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Tracer tests for investigating flow and transport in the hyporheic zone

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Steve Killeen Head of Science

Executive summary

The Environment Agency has established a research programme on groundwater–surface water interactions, specifically aimed at pollutant attenuation processes at the interface of groundwater and surface waters. This research is needed to provide understanding of the processes that control water flow and pollutant flux between groundwater (aquifers) and surface waters (principally rivers and streams). We need to understand the processes that act at this interface so that we can predict how water and pollutants move between aquifers and rivers, and how this affects the ecological health of river corridors.

The groundwater–surface water interface (including the hyporheic zone) is often overlooked by the limited research remits of hydrogeologists (who focus on groundwater quality and water resources), hydrologists (who focus on surface water resources and pathways) and freshwater ecologists (who focus on benthic and in-stream ecosystems). The hyporheic zone is, however, a critical interface between groundwater and surface water environments and has been shown to be a dynamic ecotone characterised by steep chemical and biological gradients.

The use of tracers has been well documented during both groundwater and surface water field investigations. However, due to the general lack of research into the hyporheic zone the potential for the use of tracers to develop a better understanding of this important ecotone has perhaps not yet been fully realised. This report collates and reviews existing literature documenting experimentation where tracers have been used to spatially delineate or characterise processes occurring within the hyporheic zone. The findings of this review will be used by the Environment Agency to identify the best ways of investigating the GW-SW interface by tracer testing, and to identify research needs and opportunities relating to the use of tracer tests in the hyporheic interface. This report forms part of a wider Environment Agency research programme into surface water and groundwater interactions.

Contents

1. Introduction

Hydrogeologists, hydrologists and ecologists have tended to address the surface water and groundwater interface in terms of their particular research remit, frequently failing to take a more integrated, cross-disciplinary approach. However, researchers across these disciplines are increasingly recognising the area, known as the ‘hyporheic zone’, as a transitional interface with an important role in the processing of carbon, nutrients and other pollutants, and as an important habitat. Recent legislation in the form of the Water Framework Directive (2000/60/EU) demands an integrated approach to management of the hydrological system, including surface water and groundwater resources, and to improvement of the ecological quality of surface water bodies.

With legislative requirements being placed upon scientists and government agencies to consider all water resources as a connected and dynamic system, researchers are beginning to consider the role that interfaces between traditional environmental compartments, including the hyporheic zone, plays. The hyporheic zone may act as a valuable ‘buffer zone’ between streams and groundwater.

Current literature demonstrates a reasonably coherent understanding of water and contaminant pathways and transformations in both surface water and groundwater (Smith 2005). However, little attention has been given to the potential for movement of water and contaminants across the surface water and groundwater interface.

1.1. Definition of the hyporheic zone

Workers in the field have drawn their own definitions to delineate the extent of the hyporheic zone, delineation being based upon their particular scientific discipline and research requirements:

- **Ecologists**

Ecologists have typically relied upon the distribution of indicator species in streambed and bank sediments to determine the vertical and lateral extent of the hyporheic zone. Literature based upon ecological surveys will frequently describe the hyporheic zone as a dark, nutrient-rich anoxic environment delineated by the presence of the hypogean organisms.

- **Hydrologists**

Hydrologists have often considered the hyporheic zone as an area available for flow as part of the main stream discharge, albeit with increased residence times and potential for geochemical transformations and pollutant attenuation. Little consideration is generally given to the potential for water and nutrients to be exchanged across the hyporheic zone with the surrounding aquifer.

- **Hydrogeologists**

Hydrogeologists have typically tended to consider the hyporheic zone as part of the subsurface groundwater reserve. Although a hydrogeologist may calculate surface recharge into any conceptual groundwater budget as a matter of course, specific identification of the hyporheic zone is usually omitted from conceptual models because it is a relatively small consideration at a larger scale.

Until relatively recently there has been no all-embracing consideration of the hyporheic zone as an important feature of the hydrological system. With the hyporheic zone's significant potential for pollutant attenuation, integrating groundwater and hyporheic zone ecology, biogeochemistry and hydrogeology will significantly advance our understanding of subterranean ecosystems, especially in terms of bioremediation of contaminated groundwaters (Hancock *et al.* 2005).

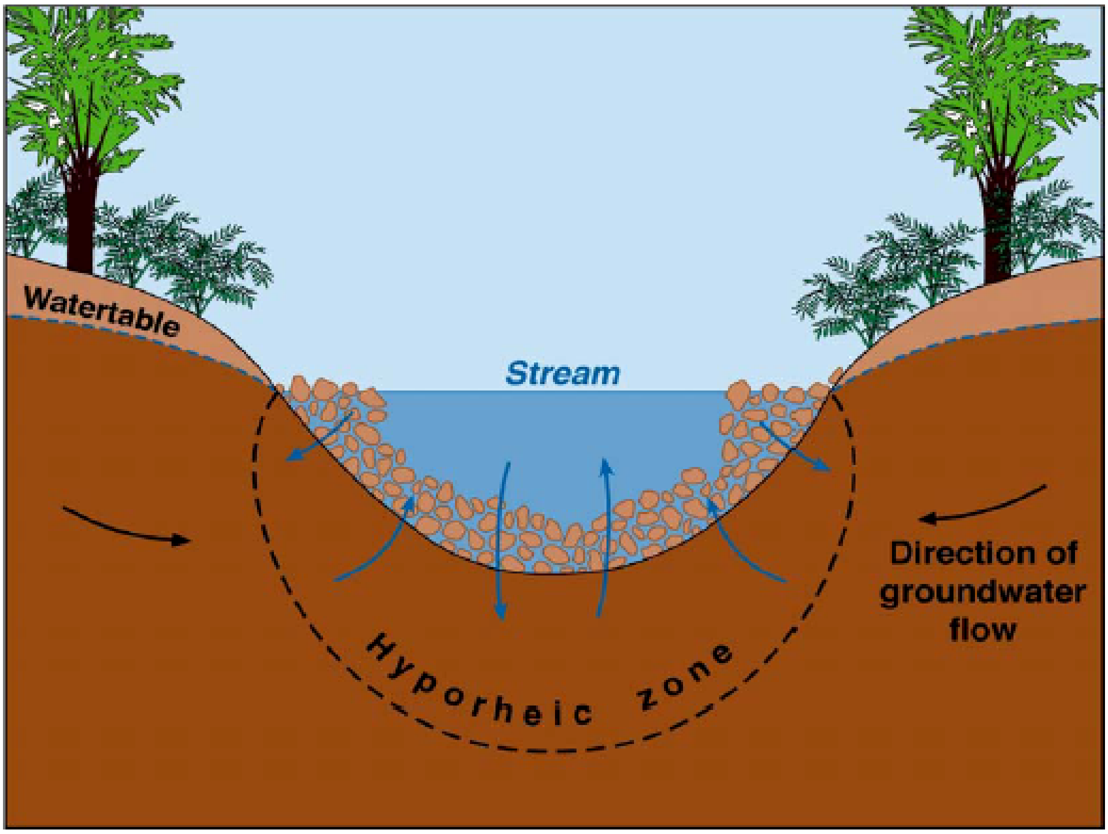

Figure 1. Schematic diagram of the hyporheic zone (reproduced with permission of United States Geological Survey)

It has been proposed that the *hyporheic zone* (Figure 1) is the region of the subsurface immediately below surface streambed sediments where stream channel water accounts for at least 10% of the total interstitial volume (Triska *et al.* 1989b). Other workers have offered alternative constraints to define hyporheic boundaries (Bencala 1983, Stanford and Ward 1988, White 1993, Boulton *et al.* 1998); however, many of these fail to be sufficiently flexible to apply in all hyporheic studies, as they are often specific to a certain stream reach. Perhaps, therefore, a definition with greater flexibility may be preferred, leaving researchers to adapt this to their area of study. Brunke and Gonser (1997) drew upon many previous attempts to define the hyporheic zone and concluded that: 'The hyporheic zone can be distinguished from its surrounding environments because it combines features of both, although each parameter develops its own gradients'. It may be concluded that any attempt to offer a more exact definition is simply too static and inflexible, and that due to the heterogeneous nature of stream and groundwater in a hyporheic zone study, researchers ought to attempt to delineate the hyporheic zone based on their own field investigations. Such investigations may benefit from the use of field tracer tests to delineate the hyporheic zone and identify groundwater and surface water interactions across this interface.

