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Diffuse nitrogen pollution control: Moving from riparian zone to headwater catchment approach—A tribute to the influence of Professor Geoff Petts

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Abstract

A lot of attention has been given to the importance of riparian zones as a nitrogen buffer during the last 30 years. Expectations were high and have resulted often in mismanagement practices. This paper aims at revisiting during this period the main research advancement, questions generated, and the progress in understanding the role of interactions between land and water in river system functioning. We describe how the seminal papers published in the 1980s on the role of riparian zone as nitrogen buffer have triggered several fundamental and applied questions related to the mechanisms at stake or their long efficiency in different hydrological and climatic contexts. We then address how this local riparian buffer capacity can be evaluated at the small drainage basin scale. We finally touch upon the restoration and protection of riparian zones in the context of climate change and especially its potential role on local and global water fluxes and other key aquatic ecosystem functions.

KEYWORDS

agricultural catchment, denitrification, diffuse pollution control, wetland

1 | INTRODUCTION

Some 30 years ago, Geoff Petts, as editor of the journal *Regulated Rivers*, took possession of a draft paper by H. Decamps and G. Pinay on the significance of riparian zones and their role in the biogeochemical cycle of key nutrients (Pinay & Décamps, 1988). As editor, Geoff had the habit of cutting the paper into paragraphs and sentences in order to physically adjust the structure and presentation of the paper. As a graduate with Geoff Petts, Haycock was presented with a box containing the paper fragments of paragraphs and sentences of the Decamps and Pinay paper, not given the original version, and told by Geoff to make sense of his mess. During an ecological conference in York, UK, in the early 90s, Geoff Petts advised Pinay to have a look at a Haycock and Burt poster. Pinay remembers Geoff saying that he should have a look at it "because it does the same thing as you, but better, since he is not only doing biogeochemistry, but sets it up in a hillslope hydrology perspective" (Haycock & Burt, 1993).

This was the start of our journey. Since then, we have been cutting and splicing information from a range of disciplines and concepts to make sense of the interactions that control the flux of nutrients within catchments, from the soil to the stream. This article seeks to present a perspective on that journey, the lessons learnt, the work of colleagues, which have added clarity to ideas that have helped build a framework of understanding on the significance of riparian zones, and their role in the hydrobiogeochemical cycles of catchments. The role of these riparian landscapes in headwater catchments, collectively, has a bearing on our understanding of the dynamics of larger catchments and, we believe, enables a clearer perspective on the long-term management of our waterscape.

2 | THE RIPARIAN BUFFER ZONE

Three seminal papers from 1984 to 1985 (Jacobs & Gilliam, 1985; Lowrance, Todd, & Asmussen, 1984; Peterjohn & Correll, 1984)

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explored the impact of agricultural pollution on freshwater ecosystems. Their focus was on the mass balance of the water and chemical flux from the hillside to the stream and enabled the quantification of the role of riparian zones in influencing the stream nutrient budgets for the first time. These papers recognized the role of denitrification over biomass uptake of N, as the principle process accounting for the degradation of nitrate within the riparian wetland soils. These papers were developed by hillslope hydrologists who were looking at the riparian zone from the field. In the meantime, stream ecologists were looking at the value of the riparian ecotone to the stream/river, through the lens of the river continuum concept, with its implicit notion of a river as a linear feature with lateral riparian habitats (Minshall et al., 1983, 1985). The ecological literature, which had focused on the animals and plant dynamics of the riparian ecotone, assimilated the biogeochemical function of the riparian zone because it supported the importance of these interfaces in the ecosystem functioning.

