ELSEVIER

Journal of Hydrology 199 (1997) 88–120

Journal
of
Hydrology

Linking the hydrologic and biogeochemical controls of nitrogen transport in near-stream zones of temperate-forested catchments: a review

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Received 3 January 1996; revised 26 September 1996; accepted 1 October 1996

Abstract

We review the status of research concerning the links between hydrologic flowpaths and the biogeochemical environment controlling Nitrogen cycling and transport in near-stream saturated zones, centering on stream environments of the northern, temperate-forested zone. N retention, transformation and mobilization occur in streamside wetlands, floodplains, riparian zones, seepage faces, and the hyporheic zone. These areas are the focal point in non-point source loading of N to stream channels. They also represent areas where rapid changes in water-table and hydrologic flowpaths occur during rainfall-runoff events. It is the combination of an abrupt change in biogeochemical environment, encountering a hydrologic boundary (the terrestrial/aquatic interface or ecotone), that make the near-stream/saturated zone critical for elucidating controls of N transport and transformation. We review published studies concerning the hydrologic controls of N transport in near-stream zones, and subsequently present several geomorphic and hydrodynamic scenarios relating N biogeochemistry and its response to hydrologic events (of both varying magnitude and seasons). It is at the critical junction between temporal and spatial conditions affecting N cycling in the near-stream zone, that research priorities must now be focused.

1. Introduction

1.1. *Excess nitrogen in the environment*

Recent concern over increased human-induced atmospheric N-deposition, in addition to

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PII S0022-1694(96)03286-6

diffuse non-point source N-inputs to surface waters from agriculture and forestry practices, has stimulated investigations of controls on the biogeochemistry and transport of N. Much of this effort has been centered on forested and agricultural catchments within the humid-temperate zone of North America and Europe. Increased N concentrations have been observed in streams in the Adirondack and Catskill Mountains in the USA (Stoddard and Murdoch, 1991; Murdoch and Stoddard, 1992; Driscoll and van Dreason, 1993; Stoddard, 1994), in mid-Atlantic Appalachian watersheds of the USA (Kramer et al., 1986; Smith et al., 1987), in the Great Smoky Mountains of Tennessee, USA (Elwood et al., 1991), as well as in Germany (Hauhs et al., 1989) and the United Kingdom (Burt and Haycock, 1992). Attempts to link increased N concentrations in streams with atmospheric N-deposition have led to the development of ''nitrogen saturation'' hypotheses (Aber et al., 1989, 1991). These hypotheses consider a combination of increasing atmospheric N-deposition, widespread forest maturation, decreased forest cutting, and stressed forest health from acidic deposition, as possible contributing factors. A categorization of watersheds by their potential N-input sensitivity has also been developed (Malanchuk and Nilsson, 1989; Aber et al., 1991; Tamm, 1991; Stoddard, 1994). Many eastern USA forests and most forests in Europe are thought to be approaching a period of steady-state in terms of biological aggradation and N demand (Sullivan, 1993). The environmental consequences of additional N-inputs to surface waters include increased surface water acidification and possible N-based downstream eutrophication (Wright, 1991; Stoddard, 1994). In addition, an increase in N-loading from agricultural areas and artificial drainage systems has been widely documented in the United States (Kohl et al., 1971; Baker and Johnson, 1976; Chichester, 1976; Burton et al., 1977; Duda, 1982; Owens et al., 1991; Jordan et al., 1993), and in Europe (Iserman, 1990; Burt and Haycock, 1992; Heathwaite et al., 1993; Armstrong and Burt, 1993). There is abundant evidence of increased N-concentration in runoff from agricultural fields and from other land-disturbance activities (Likens et al., 1977; Meybeck, 1982; Lowrance et al., 1984a, b; Burt and Arkell, 1987). Increasing NO_3^- concentrations in public water supplies have also been observed, with subsequent concerns over drinking water potability (Dillon et al., 1991; Dourson et al., 1991). The sensitivity of regional groundwater recharge areas to N inputs is being studied in the headwater catchments of several major metropolitan water supplies, including the New York City water supply catchments in the Catskill Mountains of New York, USA (Stoddard, 1992; Murdoch and Stoddard, 1992), the Chesapeake Bay (USA) watershed (Glibert et al., 1991), and in the United Kingdom (Burt and Haycock, 1992).

Galloway et al. (1995) have estimated that human activity has led to the fixation of an additional 140 Tg N per year, over and above natural processes like biotic N-fixation and lightning. Preliminary studies indicate that the fate of much of this additional N-input may involve continental processes, including storage in deep groundwater. Indeed, increasing concentrations of N in groundwater have recently been noted (Burt and Trudgill, 1993; Spalding and Exner, 1993; Sweeney, 1993; Böhlke and Denver, 1995). The correlation of increased N in stream water, with increased N in groundwater, is still somewhat unstudied. Attempts to identify sources of increased N in groundwater, along with the fate of N in near-stream environments, will be critical to a full understanding of the significance of the ''nitrogen saturation'' hypothesis to different catchments.

1.2. Nitrogen-transformation zones within the watershed

The identification of key landscape environments controlling N transport within catchments have been assisted by studies of biotic and abiotic controls of N transformation, and by the calculation of watershed N budgets. Several critical factors have been identified in both forested and agricultural catchments, including 1) the state of ecosystem maturation (age), 2) the in-situ decomposition rate (microbial status, soil fertility, moisture regime, etc.), 3) C- and N-limitation status, 4) the physical and chemical soil characteristics, and 5) the availability of moisture. Numerous investigations have shown that near-stream saturated zones and riparian wetlands are active sites of N-biogeochemical dynamics (Peterjohn and Correll, 1984; Lowrance et al., 1985; Cooke and Cooper, 1988; Cooper, 1990; Hill, 1990; Haycock, 1991; Mulholland, 1992). Furthermore, since near-stream/saturated zones are interfaces between hillslope and stream channel dynamics, they should play a critical role in determining the amount and speciation of N entering the stream channel. The juxtaposition of the near-stream/saturated zone, the stream channel, the hyporheic zone, and the catchment hillslope, are shown diagrammatically in Fig. 1. The hydrologic routing of N from the upland hillslope through the near-stream zone, is relatively unstudied, as is the interaction between "hydrologic flowpath" and "biogeochemical pathway" (Hill, 1990; Eshleman et al., 1994; O'Brien et al., 1994; Böhlke and Denver, 1995). N transformation and retention should occur where hydraulic residence time is increased and where saturated conditions prevail. Surface water–groundwater interface zones might include the hillslope–lowland interface, riparian wetlands and streambanks,

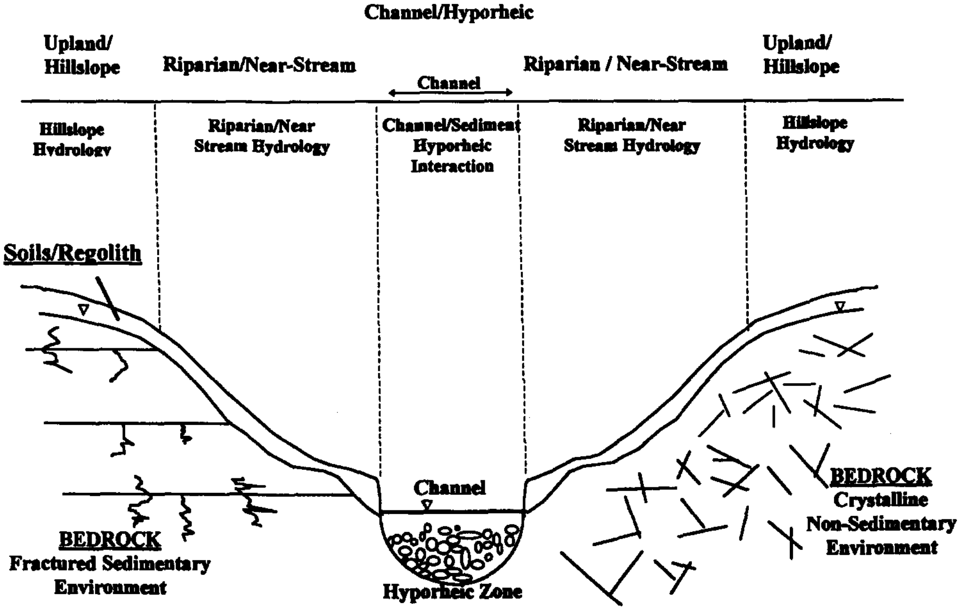


Fig. 1. Cross section of a hillslope/near-stream/riparian zone with corresponding hydrological and lithological controls.

floodplains, and the hyporheic zone under the stream channel. The water table is typically at or near the surface for much of the year in these areas, and the regolith is normally characterized by high moisture content. Hydrologic processes and dynamics controlling both hyporheic and channel solute transport have been investigated and described by Chapman (1982), Bencala (1993), Bencala et al. (1993), D'Angelo et al. (1993), Harvey and Bencala (1993), and Valett et al. (1996). In addition, Triska et al. (1989, 1990, 1993), Duff and Triska (1990), and Groffman (1994) have studied and reviewed the controls on a variety of N-transformation processes in both hyporheic zones and riparian wetlands. Some recent work on these processes has been conducted in streams of the eastern USA (Pionke et al., 1988; Mulholland, 1992; Schnabel et al., 1993; Findlay, 1995), while Hill (1990) has described N-interactions in riparian wetlands on the Canadian Shield in Ontario, Canada. Attempts to trace N through near-stream wetlands has revealed a complexity which is beyond the descriptive capabilities of current models (Hill, 1993; Waddington et al., 1993; Eshleman et al., 1994).

Recent literature in forest hydrology has been devoted to hypotheses concerning the rapid mobilization of pre-event (''old'') water to the stream during hydrologic episodes (Bonell, 1993; Buttle, 1994). However, investigations designed to study the linkages between site-specific hydrologic flowpath and biogeochemical pathway in the near-stream zone are somewhat rare (Hill, 1993; Eshleman et al., 1994). Since near-stream saturated zones and riparian wetlands may constitute the last biogeochemical environment encountered by converging hydrologic pathways, their importance in regulating stream N concentrations cannot be overemphasized. Furthermore, near-stream saturated zones are thought to expand and contract on an event and seasonal basis, as described by variable source concepts (Hewlitt and Hibbert, 1967). This necessarily places a temporal and spatial template upon descriptions of N dynamics.

