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# A Review of the Hyporheic Zone, Stream Restoration, and Means to Enhance Denitrification

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- 1 A Review of the Hyporheic Zone, Stream Restoration, and Means to Enhance Denitrification
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20 Abstract

21 The hyporheic zone is the subsurface area below and adjacent to a stream where groundwater 22 mixes with stream water, through vertical, lateral, and longitudinal flows. The hyporheic zone 23 connects the stream to uplands and other terrestrial environments. It is a zone of distinct faunal 24 communities, high biological diversity and ecological complexity, and is the site of chemical 25 processing and transformations of ground- and stream waters. The hyporheic zone is important to 26 the overall ecosystem ecology of the stream, and it can influence stream water chemistry. Flows, 27 reactions, and biota in the hyporheic zone are heterogeneous and patchy, making it difficult to 28 clearly describe the ecotone in a straightforward, general way. Nitrogen processing, especially 29 denitrification, appears to be widespread in the hyporheic zone.

The hyporheic zone, as with most aquatic systems, is often impacted by human activities. Stream restorations rarely consider potential effects on the hyporheic zone, but careful project choices can enhance the condition of the hyporheic zone, and so increase uptake of nitrogen by stream-associated environments as partial mitigation of continuing and increasing releases of reactive nitrogen, potentially reaping short-term benefits to estuarine environments that might not be as quickly realized from source control measures.

#### 37 1. The Hyporheic Zone: Definition

38 The hyporheic zone is the area below and adjacent to the streambed where surface water and 39 groundwater mix (Fig. 1). It is not at one single, easily defined place, but rather is a diverse set of 40 elements (Boulton et al. 2010) that define an ecotone (Williams et al. 2010), and its attributes 41 vary considerably over time and space (Williams 1993; Poole et al. 2006; Kaser et al. 2009; 42 Zlotnik et al. 2011), so that its defining attribute may be its dynamism (Boulton et al. 2010). It is 43 also difficult to monitor so as to produce data with wide applicability (O'Connor and Harvey 44 2008). Because the hyporhetic is an often overlooked, underappreciated element of the 45 environment, we begin with a general discussion of the traits of this ecologically important area. 46 This lengthy exposition of hyporheic zone attributes and its ability to host denitrification will 47 support details of hyporheic zone impairments, and the means by which the hyporheic zone can 48 be remediated, especially to promote denitrification. Other reviews in this journal (Birgand et al. 49 2007; Garcia et al. 2010; Kadlec 2012) have addressed aspects of the growing aquatic nitrogen 50 pollution problem, and it is our intention to supplement this literature. Potentially, this body of 51 work will affect management decisions relating to restorations, although it has been noted that 52 few stream restorations are directly shaped by scientific research and reports (Bernhardt et al. 53 2007).

The hyporheic zone has been described differently in terms of its hydrology, geochemistry, and ecology. Hydrologically, the hyporheic zone is the interstitial spaces adjacent to the stream bank and below the streambed that are saturated and contain some portion of channel water (White 1993), especially when modified to "<98% stream water and >10% groundwater" (Triska et al. 1989b; Boulton et al. 2010). Water quality that results from mixing stream and groundwater in the subsurface can be distinct from both (Fraser and Williams 1998; Hill et al. 1998; Hayashi

60 and Rosenberry 2002), and can be further modified by biologically-mediated redox reactions 61 (Jones and Holmes 1996; Storey et al. 1999). The hyporheic zone was first identified as a region 62 with unique biota (Orhigdan 1959), some associated with streams or groundwater (Boulton 63 2007), but many others that are distinctive (Boulton et al. 2010). The sum of conditions create a 64 transition area between two distinct ecological regions, and it has been suggested (Williams et al. 65 2010) that it fits the definition of an "ecotone" (Odum 1971). Water flow is the dominant driver 66 of most processes, and so here the hyporheic zone is almost always considered as the mixing 67 zone for groundwater and stream water.

# 68 2. Hyporheic Zone Attributes

#### 69

# 2.1 Hyporheic Zone Hydrology

70 A useful simplification is to consider that essentially all baseflow of streams was once 71 groundwater (Williams 1993; Winter 2000; Hayashi and Rosenberry 2002; Sophocleous 2002), 72 although it is clearly not true in all particulars (e.g., Seitzinger et al. 2006). The subsurface is key 73 for stream flows and, generally, flow through the hyporheic zone is from groundwater to surface 74 water. At some point bankward and downward from the stream, all flow is classified as being 75 "groundwater;" but, at the stream-sediment boundary, assuming permeable sediments create 76 hydraulic conductivity, there is bidirectional flow between stream and sediments (Triska et al. 77 1993), even if only driven by diffusive flows.

Any small difference in pressure between subsurface and surface water causes interchange between them: upwelling zones where subsurface water enters into the stream; and, downwelling zones where stream water enters the hyporheic zone. These zones can range from cm<sup>2</sup> to km<sup>2</sup> in area (Reidy and Clinton 2004), although most are limited in extent (Runkel et al. 2003). Under steady-state conditions, discharge dominates at stream banks and the streambed closest to the

bank, so that downward hyporheic flow is most likely near the center of the streambed; residence
time in the subsurface is less near banks and greatest at the streambed center (Boano et al. 2009).
Most stream reaches are comprised almost entirely of discharging zones (Conant 2004), although
continuous areas of discrete upward and downward flows increase downstream (Gooseff et al.
2006).

88 Flows originating in the stream can be oriented longitudinally (along the stream path) or 89 laterally into the stream bank. Small vertical head differences between the stream and the 90 subsurface waters create longitudinal flows (Williams, 1993; Holmes et al. 1996; Olsen and 91 Townsend 2003). The standard model for steady-state flows has head-driven inflows at the top of 92 riffles and outflows (including groundwater discharges) concentrated at the foot of riffles and the 93 head of pools (Williams 1993; Hill et al. 1998; Hayashi and Rosenberry 2002; Kaser et al. 2009). 94 Transitory changes in stream conditions (including flooding of previously dry areas) from 95 phenomena including run-off from precipitation, snow-melt, larger scale flooding, and/or spates 96 from dams, can create significant head differences over larger areas (Poole et al. 2006; Boano et 97 al. 2007; Kaser et al. 2009; Maier and Howard 2011). Such "event flows" may actually define 98 most flow conditions in many streams.

Longitudinal flows can be also initiated by flow-driven pressure differences on bedforms, with upstream faces serving as points where surface water enters the subsurface (Thibodeaux and Boyle 1987); this is called "advective pumping" (Worman et al. 2002), and was first described by Vaux (1968) analytically. Thus, increased flow rates in the stream can drive greater exchange (Fraser and Williams 1998), without any changes in surface water-subsurface water head differences. Pressure variations associated with turbulent flow can be sufficient to cause hyporheic exchange even in the absence of substantial bedform relief (Packman et al. 2004). The

106 frequency of bed sediment reworking means particular bedform conditions may not be 107 maintained at any one location over any long period of time (Dole-Olivier et al. 1997; Fowler 108 and Death 2001; Fischer et al. 2005; Poole et al. 2006; Boulton et al. 2010; Robertson and Wood 109 2010; Stubbington 2012), underscoring the dynamic nature of the phenomenon. 110 Lateral flows may be driven by transitory elevated stream heights (creating "bank storage"), 111 follow paleochannels across flood plains, or be created by head differences between meanders in 112 the stream path (Triska et al. 1993, Wroblicky et al. 1998; Sophocleous 2002; Cardenas 2008, 113 2009). Hill et al. (1998) also attributed lateral flows to head differences stemming from riffle-114 pool sequences (which create differences between stream and subsurface water elevations) and 115 considerable flow appears to occur parallel but outside of stream channels – in the "alluvial" 116 aquifer (Poole et al. 2008). Lateral flows have been less studied due to their longer residence

117 times (Runkel et al. 2003). Most studies of lateral hyporheic flows focus on meander-driven

118 flows, which appear to be greatest from hinge points, and may be persistent even in settings with

119 large groundwater discharge rates (Cardenas 2009). Channel sinuosity leads to variable and

120 irregular flows through point bars, too (Cardenas 2008). Horizontal flow rates, whether lateral or

121 longitudinal, span a wide range from 1 cm d<sup>-1</sup> to 43 m d<sup>-1</sup> (Kaplan and Newbold 2000).

Bank storage is a special kind of hyporheic zone feature. Bank storage is created when stream water absorbs into side sediments, often because stream levels rise faster than water tables following precipitation (Gulley et al. 2011). This dynamic storage returns stored water as water levels fall in the stream, buffering stream flow rates. Some bank storage can be formed through subsurface flows in the vadose zone associated with precipitation. Although bank storage is often connected to the water table, it is more a stream than groundwater feature

(Brunke and Gonser 1997). More bank storage occurs when stream flows are larger and where
sediment hydraulic conductivity is greater (Wroblicky et al. 1998).

130 Most flow in the subsurface is downstream (Poole et al. 2006) with a hierarchical mixture of 131 long and short flow paths that have different residence times in the subsurface (Fig. 2) (Poole et 132 al. 2008). These paths result from the synchronous mixtures of processes that are primarily 133 vertical (along the flowpath of the stream) or horizontal (across meanders) and result from the 134 heterogenous distributions of sediments (Liao and Cirpka 2011). This means that "mean" or 135 "median" measures of residence may be misleading, as the range (minutes to months to years) 136 (Harvey and Wagner 2000; Reidy and Clinton 2004) is affected by whether flow is through, say, 137 a ripple or across a major meander. 138 The amount of stream water in a reach that enters the hyporheic zone has been estimated over 139 several orders of magnitude, from  $\ll 1\%$  to as much as 460% (Jones and Holmes 1996; 140 Burkholder et al. 2008), partially because of the undefined length of a "reach", but also because 141 factors affecting hyporheic exchange are so variable. High sediment conductivity, streambed 142 roughness, and low groundwater pressures result in more surface water exchange, and fine bed 143 sediment and high groundwater pressures result in much less exchange (Duff et al. 2008). 144 Surface water tracer experiments often generate substantial "tails" (retarded tracer not advected 145 with general stream flows), which has been interpreted as evidence of much mixing between the 146 stream and subsurface (Worman et al. 2002). A model of a New England river estimated 50% of 147 run-off entered the hyporheic zone at least 2.5 times, but also found a 3:1 ratio for time in the 148 main channel to time in the hyporheic zone (Stewart et al. 2011).

