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Nutrient dynamics at the interface between surface waters and groundwaters

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SUMMARY

1. The surface water/groundwater (SW/GW) interface is a crucial control point for lateral nutrient fluxes between uplands and aquatic ecosystems and for upstream/downstream (longitudinal) processes in lotic ecosystems.
2. Hydrological and biogeochemical dynamics of the SW/GW ecotone are linked to the degree of channel constraint and the sediment characteristics of the floodplain and stream bed.
3. The availability of specific chemical forms of electron donors and electron acceptors affects the spatial distribution of biogeochemical processes at the SW/GW interface. Temporal change in discharge is also a major factor affecting the rate and extent of these processes.
4. The magnitude of SW/GW interactions in lotic ecosystems is predicted to be a major determinant of solute retention. Channel morphology, stream bed composition and discharge are predicted to be important controls on SW/GW interactions.
5. Interdisciplinary research involving hydrologists, geomorphologists, aquatic ecologists, microbial ecologists and landscape ecologists is needed to further our present understanding of this critical interface linking terrestrial and aquatic ecosystems.

Keywords: surface water/groundwater interactions, nutrient cycling, biogeochemistry, hydrogeology, terminal electron accepting processes, ecotone

Introduction

With the recognition of the importance of surface water/groundwater (SW/GW) interactions and the ensuing ecotone concept (e.g. Hynes, 1983; Gibert *et al.*, 1990; Sabater & Vila, 1991; Vervier *et al.*, 1992; Stanford & Ward, 1993; Brunke & Gonser, 1997), rates and pathways of nutrient cycling at the interface

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between groundwaters and surface waters are topics of growing interest (e.g. Wallis *et al.*, 1981; Grimm & Fisher, 1984; Triska *et al.*, 1989; Cirmo & McDonnell, 1997). Strong redox gradients commonly occur at this interface, and concentrations of many biogeochemically important solutes vary widely. The distribution of electron acceptors (e.g. oxygen, nitrate, metal oxides, sulphate, and carbon dioxide) and electron donors (e.g. dissolved and particulate organic matter, hydrogen, ammonium, methane, ferrous iron, manganous manganese and reduced forms of sulphur) is spatially and temporally heterogeneous. Therefore, redox reactions that cycle various nutrients are patterned in a complex mosaic that is closely linked to the hydrology and fluvial geomorphology of the interface. As a result, diverse and variable biogeochemical processes can occur as redox potential, solute concentrations, pH and available sources of energy vary in space and time. Many redox sensitive reactions that cycle important nutrients, such as aerobic respiration, fermentation, acetogenesis, methanogenesis, methane oxidation, nitrification, denitrification, metal oxidation (e.g. iron and manganese), metal reduction, sulphur oxidation and sulphate reduction, are of particular interest at the surface water/groundwater (SW/GW) interface.

The SW/GW interface is also a crucial control point for longitudinal nutrient interactions and for nutrient fluxes between uplands and streams (e.g. Peterjohn & Correll, 1984; Pinay & Décamps, 1988; Triska *et al.*, 1989; Valett *et al.*, 1996). The topographic location of this interface implicates the SW/GW interface as a significant regulator of nutrient transport in both surface runoff and groundwater. The fluvial history and geomorphic setting of this ecotone adds a complex three-dimensional structure to the biogeochemical processes that cycle nutrients. Temporal variability in hydrological conditions must also be considered when assessing nutrient cycling within this dynamic interface.

Gaining a better understanding of the biogeochemistry of the SW/GW interface requires effective linkage of geomorphology, hydrology and ecology. The three dimensional physical structure of the riparian zone, residence time and routing of water, plant and microbial uptake and cycling of nutrients all must be considered. The objectives of this paper are to (i) provide a general geomorphological framework for studying riparian zone ecosystems and the SW/GW interface, (ii) discuss ways to couple hydrological flowpaths and residence times to redox potential, biogeochemical pathways and nutrient cycling rates and (iii) illustrate with case studies and examples where these approaches have been effectively employed.

SW/GW ecotone structure

The intermixing of surface and groundwaters occurs at different spatial scales. At larger scales, sections and networks of streams and rivers encompass multiple reaches, varying channel units and many different substrata (Gregory *et al.*, 1991; Brunet *et al.*, 1994; Tabacchi *et al.*, 1996). At the smaller scale of a single reach, features such as pools, riffles, glides, secondary channels and relict channels exist within a given reach. Much of the research on nutrient dynamics within the SW/GW ecotone has focused on this scale, which will be the primary scale of focus for this paper.

Numerous structural elements and subsystems occur within a stream or river reach. We identify three surface compartments as organizational features for SW/GW interactions within the floodplain: riparian, parafluvial and surface zones (Fig. 1). Located within the active channel are the parafluvial and surface compartments; these vary in size with discharge. We use the term parafluvial as the region of the active channel without surface water during times of lower discharge (Holmes, Fisher, & Grimm, 1994). Although limited vegetation often covers parts of the parafluvial zone, periodic resetting disturbances and the absence of large, long-lived plant species characterize this part of the ecotone. The riparian zone is commonly defined as the interface between the terrestrial and aquatic ecosystem (e.g. Gregory *et al.*, 1991). We operationally define the riparian compartment by the presence of longer-lived, high stature vegetation within this interface (Fig. 1). The riparian zone generally does not contain surface water except during episodic floods. In larger rivers, the riparian zone is often referred to as floodplain forests or riparian forests (e.g. Décamps, 1997). These three compartments of the floodplain are hydrologically linked in the subsurface via three dimensional groundwater flow. Linking hydrological and biogeochemical dynamics within and between the

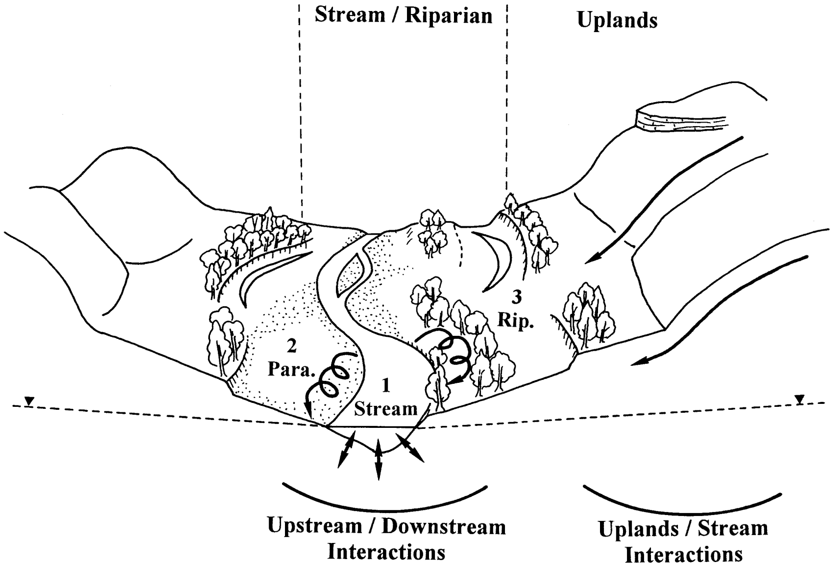


Fig. 1 Catchment geomorphology showing the uplands and stream/riparian habitats. The stream/riparian habitat is subdivided into riparian, parafluvial and stream subsystems. Lateral (upland/stream) and longitudinal (upstream/downstream) interactions are highlighted.

groundwaters of these three compartments or subsystems is a vital research and management goal.

The parafluvial and riparian subsystems contain both water-saturated and unsaturated zones. A capillary fringe between these is a major rooting zone for many parafluvial and riparian plants. Fluctuations in the height of the water table caused by periodic flooding and drying change the relative dimensions of unsaturated and saturated zones, and this influences the nutrient concentrations, organic matter content and redox potential of shallow groundwaters. Saturation of parafluvial and riparian subsystems can generate substantial surface runoff during storms or snow melt (Beven & Kirkby, 1979). Changes in the structure of the water table also affect the direction and velocity of groundwater flow. A higher water table within parafluvial and riparian subsystems commonly directs flow in a more perpendicular direction relative to the channel (Wroblicky *et al.*, 1994, 1998). The position of the water table and changes in its height may thus affect nutrient dynamics within stream and river corridors.

Two possible vectors that connect surface waters and groundwaters are: (i) groundwater flow from the uplands through riparian zones to the active channel and (ii) surface water recharging groundwater along an upstream–downstream gradient (Fig. 1). The upland interface has been the focus of many studies of nutrient retention within riparian ecotones (e.g. Peterjohn & Correll, 1984; Lowrance *et al.*, 1985; Pinay & Décamps, 1988; Knauer & Mander, 1989; Cooper, 1990; Ambus & Lowrance, 1991; Haycock & Pinay, 1993; Haycock *et al.*, 1993; Pinay *et al.*, 1994; Vought *et al.*, 1994, 1995; Hill, 1996; Hedin *et al.*, 1998). In most cases, concentration gradients in groundwater sampled perpendicular to the active channel have been used to estimate nutrient retention. Concencentrations of conservative solutes are frequently used as comparative reference data to estimate nutrient loss along gradients from the uplands to the channel. Groundwater is usually assumed to flow at right angles to surface flow and vertical gradients are generally not considered. Studies of riparian zones often point to the efficient removal of nutrients, especially nitrogen and phosphorus, at the ecotone between upland groundwaters and surface waters. Hill (1996) summarized the efficiency of stream riparian zones in regulating the transport of nitrate in groundwater flow from uplands to streams. Removal rates ranged from 0 to 99% over a wide range of streams, with most sites exceeding 80% removal.

