contribute to stream discharge have been the topic of recent attention in the hydrological literature (reviewed by McGuire & McDonnell, 2006; McDonnell *et al.*, 2010). Estimates of transit times come mostly from hydrological tracers, including the stable isotopic and radioisotopic composition of the water itself, and well as several kinds of dissolved gases. However, the gas tracers can only be applied in groundwater samples that have not been exposed to gas exchange with the atmosphere, whereas water isotope tracers are also applied in streams.

Re-evaluation of information derived from stable isotopic tracers (mainly $\delta^{18}O$ in water) or chloride versus tritium (^{3}H in water) in catchment studies has pointed to an underappreciated importance of older groundwater inputs that are revealed by tritium but often undetectable from stable isotope or solute tracers alone (Stewart, Morgenstern & McDonnell, 2010). Estimates of water transit time in catchments appear to have been biased low by the profusion of stable isotope studies in recent years. Stewart *et al.* (2010) review studies across catchments of diverse geology and size in which tritium was employed to estimate catchment-scale water transit times for the subsurface flow component, which would normally be through groundwater aquifers. Mean subsurface transit times were 15 ± 22 years in headwater catchments, in which subsurface flow comprised $60 \pm 22\%$ of the total stream discharge (mean ± SE; $N = 22$ catchments). A similar review of larger catchments indicated mean subsurface transit times of 10 ± 5 years, with subsurface flow comprising $52 \pm 26\%$ of the total discharge (mean ± SE; $N = 14$ catchments).

From the standpoint of contaminant movement through groundwater systems, it is important to note that the mean water transit time can give a misleading view of how long it takes to purge a contaminant from the system. Using the simplest model of a well-mixed groundwater reservoir in which the purging (depuration) of a contaminant follows an exponential trajectory, it takes *c.* 3 times the mean water transit time to eliminate 95% of the contaminant, assuming it behaves as a conservative solute (McGuire & McDonnell, 2006). Moreover, the movement of water through subsurface flow systems is better characterised by a distribution of transit times, and recent studies have shown how these are typically skewed with long tails, approximating a power-law distribution (Kirchner, Feng & Neal, 2000; Stewart *et al.*, 2010; Cardenas & Jiang, 2010; Godsey *et al.*, 2010). In other words, there are typically very long flow paths that will effectively cause the contaminant discharge to persist at relatively low but potentially ecologically significant levels, well beyond even three times the mean transit time.

Tritium tracing thus indicates that most of the ground water discharged from catchments, at least those which have been studied, is at least a decade old, and a substantial fraction would be much older than that (Stewart *et al.*, 2010). This conclusion is supported by studies using other tracers such as dissolved chlorofluorocarbon (CFC) gases that reveal the recharge age of ground water sampled in wells or springs (Böhlke & Denver, 1995; Böhlke, 2002; Saad, 2008; Kennedy *et al.*, 2009). This may seem surprising given that streams and rivers so readily respond to short-term rainfall and snowmelt events, but hydrological theory shows how changes in hydraulic head propagate through a subsurface flow path far faster than actual water movement; in effect, the new water input to a groundwater flow system can push older water out at a distant downhill point (Beven, 1982; Kirchner *et al.*, 2000).

Future studies need to elucidate the relationships between catchment characteristics and subsurface flows and transit times, and the implications for the groundwater flow time lag (Tetzlaff *et al.*, 2009). Groundwater flow paths with very long transit times present a challenge for tracer studies because the time scale of tracer movement through the system can greatly exceed the observation period, and hence groundwater flow systems often remain a 'black box' from the standpoint of surface-groundwater exchange.

These long transit times for subsurface flow through catchments have implications for the time scale of recovery of stream water quality in the case of contaminants that are mobile in groundwater flow systems. For example, Michel (2004) estimated that it would take 20–25 years to flush >50% of a soluble, conservative contaminant out of the catchments of the upper Missouri and Ohio rivers, major tributaries of the Mississippi River system (U.S.A.). Lindsey *et al.* (2003) estimated the streams draining into Chesapeake Bay (U.S.A.) would require, on average, at least a decade to show responses to reductions in nitrate loading from their catchments (and presumably much longer to approach pre-loading concentrations).