149 **2.2 Hyporheic Zone Geochemistry** 

150 Interactions between surface waters and the subsurface can lead to geochemically-driven 151 changes in important stream attributes (Bencala 1983). Redox chemistry, the set of reactions 152 requiring electron acceptors (these molecules become "reduced") and electron donors (these 153 moelcules become "oxidized"), is key. Carbon (C) in its various forms plays a key role in redox 154 reactions in biologically active systems. In the presence of  $oxygen (O_2)$ , the compound most 155 likely to become reduced (accept electrons) is O<sub>2</sub>. In the absence of O<sub>2</sub> (lower redox states), other 156 compounds act as terminal electron donors. As redox potentials decrease, the electron acceptors 157 that become thermodynamically favored are, in order: nitrate  $(NO_3)$  to dinitrogen  $(N_2)$  or 158 ammonia (NH<sub>3</sub>); manganese from valence state +4 to valence state +2; iron from valence state 159 +3 to +2; sulfate  $(SO_4^{-2})$  to sulfide  $(HS^{-})$ ; and carbon dioxide  $(CO_2)$  to methane  $(CH_4)$ . Most 160 redox reactions are microbially-mediated (Hedin et al. 1998). 161 In shallow flow groundwater systems, the groundwater usually has short residence in the 162 subsurface and typically is well-oxygenated (Gold et al. 2001; Storey et al. 1999) because it 163 usually does not contain great enough dissolved organic carbon (DOC) concentrations to support 164 sufficient metabolism to consume much O<sub>2</sub> over short periods of time (Gold et al. 2001). 165 Therefore, it is often only older groundwater associated with longer, deeper flow paths that may 166 be anoxic (Malcolm et al. 2003; Robertson and Wood 2010) and can support redox reactions 167 using terminal electron acceptors other than O<sub>2</sub>. 168 It is generally assumed that stream waters are well-oxygenated (Robertson and Wood 2010), 169 although low dissolved oxygen (DO) surface water conditions can be created behind natural or

- 170 artificial dams or in backwaters and channels, where organic matter accumulates and water
- 171 advection is low (Baker et al. 2000). Therefore, absent any local biological consumption of O<sub>2</sub>,

downwelling zones (stream water) are usually better oxygenated than upwelling zones(groundwater).

Hyporheic flow paths are thought to encounter enough organic C to support sufficient
respiration to deplete O<sub>2</sub> in the shallow subsurface (Jones and Holmes 1996); generally,
hyporheic zone O<sub>2</sub> concentrations are inversely related to residence time (Findlay 1995). This,
combined with increased contributions from groundwater, means upwelling water is often much
lower in DO than downwelling water.

179 The location of the hyporheic zone at the interface between the upland and the stream 180 suggests it will affect stream chemistry, especially nutrient dynamics. The hyporheic zone is a 181 transition from open water to water-sediment conditions; in it, electron donors and acceptors 182 change over a patchy mosaic; and, parcels of water appear to cycle back and forth in and out of 183 the zone. These factors produce effects on overall stream chemistry (Hedin et al. 1998; Dahm et 184 al. 1998; Baker et al. 2000). The assumed presence of a redox gradient associated with DO 185 depletion allows the hyporheic zone to be considered a geochemical "hot spot," where changes 186 in redox conditions in the presence of diverse chemical substrates (associated with sediments or 187 in solution) fosters chemical transformations (Hedin et al. 1998), particularly denitrification 188 (Baker et al. 2000). One by-product of respiration is CO<sub>2</sub>, and so pH values in the hyporheic 189 zone are often different from both groundwater and the stream (other reactions, many enhanced 190 by sediment-water connectivity, can also result in pH changes) (Runkel et al. 2003). The 191 distribution of reaction sites is spotty over both time and space (Hedin et al. 1998); shifts in 192 subsurface flows due to changes in stream or groundwater flows can cause relocation of reaction 193 sites. These shifts may be predictable, especially if seasonal patterns (flood, drought, 194 precipitation) are the drivers of changes in flow (Dahm et al. 1998).

195

# 2.3 Hyporheic Zone Biology

It is difficult to disentangle the chemistry of the hyporheic zone from its biology; in addition,
stream remediation project managers often focus on biological attributes, including invertebrate
populations which depend on hyporheic conditions (Bernhardt et al. 2007; Lake et al. 2007).
Thus, we will briefly discuss some of the more notable biological attributes of the hyporheic
zone.

201 The hyporheic zone serves two important, overt ecological purposes for stream fauna: refuge 202 for invertebrates in times of disturbance; and prime egg incubation sites. Both stem from the 203 perceived greater environmental stability of the hyporheic zone compared to open waters 204 (Orghidan 1959), a function of water velocity and temperature. Water velocity decreases upon 205 entering the hyporheic zone, by factors as much as 10<sup>-3</sup>, compared to surface water (Brunke and 206 Gonser 1997), creating shelter for stream invertebrates when water column currents increase 207 (Boulton et al. 1998). Krause et al. (2011) describe temperature as the "master variable" that 208 controls all other hyporheic zone processes. Water temperature fluctuation is generally less than 209 in surface waters, and its variability decreases with increasing depth and distance from stream 210 water infiltration sites (Brunke and Gonser 1997). Thus, the asynchronous pulses of water from 211 the hyporheic moderate stream water temperatures: on short time scales night time lows are 212 warmed, and daytime highs are reduced; on longer flow paths, hyporheic flows equilibrate with 213 groundwater temperatures, further mitigating daily or seasonal temperature fluctuations (Poole et 214 al. 2008). Careful measurements of temperature changes in streams have even been used to 215 quantify hyporheic exchange rates (Westhoff et al. 2011). Consistent temperatures are 216 advantageous for salmonid spawning, and subsurface temperatures are more constant in 217 upwelling zones (van Grinsven et al. 2012).

218 Organism sheltering generally occurs in downwelling areas, allowing benthic populations to 219 rapidly recover from events (Dole-Olivier et al. 1997), although major floods require longer 220 recovery periods (Maier and Howard 2011). Stubbington (2012) notes refuge utility is a function 221 of interactions between sediment types, taxon, the kind of disturbance, and whether the flight 222 from disturbance is active or passive, so that *which* organisms seek refuge *where* and *when*, 223 while determinable, is not consistent. In addition, at least some of these disturbance events affect 224 the hyporheic environment, altering the refuge and its functionalities (Boulton 2007; Robertson 225 and Wood 2010).

226 Changes in sediments, water flows, and associated conditions make the hyporheic zone a 227 patchwork of small, differentiated habitats. Broad generalizations of benthic sediment patterns, 228 for instance, might include downwelling gravel patches at the head of a riffle, upwelling gravel 229 areas dominated by hyporheic flows at the riffle foot, with upwelling groundwater immediately 230 adjacent (although perhaps associated with finer sediments of the pool), and other areas of 231 sediment and flows associated with meander erosion (Boulton 2007).

232 Hyporheic zone organisms include microbes (Findlay and Sobczak 2000), meiofauna 233 (Hakenkamp and Palmer 2000), and macrofauna (Boulton 2000). Most faunal characterizations 234 concentrate on insect instars (transient members of the ecosystem) (Boulton et al. 2010). For 235 many biologists, the hyporheic zone is defined by the class of micro- and macro-invertebrates 236 called "hyporheos": crustaceans, segmented worms, flatworms, rotifers, water mites, and 237 juvenile stages of aquatic insects (Williams and Hynes 1974). The eggs and alevin of salmonid 238 fish are also members, and often are the focus of hyporheic zone management programs; the 239 areas they live, excavated and then backfilled by adults, are "redds" (Environment Agency 240 2009). Differences in overall hyporheos distributions are a function of DO (Hakencamp and

Palmer 2000), but also are affected by grain size variations and vertical flow patterns (Olsen andTownsend 2003).

Bacteria are important elements of the hyporheic zone ecology, and can create biofilms. Biofilms foster the creation of micro-environments – small anaerobic zones in otherwise oxygenated settings, for instance – that appear to be required for reactions such as denitrification (Storey et al. 1999). Biofilms create specialized environments due to expressed enzymes and the restricted size of pore space environments, but the supply of nutrients and dispersion of wastes is controlled by the rate of advected waters passing them (Findlay and Sobczak 2000).