The riparian "buffer" concept was also rapidly absorbed in the United States, with the United State Department of Agriculture and farming unions adopting the idea that the preservation or establishment of riparian "buffer" zones would be a rapid fix to the attenuation of nitrate fluxes, becoming driven by the desire to define the fixed widths of these features. This sudden interest in the riparian zone, by policymakers, made a connection between the function hydrobiogeochemical functioning and the wider ecological value of riparian zones (Haycock, Pinay, & Walker, 1993). This buzz around the concept and the potential role of riparian zones as nitrate buffers raised additional questions as to their role for phosphorus, pesticides, heavy metals, sediment, and pathogen buffers, which pushed the embryonic concept into debates that the science was not equipped to answer. Scientists were been asked to define the width of these zones (Osborne & Kovacic, 1993), the most effective catchment location (Broadmeadow & Nisbet, 2004), and vegetation types (Haycock & Pinay, 1993). Questions have been raised regarding their potential saturation with nutrients (Hanson, Groffman, & Gold, 1994). At the same time, there were equally compelling concepts that catchment wetlands, sometimes large wetlands, were equally capable of attenuating catchment nutrient fluxes, and it appears that two competing camps were being formed, the diffuse riparian zones science community and its advocates (Mulholland, 1992) versus the single wetland (natural or constructed) community (Mitsch & Gosselink, 2000). As a result of the engagement of the government policy officers, model initiatives were funded to start answering these policy questions (e.g., Riparian Ecosystem Management Model), which resulted in the concept of three zone buffer zones, simply because the model had three phases of calculations to determine the performance of the riparian feature (Inamdar, Sheridan, et al., 1999b; Inamdar, Lowrance, et al., 1999a). These initial modelling initiatives showed the weakness in the understanding of the key processes and their variability temporally and spatially. Partly triggered by government policy initiatives, focused on pollution control, a diverse range of specialists were drawn into the science of riparian zones, from hillslope hydrologists, microbiologists, plant and soil ecologists, and biogeochemists. This community of applied scientists rapidly sought to develop deeper understanding of specific processes and interactions between N, P, and C cycles, in order to address key policymakers questions. A conference in 1996 brought some of the key scientists together to share perspectives and start the process of making connections between hydrology, ecology, and biochemistry (Haycock, Burt, Goulding, & Pinay, 1997).

3 | HYDROLOGICAL AND BIOGEOCHEMICAL CONTEXT

In this period, new denitrification pathways were being defined such as Anammox (Jetten, 2001) and nitrifier denitrification (Wrage, Velthof, van Beusichem, & Oenema, 2001), highlighting the complexity of microbiological community to respire oxidized nitrogen compounds. Increased attention was also being given to the interaction between N and S cycles (Burgin & Hamilton, 2008) but also with the C cycle with a wide range of research in this period on the type and form of carbon needed to drive the denitrification process and the sustainability of these sources of carbon (Weier, Doran, Power, & Walters, 1993). Questions ranged from the ideal source of carbon (Newcomer et al., 2012), could the carbon be artificially drilled into the soil, if the carbon was buried in floodplain features (relic oxbow sediment); then how long would the denitrification process be sustained (Gold, Jacinthe, Groffman, Wright, & Puffer, 1998). Research on interaction between the N and Fe cycles was also undertaken, proposing the ferrous wheel concept with the oxidation of ammonium into nitrite by ferric iron and further nitrite reduction into di-nitrogen through classic bacterially mediated denitrification (Clément, Shrestha, Ehrenfeld, & Jaffe, 2005). The ferrous wheel concept widened the range of N processing and reduced the dependency on the presence of nitrate and carbon, but still achieving a gaseous purge of N from the soil.

Hydrological monitoring was also becoming more sophisticated with the first wave of data loggers and new flow tracer chemicals becoming available (see Abbott et al., 2016, for a review). Field sampling techniques for monitoring water and gas exchanges were advancing, enabling the linkage of processes in the field to be explored at a higher resolution (Groffman et al., 2006). These parallel developments did not link/merge at this point in time, apart from the coupling of hydrology and hydro-chemical flow paths, but were still constrained by a 2D perspective on the functioning process along specific flow paths. Nevertheless, this new pluri-disciplinary approach to the nitrogen buffering capacity of riparian zones illustrated the large spatial and temporal variability of the processes and the key factors controlling the rate of these processes.

New analytical processes in the field and laboratory also exposed the spatial and temporal heterogeneity of the nitrogen buffering capacity (Groffman et al., 2006). Potential denitrification measurements were orders of magnitude greater than rates of loss of nitrate as calculated by hydro-chemical budgets (Seitzinger et al., 2006). New techniques such as denitrification enzyme analysis closed these errors, as did direct measurement of soil gas fluxes. At the same time,

coordinated field experiments in Europe (Sabater et al., 2003), the United States (Boyer et al., 2006), and New Zealand (Schipper, Cooper, Harfoot, & Dyck, 1993) further confirmed that the fabric of the riparian zones and its innate structure were responsible for the heterogeneity of their buffering capacity.