The groundwater flow time lag could explain in part why many rivers in the U.K. still carry elevated nitrate loads (Howden & Burt, 2008, 2009; Burt *et al.*, 2011b). For example, even after 12–15 years of mitigation efforts since a European Union directive to reduce nitrogen inputs, particularly from agriculture, there has been no consistent reduction in nitrate concentrations in streams draining areas designated as Nitrate Vulnerable Zones in the U.K.,

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(Worrall *et al.*, 2009a). It could also help explain why fluvial export of nitrogen from Great Britain to the sea increased from 1975–2005, in spite of an apparent drop in total *N* inputs to the terrestrial catchments since about 1990 (Worrall *et al.*, 2009b), and why the River Thames has continued to increase in nitrate load in recent decades (Howden *et al.*, 2010). However, as the Worrall *et al.* studies note, there may also be other factors at play, including long-term accumulation of soil nitrogen stocks and the possibility of a climatically induced increase in leaching losses of dissolved organic nitrogen from organic soils. Similar results have been reported in US agricultural catchments (e.g. Böhlke, 2002; Schilling & Spooner, 2006; Meals *et al.*, 2010).

In contrast to nitrate, contaminants that reversibly sorb to soils or sediments and can be gradually released from sorbed pools into subsurface flow pathways would exhibit longer recovery times than the hydrological tracer-based results suggest. A well-studied example is P, which is discussed in detail later, but other contaminants including a number of trace metals display this behaviour, although with variable conditions that facilitate their release to solution.

Many studies have shown that substantial attenuation of nitrate contamination can occur when ground water becomes depleted in oxygen (e.g. Rupert, 2008). Nitrate is consumed rapidly when conditions are conducive to denitrification (i.e. if there is enough dissolved organic matter to support heterotrophic microbial respiration), or when nitrate drives the oxidation of ferrous iron by chemolithoautotrophic bacteria (Burgin & Hamilton, 2007). Thus, one might surmise that long subsurface flow paths would provide more time for denitrification, effectively ameliorating nitrate pollution. However, this can effectively trade one problem for another. Smolders *et al.* (2010) review studies showing how nitrate leaching into the subsoil often leads to oxidation of iron sulphide minerals, producing sulphate that reaches surface waters via groundwater discharge. Eventual microbial reduction of the sulphate to sulphide generates toxic conditions in porewaters, and sulphide reacts with ferrous iron to form relatively insoluble iron sulphide minerals, thereby enhancing the release of iron-bound P from the sediments.

Dissolved and colloidal forms of P can also travel to streams via ground water, in spite of the tendency for orthophosphate to be retained in most kinds of soils. Phosphorus movement through ground water is most likely under conditions of high or prolonged P loading to soils in recharge zones, particularly where the soils are coarse or water tables are close to the soil surface, making it more likely that the P sorption capacity of the unsaturated zone would become exhausted (Driescher & Gelbrecht, 1993; Siemens *et al.*, 2004). High concentrations of P in ground water may be more common in Europe than in North America, perhaps reflecting Europe's longer history of intensive land use and associated P loading as well as extensive regions with shallow water tables.

Human alterations of catchment hydrology often result in a higher ratio of surface to subsurface runoff, and many low-lying agricultural areas have constructed drainage systems (i.e. tiles and ditches) that divert runoff or infiltrating soil water and conduct it to stream channels. These changes effectively allow water to bypass all or part of the subsurface flow path and thereby may diminish the effect of the groundwater time lag. At the same time, such hydrological alterations bypass the soil and sediment filter, conveying diffuse pollution directly and rapidly to surface waters (Gentry *et al.*, 2007, 2009; Deasy *et al.*, 2009). Measures to reduce stormwater runoff into streams often entail construction of basins to allow for infiltration, thereby returning the runoff to the groundwater flow paths.

