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High resolution in-situ monitoring of hyporheic zone biogeochemistry

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Professor Mike Depledge Head of Science

Executive Summary

Fulfilling the objectives of the Water Framework Directive (2000/60/EU) requires research in the hyporheic zone to develop:

- better methods to assess mass flux across the groundwater–surface water interface;
- the ability to predict the significance of attenuation processes within the hyporheic zone;
- the ability to link hyporheic and/or benthic chemical conditions and ecological health;
- reliable and transferable conceptual models of flow and attenuation processes at the groundwater–surface water interface.

Essential to meeting these needs is better quality and resolution of biogeochemical data gathered from the hyporheic zone.

Recent years have seen a rapid growth in the development and use of environmental measurement devices designed to be deployed *in situ* in aquatic sedimentary environments. These probes offer a potential solution to the data needs of future work on the biogeochemistry of the hyporheic zone. However, to date there is no coherent overview of the range of probes available, their capabilities and/or limitations, and the problems that must be overcome to establish *in situ* high-resolution methods in hyporheic zone research. This report provides information required by researchers in the field who wish to use high-resolution *in situ* techniques in the hyporheic zone.

The term *in situ* is used in a scientific context to describe a measurement made at the time and location in which it naturally happens. In an environmental context this usually means a process that occurs ‘in the field’ on a ‘real’ system, rather than in a laboratory or model system. The report sets out five conditions that define a high-resolution *in situ* study of hyporheic zone biogeochemistry.

Existing hyporheic zone research methods are largely based around physical sampling and removal for *ex situ* analysis. Attempts to conduct *in situ* measurements have concentrated on the use of chambers that provide some degree of environmental control to improve measurement reliability. True *in situ* measurement devices range from standard temperature, pH and redox probes to electrochemical probes, such as ion-selective and gel-integrated microelectrodes (GIMEs), and reactive surface probes, such as diffusive gradient in thin film (DGT), diffusive equilibration in thin film (DET) and semi-permeable membrane device (SPMD) probes. These can provide direct measurement of a wide variety of chemical species of interest, including sulphides, metals, trace elements, polychlorinated, organochlorine and polycyclic aromatic hydrocarbons, and a wide range of common nutrient ions.

Biosensors are an increasingly widely used tool for environmental monitoring and have the advantage of being able to distinguish bioavailable chemical species from total or active concentrations. Significant technological developments in genetic modification and biomolecular science in recent years mean that the range of targets for biosensors is increasingly broad, and includes many organic pollutants, pathogens, heavy metals and standard measures, such as biological oxygen demand (BOD) and temperature. Other techniques, including optodes, fibreoptics and those of geophysics, are discussed.

Contents

1 Introduction

1.1 Context

The Environment Agency has established a research programme on groundwater–surface water interactions, with specific focus on pollutant attenuation processes at the interface of groundwater and surface waters, sometimes called the hyporheic zone (Smith, 2004). The research aims to understand the controls on pollutant flow and behaviour within the hyporheic zone and develop a series of definitions and conceptual models to better support workers in a range of disciplines with interests in the groundwater–surface water interface. Fulfilment of policy objectives under the Water Framework Directive (2000/60/EU) will require research in the hyporheic zone to develop:

- the ability to assess mass flux across the groundwater–surface water interface;
- the ability to predict the significance of attenuation processes within the hyporheic zone;
- the ability to link hyporheic/benthic chemical conditions and ecological health;
- reliable and transferable conceptual models of flow and attenuation processes at the groundwater-surface water interface.

Essential to meeting these research needs is an increase in the quality and resolution of biogeochemical data gathered from the hyporheic zone. Modern biogeochemistry research of the hyporheic zone remains largely dependent on classic 'sample collection' methodologies. Sampling permits the use of precision laboratory analytical techniques, but logistically cannot support near-continuous time-series measurements nor the fine spatial measurement scales required to understand biogeochemistry at the groundwater–surface water interface in detail. Recent years have seen a rapid growth in the development and use of environmental measurement devices designed to be deployed *in situ* in aquatic sedimentary environments. These probes offer a potential solution to the data needs of future studies of the biogeochemistry of the hyporheic zone. However, to date there is no coherent overview of the range of probes currently available, their capabilities and/or limitations, and the problems that must be overcome to establish *in situ* high-resolution methods in hyporheic zone research.

1.2 Objectives of this report

This report provides information required by researchers in the field who wish to use high-resolution *in situ* techniques in the hyporheic zone. The report reviews the current state of the art in methodologies for the *in situ* measurement of processes that control biogeochemical reactions within the hyporheic zone at high spatial and temporal resolutions. It synthesises information on current techniques with an exploration of new methods being used in related disciplines (e.g., marine science) and developing technologies. The report then presents a critical comparison of all the potential research tools and concludes with an assessment of the main research areas in hyporheic zone biogeochemistry in which these relatively novel approaches might be effectively employed.

