Slopes: solute processes and landforms

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Abstract: This chapter reviews research on solutes by fluvial geomorphologists in the period 1965–2000; growing links with biogeochemical research are emphasized later in the chapter. Brief reference is necessarily made to some research from before and after the study period. In relation to solutes, early research sought to relate short-term process observations to long-term landform evolution. However, very quickly, research moved into much more applied fields, less concerned with landforms and more concerned with biogeochemical processes. The drainage basin became the focus of research, with a wide range of interest including nutrient loss from agricultural and forested landscapes to dissolved organic carbon export from peatlands. In particular, the terrestrial–aquatic ecotone became a focus for research, emphasizing the distinctive processes operating in the riparian zone and their contribution to river-water protection from land-derived pollutants. By the end of the period, the scale and range of fluvial geomorphology had been greatly transformed from what it had been in 1965, providing a distinctive contribution to the broader field of biogeochemistry, as well as an ongoing contribution to the study of Earth surface processes and landforms.

As the paradigm shift in fluvial geomorphology took hold in the 1960s, attention turned away from long-term landform denudation to current processes, often in an applied context. In relation to solutes, the study of process–form relationships was either limited to small features such as limestone weathering, where rapid response was evident, or to mathematical modelling. Knowledge of solute transport at the drainage-basin scale quickly advanced with the deployment of pump water samplers (which collected bottles of water over a period of hours or days), stage recorders (from which stream discharge could be estimated; originally clockwork) and laboratory analysis of the collected water samples. For geomorphologists, the question was how to relate short-term process observations to long-term denudation rates and to landform evolution (Trudgill 1986). The goal was to identify what proportion of the measured solute loss related to atmospheric deposition, and what proportion related to the passage of water through the soil, in order to establish how much of measured solute export occurred due to landform denudation. From this geomorphological start, much research evolved into more applied fields, less concerned with landforms and more with water chemistry across a wide range of topics, from nutrient loss from agricultural and forested landscapes to dissolved organic carbon export from peatlands.

An apposite example from early in our study period comes from the Mendip Hills, in England's SW county of Somerset. Research into solute processes and karst geomorphology, led by David Ingle Smith, then at Bristol University, provided a focus for PhD students studying karst hydrology like Malcolm Newson (Newson 1971) and Tim Atkinson (Atkinson 1977). However, it was soon realized that knowledge was needed about the streams flowing into the limestone cave networks, so upstream of the Burrington Combe limestone outcrop, in the East Twin Brook catchment, Darrell Weyman (supervised by Mike Kirkby, then also at Bristol) identified some key aspects of subsurface stormflow (Weyman 1973), while Mike Waylen (Waylen 1979) and Brian Finlayson (1977) studied aspects of soil chemistry. Such research helped to inspire a generation of researchers, not necessarily in relation to landforms *per se*, but in hydrology, pedology, biology and geochemistry, combined today under the umbrella of 'biogeochemistry'.

Solute process studies on hillslopes

Hillslope hydrology and solute dynamics

Information on hillslope hydrological processes emerged from specialized research within a number of disciplines, including fluvial geomorphology, from the 1960s onwards, but the foundation and context for such studies dates from the 1930s. In 1933, at the age of 58, Robert Elmer Horton published his infiltration theory of runoff (Horton 1933). He had spent most of his career as a hydraulic engineer and had long felt that a more sophisticated approach was needed for the estimation of storm runoff. He introduced two new variables: infiltration capacity (the maximum rate at which a given soil in a specified condition can absorb rainfall) and rainfall excess (that part of the rainfall that falls at intensities exceeding the infiltration capacity). Horton's ingenuity lay in his sweeping assumption that the excess of rainfall over infiltration capacity was the sole source of runoff quick enough to produce the storm hydrograph peak; meanwhile, all infiltration would percolate to groundwater and become the sole source of baseflow. Horton's idea was to dominate for several decades: the 'era of infiltration'. While infiltration-excess overland flow is not as rare as used to be thought, it is often much more localized than Horton argued – the 'Partial Area' model of Betson (1964). Surface runoff and associated erosion is reviewed in Boardman *et al.* (2021, this volume).

At much the same time as Horton was publishing his theory of infiltration, Charles Hursh was establishing the Coweeta Hydrologic Laboratory in North Carolina. Hursh quickly realized that Horton's ideas did not apply in the forested Appalachians. Hursh's work led directly to John Hewlett's definition of the 'Variable Source Area' model in 1961 (Hewlett 1961), a concept that still dominates hillslope hydrology (Anderson and Burt 1990). This emphasized the importance of subsurface flow processes, which can nevertheless contribute significantly and rapidly to storm runoff response. Such a response may involve 'new' water of low solute content moving rapidly to the stream via macropores and pipes (McDonnell 1990). However, more commonly, the rapid response is generated by displacement of 'old' water that can have a high solute content, very different from the storm rainfall. A

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full review of Horton and Hewlett is provided in Volume 4 of *The History of the Study of Landforms* (Burt 2008). Figure 1 summarizes the two runoff models proposed by Horton and Hewlett.

A great deal of fieldwork in the 1960s and 1970s sought to relate the runoff response of hillslopes to the storm hydrographs of small catchments. Much of this work is summarized in Kirkby (1978). Dunne (1978) provides great detail on these field experiments, including his own work at the Sleepers River catchment in Vermont where the speed of response of hillslope sections and the expanding variable source areas were measured in great detail. Another benchmark paper was Weyman's (1973) measurements of the downslope flow of water in permeable soil over an impermeable bedrock at the East Twin Brook, already mentioned in the introduction. Figure 2 shows typical results for the Slapton Wood catchment in SW England (Burt *et al.* 1983). Whilst much of the focus was on the displacement of 'old' water by subsurface stormflow through the soil matrix, rapid flow of 'new' water via macropores or pipes was not neglected: Whipkey (1965) was the first hillslope hydrologist to show that macropore flow can produce subsurface stormflow. Mosley (1979) emphasized the importance of macropore flow in a forested catchment in New Zealand, whilst later work by Pearce *et al.* (1986) suggested that some translatory flow through the soil matrix must also be involved since the outflow is 'old' soil water of long residence time and not 'new' soil water that reflects the precipitation input. Anderson and Burt (1990) summarize the main controls on subsurface stormflow.

Very quickly, as Figure 2 attests, attention broadened from a geomorphological interest in solutional processes to specific ions, very often in relation to pollution problems. This meant that geomorphologists began to interact with other scientists, those from agriculture and forestry in particular, exposing them to plot- and landscape-scale experimental research, such as Kneale and White's (1984) study of the thresholds controlling macropore flow on the Oxford University farm at Wytham. Experienced researchers like Steve Trudgill turned their attention from solutional denudation to agricultural runoff (e.g. Trudgill *et al.* 1983*a*, *b*). The funding agencies preferred to support applied research, hastening this process. Interdisciplinary research was very much encouraged, as illustrated by the range of authors contributing to *Nitrate; Processes, Patterns and Management* (Burt *et al.* 1993). With a growing focus on process-response systems, research on denudation rates and landform evolution inevitably dwindled. Studies of solute transport in river systems are reviewed in the section on 'Solutes in river systems' later in this chapter.