Within the context of the Environment Agency's focus on the attenuation of pollutants at the groundwater and surface water interface, this report adopts a definition for the hyporheic zone as the water-saturated transitional zone between surface water and groundwater (Smith 2005).

1.2. Tracer applications

A tracer can be any substance used to study the physical movement of water through the environment, including either surface water pathways or those in the subsurface. Tracers that track flow-paths of water by moving at the same rate and via the same physical pathways as the body of water are known as *inert* or *conservative tracers*. Tracers can also be chosen because of their potential to help us understand the chemical properties of an aquifer or stream channel sediments. Such tracers may be used to investigate the retardation or degradation potential of a substrate containing surface water or groundwater and are known collectively as *reactive* or *non-conservative tracers*. A specific tracer can be chosen based upon the parameters an investigation aims to study. There is no 'ideal' tracer, and therefore choice of tracer will depend upon the ultimate objectives of a tracer test (Ward *et al.* 1998).

Although tracers can be broadly defined as conservative or non-conservative, they can also be categorised based upon their origin and purpose in a tracer study. The main categories of tracer, and a brief description of each including possible uses, are detailed below.

1.2.1. Environmental tracers

Environmental tracers are substances occurring in the environment that can be exploited as tracers. They fit into two subclasses: *natural environmental tracers* and *anthropogenic environmental tracers*. Both natural and anthropogenic environmental tracers are used in a similar manner.

Natural environmental tracers result from naturally occurring processes. An example is the use of radon-222 (which is released from rocks containing a high uranium-238 concentration) as a hydrological tracer (Ellins *et al*. 1990, 1991, Cecil and Green 1999).

Anthropogenic environmental tracers result from their accidental release into the environment due to human activities. Frequently such tracers are widely distributed, have weak signals and result from prolonged accidental release. A particularly 'high profile' example is CFCs, which were released between the 1950s and 1980s. CFCs can be used as excellent anthropogenic environmental tracers of 'young water' (50 year timescale) at a very low detection limit (Busenberg and Plummer 1992, Plummer and Busenberg 1999). Other anthropogenic environmental tracers may result from deliberate or accidental 'catastrophic' events. Examples include radionuclides released by nuclear weapons testing or reactor failure (Cook and Böhlke 1999).

1.2.2. Artificial tracers

Artificial tracers are those purposely released into the environment during a tracer study. These may be conservative, to track the movement of surface or subsurface waters, or non-conservative, to study the effects of and potential for sorption, biodegradation and storage within a stream or aquifer system.

A wide range of substances exist that may be chosen as artificial tracers, and choice of a suitable tracer should be based upon the particular information required from an investigation. Before any tracer test, consideration must also be given to the potential risks to environmental or human receptors. Authorisation is required from regulatory bodies before any tracers are introduced into the environment. In England and Wales, the Environment Agency will authorise (or otherwise) the release of artificial tracers into controlled waters.

Many of the tracer tests cited in this review use halogen anions such as chloride and bromide. These are both readily available in forms such as potassium bromide (KBr) and sodium chloride (NaCl), though often use of the bromide ion is preferred due to lower background levels. The cations (e.g. potassium and sodium) in these common salts are generally not used as tracers as they are more likely to exchange with other cations on ion exchange sites within sediments, so they are not suited to being conservative tracers.

More comprehensive guidance can be found in Ward *et al.* (1998) ‘Groundwater tracer tests: a review and guidelines for their use in British Aquifers’ or from Environment Agency offices. This report offers detailed information on the use of tracers in aquifers and riverbed sediments but may equally be applied to surface water tracer studies.

1.3 Natural attenuation in the hyporheic zone

The Environment Agency’s definition of natural attenuation has a bias towards processes occurring in groundwater; however, it can be considered equally applicable when discussing natural attenuation in the hyporheic zone:

Natural Attenuation is the effect of naturally occurring physical, chemical and biological processes or any combination of those processes to reduce the load, concentration, flux or toxicity of polluting substances [*in groundwater*]. *For natural attenuation to be effective as a remedial action, the rate at which those processes occur must be sufficient to prevent polluting substances entering identified receptors and to minimise expansion of pollutant plumes* [*into currently unpolluted groundwater. Dilution within a receptor such as a river or borehole, is not natural attenuation*].
(Environment Agency 2000)

If, as suggested in recent studies, the hyporheic zone is to be considered as a potential ‘buffer zone’ connecting aquifers and surface waters (Atekwana and Krishnamurthy 2004, Conant *et al.* 2004), then tracer studies should be acknowledged as a viable tool to investigate the potential of the hyporheic zone to reduce the mass of a contaminant. This is of equal interest when considering a risk to surface waters of a contaminant plume in groundwater or to identify whether a hyporheic zone may be capable of reducing the mass of a contaminant carried in a stream or river. Natural attenuation is the umbrella term used to describe such processes that have the potential to reduce a contaminant's risk to receptors and should be of great interest when considering the hyporheic zone. The main processes involved in natural attenuation can be divided into three categories: advection and dispersion, sorption, and (bio)degradation. Use of tracers should be considered to assess these within the hyporheic zone. A brief description of these processes is given below.

Advection and dispersion

processes act to dilute and decrease contaminant concentrations in groundwater. Advection is the transport of dissolved solutes carried in solution with the moving groundwater, at the same rate, away from a source. Although advection acts to move a contaminant mass, there is no decrease in concentration without dispersion processes. Dispersion acts as a diluting factor to decrease concentrations of a solute within groundwater. Dispersion can be either mechanical, due to the variations and tortuosity of flow-paths (hydrodynamic dispersion), or molecular, due to the random motion and mixing of molecules in a fluid (diffusion) (Fitts 2002). As it is not possible to separate the relative contribution of mechanical and molecular dispersion, the two are combined and termed 'hydrodynamic dispersion' (Fetter 2001).

Sorption

is the process of attachment and retardation of a substance contained within water, to a surface of solid material (adsorption) or the chemical incorporation into the hyporheic materials (absorption). Generally, adsorption is most prevalent in contaminant hydrogeology and is of significant interest when considering the potential for natural attenuation processes to occur. Typically, a solute will sorb onto mineral surfaces due to cation exchange and complexation (Fetter 2001). Some organic compounds may be retarded not because of ion exchange but as a result of their non-polar nature. Water molecules are relatively polar and have a strong electrostatic attraction to each other (Fitts 2002). Hydrophobic contaminants may show retardation and accumulation on aquifer surfaces due to their polarity-induced repulsion from the surrounding water.

Degradation

If a contaminant in a particular environment has the potential to degrade by abiotic chemical breakdown or to be degraded by biotic processes, the reduction in contaminant mass will reduce its persistence and potential risk to receptors. It has been mentioned that dispersion and adsorption processes can effectively dilute and immobilise a contaminant; however, without degradation occurring to reduce a contaminant's mass it may persist indefinitely. Of particular interest to environmental scientists is biodegradation, where in situ degradation of contaminant molecules occurs by reactions within resident microbes (Fitts 2002). If field studies demonstrate that microbial populations in the hyporheic zone are active and sufficient to degrade a contaminant (originating from either a groundwater plume or surface water release) within a suitable time frame without additional risk to potential receptors, then natural attenuation may be a viable remediation option.