1.3 Definitions

1.3.1 *In situ* measurements

The term *in situ* is Latin and means, literally, 'in (the) place'. It is used in a scientific context to describe a measurement made at the time and location in which the event naturally happens. In an environmental context this usually means a process that occurs 'in the field' on a 'real' system, rather than in a laboratory or model system. Note the element of *in tempus* – 'in time';

the measurement captures the process in context with regard to time and space. In contrast, a sample is a representative element of the system that is removed from the system. Sampling thus creates a sub-system which may react to the new conditions imposed by sample storage, and hence much of sampling methodology is concerned with swift and/or careful handling of samples to preserve their integrity (e.g., Keith, 1990).

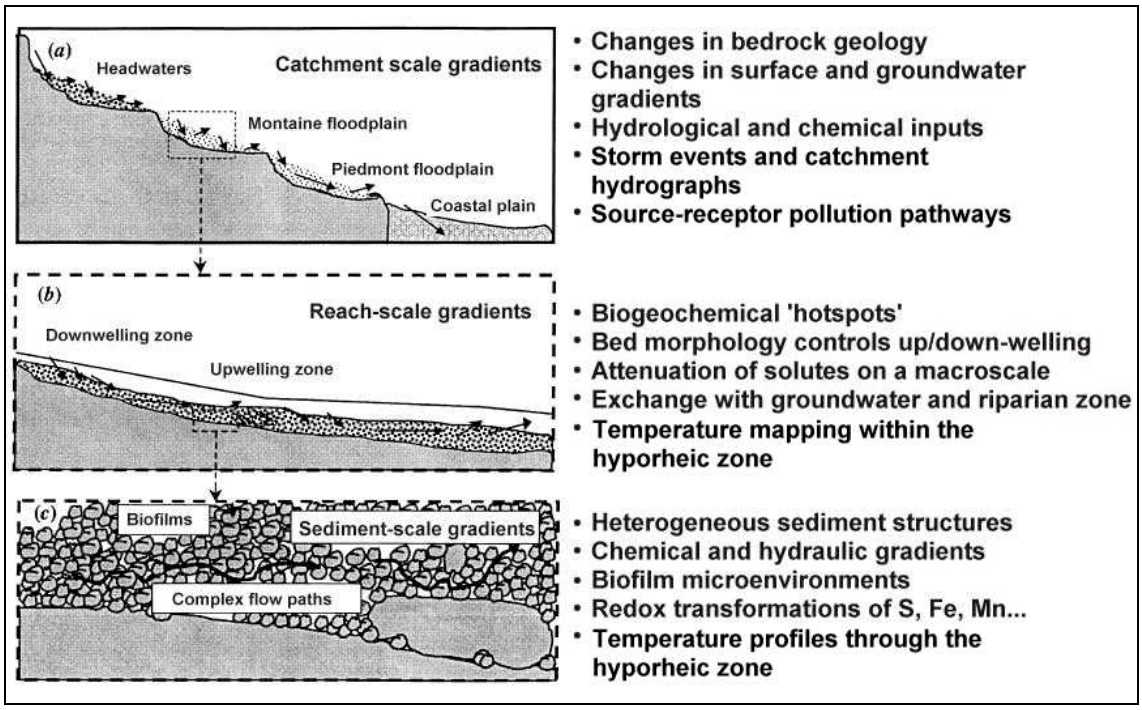

Figure 1.1 Study scales applicable to hyporheic zone biogeochemistry (after Boulton *et al*. 1998).

1.3.2 High resolution in the hyporheic zone

Data resolution has three main dimensions – spatial, temporal and analytical:

- spatial resolution of a data point is defined by the area or volume that contributes information to that data point;
- spatial resolution of a data set is defined by the separation of data points in space, relative to the external and internal dimensions of the system they seek to describe;
- temporal resolution of a data point is defined by the length of time required to make the observation;
- temporal resolution of a data set is defined by the separation of data points in time, and can vary from continuous (infinitely small separation between measurements) to a single measurement (infinitely large separation);
- analytical resolution is determined by the probe or technique used to make the measurement, and may be affected by the upper and lower limits of detection, precision, sample size, operating environment required, and the need to make repeated or replicate measurements to test the accuracy and ensure statistical strength in the dataset.

Spatial, temporal and analytical resolutions are often co-dependent and strongly characteristic of the measurement tool to be employed. Judgement of data resolution as ‘high’ or ‘low’ must be made within context of the system under study – whether its processes occur rapidly or slowly relative to the capabilities and design of the measurement plan, and whether changes in the variables within the system can be detected adequately by the analytical techniques used.