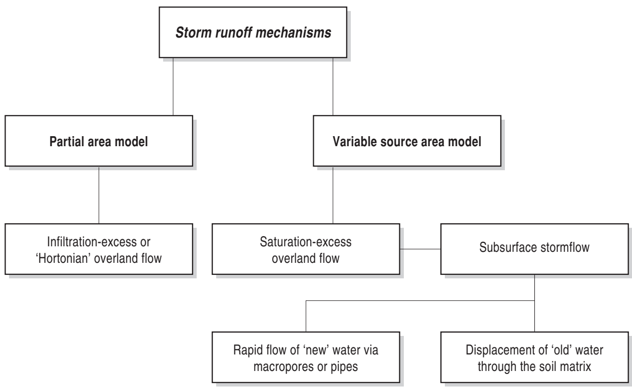

Fig. 1. Storm runoff mechanisms (modified from Burt 1989).

Solutional denudation on hillslopes

Direct measurements of solutional denudation may involve two timescales. Short-term variations in the solute content of soil water may be investigated using suction lysimeters; their use, efficiency and zone of influence within the soil is reviewed by Cryer and Trudgill (1981). A few studies have attempted to examine the short-term response of individual hillslopes sections, but usually with the aim of comparing hillslope and catchment response; given limited sampling, no information was provided about the solute yield of different

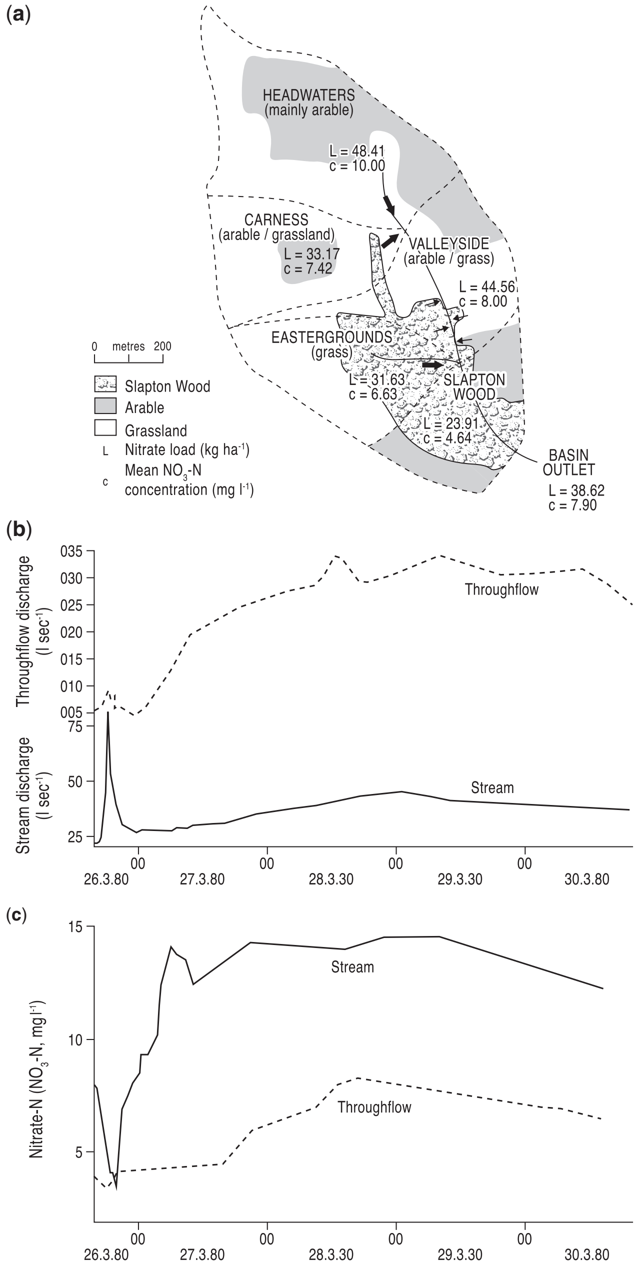

Fig. 2. Nitrate leaching in the Slapton Wood catchment, Devon, UK. (**a**) The spatial pattern of nitrate leaching as indicated by dilution gauging experiments. Large arrows indicate point sources of nitrate (springs and tributary streams); small arrows imply non-point source inputs (subsurface seepage) for that section of the stream (after Burt and Arkell 1987). (**b**) Stream and throughflow discharge for a typical double-peaked hydrograph. (**c**) Nitrate concentration in-stream and throughflow water, for the Slapton Wood catchment, Devon, UK. (b) and (c) are based on Burt *et al.* (1983), with permission of the Field Studies Council.

hillslope sections. The availability of solutes may be controlled as much by initial conditions as by the distribution of hydrological processes. At the Whitwell Wood site, described by Trudgill *et al.* (1981), analysis of soil water showed that solute uptake decreased upslope, implying a consequent upslope increase in solutional denudation. These results accord with the Carson and Kirkby (1972) model of slope evolution in humid temperate limestone slopes (see the following subsection) by implying slope decline. However, the parent material differed at the top (acid clay glacial drift) and middle sections (fluvioglacial and solifluction material) of the slope; the availability of solutes in this case was controlled as much by initial conditions as by the distribution of hydrological processes. Results from the Whitwell Wood site illustrate how a non-local material, glacial drift in this case, can dominate slope development subsequent to glaciation.

At the catchment scale, chemical denudation rates can be estimated from observations at the hillslope base or catchment outlet (e.g. Foster 1979). However, it is necessary to estimate the 'non-denudational' component of the river load, subtracting contributions from atmospheric deposition, fertilizers and biochemical processes. There are also many technical and statistical challenges in estimating solutes loads unless both discharge and concentration are measured continuously: see, for example, the much more recent study by Howden *et al.* (2018). A review of solute loads and denudation at the catchment scale is provided by Walling and Webb (1986), see also the following section.

Longer-term estimates of the relative pattern of solutional denudation may be obtained using weight-loss techniques (Trudgill 1975; Crabtree and Trudgill 1984). Rock tablets of known weight are emplaced in the soil in pits, preferably at the soil–bedrock interface. After a period of at least 1 year, the tablets are exhumed and reweighed. By using many tablets in each pit, an average percentage weight loss per tablet may be calculated. However, there are problems of preferential solution of freshly-cut rock faces, so the weight-loss technique cannot be used to calculate absolute rates of denudation. Crabtree and Burt (1983) investigated the spatial pattern of solutional denudation for the hollow and spur system described by Anderson and Burt (1978). Twenty pits were dug, with 10 tablets emplaced in each at a depth of 0.4 m; the soil was too stony to dig down to the soil–bedrock interface. There was an overall increase in weight loss upslope, related to the overall increase in soil acidity upslope (Table 1). As throughflow moved downslope, increasing solute uptake decreased the potential for solutional erosion since only long residence-time solute-rich water reached the slope base. Weight loss was greatest in the upper hollow: short residence-time soil water quickly converged into the hollow from adjacent spurs and from the interfluve plateau, allowing maximum rates of solutional erosion. In the lower hollow, weight loss was least, reflecting solute-rich water in the saturated wedge at the bottom of the slope (Table 2). The results suggested that the topographical contrast between hollow and spurs would continue to develop within a general pattern of slope decline caused by denudation rates increasing upslope. This was confirmed by a study of the spatial distribution of chemical weathering intensity on the same hillslope (Park and Burt 2000), which leads to a clear pattern of soil zonation on the study slope (Burt *et al.* 1984; Park *et al.* 1996). Patterns of hillslope solutional denudation in relation to the spatial distribution of soil moisture and soil chemistry on the same hillslope hollow and spur system are described in Burt *et al.* (1984), see below.