Other studies of hydrological and nutrient dynamics have considered the SW/GW interface along the longitudinal axis of fluvial corridors (e.g. Triska *et al.*, 1989; Triska *et al.*, 1990a,b; Valett *et al.*, 1990; White, 1990; Triska *et al.*, 1993a,b; White, 1993; Holmes *et al.*, 1994a,b; Valett *et al.*, 1994; Jones *et al.*, 1995a; Valett *et al.*, 1996). Upstream to downstream interchanges of surface waters and groundwaters exert considerable influence on the cycling of nutrients in lotic ecosystems. For example, reach-scale studies in

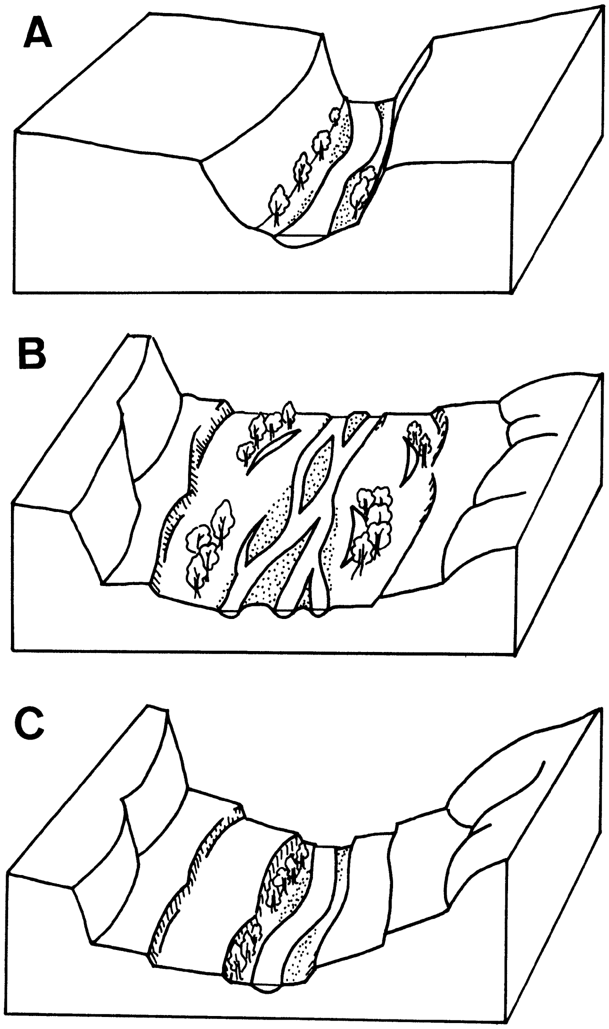


Fig. 2 Geomorphology of a stream or river ecosystem in a constrained reach (a), an unconstrained aggrading reach (b) and an unconstrained degrading reach (c).

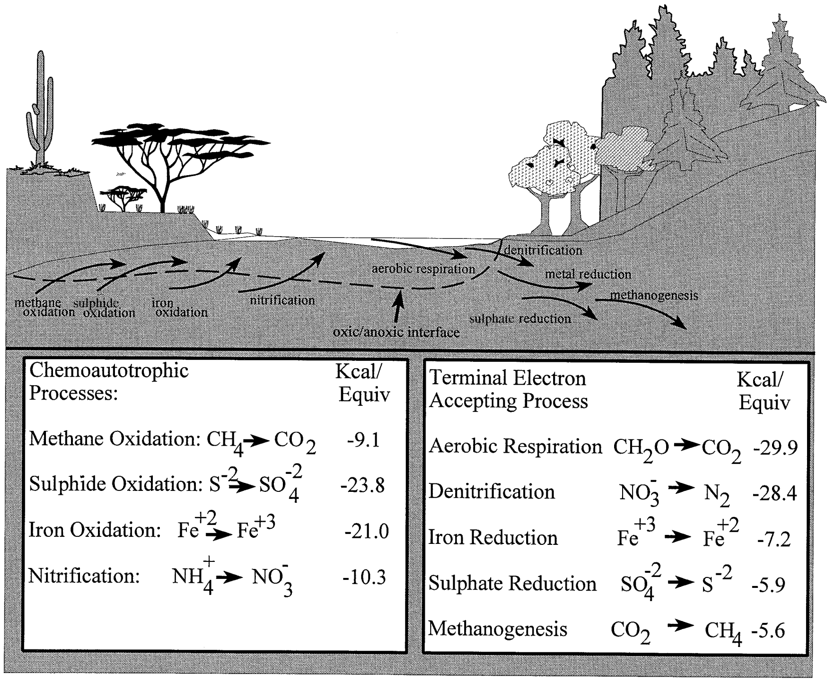
Sycamore Creek, AZ, U.S.A., have shown the importance of nitrate-enriched groundwater inputs to rates of algal growth (Valett *et al.*, 1994). Similarly, dissolved organic matter of algal origin can be a high-quality energy source to heterotrophic microbial communities in areas of groundwater recharge (von Gunten & Lienert, 1993; Jones, 1995). Exchange of surface waters and groundwaters along longitudinal pathways within lotic ecosystems provides an additional important downstream component to nutrient cycling in surface waters of fluvial ecosystems.

Streams and rivers flow through a wide variety of geomorphic landforms. Many reaches are heavily altered by human activities and channelization and straightening of fluvial corridors for flood control speeds the flow of surface waters and minimizes connectivity between the active channel and riparian subsystems. In extreme cases, canalization completely disconnects the fluvial corridor from local and regional groundwaters, and the channel functions much like a pipe for surface water transport (Bencala, 1993). Highly human-modified fluvial corridors greatly reduce the linkages between subsystems and restrict the extent of SW/GW interactions.

Fluvial reaches also can be distinguished by their relative degree of topographic confinement; one useful distinction differentiates between confined and unconfined reaches (Gregory *et al.*, 1991). Constrained reaches are physically restricted laterally, with floodplains less than four times the width of the active channel. Unconstrained reaches extend laterally for distances greater than or equal to four times the active channel width (Fig. 2). Unconstrained reaches can occur in geomorphic positions on the landscape where either aggradation (deposition of sediments) or degradation (erosion of sediments) dominates (Fig. 2). The hydrological and biogeochemical dynamics of the SW/GW interface respond to both the degree of constraint and the sediment characteristics of depositional or erosive channels and floodplains (Pinay *et al.*, 1992; Morrice *et al.*, 1997). Additional landscape elements such as tributaries and relict channels add further complexity to the SW/GW interface. Employing a hierarchical perspective and defining geomorphic conditions, however, serves as a helpful organizing structure for studying hydrogeology and nutrient dynamics where groundwaters and surface waters interact.

Biogeochemical processes

A complex array of biogeochemical processes may occur within groundwaters underlying riparian, parafluvial and surface water compartments of stream and river corridors. A variety of electron acceptors, such as oxygen (O_2), nitrate (NO_3), ferric iron [Fe(III)], manganic manganese [Mn(IV)], sulphate (SO_4) and carbon dioxide (CO_2), may be used for organic matter oxidation depending on the redox potential of the environment (e.g. Champ *et al.*, 1979; Reeburgh, 1983; Zehnder & Stumm, 1988; Lovley *et al.*, 1989; Lovley, 1991; Postma & Jakobsen, 1996). The redox potential at a specific place and time in the riparian ecotone is a function of groundwater residence time, the rates of



Chemoautotrophic Processes:		Kcal/ Equiv
Methane Oxidation:	$CH_4 \rightarrow CO_2$	-9.1
Sulphide Oxidation:	$S^{-2} \rightarrow SO_4^{-2}$	-23.8
Iron Oxidation:	$Fe^{+2} \rightarrow Fe^{+3}$	-21.0
Nitrification:	$NH_4^+ \rightarrow NO_3^-$	-10.3

Terminal Electron Accepting Process		Kcal/ Equiv
Aerobic Respiration	$CH_2O \rightarrow CO_2$	-29.9
Denitrification	$NO_3^- \rightarrow N_2$	-28.4
Iron Reduction	$Fe^{+3} \rightarrow Fe^{+2}$	-7.2
Sulphate Reduction	$SO_4^{-2} \rightarrow S^{-2}$	-5.9
Methanogenesis	$CO_2 \rightarrow CH_4$	-5.6

Fig. 3 Chemoautotrophic and terminal electron accepting catabolic processes which can occur within the SW/GW interface of streams and rivers. Energy yields for each biogeochemical process are given along with general chemical reactions. Solution pH is assumed to be 7 and CH_2O is used as an 'average' organic substance (after Stumm & Morgan, 1996).

metabolism within groundwaters and mixing between groundwaters with differing hydrological sources and chemical characteristics. Various electron transport pathways are commonly segregated in space, time or both (Lovley, 1991; Hedin *et al.*, 1998). Organic carbon decomposition can therefore be carried out through the reduction of O_2, NO_3, [Mn(IV)], [Fe(III)] or SO_4, or via methane production, depending upon the availability of different terminal electron-accepting compounds within a certain groundwater parcel (Fig. 3). Determining the rates and distribution (spatially and temporally) of biogeochemical processes that decompose organic matter within the SW/GW interface is a major challenge to understanding nutrient biogeochemistry of this dynamic ecotone.

In addition to the metabolic pathways that oxidize dissolved and particulate organic matter, there are important biogeochemical pathways that oxidize selected nutrients and elements. For example, nitrification, methane oxidation, sulphide oxidation, manganese oxidation and iron oxidation are key oxidative pathways occurring within waters of the riparian ecotone, particularly at the interfaces between anaerobic and aerobic waters and exchange points between groundwaters and surface waters (e.g. Dahm *et al.*, 1987; Triska *et al.*, 1990b, 1993b; Jones *et al.*, 1995a; Hedin *et al.*, 1998). These chemical pathways are microbially catalyzed in the presence of dissolved oxygen, and are often associated with microbial growth and maintenance through chemosynthetic pathways.