High-resolution *in situ* methods to monitor hyporheic zone biogeochemistry must therefore be able to capture biogeochemical processes at the spatial and temporal scales over which these vary, using probes that can reliably detect the reactants at the levels at which they are typically present. Boulton *et al*. (1998) define three discrete spatial scales in the hyporheic zone–sediment, reach and catchment (*Figure 1.1*). *Table 1.1* summarises some important parameters by which we define a 'high' resolution study of hyporheic zone biogeochemistry at each of these scales.

Inspection of Table 1.1 suggests that an *in situ* high-resolution study of hyporheic zone biogeochemistry must, using *in situ* measurement techniques, encompass one or more of the following:

A. Conduct general measurement of ambient conditions, physical structures, water flow and chemical gradients at spacings of less than 0.1 m;
B. Conduct measurements of chemical species at concentrations of less than 1 mg/l for major ions/nutrients and less than 1 μg/l for trace compounds, at a precision of better than ±0.1 mg/l or ±0.1 μg/l, respectively;
C. Conduct specific measurements of sediment pore structures, porewater flow paths, biofilm structures and surface chemistry at a spatial resolution of 10^{-3} m or less (sub-millimetre scale);
D. Repeat measurements at intervals of several minutes, if not continuously, to capture dynamic changes in flow patterns and chemical gradients;
E. Extend measurements over periods of weeks or months to capture seasonal changes in time-integrated biogeochemical conditions.

These conditions can be employed as standards against which to judge the performance of various hyporheic measurement techniques.

Table 1.1: Spatial, temporal and analytical standards for high resolution monitoring of hyporheic zone biogeochemistry.

Parameter		Spatial	Temporal	Analytical
Sediment scale		**10^{-6} to 10^{-2} m**		
Ambient conditions	Temperature	10^{-1} m	Minutes	0.05 °C
	pH	10^{-2} m	Minutes	0.05 units
	Redox potentials	10^{-3} m	Hours	10 mV
Biomass	Biofilm (protein content, cell nos. etc)	10^{-6} m	Hours	
Hydrology	Flow rate Flow heterogeneity	10^{-2} m	Minutes	0.01 m/s
Major ionic species	O_2, NO_3^-, NH_4^+, Ca^{2+}, CO_3^{2-}, NO_2^-	$<10^{-2}$ m	Minutes	0.1 mg/l
Metabolic indicators	O_2 flux Fe, S, acetate	$<10^{-2}$ m	Minutes	0.1 mg/l
Nutrients	N, P, K	$<10^{-2}$ m	Minutes	0.1 mg/l
Pollutants - metals	Pb, Cu, U, Cr, …	$<10^{-2}$ m	Minutes	0.1 mg/l
Pollutants - organic	PCB, PAH, …	$<10^{-2}$ m	Minutes	0.1 μg/l
Sedimentary environment	Grain characteristic Pore sizes	10^{-2} m	Months	10^{-6} m
Trace metals		$<10^{-2}$ m	Minutes	0.1 μg/l
Reach scale		**10^{-2} to 10^{2} m**		
Ambient conditions	Temperature profiles and maps Redox hotspots	10^{-1} m	Minutes	0.05 °C 10 mV
Biomass	Biofilm (protein content, cell nos. etc)	10^{-1} m	Days	
Hydrology	Up- and down-welling flow	10^{-1} m	Minutes	
Major ionic species Metabolic indicators Nutrients Pollutants – metals Pollutants – organic	Flux and gradients	10^{-1} m	Minutes	0.1 mg/l
Sedimentary environment	Ripples and riffles Sub-surface structures	10^{-1} m	Minutes	10^{-2} m
Trace metals	Flux and gradients	10^{-1} m	Minutes	0.1 μg/l
Catchment scale		**10^{2} to $>10^{3}$ m**		
Bedrock geology and relief		10 m	Years	10^{-1} m
Hydrological and/or chemical inputs	Groundwater flow	10 m	Months	
	Point source inputs	1 m	Hours	10^{-2} m
	Diffuse inputs	10^{2} m	Days	

2 Probes and technologies

2.1 Overview

Existing research methods used to study the hyporheic zone are largely based on physical sampling and removal for *ex situ* analysis. A variety of innovative sampling experiments have been used to capture biogeochemical parameters and pollutant attenuation in a range of hyporheic settings (examples of which include Baker and Vervier, 2004; Carlyle and Hill, 2001; Conant Jr. et al., 2004; Edwardson et al., 2003; Feris et al., 2004; Franken et al., 2001; Malcolm et al., 2004; Malcolm et al., 2003; Rodgers et al., 2004; Salehin et al., 2003; Storey et al., 2004). *Table 2.1* summarises the range of measurement techniques currently and potentially available to *in situ* high-resolution studies of hyporheic zone biogeochemistry together with the main references.