Retardation of a contaminant mass, by the processes described above, within the hyporheic zone acts to incorporate solutes within hyporheic sediments and increase travel times. This can be a permanent loss of substances from the advective system, or a temporary storage phase following which substances may be gradually released back into advective transport. This temporary retardation of a solute pulse is known as transient storage, and many workers have attempted to apply models to gain a greater understanding of this process, notably the ‘transient storage model’ (Bencala and Walters 1983).

1.4. Objectives of this review

This document reviews existing literature describing the use of tracer studies to investigate processes in the hyporheic zone. There is a great volume of literature describing the use of tracers solely for the investigation of groundwater, surface waters and coastal waters, and, although these may be cited, any detailed discussion is far beyond the remit of this review. We concentrate on the use of tracers in the investigation of the hyporheic interface, an area that, as mentioned above, has often been overlooked by workers focusing on adjacent parts of the environment. The findings of this review will be used by the Environment Agency to identify research needs and opportunities relating to the use of tracer tests in the hyporheic interface. This report is part of a wider Environment Agency research programme into surface water and groundwater interactions.

2. Stream water tracers

2.1. Tracer tests to study stream water exchange with the hyporheic zone

2.1.1. Streambed topography

There appears to be general agreement throughout existing literature that streambed surface forms and obstructions play a direct role in driving hyporheic exchange (Hendricks and White 1991, Harvey and Bencala 1993, Brunke and Gonser 1997, Cardenas *et al.* 2004). Surface forms and obstructions have also been cited as major determining factors controlling spatial distribution of subsurface flow-paths (Maddock *et al.* 1995). Even in gaining reaches (where stream flow is maintained from groundwater recharge), it has been accepted that streambed topography and obstacles maintain a return flow of stream water into the bed and hyporheic sediments by the water pressure (head) variations they create (Brunke and Gonser 1997, Storey *et al.* 2003).

Control on hyporheic exchange by irregularities in the streambed topography has encouraged researchers to examine these highly localised phenomena by conducting controlled laboratory studies (Marion *et al.* 2002, Packman *et al.* 2004). Field studies have focused upon pool–riffle sequences, the effect these have upon the control of exchange across the streambed interface, and the ecological implications (e.g. for salmonoid spawning success) (Hendricks and White 1991, Harvey and Bencala 1993, Brunke and Gonser 1997, Cardenas *et al.* 2004). On an even finer scale, reduced bed surface friction (e.g. due to artificial excavation) can be demonstrated from downstream tracer recovery, to lead to a reduced exchange across bed sediments (Salehin *et al.* 2003).

Streambed topography irregularities such as pool–riffle sequences cause high-pressure zones (increased head) to be formed at the head of a riffle and low-pressure zones (decreased head) at the tail. The creation of a head gradient through riffle sediments has been described as the driving mechanism to create downwelling and upwelling regions of water movement in the hyporheic zone, with connecting interstitial flow through sediments (Savant *et al*. 1987, Thibodeaux and Boyle 1987, Franken *et al.* 2001, Packman and Salehin 2003). Similarly, head gradients can also be demonstrated on the outside of meander bends where there is sufficient pressure caused by the flow-driven hydraulic head for water to breach the hyporheic interface, with water returning to channel flow downstream (Cardenas *et al.* 2004). The streambed topography induced phenomenon whereby water and solutes enter hyporheic sediments at high-pressure (high-head) zones and exit the sediments downstream back into the main flow where lower pressures (lower head) exist has been described as ‘pumping’ (Wörman *et al.* 2002). It is largely responsible for driving exchange of water from the channel into the underlying hyporheic zone (Marion *et al.* 2002).

Halogen anions such as chloride and bromide (Cl^- and Br^-) are reliable tracers for tracking water movement through the subsurface because of their conservative nature. Typically, these are delivered as tracers by dissolving a calculated amount in the form of sodium chloride (NaCl) or potassium bromide (KBr) respectively to achieve the required initial tracer concentration. Due to the conservative nature of these anions and their relatively low cost, they have been used as tracers during well-known studies to investigate the importance of streambed topography upon the movement of water across the stream/hyporheic zone interface (Harvey and Bencala 1993). The selection of Br^- and Cl^- ions delivered as LiCl and KBr to investigate hyporheic exchange in St Kevin Gulch stream, Colorado, was supported by previous work using these solutes in similar acidic mountain streams (McKnight *et al.* 1988, Bencala *et al.* 1990). A detailed list of other earlier studies that describe the use of lithium as a stream tracer has recently been compiled by the United States Geological Survey (USGS) and is provided in Appendix 2 of this report.

At St Kevin Gulch, Br^- and Cl^- labelled solutions were injected at a constant rate and concentration into both the stream water and local groundwater. From this it was possible to relate the downwelling and upwelling of tracer-labelled water across the hyporheic zone/stream water interface to the varying streambed topography (Harvey and Bencala 1993). In particular, concave and convex bedforms associated with pool–riffle sequences were highlighted as features that led to convective exchange across the streambed. Recharge to the subsurface was seen to increase when streambed slope increased at the transition from a pool (slope < 1%) to a riffle (slope 5–20%), with the return of hyporheic water to the stream dominating when streambed slope began to decrease with the formation of a pool. This important tracer study evidence supports the theory that bedform-induced hyporheic exchange is a result of pressure changes known as ‘pumping’ (Savant *et al.* 1987, Wörman *et al.* 2002).

Effects of pool–riffle sequences upon the exchange of water across bed sediments may occur on a relatively small spatial scale. However, the influence of these substream flows may play a significant role in determining wider hyporheic zone flow patterns. It was concluded from tracer studies at St Kevin Gulch that the control of streambed topography to hyporheic exchange could have a significant effect upon solute transport and fate at a catchment scale (Harvey and Bencala 1993). Solutes carried by water entering hyporheic flow-paths have greater potential to be retarded onto sediments or degraded by biological processes than if they were to remain entrained in the stream channel flow.

It was also noted from the field tracer experiments that in areas where hyporheic flow-paths are recharged by streambed topography induced ‘pumping’ there was little or no upward recharge from local groundwater (Harvey and Bencala 1993). Groundwater recharge to the hyporheic zone was only seen to be of influence in reaches where stream to hyporheic exchange was not occurring. With transport through the hyporheic zone, initiated by bed topography induced ‘pumping’, biogeochemical transformations in the chemistry and solute content of the original stream water have the potential to occur in hyporheic sediments. On later return to the main stream channel, often at the base of a riffle sequence a short distance downstream, the returning water’s altered chemical properties may then have the potential to affect the overall downstream water chemistry. The alteration of stream water chemistry by its transport within the hyporheic zone may benefit from further research, especially if the hyporheic zone is to be considered as a zone with natural attenuation processes occurring, acting to reduce the mass of a contaminant carried within the stream or shallow groundwater.

To support their field investigations, Harvey and Bencala (1993) also employed numerical hydrological simulations demonstrating that the exchange of water between the stream channel and hyporheic zone was significantly influenced by pressure differences caused by topographical features of the streambed. This was later developed into the ‘pumping exchange model’ (Elliott and Brooks 1997a). Modelling was subsequently developed further with the ‘Advective Storage Path model’ (ASP model), which uses conservative tracer data to approximate hyporheic exchange and related longitudinal transport (Wörman *et al.* 2002). The focus of this modelling work conducted by Wörman *et al.* (2002) was to try to simulate the hyporheic exchange and transport properties of the Säva Brook, Sweden, from earlier ^3H_2O (tritium) tracer data (Jonsson & Wörman 2001). This work involved the integration of a model for longitudinal in-stream solute transport with a physically based representation of flow-induced uptake in the hyporheic zone to form the ASP model.