Geoff Petts, when reviewing this work in the early 2000s, challenged those involved in these detailed site investigations to find ways to scale this site-specific information to a catchment scale. In other words, how could we appraise the nitrogen buffering capacity of riparian zones at a catchment scale without resorting to the detailed site measurements? What are the proxy indicators of the riparian zone functions at the landscape scale? Typical Geoff, you solve one question, and he would jump up and raise the bar higher.

4 | HOW EFFICIENT ARE RIPARIAN ZONES FOR BUFFERING DIFFUSE NITRATE POLLUTION?

The breakthrough in scaling our understanding of how riparian buffers could be assessed at a catchment scale was moving away from a site-specific and mechanistic assessment to a geo-statistical appraisal that examine the likelihood of denitrification occurrence within a given habitat mosaic (Tabacchi et al., 1998). If the three critical drivers, that is, nitrate, bioavailable carbon, and an anaerobic environment, were present, then denitrification would occur, although the estimated rate of denitrification could not be defined. It could not be assumed that the presence of nitrate was certain. For example, a wetland may exist in a catchment, with bioavailable carbon and an anaerobic environment, but the hydrological flow pathways would not necessarily pass into the wetland, either from the upslope land or from the river environment. In this context, this wetland would not have an appreciable level of denitrification to influence the flux of nitrogen at a catchment scale. This has led to the concept of the biogeochemical hot spot, with the implicit assumption that this environment was connected to a source of nitrate (McClain et al., 2003; Figure 1). The hot spot concept has been further refined with the Damkhöler concept taking into account the residence time of nitrate within the active zone relative to biochemical reaction rates (Ocampo, Oldham, & Sivapalan, 2006; Figure 2). This further refinement enabled the relative capacities of hot spots to be scaled, namely, short hydraulic resident times would be associated with limited opportunities to denitrify the incoming nitrate. The combination of geo-statistical information on land cover and nutrient loads, combined with soil wetness indices (potential wetness areas/variably saturated zones), could enable the assessment of the cumulative area of potential denitrification zones (hot spots) within a catchment (Frei, Knorr, Peiffer, & Fleckenstein, 2012; McGlynn, McDonnell, Seibert, & Kendall, 2004). Again, developments in spatial hydrological modelling, more powerful desktop computing, enabled the resolution of terrain flow models to increase dramatically, and thus, the mapping of soil wetness and saturation zones became more sophisticated (Ficklin, Luo, & Zhang, 2013; Lam, Schmalz, & Fohrer, 2010; Poudel, Lee, Srinivasan, Abbaspour, & Jeong, 2013; Sahu & Gu, 2009).

The three drivers of denitrification (see above) are mostly found at the upslope wet area interfaces, which includes riparian zones, but also upslope seepages faces associated with hedges, ponds, and artificial ditches. Given the dendritic nature of drainage networks, the vast majority of these dry/wet interfaces occur in small headwater catchments, indeed typically "75%" of terrestrial land drains into these seepage channels, classified as the first- and second-order streams (Bishop et al., 2008; Riley et al., 2018). A very small portion of the catchment land drains into the third- to fifth-order streams directly. These first- and second-order streams are everywhere and not only occur in mountainous areas; for example, you can have a first-order stream on a field locally to a large river, but the majority of the hillside run-off will be through this first-order stream, thus the disproportionate interest in this interface. Moreover, nutrient loads vary widely despite similar land cover in drainage basins smaller than 20 km^2 (Abbott et al., 2016; Brookshire, Valett, & Gerber, 2009; Burt & Pinay, 2005; Lefèbvre et al., 2007; Schilling, Jones, & Seeman, 2013; Strayer et al., 2003). Yet amplitude and frequency of chemical variation in stream networks decrease moving downstream (Burt & Pinay, 2005; Creed et al., 2015; Lefèbvre et al., 2007). We postulate that the