A predictable cascade of microbial processes based upon thermodynamic energy yield would be expected to occur along an idealized groundwater flowpath (Fig. 3). Groundwater containing dissolved O_2 supports aerobic metabolism and such microbial chemosynthetic pathways as nitrification, methane oxidation and sulphide oxidation, if the necessary chemically-reduced substrates are present. Where dissolved O_2 supplies are exhausted, alternative electron acceptors are used in organic matter catabolism. Denitrification yields the most free energy once dissolved oxygen is no longer available, and this biogeochemical pathway is of great interest in riparian ecotones since it provides a permanent sink for excess nitrate (e.g. Lowrance, 1992; Haycock *et al.*, 1993; Pinay *et al.*, 1993; Gilliam, 1994; Jansson, Leonardson & Fejes, 1994; Pinay *et al.*, 1994; Groffman *et al.*, 1996; Hill, 1996).

Alternative electron acceptors such as Mn(IV), Fe(III) and SO_4 become important once supplies of dissolved oxygen and nitrate are exhausted. Energetically, Mn(IV) reduction, Fe(III) reduction and SO_4 reduction, respectively, are predicted to occur sequentially along groundwater flowpaths where these electron acceptors are present (e.g. Berner, 1981; Stumm & Morgan, 1996). Alternatively, microbial competition for an electron donor such as hydrogen also might determine where certain microbial processes occur along groundwater flowpaths (e.g. Lovley & Chapelle, 1995). Electron donors formed as a byproduct of microbial fermentation during organic matter degradation also could be rate limiting for specific anaerobic biogeochemical pathways such as metal reduction, sulphate reduction and methanogenesis (e.g. Postma & Jakobsen, 1996). The appearance of manganous manganese [Mn(II)] and ferrous iron [Fe(II)] in solution along known flowpaths is good evidence that metal-reducing microbial biogeochemical processes are occurring. Once the major forms of Fe(III) available for microbial reduction are chemically reduced, sulphate becomes the dominant electron acceptor and sulphate reduction can occur. The metabolic byproduct of microbial sulphate reduction is sulphide, which either remains in solution or produces a metal sulphide particulate when solubility is exceeded.

The distribution and rates of nutrient cycling processes within the SW/GW interface are linked to interdependencies between hydrology, chemistry and biology. Riparian zones are geomorphically complex interfaces with a substantial three-dimensional structure. A clear understanding of the biogeochemistry of this ecotone requires a basic knowledge of system hydrology. Regions of relative hydrological constancy through time, for example at locations of continual infiltration or exfiltration, often maintain relatively invariant chemical patterns and distributions of microbial processes spatially and temporally (Hedin *et al.*, 1998). Locations within the SW/GW interface with variable hydrological conditions may have more temporally variable microbial processes, process rates, and chemical conditions. Similarly, sediment and soil characteristics, such as hydraulic conductivity, markedly alter hydrological residence times, redox conditions, and biogeochemical pathways. Biogeochemical processes need to be studied within the context of the hydrology and sediment/soil characteristics of the SW/GW interface. A major challenge lies in effectively linking the geomorphology, hydrogeology and biogeochemistry of these dynamic interfaces.

Riparian zone biogeochemistry: an historical overview

Current perspectives on riparian zone biogeochemistry have roots in both forest (catchment) ecology and stream ecology (Fig. 4). Typifying the catchment approach is the Hubbard Brook ecosystem study (e.g. Likens *et al.*, 1977; Bormann & Likens, 1979; Likens & Bormann, 1995). Catchment nutrient budgets considered precipitation as inputs (I) and streamflow as outputs (O), thus retention ($I - O$ is positive) or loss ($I - O$ is negative) are integrated through upland, riparian and stream components of the catchment upstream at the point of sampling.

Quantification of nutrient inputs and outputs has a long history in ecosystem science, yet seldom are individual budgets of linked subsystems simultaneously considered. The classic approach to catchment budgets (Fig. 4a) was to attribute changes between precipitation and streamflow to terrestrial vegetation or soils (Vitousek & Reiners, 1975; Likens *et al.*, 1977), with the assumption that within-stream and riparian zone processes were minimal or included in the estimate. One of the first studies linking nutrient budgets of adjacent ecosystems connected by water flow is that of Giblin *et al.* (1991), conducted in a toposequence in northern Alaska. This approach, and recent hydrological–biogeochemical work in riparian and hyporheic zones (e.g. Peterjohn & Correll, 1984; Triska *et al.*, 1989, 1990b; Hill, 1990, 1993; Haycock & Pinay, 1993; Valett *et al.*, 1996; Wondzell & Swanson, 1996b), considers the spatial arrangement of different landscape components. Chemical changes in water moving from upland ecosystems through riparian zones and into surface stream zones strongly suggest riparian zones are major sites of nutrient transformation (Triska *et al.*, 1990b; Mulholland, 1992; Hill, 1993; Hedin *et al.*, 1998).

An interesting variant on the catchment nutrient budget approach was that of Lowrance *et al.* (1984). They viewed the system of interest as the riparian 'ecosystem' (Fig. 4b), and measured inputs to the riparian zone from the atmosphere and from subsurface hydrological routes, while outputs from this ecosystem were measured in streamflow at the weir. Thus, a tacit assumption of homogeneous internal dynamics remained despite the innovative focus upon the riparian zone. Any differences between nutrient retention in riparian zones and stream or groundwater

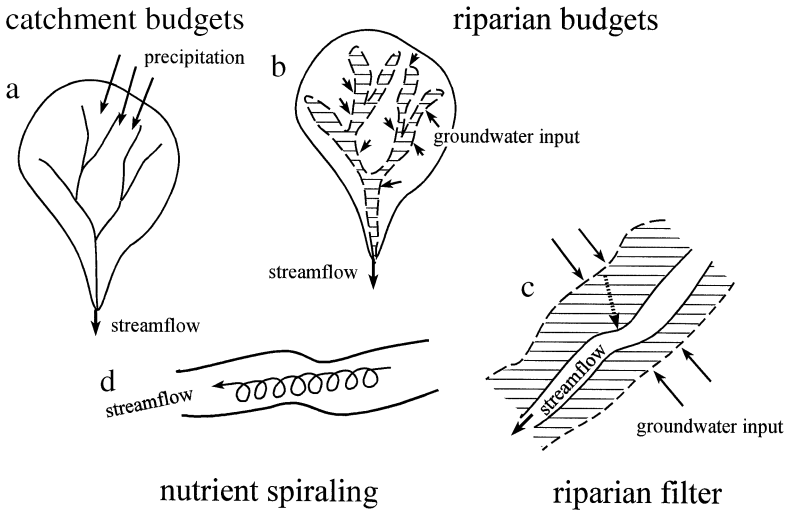


Fig. 4 Historical roots of current concepts of riparian zone biogeochemistry. (a) In the watershed approach, biogeochemical budgets are constructed based on inputs in precipitation and outputs in streamflow. Retention (i.e. the difference between input and output) is assigned to the watershed as a whole, but in practice is often seen as a consequence of terrestrial biogeochemical processes. (b) The riparian nutrient budgets of Lowrance *et al.* (1984) defined the 'ecosystem' as the area enclosed between the riparian edges on either side of the stream channel. Retention in this case is calculated as the difference between meteorologic and hydrological (subsurface) inputs to the riparian zone and outputs in streamflow. (c) Biogeochemical cycles are seen as spirals by stream ecologists. The 'system' of interest here is the wetted stream, including the benthic (biogeochemically active) component. (d) Current concepts of riparian-stream biogeochemistry merge the view of riparian zones as nutrient filters with the spiraling concept. In this construct, both lateral (upland-stream) and longitudinal (along the stream-riparian corridor) flowpaths are important.

subsystems were averaged over the area encompassed by all these subsystems upstream of the weir.

Many stream ecologists have approached nutrient dynamics from the perspective of the flowing water. In early work, nutrients were studied mainly for their role in potential limitation of primary production (Wuhrmann & Eichenberger, 1975; Stockner & Shortreed, 1978; Elwood *et al.*, 1981; Peterson *et al.*, 1983; Triska *et al.*, 1983; Grimm & Fisher, 1986) or decomposition (Howarth & Fisher, 1976; Elwood *et al.*, 1981; Aumen *et al.*, 1983). Nutrient budgets also were constructed for streams, an idea which borrowed from the catchment approach but considered only the wetted perimeter of a stream reach (Meyer & Likens, 1979; Naiman & Melillo, 1984; Grimm, 1987) or first-order stream drainage channel (Triska *et al.*, 1984). Finally, a conceptual basis for studying biogeochemistry in lotic ecosystems came from the nutrient spiralling models (Fig. 4c; Webster & Patten, 1979; Newbold *et al.*, 1981, 1983; Elwood *et al.*, 1983). In this view, elements are alternately transported and removed from the water by biotic or abiotic uptake. Thus biogeochemical cycles are stretched into spirals, and whole stream retention reflects the balance between uptake and transport.

The past decade has seen rapid expansion of work on surface and groundwater interactions from the uplands to the channel and between surface waters and groundwaters along the longitudinal axis of the channel. An important objective of research on riparian zone biogeochemistry is merging the stream spiralling perspective and the concept of the riparian zone as an effective nutrient filter (Fig. 4d). This can best be accomplished by viewing stream and riparian zones as interacting parts of the same ecosystem, and by carefully describing hydrological connections and aspects of nutrient cycling or spiraling in each.