By contrast to cases like Whitwell Wood, where soil types vary locally with parent material, in cases where the soil has developed *in situ* on a single bedrock formation, mutual adjustment of soil characteristics and bedrock form will occur, with the soil catena – the distinctive sequence of different soil profiles found along a slope – of particular significance. At one point in time ('static equilibrium': Chorley and Kennedy 1971), soils can be seen as a function of topography, with more leached soils on the slope crest with better-drained conditions and more solute-rich soils at the slope base. However, in the long term ('dynamic equilibrium'), mutual adjustment of soil and slope form will occur, and soil characteristics can be studied to indicate what pattern of solutional denudation is likely down the slope. In practice, most soil catenas show a downslope increase in solutes or weatherable mineral content (e.g. a slope-crest podzol to a brown earth further down: Gerrard 1981), suggesting that slope decline will be the dominant pattern of slope evolution for most soluble material. Burt *et al.* (1984) describe a series of soil profiles for the Bicknoller hollow-and-spur system previously described. The contrast between hollow and spur was confirmed by soil properties, in particular analysis of extractable iron, with a marked contrast between brown earth soil on the spur and gley soils in the hollow. In the hollow soils, low iron ratio values confirmed the continued presence of saturated conditions, which favour higher rates of solutional denudation compared to the spurs. Profiles near the base of the slope had the greatest extractable iron values, suggesting that iron removed in solution upslope is accumulating lower down the slope.

Modelling solutional denudation and hillslope form

Carson and Kirkby (1972, p. 257) proposed a slope development model for solutional denudation. It is assumed that rainfall input is uniform across the slope and that infiltrating water comes rapidly to equilibrium with the soil solutes. Without lateral flow, all infiltration would be vertical and only parallel slope retreat would be possible. With lateral flow, soil moisture tends to increase downslope and so too evaporation (Fig. 3a). The quantity of each solute removed at any point is assumed to be equal to the rainfall input multiplied by the proportion of the oxide, p, present in the soil, or to the product of net runoff times 1.0 (i.e. the solute has reached its saturated concentration), whichever is the less (Fig. 3b). Assuming an

Table 1. *Micro-weight-loss tablet results for the Bicknoller Combe experimental hillslope (Crabtree and Burt 1983): upslope changes in mean tablet weight loss from five pits across the slope combined*

	Distance upslope from stream (m)	Mean tablet weight loss (%)
1	115	0.42 ± 0.17
2	75	0.38 ± 0.13
3	43	0.35 ± 0.08
4	15	0.30 ± 0.08

Table 2. *Micro-weight-loss tablet results for the Bicknoller Combe experimental hillslope (Crabtree and Burt 1983): mean weight loss for each slope profile combining four pits up the slope*

	Profile	Mean tablet weight loss (%)
A	Downstream spur	0.34 ± 0.07
B	Downstream spur flank	0.35 ± 0.07
C	Hollow	0.42 ± 0.09
D	Upstream spur flank	0.33 ± 0.07
E	Upstream spur	0.31 ± 0.15

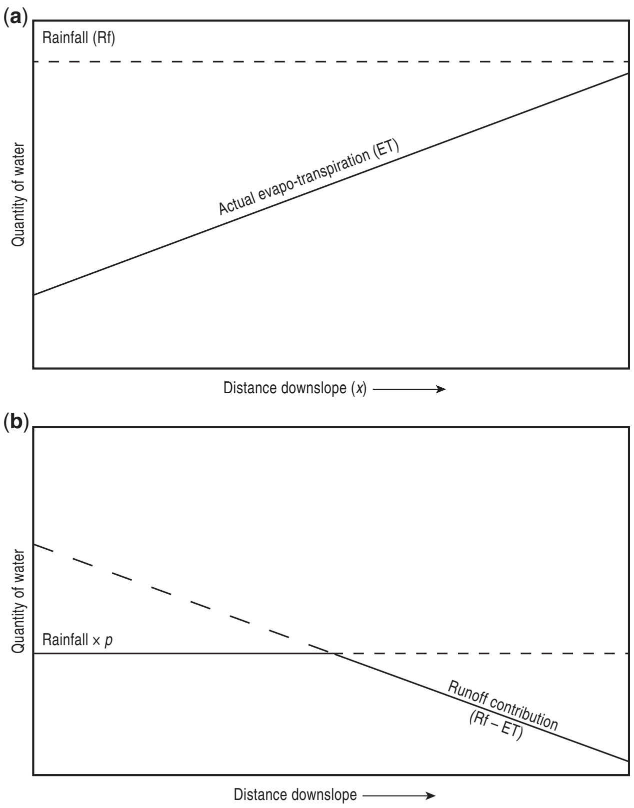

Fig. 3. Conceptual model of hillslope solutional denudation proposed by Carson and Kirkby (1972): (a) distribution of rainfall and evaporation; and (**b**) runoff contribution; equal to rainfall minus evaporation and rainfall multiplied by the proportion, *p*, of oxide present. The lower of these two values, shown by the solid line, is proportional to the net rate of chemical removal. Where the runoff contribution is lower, the difference between the two values is proportional to the amount of material redeposited in the soil. Reproduced with permission of Cambridge University Press through PLSclear.

initially straight slope with solution acting alone on the slope, Carson and Kirkby (1972) show that three downslope patterns of solutional denudation can be distinguished:

(a) Rainfall. p < runoff for the whole slope: solute removal is constant over the slope and parallel retreat will occur.
(b) Rainfall. p > runoff for the whole slope: solute removal decreases downslope and slope decline will occur.
(c) An intermediate case with solute removal constant at the top of the slope but then decreasing downslope in the lower part of the slope. In this case, parallel retreat occurs at the top of the slope with slope decline below.

For a limestone, Carson and Kirkby argue that the proportion of calcium carbonate, *p*, present is almost 1 so that case (b) applies, with slope decline whatever the climate (Fig. 4a). For igneous rocks, the pattern of solutional denudation would progress from case (b) through (a: Fig. 4b) to (c: Fig. 4c) as the ratio of runoff to rainfall increases in more and more humid areas. Despite its simplicity, few field experiments have attempted to verify the Carson and Kirkby model, the use of micro-weight-loss tablets at Whitwell Wood and Bicknoller Combe as described above being rare exceptions. Solutional denudation is not included in Kirkby's (1984) modelling of the 'Savigear' slope sequence, nor in Burt's (2003) extension of the same approach, although it might easily have been. However, note that Kirkby (1985) developed a mathematical model for soil profile evolution in three parts: for the weathering profile, for the organic profile and for the inorganic profile associated with nutrient cycling,

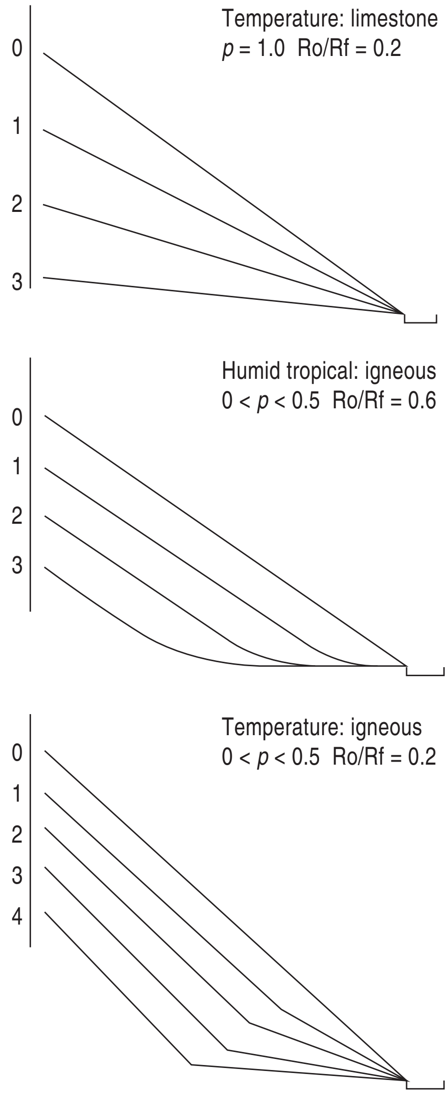

Fig. 4. Models of slope profile evolution as predicted by the Carson and Kirkby (1972) model for different rock types and climates.Rf, rainfall; Ro, runoff. Reproduced with permission of Cambridge University Press through PLSclear.

respectively. This shows how a hillslope denudation model could be developed on a 2D or even a 3D basis (see also Kirkby 2021, this volume). Relevant soil profile processes are reviewed in Trudgill (1987).