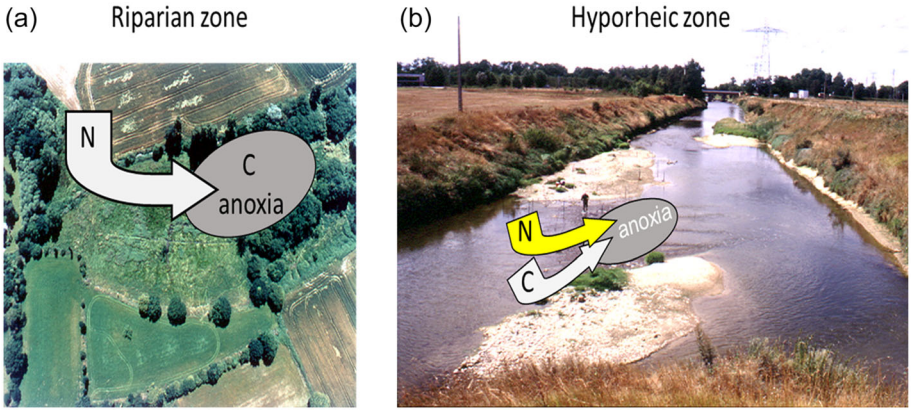


FIGURE 1 (a) Denitrification hot spot in riparian zone where nitrate is transported via surface and subsurface flow to an anaerobic environment rich in carbon. (b) Denitrification hot spot in a hyporheic zone where both nitrate and organic carbon are transported by surface water downwelling to an anaerobic environment

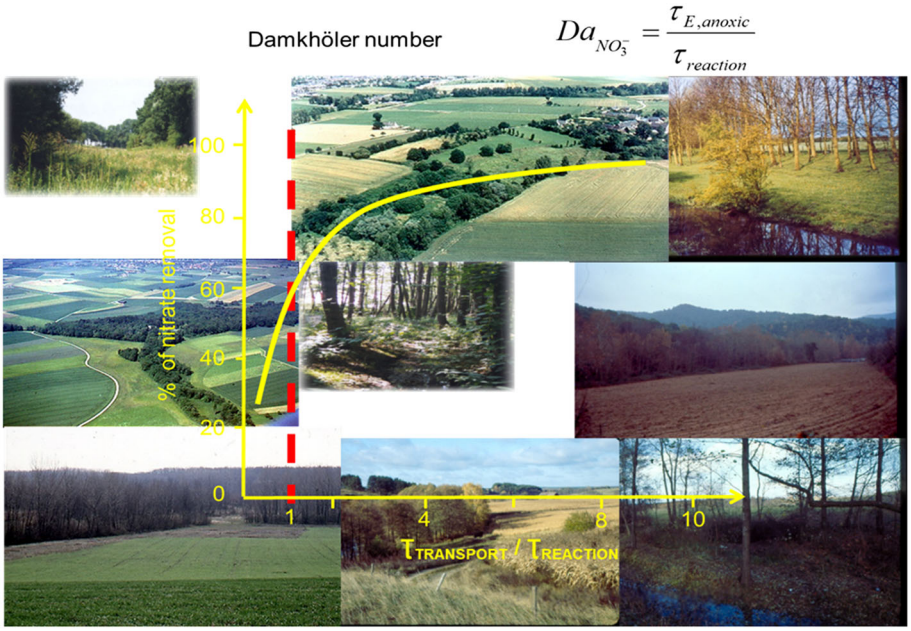


FIGURE 2 Relationship between the Damkhöler ratio of the rate of nitrate transport to the rate of denitrification in riparian zones and their nitrate removal capacity. Adapted from Ocampo et al. (2006)

breakdown in the relationship between land cover percentage and nutrient loads at small catchment scales is due to the fact that spatial arrangements of land covers and interfaces such as riparian zones, hedgerows, ponds, hyporheic zones, and wetlands matter (Burt & Pinay, 2005). Therefore, this is at these small catchments scale that the nitrate buffering capacity of riparian zones should be appraised.

The knowledge position in the early 2000s enabled the denitrification process to be scaled and the probability of hot spots mapped, but Geoff Petts raised the bar again. Could we evaluate the overall contribution of these hot spots and how they influenced the movement of nutrients from the catchment, at a meaningful catchment scale. This was the period in Europe of the merger of water policy initiatives and the formation of the Water Framework Directive (WFD, 2000) that incorporated the nitrate directive. This brought new compliance standards to members of the European Union (EU) and new challenges to the science community to find ways to preserve or enhance the quality of the aquatic environment; thus, scaling smaller catchment experiments to larger representative river basins datasets was now a key policy and funding driver.