It would be useful for conceptual purposes and model development to link runoff production from hillslopes with spatial and temporal variations in the biogeochemical environment characteristics of near-stream/saturated zones, to assist in predictions of N transport and fate in the landscape. Studies designed to track the spatial and temporal routing of water through hydrologic transition zones in diverse topographic, geologic and hydrogeomorphic settings, would also allow more-informed predictions of the effects of changing land-use patterns on N transport. Therefore, we need to link predictions of N dynamics with seasonal (''long-term'' temporal), hydrologic event (''short-term'' temporal), and spatial (microtopographic or hydrogeomorphic) variations in the environment.

1.3. Ecotones and hydrobiogeochemical interfaces

Terrestrial–aquatic boundaries can be considered environmental transition zones, and are normally characterized by abrupt changes in hydrologic flowpath and biogeochemical environment (Johnston et al., 1984; Wiens et al., 1985; Nixon and Lee, 1986; Risser, 1990). Ecological zones of transition are referred to as ''ecotones'' (Holland, 1988). Abrupt transitions in antecedent moisture conditions normally lead to corresponding changes in the subsurface biogeochemical environment (e.g. redox potential, pH, etc.). A gradient of vertical and horizontal zones can be defined within the soil/regolith profile in the riparian and near-stream zone, depending on the stratification of both hydrologic and physical properties of the matrix (as defined by hydraulic conductivity, porosity, and texture). This can result in a stratification of biogeochemical environments constrained by redox potential, pH, mineralogy, organic matter content, and microbial community dynamics. Recent findings point to linkages between temporal hydrologic variability (high- and low-flow regimes), biogeochemical conditions, and antecedent soil moisture, in controlling N dynamics. The zonation of hydrologic/biogeochemical gradient can be both vertical (within the regolith), and longitudinal (in an upstream/downstream direction).

It has been shown that wetlands and saturated zones near the stream channel (i.e. discharge areas or surface expressions of the groundwater table), are important in the mediation of nutrient retention (Johnston, 1991) and in the biogeochemical transformations of both N and P. Recent land-use and management decisions concerning cropland and feedlot practices have included protection of these interface zones as "green belts" (Burt and Haycock, 1993). A steepening of the hydraulic gradient can be effected by topographic and subsurface water convergence leading to surface expression of the water table (surface saturation) and exfiltration at the toe of the hillslope (Anderson and Burt, 1978; Fig. 2). This can, in turn, lead to rapid material flux (including N) mediated by hydrology. The near-stream environment can determine water source satisfying both stormwater hydrograph volume and episodic streamwater biogeochemistry. Since water entering the stream channel from the hillslope may traverse this boundary, the dynamics of subsurface flow must be described to adequately predict the timing of N attenuation or release (Haycock et al., 1993). Changes in hydrologic flowpath, as well as variations in areal N-loading rates, should determine whether N in the saturated zone originates from near-surface flow during hydrologic events, or from deeper subsurface water.

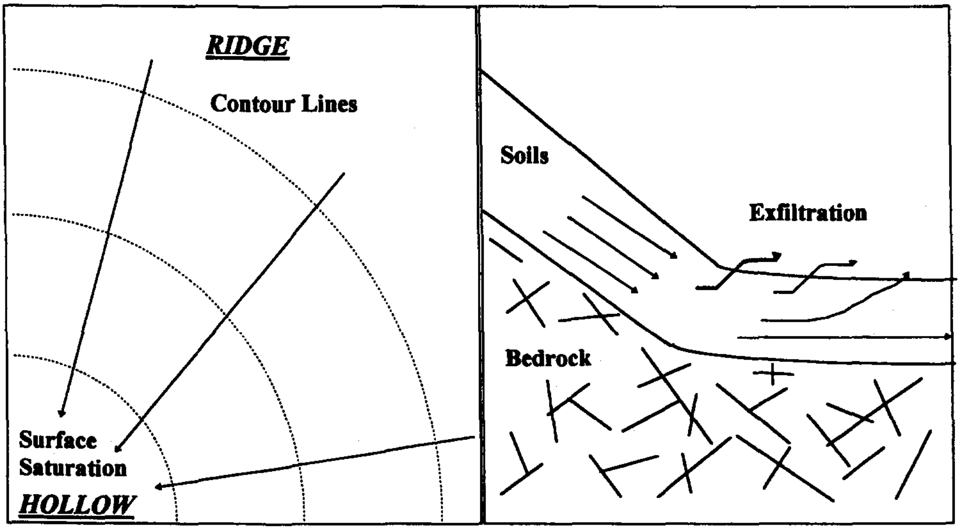


Fig. 2. The effects of topographic convergence on hydrologic flowpath at the hillslope–lowland boundary.

1.4. A working review framework

In this paper, we review studies of the interaction between hydrologic flowpath and the biogeochemical environment which may control N-cycling and transport, in near-stream/ saturated zones. We then propose scenarios of N dynamics and its response to changes in hydrology. It is at this critical juncture between temporal, spatial and biogeochemical conditions that research on environmental and landscape controls of N-flux should be focused. Although this review centers on phenomena related to N transport, examples of other solutes, both conservative and non-conservative, will be used as illustrative of the processes involved.

In Fig. 3, we propose an environmental template of factors controlling both hydrologic routing and the transport of N in streamside saturated zones within northern temperate-zone forested watersheds. In this template, control of N dynamics (both temporal and spatial) is based primarily on soil moisture. This model includes 1) antecedent moisture conditions (seasonal and hydrologic event), 2) soil and regolith controls (an ''edaphic'' template), 3) drainage position in the catchment (a topographically controlled ''hydrogeomorphic'' template), and 4) the biogeochemical environment (a ''biogeochemical'' template based on redox status and other chemical conditions). The first three templates would be expected to determine the dominant flowpath and hydrologic dynamics of N transport, while the biogeochemical environment should control vertical stratification of

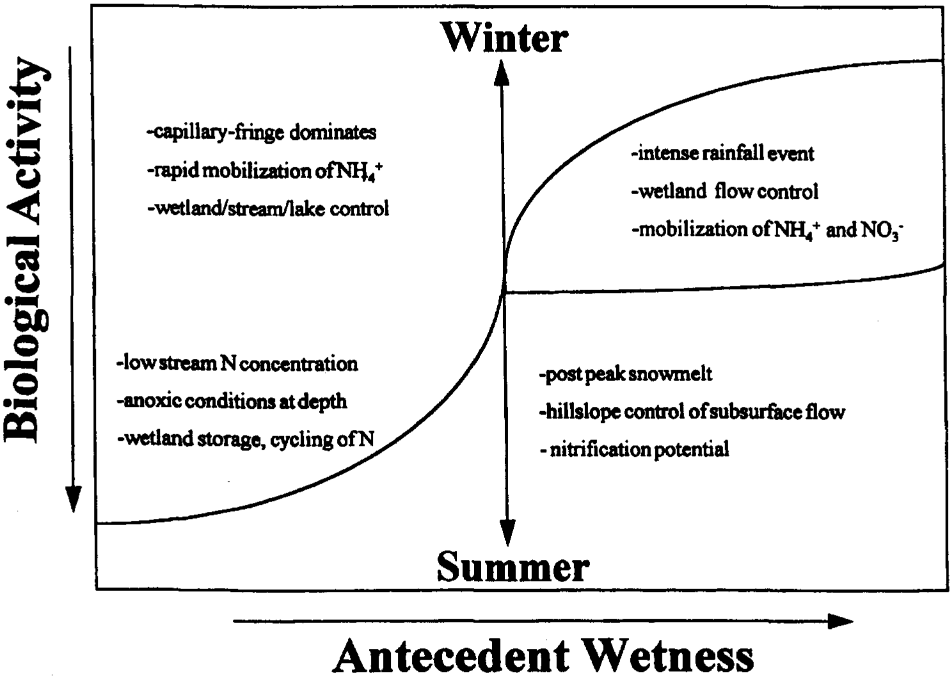


Fig. 3. Hypothetical environmental template controlling the hydrologic routing and biogeochemical expression on nitrogen species in the near-stream zone of a northern temperate stream.

redox zones and microbial communities. The biogeochemical template could include soil fertility and nutrient status (e.g. C content, C:N ratio of litter and vegetation, etc.), and would be controlled indirectly by the moisture, edaphic, and hydrogeomorphic templates. The interaction of these templates presents a matrix of effects thought to determine sources, sinks and transformation zones for N. We also attempt to describe the near-stream–riparian zone interactions thought to be important to the hydrologic and biogeochemical fate of N entering from watershed drainage.

2. Cycling and fate of nitrogen in near-stream zones

The biogeochemical control of N dynamics in saturated zones is accomplished through biotic transformations, soil and sediment adsorption, or long-term storage in a slowly cycling organic-N pool (Bowden, 1987; Howard-Williams and Downes, 1993). The size of the potential mineralizable pool of N in wetlands and riparian zones can be relatively large in some moist, temperate systems, while it is quite low in streams in arid zones and in some highly incised systems of sedimentary lithology. Internal N-cycling within the near-stream zone can predominate in some wetland environments (Bowden, 1987). Whether saturated zones are sources or sinks for N depends largely on biological N requirements, and on the availability of C. Some N-transformation pathways, in relation to the anoxic–oxic boundary (normally determined by the relative depth of the water table), and the chemistry of the subsurface hydrological environment, are illustrated in Fig. 4. Many of these processes are mediated by microorganisms, and can be described kinetically (Atlas and Bartha, 1987; Bouwer and Cobb, 1987; Bencala et al., 1993; Brown, 1988). As a result, the fate or chemical speciation of N at a particular site will depend on the water residence time, as well as on the biogeochemical environment encountered along the hydrologic flowpath.