Solutes in river systems

As interest in fluvial processes in geomorphology grew rapidly in the 1960s, geomorphologists began to take an interest in solute transport in rivers, using water sample data for a variety of purposes including estimating rates of chemical denudation, quantifying biogeochemical cycling in small drainage basins, identifying the impact of non-point pollution, and using solute data to elucidate runoff processes and sources. Studies of solute transport by rivers ranged from spatial scale from small catchments, through to larger basins and regions to the continental scale, whilst temporal variations from individual storm events to long-term trends have been studied (Walling and Webb 1986). At whatever scales the research was conducted, it was essential to recognize that the chemical character of water flowing in a river channel reflected the spatial and temporal integration of a complex sequence of pathways interposed between precipitation input into the drainage basin and output as channel flow and the associated evolution of stream water chemistry. Examples of nitrogen and carbon dynamics will be described in more detail below; this section looks briefly at solutes more generally.

Studies of national, regional and local scales are well exemplified by the research of Des Walling and Bruce Webb in the River Exe Basin in SW England. The catchment is free from major industrial or domestic pollution, and exhibits a considerable diversity of lithology, topography and land use. Walling and Webb (1978) decided that the measurements obtained at a small number of permanent gauging stations were too lumped to allow useful maps of solute loadings to be constructed. They undertook a reconnaissance survey of low-flow solute concentrations at a large number of small catchments over the study area, using these results to produce maps of total solute loadings and chemical denudation rates. Specific conductance data were collected to show total solute loadings rather than individual solutes. Such results provided an important bridge between more traditional studies of denudation chronology at a regional scale and the small-scale studies of hillslope form described above. Walling and Webb set the trend for mapping solute distributions across drainage basins; these increasingly moved away from measurements of bulk solute loading and towards individual solutes of interest. Their research into temporal behaviour of solutes often took a similar approach, with a comparison of solute rating curves at different gauging stations across a large basin such as the Exe. Storm-period response became an increasing focus in an attempt to use solute data to explain runoff processes and sources. Whilst specific conductance continued to be used to identify the major pattern of solute variation, individual cations and anions were used more and more, including calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), bicarbonate (HCO_3^{-}) and chloride (Cl^{-}). Contrasts in the chemical concentration and timing of surface and subsurface runoff exert an important influence on the in-stream pattern of storm-period solute response, often leading to a hysteresis effect whereby there are markedly different solute concentrations for the same discharge on the rising and falling limbs of the storm hydrograph. Studies of stream solute response soon became accompanied by studies of runoff production on hillslopes, helping to link process and response (e.g. Burt 1979).

As an example from the Exe Basin itself, as part of a detailed investigation of solute behaviour undertaken in a small catchment in East Devon, England, Ian Foster measured concentrations of K, Ca, Na, Mg, Cl and nitrate nitrogen (NO_3-N) in bulk precipitation, throughfall, soil water and stream water samples obtained weekly from a small, forested catchment of approximately 0.8 ha (Foster 1979). He showed that relative enrichment of ions is selective, with Ca and Mg concentrations in soil water increasing, probably as a result of the high levels of both ions on the soil exchange sites. In contrast, relative K enrichment occurred in throughfall samples, but was not translated to the stream, possibly as a result of soil buffering and nutrient cycling effects. Na and Cl concentrations were high in bulk precipitation samples, hardly surprising given the proximity to the sea; the Na : Cl ratio in bulk precipitation closely approximated the same ratio as in seawater. In contrast, the ratio between Cl and K, and Ca and Mg showed a marked increase in bulk precipitation indicating the likely input of dry fallout. Results from a larger catchment, of which the site previously described formed a small part, indicated that the 1976 drought produced a unique solute response, with levels rising markedly during the autumn flush. Concentrations of several ions increased 3–4 times with nitrate levels increasing by up to 50-fold (Foster and Walling 1978). The delayed solute response mirrored those observed elsewhere at the end of the drought (Burt 1979), very similar to those already described from the Slapton Wood catchment (Fig. 2). Such results exemplify how the study of solute distributions across large river basins was soon accompanied by smaller-scale process studies linking runoff and solute response.

In the USA, the most prominent research on solutes came from research programmes run by the USDA Forest Service, most notably the Hubbard Brook Experimental Forest (New Hampshire: Likens *et al.* 1977), the Coweeta Hydrologic Laboratory (North Carolina: Swank and Crossley 1988) and the HJ Andrews Experimental Watershed (Oregon: Robbins 2020). Such studies were based on paired-catchment experiments: after a control period lasting several years, one catchment was ‘treated’ (e.g. clear felling of forest), and the impact on streamflow and solute transport was assessed by comparison with the control catchment where conditions remained unchanged. Nutrient losses following deforestation were of particular interest. Many of the key papers on forest hydrology during the second half of the twentieth century are brought together in DeWalle (2011). Much of this research was not carried out by geomorphologists but provided an important foundation for them once they began to look at transport of solutes through the drainage basin.

Nitrogen dynamics in the catchment system

Scale and dimensions

It has already been mentioned that the attention of some hillslope geomorphologists moved from an interest in solutional denudation to specific ions, very often in relation to pollution problems. With nitrate, they rubbed shoulders with a wide variety of other scientists, from aquatic ecologists, often working in forested catchments, to agricultural scientists working at the field scale to understand nutrient loss from farmland soils. Fluvial geomorphologists contributed by broadening the scale of approach from plot experiments at agricultural research stations and ecological field studies of the links between riparian and in-stream processes, often undertaken in first-order tributaries, to much larger river basins, the scale at which water pollution management is inevitably focused. Concerns about potential links between nitrate and human health initially focused on ‘cure’ rather than ‘prevention’, notably nitrate removal from abstracted water using biological denitrification. In terms of catchment sources, the focus was initially on wastewater from heavily urbanized catchments. However, it was gradually realized that nitrate losses from heavily fertilized farmland were on the increase, and that ‘prevention’ might be a more appropriate approach, especially since water treatment does nothing to prevent the eutrophication of freshwater and marine ecosystems. What emerged was a multidimensional approach: experimental field experiments at the hillslope scale and, often within the same project, catchment-wide monitoring and modelling. Catchment management also adopted the same split-scale approach.

Spatial and temporal patterns of nitrate transfer

Walling and Webb (1986) describe the spatial distribution of solutes in river systems, from the global to the local. In rural catchments free from major industrial or domestic pollution, the main controls are geology, topography and land use. For nitrate, at the UK national scale, they demonstrated a marked west–east gradient; much higher concentrations in the lowland east reflected the increased intensity of agricultural activity, particularly arable farming (Betton *et al.* 1991), and the lack of diluting rainfall. Even in small, low-order drainage basins, land use controls the pattern on nitrate input into the stream. Burt and Arkell (1987) mapped nitrate concentration and load along the 1 km^2 Slapton Wood stream, with larger inputs from arable fields compared to grassland and woodland (Fig. 2a). Given the importance of land use, Johnes and Burt (1993) were able to use a simple export coefficient model to predict nitrate loading from an entire catchment; the model was calibrated using information on land use, livestock numbers and human population. Such models can then be used to formulate a basin-specific management strategy to reduce nitrate loading.