# 249 **3.0** Hyporheic Zone Nitrogen Transformations: Research Findings

250 Krause et al. (2011) summarized current research on N in streams, finding it can be 251 transformed, mobilized, or returned to the atmosphere at different rates over relatively small 252 scales, and that these processes differ for particular streams. The concept of nutrient "spiraling" 253 (Webster and Patten 1979) is helpful: it illustrates, in this case, N moving from organisms to a 254 variety of reservoirs, and being carried (predominantly) downstream via diverse pathways, 255 including subsurface routes, with repetitive cycling of flows, forms, mineralization, and 256 organism uptake. The retention of nutrients for at least some time is necessary in order to 257 maintain ecosystem processes in streams, and so the spiraling concept illuminates stream 258 ecological dynamics (Triska et al. 1989a, Ensign and Doyle 2006). In headwater streams, 259 groundwater is the primary source of N, although much N enters the system as organic N from 260 leaf litter and sediment inputs (Duff and Triska 2000). Transformation from organic to inorganic 261 forms is expected, along with considerable lags due to incorporation into organisms or sorption 262 onto sediments, so that the transport of N is considerably delayed along each stream reach 263 compared to a non-reactive tracer (like chloride). Nitrogen spiraling (Mulholland and DeAngelis

264 2000) describes the repeated transformation of N from inorganic to organic forms, and its track 265 from the main body of the stream into sediments. The spiral has "uptake length" (the distance an 266 atom travels before being biologically retained) and "turnover length" (the distance traveled by 267 the atom as organic matter) (Duff and Triska 2000). Hyporheic exchange should reduce uptake 268 length and increase turnover length by increasing interaction between sediments and the water 269 column (Mulholland and DeAngelis 2000). Denitrification is, in a sense, a form of completion of 270 the spiraled pathway as the N-atoms are thus lost to the system.

271

#### **3.1 Denitrification**

273 Denitrification measurements are affected by the development of techniques that accurately 274 capture data but are not universally used. Direct measurements of N2 creation can be made in 275 aquatic systems using gas chromatography, and changes in N<sub>2</sub>:argon (Ar) ratios can be measured 276 using membrane inlet mass spectrometry (Davidson and Seitzinger 2006). However, many often-277 cited papers used the acetylene inhibition technique, which often understates denitrification rates. 278 Acetylene inhibition has great advantages in that it is simple to conduct and can support many 279 measurements over small spaces, which is useful to measure a patchy, inconsistent phenomenon. 280 The method can be confounded by slow diffusion into fine sediments, the presence of sulfide, 281 and insensitivity to low concentrations of NO<sub>3</sub><sup>-</sup>. Wide testing of cores and other disturbed 282 samples instead of making in situ measurements also affects the usability of many acetylene inhibition results (Groffman et al. 2006; also see Powell and Bouchard 2010). Use of N15 tracer 283 284 techniques to track denitrification result in higher estimates of denitrification than would be 285 "expected" for acetylene inhibition approaches, given understandings of how site conditions 286 affect denitrification (Mulholland et al. 2004). Another approach is to track potential

denitrification by inducing conditions that lead to denitrification and measuring losses of N fromthe system, which lead to overestimates of actual denitrification.

289 The necessary elements for hyporheic zone denitrification are subsurface organic C, low  $O_2$ 290 concentrations, and bacterial biofilms to metabolize the organic matter. Surface-subsurface 291 exchange flows create organic C pools from DOM and particulate organic matter (POM). 292 Entrained dissolved inorganic nitrogen (DIN) is then transformed by hyporheic bacteria into N<sub>2</sub> 293 (Boyer et al. 2006; Harvey et al. 2011; Zarnetsky et al. 2011). The hyporheic zone is not uniform 294 in sediment size, O<sub>2</sub> availability, temperature, and other parameters, creating discrete zones of 295 denitrification instead of the entire zone being a  $NO_3^{-1}$  sink (Craig et al. 2010). The controls on 296 denitrification have been found to be different under differing conditions. Sometimes a particular 297 factor (nitrate concentration or carbon availability or grain size) is the variable that best describes 298 differences in rates of denitrification, but often there is a complicated interplay among the factors 299 so that no one parameter can predict changes in nitrogen concentrations. 300 So, for instance, hyporheic zone hydrology and stream N export are linked, but not in a 301 consistent manner (Zarnetske et al. 2011). Generally, increased water residence time in stream 302 environments with suitable denitrification conditions results in increased denitrification rates 303 (Seitzinger et al. 2006; Flewelling et al. 2012; Mayer et al. 2010), a relationship characterized as 304 the Damkohler number (the residence time:reaction time ratio) (Gu et al. 2008a). Thus, at five 305 low gradient, high N concentration streams, residence time correlated with denitrification 306 (Puckett et al. 2008), and comparisons across differing stream conditions found hydrologic

307 residence time increased denitrification rates (Kaushal et al. 2008). Flowpaths where at least 2

308 days were needed to traverse a 30 cm thick zone where denitrifying activity was greatest had

309 complete N-removal; shorter residence times resulted in less N-removal (Flewelling et al. 2012).

310 Generally, it is expected that long hyporheic zone residence times will increase denitrification 311 (Hill et al. 1998), and in many sedimentary environments residence time correlates to flowpath 312 lengths, and the effect of increasing flowpaths is often to reduce N concentrations. Still, 313 denitrification of injected N into a gravel bar was largely completed in 1 hr travel time; very little 314 measurable dentrification occurred farther along the flow paths (Pinay et al. 2009). Most river 315  $NO_3^-$  (60-80%) was removed in the first 50 m of hyporheic flowpaths for a river in a boreal 316 forest floodplain (Cliverd 2008). In the Platte River, depletion of DO occurred not in shallow 317 sediments but 30 cm below the subsurface-stream interface, which was assumed to be the result 318 of denitrification (in part) (Duff and Triska 2000).

319 A process-free model, the transient storage model, has been used for more than 25 years to 320 estimate water retained rather than advected in stream reaches. Strictly speaking, it simulates in-321 stream storage (such as pools and back flows); but its results have been interpreted as including 322 some flow through the hyporheic zone (typically, shorter duration shallow-flow pathways) 323 (Bencala and Walters 1983; Boano et al. 2007). Use of a fluorescent tracer (resazurin) that is 324 transformed by microbial respiration into another fluorescent tracer (resorufin) can differentiate 325 between biologically active and inactive storage areas, and help interpret the degree of hyporheic 326 exchange associated with transient storage (Haggerty et al. 2008; Gonzalez-Pinzon et al. 2012). 327 For some, transient storage poorly explains N processing (Hall et al. 2002; Lautz and Siegel 328 2007) but it has produced good correlations (although these N-reductions may have resulted 329 from benthic not hyporheic functions) (Ensign and Doyle 2005). Denitrification rates were found 330 to be greatest at "separation zones": still pools found in the lee of point bars, where water storage 331 occurs, and greater residence time in contact with fine, organic-rich sediments apparently leads 332 to more sediment denitrification (Opdyke et al. 2006). Alternately, increased flow causes less

333 contact time and creates smaller sediment surface:water volume ratios, and so must result in less 334 denitrification (Ranalli and Macalady 2010). Slowed stream flow was responsible for greater N-335 uptake in a restored stream compared to pre-alteration conditions, with the greatest rates 336 observed in a side pool (Bukaveckas 2007). Conversely, observations at human-impacted 337 streams in the southwest U.S. found that denitrification at these sites was greater than that 338 measured at reference sites, although connectivity and interchange with the hyporheic zone was 339 greater at reference streams (Crenshaw et al. 2010). Thus, Botter et al. (2010) argue that factors 340 other than sediment contact times are also important in determining N-removal efficiencies. 341 One of these is sediment quality. Decreasing sediment grain size theoretically adds to 1) 342 surface area availability for bacteria; 2) overall residence time; 3) in particular, slower transport 343 rates of dissolved N and C through potential reaction sites; and 4) retention of C to fuel reactions 344 (Baker et al. 2000). Fine-grained sediments were associated with greater dentrification in one 345 study (Opdyke et al. 2006), and residence time in the denitrification zone controlled N-reduction 346 extent, with residence time being inversely proportional to sediment hydraulic conductivity 347 (Flewelling et al. 2012). Sediment surface area:stream volume ratios predicted denitrification in 348 small streams (Peterson et al. 2001) and were used to explain N-uptake dynamics (Ranalli and 349 Macalady 2010), under the assumption that benthic processes control denitrification reactions. 350 Stream flow rate variations across seasons (greater in spring, less in winter) controlled 351 denitrification because more water and faster flows decreased contact time with sediments 352 (Alexander et al. 2009). 353 Alternately, availability of  $NO_3^-$  was said to be the major control on dentrification (Duff and

355 Alternately, availability of  $NO_3$  was said to be the major control on dentrification (Duff and 354 Triska 1990); denitrification in high flow downstream areas of the Elbe River were greater where 355  $NO_3^-$  concentrations in the river were higher (Fischer et al. 2005). More commonly,

356	denitrification rates are related but not proportional to available NO <sub>3</sub> <sup>-</sup> concentrations. The Lotic
357	Intersite Nitrogen experiment (LINX II) at 72 streams in 8 US regions used N <sup>15</sup> tracers and found
358	that denitrification increased with $NO_3^-$ concentrations, but the efficiency of the reactions
359	decreased, meaning the relative proportion of N removed was less in higher NO3 <sup>-</sup> streams.
360	Smaller streams lost efficiency more rapidly than larger streams, perhaps because they remove a
361	"maximal amount" of N, so that downstream larger order streams have unfilled assimilative
362	capabilities (Mulholland et al. 2008). The absolute amount of NO <sub>3</sub> <sup>-</sup> denitrified comparing
363	seasonal flows in two streams was greater under higher NO3 <sup>-</sup> concentration conditions – but not
364	proportionally to increases in inputs (Alexander et al. 2009). Nitrate concentrations in streams,
365	when comparing agricultural, urban, and forested land uses, were greatest in the agricultural
366	areas, and denitrification rates were also greatest in agricultural area stream sediments. But,
367	increases in denitrification did not compensate for increases in N, so stream reaches leaving
368	agricultural and urban areas had higher NO <sub>3</sub> <sup>-</sup> concentrations (Inwood et al. 2005).
369	Carbon is essential to denitrification, but it may not be the rate-determining factor, either
370	considered theoretically (Bardini et al. 2012) or through extensive measurements (Bohlke et al.
371	2009). Generally, the amount of C in sediments has been found to regulate denitrification, as C
372	is needed to fuel reactions that consume DO. It is also needed for the metabolic reactions that
373	cause denitrification, so that C concentrations were the best correlation for denitrification in one
374	urban setting (Mayer et al. 2010). Augmenting subsurface C where both groundwater and stream
375	water had low $NO_3^-$ concentrations increased denitrification rates (Triska et al. 2007). Sediment
376	instability in the Elbe River meant C concentrations were well distributed with depth, and so
377	high denitrification rates were measured throughout the hyporheic zone. Denitrification rates
378	were lower outside of the main channel where sediment C concentrations were lower (Fischer et

al. 2005). When stream  $NO_3^{-1}$  concentrations exceeded half of the saturation concentration,

380 sediment C content was a good predictor of denitrification rates. At less than half-saturation

381 concentrations, stream NO<sub>3</sub><sup>-</sup> concentrations best predicted denitrification rates (Arrango et al.