2.1.2. Bed sediment properties

Existing documentation on the effects of streambed sediments on hyporheic exchange appears to be based mainly upon laboratory-scale experimentation (Nagaoka and Ohgaki 1990, Eylers *et al.* 1995, Elliot and Brooks 1997b, Packman *et al.* 2000, 2004, Marion *et al.* 2002, Packman and MacKay 2003). Despite this, laboratory flume experiments should still act as a reliable analogue to explain processes occurring in the field, and may offer greater control and resolution during a tracer study than could possibly be achieved under field conditions.

Streambed heterogeneity

Discussion of the pumping exchange model (Elliot and Brooks 1997a, Wörman *et al.* 2002) has been made in earlier sections. Recent literature has described laboratory flume experiments that attempt to relate this advective pumping exchange model theory to streambed heterogeneities (Packman and Salehin 2003, Salehin *et al.* 2003). Of particular interest when discussing streambed heterogeneity are variations in grain size distributions, hydraulic conductivities and sediment anisotropy. One limitation of many recent studies is that they assume the hyporheic zone to be homogeneous and isotropic (Fox and Durnford 2003, Salehin *et al.* 2003). In reality, this would be extremely unlikely to occur in natural sediments, including streambeds, where depositional processes lead to layering and an anisotropic structure.

Laboratory-scale flume experiments using a streambed of varying heterogeneity and anisotropy are presented by Salehin *et al.* (2003). Sodium chloride (NaCl) was injected into recirculating stream flow to determine the exchange of stream water into bed sediments, by measurement of changing solute concentrations in the recirculation flow. Coloured conservative dyes were additionally used to allow visual interpretation of the subsurface flow-paths. From these observations it was determined that solute transport in a heterogeneous streambed follows near-surface streamlines within the sediments due to the high horizontal hydraulic conductivity (Salehin *et al.* 2003). This experimentation offered a more realistic representation of residence times and flow-paths occurring in the field.

Not only has it been demonstrated that streambed heterogeneities have major control upon hyporheic zone exchange and flow-paths but also the grain size of bed surface material is described as a major controlling factor upon the penetration of stream water into the hyporheic zone (Packman and Salehin 2003). Sodium chloride was highlighted as a commonly used conservative tracer to examine the effect that sediment grain size has upon hyporheic exchange. From this it was concluded that the rate of hyporheic exchange was proportional to the permeability and inversely proportional to the porosity of bed sediments (Packman and Salehin 2003). The authors draw attention to an increase in turbulent interactions, in addition to advective flows, that occurs as a result of a predominantly gravel streambed. This turbulent flow is determined as one of the driving forces that acts to ‘inject’ stream water through bed sediments and is dependent upon the presence of larger streambed grain sizes. These observed increased rates of stream water penetration in gravel bed sediments as a function of increased stream-driven turbulence are also discussed in earlier work by Nagaoka and Ohgaki (1990) and Zhou and Mendoza (1993).

Colmation of surface sediments

Colmation is a process that occurs in streambed sediments which can impede the exchange of water across the hyporheic interface. Colmation has been defined as the clogging of the top layer of the sediment matrix and the subsequent decrease in permeability of the streambed (Brunke and Gonser 1997). Fine particles can become trapped within the surface layers of a coarser bed material leading to reduced permeability (Schälchli 1992, Wood and Armitage 1997). Colmation will generally not occur in streambeds through which groundwater is upwelling, as the upward movement of groundwater will purge any siltation at the surface, maintaining hydraulic conductivity (Schälchli 1993). Reduced permeability of streambed sediments will inevitably lead to a reduction in surface water and groundwater exchange across the hyporheic interface. For a basic overview of colmation processes and further related references refer to the review by Sophocleous (2002).

There appears to be a lack of tracer studies which study the effect of colmation on flow dynamics through streambed sediments in the field. However, one study, although conducted in a laboratory flume, used sodium chloride as a conservative tracer to measure solute exchange between stream water and a streambed affected by colmation (Packman and MacKay 2003). During this experiment, the addition of kaolinite clay in suspension to the recirculating flume water caused colmation of the silica-sand bed sediments, which led to alteration of the pore-water flow environment. If occurring in an actual stream this would be likely to result in reduced hyporheic exchange and a possible degradation of the streambed habitat (Packman and MacKay 2003). Colmation is a process that to date has only been studied accurately in controlled flume experiments, as a similar experiment in the field may prove difficult to replicate. The use of tracers to examine the process and effects of colmation on streambed sediments is clearly an area with little research so far, and may benefit from future investigation.

2.1.3. Effect of vegetation on hyporheic exchange

In order to elucidate the effect vegetation may have upon solute transport within a stream channel and associated hyporheic exchange, it is necessary to compare vegetated and unvegetated reaches, ideally of the same stream. Salehin *et al.* (2003) describe field experimentation along a 10 km reach of the Säva Brook in Sweden, the same stream as described in earlier detailed experimental work focusing on the behaviour of conservative and reactive tracers in the stream channel and adjacent hyporheic zones (Johansson *et al.* 2001, Jonsson and Wörman 2001, Jonsson 2003, Jonsson *et al.* 2003).

Iodine (I^-) delivered as potassium iodide (KI) was employed as a conservative tracer to assess stream–subsurface mixing in this agricultural stream with dense channel vegetation, and again following artificial channel excavation which left the channel devoid of vegetation (Salehin *et al.* 2003). Following injection of 17.7 kg potassium iodide dissolved in 20 litres of deionised water as tracer, breakthrough curves from various downstream locations were analysed using the Transient Storage Model (TSM) (Bencala and Walters 1983) and the Advective Storage Path model (ASP model) (Wörman *et al.* 2002, Jonsson *et al.* 2004).

Salehin *et al.* (2003) make some general observations upon the effect that in-channel vegetation has upon in-stream transport and hyporheic exchange. From field observations and earlier literature it can be assumed that the resistance to flow resulting from vegetation leads to an increase in water depth and a decrease in velocity, with these changes having an influence on hyporheic exchange (Salehin *et al.* 2003). In other work it is demonstrated that vegetation alters streambed permeability, with the introduction of organic matter to hyporheic sediments and intrusion of plant roots having a pronounced effect (Packman and Salehin 2003). Dense vegetation also increases solute storage in 'dead zones', areas of stagnant flow, which when considered in terms of a solute tracer test would lead to a pronounced delay in tracer recovery at downstream stations and ought to be considered so that it is not assumed to be storage occurring in hyporheic sediments. The reduction in exchange across the bed of a vegetated stream reach resulting from stream water flowing over bed irregularities occurs because of the general reduction in stream water kinetic energy caused by the presence of vegetation. Additionally, where the flow of stream water is slowed by the presence of macrophyte (plant) beds, the deposition of fine sediments at the bed surface may further reduce hyporheic exchange. It would appear that the presence of in-stream vegetation may cause a very pronounced reduction in hyporheic exchange (Hendricks and White 1991, Harvey and Bencala 1993, Brunke and Gonser 1997, Cardenas *et al.* 2004).

It is noted that investigations using a conservative tracer injected in vegetated and unvegetated stream reaches have neither the resolution nor scope to identify specific effects stream vegetation has on the stream hydrological or hyporheic exchange characteristics (Salehin *et al.* 2003). Instead, the authors suggest that their work is used as a guide when considering the effect in-channel vegetation has upon the bulk transport of solutes, to allow other workers to distinguish true hyporheic exchange from in-stream transient storage resulting from in-stream vegetation.