Retention and stream geomorphology

The retention (or loss) of nutrients in lotic ecosystems is a collective measure of ecosystem processes (Fisher & Likens, 1973; Elwood *et al.*, 1983; Grimm, 1987; D'Angelo *et al.*, 1991). Recently, emphasis has been placed on the role of geomorphic structure (Lamberti *et al.*, 1989; Munn & Meyer, 1990; D'Angelo *et al.*, 1993) and associated changes in SW/GW interactions (Bencala, 1984; Triska *et al.*, 1990b; Valett *et al.*, 1994, 1996) on stream retention. Hydrological retention (*sensu* Morrice *et al.*, 1997), caused by the interaction between surface water and the alluvial aquifer (Bencala *et al.*, 1993; Wondzell & Swanson, 1996a) results in increased water residence time (Findlay, 1995; Valett *et al.*, 1996; Morrice *et al.*, 1997). This may result in increased nutrient retention because of greater contact between dissolved solutes and the microbial biota attached to alluvial materials of the bed and aquifer (Bencala *et al.*, 1993; Findlay, 1995; Valett *et al.*, 1996).

The extent and nature of SW/GW hydrological interactions have been investigated with introduced conservative chemical tracers (e.g. Triska *et al.*, 1989, 1990b, 1993a,b) and hydrogeologic models (Bencala, 1984; Harvey & Bencala, 1993; Wroblicky *et al.*, 1994; Harvey *et al.*, 1996; Wondzell & Swanson, 1996a; Wroblicky *et al.*, 1998). Application of solute transport models in streams have shown that measurements of 'transient storage' usefully represent increased residence time due to SW/GW interaction (e.g. D'Angelo *et al.*, 1993; Bencala, 1993; Harvey *et al.*, 1996; Morrice *et al.*, 1997). Exchanges between surface waters and groundwaters have been shown to be important pathways for stream metabolism (Jones *et al.*, 1995a), nutrient retention (Pringle & Triska, 1991; Valett *et al.*, 1996) and material budgets (Triska *et al.*, 1990a; Fiebig, 1995).

Geomorphologists have addressed spatial organization in streams and rivers emphasizing their function as 'stimulus–response' systems that can be viewed at multiple scales (Frissell *et al.*, 1986; Schumm, 1988; Grant *et al.*, 1990; Gregory *et al.*, 1991). Gregory *et al.* (1991) described a geomorphic categorization of running water systems that represents an ecosystem perspective of streams and their riparian zones. In Fig. 5, we present seven hypothetical geomorphic categories for a river channel based primarily on those reported by Gregory *et al.* (1991), but include categories that directly reflect human intervention. We hypothesize that these categories vary in their retentive capacity for solutes primarily because the associated hydrological and geomorphic features interact to alter the volume and direction of interactive exchange among the river, riparian zone and alluvial aquifer. These alterations change water residence times and the amount of water exchanging between surface waters and groundwaters, thereby influencing the rates and nature of biogeochemical cycling.

In Fig. 5, we present theoretical relative magnitudes of nutrient retention within geomorphic categories. Differing types of exchange scenarios for a hypothetical river and its alluvial aquifer are shown and the extent of SW/GW interactions within these categories is hypothesized to be a function of channel geomorphology. Channelization and canalization largely disconnect interfaces between surface waters and groundwaters. Tributaries and aggrading reaches are hypothesized to be locations where SW/GW interactions are high. Transitional reaches where constrained channel morphology opens up to unconstrained conditions, are also regions where SW/GW interactions are predicted to be greater. Degrading reaches are hypothesized to diminish the extent of SW/GW interactions relative to aggrading reaches. Below, we briefly discuss examples of research that consider the effect of system geomorphology and its interplay with surface–subsurface exchange. We also identify areas where our understanding is poor and there is need for increased research effort.

Large-scale studies

At the scale of the drainage network, Vannote *et al.* (1980) presented a series of hypotheses about the retention and processing of materials by lotic ecosystems. While their River Continuum Concept recognized the important interactions among riparian, benthic and water column environments, the model did not explicitly incorporate SW/GW interactions. For example, Minshall *et al.* (1983) documented decreased retention of benthic and transported organic matter with increasing numbers of tributary linkages along a river channel. No comparable studies of the role of SW/GW interactions in nutrient retention as a function of stream order or link number yet exist. Hypotheses addressing large-scale organization of SW/GW interactions are only now being formulated (e.g. Creuzé des Châtelliers, 1991; Stanford & Ward, 1993; Creuzé des Châtelliers *et al.*, 1994).

Creuzé des Châtelliers (1991) and Creuzé des Châtelliers *et al.* (1994) reasoned that for large river systems, alluvial floodplains may be dispersed along the river much like 'beads on a string.' They argued that large scale (i.e. river sections, *sensu* Gregory *et al.*, 1991) variation in erosion and sedimentation influ-

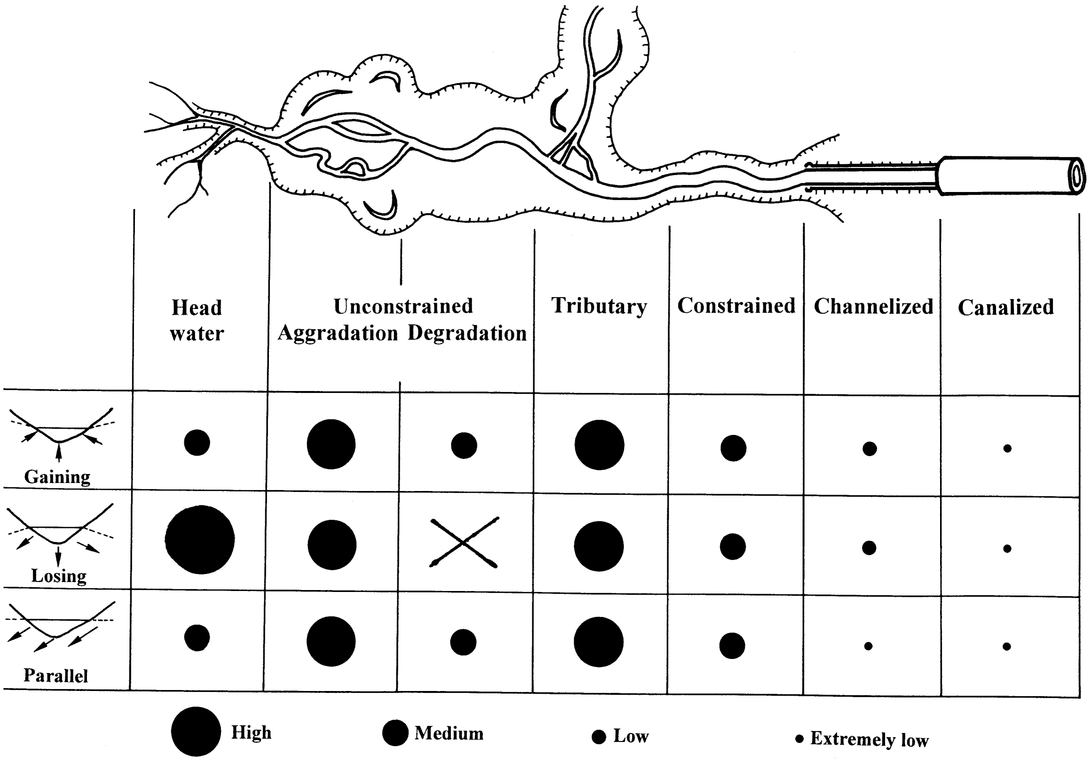


Fig. 5 Hypothesized retention efficiency of various channel configurations in gaining reaches (groundwater discharge), losing reaches (groundwater recharge), and parallel flow (limited SW/GW interactions). Losing reaches rarely occur in degrading reaches of unconstrained rivers.

ences the dynamics of river channel features and exchanges between surface water and groundwater flowing through the substratum. Because of great spatial heterogeneity in geomorphic processes, river/groundwater interactions include a number of 'discontinuities' (*sensu* Creuzé des Châtelliers *et al.*, 1994) caused by variations in grain-size distributions, influence of tributary inputs and vertical segregation that results from aggradation or degradation.

In contrast, Stanford & Ward (1993) emphasized that the continuum of lotic ecosystems that extends from headwaters to large rivers also includes 'serial convergences of surface and groundwaters connected by variable accumulation of porous alluvium.' While acknowledging that local geomorphological conditions may dictate the nature of hyporheic zone development, they proposed that there are predictable changes in extent of alluvial aquifer development and the nature of SW/GW interaction. Such changes are commonly associated with transitions from montane systems of alternating floodplain development and bedrock 'nick points' to piedmont regions of low-gradient rivers.

Channel gradient, width-to-depth ratio and sinuosity are other geomorphic variables which can influence SW/GW interactions. Larkin & Sharp (1992) predicted that regional groundwater flow would have a significant underflow or downstream regional-flow component as long as channel gradient exceeded 0.0008, the width-to-depth ratio was greater than 60, the sinuosity was less than 1.3 and the fluvial deposition system was either valley fill or bedload. A geomorphic perspective appears to offer a fruitful approach for characterizing SW/GW interactions for larger drainages, and can be useful for predicting the extent and location of such interfaces.

Catchment-level studies

At the catchment level, a few studies have begun to link retention to the geologic composition of parent material and its impact on alluvial composition. For example, Nelson *et al.* (1993) suggested that notable differences in stream water DOC in adjacent river systems in Australia resulted from very different sorptive capacities of soils and sediments formed from differing geological material. In addition, differing nutrient uptake lengths in streams have been attributed to catchment geology (Munn & Meyer, 1990; Martí & Sabater, 1996).