382 2007).

383 At least one study concluded denitrification was controlled by temperature (Alexander et al. 384 2007) but no temperature effect was found by Triska et al. (2007). Because the hyporheic zone 385 buffers temperatures, most likely temperature is usually not a dominant factor affecting 386 denitrification processes. Nonetheless, seasonal effects (seasons correlate to temperature 387 changes) were found where lateral flow through a gravel bar resulted in some denitrification, 388 especially in summer (Deforet et al. 2009). However, flow rate variations and/or groundwater 389 inputs appeared to be the underlying cause of a seasonal component in denitrification rate 390 differences for two streams draining agricultural areas (Bohlke et al. 2009). A seasonal effect 391 was associated with snowmelt flooding, which had been expected to increase N exports from a 392 high gradient mountain stream, but because the higher flow rates increased hyporheic exchange, 393  $NO_3^{-}$  removal rates were much higher during floods. Although the mass of N exported was 394 greater, it was not proportional to the increase in flow (Hall et al. 2009). Seasonal differences in 395 flows and nitrate inputs, based on a regression on 300 published measurements, were found to 396 explain differences in N removal (low flow and low N-inputs resulted in higher N-removal rates) 397 (Alexander et al. 2009). Daily fluctuations in N-removal in open waters were found, but this was 398 related to fluctuations in both  $NO_3^-$  and C concentrations due to photosynthetic organism 399 elemental cycling (Heffernan and Cohen 2010) rather than diurnal temperature patterns; open 400 water conditions often affect subsurface conditions with a time delay.

401 Some studies have tried to capture the apparent interplay among multiple factors. So, a 402 forested area had increased denitrification; this was linked due to increased debris inputs, which 403 slowed stream flows and increased organic matter content on the stream bottom (although it was 404 not determined if the N was lost at the stream-surface sediment interface or in the hyporheic 405 zone) (Weigelhofer et al. 2012). A study of 18 streams found links among seasonality,  $NO_3^{-1}$ 406 concentrations, sediment C content, and denitrification rates. Sediment C was the best predictor 407 of denitrification rates, but stream  $NO_3^-$  concentrations were highest in winter, when the greatest 408 denitrification rates were measured. Agricultural land uses resulted in higher stream  $NO_3^{-1}$ 409 concentrations compared to urban areas (Arrango and Tank 2008). Biological activity was 410 increased with warmer water in summer, but denitrification was greater in winter due to 411 increased available N from greater groundwater discharge rates. The flux of denitrified N per 412 unit streambed area was inversely related to hyporheic flow rates, suggesting that residence time 413 was important, and, denitrification was higher for areas with finer sediments (which also 414 contained more C) (Bohlke et al. 2009). 415 Denitrification mechanisms create some of these complications. Biofilms generate zones 416 where local conditions can vary tremendously from bulk water states. This is a potential mechanism for patchy biochemistry, such as denitrification; this is true even though there are 417 418 general oxidizing states in the overall flow line (Mulholland et al. 2004). Variations at these 419 small scales fit with accounts of sudden changes in  $NO_3^-$  concentrations over distances <1 m

420 (Storey et al. 1999); if small, idiosyncratic single sites are determinants of reactions, notions like

421 the Damkohler number that apply to bulk conditions (Gu et al. 2008a) would not be pertinent,

422 although remaining descriptive of changes in water quality at the reach scale.

423 Downwelling zones are hotspots for denitrification (Holmes et al. 1996). Highest 424 denitrification rates were found in these areas, although rates can be inhibited by higher DO 425 concentrations associated with downwelling, and short residence times make it difficult for 426 microbial respiration to deplete the available DO. Denitrification was minimal in upwelling 427 zones due to a lack of  $NO_3^-$  (Storey et al. 2004). In an N-rich agricultural stream, downwelling 428 areas resulted in losses of DO and NO<sub>3</sub><sup>-</sup>, while more anoxic upwelling areas transported NH<sub>4</sub><sup>+</sup> 429 from groundwater to the stream (albeit in reduced concentrations), so that the hyporheic zone 430 was a sink for  $NO_3^-$  and a source of  $NH_4^+$  for the stream (Hill et al. 1998). Similarly, in a gravel 431 bed of an NO<sub>3</sub><sup>-</sup>-rich stream denitrification rapidly commenced as DO was reduced below 1 mg L<sup>-</sup> <sup>1</sup>, and NH<sub>4</sub><sup>+</sup> concentrations increased (Peyrard et al. 2011). 432

433 Floods enhance denitrification, as they increase flow through the hyporheic zone and expand 434 its extent (Cliverd 2007); however, they also have the potential to reduce reactions by changing 435 biochemical conditions - "washing out" the needed redox state (Gu et al. 2008a), which also 436 may occur with high flow-high groundwater conditions (Ranalli and Macalady 2010). Low flow 437 conditions correlated well with higher denitrification rates in Baltimore. The water table was 438 closely linked to stream flow rates, so that head in the aquifer decreased with decreased flow, 439 causing less hyporheic discharge, and greater hyporheic zone residence time – thus, greater 440 denitrification (Mayer et al. 2010).

In a desert stream, nitrification and denitrification occurred in the subsurface; denitrification rates were higher in the banks than the sub-benthic hyporheic sediments (Holmes et al. 1996). A modeling solution of bedform-induced flows suggested that in the flow cells created by hyporheic exchange, the shallower portion of each cell would be a nitrifying area and the deeper portion would denitrify. Consumption of DO (due to available C) would determine the relative

proportions of each (Bardini et al. 2012). And, at one stream where denitrification occurred in
the hyporheic zone, the hyporheic zone (as determined by comparisons to groundwater
chemistry) was very shallow and was not the locus for most denitrification of the incident
groundwater. More denitrification occurred below the hyporheic zone, as O<sub>2</sub>-rich groundwater
became depleted of DO, after coming into contact with buried organic C. Therefore, only
tracking hyporheic zone processes may lead to underestimates of total subsurface reactivity
(Stelzer et al. 2011).

453 Generally, despite recent advances in theory (Botter et al. 2010) and field techniques 454 (Haggerty et al. 2009), because hyporheic exchange rates are often not well-defined over larger 455 scales, quantifying the impact of the hyporheic zone on N-attenuation is difficult beyond single site evaluations (Krause et al. 2011). Reports of large reductions include 12 mg N L<sup>-1</sup> to 0.1 mg 456 L<sup>-1</sup> over 30 cm of flow path (Gu et al. 2008b), 21% removal of total inorganic N over the entire 457 458 river network (nearly 75% removal by all river processes) (Stewart et al. 2011), 30% of NO<sub>3</sub><sup>-</sup> 459 additions removed in a 300 m reach (Triska et al. 1989b), differences of >80% between 460 groundwater N concentrations (approximately 15 mg N L<sup>-1</sup>) and stream water concentrations (mean of 2 mg N L<sup>-1</sup>) (Gu et al. 2007), and overall losses of N in the subsurface in the vicinity of 461 462 90% (by various mechanisms that varied with depth) (Lansdowne et al. 2012). High 463 denitrification rates (2.0-16.3 mg m<sup>-2</sup> h<sup>-1</sup>) were reported for agricultural streams in three varying 464 settings (but note NO<sub>3</sub><sup>-</sup> concentrations increased over the reaches due to larger inputs from 465 groundwater) (Duff et al. 2008).

466

#### 3.2 Nitrification

467 Nitrification occurs when bacteria oxidize  $NH_3$  to  $NO_3^-$  (Hedin et al. 1998); conditions that 468 allow for nitrification include the presence of: 1)  $O_2$ ; 2)  $NH_4^+$ ; and 3) a carbon source (to allow

for bacterial growth and reproduction) (Triska et al. 1993). However, nitrifying bacteria are
relatively inefficient, and so on theoretical grounds alone will only constitute a small portion of
microbial production compared to other heterotrophs (Storey et al. 1999). There have been
reports that the hyporheic zone is an area of net nitrification, transforming organic N or NH<sub>3</sub>-N
to NO<sub>3</sub><sup>-</sup> (Boulton et al. 1998).

Generally, subsurface waters have higher  $NH_4^+$  concentrations than surface waters do. This suggests, given overall subsurface to surface transport, that the hyporheic zone generally nitrifies some  $NH_4^+$  (Baker et al. 2000). Triska et al. (1993, 2007) describe the organic-rich subsurface therefore as a patchwork of zones where nitrification and denitrification occurred discretely, depending on the species of N and the redox status of the sediments.