2.2. Stream water tracers to assess storage and transport within hyporheic sediments

The importance of shallow gravels and deeper alluvial deposits beneath a stream in the subsurface transport of stream water and solutes is described by Castro and Hornberger (1991). Potassium bromide (KBr) was chosen to deliver bromide anions (Br^-) as a conservative tracer. With low background concentrations naturally occurring in the stream and hyporheic waters this made detection limits of bromide ions sensitive to any downstream changes. Downstream concentrations of this tracer were monitored in wells positioned in surrounding alluvial sediments. Castro and Hornberger (1991) point to the prevalence of a 'storage phase' of tracer travel as initially described by Bencala & Walters (1983). Their study illustrates that there is active transport and storage of stream water and solutes away from the stream, which may gradually be released once hyporheic flow-paths rejoin the main stream flow. The authors describe this as 'long-term storage', as opposed to the shorter-term storage effect of stagnant pools and gravel bars, which in practice may have an important effect on the geochemistry of similar streams.

2.2.1. Radioisotopes

In order to gain greater experimental control during an investigation such as that described by Fuller and Harvey (2000), the addition of an artificial tracer to stream water may be used to provide improved understanding of hyporheic zone solute retention and natural attenuation processes. This has been the experimental protocol for some of the most recent and informative studies that address the use of tracers to quantify retardation of solutes within the hyporheic zone (Johansson *et al.* 2001, Jonsson and Wörman 2001, Jonsson *et al.* 2003).

Field studies that formed the experimental grounding for this suite of papers, in the Säva Brook, Sweden, involved the simultaneous injection of conservative (inert) and non-conservative (reactive) radioisotope tracers into the stream water. The tracers used were tritium (^3H as tritiated water) and chromium (^{51}Cr as Cr(III) (aq.)) respectively. By simultaneous injection of these two tracers into the stream water, the investigators were able to detect the retardation of the non-conservative (reactive) tracer relative to the conservative (inert) tracer (Johansson *et al.* 2001). During the passage of the tracer pulses in the stream flow, water samples were collected to build a breakthrough curve for each tracer for various locations along the 30 km reach. In addition, sediment cores and water samples were collected from the hyporheic zone surrounding the stream channel for several months following tracer injection to determine the uptake of the reactive tracer into the sediment (retardation) and subsequent gradual release over time (Jonsson *et al.* 2004).

Results demonstrate a significant retardation of the reactive ^{51}Cr(III) tracer from stream water samples. It was determined that over the 150 hours it took for the conservative tracer pulse to travel the length of the 30 km reach, the reactive ^{51}Cr(III) tracer had lost 76% of the mass initially injected (Jonsson *et al.* 2003). Retardation processes within stream sediments, including the hyporheic zone, clearly had a significant impact upon the progress of the reactive solute.

Sediment cores taken from the hyporheic zone of the streambed during this investigation illustrated a greater tendency for ^{51}Cr(III) to retard to hyporheic sediments than was recorded for the tritium. ^{51}Cr(III) was consistently found to penetrate only a relatively short distance into bed sediments as it was immobilised onto hyporheic sediments within the first few centimetres. Tritium was shown to have penetrated to a greater depth, and was unaffected by any retardation processes (Jonsson *et al.* 2004). Due to retention within hyporheic sediments, downstream recovery of ^{51}Cr(III) was significantly less than that of tritium, demonstrated by breakthrough curve data.

Both tritium and ^{51}Cr(III) were transported into hyporheic sediments as part of the stream water–hyporheic water exchange. Tritium was seen to follow the advective flow of water within the hyporheic flow-paths, and was suitable as a conservative tracer because it formed part of the water molecule itself (Ward *et al.* 1998). In contrast, ^{51}Cr(III) was not fully 'washed out' of the sediments even after 1,510 hours (63 days), highlighting the capability of hyporheic sediments to retard and immobilise for some time much of the ^{51}Cr(III) tracer mass. This wash-out time for ^{51}Cr(III) was 85 times greater than for tritium, clearly illustrating the potential for sorption by a non-conservative tracer, or for ^{51}Cr(III) pollution in these particular hyporheic sediments (Jonsson 2003).

Using the same Säva Brook experimental ^{51}Cr(III) and tritium tracer data, the conclusion is drawn that kinetic sorption plays an important role in the retardation of solutes in the bed sediments (Jonsson and Wörman 2001). Support for this theory is drawn from earlier work, which demonstrates that kinetics has an important influence on the sorption of strontium (Sr) and potassium (K) tracers in bed sediments (Bencala *et al.* 1983). It was postulated that it is the larger streambed particles, as opposed to finer sediments suspended in the main flow, which feature sorption regulated, to a significant degree, by kinetic processes (Bencala 1983). In addition, Jonsson and Wörman (2001) also cite earlier workers where caesium (Cs) sorption in aquatic sediments is considered as a kinetically controlled process (Nyffeler *et al.* 1986, Comans *et al.* 1991, Comans and Hockley 1992, Smith and Comans 1996). It should be noted that the use of ^{137}Cs as described in these papers is as a 'natural tracer', with elevated ^{137}Cs concentrations originating from the 1986 Chernobyl accident in the Ukraine.

In summary, it can be demonstrated by use of reactive tracers that sorption and transient storage by hyporheic sediments has a pronounced effect upon the transport and fate of reactive solutes carried in stream water. In addition, the active zone of stream water exchange with the hyporheic zone was found, from conservative tritium tracer data, to extend to only 10 cm beneath the streambed in the Säva Brook. However, one could argue that the tracer recovery was only indicative of shorter, shallower flow-paths, and if the experimental time was increased in order to capture more of the tracer signal it may show the active exchange zone to extend into deeper alluvial sediments with longer flow-paths and residence times (Harvey *et al.* 1996).

The reactive ^{51}Cr(III) tracer was found to extend to a depth of 6 cm in the hyporheic sediments and showed a seven-fold increase in retardation when compared to the conservative tritium tracer. Release of both tracers from the hyporheic zone was slower than their initial entry due to the lower concentration gradient. ^{51}Cr(III), however, showed considerably slower release from storage than tritium, as much of the ^{51}Cr(III) mass in transient storage was retarded by sorption to hyporheic sediments (Johansson *et al.* 2001). These results should be considered in the context of natural attenuation. Although micro-organisms are unable to degrade ^{51}Cr(III), if retardation had occurred to another reactive solute that could be degraded by microbial action, the increased residence time resulting from hyporheic transient storage may allow for biodegradation to occur, resulting in a reduction in contaminant mass.

2.2.2. Storage and retention of trace metals in the hyporheic zone

Contamination of surface waters is often particularly severe where trace metals have been introduced as a result of mining activities. Fuller and Harvey (2000) demonstrated the reactive uptake of trace metals in the hyporheic zone of a stream contaminated by mining in Arizona. In this study, bromide (Br^-) was used as a conservative tracer to delineate the spatial variability and extent of the hyporheic zone along a stream reach and to identify locations where groundwater was recharging to surface waters. This offered inert hydrological tracer information with which monitored trace metal concentrations could be compared and explained.

Analysis of in-channel stream water samples indicated a significant decrease in trace metal concentration downstream from the source of release. When assessed together with the sampling of hyporheic sediments, the study demonstrated active uptake and retardation of these metals by hyporheic flow-paths along the study reach (Fuller and Harvey 2000). Hyporheic sediments through which the metal contaminated water was upwelling showed little retardation of the trace metals. This perhaps indicates that trace metal concentrations were too high and had saturated the hyporheic zone where the contaminated groundwater entered the stream. The hyporheic corridor further downstream was able to retard the trace metals once diluted by the stream flow to concentrations and delivery rates that could be managed given the natural retardation capacity of the hyporheic zone sediments. Significant metal uptake was observed at 75–96% of hyporheic sites, indicating significant capacity for retardation, and therefore natural attenuation, along much of the reach (Fuller and Harvey 2000).