In relation to temporal variations, fluvial geomorphologists initially turned their attention to the links between runoff processes and delivery of nitrate to the river channel. In small catchments, such as the Slapton Wood catchment shown in Figure 2a, the role of hillslope hollows proved important as conduits for subsurface runoff, linking the intensively farmed fields on the interfluve plateau to the stream channel. The major episodes of nitrate loss happen during delayed hydrographs a few days after a storm rainfall event: the stream tends to dilute during the immediate period of storm runoff but then the delayed hydrograph is accompanied by a rise in concentration, reflecting leaching and then downslope transport (Fig. 2b, c). Note that in this case the throughflow concentration is lower than in the stream because the throughflow measured was derived from a wooded hillslope, but the same pattern is seen during the delayed throughflow hydrograph for the stream as a whole. The higher concentrations in the stream reflect subsurface drainage from the farmed areas of the catchment (Burt and Arkell 1987). Such research shows how an interest in the links between hillslope topography and hydrology could easily move to the study of nitrate pollution in subsurface runoff.

At much longer timescales, increasing attention was paid to long-term trends in nitrate concentration. In the UK, it became a matter of increasing concern in the 1970s that nitrate concentrations in rivers were increasing. This prompted the UK's Royal Society to organize a study group to collate, assess and present the scattered, but substantial, information concerning nitrate in UK waters (Royal Society 1983). Prominent evidence in the report were the trends in annual nitrate concentration for large rivers for which long-term data were available, including at that time the Thames from 1928. Figure 5 shows a much longer nitrate record than was then available, extended back to 1868 and updated to the end of 2019. The upward trend started with the effects of large-scale ploughing of grassland at the start of World War II. The steep rise in the 1960s and 1970s related both to the mechanization of agriculture and the greatly increased use of inorganic fertilizers, as well as to the delay caused by water flow through the Chalk aquifer: nitrate leached in the early 1940s would take several decades to travel down through the unsaturated Chalk limestone before being transmitted quite quickly through the saturated zone to the river (Howden *et al.* 2010, 2011).

Management strategies

In 1980 the EC Directive on Drinking Water 80/778 set a maximum admissible nitrate concentration of 50 mg l^{-1}. This was followed by the Nitrates Directive (91/676) in 1991, which aimed to protect water quality across Europe by preventing nitrate from agricultural sources polluting ground and surface waters, and by promoting the use of good farming practices. The significance of such measures is that they were proactive and preventative, coupling input management with water protection and restricting intensive agriculture for the sake of water quality. The Nitrates Directive acknowledged that nitrate pollution was not just a matter of public health, but was related to the health of the aquatic environment too. The establishment of Nitrate Vulnerable Zones in which sources of nitrogen were carefully managed was a direct outcome of research that had linked land use and nitrate pollution at the landscape scale. More local-scale management using buffer zones was funded through national-scale 'stewardship' schemes; further acknowledgement that applied research can have a direct policy outcome. The impact of better management strategies is shown in Figure 6 with a levelling out of nitrate concentrations from the 1980s onwards. The reason for the renewed upward trend in the 2010s and the loss of a clear annual cycle in that period are not known, but is a cause for concern nevertheless.

Carbon dynamics in the catchment system

Fluvial carbon consists of both organic and inorganic components. The fluvial organic matter consists of both dissolved and particulate organic matter (DOM and POM), which in turn are in part made up of carbon (C); typically, DOM and POM are *c.* 50% C. The difference between dissolved organic carbon (DOC) and particulate organic carbon (POC) is operationally defined by the size of the filter used on the water sample (typically between 0.2 and 1 µm in nominal filter size), with DOC being the component of the DOM that passes through the filter with the particulates retained on the filter. Although called 'dissolved', DOC is made up of both truly dissolved and colloidal organic carbon. The inorganic

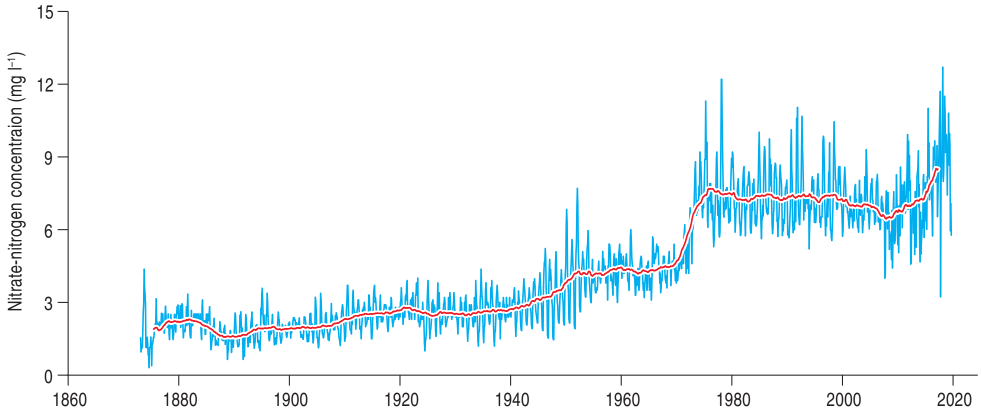

Fig. 5. Monthly nitrate concentrations for the River Thames with a 5-year running mean (based in part on Howden *et al.* 2010).

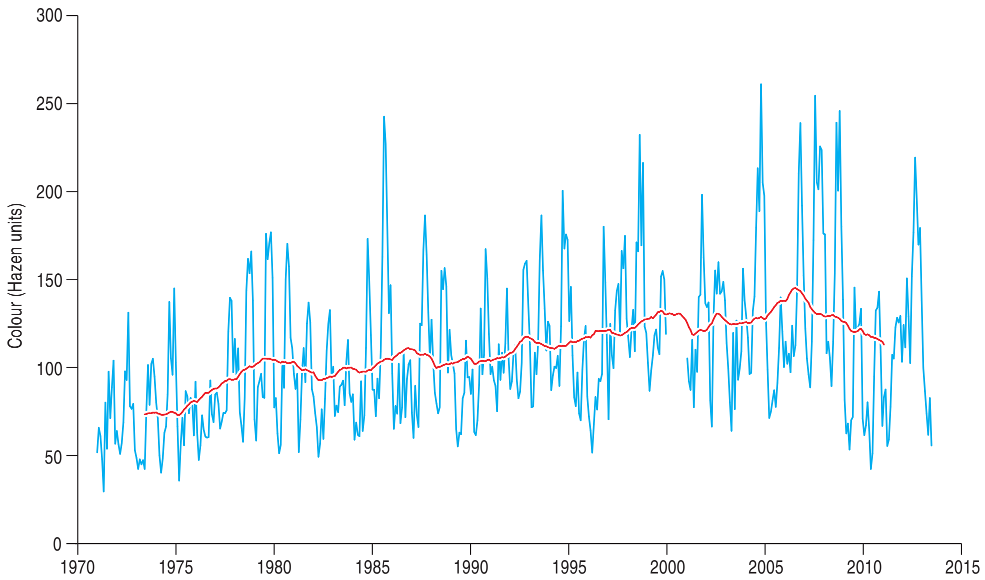

Fig. 6. Monthly means of water colour (Hazen units) for the Broken Scar water treatment works at Darlington on the River Tees with a 5-year running mean (updated from Worrall *et al.* 2002).

component, DIC, is made of the species of dissolved CO_2. In surface waters in contact with the atmosphere, there will always be DIC as CO_2 equilibrates across the air–water interface. Therefore, it is common to measure the excess CO_2 present ($EpCO_2$) as this is measure of the inorganic carbon species present above that which would be present in equilibrium with the atmosphere.