The sediment storage time lag

Natural risk factors that predispose a catchment to a long sediment storage time lag are largely geomorphological (Fig. 2). Sediment movement through river networks can exhibit a protracted time lag because of storage and remobilisation processes involving stream beds as well as fringing bars and floodplains, and this storage capacity has often been augmented by construction of impoundments from the headwaters to the lowermost reaches. Conveyance capacity of sediment through fluvial systems is limited, and therefore, it can take decades or, where there are extensive floodplains, even centuries for sediment inputs to move through the fluvial system. There is a large literature on this topic, recently reviewed by Burt & Allison (2010), and I will only briefly discuss it here.

The sediment storage time lag is most readily observed where a new sediment input is imposed on a previously unimpacted fluvial system, a situation more common in North America than Europe. Classic studies from the United States demonstrate time lags for sediment transport in stream channels lasting over decadal scales or longer (Schumm, 1977; Trimble, 2010). These include the Sacramento River system in California, where sediment inputs generated by hydraulic mining in the late 1800s took nearly a century to move through the entire river system (Meade, 1988). Conversion of forest to agriculture upon European settlement of the eastern United States caused massive sediment mobilisation and transport, as

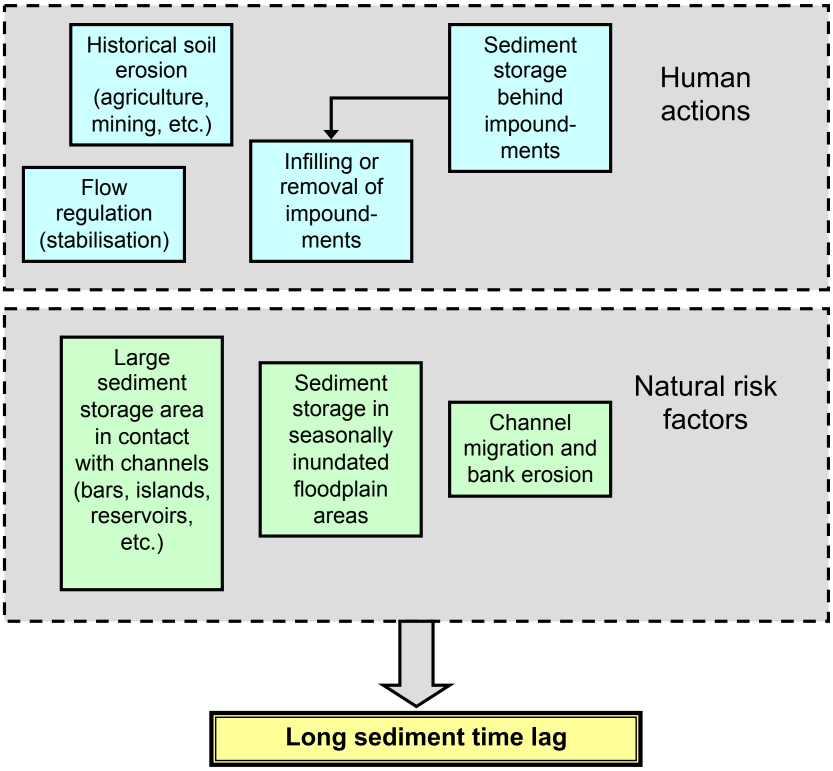

Fig. 2 Human actions and natural risk factors likely to lead to protracted time lags for the movement of sediment through streams and rivers. See Fig. 1 for more explanation and the text for sources of information.

illustrated by detailed studies at Coon Creek, which drains a 360-km^2 catchment of the upper Mississippi River system in Wisconsin (Trimble, 2009). Sediment delivery from that catchment into the Mississippi River has continued unabated as conservation measures dramatically reduced soil erosion inputs, apparently because of erosion of stream banks containing the accreted sediment. However, Meade & Moody (2010) report that part of the decline in sediment transport in the Mississippi River in recent decades may be attributable to soil conservation measures.