The importance of a clear understanding of the hyporheic zone and its potential for the attenuation of substances otherwise harmful if free in the aquatic environment is well illustrated in the work of Fuller and Harvey (2000). Their use of a deliberately released tracer is limited to the conservative solute bromide (Br^-) to delineate the hyporheic zone. However, the use of anthropogenic environmental tracers (trace metals mobilised by mining activities) is fundamental to this study, even though the researchers could only measure initial concentrations of trace metals at the upstream end of the reach and had no control over initial tracer delivery concentrations. Discharge rates and concentrations of trace metals may vary depending upon a variety of temporal spatial factors beyond the control of the authors, therefore use of artificial tracer additions may offer greater experimental control.

2.2.3. Denitrification processes within the hyporheic zone

A suite of frequently cited papers exist describing a series of field tracer studies, conducted over several years, designed to investigate the transport and retention of nitrate in the hyporheic zone (Triska *et al.* 1989a, 1989b, 1990, 1993, Duff and Triska 1990). Continuous injection of inert tracer (chloride or bromide) was used to indicate groundwater input to the stream over a reach. The recovery of these inert solutes from the hyporheic zone by wells positioned in transects laterally to the channel and at varying depths offered spatial delineation of hyporheic flow-paths and observation of the relative contribution of stream water and groundwater to the hyporheic zone (Triska *et al.* 1989a, 1993). It was observed that stream water accounts for much of the hyporheic interstitial water for a considerable distance from the stream channel; at 4 m from the channel 88% of hyporheic water was of stream origin. With samples further from the channel, stream water continued to dominate. It was only with a distance of 10 m normal to the channel that groundwater accounted for over 50% of hyporheic water (Triska *et al*. 1989b).

Inert chloride tracer data indicates that transient storage in the hyporheic zone, in this particular study, was a large component of overall physical storage (Triska *et al*. 1989b). The use of an inert solute as a hydrological tracer, as in this suite of studies, is a common method to offer ‘control’ data to which subsequent reactive tracer tests can be compared to derive information on the retardation and biological properties of the hyporheic zone. Such methods have not only been described in literature by Triska *et al.* (1989a, 1989b) but also in studies where inert hydrological tracers such as bromide (Fuller and Harvey 2000) or tritium (Jonsson *et al*. 2001) are used to provide data for similar comparison purposes for accompanying reactive tracer injections.

By injecting nitrate ($NaNO_3$) into the stream water, it was demonstrated that biotic uptake within the hyporheic zone sediments acted as the major retention and storage mechanism (Triska *et al.* 1989a). A slightly different technique was adopted during a later study, believed to provide the first direct evidence for denitrification in a headwater stream hyporheic zone, in which stream water with increased nitrate levels was injected into hyporheic sediments 8.4 m inland from the stream channel (Duff and Triska 1990). A particularly interesting finding from this later investigation was the identification of a correlation between the flux of groundwater and surface water into the hyporheic zone and the denitrifying capacity of hyporheic sediments. This was due to the different dissolved oxygen concentration (DOC) provided by the particular source of hyporheic waters (Duff and Triska 1990).

Nitrogen cycling and uptake in stream hyporheic zones may also be assessed using the ^{15}N isotope in amended water as tracer. Rates of denitrification can be calculated by monitoring and comparing the denitrification rates of added ^{15}N tracer and naturally occurring ^{14}N tracer. Storey *et al.* (2003) offer a description of how denitrification may be assessed in this manner by use of sediment cores in laboratory column experiments. However, field application of ^{15}N offers reach-scale understanding of the uptake and transformation of nitrate in the hyporheic zone. Recent studies by Crenshaw *et al.* (2005) and Kaushal and Groffman (2005) provide further information on the use of the ^{15}N isotope in studies designed to assess the denitrification processes within the hyporheic zone, and expand on the earlier work using inert solutes or nitrate as tracers (Triska *et al.* 1989a, 1989b, 1990, 1993, Duff and Triska 1990).

3. Groundwater tracers

In previous sections we have discussed use of tracers to identify localities and causes for stream water to enter the hyporheic zone. We have also noted literature that refers to physical transport and storage properties of the hyporheic zone and the effect these may have on water chemistry when the water is released back into the main stream flow. This next section will attempt to summarise tracer methodologies used in the field in an attempt to identify and quantify groundwater flow to the hyporheic zone. These methods appear rather limited as they generally rely upon the detection in the hyporheic zone of solute or heat signatures that are indicative of the local groundwater. In essence, these heat or solute signatures are being used as natural environmental tracers.

3.1. Naturally occurring solutes

In any location within an aquifer, groundwater will possess a chemical signature that is controlled by concentrations of solutes mobilised from the geological formation in which it is contained. Other species transported from external sources, such as adjacent aquifers or surface recharge, may also show a lesser presence. Unless locally contaminated by a foreign substance, the geochemical signature of groundwater may be considered as relatively constant. Therefore, if hyporheic or stream waters show local increases in solutes typically found in the underlying aquifer, then the assumption can be made that the particular stream reach is receiving upwelling groundwater flow. Several studies attempt to monitor hyporheic solute signatures as natural environmental tracers along a reach to determine the pattern of groundwater flow to hyporheic sediments (Hendricks and White 1991, Franken *et al.* 2001, Malcolm *et al.* 2004).

3.2. Heat

Groundwater is often presumed to have a relatively constant temperature, with any variation only likely to be noticeable on a seasonal basis if at all. Groundwater temperatures can be demonstrated to be relatively stable temporally compared to those of surface or stream waters (Constantz 1998). Measurement of the temperature profile along a reach, by using arrays of thermometers/thermistors installed in the streambed has been demonstrated as a viable method to identify groundwater–surface water fluxes over a time series in a UK lowland stream (Keery *et al.* 2005). Using heat profiling for the identification of gaining and losing stream reaches, Conant (2004) recognised that stream water temperature changes along a reach and through a depth profile of hyporheic sediments. This relatively simple experimental procedure, which lets us identify areas of groundwater recharge (downwelling stream water) and discharge (upwelling groundwater) at reach and point scales, now benefits from a range of relatively inexpensive yet high quality instruments and dataloggers being available (Anderson 2005).

Confirmation of the delineation of zones of groundwater discharge or recharge within the hyporheic zone derived from temperature measurements can be provided by the simultaneous injection of conservative solute tracers in the study reach. By monitoring the solute presence in the downstream hyporheic zone, support can also be given to identification of areas of groundwater flow to the hyporheic zone derived from temperature data (Constanz *et al*. 2003). Field demonstration using heat as a tracer to complement incremental stream flow measurements assessing the contribution of groundwater to stream flow is well documented in a hydrological study by Becker *et al.* (2004). Additionally, the upwelling of groundwater and the associated temperature control this has upon hyporheic sediments may also be of significant interest to ecologists studying benthic fauna and fish spawning. Such information may allow correlation between the source of hyporheic water and the benthic communities the sediments can support (Malcolm *et al*. 2002, 2004). Further information is presented in a recent paper by Anderson (2005), in which the use of heat as a groundwater tracer is discussed. The paper also mentions the use of heat tracers in the hyporheic zone and surface waters, and offers a comprehensive background and a thorough review of existing literature.

3.3 Alkalinity

Alkalinity can be used as a natural tracer to identify hyporheic zone areas and stream reaches which are influenced by groundwater discharge. Typically the presence of groundwater makes the water more alkaline than the generally acidic, organically enriched, soil water of streams with flow dominated by surface waters (Rodgers *et al.* 2004). Rodgers *et al*. used Gran alkalinity as a secondary tracer in an attempt to pinpoint the hydrological sources contributing to flow in the braided section. This study focused upon a braided stream reach in Scotland and found from simple analysis of hyporheic samples that groundwater influx was much greater in braided sections, with a significant buffering of stream water being caused by groundwater input under moderate flow conditions (Rodgers *et al.* 2004). The authors note the importance of the buffering effect of groundwater input to the stream reach for successful salmon spawning, and cite work by Malcolm *et al.* (2004), which has also been mentioned in this review.