In an attempt to better constrain the measurement environment while maintaining a representative equilibrium with the streambed environment, *in situ* experimental chambers (benthic chambers, microcosms, hyporheic chambers, flow or flux chambers) and controlled plot methods have been developed (e.g., Craft et al., 2002; e.g., Crenshaw et al., 2002; Dodds and Brock, 1998; Uzarski et al., 2001; Uzarski et al., 2004). Many of these rely on sampling methodologies to extract data from the chambers. Hyporheic chambers share many design principles with similar devices use to measure chemical and water flux across sediment–water boundaries in lakes (e.g., Thorbergsdottir et al., 2004) and in marine environments (e.g., Forster et al., 1999). The latter field represents a significantly advanced state of development of these methodologies and a valuable potential resource for future hyporheic zone research (e.g., Viollier et al., 2003).

True *in situ* measurement devices range from analytical standard temperature, pH and redox probes to established electrochemical probes, such as ion-selective and gel-integrated microelectrodes (GIMEs, here classed as electrochemical microsensors) and diffusive gradient in thin film (DGT), diffusive equilibration in thin film (DET) and semi-permeable membrane device (SPMD) probes (here grouped as reactive surface probes). These are able to provide direct measurement of a wide variety of chemical species of interest, including heavy metal trace elements (e.g., Herdan et al., 1998; Pei et al., 2001; Tercier-Waeber et al., 1999; Wang et al., 1995), polychlorinated and organochlorine compounds (PCDD/Fs, PCBs, PAHs, e.g., McCarthy and Gale, 2001), a wide range of nutrients (e.g. NH4+, Ca, Cl, NO3, Mortimer et al., 1998), and sulphide and related species (e.g., DeVries and Wang, 2003; e.g., Naylor et al., 2004).

Chalcogenide and chalcohalide glasses have been recognised as ion-selective materials for heavy metals and anions for some years (e.g., Bychkov, 1995) and have recently found application for the *in situ* measurement of sulphide in wastewaters (Miloshova et al., 2003). Optical fibres based on chalcogenide glasses have made possible *in situ* infrared (IR) spectroscopy (Michel et al., 2004). Other optical microsensors (micro-optodes) and other techniques based on ultraviolet (UV) fluorimetry and light scattering have been introduced to marine benthic studies and industrial wastewater monitoring (e.g., Thomas and Constant, 2004; Vanrolleghem and Lee, 2003; e.g., Viollier et al., 2003). These techniques are able directly to measure oxygen and nitrate concentrations, salinity, phenols, total organic carbon (TOC), ammonia, suspended solids, biological oxygen demand (BOD) and biomass metabolism (Thomas and Constant, 2004), but their *in situ* applicability in the riverine environment is as yet unproved.

Biosensors are increasingly widely used for environmental monitoring (Rodriguez-Mozaz et al., 2005) and have the advantage of being able to distinguish bioaccessible chemical species from total or active concentrations. Significant technological developments in genetic modification and biomolecular science in recent years mean that the range of analytes for biosensors is

increasingly broad, and includes many organic pollutants, pathogens, heavy metals and standard measures, such as BOD and temperature (e.g., Nivens et al., 2004).

Finally, several geophysical techniques offer a largely non-invasive, real-time method to collect important contextual data for high-resolution biogeochemical studies. These include borehole gamma ray and conductivity logging, borehole tomography and cross-stream electrical imaging (Acworth and Dasey, 2003) used to delineate the hyporheic zone of a tidal creek based on variations in porewater salinity, acoustic imaging techniques to measure real-time changes in sediment surface profiles (Betteridge et al., 2003) and ground-penetrating radar, which can detect fine-scale structures in shallow sediments (e.g., Neal, 2004).

Table 2.1: Biogeochemical targets for monitoring devices and technologies discussed in this report.

Measurement / Probe type	Biogeochemical target										Example reference
	Ambient conditions	Biomass	Hydrology	Major ionic species	Metabolic	Nutrients	Pollutants – metals	Pollutants –	Sediment environs	Trace metals	
Piezometer-based sampling	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	Conant Jr *et al*. (2004) Malcolm *et al*. (2003)
Flux chambers and microcosms	✓	✓			✓	✓					Uzarski *et al*. (2004)
Standard analytical electrodes	✓				✓						Conant Jr (2004)
Ion-selective electrodes (ISEs)				✓	✓	✓	✓	✓		✓	Muller *et al*. (1998) Muller *et al*. (2003a)
Stripping electrodes (ASV, CSV)					✓			✓		✓	Tercier-Waeber *et al*. (1998)
Ultramicroelectrode arrays (UMEAs)				✓			✓			✓	Tercier-Waeber *et al*. (1999)
DET/DGT/redox gel probes	✓			✓	✓		✓	✓		✓	Mortimer *et al*. (1998) Zhang *et al*. (1998b)
SPMDs								✓			McCarthy and Gale (2001)
Optical microsensors (optodes)	✓			✓	✓	✓	✓			✓	Glazer *et al*. (2004) Holst and Grunwald (2001)
IR spectroscopy		✓			✓	✓		✓			Michel *et al*. (2004)
Biosensors	✓	✓		✓	✓	✓	✓	✓		✓	Nivens *et al*. (2004) Paitan *et al*. (2003)
Electrical tomography and imaging	✓		✓						✓		Acworth and Dasey (2003)
Ground penetrating radar (GPR)									✓		Neal (2004)
Acoustic imaging			✓						✓		Betteridge *et al*. (2003)