479 Nitrification requires relatively large amounts of O<sub>2</sub> to occur, and so nitrifiers may be an 480 important link in the reduction of DO that may allow for denitrification. Coupled nitrification-481 denitrification will only occur with a substantial change in redox potential (from +200 mV to -482 200 mV), which implies a change in time and distance; however, these kinds of coupled 483 reactions appear to occur across short distances in sewage plant trickling filters, which use 484 biofilms to treat sewage, and so it has been hypothesized similarly linked reaction sites could 485 exist in the interstices of the hyporheic zone (Storey et al. 1999). This apparently was the case 486 for one stream where pressure dynamics changed the extent of the hyporheic zone so that it often 487 extended beyond its "permanent" depth. When the zone was extended, NO<sub>3</sub><sup>-</sup> concentrations 488 sometimes increased in the stream, and sometimes decreased – suggesting that the particular 489 relations between nitrification and denitrification were contingent on small local variability 490 (Krause et al. 2009). A modeling study suggested that the upper portion of flow in the hyporheic

491 zone would support nitrification, while deeper flows would be more likely to result in 492 denitrification (assuming needed distributions of N-species, C, and DO) (Bardini et al. 2012). 493 In an anthropogenically-impacted, N-limited, losing, desert stream, NO<sub>3</sub><sup>-</sup> concentrations 494 increased following hyporheic zone residence, with the largest increases in  $NO_3^{-1}$  concentrations 495 being found in the summer at the head of the flowpath (Holmes et al. 1994). The hyporheic zone 496 was also found to be a net source of  $NO_3^{-1}$  in the alluvial system of an arctic tundra stream 497 (Greenwald et al. 2008). In a stream with low DIN concentrations, organic N (as DOM and 498 POM) was first ammonified and then nitrified; there was no measurement of denitrification, 499 although DO concentrations decreased along the hyporheic flowpaths. All reactions appeared to 500 occur within the first 10 cm of flow (Harvey et al. 2011). Nitrification was found to be affected 501 by temperature, much more so than denitrification, so that with low temperatures, net 502 denitrification was found, and high temperatures led to a net increase in  $NO_3^-$  (Triska et al. 503 2007). Concurrent nitrification and denitrification were measured in the Elbe River; nitrification 504 occurred in sediments closest to the bank, and declined with sediment depth due to decreasing 505 DO concentrations (Fischer et al. 2005).

Jones and Holmes (1996) suspected that hyporheic zones in N-poor streams are generally a NO<sub>3</sub><sup>-</sup> source, and hyporheic zones in N-rich streams act as an N sink. Duff and Triska (2000) agreed nitrification is more important in low-N streams, but thought nitrification was a pathway to transform organic N to forms that could subsequently be denitrified, as part of subsurface metabolic processes. Arrango and Tank (2008) measured substantial nitrification in agricultural streams with high NO<sub>3</sub><sup>-</sup> concentrations, and the occurrence of peak nitrification did not accord with peak denitrification, suggesting no explicit linkages.

# 513 **4. The Riparian Zone and the Hyporheic Zone**

514 Although the riparian zone is imprecisely defined, for many it excludes classic wetlands with 515 open water (swamps and marshes) (sensu Mitsch et al. 2012). Rather, it is characterized by 516 specific vegetation communities and is physically located between uplands and the stream. 517 Underground water flow in the riparian zone tends to be dominated by groundwater (surface 518 water inputs from bank storage or infiltrating flood water can be important at times), and riparian 519 zone water tables tend to be very shallow (within 1-2 m of the ground surface) (Dahm et al. 520 1998; Hill 2000; Kaplan et al. 2010). The hyporheic zone is not defined by any surface 521 vegetation features, and so there can be some overlap between these two features. Typically, 522 some bank storage and lateral flows between meanders have been classified as both hyporheic 523 and riparian zone waters (Duval and Hill 2007; Pinay et al. 2009); some prefer not to distinguish 524 between the two processes (Vidon et al. 2010).

525 Riparian zones are often found at the base of hills, where the surface topography intercepts 526 the water table, or, at least, comes close to doing so. There is often an accumulation of fine, C-527 enriched sediments at the base of the slopes (Hill et al. 2004). The flatter portion of the riparian 528 zone should accumulate C-rich sediments from flood overflows, which should increase closer to 529 the riverbank (Kellogg et al. 2005). Riparian zones have been identified as hot spots for 530 denitrification (Holmes 2000), although these denitrification zones are often only meters wide 531 (McClain et al. 2003), often at the uphill edge of the zone (Schipper et al. 1993), and at or near 532 the groundwater discharge point into the stream, as well (McClain et al. 2003; Flewelling et al. 533 2012). Hydric (low redox state) soils, created by high organic content, low  $O_2$  transfer rates from 534 the ground surface, and saturated conditions, support denitrification, and are a signature element 535 of riparian zones (Gold et al. 2001). Nitrogen removal from groundwater can be as much as 536 100% for riparian zones (Dosskey 2002), but conditions that lead to substantial denitrification

are patchy and are not found in all shallow groundwater transition zones near streams (Stutter etal. 2012).

### 539 5. Hyporheic Zone Management Issues: Research Findings

## 540 **5.1 Degradation of the Hyporheic Zone**

541 Anthropogenic degradation of the hyporheic zone results because it lies between surface 542 water and groundwater, two resources exploited by humans and both intentionally and 543 inadvertently affected by their activities. Impacts to the hyporheic zone often affect water 544 exchange and may poison bacteria and invertebrates (Hancock 2002). Direct changes to streams 545 and groundwater flows, such as through water withdrawals and discharges, or to physical 546 morphology such as with dams, channeling, and shoreline and bottom hardening cause impacts 547 to chemical and biological functions, too (Pringle and Triska 2000). Indirect effects come with 548 mining activities, urban and industrial discharges, changes in land use, and agriculture and 549 forestry practices, including removal of sediment and/or water, impairment of surface and/or 550 groundwater quality, disruption of hydrological connectivity between the hyporheic zone and the 551 surface and groundwater systems, and changes in hyporheic biota (Boulton 2007). 552 Changing stream flow or groundwater heads will affect the hyporheic zone. Flow patterns are 553 generally defined by head differences (Sophocleous 2002), which are affected by changes in 554 stream conditions and groundwater levels (Packman and Bencala 2000; Gu 2008a). Advective 555 pumping can be increased by higher flow rates (Fraser and Williams 1998). Flooding across 556 previously dry areas (Maier and Howard 2011) or drying of previously flowing areas (Gu et al. 557 2008a, b) can reverse or substantially change hyporheic flow patterns. Lateral flows are also

affected by changes in the stream flow or groundwater head, as these will change bank storage

and may affect the head differences between meanders (Triska et al. 1993; Wroblicky et al.
1998; Sophocleous 2002; Cardenas 2009).

561 Constructing dams can induce channel migration and bank erosion, moving the stream away 562 from its original course, and, as a result, changing relationships with the hyporheic zone. 563 Downstream erosion, a common feature for dams, could reduce the size of the hyporheic zone 564 (Hancock 2002). Dams change sedimentation rates and sediment flushing, which can affect the 565 interstitial spaces of the hyporheic zone. If particulates are trapped by the dam, there may be 566 fewer inputs of organic matter downstream, which could affect microbial respiration rates and 567 geochemical reactions (Environment Agency 2009). Dams can either increase or decrease 568 temperatures downstream, with the controlling factors being the size of the impoundment and its 569 management (Webb et al. 2008); temperature is a key element in hyporheic ecological processes 570 (Krause et al. 2011). Releases of water from dams also change rates by which surface-subsurface 571 exchange occurs; rapid changes resulting from dam spates may not allow organisms to 572 accommodate to the new conditions. In addition, subsurface residence time may be substantially 573 reduced under higher flows (Maier and Howard 2011). Dams also affect general downstream 574 groundwater head levels, and the biology and geochemistry of water from reservoirs can be very 575 different from that in native streams (Pringle and Triska 2000).

Simplification of bedforms and channels due to canalization or other channeling and
constraining of stream flows reduces exchange potentials between the stream and the subsurface.
A smooth stream bottom minimizes advective pumping (Packman et al. 2004; Poole et al. 2006).
A stream with fewer meanders had less lateral flow (Cardenas 2009) and overall less
connectivity with the subsurface (Crenshaw et al. 2010); all of these lead to a reduced portion of
stream water entering the hyporheic zone (Dahm et al. 1998). Fewer stream obstacles mean

582 decreased transient storage (Ensign and Doyle 2005). Straightening channels decreases the 583 overall amount of sediment area per linear distance traversed by the stream, and so decreases 584 water exchange and associated subsurface reactions (Opdyke et al. 2006). In addition, 585 canalization of waterways changes subsurface entry points into the stream, so groundwater may 586 not flow through the riparian zone (Gold et al. 2001). Urban environments are characterized by 587 altered stream channels; in one, Groffman et al. (2005) found that although substantial 588 denitrification appeared to occur, a lack of debris accumulations limited the number of locations 589 where proper reaction conditions could occur. Streams where channels have been modified often 590 have greater erosion rates; locations with higher erosion rates or where flows were constrained 591 and/or straightened, were characterized as being less likely to retain nutrients (Dahm et al. 1998). 592 Mining in a stream basin can add excess silt, introduce heavy metals, and change channel 593 morphological features. Runoff can introduce additional silt to the hyporheic zone leading to 594 colmation (the clogging of interstitial spaces), which limits surface water exchange, and so 595 decreases hyporheic zone  $O_2$  and nutrients. Mining that occurs directly in a stream increases 596 colmation by causing sediment resuspension (Hancock 2002). Overall, the occurrence and 597 amount of colmation is affected by stream bed transport properties, as small differences in 598 velocity affect settling and resuspension (Rehg et al. 2005). Mining activities that change stream 599 pH (by exposing sulfidic minerals) increase dissolved metals concentrations, and could prove to 600 be toxic to the hyporheos (Hancock 2002). The hyporheic zone was shown to immobilize 601 manganese from copper mining in Arizona (Harvey and Fuller 1998) and, because changes in 602 redox zonation occur generally in hyporheic zones and residence time in reactive sediments 603 promotes sorption, generally the hyporheic zone does a fair job in removing many metals of 604 concern from mining waste-impacted groundwater and surface water (Gandy et al. 2007).