While these studies and others have recognized that nutrient composition and utilization will vary with geological setting, less work has been directed at resolving the extent of SW/GW interaction among catchments differing in geological composition. Recent results suggest, however, that the nature and extent of exchange vary predictably with alluvial composition and, in turn, influence efficiency of nutrient retention. Morrice *et al*. (1997) used injections of a conservative tracer and one-dimensional modelling of solute transport to compare SW/GW interaction and quantify transient storage in three first-order streams that occurred in catchments of contrasting alluvial composition (granite/gneiss, volcanic tuff, sandstone/siltstone). Hydrological retention increased as average particle size of the alluvial substrate increased (granite/gneiss > volcanic tuff > sandstone/siltstone) and these differences lead directly to predictable variation in nutrient retention. Valett *et al*. (1996) reported that nutrient retention (measured as uptake length, *sensu* Elwood *et al*., 1983) at baseflow was closely correlated to transient storage in these same systems. They showed that uptake length for nitrate-nitrogen decreased from 1178 m to 782 m to 133 m among the three catchments as predicted by increasing alluvial hydraulic conductivity and associated transient storage (Valett *et al*., 1996). These results suggest a close link between SW/GW interaction and nutrient retention by streams, but also indicate that stream/aquifer relationships will vary among catchments.

Constrained and unconstrained reaches

At the reach scale (i.e. lengths of stream 100–1000 times the channel width, *sensu* Grant *et al*., 1990), there has been a clear recognition of the importance of hydraulic residence time as a critical component of nutrient retention. Tracer releases have shown that constrained reaches are far less retentive of ammonium-nitrogen than reaches of unconstrained geomorphology (Lamberti *et al*., 1989). While these results suggest an important role for geomorphic control of hydraulic residence time, the role of SW/GW interactions was not directly assessed. Later research in the same stream verified that SW/GW interaction was, indeed, enhanced in unconstrained reaches (D'Angelo *et al*., 1993). Using hydrological models to describe solute transport, D'Angelo *et al*. (1993) showed that transient storage in an unconstrained reach of Lookout Creek, Oregon (USA) was six times that in a nearby constrained reach. Taken together, these results indicate a strong influence of SW/GW interaction on both hydrological and nutrient retention that is constrained by geomorphology within catchments (see also Valett *et al*., 1996).

Geomorphic characteristics and human influence: degradation, aggradation, channelization and canalization

Impoundment of streams and rivers has a dramatic effect on the hydrology, geomorphology and ecology of impacted river/riparian ecosystems (Stanford & Ward, 1979; Junk *et al*., 1989; Bayley, 1995). Except for the Yellowstone River, all large river systems of the contiguous United States have been altered for hydroelectric power, flood control, irrigation or navigation (Benke, 1990). In Europe, the Rhine and Rhône have long histories of modification and regulation (Bravard, 1987; Carbiener & Tremolieres, 1990).

In the River Rhône, a series of diversions route 90% of the base flow through headrace canals that supply hydroelectric facilities, leaving a reserved discharge to occupy the by-passed river channel. Hydrological regulation of the Miribel–Jonage sector (approximately 18 km of river length) has resulted in distinct alterations in river bed geomorphology (Creuzé des Châtelliers & Reygrobellet, 1990). An 8-km upstream region of degradation has lowered the river bed by as much as 4 m and, conversely, a downstream region of approximately equal length has experienced aggradation by as much as 5 m. These geomorphic changes have altered the nature of aquifer/river interaction and the biogeochemistry of SW/GW interactions. In the degrading sector, the lowered water table results in enhanced nitrate-rich groundwater (> 5 p.p.m. NO_3-N) inputs that increase solute loads in surface water. Conversely, the raised river bed in the aggraded sector farther downstream promotes unidirectional exchange in the form of extensive groundwater recharge. Thus hydrological interactions between the lateral floodplain riparian forest, the interstitial zones of the river bed and the regional phreatic aquifer have all been heavily modified by hydrological regulation. Given this decreased linkage among critical subsystems, we hypothesize decreased nutrient retention in degrading sectors as compared to aggrading regions where subsystem transfers are retained or possibly enhanced (Figs 2 and 5).

Carbiener & Trémolières (1990) detailed a similar decoupling of the riparian, river and aquifer subsystems along the Rhine due to geomorphic and hydrological manipulation. Over the past 150 years, two phases of alteration have influenced the river/riparian/aquifer relationships along the Rhine. The phase of 'straightening and containment' generally occurred from 1830 to 1880, during which dikes were erected at lateral distances of 0.5–2 km from the 'straightened' main channel. The floodplain continued to function as an 'efficient hydrological regulator and self-purifying system' (Carbiener & Trémolières, 1990). During this phase, room for lateral interaction maintained the flood pulse (*sensu* Junk *et al.*, 1989) and hydrological linkage continued to promote subsystem interaction. The second phase of development (1950–76 and recent hydroelectric canalization) has profoundly modified the hydrological system of the upstream sector of the Rhine. Where conditions previously promoted hydrological linkage and nutrient retention, such linkages and processes are substantively removed. The upstream portions of the Rhine have down-cut and entrenched, isolating the river from lateral interactions with the floodplain. This restricts recharge to areas of the river bed within the constraints of the canal system, similar to the response of the River Rhône. Carbiener & Trémolières (1990) describe increased levels of organophosphorus compounds in the waters of spring-fed streams located on the Rhine floodplain and a distinct shift toward 'eutrophic' status after these geomorphic alterations. In addition, mercury levels have increased strikingly within these groundwater-fed subsystems. Diminished SW/GW interactions where lateral interactions between the channel and floodplain are minimized often lead to increased solute concentrations in groundwater discharge.

Scaling nutrient dynamics at SW/GW interfaces

Spatial scaling

How do nutrient cycling processes among subsystems change across scales? To answer this question, it is useful to examine some principles developed by an 'emerging science of scale' (Wiens, 1989). In any hierarchy, such as that represented by a geomorphic scaling perspective, processes of interest are *constrained* by processes occurring at the next $(n+1)$ hierarchical level, and *mechanistic explanations* for those processes can be found at lower hierarchical levels $(n-1)$ (O'Neill *et al.*, 1986; Pickett *et al.*, 1994; Wu & Loucks, 1995). An example of a constraint on nutrient biogeochemistry processes is the variation in nutrient filtration by riparian vegetation (upland–stream linkage) in large catchments as a function of land-use patterns (e.g. Correll *et al.*, 1992; Jordan *et al.*, 1993; Hanson *et al.*, 1994; Nelson *et al.*, 1995). At another scale, point-source loading of dissolved organic carbon (e.g. wastewater effluent, agricultural wastes, pulp mill effluents) can cause shifts from aerobic to anaerobic biogeochemical processes, and changes in the terminal electron accepting process used in organic matter catabolism.

Mechanisms explaining patterns at higher hierarchical levels are processes that occur within subsystems. For example, the retention capacity of an unconstrained stream or river reach is a function of retention within each of the linked subsystems that comprise the reach: subsurface water in the parafluvial zone, the surface stream, and the riparian zone. In turn, different mechanisms may underlie patterns exhibited by each of these subsystems. For example, surface stream water is primarily oxic and autotrophic assimilation of phosphorus dominates, whereas phosphorus may be mobilized from mineral complexes due to metal reduction and decreased pH in subsurface environments.

In considering how biogeochemical processes might change with scale, knowledge of how hydrological flowpaths change will be critical. For example, small variations in depth of alluvium within channel units (approximately 100–300 m in length) result in vertical exchange in Sycamore Creek (AZ, U.S.A.). Upwelling zones are characterized by higher concentrations of nutrients, but at the scale of the channel unit, zones of exchange simply represent spatially segregated sites of nutrient recycling. In other words, the inorganic nutrient is taken up in the surface stream and then released in the hyporheic zone; there are no true inputs or outputs within this channel unit as a whole. In contrast, discharge of deep groundwaters into the surface stream at the upstream ends of constrained reaches (approximately 1–2 km in length) brings high nutrient concentrations to these sites. At the reach scale, these discharges can be viewed as true inputs. However, at the section scale, these inputs may represent nutrients that are recycled within the system, albeit at a much slower rate.

Temporal scaling

Rates of biogeochemical processes and solute retention efficiencies in riparian–stream ecosystems are temporally variable. A key factor affecting the temporal dynamics of SW/GW interactions is discharge. Poff & Ward (1989) used streamflow patterns and a hydrograph analysis scheme to predict lotic community structure based on streamflow variability. A similar approach for classifying the temporal dynamics of SW/GW interactions could also employ this type of hydrograph analysis. Richter *et al.* (1996) developed a method for assessing hydrological alteration within ecosystems by analysing the magnitude, frequency, duration, timing and rate of change in flow regime. Poff *et al.* (1997) expanded this assessment technique into a central component for determining the ecological integrity of flowing water ecosystems. This approach, especially when linked to a geomorphic classification scheme, could provide a strong organizational basis for predicting temporal dynamics of SW/GW interactions.

An example of the effects of regular variation in discharge associated with snowmelt on nutrient cycling processes comes from studies of nitrogen retention in mountain streams of New Mexico (U.S.A.). Hydrological retention through interaction with the alluvial groundwater was much greater during low flow seasons (summer, autumn) than during high flow periods in winter and spring in a stream containing bed sediments with high hydraulic conductivity (Morrice *et al.*, 1997). As a result, nitrate retention (expressed as uptake length) was much higher (shorter uptake length) during low-flow seasons (Valett *et al.*, 1996). The extent of SW/GW interaction was impacted by discharge, and this interaction affected nutrient retention.

Regular discharge variations associated with winter (wet) and summer (dry) seasons produced threshold responses in nitrogen transport from a gravel bar and the floodplain in an unconstrained reach of McRae Creek in the Cascades Mountains of Oregon (U.S.A.) (Wondzell & Swanson, 1996b). Rapidly increasing N concentrations (especially nitrate) in subsurface water during high baseflow discharge (winter) and during specific storm events, could not be explained by replacement of N-poor water parcels by N-rich water. Rather, Wondzell & Swanson (1996b) concluded that increases were caused by leaching of previously dry gravel bar and floodplain sediments by the rising water table. This study raises general questions about the importance of solute storage in seasonally unsaturated zones, which in turn may be viewed as a mechanism producing threshold responses to discharge variation.