2.2 State of the art sampling – the current approach

A brief examination of some recent hyporheic zone investigations is useful not only to assess where *in situ* and high-resolution technologies can be employed most usefully, but also as an attempt to understand why they have not been used to date. What barriers existed in the past, and can they be overcome now or in the near future?

The hyporheic zone has been sampled at all scales from catchment (e.g., Salehin et al., 2003) through reach (e.g., Baker and Vervier, 2004; Carlyle and Hill, 2001; Conant Jr. et al., 2004; Edwardson et al., 2003; e.g., Rodgers et al., 2004) to studies of individual up- and down-welling zones (e.g., Feris et al., 2004; Franken et al., 2001; Malcolm et al., 2004; e.g., Malcolm et al., 2003; Storey et al., 2004) and sediment-scale processes using core sampling techniques and microcosms (e.g., Moser et al., 2003; Sheibley et al., 2003). The studies quoted here represent only a fraction of the total published material. Most pertinent here are those studies that provide context for, or attempt to address, a phenomenon to which *in situ* high-resolution techniques can be applied. These are typically the reach-to-riffle scales and studies based on cores and/or microcosms, examples of which are introduced in the following sections

2.2.1 Sediment-scale – core sampling

Moser *et al*. (2003) investigated the potential of biogeochemical processes in the Columbia River, Washington State, USA, to contribute to the natural attenuation of contaminants that leached from the Hanford site, the USA's centre for the production and research of nuclear weapons during the Cold War. The 'freeze core' method was used to sample intact columns of hyporheic zone sediment. Liquid nitrogen is pumped into a tube driven vertically into the streambed, which freezes sediments, porewater and biota in place and thus maintains the spatial integrity of geochemical and microbiological gradients within the extracted core. This method may permit high-resolution spatial and analytical data in the vertical plane, but has poor horizontal spatial resolution unless cores are closely spaced. The time required to freeze the core is around 40 minutes in a temperate stream (Moser et al., 2003). Clearly, exact repeat measurements are not possible since this is a destructive sampling method. However, these authors sampled the same sites over a 13 km reach on three occasions (March, May and November).They analysed porewater chemistry, microbial communities and chromate reduction potential using ion chromatography, continuous intracranial pressure (ICP) analysis, ^{14}C acetate mineralisation, phospholipid fatty acid (PLFA) analysis, plate culture and incubation experiments in the laboratory. They do not report spatial (vertical) profiles in the data. Major ions were measured at 0.1 mg/l.

Moser *et al*. (2003) conclude with a typical sentiment: 'The spatial and temporal controls governing microbial abundance and activity … remain poorly understood … and the development of insights into these controls should be a focus of future research'. Core sampling techniques can provide useful data to characterise hyporheic zone sediments, porewater and microbiology, but significantly fail to capture lateral and temporal heterogeneity.

2.2.2 Sediment-scale – studies at riffles

Sites of up- and down-welling flow between the stream and hyporheic zone are the main targets for sample-based studies. Two studies by Malcolm *et al*. (Malcolm et al., 2004; Malcolm et al., 2003) demonstrate the use of a suite of techniques emplaced in the stream, including buried hyporheic-sample collection devices (*Figure 2.1*), bankside piezometer nests and borehole sampling for groundwater chemistry. Using several such instruments at several sites over a 150 m reach, Malcolm *et al*. (2003) were able to characterise the spatial and temporal variability of groundwater–surface water exchange simultaneously at sediment and reach scales. Using the buried samplers, hyporheic water at 150 and 300 mm depth below the streambed was sampled

and analysed for dissolved oxygen (DO) and pH (both on site), conductivity, alkalinity, major cations, anions and nutrients (standard laboratory methods with a precision of 0.01 mg/l). Samples and simultaneous hydrological measurements (vertical head gradient) were made weekly and 'more frequently' during rainfall events (Malcolm et al., 2003). *In situ* automated measurements of stream stage were made at intervals of 15 minutes throughout the experiment using a pressure transducer and datalogger.