Peatland erosion can contribute significantly to sediment yield; in the UK, peat-covered headwater catchments influence the pattern of streamflow and erosion in most of the major British rivers. These areas are often crucial for water supply and, having a flashy runoff response, reservoirs were needed from the nineteenth century onwards to store drinking water. Many of these reservoirs are now seriously full of sediment of which POM is a significant fraction. Research on gully erosion in blanket peat is described in the next subsection, an example of geomorphological investigation linking process and form, yet with important implications downstream.

DOC is a major component of river water: it contributes to the transport of metals and organic micropollutants; it aids the transport of pollutants; it acts as an energy or nutrient source; it affects light penetration; it contributes to pH buffering; and, perhaps most importantly, it is a major limitation to the treatment of drinking water (Worrall *et al.* 2002). Research on DOC production and fluvial transport is described in the subsection 'DOC in potable water supplies' later in this section.

Gully erosion of blanket peat

Blanket peat is characteristic of areas with cool, wet climates, with low infiltration capacities, high surface runoff and flashy flow regimes. In such dynamic hydrological systems, understanding fluvial processes is central to an understanding of sediment and solute transport (Evans and Warburton 2007). In the British Isles, the drainage density of peat moorlands is very high compared to most other areas (Burt and Gardiner 1982). Hydrological studies have tended to focus on the headwaters, particularly the zero-order 'peat flush' channels. Two types of network occur: a very dense branching network on the deep peat of the flat interfluves and a more open network of unbranching tributary streams on the thinner peat of slightly sloping ground (up to 5°); Bower (1961) termed these two types Type I and Type II, respectively.

As research in fluvial geomorphology developed following work by Horton (1945) and others (see Burt 2008; and Boardman *et al.* 2021, this volume), the morphology of eroding blanket peat was soon of interest in the UK with a series of papers including Johnson (1958), Bower (1961), Radley (1962) and Mosley (1972). Using evidence from pollen analysis, Tallis (1964) argued that the start of the network extension coincided with the loss of the sphagnum moss species from the peat surface due to air pollution emissions from nearby industrial areas, from about 1750 onwards. Studies of runoff processes followed, in both the Southern Pennines (Burt and Gardiner 1984; Labadz *et al.* 1991) and at the Moor House National Nature Reserve in the Northern Pennines (e.g. Crisp 1966; Holden and Burt 2003; Clark *et al.* 2008). As already noted, the hydrology of blanket peat is dominated by surface runoff processes; overland flow is produced even during small storms. Burt and Gardiner (1984) show a clear difference in runoff generation between the heavily eroded Type I gullies, where source areas are relatively constant, and the Type II areas, where antecedent conditions are more important, with a more variable source area depending on how wet the peat is prior to the storm event.

Surveys of four reservoirs in the Wessenden Valley in the Southern Pennines were used by Labadz *et al.* (1991) to derive the sediment yield. Reductions in reservoir capacity since construction were estimated by field survey and combined with analysis of sediment samples to produce a total sediment yield of 204 t km^{-2} a^{-1}. The organic fraction, assumed to be derived from peat erosion, was 39 t km^{-2} a^{-1}. Although not excessive in gravimetric terms, the low density of peat means that there is a serious erosion problem. Estimates of erosion rates for the peat gully network at Shiny Brook appeared to confirm earlier evidence (Tallis 1964) concerning the relatively recent occurrence of the peat erosion, within the last three centuries.

It has been argued that the erosion of POC from soils constitutes a global carbon sink because the eroded soil organic carbon lost to POC is replaced whilst the eroded POC is stored by downstream burial (Stallard 1998; Harden *et al.* 1999). However, the real impact of soil erosion on the atmosphere must include consideration of greenhouse gas fluxes too. Organic matter can be released to the atmosphere as a range of greenhouse gases, not only CO_2, but also the more powerful greenhouse gases CH_4 and N_2O. Recent research has shown that soil erosion is a net source of greenhouse gases (Worrall *et al.* 2016). Gross soil erosion will only be a net sink of both carbon and greenhouse gases if all the following criteria are met: the gross soil erosion rate is very low; the eroded carbon is *completely* replaced by new soil organic matter; and less than half of the eroded POC makes it into the stream network. Concerns about peat moorland degradation were first evident in the 1950s for a variety of reasons. More recently, the benefits of good peatland management have come to include minimizing losses of greenhouse gases to the atmosphere, as well as protecting water quality, reservoir capacity and landscape quality (see also Boardman *et al.* 2021, this volume).

DOC in potable water supplies

Discoloration of runoff from peatlands began to receive attention at much the same time as the field studies of runoff and erosion were started, with growing awareness of its scientific and economic importance. Colour levels from the UK's moorland catchments rose markedly after the major droughts of 1976 and 1984, resulting in many consumer complaints and increased costs of water treatment. As noted above, both truly dissolved and colloidal organic carbon contribute to the discoloration.

Upland catchments are major water supply catchments in the UK and the loss of carbon from their peat soils very often results in the release of DOC. Removing DOC is often the largest recurrent water treatment cost, and its incomplete removal leads to domestic water supply with low aesthetic quality, low residual chlorine thus limiting its protection against biological contamination, and the potential for formation of disinfection by-products (Worrall *et al.* 2002).

Whilst temporal analysis was hampered by a lack of water quality records, it soon became clear that discoloration was greatest in autumn and early winter as the peat rewetted after the relatively dry conditions of summer; after a major summer drought occurred, there was clear evidence of a major spike in colour the following autumn. There was also growing evidence of an upward trend (Edwards *et al.* 1987; Naden and McDonald 1989; Freeman *et al.* 2001*a*, *b*). The causes of the observed increases in surface water DOC concentrations have long been debated. Most of the relevant research is relatively recent; being beyond the scope of this volume, this will only be briefly reviewed here therefore. Possible causal factors include: reduction in atmospheric sulfur deposition; increase in atmospheric CO_2 concentration; changes in precipitation and runoff; increased frequency of severe drought; eutrophication; and changes in land management. Often, a combination of causal factors is involved, and these may differ between catchments. Freeman *et al.* (2001*a*) and Worrall *et al.* (2003) showed that the upward trend in water colour was correlated with air temperature. Long-term degradation of carbon stores happens as the peat is subject to ever higher temperatures combined with an increased frequency of drought. Figure 6 shows the long record of water colour for the River Tees in NE England. The upward trend is clear with inter-annual variability relating in particular to periods of drought and post-drought response; for example, the severe drought of 1975–76 had low colour values but the post-drought period was characterized by high colour in the following winters as the peat gradually rewetted. Freeman *et al.* (2001*b*) showed that increased peat aeration, as a result of drought, has the potential to eliminate a critical mechanism restricting the release of CO_2 to the atmosphere, the so-called 'enzymic latch' mechanism. Figure 6 shows that it can take several years for the peat to recover from the effects of a severe drought, with persistent highly coloured runoff in autumn and winter.

The interest of geomorphologists and others in the runoff and erosion processes operating in peat-covered catchments, which began in the 1970s, moved naturally to examine patterns of DOC rather than just POC. Research in the twenty-first century has focused increasingly on the carbon cycle and the importance of peat as a carbon store. There has also been consideration of the role of DOC and POC in downstream nutrient cycling. Extensive restoration of eroded peatland is helping to minimize downstream impact, as noted above, as well as rebuilding intact, functioning moorland ecosystems.