2.1. *Loss to the system by denitrification*

Denitrification results in removal of N from the terrestrial and aquatic ecosystem and is considered a mode of N-attenuation in catchments with excess NO_3^- in runoff. Despite the development of anoxia in saturated soils, the denitrification rate may still be limited by other environmental factors such as acidity, C and P availability, and temperature (Urban and Bayley, 1988; Verhoeven, 1992; Pinay et al., 1993; Schipper et al., 1993; Groffman, 1994). Denitrification is thought to constitute a minor route of N loss from upland soils, and is usually ignored in watershed modelling efforts for upland systems (Van Miegroet and Johnson, 1993). Conversely, N losses from denitrification may be much higher from soils and sediments that are saturated and develop anoxic conditions. Schipper et al. (1993) observed rates of denitrification in riparian soils three orders of magnitude greater than those from upland soils in the same catchment. Simmons et al. (1992) and Groffman et al. (1992) linked N concentrations in riparian-zone groundwater to microbial potentials (both denitrification and nitrification), soil depth, and texture, in a agricultural watershed. Nitrate retention was positively

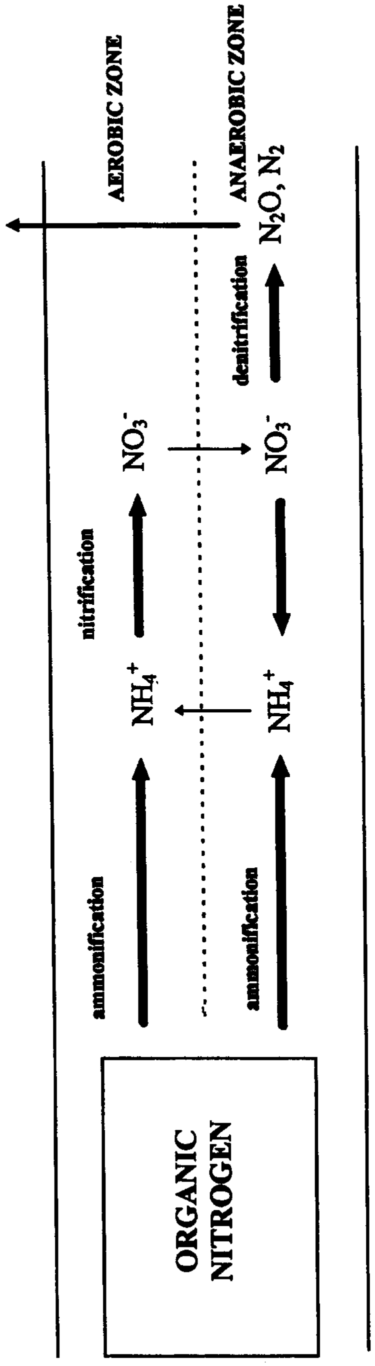


Fig. 4. General model for nitrogen cycling in relation to the subsurface biogeochemical environment.

related to both soil organic-C content and depth to the water-table. Denitrification has also been shown to be responsible for NO_3^- losses at a hillslope–riparian swamp–forest boundary (Jordan et al., 1993). Seitzinger (1994) found that denitrification was strongly correlated with organic matter mineralization rate in several New Jersey and Pennsylvania, USA, wetlands. The vertical and horizontal location of soil moisture gradients within a wetland–upland transition zone appears to be critical for determining NO_3^- attenuation rate and denitrification potential. The addition of NO_3^- through diffuse sources in agricultural catchments can, for example, stimulate its own removal by ''priming'' the populations of denitrifiers in the soil (Gersberg et al., 1983; Howard-Williams and Downes, 1993).

Groffman (1994) reviewed the environmental controls on denitrification in wetlands, emphasizing the differences between saturated zones and wetlands with variable N-availability. Nitrogen-''rich'' wetlands normally have higher denitrification rates and respond rapidly to NO_3^- additions (i.e. denitrification of added NO_3^- occurs rapidly); N-poor wetlands respond much more slowly to NO_3^- additions. These N-poor sites may not be immediate sinks for N, but may respond after a period of ''priming''. Either kind of near-stream wetland could be bypassed by N-fluxes during large hydrologic events, or snowmelt. This implies that N-poor wetlands in areas with increasing atmospheric N-inputs may be at risk of being artificially ''fertilized'' by atmospheric N-inputs.

2.2. *Other nitrogen-transformation pathways*

Updegraff et al. (1995) demonstrated the dependence of C and N mineralization on substrate quality in wetland soils representing several different vegetative community histories. They found that both depth in the peat horizon and the quality of the substrate (i.e. C and N content) controlled the N-mineralization rate. High temperature and aeration of surficial peat layers were found to accelerate mineralization rates. These findings imply that inorganic-N mobility and availability in the near-stream/saturated zone may control the mineralization ''potential'' of peat and soil.

Riparian wetlands may also be a source of N to downstream waters owing to nitrification of NH_4^+ released from the mineralization of organic N. Release of NH_4^+ from underlying soils or peat would depend on depth to the water table and, consequently, on the redox status of the substrate. The supply of NH_4^+ for nitrifiers may originate from upland or external sources, although most NH_4^+ from the catchment will be taken up by the vegetation and/or adsorbed to soil exchange sites. Atmospheric sources of NH_4^+ are usually minor for North American forested catchments; this is not the case for European watersheds where NH_4^+ may constitute a major portion of the atmospheric N load. In most agricultural watersheds, much of the NH_4^+ load is transported during hydrologic episodes as surface-water runoff from compacted cropland or feedlots. In forested catchments, where soils in the near-stream zone may be draining owing to a water-table drawdown, mineralization of organic N in the substrate may be accelerated owing to aerobic oxidation. This may, in turn, result in increases in N input to the stream, stimulating nitrifiers in the aerobic zone. Depending on other factors, the wetland could, thus, become a net source of N to the stream.

3. Hydrology and nitrogen transport in the near-stream/saturated-zone

3.1. Groundwater nitrogen-inputs to the near-stream zone

Capone and Bautista (1985) have suggested that groundwater NO_3^- may be an important source of N to surface waters in near-stream and riparian wetland zones. Nitrate concentration patterns in groundwater in the USA have been reviewed by Spalding and Exner (1993), as well as Hamilton and Helsel (1995), and trends in NO_3^- in deep aquifers in the United Kingdom have been discussed by Burt and Trudgill (1993). Notable increases in N concentrations in groundwater have been observed over the past 20 years. Recent studies in layered sedimentary geologic environments of the Appalachian Plateau (Burns et al., 1993) have revealed large groundwater inputs of NO_3^- to surface streams during baseflow. Stoddard and Murdoch (1991) demonstrated a positive but diminishing relationship between NO_3^- concentration and discharge in selected Catskill Mountain streams. These findings were similar to those observed in hillslopes in a central Pennsylvania watershed (Pionke et al., 1988; Schnabel et al., 1993), and in a mixed agricultural/forested watershed in Ohio (Owens et al., 1991) where high baseflow concentrations of NO_3^- from groundwater were diluted by stormflow. Sweeney (1993) observed increasing NO_3^- concentrations in deeper wells and surface springs in Pennsylvania, USA. Much lower NO_3^- concentrations were found in shallow, stream-side wells in the riparian zone. Burns et al. (1993) found elevated NO_3^- concentration in groundwater seeps, suggesting that older, deeper groundwater-N may have been transported directly to the stream channel via bank cuts in the layered sedimentary strata. It would be expected that preferential flow along large-scale fractures and bedding planes would short-circuit any interaction between groundwater and the saturated near-stream zone in certain geologic settings. Subsurface water emerging as seeps and springs may affect the extent and timing of N input to receiving streams in these watersheds (Pionke and Urban, 1985). Owens et al. (1991) found that even though more total-N was transported during surface stormflow in an agricultural watershed, substantial percentages (25% of inorganic N and 50% of total N) were transported via groundwater-controlled baseflow. In this case, the riparian zone was a N sink on an annual basis, but hydrologic-event water appeared to short-circuit the riparian zone during events. Carbon resources for the microbial community may also limit or control N transformations (e.g. denitrification, sensu Groffman et al., 1992) in certain watersheds. Carbon tends to accumulate in near-stream zones in cool temperate zone watersheds. The presence of C in the near-stream saturated zone may be a critical limiting factor to populations of denitrifiers. Overlying this response might be the effects of vegetative uptake and season (Stoddard and Murdoch, 1991). This subtle interaction of hydrology (particularly subsurface hydrology) and biogeochemistry may be overlooked in attempts to describe the differential regional response of watersheds to N inputs.

The interaction of groundwater-N with riparian and near-stream forested wetland zones, has been found to play a critical role in the control of N-retention and release in the Delmarva Peninsula, USA (Phillips et al., 1993). In this study, total NO_3^--release in a watershed was found to be dependent on current groundwater recharge/discharge status, and on the spatial association of microbial denitrifier communities. The development of anoxic zones in deeper, saturated soils led to a reducing environment which favored denitrification. Factors found to be important in this linkage included temperature, soil texture, redox status, organic-C abundance, depth to water table, hydrologic flowpath, anisotropy of confining layers, vegetation and land use, and hydraulic residence time.

Galloway et al. (1995) hypothesized that deep groundwater within the continental environment may be a major sink for N which has been fixed by human activities. Losses to deep groundwater are normally assumed to be permanent losses from the surface hydrological system. While this may be true in the short-run for systems dominated by surficial processes, increasing concentrations of N in groundwater may be expressed as increased N-concentrations in baseflow in layered sedimentary environments, with groundwater which may be relatively older (e.g. the Catskills, Allegheny Plateau, etc.). This potential needs to be addressed when considering the impacts of inputs of N from groundwater to downstream water supplies and rivers. Evidence reviewed by Burt and Trudgill (1993) has also indicated that water rich in NO_3^- may be lost to deep aquifer groundwater, particularly in agricultural catchments, and may reappear in baseflow at later times. This is particularly true if the near-stream zone is less important to N attenuation (i.e. those with narrow or steep riparian zones, highly incised or meandering systems of the western USA, near-stream zones which lack abundant organic carbon, etc). This avenue of research holds promise as well in attempts to sort out the contribution of either atmospheric or deep groundwater-based N to observed increases in N concentrations in streamwater within catchments believed to be approaching N saturation.