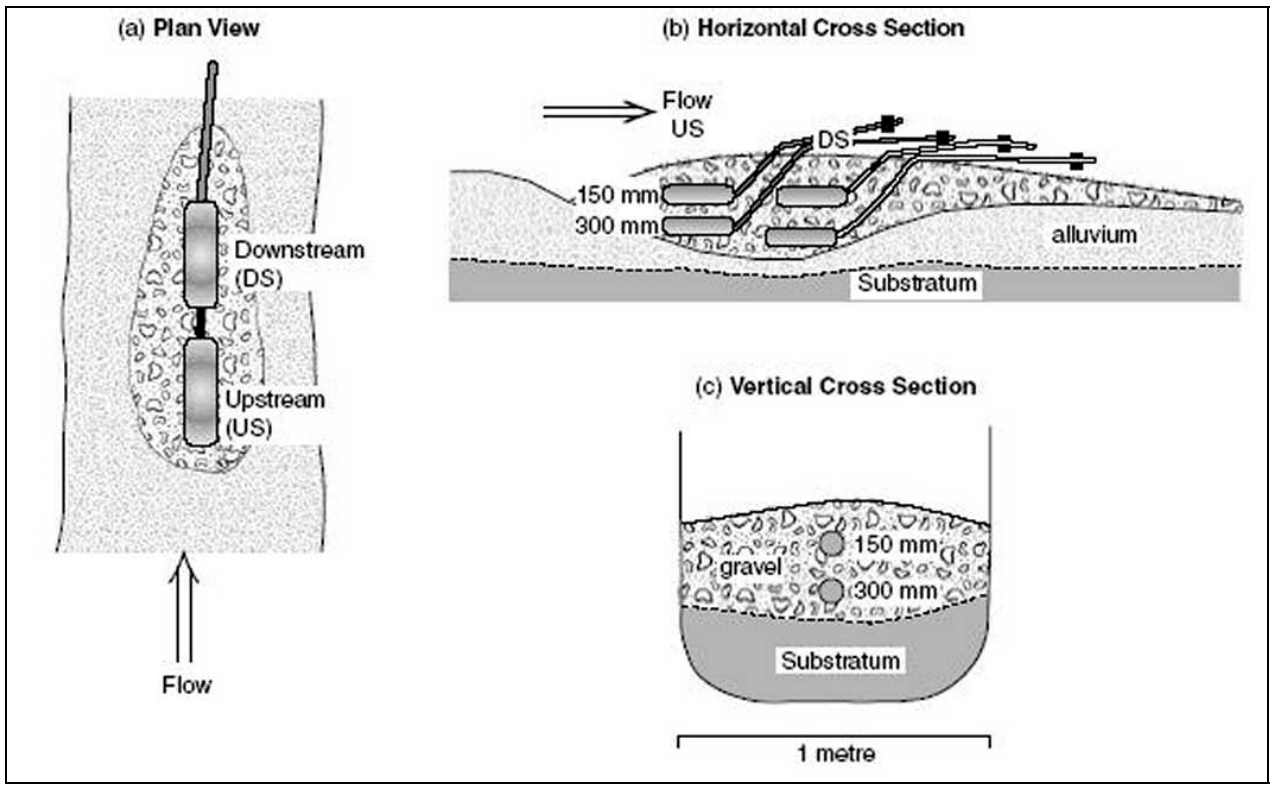

Figure 2.1 Hyporheic sampling infrastructure described by Malcolm *et al*. (2003). Water sampling chambers are buried in artificial riffles which become integrated into the hyporheic zone system. Similar methodology could be used for deployment of *in situ* probes. Copyright 2002 John Wiley and Sons, Ltd**.**