Changes in channel geomorphology associated with in-stream mining, such as widening or
deepening of the channel with the removal of sediments, can cause loss of riffle-pool sequences
and river bends, and lower floodplain water levels, thus also changing hyporheic flows (Hancock
2002).

609 Negative impacts to the hyporheic zone from urban and industrial activities come from 610 effluents, stormwater, and other discharges, as well as from groundwater pollution, and general 611 colmation effects. Nutrients from effluents and stormwaters increase N concentrations; 612 discharged metals and organics may affect the hyporheos; and colmation results from excess 613 sediment inputs (Hancock 2002). High levels of sewage-polluted groundwater prompted a faunal 614 composition change in one hyporheic zone (Mallard et al. 1994), a finding which does not 615 support a more general hypothesis that the hyporheic zone can serve as a refuge from pollution 616 for stream invertebrates (Hancock 2002). Inputs of sewage-derived DOM into groundwater 617 systems caused a change in invertebrate community structure to more pollutant-tolerant 618 organisms (Hartland et al. 2011). It is thought that urban environments support a less diverse 619 hyporheic biology that has less production (Environment Agency 2009). Overall, however, 620 determining impacts to biota from pollution is hampered by a lack of detailed information for 621 many subsurface taxa (Hakencamp and Palmer 2000); nonetheless, it has been proposed that 622 larger hyporheic zone organisms would be suitable for use as biomarkers, as their distributions 623 are affected by pollutants in streams (Boulton 2000). 624

Water quality impairments in many streams correlate to the amount of agriculture in the
surrounding basin. Agriculture (including range activities which often affect fluvial landscapes)
and forestry introduce excess nutrients and silt to stream ecosystems, change vegetation
distributions and the physical landscape (including stream morphology and positioning),

628 discharge pollutants of various kinds, and also alter flows in the hyporheic zone through 629 groundwater and surface water extraction (Pringle and Triska 2000). Unregulated forestry has 630 been found to reduce inputs of large wood, alter riparian zone vegetation (leading to hyporheic 631 zone effects), and increase sedimentation (Environment Agency 2009). Any residual poor 632 practices will also have some impacts similar to these. Nutrients may be introduced to aquatic 633 systems through fertilizers, waste from livestock, and ash from forestry waste management. 634 Augmented nutrient levels in streams lead to reduced DO and can change hyporheic conditions 635 from oxidizing to reducing (Hancock 2002). In many agricultural areas adjacent to streams, the 636 streams are physically modified (channelized and tiled) to drain high water tables or encourage 637 run-off to prevent saturated soils; this was found to diminish riparian and hyporheic cycling of N 638 (Triska et al. 2007), and also affected the general ecology of the impacted streams (Freeman et 639 al. 2007). Anoxic conditions associated with stream degradation may increase denitrification, a 640 potential environmental benefit, but only if net N removal equals or exceeds N inputs (Boulton et 641 al. 1997).

642 Agriculture and forestry can increase colmation. Generally, the loss of riparian vegetation 643 (from field expansion or livestock browsing or trampling) can lead to bank collapse, burying the 644 hyporheic zone and limiting parafluvial exchange. Native riparian vegetation was found to 645 support a more diverse and abundant hyporheos than pasture land (Boulton et al. 1997). 646 Deforested riparian areas have narrower streams with less bed roughness and higher stream 647 velocities. This was thought to lead to lower denitrification rates because of less connectivity to 648 subsurface processes (Sweeney et al. 2004). Livestock moving through streams can affect the 649 hyporheic zone by contributing nutrients through waste, compacting gravel and clogging 650 interstitial spaces, resuspending sediments, and consuming or trampling riparian vegetation

651 (Hancock 2002). Sediment inputs are also increased by near-stream construction (Hester and 652 Gooseff 2010). Erosion generally changes bedform conditions; the introduction of substantial 653 sediments into streams can lead to sand slugs, which, while comprising new hyporheic habitat, 654 are not natural features, and have not proved amenable to restoration projects intending to restore 655 habitat heterogeneity (Lake et al. 2007). Generally, agricultural impacts to streams are thought to 656 result in simplified hyporheic population structures that have less overall production 657 (Environment Agency 2009).

#### 658

## 5.2 Stream Restoration, Nitrogen Dynamics, and the Hyporheic Zone

659 Environmental management requires making selections from a suite of goals, which are 660 developed from identified and sought values and functions for the restoration site. Natural systems do not have such pre-selected goals, per se, although our analyses often impute 661 662 intentions and directions to them. However, when we take steps to undo our effects on a system, 663 we must choose the directions and aims for the project, as our general alterations of the world 664 make it impossible to simply return to pre-anthropogenic conditions.

665 The most common explicit goal for stream restoration projects is to improve habitat for one 666 or more commercial fish species; this is closely related to project rationales to improve habitat 667 for stream macroinvertebrates, either as habitat indicator species or to support the charismatic 668 fish species (Bernhardt et al. 2007; Lake et al. 2007). Often these goals are achieved through 669 alteration of stream morphology (Bond and Lake 2003) – what has been described as the "field 670 of dreams" hypothesis ("if you build it, they will come") (Palmer et al. 1997). Although 671 management programs seeking to increase salmonid fish populations sometimes specifically seek 672 to improve the hyporheic zone, as these species lay eggs and have young fish that live in the top 673 5-50 cm of stream sediments (Environment Agency 2009), even comprehensive stream

674 restoration designs usually do not explicitly address any subsurface hydraulic connectivity issues675 (e.g., Shields et al. 2003).

676 General restoration efforts for stream and benthic habitats can also enhance the hyporheic 677 zone and affect its ability to transform N, even if not implicitly included in project planning, as 678 hyporheic zone improvements are a byproduct of efforts aimed at other goals (Welti et al. 2012). 679 For instance, one common stream restoration approach to improve fish habitat is to flush fine 680 sediment from benthic gravel areas (Arthington and Pusey 2003), which should also improve 681 connectivity into the hyporheic zone. Adding woody debris to streams is another common 682 surface water ecosystem rehabilitation technique that also helps hyporheic zones. If the log is 683 partially embedded in sediment, across a flowpath, this will create two downwelling areas: one 684 just before the water hits the log and another right at the downstream plunge pool. There will 685 also be an upwelling area shortly after the plunge pool (Fig. 3). This should also reduce 686 colmation, which will improve connectivity (Boulton 2007).

687 If the hyporheic zone is a foundation for overall stream health, then its significance in 688 restoration plans is thought to be severely underappreciated (Boulton et al. 2010). To address this 689 failing, the British Environment Agency issued a 250 page handbook on science issues 690 associated with the hyporheic zone. One chapter discussed how common stream restoration 691 efforts affect the hyporheic zone. The addition of in-stream deflectors and large wood was 692 identified as the most common activity (43% of projects). This increases hyporheic exchange, 693 increases subsurface DO, and generally enhances subsurface chemical reactions. It tends to 694 redistribute fauna because of habitat changes. Plantings to enhance fish cover was the second 695 most common restoration technique affecting the hyporheic zone (18% of projects), and was 696 thought to create very local changes in flows, chemistry, and habitats. Bed raising and substrate

697 changes (8% of all projects) increases stream connectivity, could enhance chemical reactions, 698 and could have a major effect on habitat types and distributions. Increasing the sinuosity of the 699 stream (6.5% of all projects) increases lateral hyporheic flows and tends to increase subsurface 700 residence time, and creates more diversity of benthic and hyporheic habitats. Removing 701 dams/weirs (6% of all projects) increases lotic environments and may increase exchange 702 processes but probably decreases overall storage times; it causes major shifts in fauna due to 703 habitat change. Removing artificial banks and beds (5% of all projects) causes a substantial 704 increase in exchange and adds the subsurface-banks as potential habitat zones. Creating riffles 705 (4.5% of all projects) increases exchange rates and subsurface residence time, increasing the 706 potential for chemical reactions, and, at a minimum, relocates subsurface habitats (Environment 707 Agency 2009). Although not explicitly mentioned in the handbook, other improvements to 708 riparian zone conditions, such as plantings or vegetation restoration should also indirectly 709 improve hyporheic zone functions.

710 However, increased connectivity with surface water or groundwater can have negative 711 consequences. Contaminated groundwater can degrade surface water if it is transmitted through 712 the hyporheic zone (Hancock 2002) or contaminated surface water can affect groundwater or 713 hyporheic zone water quality (Environment Agency 2009). Restoring connectivity can also allow 714 invasive species to spread and expose endemic species to new competitors, changing community 715 dynamics (Kondolf et al. 2006). Even increased hyporheic zone denitrification (see below) can 716 have negative consequences: one estimate is that the equivalent of 10% of anthropogenic 717 emissions of nitrous oxide (a potent greenhouse gas) are generated from river denitrification 718 processes (Beaulieu et al. 2011).