3.2. *Observations of nitrogen transport in near-stream zones*

Recent studies of hydrological and biogeochemical interactions in near-stream saturated zones in Canada (Hill, 1990, 1991, 1993), in the western USA (Triska et al., 1989, 1990; Duff and Triska, 1990; Valett et al., 1993), and in the Catskill Mountains of New York (Burns et al., 1993; Kendall et al., 1995), have revealed a variety of possible controlling mechanisms on N transport. The importance of seasonality, substrate permeability, and hydrologic flowpath have been demonstrated in the fate of natural and introduced N (Triska et al., 1990; Duff and Triska, 1990; Hill, 1993). Stream-channel simulations (Kim et al., 1992; Harvey and Bencala, 1993) coupling transient hydrologic storage and biotic submodels have demonstrated the importance of linking physical and biotic processes in describing NO_3^- retention. Kim et al. (1992) showed that channel transport dominated N-flux in the initial periods of their stream N addition experiment. Biotic uptake became increasingly important only after an initial "priming" period.

The importance of boundary zones in the hydrological control of NO_3^- and NH_4^+ transport has also been demonstrated by comparing the $\delta^{18}O$ of "pre-event" and "event" water in short-term storage within saturated zones and wetlands in Ontario (Buttle and Sami, 1992; Hill, 1993). Event-water contributions to streamflow generally increase with storm duration and intensity, supporting the notion that event water mixes with pre-event surface water (surface or depression storage) giving an increasing event-induced N-signature with time. Subsequent transport of this "mixed" water occurs at an increasing rate after surface storage is exceeded, and would be expected to occur predominantly as saturation-excess overland flow. Waddington et al. (1993) showed that mixing occurred between event water (transported as overland flow) with the return-flow of groundwater from saturated areas. The speciation of N was partially dependent on this mixing. Hill (1993) also found that variable mixing-ratios of groundwater and surface water were important in N speciation and export.

Simmons et al. (1992) demonstrated the retention of NO_3^- in both wetland soils and in the transition zone between streamside wetlands and uplands. Transition-zone retention was correlated with both water-table fluctuations and season, while the retention of NO_3^- was positively correlated with the organic-C content of the soil. It is evident that hydrology and biogeochemical status are linked in determining the observed N-signature in receiving waters; knowledge of the dominant hydrologic flowpath may allow extrapolation of a predicted N-response.

3.3. *Hydrologic events and nitrogen biogeochemistry in the near-stream zone*

It is assumed that many northern mid-latitude forests and wetlands are N limited and should act as net sinks for N inputs from anthropogenic sources (Vitousek and Howarth, 1991; Schindler and Bayley, 1993). This would imply that the proposed "biogeochemical template" is controlling N transport throughout the terrestrial watershed. However, the transport of N through saturated wetland and riparian zones during hydrologic events may be more closely linked with underlying geology and the relative biogeochemical activity of soils in the near-stream zone. The initially positive but diminishing correlation of NO_3^- concentration to episodes in both the Catskill Mountains (Murdoch and Stoddard, 1992) and in Pennsylvania (Pionke et al., 1988; Schnabel et al., 1993) suggests a decoupling of biogeochemical control from hydrology in layered sedimentary geologic environments, with the progress of storm events. Control of N transport by baseflow may be overcome during these episodes, the role of the near-stream zone in controlling N-transport being less important during these events (Schnabel et al., 1993). In contrast, (Hill, 1993) found that more-highly variable discharge relationships existed between NO_3^- concentrations and the rising and falling limbs of storm hydrographs, for stream/riparian zones in Ontario. These relationships have been noted in the Adirondack Mountains, USA as well (Schaefer et al., 1990; Wigington et al., 1990), and in other studies centered on non-layered metamorphic or crystalline lithologies mantled with glacial till and outwash. Streamside wetlands and saturated zones are more prevalent in such environments, and hillslope-derived water is more often routed to the channel through riparian and valley-bottom wetlands. In such geomorphic settings, streamwater may have greater opportunity to interact with saturated sediments, soils and peat before reaching the stream channel. An increase in shallow or near-surface flow with the progression of storms, has been suggested as a possible mechanism. Differences in the source of N in these two different geologic settings may be illustrative of the hydrologic flowpath variation thought to exist between "baseflow" and "event flow" in complex riparian zones. N attenuation in the near-stream/saturated zone may depend on both the upland source of N, and on the particular hydrologic flowpath in the saturated zone. Regardless of the source of N, or the concentration–discharge relationships, the possibility of N retention should be directly proportional to the topographic and hydrogeomorphic location of the wetland areas in relation to both static and episodic flow.

Rainfall events and snowmelt may result in large contributions of N from uplands to receiving streams and lakes. Increased flow and reduced water residence time (in the soils or wetlands) may increase short-circuiting or bypassing at the aquatic–terrestrial interface between the hillslope and the stream (Wigington et al., 1990; Stoddard and Murdoch, 1991; Murdoch and Stoddard, 1992; DeWalle and Swistock, 1994). The N transported by snowmelt is variously attributed to an accumulation of atmospherically deposited N in developing snowpacks, active nitrification in the snowpack, mineralization of organic N in the insulated soils beneath the snowpack, or to accumulation of N eluted from the snowpack in surficial soil layers (Rascher et al., 1987; Kendall et al., 1995). The flushing of NO_3^- during episodic snowmelt and spring storms constitutes a large annual source of N pollution from many forested ecosystems in both the eastern and western USA. Earlier models describing N transport during events used biogeochemical processes and changes in flowpaths thought to dominate in upland soils. Models built around these assumptions do not take the near-stream zone into account. Efforts to incorporate these variably saturated zones into current and future models will lend confidence to their applicability to different regions.

The interaction of hydrology with N biogeochemistry was studied in a wetland complex in Ontario (Hill, 1993; Hill and Waddington, 1993) where constant discharge from deeper groundwater precluded rapid water-table response mechanisms. This situation may be common in glacially mantled areas (Roulet, 1990). Saturation-excess overland flow was the major runoff mechanism during storms at this site. This was similar to the results of Burt et al. (1990) in a peatland in the United Kingdom. Event or ''new'' water percentages were high (63%) during a high-intensity, short-duration storm, but more commonly low (20–25%) in moderate-intensity, short-duration storms. Variable event/pre-event response was also observed in a wetland within a catchment in New Zealand particularly when the water-table was close to the wetland surface (Bonell, 1993). The variation in contribution from saturation-excess overland flow or from subsurface stormflow, to the receiving stream, seems to be related not only to the intensity and duration of the event, but also to the proximity of the water table to the surface, and the topographic position of the wetland area in relation to a stream or valley bottom.

Using $\delta^{18}O$ and NO_3^-/NH_4^+ data collected during a storm in a wetland, Hill and Waddington (1993) demonstrated that the dynamics of N-transport were related to hydrologic response, revealing a relatively conservative mixing of event-related (precipitation) NO_3^- with groundwater/swamp surface NO_3^-. This response included a non-conservative and non-linear relationship between NH_4^+ concentration and discharge. Indications of biotic uptake or abiotic adsorption of NH_4^+ were suggested, and the potential role for an in-situ source of NH_4^+ was proposed. Similar NH_4^+ responses have been observed in peat-covered catchments in Finland (Sepponen and Haappala, 1979) and in England (Heathwaite and Ross, 1987). In the later study, peak NH_4^+ concentration lagged discharge at an outfall from a peat drain after a storm event. This indicated that subsurface flow paths were important; delayed hydrologic response was controlled by the biogeochemical environment (in this case, the anoxic zones of the peat).

4. Hydrologic flowpath determinations in boundary zones

4.1. The hillslope–lowland boundary

Catchment runoff dynamics have traditionally been described by combinations of Hortonian overland flow (Horton, 1933), saturation overland flow (Dunne and Black, 1970), near-stream groundwater ridging (Ragan, 1968), shallow near-surface flow through more transmissive soil layers (Rodhe, 1989), and macropore flow (McDonnell, 1990). For N transport, it is important to distinguish between these possible flowpaths and their link to the near-stream zone. The aforementioned flowpath mechanisms are response mechanisms that allow for rapid "event" water movement and/or "pre-event" water mobilization. However, though these mechanisms may differ in their actual hydrologic dynamics, the resulting isotopic or geochemical mixture observed within the stream channel may be identical. Buttle (1994) describes this as an example of "equifinality", a concept from geomorphology in which a range of response mechanisms may evoke a similar endpoint observation (in this case, observed stream chemistry).

The presence of steep physical, chemical or biological gradients between hydrologic environments is common. Surface vegetation, soil moisture, or other observable surface characteristics may not be reliable indicators of "subsurface" conditions which may control hydrologic and biogeochemical response. Dynamic hydrologic changes within wetlands and between hillslopes and wetlands, can vary with changes in seasonal, annual or decadal water-regimes (Taylor, 1982; Carter, 1986). Hydrologic functions of near-stream saturated zones include flood storage and peak flow moderation (Daniel, 1981), discharge or exfiltration (and occasionally recharge) to local surface waters, and maintenance/moderation of baseflow (Novitzki, 1979). Some hydrologic studies have centered on the interactions between surface and subsurface water within wetland areas (Verry and Boelter, 1978; LaBaugh, 1986; Ford and Bedford, 1987; Siegel and Glaser, 1987; Fortin et al., 1991) while investigations designed to determine hydrologic flowpaths between terrestrial–aquatic interfaces are rare (Böhlke and Denver, 1995). Winter and Woo (1990), in a review of wetland–lake subsurface-water interactions, pointed out that reversals in groundwater flow direction are probably common between these compartments, especially during snowmelt and hydrologic episodes. Abrupt hydrologic changes are likely the norm at the interface between a hillslope (steep gradient) and a stream valley or wetland area (with a low topographic and hydraulic gradient). The hydraulic residence time and the hydrologic characteristics of the soil matrix can change substantially within a relatively small area of the watershed. Eshleman et al. (1994) showed that the spatial extent of the near-stream/saturated zone was directly related to the volume of event water in a North American Piedmont stream. It was hypothesized that rapid overland flow of rain falling onto the expanding surface-saturated zone made its way into the channel physically and chemically unchanged. Other studies (Waddington et al., 1993; Titus et al., 1995) have shown that the areal extent of surface-saturation, and, in turn, the amount of event-related channel water, cannot be predicted a priori, owing to mixing between exfiltrating groundwater and incident precipitation.