3.4 Radon

Radon (^{222}Rn) is typically found in higher concentrations in groundwater than in surface water, as it is released from radon-bearing rock. Therefore, radon can be used as a reliable tracer to identify local areas of groundwater input to a stream (Yoneda *et al.* 1991) or larger reach scale inputs from groundwater (Ellins *et al.* 1990). Radon levels in stream or hyporheic waters are not only able to offer an indication of the groundwater input but also may be used in conjunction with other natural tracers (e.g. heat) to infer the age of the groundwater component from radon concentrations (Hoehn and Cirpka 2006).

3.5. Artificial solute injection

If a reach-scale measurement of groundwater flow to a stream across the hyporheic zone is required then a simple continuous injection of a conservative solute can be conducted. The continuous injection of sodium chloride (NaCl) over a 10-day period is documented by Triska *et al.* (1989a). With continuous tracer injection, a plateau in the concentration of tracer solute will be achieved a short distance downstream of the injection point. By making use of a further sampling point downstream, measurement can be made of the solute concentration at that location. If a stream is in receipt of flow from groundwater, this will be indicated by a lower plateau concentration of tracer solute observed at the downstream sampling point due to dilution of tracer mass; it should therefore be possible to calculate the net input to the stream from groundwater.

4. Planning a hyporheic zone tracer study

This section describes things that need to be considered during the design and implementation of a tracer investigation of the hyporheic zone.

4.1. Health and safety

Tracers should be non-toxic and non-polluting and should not give rise to environmental damage or harm. Tracers should not normally be substances listed under the European Union's groundwater and dangerous substance directive that have to be prevented from being released to controlled waters (Groundwater Directive (80/68/EEC)). In England and Wales further information and, where required, permissions for tracer release can be obtained from the Environment Agency.

As with any experimental work in the field, investigators should ensure a full risk assessment is conducted so that any potential risks while on site are identified and, where necessary, action is taken to make sure these are reduced.

4.2. Stream flow conditions

When designing a tracer test to identify hyporheic exchange, consideration should be given to the work of Harvey *et al.* (1996). This paper provides a useful comparison of tracer and hydrometric approaches to assess the rate of hyporheic exchange and storage in a stream under varying base flow conditions. Results demonstrated that hyporheic exchange occurred during all flow conditions. However, when base flow was particularly high (high flux of groundwater across the hyporheic zone) the stream tracer approach using the conservative tracer Cl^- as LiCl was less reliable compared to when base flow was lower, as the force of groundwater inflow to the hyporheic zone reduced the penetration of stream water (Harvey *et al.* 1996).

If, therefore, a conservative tracer such as Cl^- anions delivered as LiCl is to be injected into stream water to identify the extent of hyporheic zone flow-paths, consideration ought to be given to the amount of stream discharge that is derived from base flow (Harvey *et al*. 1996, Wagner and Harvey 1997). A suitable period for conducting the experiment should also be chosen where it is likely that the rate of groundwater flux across the hyporheic zone will be sufficiently low to allow tracer to penetrate into the hyporheic sediments. The subsequent downstream recovery should then more accurately reflect the extent of the hyporheic zone and its flow-paths.

4.3 Test duration

Harvey *et al.* (1996) concluded that the selection of suitable flow conditions to gain accurate information to identify the extent of hyporheic flow-paths and their contribution to transient storage was a vital prerequisite to any tracer study design. Their study also found that it was important to consider test duration. They concluded that the tracer study described was likely to have shown only the influence of shallow hyporheic sediments of high permeability (such as gravel bars). A longer duration test might have captured the later release of tracer travelling in flow-paths in the deeper and hydraulically less conductive alluvial deposits that make up the hyporheic zone further from the channel (Harvey *et al.* 1996). Equally, if a reactive tracer test is planned to investigate the retardation properties of hyporheic sediments, it will have to be conducted over a significantly longer timescale than for a conservative tracer test.

4.4 Tracer selection, injection and sampling strategy

Clearly, it is critical in the design of any investigation studying the hyporheic zone to select a suitable tracer for the information sought (spatial delineation of the hyporheic zone, groundwater recharge, transient storage and retention etc.). There is currently no specific guidance on the use of tracers for hyporheic zone studies. However, existing Environment Agency documentation for the use of tracers in groundwater may offer some transferable techniques and information on tracer suitability (Ward *et al*. 1998). Additionally, the studies referred to in this review should be consulted as sources of guidance for the design of a hyporheic zone tracer study, including further detail regarding tracer injection, sampling and monitoring methods. Ultimately, any field experimentation will demand careful, well-considered design based upon the information required and reference to published literature on previous studies. Literature referred to in this report regarding previous use of tracers in the hyporheic zone is fully referenced in section 6. Appendix 1 provides a summary list of tracers from cited literature in this report, while a recently complied list by the USGS citing studies specifically using lithium as a tracer is provided in Appendix 2.

5 Conclusions and future research

This report has attempted to review existing literature that describes the use of tracers in the hyporheic zone. From this exercise it appears that much of the existing literature comes from a relatively small number of researchers using tracer investigations as a novel experimental approach to better delineate and characterise the hyporheic interface. The relatively sparse library of literature from a handful of investigators shows that neither the hyporheic zone nor the use of tracer tests to achieve a better understanding of this dynamic ecotone have received much attention or research development from a wider scientific audience.

From a holistic hyporheic zone research perspective, Smith (2005) offers a comprehensive outline of knowledge gaps and future research needs as part of the Environment Agency's research programme on groundwater–surface water interactions. Many of the identified knowledge gaps relating to the hyporheic interface and in particular its potential for pollutant attenuation could be addressed to varying degrees by the further development and field use of tracer investigations. Smith (2005) lists the main topics that would benefit from further hyporheic zone research as:

- hyporheic zone architecture;
- flow and hydrology;
- chemical cycling and pollutant attenuation;
- ecology and microbiology.

A review of literature presented in this report suggests that tracer studies have been employed to address the four research requirements listed above, albeit to differing extents. For ecology and microbiology, the potential for the use of tracer studies is perhaps rather limited. However, there remains scope if use of a tracer is considered to determine biotic processes in the hyporheic zone such as when considering biodegradation for pollutant attenuation, or, as in the case of experimental work by Triska *et al.* (1993), to assess nitrification and nitrogen processing. The use of reactive or degrading tracers to identify the capacity of the hyporheic zone to attenuate contaminants is an area which would benefit from greater experimentation, in a similar manner to the increased use of tracers for the assessment of natural attenuation in groundwater over recent years. Further development of such tracer methodology in the hyporheic zone could potentially offer a greater insight into the hyporheic zone as a natural attenuation 'buffer' for agricultural, industrial and mine-water pollution. These were highlighted by the Environment Agency as specific research topics requiring further research in the context of the hyporheic zone (Smith 2005). Similarly, guidance can be sought from literature presented in this report to develop tracer studies to address research focused upon hyporheic zone architecture and flow and hydrology. From a regulatory perspective, perhaps the development of tracer studies to assess natural attenuation within the hyporheic zone may be of most immediate value. This area warrants further support to develop an improved understanding to supplement the relatively limited studies to date.