Flash floods or spates can produce nearly instantaneous shifts in state that alter nutrient cycling pathways. The concept of threshold responses is relevant to this type of temporal variation. Floods are also disturbances because they result in changes in biota, physical structure and chemistry and open up space for recolonization. Intensity, timing and spatial extent of single events can initiate rapid changes in nutrient dynamics. Disturbance regime (temporal distribution and frequency of multiple events) has a strong impact on the time-averaged rates of biogeochemical transport, retention and transformation.

Examples from Sycamore Creek (U.S.A.), where disturbances have been intensively studied, provide illustrations of the kind of temporal variability in nutrient cycling induced by flash floods. The most obvious impacts of a flash flood are on stream primary producers – extensive algal mats are obliterated by spates, but re-establish within a few weeks (e.g. Fisher *et al.*, 1982; Grimm & Fisher, 1989). Algae are a major food base for the stream; they also provide an important subsidy of labile carbon to microbial communities within groundwater downwelling (groundwater recharge) zones. Research has shown that respiration, nitrification (which is linked to mineralization in subsurface zones; Holmes *et al.*, 1994a,b; Jones *et al.*, 1995a) and denitrification all are reduced at downwelling locations after floods remove the algae (Jones *et al.*, 1995a,b). Interestingly, the activity of bacteria in groundwaters of parafluvial zones is muted at distances farther along groundwater flowpaths, where the organic carbon subsidy from the surface stream is depleted.

A reciprocal linkage between groundwater discharge zones and surface water influences the post-flood recovery of algae. Where nitrification is a predominant N transformation along groundwater flowpaths in the parafluvial zone (Holmes *et al.*, 1994a,b; Jones *et al.*, 1995a), nitrate-rich water emerges at points of groundwater discharge to the stream. These locations support higher standing crops of algae and significantly faster recovery after floods than do downwelling sites (Valett *et al.*, 1994).

These examples of temporal dynamics in SW/GW interactions come from streams where snowmelt (New Mexico), winter rainfall (Oregon) and monsoonal thunderstorms (Arizona) dominate peak flows in the hydrographs. These sites would be classified as snowmelt (New Mexico), winter rain (Oregon) and perennial flashy (Arizona) in the regional analysis by Poff & Ward (1989). Other stream types identified by Poff & Ward (1989) include harsh intermittent, intermittent flashy, intermittent runoff, perennial runoff, snow plus rain and mesic groundwater. Characterization of the temporal dynamics of SW/GW interactions across a continuum of stream types with differing streamflow patterns would lay a strong foundation for generalizations about the importance of these interactions at terrestrial/aquatic ecotones.

Case studies

Research on nutrient dynamics at the SW/GW interface has increased substantially in the past decade. Geomorphic and hydrological processes have also been increasingly considered. Both lateral linkages between uplands and lotic ecosystems and longitudinal linkages examining upstream–downstream interactions have received increased attention. In addition, spatial and temporal variation in rates of terminal electron accepting processes (TEAPs) that are utilized in the microbial metabolism of organic matter under aerobic and anaerobic conditions have begun to be characterized. No one study has yet fully characterized the full suite of primary anabolic and catabolic processes which are likely to occur, but specific processes (e.g. denitrification, nitrification, methanogenesis and methane oxidation) are being examined along with the distribution of key electron acceptors (e.g. O_2, NO_3, metal oxyhydroxides and SO_4) and electron donors (DOC and POC). This section of the paper highlights examples of research by the authors on lateral and longitudinal interactions at the SW/GW interface in streams and rivers. The focus will be on redox-sensitive solutes and important aerobic and anaerobic biogeochemical processes.

Upstream–downstream interactions in Sycamore Creek, Arizona, U.S.A.

Sycamore Creek drains a catchment of 500 km^2 located in the northern Sonoran Desert of central Arizona, U.S.A. Headwaters are ephemeral streams draining mountainous terrain to an elevation of greater than 2000 m. The lower reaches of Sycamore Creek, at 400–600 m altitude, are dry and support only deep subsurface flow except during large floods. Study sites, at 600–800 m altitude, are in the transitional zone where baseflow is disconnected (spatially intermittent). Constrained canyon reaches contrast with unconstrained reaches, but even in the former, the total width of the riparian-stream ecosystem is 2–10 × stream width during summer low flow. The riparian zone is quite distinct from the desert uplands and, in turn, the surface boundary between the riparian zone and active channel is clearly delimited by a shift from shallow soils to coarse sand/fine gravel alluvial sediment. The parafluvial zone is wide relative to the surface stream, and surface–subsurface water exchange (both lateral and vertical within the stream) is high. Baseflow discharge is 0.01 $m^3 s^{-1}$ in summer and 0.1 $m^3 s^{-1}$ in winter. Flood discharge on a 1-year recurrence interval is approximately 11 $m^3 s^{-1}$, and the maximum recorded flood was 705 $m^3 s^{-1}$. Studies of biogeochemical processes emphasizing upstream–downstream linkage are a major research focus (e.g. Jones & Holmes, 1996).

Valett *et al.* (1994) identified localized areas of vertical exchange using measurements of vertical hydrological gradients (VHGs) and confirmed exchange with injections of dye (fluorescein). Subsurface water is higher in nitrate than surface water. Thus at upwelling zones (groundwater discharge), nitrogen delivery to the benthos can be high. Valett *et al.* (1994) showed that recovery of algae following a flash flood was significantly faster at upwelling zones than at downwelling zones, suggesting that algae benefit from the nutrient subsidy resulting from subsurface–surface linkage. As water flows downstream, nitrate is taken up by growing algae, resulting in nitrogen limitation at downwelling zones (groundwater recharge).

High nitrate at upwelling zones, or at points where flows through lateral gravel bars in the parafluvial zone discharge to the stream, appears to be caused by nitrification in subsurface flow paths. Nitrification rates are highest at the interface of surface stream and parafluvial/hyporheic subsystems, both in the case of downwelling, or vertical, exchange zones (Jones *et al.*, 1995a) and along gravel bar flowpaths (Holmes *et al.*, 1994a,b). Compression of biogeochemical activity to interfacial areas may result from exhaustion of labile carbon supply from the surface stream. Although DOC concentration does not change significantly along subsurface flowpaths, bacterial numbers and activity, respiration rates (Jones *et al.*, 1995b), net nitrification rates (Holmes *et al.*, 1994a,b; Jones *et al.*, 1995a), and even denitrification potentials (Holmes *et al.*, 1996) all are highest at the influent interface.

Jones *et al.* (1995b) hypothesized that subsurface respiration is fueled by algal-derived carbon from the surface stream. In support of this hypothesis, they reported that (i) respiration was higher at downwelling than at upwelling zones and (ii) rates were reduced following flash floods at downwelling zones and increased with successional time as algal biomass increased in the surface stream. Similarly, bacterial numbers at the stream–parafluvial interface dropped dramatically after a flash flood and increased thereafter, while postflood increases in bacteria were more muted at greater distances along parafluvial flowpaths.

Together, these studies reveal the importance of longitudinal subsystem linkage within the active channel in a desert stream. An important pattern is high biotic activity at interfaces. If interfaces between subsystems generally support higher rates of biogeochemical processes than locations downflow, researchers should be cautioned not to average process rates and thereby miss significant gradients. Similar patterns may exist at other subsystem boundaries, but published data in support of this generality are lacking. In addition, the availability of electron donors such as labile DOC may be an important control on the rate of aerobic and anaerobic catabolic processes occurring longitudinally along hydrological flowpaths at the SW/GW interface.

Temporal and spatial dynamics of DOC within gravel bars of the Garonne River, France

The Garonne River near Toulouse, France, is a seventh-order channel draining about 10 000 km^2. The Garonne River begins in the Pyrénées with maximum discharge in spring due to precipitation and snow melt. Low water period generally lasts from August to October. The study site has a channel slope of 0.1%, and average annual discharge is 200 m^3 s^{-1}. The Garonne River meanders irregularly where natural migration of meander bars is accompanied by lateral accretion of sediment over the floodplain. Willow and poplar stands dominate the riparian forests in the study area.