4.2. The rapid water-table response phenomenon

The rapid vertical response of the water table to additions of precipitation, in areas where the capillary fringe is close to the surface, may play a role in N mobilization during hydrologic events. The capillary fringe is a zone of ''tension'' saturation, since it contains soil water held at below atmospheric pressures (Abdul and Gillham, 1984; Gillham, 1984). The thickness of this zone is theoretically inversely proportional to median particle size, and can be affected by porosity, permeability and particle size distribution. Indirect evidence for rapid water-table rise within the capillary fringe has been observed in wetlands and saturated zones, but it has not been demonstrated definitively under field conditions, nor is the concept of the capillary fringe response universally accepted (Abdul and Gillham, 1989; Zaltsberg, 1986; Buttle and Sami, 1992). Nevertheless, the presence of a large ''theoretical'' capillary fringe in near-surface layers of soil or peat (based on calculations using substrate texture and transmissivity), may result in rapid water-table storm responses (Gillham, 1984; Heliotis and DeWitt, 1987). Rapid vertical upward movement of the water-table in response to small amounts of rainfall or snowmelt (in excess of the response expected based on calculation of specific yield) can result in the movement of the redoxcline. The relationship between water potential and soil moisture content, for a hypothetical wetland soil or peat, is illustrated in Fig. 5. The shape of this relationship depends on whether one is observing a drying or wetting phase. The steepness of the curve on the wetting phase results in the rapid mobilization of water which may reflect micro-reducing environments or N in occluded water. The hysteresis implicit in the soil wetting/drying curve has implications for the amount and types of soil microenvironment which may be in contact with soil water at any point in time (Jaynes, 1990). The nature of this contact will

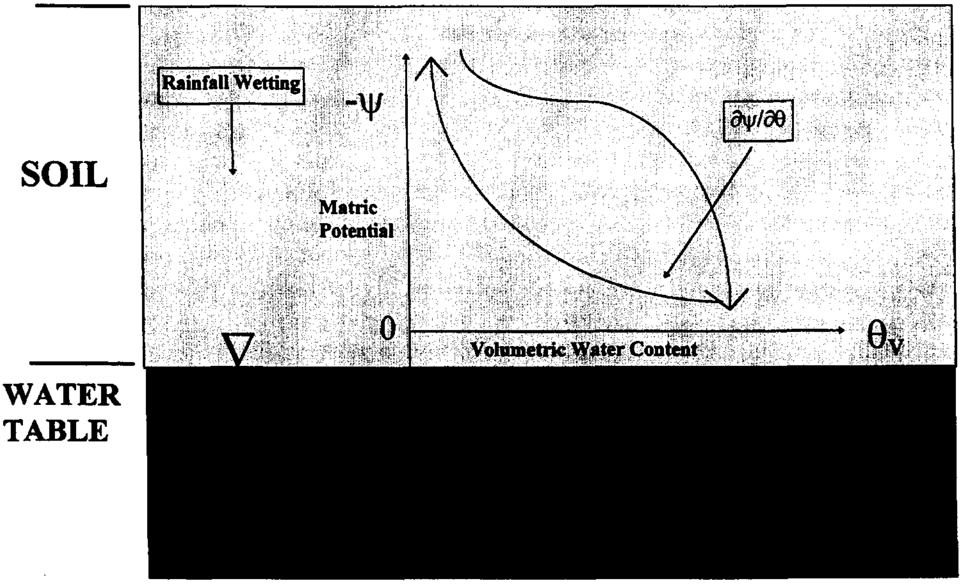


Fig. 5. Relationship between volumetric soil moisture content and matric potential in the capillary-fringe zone above a water-table surface.

depend on the most recent soil moisture history of the site. Rapid mobilization of organic or NH_4^+-rich water within micropores of the soil matrix (within the capillary fringe), and subsequent upward transport this N-rich water to the stream channel, needs to be investigated in the field.

The rapid change from capillary to phreatic water in areas of rapid water-table response could lead to the concurrent mobilization of subsurface water previously in a different redox state (i.e. anoxic or near-anoxic). High concentrations of NH_4^+ and organic N, representative of pre-event or "old" water, might be quickly mobilized into dynamic surface storage, or to surficial peat layers (Heathwaite and Ross, 1987), along with other chemical indicators of a reducing environment (e.g. higher pH, elevated DOC, S^{2-} and Fe^{2+} concentration, etc.). A sudden flush water of higher pH from the subsurface, with higher NH_4^+ concentration, could also stimulate nitrifying bacteria within more oxidized surface layers. This could result in an increase in the concentration of NO_3^- in surface water. In this regard, hypotheses concerning capillary fringe effects are an attempt at understanding the rapid movement of "pre-event" water to stream channels through saturated riparian zones. How this "pre-event" or "old" water interacts with "event" or "new" water to give a predominant "pre-event" signature (in terms of water age), is an area of active investigation. Novakowski and Gillham (1988) demonstrated a disproportionate rise in water table in low-lying areas during an event on the Canadian Shield, while recent studies on a wetland in Ontario refuted this observation (Hill and Waddington, 1993; Waddington et al., 1993).

McDonnell (1990) has shown that macropore flow involving preferential flowpaths around root channels and bedrock–soil interfaces can also evoke a rapid water-table response. In fact, the measured water-table response was as large or greater than in many studies in which it was attributed to the presence of a capillary fringe (Fig. 6). In addition, hillslope-derived water was well-mixed, indicating a possible interaction between micropore and macropore waters. Similar findings of macropore-induced rapid water-table rise, as well as old–new water mixing have been reported by Peters et al. (1995), and reviewed by Germann (1990). The hydrologic and biogeochemical influences of macropores in low-relief stream valleys may be limited during times of maximum saturation. In support of this, Gerla (1992) noted that the rise in a wetland water-table may have been limited by the presence of large macropores in a wetland in Wisconsin. The possibility of such macropore flow being important to N movement and mobilization in near-stream areas may come into play when there is extensive drying of peat layers and subsequent cracking of the surface. In addition, formerly glaciated areas (e.g. the Canadian Shield region of eastern and northern North America) are often characterized by extensive boulder fields, abundant erratics, and shallow-rooted trees, all of which could contribute to the preferential movement of hydrologic "event" water and rapid N-movement downslope. Models describing the movement of N species through different biogeochemical zones in such an environment would need to account for this heterogeneity.

Under snowmelt conditions, there is a large and prolonged input of water somewhat uniformly distributed over the landscape, with subsequently uniform and rapid surface saturation with spring thaw. Recent work by Buttle and Sami (1992) suggests that surface depression storage of meltwater (in hummocks and surface channels) played a large role in regulating streamflow in a catchment on the Canadian Shield, even in areas with extensive

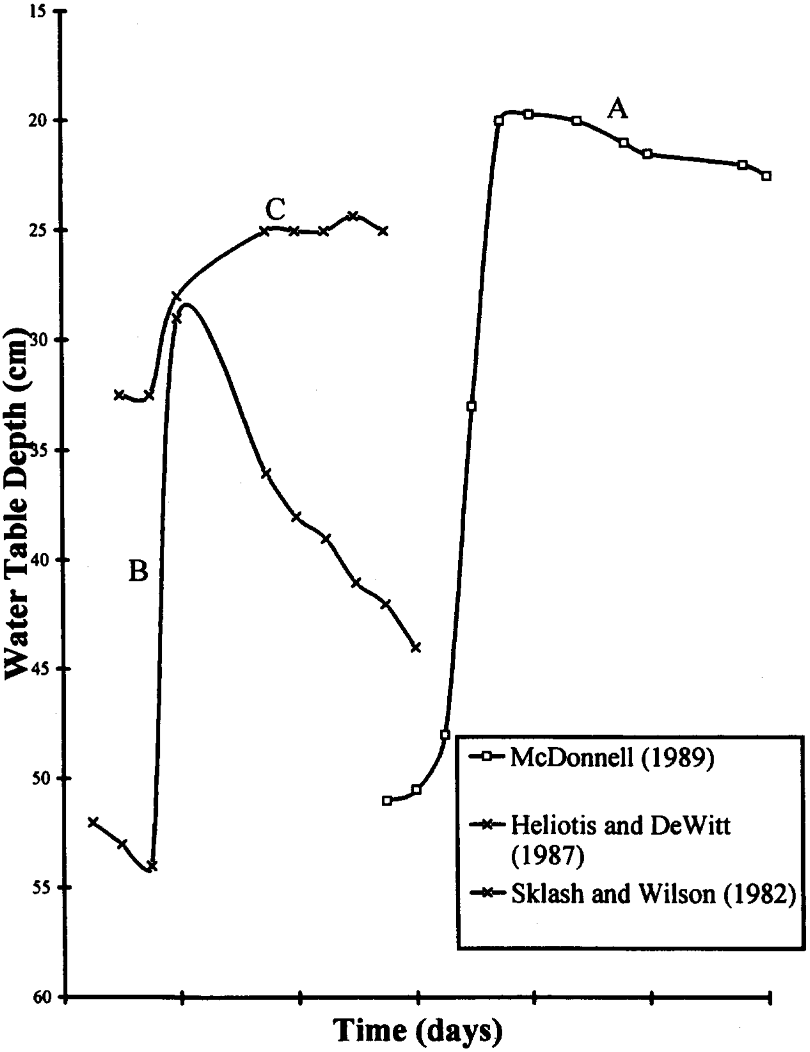


Fig. 6. Measured water-table response to hydrologic events for studies invoking a macropore bypassing (A) and capillary fringe response (B and C); (modified after McDonnell, 1989).

saturated zones. It would seem reasonable that filling the storage compartment within wetlands and saturated zones allows precipitation water the opportunity to react and mix with underlying soil water, formerly in a reducing redox state. Nitrate from atmospheric or snowmelt input may have the opportunity to interact with anoxic zones which move upward with the water-table surface. In a near-stream riparian zone within a watershed in Northeast Vermont, Titus et al. (1995) demonstrated that considerable mixing occurred between overland flow and groundwater, both along the overland flowpath and in and around hummocks, while en route to the stream channel.