719 One broad stream restoration review identified vertical connectivity with the hyporheic zone 720 as an important element in creating proper ecological functions, but no explicit actions were 721 identified to achieve the connectivity goal (Lake et al. 2007). However, a similar review included 722 specific design elements to improve hyporheic zone functions: creating features such as pools, 723 riffles, steps, log dams, bars, meanders, and side channels, along with in-stream placement of 724 debris dams and large wood, and increasing bed complexity (or at least matching historical 725 patterns), coarsening sediments, and restoring the riparian zone (Hester and Gooseff 2010). 726 Stream restoration projects aiming to increase bedform heterogeneity will strengthen 727 connections in longitudinal, lateral, and vertical dimensions and increase surface-subsurface 728 exchange flowpaths, although predictive capabilities for such efforts were said to be lacking 729 (Boulton et al. 2010). Several weir variants (cross vanes and J-hooks) were installed in a New 730 York mountain stream to reduce stream erosion, and also to increase hyporheic zone 731 connections. Temperature testing largely corresponded with modeling of the project, suggesting 732 that design water exchange patterns can be largely achieved in practice (Crispell and Endreny 733 2009). A Nevada project undertaken to restore riparian functions by elevating downcut sections 734 and adding riffles and pools was found to have greater transient storage, as measured by 735 retention time, compared to unrestored areas. Modeling supported longer flow intervals in the 736 hyporheic zone, which suggested denitrification would have also increased (Knust and Warwick 737 2009). Several small weirs (1.5 m high) were constructed in another stream to mimic beaver 738 dams; a complex flow pattern of shallow pools, plunge pools, glides, and riffles with a variety of 739 sediment distributions and bedforms resulted. Indirect measurements (temperature and water 740 chemistry) along with modeling found distinct areas of inhibited and enhanced hyporheic 741 exchange, with evidence of much denitrification found in downwelling zones, and some more in

upwelling areas (Fanelli and Lautz 2008). Conversely, installation of a flat gravel bed, although
conformed to the preferred depths used by salmon for spawning, did not replace lost habitat from
dam construction. Salmon did not use the artificially formed sediments, and it was suggested that
the lack of bedform definition impeded hyporheic flows. Salmon possibly found the space subpar
due to the absence of hyporheic environmental modifications (particularly temperature control)
(Kondolf et al. 2006).

748 Instead of proposing in-stream modifications, Vaux (1968), using analytical solutions of flow 749 equations, determined that subsurface flows could be enhanced by changing hydraulic 750 conductivity in sediments (explicitly intended to increase DO availability for salmon alevins). 751 Structural changes included various high or low conductivity blocks of material, or sheet pilings. 752 Ward et al. (2011) simulated the structural changes proposed by Vaux, and, using reasonable rate 753 values derived from high gradient streams, estimated the impacts on processes such as 754 denitrification, respiration, and temperature buffering from various designs. A template to 755 achieve various effects was proposed. It was noted, on a practical note, that high conductivity 756 subsurface features can be difficult to retain as they will have their effectiveness reduced by 757 sediment clogging, but that some of the same results could be achieved through selection of 758 various low conductivity structures (the functions of which are unlikely to be easily degraded). 759 Currently, there are few broad guides focusing on improving stream N-management, as there 760 are for increasing bank stability and some other stream attributes. One explicit management approach suggested an emphasis on 2<sup>nd</sup> and 3<sup>rd</sup> order streams with low flow rates, calling for 761 762 enhanced C availability and increased transient storage and interchanges with surrounding 763 terrestrial environments (Craig et al. 2008). The program targeted in-stream N, not subsurface 764 concentrations. The low order streams were preferred in accord with N-removal efficiencies

identified by Ensign and Doyle (2006). Carbon enhancement was not selected based on any cited
studies, but rather to ensure stream metabolism was maintained to allow for denitrification.
However, Hartland et al. (2011) determined that enhancing DOM in subsurface environments
caused a change in invertebrate populations to more pollution tolerant species, and so this
remedial approach for N may have unintended consequences.

770 A stream restoration project in Maryland that was intended to decrease stormwater-driven 771 erosion also led to improved N-removal rates. Cobbles and boulders and coarse sediments were 772 set into the stream, and features such as point bars, pool-riffle sequences, and meanders were 773 constructed. The riparian zone had trees planted, and banks were cut to be closer to the stream 774 surface in places. Tracer tests found that mean denitrification rates were twice as high for 775 restored areas as unrestored areas, and groundwater and stream water NO<sub>3</sub><sup>-</sup> concentrations were 776 lower in the upstream restoration areas. Low bank riparian reaches had greater overall 777 denitrification rates, which was attributed to wider channels and less stream incision creating 778 greater overall system hydrological connections (for both the hyporheic and riparian zones) 779 (Kaushal et al. 2008). Approximately 40% of nitrate loadings were removed, due to "greater 780 whole stream connectivity" and especially to increased residence time (especially in the 781 hyporheic zone, where most dentrification was assumed to occur) (Klocker et al. 2009). 782 A long-time (ca. 100 yr) channelized stream in Kentucky was relocated to its former 783 floodplain. Its flow patterns were altered by creating meanders and pool-riffle sequences; the 784 restored segment was wider and shallower and approximately 15% longer than the channelized 785 segment had been. Significantly slower flow rates, higher temperatures, greater transient storage 786 areas, and more connectivity with the hyporheic zone were created. Nitrogen uptake was 787 estimated to be 30 times greater than the channelized segment used to have, and approximately
an order of magnitude greater than a reference site (which had a thriving, forested riparian zone)(Bukaveckas 2007).

790 Constructing artificial riffles (adding stones or cobbles) or gravel bars, or recreating 791 meanders are also common habitat restorations. Constructed riffles and a constructed step in N-792 rich agricultural and urban streams induced additional hyporheic exchange, with clear 793 downwelling and upwelling trends (Fig. 4). The hyporheic zone at the restored sites was a NO<sub>3</sub><sup>-</sup> 794 sink; the streams had steeper longitudinal hydraulic head gradients and coarser substrates than 795 reaches with natural riffles and steps, suggesting the restored sites had enhanced NO<sub>3</sub><sup>-</sup> removal 796 capabilities (Kasahara and Hill 2006). At another site, a constructed gravel bar and re-meandered 797 stream reach caused enhanced lateral hyporheic exchange flow. Vertical exchange was increased 798 at the gravel bar by adding a riffle-pool sequence. The need to manipulate sediments in 799 restorations was underlined, especially in agricultural and urban settings where fine-grained 800 sediments predominate and cause colmation (Kasahara and Hill 2007). Construction of baffles 801 also lead to increased denitrification – however, the effect was thought to be due to increased 802 transient storage due to stream velocity decreases, and not increased hyporheic zone exchange 803 (Ensign and Doyle 2005). Adding debris dams and gravel bars to streams in urban and suburban 804 settings caused greater denitrification rates, more than other management steps, even when 805 compared to forested reference sites. These sites supported organic-rich matrices, which seemed 806 to be the key factor for added N-losses (Groffman et al. 2005). 807 Indirect effects on the hyporheic zone may be achieved through alternative restoration

808 efforts. Forested riparian zones, for instance, were associated with greater hydrologic retention

times in stream reaches, apparently from slowing stream flows through debris additions. The

810 debris may have increased hyporheic zone inputs or created surface backwaters. In any case, N-

811 reductions greater than degraded, non-forested areas were measured (Weigelhofer et al. 2012). 812 Stream fencing can be useful in preventing cattle from encroaching on the riparian zone (Vidon 813 et al. 2010); not only might that lead to indirect hyporheic zone benefits from a restored riparian 814 buffer, but keeping cattle out of a stream is a good direct hyporheic zone remediation activity. In 815 the Danube River, changes to channels to restore more natural flow conditions increased surface-816 subsurface connectivity, and resulted in greater rates of denitrification (among other enhanced 817 hyporheic zone functions) (Welti et al. 2012). It has also been suggested that restoring variable 818 flow conditions in controlled streams can improve nutrient uptake, as this may increase contact 819 with subsurface C pools (Faulkner 2008).

820 Agricultural drains are designed to have flat bottoms and steep, unvegetated sides to facilitate 821 water flows. These ditches lose functionality as they erode and with increasing plant 822 colonization, and the narrow-bottomed, vegetated, and often benched ditches that result have 823 been called "2-stage" ditches. Testing of sediments found that the benches in 2-stage ditches 824 function like floodplains, and have good denitrification potential (greater than sediments in 1-825 stage ditches). Although this potential decreases some effects associated with excessive fertilizer 826 use, drains also foster direct transport of excess N from fields to streams; overall, it is likely that 827 areas with drains have quicker transport of more N to surface waters than areas that are not 828 drained (Powell and Bouchard 2010). In one setting, a bioreactor was installed in a ditch instead 829 of relying on natural deterioration of the ditch structure. The woodchip bioreactor generated 830 impressive denitrification rates, estimated to exceed those associated with natural wetlands in the 831 region by a factor of 40 (Robertson and Merkley 2009).