At larger scales, it is similarly estimated that 90% of the anthropogenic sediment inputs to fluvial systems across the coterminous United States remain in storage in channels, floodplains and reservoirs (Meade, 1988). Trimble (2010) reports similar conclusions from a number of catchments in Europe. Recent studies in the eastern United States have shown the importance of innumerable small impoundments, many built as mill ponds between the late 1600s and early 1900s, in sediment storage (Walter & Merritts, 2008; Schenk & Hupp, 2009; Foster, 2010). Most floodplains above such impoundments are fill terraces produced since dam construction, often containing 1–5 m of sediment accumulation that has fundamentally altered stream channel and floodplain geomorphology. Many of these old dams are now breached, but the sediment deposits remain and are subject to gradual conveyance downstream as incised channels meander through them. Similar widespread damming of streams occurred in Europe, but began several centuries earlier (Walter & Merritts, 2008). Stream channel restoration that entails removal of impoundments often must anticipate a protracted mobilisation of large volumes of legacy sediment and associated nutrients and contaminants (e.g. Burroughs *et al*., 2009).

Thus, a decrease in sediment loading from the catchment may not produce a proportionate decrease in problems resulting from excess sediment within stream channels until the legacy of past sediment loading has been flushed from the river system. Nutrients and trace contaminants associated with sediments will remain in the river-floodplain system and continually be subject to remobilisation until stored deposits become depleted (e.g. Walling *et al*., 2003; Dunlap *et al*., 2008; Walling, Collins & Stroud, 2008), and in some cases, the resultant protracted recovery time presents a great challenge for ecological restoration. Removal of contaminated sediments is employed in the most extreme cases, but is expensive and impractical at larger scales (NRC, 2007; Clements, Vieira & Sonderegger, 2010).

The phosphorus buffer time lag

Phosphorus availability is particularly subject to time lags because P tends to associate with minerals, resulting in a potentially large yet exchangeable P reserve in upland soils as well as in alluvial and stream-bed sediments. Thus, soils and sediments can remain rich in P long after new inputs are reduced and can release soluble P to surface or ground waters. The concept of a reservoir of P bound to particulate matter that is potentially released to solution has been termed the 'phosphorus buffer' because it effectively buffers soluble P concentrations and augments the total P pool that is potentially available for biotic uptake (Froelich, 1988). This P buffer concept can be extended from individual mineral particles to soils, sediments and entire catchments (Schippers *et al.*, 2006). The P buffer time lag is therefore related to both the sediment and groundwater time lags discussed above, although it also involves intact soils in upland areas of catchments.

The P buffer time lag has received considerable scientific attention. Reviews of P biogeochemistry that are pertinent to the P buffer time lag include Haygarth *et al.* (2005a) and Ulén & Jakobsson (2005) for land-water transport of P, Mainstone & Parr (2002), Withers & Jarvie (2008) and Neal *et al.* (2010) for streams and rivers, Marsden (1989) for lakes and Reddy *et al.* (1995, 1999) and Smolders *et al.* (2006) for wetlands. These reviews point to the important role of minerals in P sorption (particularly iron oxyhydroxides) or coprecipitation (particularly calcium carbonate). They also summarise numerous studies that show the potential for release of soluble P from these mineral-P associations in response to changing conditions including decreased P concentrations in water, increased *p*H or decreased redox potential (i.e. following depletion of dissolved oxygen). The entire pathway of P flow through ecosystems can be conceptualised as a continuum from P sources into storage pools, from which P is eventually subject to remobilisation followed by transport to sensitive waters where eutrophication impacts occur (Haygarth *et al.*, 2005a).

Natural risk factors that predispose a catchment to long P buffer time lags include geomorphological features that result in high contact of surface water with sediments in depositional areas, either seasonally or in shallow permanent water bodies (Fig. 3). Human actions contribute to elevated P loading of soils and sediments, and this becomes a problem for downstream waters when the soils erode, or when the P retention equilibria in soils or sediments change to favour net P release to the water. Net P release can be invoked by flooding previously dry soils (e.g. reservoir creation or wetland restoration) and can be exacerbated by sulphur pollution (see discussion above). An alternative pathway involves constructed drainage systems that deliver P directly to water bodies. Dissolved oxygen depletion, a common indirect effect of eutrophication, can also increase P release to water overlying sediments. These various ways in which human actions can influence P storage and remobilisation are discussed in greater detail below.