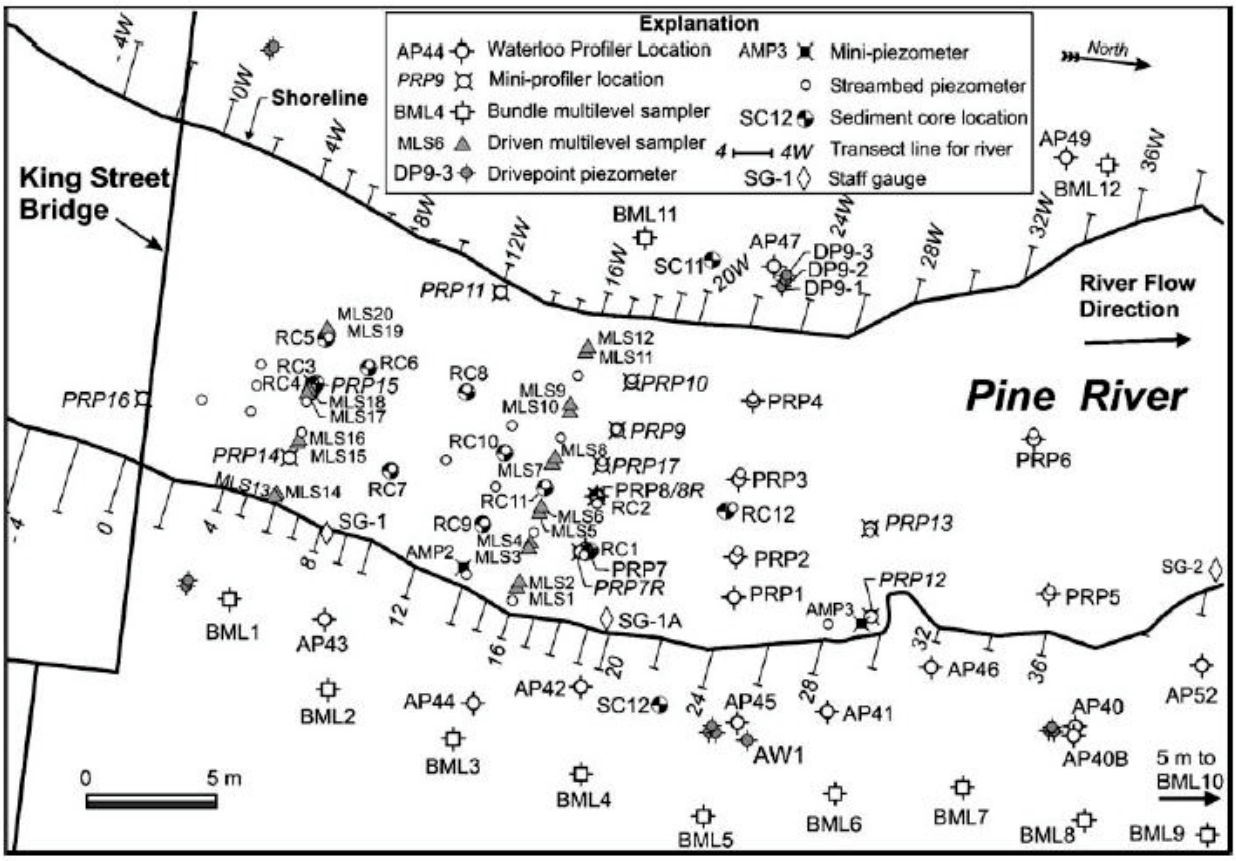

Figure 2.2 Plan view of instrumentation and sampling infrastructure deployed by Conant Jr *et al*. (2004) for an intensive study of PCE degradation in an hyporheic zone. Copyright 2004 Elsevier B.V.

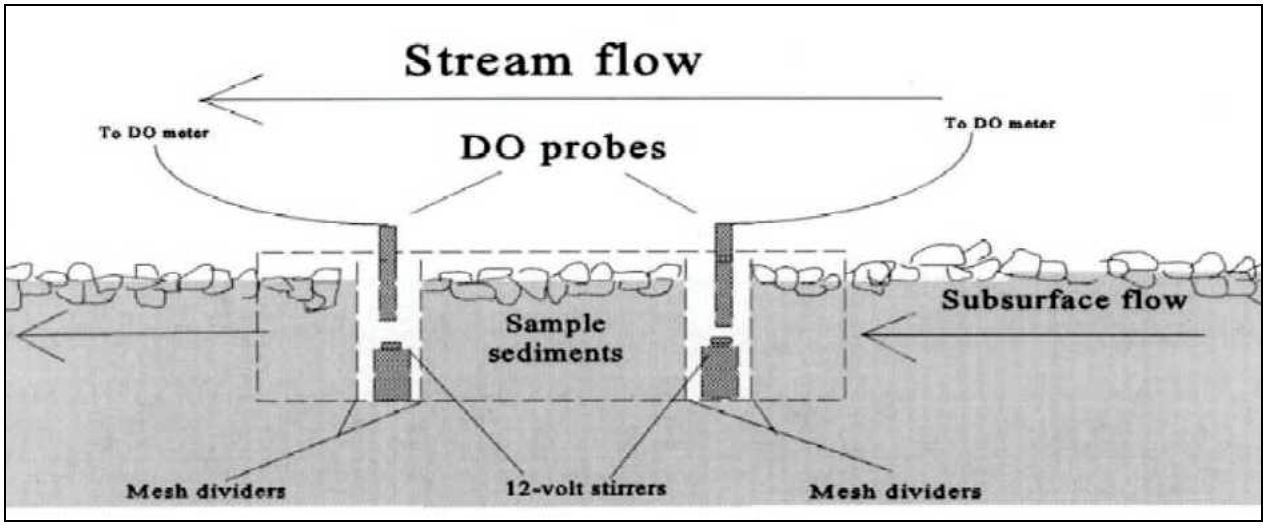

Figure 2.3 Schematic diagram showing a hyporheic chamber (Uzarski *et al*. 2001). The chamber is an open-ended steel cylinder of square cross-section. The chamber contains sediment taken directly from the point of emplacement and hydraulically connected to the wider hyporheic zone. This design enables *in situ* monitoring of dissolved oxygen (DO). The cylinder has a clear acrylic top to enable sunlight to reach the sediment surface within. Copyright 2001 Kluwer Academic Publishers.