Work done on a riparian forested wetland area in a small watershed in southern Ontario has assisted in identifying mechanisms important in the determination of the flowpaths and N-reaction pathways in a wetland complex (Hill, 1990, 1993; Warwick and Hill, 1988; Hill and Waddington, 1993). These studies moved from a whole-catchment perspective on N transport, through site-specific stream investigations, to a determination of wetland soil-N utilization rates, and finally to detailed investigations of the flowpaths and reaction pathways in the saturated zone. The denitrification potential of the substrate beneath small rivulets in the wetland were found to be low (Warwick and Hill, 1988). Attempts were then made to identify water source and vertical/horizontal N-chemistry from isotopic signatures and piezometric information (Hill, 1990). The identification of three distinct water sources in the wetland included: a) well-oxygenated surface water, feeding preferential flowpaths, created by decaying logs and litter; b) sub-surface flow, originating deeper but travelling for some distance within the organic soils; and c) deeper groundwater, originating in a regional flow system through deeper till, contributing to both the wetland surface and stream water. These findings suggest that water sources have distinct and evolving NO_3^- and NH_4^+ signatures which can vary both vertically and horizontally, depending upon their specific flowpath. Results revealed that deep groundwater gained both NO_3^- and NH_4^+ during its travel upward to the wetland surface. Also, a narrow boundary of low dissolved oxygen and NO_3^- was observed within the profile (Fig. 7). Similar studies that include measurements of the dynamic in-situ response of the water-table, along with real-time monitoring of the soil moisture-content change with matric potential in wetland soils and peat, will aid in attempts to understand the dynamics of hydrologic response coupled to N biogeochemistry.

4.3. *Stable isotopic ratios as a tool in saturated zones*

The use of stable isotopic signatures (e.g. ^{18}O) as a water-source tracer has aided investigations of event and pre-event water mixing on hillslopes. Nevertheless, their use in the saturated near-stream zone and in wetlands may be complicated by complex hydrologic and biogeochemical mixing from, as yet undetermined, pools of "old" water within the zone. Isotopic hydrograph separation techniques for water "sources" have been used in areas of extensive surface saturation (Buttle and Sami, 1992; Hill and Waddington, 1993). These studies revealed that standing water in hollows can obtain a distinctly "pre-event" isotopic signature. However, as pointed out by Buttle (1994), it is the operation of "a number of in-channel, down-valley mechanisms and factors that are distinct from the hillslope-scale processes...which may exert an important control on the isotopic signature seen at the basin outflow." In this way, assumptions about the biogeochemistry of N and its fate and movement at hydrological interfaces must account for the last biogeochemical environment encountered in order to adequately describe the observed N-signature. The determination of intracompartmental flowpaths and biogeochemical evolution pathways using $\delta^{18}O$ and δD, may be obscured by both the timing and site of sampling in the field (Buttle, 1994). Also, ^{18}O and D only truly provide information on runoff sources and say nothing about flowpaths. A stable isotopic ratio of a non-conservative species (e.g. $\delta^{13}C$) is needed before any flow history information may be determined. The isotopic signature of the non-conservative chemical species in question (in this case, $\delta^{15}N$ of the N species

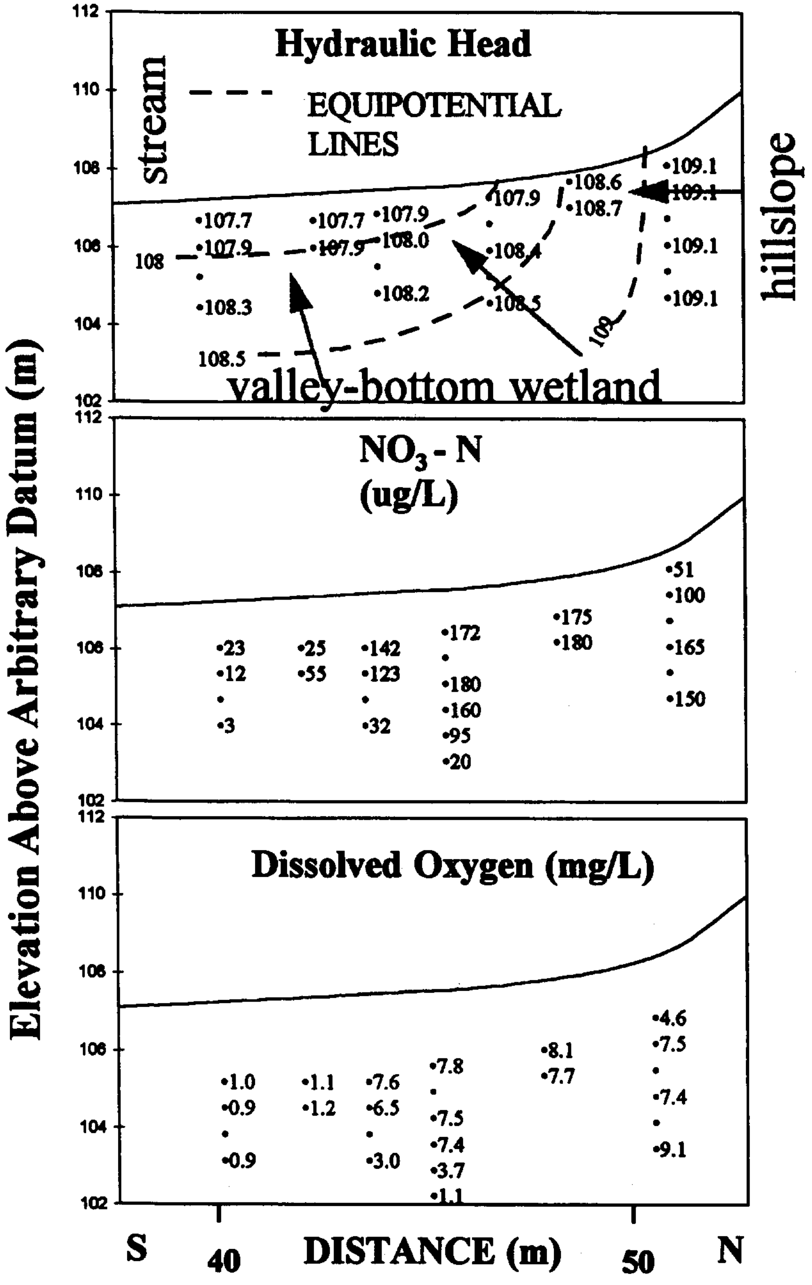


Fig. 7. Depth profiles of (a) hydraulic nitrate (c) dissolved oxygen in the near-stream zone of an Ontario, Canada wetland (modified from Hill, 1990).

involved or the $\delta^{18}O$-NO_3^-) is amenable to at least qualitative determinations of biogeochemical source or environment (Durka et al., 1994; Kendall et al., 1995). Nadelhoffer and Fry (1988) have suggested that different pools of soil N can be similarly discriminated since surface soil and litter layers have lower $\delta^{15}N$ values than subsurface soils. This may be the result of differences in litter layer decomposition processes (Mariotti et al., 1980; Karamanos et al., 1981). Soils on lower slopes have also been shown to have higher $\delta^{15}N$ values than those on well-drained soils, owing, hypothetically, to higher rates of denitrification in the more poorly drained saturated zones (Karamanos et al., 1981; Shearer and Kohl, 1989).

The ability to further discriminate the actual source of NO_3^- (e.g. atmospheric NO_3^- versus soil-derived NO_3^- from bacterial nitrification of soil NH_4^+) has been enhanced by using the combined $\delta^{18}O$ and $\delta^{15}N$ signatures of NO_3^- in various surface and subsurface waters (Durka et al., 1994; Kendall et al., 1995). Preliminary results indicate that the method is useful in discriminating sources of N during snowmelt (Kendall et al., 1995) and for comparing healthy, undisturbed forested watersheds, to disturbed and acidified watersheds (Durka et al., 1994). The major challenge to investigators using this technique includes identifying changes in flowpaths as reflecting biogeochemical environment. This may assist in efforts to elucidate near-stream zone N biogeochemistry and hydrology.

5. Near-stream/saturated-zone hydrological and biogeochemical nitrogen modelling

Generally, biogeochemical modelling (of N, for example), and field studies of hydrologic pathways, are not well coordinated (McDonnell et al., 1993). For any given catchment, the spatial and temporal variability of hydrological and biogeochemical environments, along with the position of the saturated zone in relation to drainage water, should play a large role in controlling the release of N. Owing to the kinetic control of many biogeochemical processes involving microbial communities (particularly for N transformation) the biogeochemical composition of waters may be largely a function of residence time, especially within areas which have a high diversity of microenvironments. Residence time within a "hydrologic unit" (e.g. wetland, riparian zone, hyporheic zone, etc.), "effective" soil:water ratios, and antecedent soil/matrix moisture conditions, are all factors which need to be incorporated into models linking hydrologic flowpath and biogeochemical pathway. The findings of Robson et al. (1992) in Plynlimon, Wales, indicate that the chemical compositions of all flowlines may be reset in the riparian zone of the stream. These zones are not chemically inert, and likely impart a unique chemical signature on water from various sources. As an illustration of the modelling of a non-conservative solute, Hornberger et al. (1994) tested a hypothesis concerning sources of dissolved organic carbon (DOC), by delineating three compartments which might be end-member sources of variability, including the riparian/hyporheic zone. In this model, temporal variations in DOC concentration in the upper-soil layer were accounted for as a simple function of time and temperature, and successfully connected to a hydrological component of the submodel describing the temporal variations in flow amounts through the upper-soil horizons. Such an approach may prove useful to attempts at modelling contributions to the N signature of streamwater from vertically or longitudinally different biogeochemical environments within the near-stream saturated zone. One could designate the redox "boundary" (between oxic and anoxic environments) as an upper limit to NO_3^-, NH_4^+, or organic-N transport, and incorporate a temporally variable hydrological submodel describing variations in water-table level and antecedent soil moisture.