Evaluating the impact of overall buffering capacity of riparian zones on nitrogen fluxes at small catchment scale requires calculating the time water takes to move through the drainage basin (Toth, 1962). Numerous studies, using seasonal fluctuation of stable isotopes in precipitation and streamflow, had estimated that mean residence time in small catchments ranged from 1 to 5 years (Klaus & McDonnell, 2013; McDonnell et al., 2010). Yet it seems now that these methods were not appropriate to calculate mean residence time and significantly underestimated the average residence time of water in headwater catchments, which would rather range between decades (Kirchner, 2016a, 2016b). A larger mean residence time of water in head catchments can however hide a large variability of residence times depending on their flow paths. Indeed, a recent study of more than 250 catchments around the world demonstrated that ~25% of the stream run-off was less than 3 months old (Jasechko, Kirchner, Welker, & McDonnell, 2016). Hence, as a first approximation, one fourth to one third of the precipitation water will take a short superficial flow path towards the stream, transferring during its short journey dissolved and particulate elements, including nitrate to riparian zones, whenever it exists. Water partitioning between old and recent water underlines that as a first estimate, riparian zones can potentially influence one fourth to one third of the water drained by headwater catchment streams. This "magic" number has a great virtue; it allows us to underline that riparian zones cannot do it all. Indeed, this means that approximately two third of the precipitation water will take a longer journey to the stream outlet, most likely bypassing the riparian zone and reaching the stream via the hyporheic zone, whenever it exists. Let us have a look at this longer travel path and the potential nitrate buffer the water might encounter during its journey.

5 | THE DRAINAGE BASIN APPROACH

The first hydrobiogeochemical landscape feature the precipitation water will encounter is the soil (Figure 3). This is indeed a key player in the determination of water quality, but also it has long been known that it has the capacity to recycle and remove nitrate (Gayon & Dupetit, 1886; Groffman & Tiedje, 1989). This capacity is strongly mediated by soil microbial activity and the quality and amount of organic matter. A recent study using ^{15}N isotope tracer on lysimeters found that ~15% of the applied N fertilizer was still present in the soil 40 years after the application (Sébilo, Mariotti, Mayer, & Pinay, 2013). Hence, this result underlines that soil can be a very effective N buffer

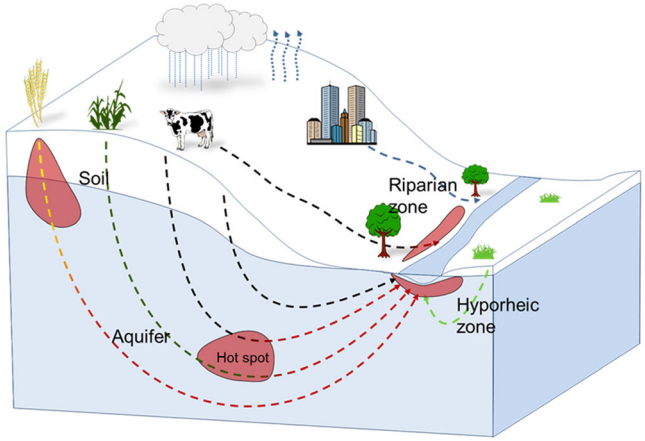


FIGURE 3 Schematic representation of the surface, subsurface, and deep water flows in headwater catchments and the potential hot spot of denitrification. Adapted from Toth (1962) and Pinay et al. (2015) [Colour figure can be viewed at wileyonlinelibrary.com]

system providing that organic matter and microbial community are present. Unfortunately, our current agricultural practices that tend to reduce the soil organic matter, and in turn its microbial community, have strongly reduced soil nitrogen buffering capacity (Bronick & Lal, 2005; Guo & Glifford, 2002; Sébilo et al., 2013). This result also stresses the long legacy of N input in soils, affecting the response time of the whole catchment to a given change in land use activity. Water and nitrate can then continue their journey below the soil and reach the aquifer, where they can be stored for another long period. Estimation of average residence time in head catchments aquifers has long been estimated to range between 3 and 5 years, whereas recent evaluation using Chlorofluorocarbon (CFC) (Aquilina et al., 2012) as a tracer revealed that it would rather be measured in decades (Kolbe et al., 2016). This fuels the lines of evidence of a much longer response time of headwater catchments to land use and land cover change than previously estimated. This is an important issue to be taken into account when setting up water quality restoration objectives. We shall get back to this point later on in the text. Once nitrate is in the aquifer, it can be also subject to denitrification in anaerobic environments where either organic carbon or pyrite is present (Hosono, Tokunaga, Tsushima, & Shimada, 2014; Pauwels, Kloppmann, Foucher, Martelat, & Fritsche, 1998). A recent study proposed a new method combining a particle tracking modelling approach with the use of biochemical proxies to infer the spatial organization of existing denitrification structures within aquifers and evaluate its nitrogen buffering capacity (Kolbe et al., 2019).