832 There appear to be correlations among land use, channelization, and the hyporheic zone's 833 ability to retain  $NO_3^-$ , but the exact linkages have not been made yet (Robertson and Wood

834 2010). Although some studies have quantified the effect of stream restoration on nutrient 835 dynamics, it is difficult to determine general effects that extend beyond the specific examples 836 (Bukaveckas 2007). Clearly, understanding denitrification better is an important element in the 837 construction of accurate watershed nutrient management plans (Davidson and Seitzinger 2006). 838 Because denitrification is limited in time and space within the hyporheic zone, meeting the 839 definition of "hot spots"/"hot moments," it may not be possible to manage specific stream 840 elements to create increased denitrification rates. Instead, increasing overall stream-hyporheic 841 zone connectivity may be the most feasible means of achieving the desired end (McClain et al. 842 2003), although such a restoration approach becomes a "black box" solution, resistant to further analysis. 843

## 844 **6.** Conclusions

845 Regional mass balances (e.g., Howarth et al. 1996; van Breeman et al. 2002) find that sources 846 of N to the environment exceed identified sinks, and so denitrification is assumed to account for 847 the lost N, based on data collected in experimentation over physically small spaces and short 848 durations (Grimm et al. 2003). Use of N<sub>2</sub>:Ar ratios and very precise direct measurements of N<sub>2</sub> 849 appear to be resolving some of the analytical issues (Laursen and Seitzinger 2002; McCutchan et 850 al. 2003). However, historically, it has very difficult to measure denitrification well at any scale, 851 from the regional to site-specific. This has led to the invocation of "hot-spots," variable over 852 time and space, to account for inabilities to repeat measurements or to find the expected 853 phenomenon that is predicted by mass-balance and other modeling (Boyer et al. 2006). 854 Denitrification of groundwater N in the hyporheic zone has been consistently found for streams 855 across the U.S.; the amount of denitrification is site specific, but generally relates to residence 856 time in the reaction zone beneath the stream (Puckett et al. 2008). The absolute impact of the

857 hyporheic zone is a function of still poorly determined relationships defined by Findlay (1995): 858 short residence times with high reaction activity lead to as much alteration of water chemistry as 859 longer residence times with slower reaction rates. Long residence times imply that not very much 860 water volume can be processed through the subsurface. Short reaction times allow for greater 861 volumes to be treated, but then require resolution of conundrums such as quick depletion of DO 862 (which appears to require residence time), DOC availability to fuel reactions, and whether small 863 biofilm zones can suffice to explain how otherwise well-oxygenated sediments can host 864 denitrification. Denitrification in the hyporheic zone occurs in spatially discrete zones, and 865 requires specific geologic and nutrient conditions. Although best estimates are that river basins 866 are the site of significant denitrification (for instance, van Breeman et al. 2002), a skeptical 867 analysis of extent of hyporheic conditions could conclude that there is often not enough 868 upwelling and downwelling relative to the size of the stream to generally create meaningful 869 effects on stream N-cycling.

870 Riparian zones cannot be separated from the hyporheic zone, given their close spatial and 871 functional proximity in many streams. Riparian zones have been described as poor "end-of-pipe 872 solutions" for increasing nutrient content in run-off and groundwater; where conditions are 873 suboptimal (deep groundwater flow paths, non-hydric sediments), only minor (<10%) N-874 reduction can be expected (Stutter et al. 2012). The strongest correlations for N reductions in 875 streams have been found to wetlands acreage, not riparian or hyporheic conditions (McClain et 876 al. 2003). In fact, factors other than denitrification potential (such as land use, population 877 density, soil quality, and N atmospheric deposition rates) correlate much better with stream N 878 concentrations (Smith et al. 2008).

879 This supports the proposition that augmenting subsurface denitrification is unlikely to be 880 more effective at reducing stream N-concentrations than reducing input N concentrations 881 (Ranalli and Macalady 2010). Various land use programs have been proposed to achieve lower 882 N-inputs (Howarth 2005; Silgram et al. 2005; Hiscock et al. 2007), with one estimate being that 883 major changes in N-loading in 25% of headwater streams could "easily" lead to 10-15% 884 reductions in river discharge N loadings (Alexander et al. 2007). However, most input control 885 programs have not been able to achieve their goals (Boesch et al. 2001; Howarth 2005). One of 886 the few clear reductions in the delivery of N to coastal waters occurred in the Black Sea in the 887 1990s. This was not due to management success, but rather reflected the substantial, negative 888 impacts of economic chaos on agriculture in the former Soviet Union (Howarth 2005). 889 General prescriptions to reduce world-wide releases of reactive N by 25-30% include 890 controlling emissions from fossil fuel combustion, increasing efficiency of N applications to 891 crops, improving animal waste management, and, in cities without sewage treatment, treating at 892 least half of all human septic wastes (Galloway et al. 2008). Howarth (2005) identified steps to 893 be taken in the U.S. that could reduce coastal impacts from increased N releases. These included 894 source reduction steps, and additional treatment possibilities including: 895 1) changing agricultural drainage systems so as to improve nutrient uptake 896 This has been identified as feasible and generally creating few impacts to overall agricultural 897 output. Mostly this kind of project appears to require changes in perception of desired aesthetics 898 and some changes in general ditch management (Birgand et al. 2007), although more substantial 899 projects are also feasible (Robertson and Merkley 2009). Agricultural drainage systems do not 900 affect N that was exported directly to groundwater, however.

901 2) adding wetlands to riverine systems wherever feasible and desired.

902 It has been argued that above-ground, flow-through marshes are the most effective means of 903 reducing NO<sub>3</sub><sup>-</sup> concentrations, especially if flow short-circuiting is avoided through careful 904 design (Kadlec 2012). Greater removal efficiencies (although greater space requirements are 905 needed too) can be achieved using constructed subsurface wetlands (Garcia et al. 2010), although 906 subsurface treatment is most beneficial when pathogen exposure is a major concern (Kadlec 907 2012). Marsh projects like these can be monitored and assessed more easily than less intrusive 908 changes to foster subsurface  $NO_3^-$  removal in riparian and/or hyporheic zones. Marsh 909 construction requires large expanses of space, however, and may not be the landscape feature 910 that is possible, needed, or desired in all settings.

911 3) restoring riparian areas as is possible.

912 A nation-scale modeling exercise in England suggested that substantial attenuation of N-inputs 913 through subsurface reactions is possible in many lotic environments (although certainly not all) 914 (Smith et al. 2009). Bayesian simulations using literature search denitrification values suggested 915 that basic riparian restoration techniques would lead to approximately 25% more N-assimilation 916 in restored reaches compared to impacted reaches (Faulkner 2008). Still, although higher 917 concentrations of  $NO_3^{-1}$  lead to higher denitrification rates, the increase in denitrification is not 918 proportional to increases in inputs (Alexander et al. 2009), and so only mitigates (not resolves) 919 the issue of increasing N-releases.

920 The degree that restoration efforts should focus on the hyporheic zone and its potential for

921 denitrification is not clear. Estuarine N-loads are a function of prior loadings in the upriver

922 region: e.g., water quality in the Gulf of Mexico is closely linked to historical fertilizer

923 applications throughout the Mississippi-Missouri River basin (Alexander et al. 2007).

924 Degradation and alteration of headwater streams (in particular) was identified as a major element

925 in coastal hypoxia due to a loss of nutrient processing capabilities (Freeman et al. 2007). This 926 seems to imply that restoration efforts in these areas, assuming that denitrification potential is 927 part of the selected approach, could be effective in improving a major regional problem. But, 928 determining the impact of a potential denitrification zone depends on the degree and reliability of 929 the connection between N-source and the denitrification zone (McClain et al. 2003). There is 930 good evidence that denitrification occurs in the riparian and hyporheic zones, reducing 931 groundwater N inputs and mitigating stream  $NO_3^-$  concentrations. Denitrification in riparian 932 zones requires groundwater to be funneled through particular small regions of the streamside 933 environment, and many groundwater pathways do not intersect these zones. Hyporheic processes 934 depend on generating micro-scale patches of favorable conditions, or appear to be governed by 935 Freundlich reaction kinetics: denitrification increases as ambient concentrations of NO<sub>3</sub><sup>-</sup> 936 increase, but denitrification rate increases are not fast enough so as to keep pace with the 937 increases in the stream water  $NO_3^-$ . Slower flow rates through sediments compared to flow rates 938 in the stream and the relatively small volume of the hyporheic zone imply that, in most settings, 939 water in a particular reach cannot have much residence time in the subsurface. Thus, there can 940 only be a limited role for these environments as checks on increasing stream  $NO_3^-$  content and 941 deliveries to marine systems. Increasing treatment of water through wetlands appears to return 942 greater dividends than enhancing subsurface NO<sub>3</sub><sup>-</sup> treatment potentials. 943 Incorporating better knowledge of these ecotones into stream remediation plans is not 944 pointless, however; understanding the functionalities of these zones better could lead to better

945 crafting of environmental initiatives. On Long Island (New York, U.S.), management concerns

946 regarding  $NO_3^-$  concentrations in a shallow lagoonal estuary have focused on direct groundwater

947 discharges to the estuary (Kinney and Valiela 2011). However, although the fresh water entering

948 the estuary is derived from groundwater, most enters the estuary via short stream systems. A 949 focus on improving riparian and hyporheic zone processes in these canalized, heavily altered 950 streams, where sufficient space for wetland construction appears to be lacking, might pay a 951 greater short-term dividend than trying to change overall N-inputs to groundwater (where 20-50 952 year residence times have been modeled). In this way, rehabilitation of hyporheic zones could 953 reduce estuarine N-loadings within timescales appreciated by funding agencies and politicians. 954 Therefore, there is virtue in addressing the hyporheic zone, and improving its connectivity 955 with surface waters as stream modifications are made. Even greater returns might be realized by 956 treating the hyporheic and riparian zones together. Although source controls on  $NO_3^-$  appear to 957 be the most effective means of reducing NO<sub>3</sub><sup>-</sup> inputs to sensitive marine environments, greater 958 water flows through subsurface zones will help to ameliorate increases in NO<sub>3</sub><sup>-</sup> releases from 959 agriculture and other human endeavors, especially if short-term effects are desired.

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965	

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## 1489 List of Figures

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1501 1502 1503 Figure 1. The hyporheic zone



- 1506

Figure 2. Diverse subsurface flowpaths (adapted from Poole et al. 2008): paths range from very

short and shallow (s. to min.) to those that are very long (mos. to yrs.). Temporally longer 

pathways tend to traverse physically longer subsurface pathways. Groundwater controls the overall directionality of flow.


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Figure 3. Micro-pressure effects on hyporheic flow, caused by a partially embedded log in a gravel-bed riffle (adapted from Boulton 2007) 



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1523 1524 1525 Figure 4. Hyporheic flowpaths through a riffle (adapted from Boulton 2007)