Upland soils used for agricultural row crops or livestock production often accumulate surplus P in the surface horizons (Blake *et al.*, 2003; McLauchlan, 2006; Schippers *et al.*, 2006), particularly where manure is applied because it supplies P in excess of crop require-

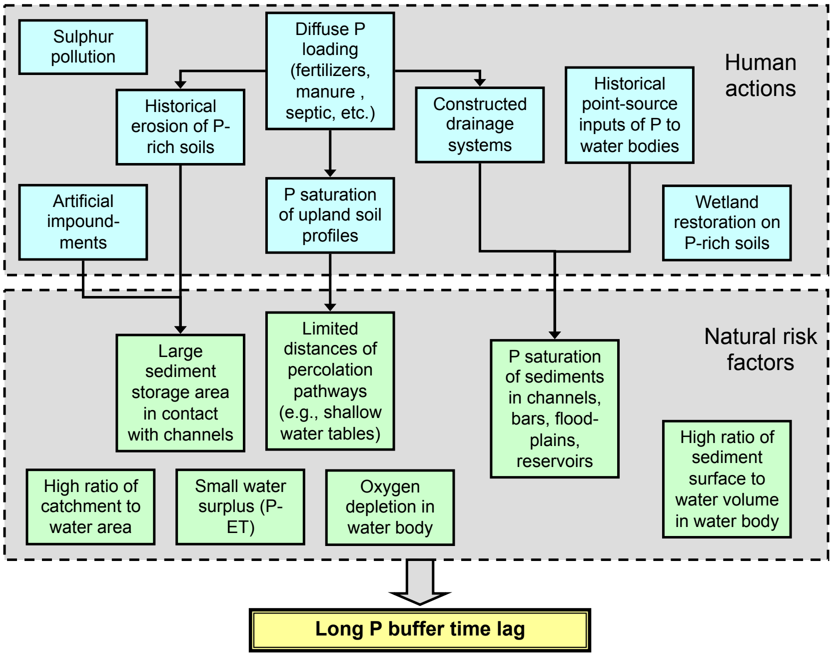

Fig. 3 Human actions and natural risk factors likely to lead to protracted time lags for the response of streams and rivers to changes in catchment phosphorus (P) loading. See Fig. 1 for more explanation and the text for sources of information.

ments relative to N (Edmeades, 2003). Soils may retain excess P for several decades after reduction of inputs (McLauchlan, 2006; Schippers *et al.*, 2006). Much of the soil P reservoir will be adsorbed onto fine silts and clays. In many settings and particularly in agricultural landscapes, most of the transport of P from soils to water occurs by overland flow of fine particulate and colloidal matter (Haygarth *et al.*, 2005a,b; Withers *et al.*, 2009a), but can also occur via subsurface flow where artificial drainage systems exist (Ulén & Jakobsson, 2005; Deasy *et al.*, 2009). However, under conditions of long-term loading that leads to P saturation of surface soils, P can move downward into the unsaturated zone and underlying ground water; areas with shallow groundwater tables and coarse soils are most at risk for groundwater P contamination (Schippers *et al.*, 2006). Holman *et al.* (2008, 2010) have documented the extent of groundwater P contamination across the U.K. and Ireland and shown many instances where groundwater P concentrations are elevated enough to contribute to the eutrophication of surface waters, suggesting saturation of the soil P retention capacity.

Phosphorus associated with colloidal or particulate matter entering streams and other surface waters may eventually reach depositional areas, where it is potentially exchangeable with the water column or otherwise available for biotic uptake (House & Denison, 2002; House, 2003; Withers *et al.*, 2009a; Neal *et al.*, 2010). Storage in depositional areas of stream channels or flood plains may also be temporary, subject to resuspension in future high flow events or as stream channels migrate laterally (Walling *et al.*, 2008; see also sediment time lag discussion above).