It appears that often a tracer investigation has been conducted only to provide a supplementary dataset to a larger programme of field experimentation. Given the broad potential spectrum of tracer tests for investigation of the hyporheic zone, those documented to date appear rather limited in their overall remit. In particular, these tests appear to focus on monitoring a natural signature such as heat (Malcolm *et al*. 2002, 2004, Conant 2004, Anderson 2005) or solutes (Hendricks and White 1991, Franken *et al.* 2001, Malcolm *et al.* 2004) to determine the source of hyporheic water; the specific experimental injection of tracers to assess the exchange of stream water to hyporheic pathways (Hendricks and White 1991, Harvey and Bencala 1993, Brunke and Gonser 1997, Cardenas *et al.* 2004); and transient storage and retardation in hyporheic sediments (Fuller and Harvey 2000, Johansson *et al*. 2001, Jonsson and Wörman 2001, Jonsson *et al.* 2003). The existing literature does, however, demonstrate the potential for conducting further field tracer experiments to address some of the research gaps outlined as part of the Environment Agency's research programme on groundwater–surface water interactions (Smith 2005).

The literature reviewed in this report also shows there is scope for the use of tracers in almost all investigations of the hyporheic zone. This scope has been shown at differing scales: at small scales such as the monitoring of temperature or solute profiles to identify localities of groundwater flow to surface waters, or the injection of inert solutes to identify local hyporheic flow-paths, and at larger scale with injection of reactive tracers to assess the performance of attenuation processes for an entire stream reach. If a hyporheic zone investigation is planned, monitoring of a tracer has the potential to offer high resolution, in situ data for the required parameters. Any further development and carrying out of tracer investigations, therefore, can only act to offer greater understanding of processes occurring within the presently under-researched hyporheic zone and its role as a transitional interface between groundwater and surface water.

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7 Glossary of terms

Aerobic	An environment that contains oxygen; biodegradation or other process that operates in the presence of oxygen
Anaerobic	An environment that contains no oxygen; biodegradation or other process that operates in the absence of oxygen
Anoxic	Deficient in oxygen
Benthos	Organisms that live primarily on (not in) stream sediments
Biodegradation	The reduction of mass (usually considered a contaminant) by biotic processes. Important factor when considering natural attenuation
Colmation	(Formation of) low permeability deposits due to filtration of fine-grained material within riverbed sediments
Ecotone	Ecosystem at the interface of environmental compartments
Groundwater	Volume of groundwater within an aquifer
Hyporheos	Assemblage or community of organisms that live in the hyporheic zone; organisms that live among (between) sand grains
Natural attenuation	The reduction of a contaminant mass or flux by processes naturally occurring within a particular environment
Oxic	In the presence of oxygen
Programme of Measures	Collection of regulatory, management and fiscal methods to improve environmental quality under the Water Framework Directive
Retardation	The reduction in transportation rate of a solute compared to the rate of advective flow
Riffle	Deposit of gravel and other coarse sediments within a river; often associated with a deeper pool
Riparian zone	Flood plain and associated areas adjacent to a river
Sorption	The attachment of a solute to a mineral surface
Transient storage	Temporary storage of solutes within sediment pathways due to a tortuosity of pathways and/or retardation processes

Appendix 1

Summary of tracers referred to in this report, and corresponding authors

Natural environmental tracers

- **Heat** (Constantz 1998)
  (Constantz *et al*. 2003)
  (Becker *et al*. 2004)
  (Malcolm *et al.* 2002)
  (Malcolm *et al*. 2004)

A thorough review of the use of heat as a groundwater tracer is made in a recent paper by Anderson (2005).

- **Groundwater solute signature** (Hendricks and White 1991)
  (Malcolm *et al.* 2004)
  (Franken *et al.* 2001)

- **Radon-222** (Cecil and Green 1999)
  (Ellins *et al.* 1990)
  (Ellins *et al*. 1991)

Anthropogenic environmental inert (hydrological) tracers

- **CFCs** (Busenberg and Plummer 1992)
  (Plummer and Busenberg 1999)

- **Caesium (^{137}Cs)** (Nyffeler *et al*. 1986)
  (Comans *et al.* 1991)
  (Comans and Hockley 1992)
  (Smith and Comans 1996)

Anthropogenic environmental reactive tracers

- **Acid mine water derived trace metals** (Fuller and Harvey 2000)

Artificial inert tracers (hydrologic tracers)

- **Chloride anions (Cl$^-$)** (Triska *et al*. 1989a, 1989b)
  (commonly as NaCl or LiCl) (Triska *et al.* 1990)
  (Triska *et al*. 1993)
  (Duff and Triska 1990)
  (Salehin *et al.* 2004)
  (Packman and Salehin 2003)
  (Packman and MacKay 2003)

○ **Potassium iodide (KI)**	(Salehin *et al.* 2003)
○ **Tritium (^3H_2O)**	(Jonsson *et al*. 2001) (Jonsson and Wörman 2001) (Jonsson *et al*. 2003)
○ **Dyes**	(Salehin *et al.* 2004)
○ **Bromide anions (Br^-)** *(commonly as KBr)*	(Fuller and Harvey 2000) (Triska *et al*. 1989a, 1989b) (Triska *et al.* 1990) (Triska *et al*. 1993) (Duff and Triska 1990)

Artificial reactive tracers

○ **Chromium (as $^{51}Cr(III)$)**	(Jonsson *et al.* 2001) (Jonsson and Wörman 2001) (Jonsson *et al.* 2003)
○ **Nitrate (as $NaNO_3$)**	(Triska *et al*. 1989a) (Duff and Triska 1990)

Appendix 2

USGS reading list on the use of lithium as a stream tracer

Compiled by M. Cox and K. Bencala – original 11 July 2005, revised 23 September 2005. Available online at http://water.usgs.gov/nrp/proj.bib/bencala.html

Lithium Tracer

Assessment of metal loads in watersheds affected by acid mine drainage by using tracer injection and synoptic sampling: Cement Creek, Colorado, USA. BA Kimball, RL Runkel, K Walton-Day, KE Bencala, *Applied Geochemistry*, **17**: 1183–1207, 2002.

Testing and comparison of four ionic tracers to measure stream flow loss by multiple tracer injection. GW Zellweger, *Hydrological Processes*, **8**: 155–165, 1994.

Characterisation of transport in an acidic and metal-rich mountain stream based on a lithium tracer injection and simulations of transient storage. KE Bencala, DM McKnight, GW Zellweger, *Water Resources Research*, **26**(5): 989–1000, doi: 10.1029/89WR03235, 1990.

Interactions of solutes and streambed sediments 2. A dynamic analysis of coupled hydrologic and chemical processes that determine solute transport. KE Bencala, *Water Resources Research*, **20**(12): 1804–1814, 1984.

Lithium Background

Lithium isotopic composition and concentration of the upper continental crust. FA Teng, WF McDonough, RL Rudnick, C Dalpe, PB Tomascak, BW Chappell, S Gao, *Geochimica et Cosmochimica Acta*, **68**(20): 4167–4178, doi: 10.1016/j.gca.2004.03.031, 2004.

Lithium and its isotopes in major world rivers: implications for weathering and the oceanic budget. Y Huh, L-H Chan, L Zhang, JM Edmond, *Geochimica et Cosmochimica Acta*, **62**(12): 2039–2051, 1998.

Lithium Stream Tracer Examples

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pH dependence of iron photoreduction in a rocky mountain stream affected by acid mine drainage. DM McKnight, BA Kimball, RL Runkel, *Hydrological Processes*, **15**(10): 1979–1992, doi: 10.1002/hyp.251, 2001.

The contribution of old and new water to a storm hydrograph determined by tracer addition to a whole catchment. R Collins, A Jenkins, M Harrow, *Hydrological Processes* **14**: 701–711, 2000.

Analysis of transient storage subject to unsteady flow: diel flow variation in an Antarctic stream. RL Runkel, DM McKnight, ED Andrews, *Journal of North American Benthological Society*, **17**(2): 145–154, 1998.

Reactive solute transport in acidic streams. RE Broshears, *Water, Air and Soil Pollution*, **90**: 195–204, 1996.

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