Pinay and DeCamps (1988) developed a model describing an agricultural riparian zone of a large river in France, incorporating the seasonal and hydrologic variations expected to affect the cycling of N in these saturated zones (Fig. 8). In this model, ammonification of organic N and subsequent diffusion of NH_4^+ are considered to control nitrification rate, and, indirectly, denitrification rates. The model was applied to various hydrologic conditions including a) a zone containing an aerobic surface layer which was never submerged, b) a zone of fluctuating inundation and submergence, and c) zones permanently inundated. Results indicated that the intensity and duration of flooding was a controlling factor, and that denitrification capacity was quite heterogeneous and rarely achieved in any of the riparian zones studied. An expansion of this conceptual model to incorporate stormflow volumes linked to water-table response in a forested watershed would be a useful initial effort at linking both groundwater and surface-water hydrology to the functioning of these zones. A simulation model presented by Brown (1988) attempted to directly link site hydrology to nutrient dynamics for wetlands. This model used the coupling of a hydrologic submodel with nutrient uptake processes. Although this model was constructed to represent most of the hydrologic and N-transformation processes discussed in this paper, it did not explicitly address the complications presented by the subtle hydrologic flowpaths present at the interface between terrestrial and aquatic ecosystems (e.g. rapid water-table rise, macropore flow, groundwater ridging, etc.). Creed and Band (1995) simulated N release from a watershed based upon both temporal and spatial variations in the saturation deficit of the catchment. Their results indicated an N-flushing mechanism whereby N was flushed from an accumulation pool in the upper-soil layer. This is similar to the successful modelling of DOC flushing described by Hornberger et al. (1994). This conceptual flushing model holds promise for modelling the dynamic spatial and temporal link occurring in saturated zones in regards to N.

6. Scenarios for consideration in near-stream/saturated-zone nitrogen dynamics

In Fig. 9, we illustrate some hypothetical temporal profiles of biological activity, streamflow and stream concentrations of N species, based on a cross-section of studies within the saturated near-stream zone of a typical headwater stream in a temperate-zone forested catchment.

Following the assumptions implicit in these profiles (following the template presented in Fig. 2), four scenarios involving theoretical hydrologic phenomena discussed in this paper, are presented in Fig. 10. The scenario presented in Fig. 10(A) represents a rapid water-table rise when the capillary fringe extends to the wetland surface. Hypothetically, this situation would allow little interaction and little-to-no mixing of event and pre-event water. In addition, the wetland surface is depicted as being relatively flat, where the effects of topography would be minimal, and microtopography-microenvironment would control

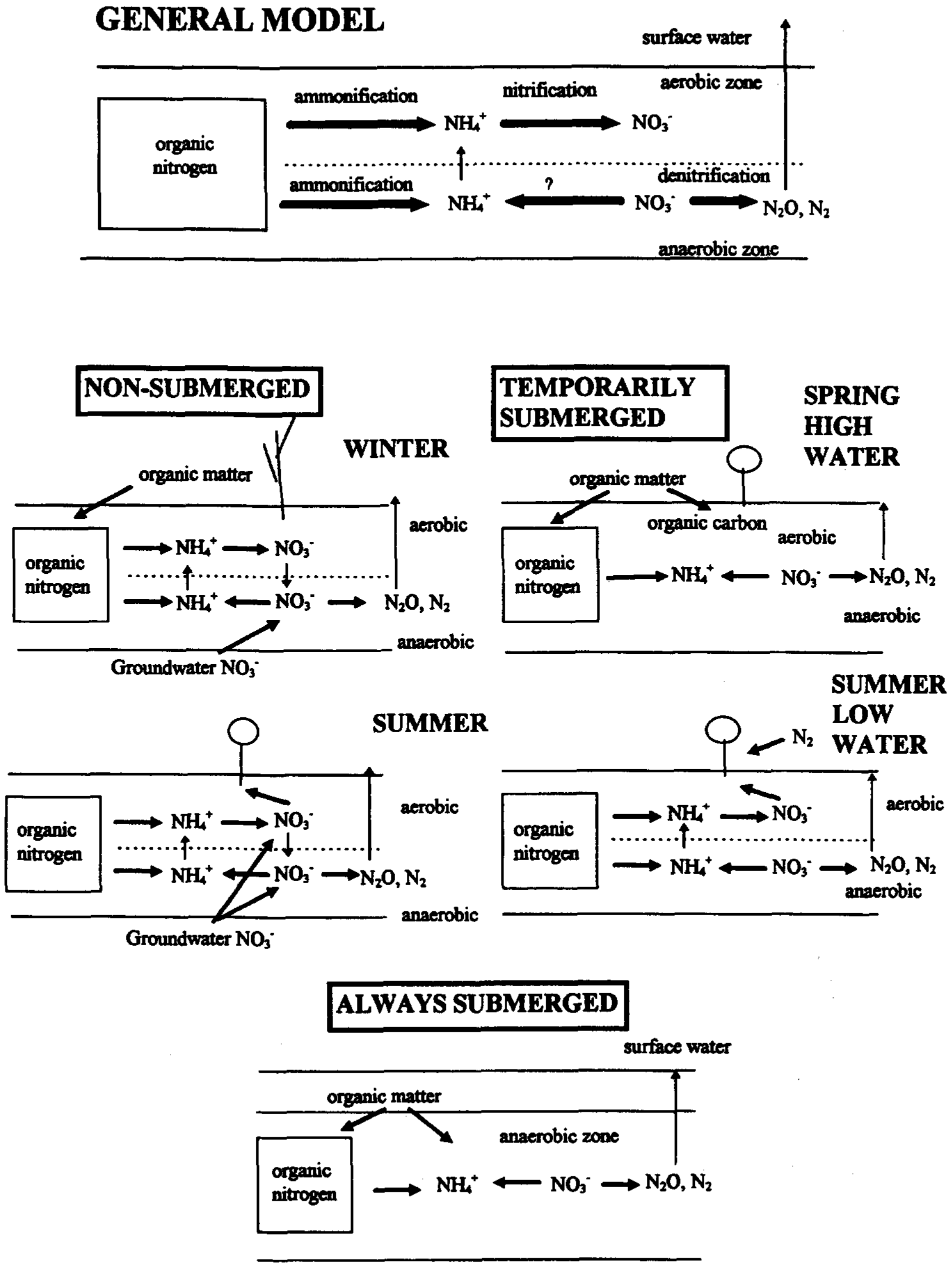


Fig. 8. Hydrological and biogeochemical model of nitrogen cycling and transport in an agricultural riparian zone in France (modified from Pinay and DeCamps, 1988).

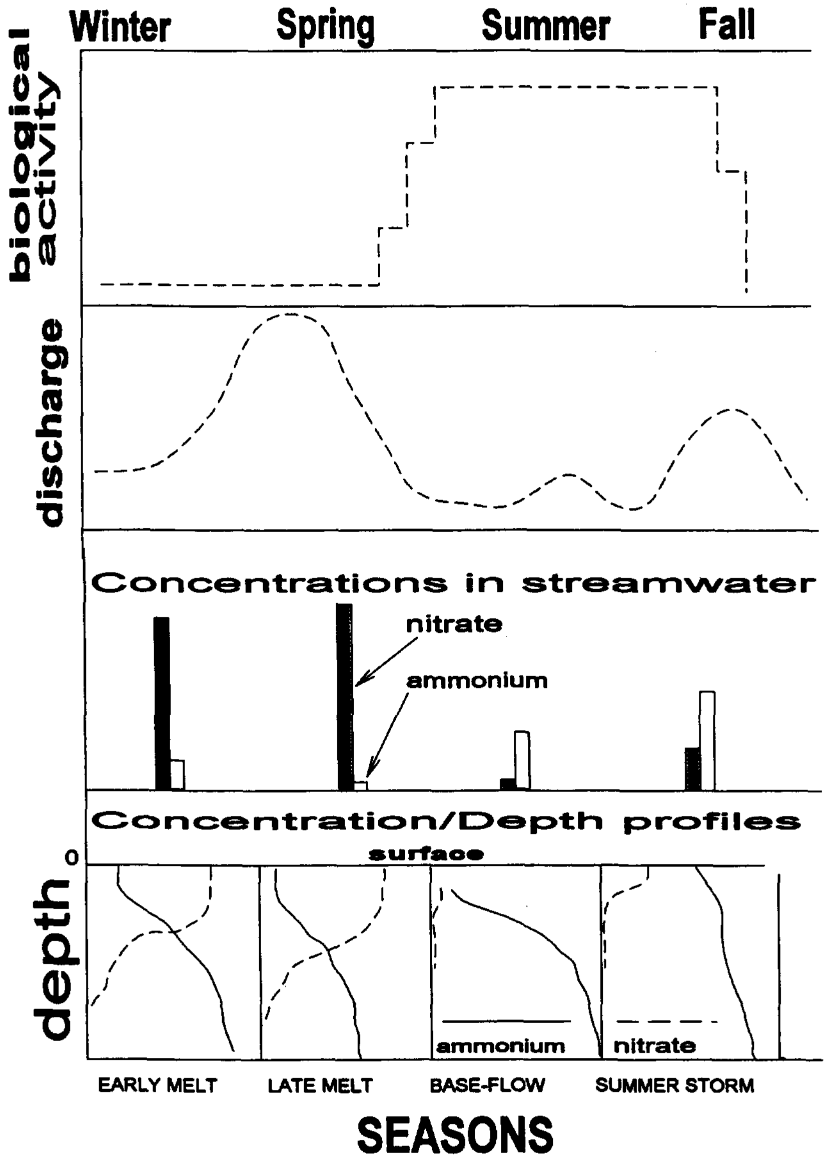
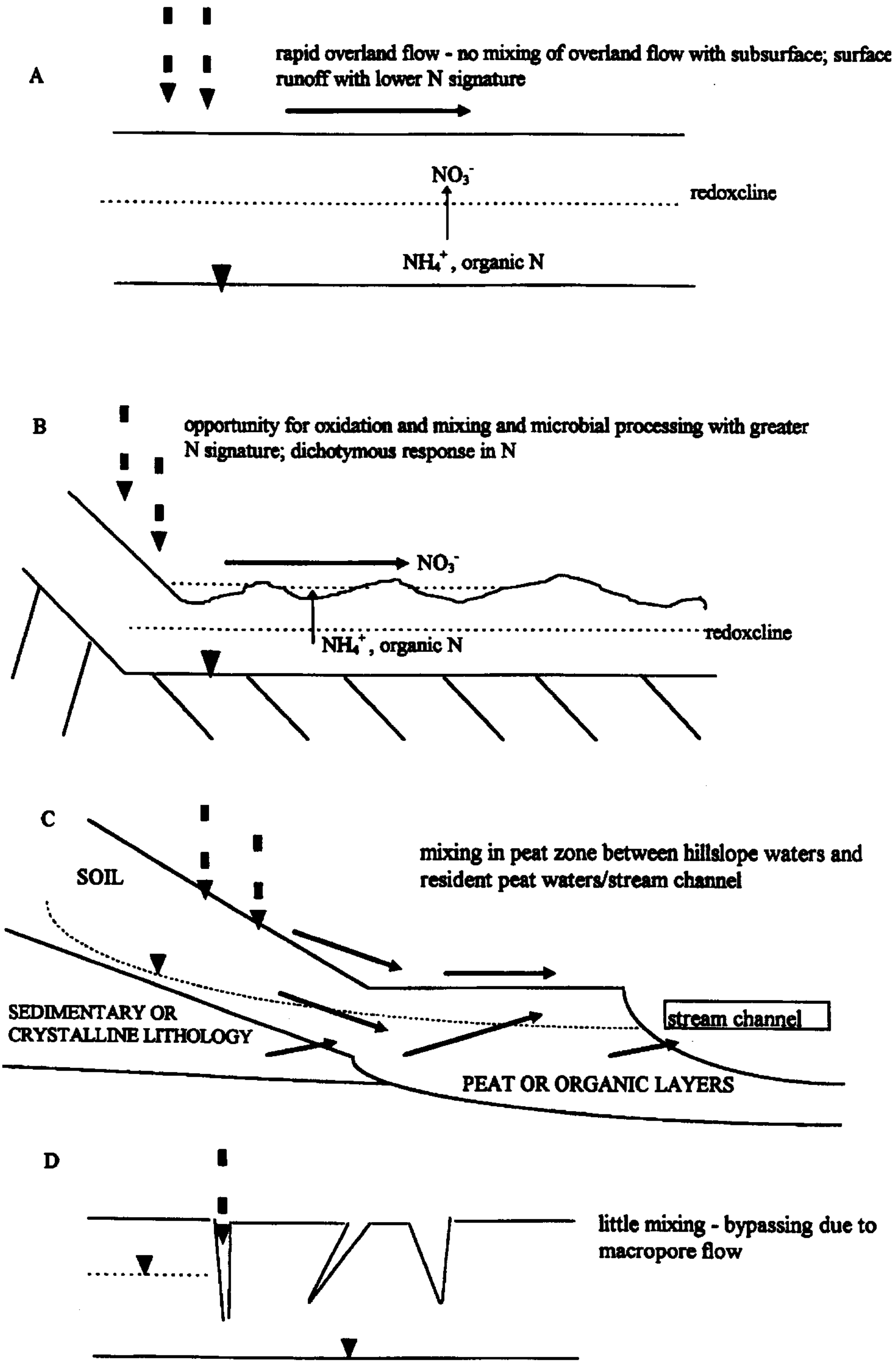