Dissolved P inputs to streams and rivers can be particularly important where there is sewage or septic effluent, or runoff from impervious surfaces (White & Hammond, 2009; Withers *et al.*, 2009b; Neal *et al.*, 2010). Often under these circumstances, aquatic sediments in the fluvial system act as a sink for excess P (Neal & Jarvie, 2005). However, this equilibrium between sediment-sorbed P and dissolved P can be altered when P loading is attenuated, as for example when point sources are reduced, and as a result, the sediments can become a source of P to the overlying water (Jarvie *et al.*, 2005, 2006; Ballantine *et al.*, 2009). There can also be a seasonal offset between inputs of P-rich sediments in storm events and their eventual release of P during an ensuing low-flow period, which is typically a season of high biological demand for P (Jarvie *et al.*, 2005).

Sediment-water exchanges of P have long been studied in lakes, where delayed responses to mitigation of P inputs have often been ascribed to 'internal loading' from the lake sediments, most commonly during seasonal oxygen depletion of the hypolimnion (Marsden, 1989). Internal P loading in seasonally stratified lakes can remain an important driver of eutrophication for several decades after new P inputs are reduced (e.g. Dørge & Windolf, 2003: 20–25 years; Carpenter, 2005: 50 years under P-rich conditions; Schippers *et al.*, 2006: 70 years for a model lake; more examples provided in Marsden, 1989). In shallow lakes, internal P loading may be less persistent but may remain important as long as 15–20 years after mitigation of point-source P inputs (Phillips *et al.*, 2005; Jeppesen *et al.*, 2005 & 2007). Dissolved oxygen at the sediment-water interface is a key variable controlling P release, with increased release rates upon depletion of oxygen, likely due mainly to consequent reduction of oxidised forms of iron that would otherwise bind P at the sediment surface (Marsden, 1989; House & Denison, 2002; House, 2003). Thus, the productivity of the lake is an important factor, providing the source of sedimented labile organic matter whose decomposition results in oxygen depletion at the sediment surface (Marsden, 1989).

In temperate lakes and reservoirs, dissolved oxygen depletion is generally observed in hypolimnetic waters during seasonal stratification, but in shallow, productive waters of wetlands and shallow lakes, depletion of oxygen at the sediment surface can occur episodically or erratically in response to fluctuating water levels and vegetation growth cycles (Reddy & Delaune, 2008). The well-studied P release processes that operate in an anoxic lake hypolimnion are also important in shallow waters subject to oxygen depletion (Smolders *et al.*, 2006). Also, as discussed above, increased inputs of sulphate to lakes and wetlands can enhance sediment P release from iron oxyhydroxides by sequestering the reactive iron in iron sulphide minerals (Smolders *et al.*, 2010).

Restoration measures that entail re-wetting of previously dry soils or desiccation of previously inundated sediments often induce high rates of P release from organic and inorganic (mineral) pools (Venterink *et al.*, 2002; Pant & Reddy, 2003; Duff *et al.*, 2009; Ardón *et al.*, 2010; Zak *et al.*, 2009 & 2010). The aforementioned biogeochemical interactions involving iron, sulphur and nitrogen can change the sediment-water P equilibrium over time after re-wetting (Smolders *et al.*, 2006; Grunth, Askaer & Elberling, 2008). Modelling that only considers P exchange between stream-bed sediments and the water column under present conditions (e.g. Wade *et al.*, 2007) may vastly underestimate the potential P release that could be invoked upon restoration of natural flow and flooding regimes, which may entail the creation of expansive areas of shallow, often seasonal flooding (Zak & Gelbrecht, 2007). However, in many cases, the sediments of newly created wetlands can function as a sink for P, particularly if their soils were not subjected to high rates of historical P loading (Reddy *et al.*, 1995).