Hydraulic continuity between the free flowing surface water and the interstitial water flowing within the sediment is greater within meanders and associated bars. Therefore, dissolved solutes, such as DOC, are exchanged between these two subsystems of the river (Vervier *et al.*, 1997). Spatial and temporal patterns of DOC concentration within gravel bars have been studied in a variety of streams and rivers (Vervier & Naiman, 1992; Findlay *et al.*, 1993; Vervier *et al.*, 1993; Bernard *et al.*, 1994; Findlay, 1995). From these studies, a conceptual model has been developed (Vervier *et al.*, 1993) that incorporates spatial fluctuations of DOC concentration within gravel bars responding to changing hydrological conditions. During moderate discharge or when small increases in discharge occur, DOC gradients decrease from the head to the downstream part of the gravel bar. Under these conditions, a gravel bar is considered as a single unit in which microbial processes modifying DOC concentrations are linked from upstream to downstream by flow. During low-water periods, decreasing gradients of DOC concentration from upstream to downstream do not occur. It is hypothesized that flow within the porous matrix is not strong enough to create hydraulic connectivity through the gravel bar. Therefore local conditions, such as grain size or particulate organic matter content, are more likely to govern microbial processes and DOC concentration. Under these conditions, DOC concentrations are patchy, and gravel bars cannot be considered as single units but rather as a set of patches. The dynamics of DOC during floods are difficult to observe, but sampling before and immediately following a flood suggests dilution decreases DOC concentrations within the gravel bar immediately after a flood (Bernard *et al.*, 1994). It is hypothesized that an elevated water table in the floodplain

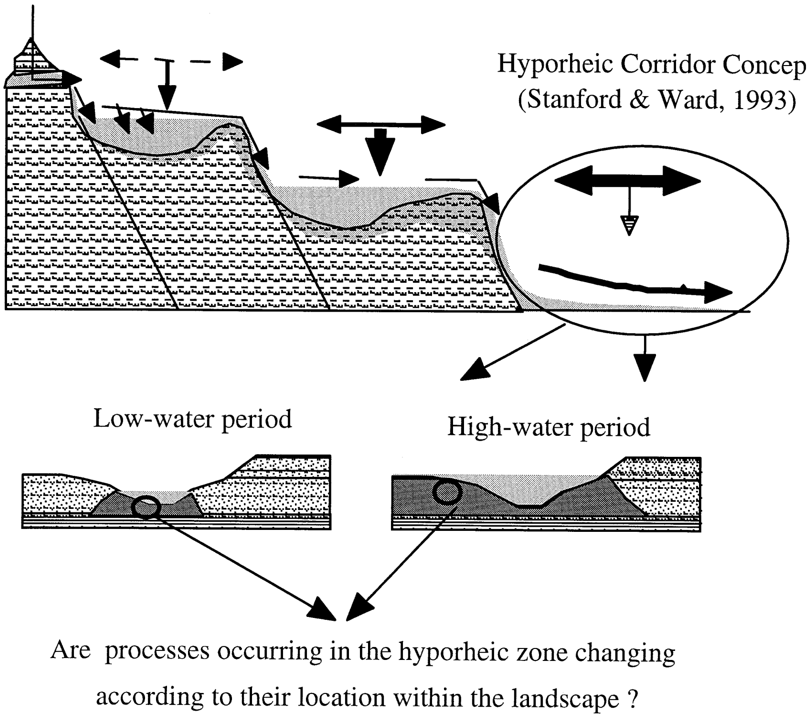


Fig. 6 Processes occurring in the SW/GW interface are hypothesized to be changing according to the location where the surface waters enter the alluvial porous medium (adapted from the hyporheic corridor concept of Stanford & Ward, 1993).

during floods enhances exchange with low DOC groundwater from upland sources.

Locations of groundwater recharge and the linkage strength between surface waters and porous alluvium change along a river in response to hydrogeomorphic gradients (e.g. Stanford & Ward, 1993; Fig. 6). Characteristics of the recharge zone within a given segment of river can change seasonally in association with different hydroperiods (Fig. 6). An important question is whether biogeochemical processes occurring within groundwater recharge zones change according to location within the landscape, and data obtained through studies conducted in the riparian zone of the Garonne River can be examined to consider this question (Ruffinoni, 1995). Piezometers have been installed in the riparian zone to analyse nitrate fluxes and transformations within groundwater discharging into the river (Fig. 7). Seven wells of 6 cm diameter were buried to bedrock along a transect following the dominant groundwater flow direction. Four piezometers were located in an upland part (a poplar plantation) and three wells were in a lowland (riparian forest) portion of the riparian zone. Seven wells were sampled for DOC five times between February and April 1994, corresponding to different hydrological periods.

Results showed that DOC concentrations were relatively low and stable within the upland part, whereas within the natural riparian forest, DOC concentration increased towards the river channel (Fig. 7). This suggests that groundwater in this sector is influenced by surface water with high DOC content. The strength of this influence changes according to the hydrological regime. Increased DOC concentrations extended further into the riparian zone during floods relative to low flow periods. This influence of hydrological stage was shown by the highest values of DOC being found in piezometers further inland in April, whereas at other periods the highest values were found closer to the river. These data show that the availability of electron donors for biogeochemical processes within the interactive SW/GW ecotone is spatially variable in large rivers.

Upland/surface water interactions: examples from the Rhône River, France

The Rhône River is a seventh-order, submontane river where upland/stream interactions are influenced by three major characteristics. First, lateral aquifers are generally well developed (greater than 15 m deep in the Jons sector, for example; Dole-Olivier *et al.*, 1994).

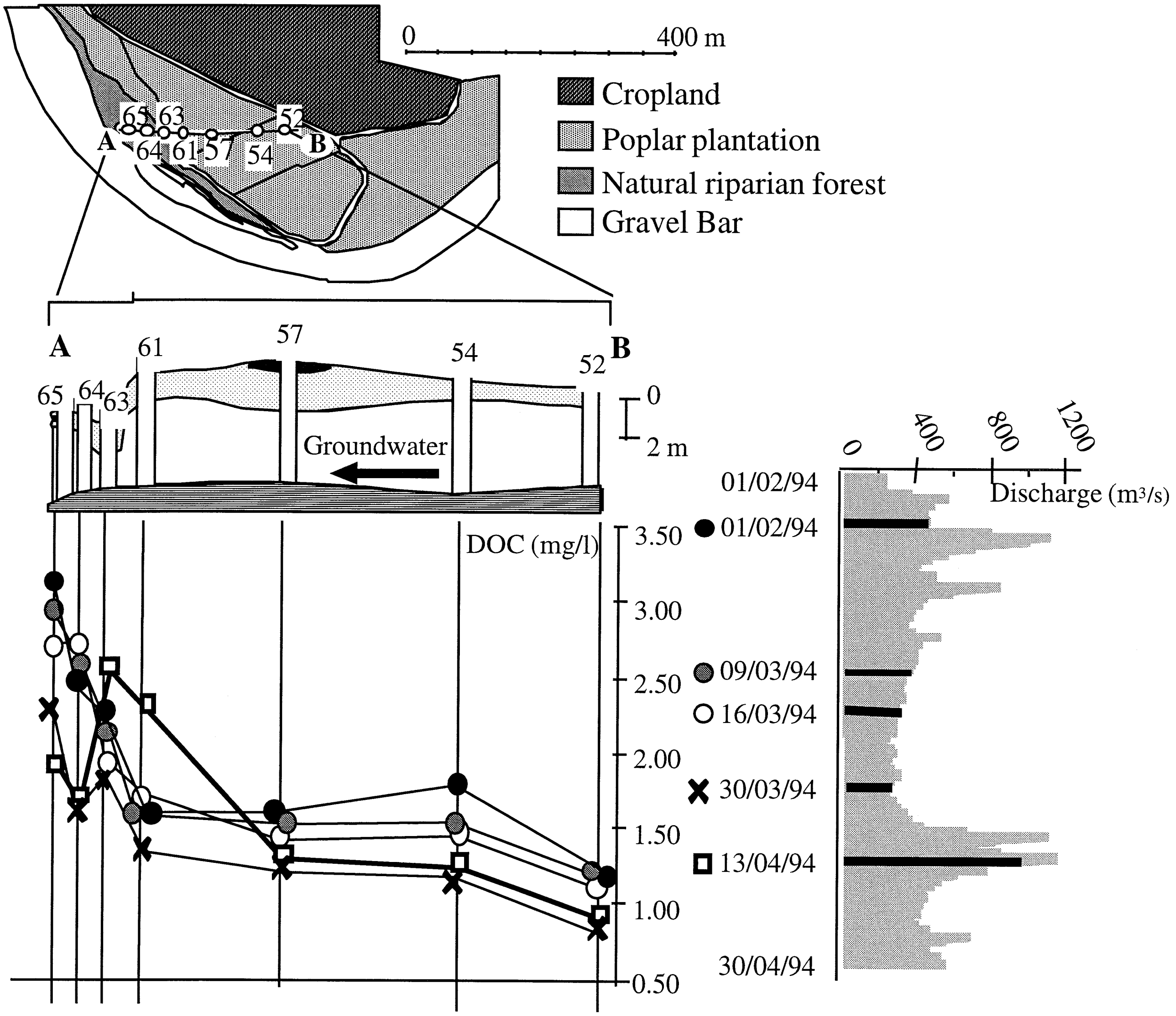


Fig. 7 Dynamics of DOC concentrations through space and time within the groundwater in the riparian zone of the Garonne River (adapted from Ruffinoni, 1995).

Second, the river is bordered by a large floodplain with numerous side channels (around 5 km width in the same sector; Marmonier *et al.*, 1992). Third, river sediment is coarse with a reduced sandy matrix that promotes high permeability (10^{-2}–10^{-3} m s^{-1}) with high vertical and lateral exchanges between the river and the groundwater (Gibert *et al.*, 1977; Dole-Olivier & Marmonier, 1992a,b; Dole-Olivier *et al.*, 1994). In this hydrogeological and geomorphological context, three examples of upland/stream interactions are presented: (i) a comparison of solute and nutrient inputs from parafluvial and riparian groundwaters to the river during an artificial drought; (ii) seasonal dynamics of nitrate and sulphate in a side arm fed by riparian groundwater and (iii) a survey of long-term changes in nutrient content after erosion of bottom sediment of a side channel by a large flood.

1 Quantification of nutrient inputs from groundwaters to surface waters is difficult because subsurface springs are generally diffuse and have variable flow. Recently, these inputs were estimated during an artificial drought of the Rhône River. Groundwater chemistry of discharge from parafluvial and riparian zones was compared (Boissier *et al.*, 1996). The study took place in a bypassed section of the Rhône River in the Chautagne sector. In this sector the right side of the river is naturally forested (poplar, willow, alder) and the river channel is bordered by several gravel bars made up of coarse sediment. During three days in June 1993, this channel was dewatered because of maintenance work performed on an upstream dam. During this period of low flow, springs fed by groundwater in the riparian zone (alluvial aquifer groundwater) appeared at the bottom of the right bank and others fed by groundwater in the parafluvial zone appeared at the downstream end of the gravel bars. Four springs were sampled at the bottom of the bank (riparian zone groundwater) and four at the downstream end of the gravel bar (parafluvial zone groundwater). Water temperature and chemical characteristics of springs in the parafluvial zone confirmed a recent surface water origin (Boissier *et al.*, 1996).