Fig. 9. Hypothetical profiles of: (a) biological activity; (b) stream discharge; (c) streamwater nitrogen concentration; and (d) depth nitrogen concentration profiles through the seasons in a northern temperate-zone stream.

Fig. 10. Scenarios representing theoretical hydrological and nitrogen biogeochemical responses of various near-stream environments to hydrologic events. (A)–(D) as described in text.


A
rapid overland flow - no mixing of overland flow with subsurface; surface runoff with lower N signature
NO_3^-
redoxcline
NH_4^+, organic N
B
opportunity for oxidation and mixing and microbial processing with greater N signature; dichotymous response in N
NO_3^-
redoxcline
NH_4^+, organic N
C
SOIL
mixing in peat zone between hillslope waters and resident peat waters/stream channel
SEDIMENTARY OR CRYSTALLINE LITHOLOGY
stream channel
PEAT OR ORGANIC LAYERS
D
little mixing - bypassing due to macropore flow

N dynamics. Rapid saturation overland flow would likely occur, along with a rapid rise of the redoxcline. This would, in turn, allow the accumulation of reduced N-components (e.g. organic-N and NH_4^+), and subsequent rapid wash-out of surface N to the stream channel. Rapid mobilization of N from the wetland, with little retention of N inputs, would be predicted. In this situation, the near-stream zone might be considered a net source of N to receiving waters. A lag time in the appearance of reduced N-species in the receiving stream might also be noted, depending on the width and saturation depth of the near-stream wetland. In Fig. 10(B), we depict a rapid water-table response within a near-steam wetland with hummocky topography. In this situation, depression storage and mixing of event with pre-event N-species would occur. Sufficient time would be available to allow the oxidation of reduced N-species from deeper soils. Not only would downstream N concentrations rise at a slower rate, but opportunities for N retention and loss owing to denitrification might also exist. A dichotomous stream N-signature might be expected, with initially lower N-input, but with increasing event N-signature owing to the filling of depression storage and commencement of saturation excess overland flow.

Hillslope–wetland boundary dynamics that might occur during a hydrologic event, before water is mobilized to the stream channel, are shown in Fig. 10(C). In this case, watershed inputs of N from uplands are allowed to mix before entering the stream, with a combination of (1) flow over the surface in the near-stream zone, (2) upland water, and (3) pre-event soil water. Both crystalline and sedimentary lithologies are possible in the underlying hillslope bedrock environment. A variable response would be anticipated, depending on reservoir size and antecedent moisture conditions in both the upland and wetland. Much would also depend on the presence of glacial deposits (till, outwash, etc.) which may be a source of older water to the stream channel. Changes in saturated hydraulic conductivity of the wetland soil, along with more-rapid flow through more-transmissive surficial layers could allow a predominant pre-event water signature, along with mobilization of N from deep storage within the wetland. In addition, more time for nutrient transformations might be available in the saturated zone, depending on initial water-table height and flowpaths. Consequently, the near-stream zone might be a net sink for N. In a layered sedimentary lithology, deeper groundwater seepage along bedding planes and fractures might allow additional inputs of deeper and older groundwater. This scenario would be characterized by variable N responses during storms, depending on the concentration of N in, and the volume of, deep groundwater inputs. The scenario depicted in Fig. 10(D) constitutes a short-circuiting or bypassing of the near-stream zone along cracks, root channels or along the bedrock–soil interface (macropore flow). In this example, an immediate increase in N concentration of streamwater might be expected, including an increasing event-water N-signature.

It is possible to discuss the changes in antecedent hydrologic conditions for these scenarios, in relation to hypothetical seasonal and event changes typical in forested watersheds. Water-table drawdown during late summer, early fall, or during drought periods, with subsequent drying of surficial soil and peat, might result in the mineralization of accumulated organic-N. Surface soils and peat high in organic N would be oxidized through increasing exposure to oxygen and higher temperatures, resulting in the potential accumulation of NO_3^-. This accumulated NO_3^- might be mobilized rapidly by a rising water-table or saturation excess overland flow and storage within the riparian wetland.

This scenario could also result in rapid nitrification of any previously stored NH_4^+ at depth in an anoxic layer, particularly in hummocky topography. A temporary increase in NO_3^- release from wetlands or saturated zones around streams and lakes, might also occur. Another consequence of drying or draw-down of the local water-table would be a change in the physical properties of the soil or peat matrix (Chason and Siegel, 1986), including cracking and hardening of the surface, bulk density reduction, and possible macropore formation through cracking and shrinkage of the peat matrix (Jones and Crane, 1984). Alterations in the physical matrix would likely produce changes in hydrologic flowpath and the development of preferential flow along macropore conduits (McDonnell, 1990). Indeed, peat soils have been shown to expand and contract with associated ground-surface movement noted by Ingram (1983). Depending on hillslope antecedent moisture conditions and saturated-zone water-table response, hydrologic events could then elicit a large flush of inorganic N from the system.

Nitrogen may accumulate in the subsurface of saturated zones during seasonal water-table drawdown during periods of minimal biological uptake of N (e.g. in early to mid-autumn in northern-temperate zones), along with residual accumulation of N from litter decomposition and increased soil temperature (during the open canopy period). Subsequent mobilization of this accumulated N by wetting up later in the season and through the winter, could lead to higher N-concentrations in stream water during these periods. A pulse of NO_3^- could result during a time when it is less likely to be biologically assimilated. In this example, the biotic control of N may be decoupled seasonally from hydrology.

7. Conclusions and recommendations

Increases in anthropogenically induced atmospheric N-deposition have stimulated a number of studies examining increased surface-water acidification and possible N-based downstream eutrophication. Numerous studies have indicated that the near-stream zone of saturation can effect an increase in N retention, transformation, or transport. Nevertheless, the interaction between hydrologic flowpath and biogeochemical pathway in saturated/near-stream zones has only recently been addressed. These ecological zones of transition, or ecotones, constitute surface-water–groundwater interfaces where the biogeochemical environments controlling the fate of N change rapidly on the timescale of hydrologic events. Factors that affect the hydrologic routing and transport of N in these zones include: a) antecedent wetness conditions; b) soil/peat physical and nutrient status; c) proximity to the channel; d) vertical stratification of redox zones and microbiological communities which control N speciation; e) biological uptake and net retention of N. In addition, near-stream variable source areas typically control the stormflow hydrologic response of upland forested catchments and are the sites of rapid water-table response owing to capillary-fringe-induced groundwater ridging, macropore flow or return flow during saturation overland flow. Consequently, this zone is dynamic, both in its hydrologic response and biogeochemistry.

Hydrologic routing through a variably saturated biogeochemical environment constitutes an area of uncertainty in regards to efforts at watershed modelling of the controls of N transport. There is a need for future studies to track the spatial and temporal routing of water through the hydrologic transition zone in diverse topographic, geologic and hydrogeomorphic settings in order to allow prediction of the effects of changing land-use patterns on N transport. In this paper, we have presented four scenarios of near-stream saturated-zone N dynamics, and have illustrated hypothetical temporal profiles of biological activity, streamflow and stream concentrations of N species. We hope that our review, and these examples, may serve as a catalyst to unite the hydrological and biogeochemical community to link predictions of N attenuation (both biotic and abiotic) with seasonal, event-based and spatial variations in the hydrologic environment in forested catchments.

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