The protracted time scales for catchment-wide responses of the P buffer were demonstrated in a modelling study by Schippers *et al.* (2006) based on a model catchment of a shallow lake with its catchment subjected to hypothetical scenarios of terrestrial P loading. The responses of surface soils and lake sediments to a dramatic decrease in P loading extended over several decades. In the case where substantial P loading occurred belowground in the 'percolation pathway', affecting P sorption on minerals as well as groundwater P concentrations, responses took centuries, far exceeding water transit times. This is because substantial stores of sorbed P had accumulated belowground, and that P was gradually released to solution after the loading was diminished. Similar conclusions were reached by Carpenter (2005) in simulations of Lake Mendota (Wisconsin, U.S.A.) and its catchment. These studies demonstrate how long-term P loading to soil profiles could be setting the stage for future increases in P transport to water bodies. Once such increases become evident, they are likely to persist for a very long time, even if anthropogenic P loading to the surface is curtailed.

Time lags, nutrient availability and ecosystem restoration

In considering these potential time lags, one must bear in mind the current condition and the desired target for ecosystem restoration. Many streams and rivers in agricultural landscapes of North America and Europe carry concentrations of nutrients that are far above their natural levels (Sharpley *et al.*, 2009; Dubrovsky *et al.*, 2010). In the United States, Alexander & Smith (2006) reported a median and 75th percentile for the total P concentrations in 250 gauged river sites of 0.12 and 0.46 mg L^{-1}, respectively. In England and Wales, the majority of large lowland rivers carry soluble reactive P concentrations above 0.3 mg L^{-1}, with many exceeding 1 mg L^{-1} (Mainstone & Parr, 2002). Such levels of P enrichment are far above the threshold for biological limitation of primary production, which for algal production in both streams and lakes has been estimated at around 0.030 mg L^{-1} total P (Dodds, 2007). Most streams and rivers in North America and Europe were probably below these thresholds prior to the intensification of agriculture and the increase in human population densities in their catchments (Mainstone & Parr, 2002; Smith, Alexander & Schwarz, 2003). Thus, the more eutrophic streams and rivers are so replete with nutrients that they may require large decreases, on the order of 90% or more in concentrations of available nutrient forms, before nutrient limitation would become a structuring force and the symptoms of eutrophication would be relieved in the fluvial system and its receiving water bodies.

Therefore, aquatic ecosystem restoration can be a long-term undertaking, and where there are indications of a long time lag for the return to pre-loading conditions, that prospect needs to be understood by policy makers as well as the public (Meals *et al.*, 2010). Indeed, if expectations are set too high, then support for restoration may wither as quick improvements fail to materialise (Gregory *et al.*, 2007). Whilst even substantial decreases in nutrient concentrations in the more eutrophic streams and rivers may not result in desirable ecological outcomes until the much lower thresholds are reached, at least a demonstrable decrease in nutrient concentrations would show that the catchment-stream system is on a trajectory of change towards a less nutrient-enriched condition. If steps are not taken to reduce the root causes of eutrophication, then the eventual restoration becomes ever more difficult and the problem is left for ever more future generations.

Anticipating time lags in stream restoration

The ranges of time lags discussed above are summarised in Fig. 4, which is intended to provide examples rather than a comprehensive indication of likely ranges and is biased by the relatively small number of available studies. For the groundwater time lag, the estimates of mean transit times based on tritium compiled by Stewart *et al.* (2010) were multiplied by three to estimate the approximate time for 95% of the water to be exchanged, as discussed above. Estimates of the sediment time lag come mainly from North America and may be biased towards studies of catchments where soil erosion and sedimentation were recognised problems. The P buffer time lag includes estimates for its four major components, including the subsurface percolation flow path, as distinguished by Schippers *et al.* (2006). The potential for protracted groundwater, sediment or P buffer time lags in a particular fluvial system can be ascertained by consideration of the human actions in the catchment in combination with natural features of the catchment and its streams and rivers that represent risk factors for time lags (Figs 1–3).