Sulphate, nitrate and phosphate content over the three days was always higher in spring water within the parafluvial zone compared to that from the riparian zone. Higher dissolved nutrient concentrations measured in springs from the parafluvial zone do not mean, however, that the parafluvial zone is always a source of nutrients for surface waters. For example, sulphate and phosphorus concentrations in groundwater springs in the parafluvial zone were similar to those of Rhône River surface water. In this system, where groundwater in the parafluvial zone originates from surface water infiltration in gravel bars, and where oxygen content of subsurface water is high (4–11 mg L^{-1} during the study period), sulphate and phosphorus were transported conservatively through the gravel bar without net enrichment or consumption. In contrast, nitrogen concentration (predominantly nitrate) was higher in groundwater springs from the parafluvial zone compared to Rhône River surface water. Limited development of gravel bar vegetation and high oxygen content of interstitial water appears to have stimulated nitrification. The parafluvial zone was a net source of inorganic nitrogen for the river. On the other hand, groundwater inputs from the riparian aquifer dilute surface water with cold and nutrient poor groundwater that maintains local oligotrophic areas within the river system.

2 Nutrient inputs from floodplain backwaters (for example from abandoned channels) are a direct and an indirect contribution to river nutrient budgets. A part of these nutrients is directly transported to the main channel through backwater outlets (Cellot & Rostan, 1993), while another part is stored (assimilated by organisms or trapped in sediment) and released to the river channel during floods (Grubaugh & Anderson, 1989; Cellot, 1996). These nutrient inputs from floodplain backwaters probably show seasonal variations, but seasonality is poorly studied for solutes transported through groundwater subsystems of river ecosystems. For example, Marmonier *et al.* (1992) showed that nitrate and sulphate contents in interstitial water in an adandoned channel had very different seasonal dynamics according to the origin of the interstitial water and the grain size characteristics of bottom sediments. The downstream part of the channel was unclogged and fed directly by terrace groundwater through large artesian springs. There, nitrate and sulphate concentrations of interstitial water did not vary or varied slightly with season. In contrast, the upstream end was partially clogged and fed by riparian groundwater from the surrounding alluvial plain. There, nitrate and sulphate concentrations significantly decreased from spring to autumn, most likely due to sulphate reduction and nitrate reduction (denitrification) in anaerobic interstitial water. Sulphate and nitrate dynamics in these riparian zones appear to be governed by geological (groundwater origin), geomorphological (sediment grain size), and biological (oxygen consumption, denitrification, and sulphate reduction) processes.

3 The importance of geomorphological processes in influencing nutrient inputs from floodplains to river channels has been highlighted in two other abandoned side channels of the Rhone River (the 'Vieux Rhone' and 'Grella' side channels). Bornette & Heiller (1994) have studied the effect of erosion of bottom sediment by floods on surface water chemistry. Because of gravel extraction from the river bed, the rate of river incision increased between 1989 and 1993. The water table at base flow decreased by approximately 0.5 m compared to before the period of gravel extraction. This erosion induced a reduction of surface water infiltration into bed sediments and increased riparian water inputs into the side channels. This caused a decrease in ammonium and phosphate concentrations, while conductivity and nitrate content increased. These changes in water chemistry produced changes in the functioning of the surface subsystem. This is evident for aquatic vegetation, with the appearance and development of oligotrophic species (such as *Chara hispida*) and decrease of spatial and temporal heterogeneity of aquatic macrophytes in these former channels.

These three examples underscore that nutrient exchanges between upland aquifers and river channels through riparian floodplain aquifers are fundamentally heterogeneous in space and time. Long-term biotic and geomorphic processes (such as revegetation of abandoned channels, erosion of side channels, or deposition of gravel bars in main channels) maintain this heterogeneity and directly modify nutrient dynamics. These processes can alter the mean annual nutrient content of groundwater recharging into surface waters and potentially increase seasonality in available nutrient concentrations.

Headwater montane streams in New Mexico, U.S.A.

The extent of lateral and longitudinal interactions between the SW/GW interface and the role of geologic and geomorphic heterogeneity upon this interface is a major focus of research on three instrumented montane catchments in New Mexico, USA (e.g. Coleman & Dahm, 1990; Dahm *et al*., 1991; Wroblicky *et al*., 1992, 1994; Baker *et al*., 1994; Henry *et al*., 1994; Valett *et al*., 1996; Morrice *et al*., 1997; Valett *et al*., 1997; Wroblicky *et al*., 1998). Seasonality and spatial variability of the hydrology and biogeochemistry of the SW/GW interface are strongly influenced by the stage of the hydrograph and differences in geomorphology and lithology of alluvial materials within the catchments.

The strength of lateral interactions between groundwater of upslope origin and surface waters within the stream varies with hydrological stage. For example, flow lines which indicate the direction of movement between groundwaters and the active channel are directed more perpendicular to the channel when stream stage and water table are high, such as during snowmelt runoff or following periods of heavy precipitation (Wroblicky *et al*., 1994; Wroblicky *et al*., 1998). In addition, the VHG between surface waters and piezometers installed 30 cm below the wetted channel are strongly positive (upwelling) throughout almost all of the study reaches at times of high stream discharge (Henry *et al*., 1994; Wroblicky *et al*., 1998). This indicates the flow of groundwater is primarily directed from the subsurface to the surface. When stream discharge is low, longitudinal interactions at the SW/GW interface become increasingly dominant. Complex patterns of upwelling (groundwater discharge) and downwelling (groundwater recharge) establish along the study reaches. Groundwater flow lines show a much stronger longitudinal component (Wroblicky *et al*., 1994; Wroblicky *et al*., 1998).

Morrice *et al*. (1997) showed through tracer experiments that hydrological retention is strongly discharge dependent and is also influenced by differing alluvial characteristics between catchments. Valett *et al*. (1996) determined that nitrate retention was facilitated by SW/GW interactions with groundwater recharge zones generally acting as sinks for nitrate. Coupling knowledge of system hydrology and biogeochemistry using paired conservative and nonconservative tracers provides a powerful method to evaluate the overall role of the SW/GW interface on nutrient dynamics. The strength of lateral and longitudinal linkages at the SW/GW interface varies markedly as a function of discharge and lithology.

Seasonal variations in the distribution of redox-sensitive solutes and gases at the SW/GW interface indicate the likely importance of the full suite of terminal electron accepting processes (TEAPs) occurring within this zone at various times and at different locations. Strong seasonal patterns in concentration within the alluvial groundwater at Rio Calaveras, New Mexico, U.S.A., occur for many solutes and gases. For example, Fig. 8 shows the concentrations of dissolved oxygen, nitrate, and ammonium before, during, and after snowmelt. Spring snowmelt with high stream discharge is characterized by increased concentrations of oxygen and nitrate at the SW/GW interface. Summer and autumn are times of decreased oxygen and inorganic nitrogen is dominated by ammonium. The extent to which these distributions reflect *in situ* microbial processes vs. hydrological control remains to be determined. However, substantial temporal biogeochemical heterogeneity within the SW/GW interface is clearly evident as is variability among catchments containing different parent lithology, alluvial composition, and channel geomorphology (Valett *et al*., 1997).

Future directions for research

Much remains to be learned about nutrient dynamics at the SW/GW interface of streams and rivers. Although recent research has added substantially to our understanding of this critical ecotone, there are

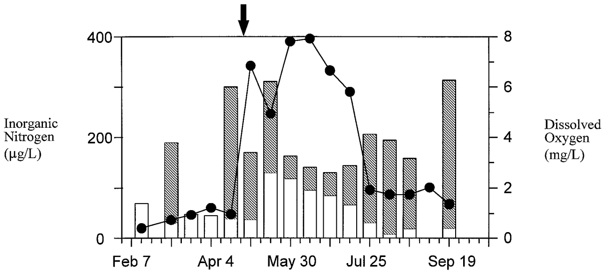


Fig. 8 Inorganic nitrogen (ammonium-nitrogen, shaded bar, nitrate-nitrogen, open bar) and dissolved oxygen (filled circles) for a floodplain well before, during, and after snowmelt at Rio Calaveras, New Mexico, U.S.A. The black arrow denotes the onset of flooding in the stream resulting from snowmelt runoff.

many areas where progress is yet needed. These recommendations are undeniably incomplete, but reflect our opinion of where further progress is clearly required.

1 The full suite of terminal electron accepting processes and redox sensitive gases and solutes needs to be studied, preferably along known flowpaths.

2 The quantitative role of lateral and longitudinal linkages in the amount and chemical form of nutrient delivery and/or uptake within groundwaters at the ecotone needs to be determined under varying hydrological conditions.

3 The spatial and temporal dynamics of groundwater discharge and recharge along active channels in varying geomorphic settings needs further elucidation. Quantification of the temporal dynamics of nutrient and water flux through these boundaries is essential.

4 The role of the interface zone in the alluvial floodplain where periodic inundation and drying occurs as a result of water table changes should be studied as a possible source for organic matter and nutrients during periods of increasing discharge.

5 Methods for extrapolating results accurately from small instrumented catchments, channel units, or reaches to the sector or network scale need to be devised.

Progress in addressing these topics will require interdisciplinary research including hydrologists, geomorphologists, aquatic ecologists, microbial ecologists and landscape ecologists. The returns, however, in improved understanding of this critical interface will prove extremely beneficial for management, protection and restoration of stream and river ecosystems worldwide.

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