The next step water and nitrate would take before reaching the stream is through the hyporheic zone, which has generated a lot of exciting research for decades since Karaman (1935) demonstrated its role as a refuge for aquatic invertebrates. Numerous studies were then undertaken on the ecology (Bretschko, 1992; Marmonier, Vervier, Gibert, & Dole-Olivier, 1993; Stanford & Ward, 1988; Wood & Petts, 1994) and the biogeochemical processes (Bencala, 1984; Triska, Kennedy, Avanzino, Zellweger, & Bencala, 1989; Zarnetske, Haggerty, Wondzell, & Baker, 2011). Many expectations were placed in the role of hyporheic zone in controlling nitrogen diffuse input from groundwater. Yet some recent modelling results (Trauth, Schmidt, Maier, Vieweg, & Fleckenstein, 2013) showed that the Damkhöler ratio in hyporheic zone was not favourable for significant removal of nitrate originated from groundwater.

So, Geoff, what is the overall conclusion of this water and nitrate journey through the headwater catchment? Well, riparian can do a bit of the N buffering, but probably no more than a few tens of per cent. The main biogeochemical player is the soil, given that its microbial community is still active after all these years of pesticides application and carbon depletion under intensive agricultural practices. One should not rely too much on the aquifer to do the job, although denitrification can occur, thanks to pyrite and or buried carbon if any. Hyporheic zone, despite its tremendous role for instream metabolism and aquatic community dynamics, should not be accounted for to clean up aquifers' nitrate loads before entering the stream. These findings reinforce the need to formulate management questions such as the design of the riparian width or the optimal localization in the drainage basin at the appropriate scale of appraisal and with the right scientific disciplines (Figure 4). We know what you would say: "All that noise for that?" Well, we can argue that highlighting a particular landscape element such as the riparian zone, so intimately dependent on water, allowed to progress in understanding the structural and functional interactions between the drainage basin and its streams. We can see you goggling that "it is about time since Hynes (1975) advocating that in his paper about the stream and its valley." Indeed, Geoff, it took time, but now we are there, at last ….

6 | WHAT NEXT?

The development of detailed headwater catchment hydrological budgets and the quantification of the significance of various flow pathways has also challenged our concepts of how important certain

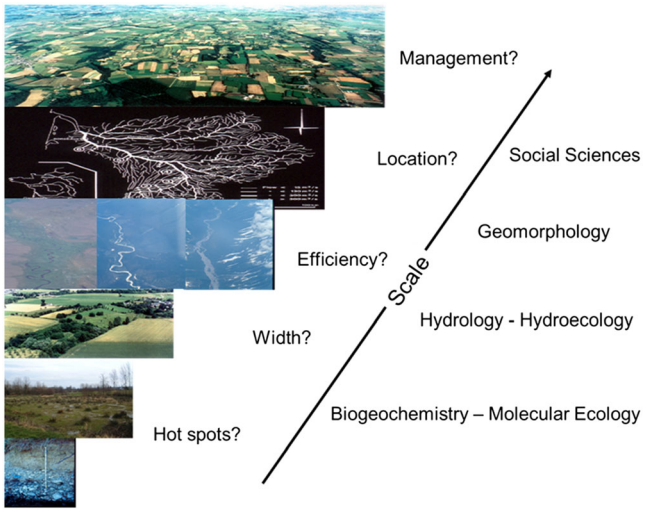


FIGURE 4 Scale-dependent management issues related to nitrate diffuse pollution control and the corresponding relevant research disciplines