Modelling is useful to integrate this information and provide a picture of the likely dynamics of recovery of specific catchments from eutrophication, provided there is

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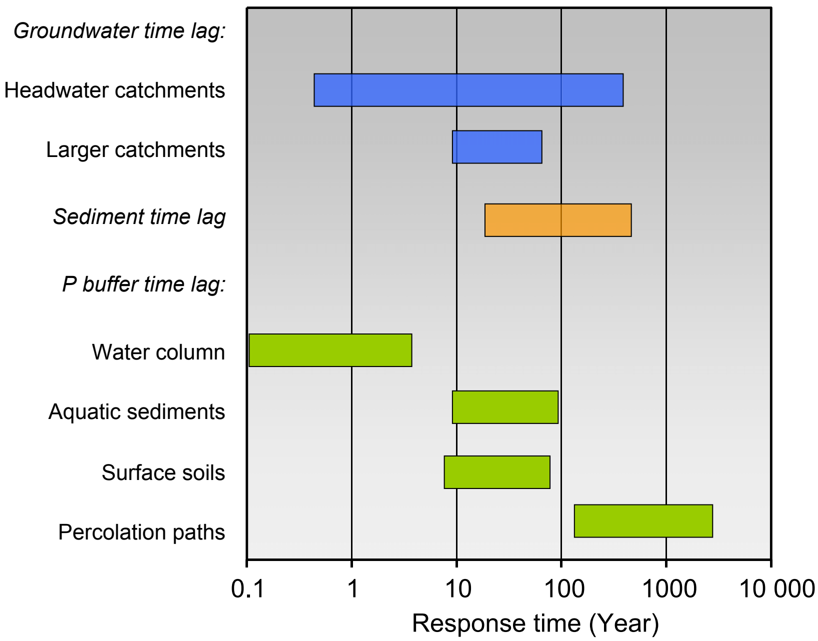

Fig. 4 Estimated ranges of response times for recovery of fluvial systems and their catchments from sediment and nutrient pollution. The groundwater time lag is considered the time for *c.* 95% of the reservoir water to be exchanged, estimated as three times the mean water transit times for a diverse set of catchments (data compiled by Stewart *et al.*, 2010). The sediment and P buffer time lags are based on observations (see studies cited in text) and, in the case of percolation pathways, modelling by Schippers *et al.* (2006).

sufficient information for the catchment (Dørge & Windolf, 2003). The insights provided by modelling are exemplified by the coupled catchment-shallow lake model of Schippers *et al.* (2006), which suggests that a mere 50 years of today's typical agricultural P loading to the landscape (e.g. half of a catchment receiving 15 kg P ha^{-1} $year^{-1}$) could take >1000 years to be fully flushed from the system such that the lake would return to its initial oligotrophic state! In spite of the uncertainty in this kind of modelling, the obvious conclusion is that current P loading rates are leading to long-term catchment eutrophication, and therefore, it is prudent to seek measures to reduce the loading. Even though such models may be quite uncertain in their longer-term projections, they allow for generation of scenarios that can guide policy choices. For policymakers, what may be most important to know is whether ecological outcomes are anticipated in the short-, medium- or longer-term time horizons.

These hydrological and biogeochemical time lags can obscure the short-term responses of streams and rivers to restoration and management and may help explain the apparent lack of readily measurable ecological responses in many aquatic systems. Considering that most catchment and in-stream restoration has been conducted in the past 30 years, and most monitoring of specific projects occurs on time scales shorter than decadal, such delays may account in part for the lack of demonstrable responses. Nonetheless, it is important to point out that recovery of streams and other aquatic ecosystems from diffuse pollution is not necessarily a protracted process and can be fast in some cases (Yount & Niemi, 1990; Gregory *et al.*, 2007). Chambers *et al.* (2006) provided evidence of a rapid reduction in N and P export from headwater catchments taken out of agricultural production. A paleolimnological investigation of a shallow lake in Ireland provided evidence for rapid response of the lake's trophic status to depopulation of its catchment during and in the decade following the Great Irish Famine of 1845–1850 (Donohue *et al.*, 2010). Even larger rivers may respond quickly: for example, in a medium-sized river in Michigan (U.S.A.), Lehman, Bell & McDonald (2009) reported evidence for an immediate reduction in P concentrations following a ban on P in lawn fertilisers, suggesting that much of the movement of fertiliser P to the river occurred by fast runoff pathways. Unfortunately, the evidence suggests that many catchments are unlikely to recover so quickly as in these examples.

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