Research on other solutes in the drainage basin

Acid rain and rock weathering

Acidification became one of the major global issues of freshwater pollution from the 1960s onwards. In large regions of Europe and eastern North America, thousands of lakes, rivers and streams were damaged by acidification. As early as 1920, freshwater acidification and problems with fisheries were reported in southern Norway but the cause remained unexplained until the 1960s. By the 1970s, acid deposition, acidification of surface waters and loss of fisheries had been reported in many countries (Steinberg and Wright 1994). Natural acidification was significantly accelerated by industrial emissions of various sulfur and nitrogen gases, by exhaust fumes from motor vehicles, from excessive application of nitrogenous fertilizers, and from ammonia emissions from livestock. Research in drainage basins included spatial and temporal surveys of precipitation, river and lake water quality, process studies of water quality and runoff generation in soils and on hillslopes (e.g. Pilgrim *et al.* 1979; Trudgill 1986; Soulsby and Reynolds 1994), and palaeolimnological reconstruction of lake sedimentation (e.g. Battarbee 1990; Birks *et al.* 1990). For the UK Acid Waters Monitoring Network (AWMN: 1988–2002), regional-scale reductions in sulfur deposition were found to have had an immediate influence on surface water chemistry, including increases in acid neutralizing capacity, pH and alkalinity, and declines in aluminium toxicity (Monteith and Evans 2005). Despite a general trend towards recovery, there was nevertheless substantial between-site variation: local factors such as catchment hydrology, sea-salt inputs, forest cover, soil and bedrock chemistry, and N saturation could all affect patterns of recovery in response to sulfate decline (Davies *et al.* 2005).

Research on the effects of acidification on rates of weathering involved not only the study of drainage basin systems, weathering of soil and bedrock, and its effect on soil profiles in particular, but also the built environment where weathering of heritage stonework was an important focus (see Goudie 2021, this volume; Trudgill *et al*. 2022, this volume).

Phosphorus

One solute that does not appear much in the geomorphological literature during this time period is phosphorus (P). As already described, studies of nitrate nitrogen began to appear in the 1980s, largely because of concerns over drinking water quality. Phosphorus remained largely the realm of aquatic scientists and biogeochemists until much nearer the end of the twentieth century (e.g. Johnes 1996) when links between source areas and stream concentrations began to be explored. Until then, in-stream studies related to the river continuum concept (Vannote *et al.* 1980) and nutrient spiralling (Webster and Patten 1979; Newbold *et al.* 1982), and the effects of pollution on aquatic ecosystems remained much more common, although it must be acknowledged that agricultural scientists had been exploring links between soils and phosphorus in runoff for some time. Given that much P is transported bound to soil particles, studies of soil erosion could link to P transport, but an integrated approach to transport of P, N and C would have to wait largely until the present century.

Ecotones in catchment systems

The terrestrial–aquatic ecotone

Today, there is an intuitive assumption that the condition of the river and the condition of the surrounding catchment are intimately linked, but it was not always so (Burt *et al.* 2010). A series of papers in the 1970s created a new paradigm for aquatic ecology (Cummins 1974; Hynes 1975; Vannote *et al.* 1980), borrowing a concept from fluvial geomorphology that stressed the drainage basin as the fundamental unit of analysis (Leopold *et al.* 1964; Chorley 1969). The 'river continuum concept' is based on the notion of dynamic equilibrium involving continuous interaction between the channel and its riparian zone; moving from source to mouth, this balance is constantly changing. At much the same time, another group of researchers developed the 'nutrient spiralling concept' (Webster and Patten 1979; Newbold *et al.* 1982), which recognizes that as organic matter and nutrients move downstream, they are incorporated, released and reincorporated by various groups of living organisms. At much the same time, yet another group of researchers began to focus their attention on the riparian zone but from a catchment perspective. Peterjohn and Correll (1984) measured a significant decrease in nitrogen concentration as subsurface water drained through the riparian zone, due to a combination of denitrification and plant uptake. Parallel research in other agricultural contexts confirmed this phenomenon (Lowrance *et al.* 1984; Jacobs and Gilliam 1985). Given this intimate connection between land and stream, it is hardly surprising that the terrestrial–aquatic ecotone has become a focus of attention. Given their interests in hillslope topography and runoff processes, fluvial geomorphologists were well placed to collaborate with ecologists in such research.

The ecological importance of terrestrial–aquatic ecotones

The ecotone concept has been in the literature for quite some time, defined as a transition zone between two different vegetation zones (Weaver 1960). A more recent understanding of the inherent process dynamics of ecotones has led to a more detailed definition of an ecotone as:

> [A] zone of transition between adjacent ecological systems, having a set of characteristics uniquely defined by space and time scales, and by the strength of the interactions between adjacent ecological systems
>
> (Holland 1988, p. 106).

Ecotones can be observed at any spatial scale from micrometre-scale biofilm to the kilometre scale of the land–water riparian zone. Freshwater ecologists have long recognized the importance of riparian zones, for instance in controlling organic matter supply for the aquatic food web (Thienemann 1912), flood peak adsorption (Schlosser and Karr 1981), stream primary productivity (Vannote *et al.* 1980) and providing habitat for fish (Welcomme 1979). The value of land–water ecotones in the functioning of aquatic ecosystems is now widely recognized; amongst the most cited and influential publications is 'The ecology of interfaces: Riparian zones' by Naiman and Décamps (1997). At the same time, the importance of land–water ecotones was recognized far beyond the riparian zone area and encompassed the entire drainage basin following Hynes' (1975) idea in his seminal paper 'The Stream and its valley'. This recognized the need to move beyond the river bank (Likens 1984) and to consider the terrestrial–aquatic interactions across the entire drainage basin (Wetzel 1990), linking concepts of aquatic ecosystem functioning to concepts in landscape ecology, considering landscape boundaries as one of the key controls of energy and matter (Hansen and di Castri 1992).

Riparian buffer zones

Following the seminal papers of Lowrance *et al.* (1984), Peterjohn and Correll (1984) and Jacobs and Gilliam (1985), a lot of attention has been given to the role of riparian zone ecotones as buffers of nitrate generated in the drainage basin (Haycock *et al.* 1997). Several questions were raised regarding the potential buffering capacity of nitrogen. One of the main ones was the potential saturation of the capacity to store or remove nitrogen (Hanson *et al.* 1994). It was confirmed that if both vegetation uptake and denitrification were involved in the nitrogen-buffering capacity of riparian zones, microbial denitrification (Knowles 1981) removes nitrogen from the ecosystem (Pinay and Décamps 1988) and hampers its saturation. In addition, new denitrification pathways were defined such as anammox (Jetten 2001) and nitrifier denitrification (Wrage *et al.* 2001), highlighting the complexity of the microbiological community to respire oxidized nitrogen compounds. Moreover, interaction between the nitrogen cycle with the carbon (Weier *et al.* 1993), sulfur (Burgin and Hamilton 2008) or iron (Clément *et al.* 2005) cycles underlined the complexity of biogeochemical interactions within riparian buffer zones. This has led to consideration of riparian zones as biogeochemical 'hotspots' that show disproportionately high reaction rates relative to the surrounding area (or matrix), with the implicit assumption that this environment is connected to a source of nitrate (McClain *et al.* 2003). Scientists have also been asked to define the width of these buffer zones (Osborne and Kovacic 1993). It was clearly demonstrated that there was no rule of thumb to assess the optimal width since their efficiency was under the control of local hydrogeomorphic conditions (Sabater *et al.* 2003) and a function of the ratio of rate of denitrification activity to the rate of nitrate supply to the site: that is, the Damköhler ratio (Ocampo *et al.* 2006). In the meantime, a broader catchment perspective allowed identification of other landscape features such as hyporheic zones, which also provided suitable environments for denitrification to occur, depending on anaerobiosis, bioavailable carbon and nitrate input (Bencala 1984).