pathways are and the importance of shallow flow routes through the soil, especially in the overall transfer of nutrients to the stream environment. One re-emerging issue is the role of headwater catchments in the recirculation of water and the importance of terrestrial evapotranspiration in the land-based hydrological water cycle (Ellison et al., 2017). Our concept of the hydrological cycle, from schools onwards, has fixed an image in our minds that water vapour is from the sea, and rainfall on land. Even this simple axiom of faith hides a more complex terrestrial water cycle (Abbott et al., 2019). When the biochemical role of riparian buffer zones emerged some 30 years ago, there was concern that renaturalization and or afforestation of riparian zones would result in less stream flow because of the higher evapotranspiration rates from the wet woodland areas. See Bennett and Barton (2018) for a review. Terrestrial rainfall, it has now been shown, is highly dependent on terrestrial evapotranspiration with many inland catchments dependent on their upwind catchment for their atmospheric stream of vapour and resultant rainfall. In the summer period, when evapotranspiration loss from fields is limited by their soil moisture deficit, the vegetated and wetter riparian zones have a disproportionate significance in maintaining the water vapour export to its and adjoining catchments and maintaining the terrestrial hydrological cycle (Keys, Wang-Erlandsson, Gordon, Galaz, & Ebbesson, 2017). This holistic understanding of the linkages of water, nutrient, and gases within and between catchments is fundamental to wider questions of water resource management. Loss of water to the catchment atmosphere is not a negative, it is a positive gain and sustains the water vapour within and to adjoining catchments, which in turn benefits land uses of the whole catchment.

The second issue resulting from this long and meandering journey through the role of riparian zones in buffering diffuse nitrogen pollution is that the "aqua incognita" that still represent today the headwater catchments (Bishop et al., 2008) should be better monitored and understood because they are playing a fundamental role in water quality acquisition. So far, there is a poor legal protection (e.g., EU WFD and U.S. Clean Water Act) of headwater catchments smaller than 50 km^2. Headwaters account for about 75% of global stream length and constitute our main agricultural areas and fresh water resources. Yet the lack of legal focus on small catchments has led to a shortfall of information and long-term monitoring data, thus limiting our ability to conduct evidence-based resource management, especially under current climate change (Loecke et al., 2017; Milly, Kam, & Dunne, 2018). The endeavour might seem unrealistic because there are so many streams to be monitored. Yet a recent analytical framework informed by landscape ecology and catchment hydrology was developed to quantify spatio-temporal variability across scales (Abbott et al., 2017). Unexpectedly, spatial patterns of water chemistry were stable on annual to decadal timescales. These findings suggest that periodic sampling of headwaters could provide valuable information about major head catchments contribution to solute sources and help hierarchizing management restorations. Moreover, the long response time of head catchment to pollution control measures, due to long residence time of nitrate both in soils and in aquifers, calls for revisiting the targeted expectations in terms of time for recovery, set up by the WFD and other water policies. Hence, current incentives of agri-measures for diffuse pollution control through EU need to be far more focused on headwater catchments. It also advocates for monitoring trends of water quality evolution, even though large-scale hydroclimatic variation can influence trends (Mellander et al., 2018), rather than target concentration limits, which do not have much ecological relevance (Le Moal et al., 2019).

This wider function of riparian landscapes also links back to the ecological health of a catchment. In the 1990s, the awareness of how many species of plants and animals depended either completely or for part of their life cycle on the riparian landscape was initially quantified with, for example, 80% of catchment invertebrates dependent on this riparian areas (Nakano, Miyasaka, & Kuhara, 1999; Sponseller, Benfield, & Vallett, 2001; Wallace, Eggert, Meyer, & Webster, 1997). If we now start to factor in the disproportionate role these landscapes have in the recirculation of moisture within and between inland catchments, then the influence of this ecotone habitat on the ecology and functioning of its catchment is far more extensive. This then raises questions as to what portion of the headwater catchments needs to be maintained and/or restored in order to deliver a vast array of benefit but critically how much needs to exist in order to sustain inland recirculation of water for the health of the whole catchment, and all it associated habitats and land uses. With hotter summers for most European nations occurring more frequently, does this necessarily mean dryer landscapes if the inland recirculation of water can be enhanced? We have raised the bar again and the integrated vision and connectivity of issues, which was so central to Geoff Petts' science, is becoming denser and more exciting. Yet we know that he would find the next big question. Sadly, we now have to find it ourselves.

DATA AVAILABILITY

The authors confirm that the data supporting the findings of this study are available within the article.

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