In-stream ecotones

The hyporheic zone is an ecotone between the stream and its subsurface channel sediments; it is a dynamic area of mixing between surface water and groundwater at the sediment–water interface. Hydrobiologists (Karaman 1935; Angelier 1953; Gibert 1976) identified specific micro- and macro-invertebrate fauna, distinct to both surface and groundwater zones. This mixing zone of surface and groundwater is not easy to quantify since the proportion of the mixing varies both spatially as a function of local hydrogeomorphic context, and temporally as a function of stream discharge. Hydrologists had long neglected this landscape feature, most probably because it does not influence the overall water budget at the catchment scale. Apart from its role as a biodiversity reservoir and refuge, the hyporheic zone can also significantly affect stream water quality: longer retention times of surface water and groundwater mixed in the hyporheic zone can significantly improve stream water quality (Triska *et al.* 1989). Biogeochemical research on the role of the hyporheic zone in processing stream carbon, nutrients and chemicals then increased rapidly and generated a workshop (Stream Solute Workshop 1990) that paved the way for further interdisciplinary research combining hydrogeology, hydrology, geomorphology, microbiology, biogeochemistry and ecology. Nowadays, streams can no longer be considered as simply the conduit of surface water; they are connected to the riparian zone (Valett *et al.* 1996), to the wider floodplain (Stanford and Ward 1988), and to shallow and deep groundwater (Toth 1962).

Management implications

Understanding the role of land–water ecotones in the hydrological and biogeochemical functioning of the drainage basin has been triggered by basic management questions: What are the underlying biogeochemical mechanisms? What is the necessary ecotone width needed to buffer diffuse nitrogen fluxes? What is its overall efficiency at the catchment level? What is its optimal location within the drainage basin (see Fig. 7)? These questions require the linking of different scientific disciplines at different levels of organization, from the soil hotspot to the landscape level. It is nowadays well established that the addition of land–water interfaces, along the stream network (riparian zones), in-stream (hyporheic zone) and further upslope, can increase the retention time of the water within the catchment. This will in turn increase the likelihood for the transported nitrate to encounter suitable environmental condition for denitrification to occur (Naiman and Décamps 1990; Pinay *et al.* 2015; Pinay and Haycock 2019). Sadly, land use change in agricultural drainage basins all over Europe in the 1970s and 1980s has simplified landscape structures, draining wetlands, removing hedgerows, straightening stream reaches, and reducing meandering features and associated hyporheic zones. All these transformations have reduced tremendously the number of land–water ecotones within drainage basins. Consequently, this has dramatically limited their potential buffering capacities for nitrogen, and their terrestrial and aquatic biodiversity, impacting on eutrophication of freshwater and coastal areas (Le Moal *et al.* 2019).

Perspectives on the links between geomorphology and biogeochemistry

If Robert Horton's work on infiltration, overland flow and erosion marked the start of the process revolution in hillslope geomorphology, then Leopold, Wolman and Miller's *Fluvial Processes in Geomorphology* (Leopold *et al.* 1964) may be regarded as marking the high point of the paradigm shift (Burt 2008). Research moved rapidly away from denudation chronology to current processes and forms, with field and laboratory measurements providing quantitative evidence of process and response. Initially, interest continued into the link between solute transport and hillslope denudation, but very quickly this broadened, less concerned with landforms per se, and more with biogeochemical processes and responses, with the drainage basin being seen as the fundamental unit of study. Studies of larger river basins soon were accompanied by small-scale field experiments, quantifying the sources and rates of input to the local river channel. Applied research, for example on nitrate pollution, riparian buffer zones and carbon loss from peatlands, soon followed. Observations made at the end of the UK's severe drought of 1975–76 show just how greatly the subject was changing, barely a decade after Leopold, Wolman and Miller had codified the new discipline. By the end of the century, computer-based modelling, statistical analysis and high-frequency monitoring transformed the field still further, but these innovations lie beyond our period of study. Certainly, by the end of the twentieth century, the scale and range of fluvial geomorphology had been greatly transformed from what it had been in 1965, providing a distinctive contribution to the broader field of biogeochemistry,

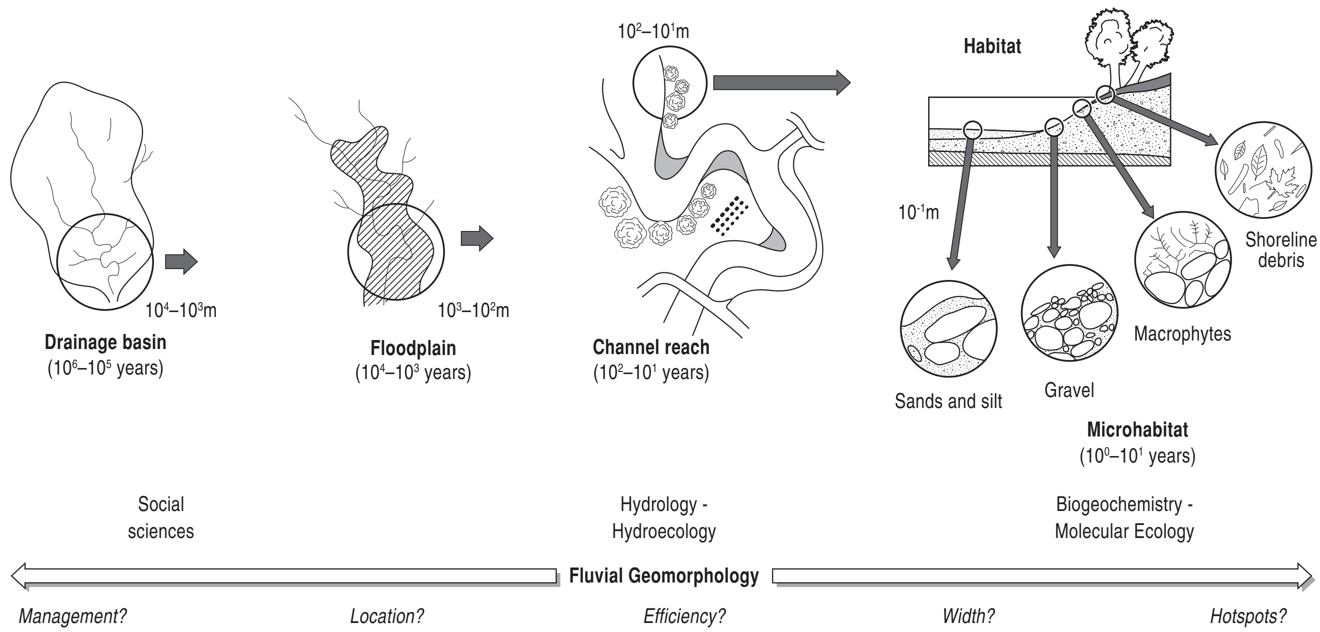

Fig. 7. Scale-dependent management issues related to nitrate diffuse pollution control and the corresponding relevant research disciplines, emphasizing the key influence of fluvial geomorphology. Adapted from Pinay and Haycock (2019).

as well as an ongoing contribution to the study of Earth surface processes and landforms.

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