Malcolm *et al*. (2003) were able to distinguish vertical gradients in DO, conductivity and NO_3, and to interpret these in terms of surface and groundwater mixing, up- and down-welling flow, hyporheic residence times and dynamic variations in groundwater–surface water exchange during and after individual rainfall events. A later study (Malcolm et al., 2004) on a different stream, using the same instrumentation plus vertical temperature profiles measured *in situ* at depth intervals of 0.2 m across streambed riffles, was similarly able to measure and interpret patterns of porewater chemistry and water exchange through the hyporheic zone in the context of detailed hydrological data. In both studies, local spatial resolution of measurements was less than 1 m horizontally and 0.15 m vertically, with practically simultaneous data collection at sites several tens of metres apart at a temporal resolution of a week, supported by contextual stream flow data at 15 minutes resolution. Greater temporal resolution around storm events was able to capture dynamic variation in hyporheic zone hydrochemistry in direct response to hydrological variability.

An earlier study by Franken *et al*. (2001) investigated biological, physical and chemical processes across a riffle using core sampling to retrieve data at depth intervals of 0.2 m. Simultaneous hyporheic water samples were taken from permanent piezometer nests across the same riffle. Data gathered included temperature, conductivity, pH, redox potential and DO (field measurements using a 'multiprobe'), nitrogen species by spectrophotometry, sediment protein content, bacterial and faunal counts, and organic matter content. Although horizontal spatial resolution was better than 1 m between core samples, temporal resolution was poor, with a single repeat measurement after 1 month. Hydrochemical data gathered was averaged spatially upstream and downstream of the sediment sampling sites.

Franken *et al*. (2001) were able to report variations in hydrochemical and biological gradients with depth related to both up- and down-welling locations within the riffle–pool complex they studied. However, because of both the lack of contextual hydrochemical data for the local stream and groundwater and the absence of a time-series data set for hydrological conditions, they were unable to draw conclusions about dynamic change in the hyporheic zone.

These approaches are able to characterise decimetre- (vertical) and metre-scale (horizontal) variations in physical, chemical and biological characteristics of the hyporheic zone and, with useful supporting data, interpret them in the context of dynamic groundwater–surface water interactions over hydrologically important time intervals.

2.2.3 River reach-scale

Of the many stream and hyporheic zone investigations that approach the subject at the reach scale, few can claim to be as extensive and detailed as that of Conant Jr *et al*. (2004). The 30 month study of a 60 m long reach of the Pine River, Ontario, Canada, and its immediate environs deployed 80 piezometers and mini-piezometers, numerous profilers and multi-level samplers, took 25 sediment cores, collected surface water samples and probed the sub-surface with ground-penetrating radar (GPR). *Figure 2.2* shows the density of instrumentation involved.

The target of the investigation was a groundwater pollutant plume composed of the volatile organic contaminant tetrachloroethene (polychloroethene, PCE) and its degradation products, which was known to be moving down the groundwater gradient towards the stream. How would these behave in the complex biogeochemical environment of the hyporheic zone? Cores, geophysics and borehole piezometry provided detailed information about groundwater hydrogeology adjacent to the river and demonstrated constant flow from the groundwater to the stream across the hyporheic zone within the reach, regardless of in-stream flow variations. A detailed map of streambed hydraulic conductivity and discharge was made possible by *in situ* temperature profiling (Conant Jr., 2004), which showed that the discharge correlated more closely with the deeper geology than with the surficial deposits and streambed morphology. Detailed sampling of the streambed hyporheic zone showed intense anaerobic biodegradation of the PCE to its degradation products within the top 2.5 m of the bed, compared to almost zero

degradation over 195 m in the adjacent aquifer. Vertical and horizontal gradients in contaminant concentrations and biodegradation rates could be resolved at the centimetre scale, and these could be correlated with sub-surface hydrogeology.

The results presented by Conant Jr *et al*. (2004) demonstrate that a sampling-based investigation can provide high-resolution spatial and temporal datasets that characterise the heterogeneity in structure and process across a reach-scale hyporheic zone. In fact, this study could be considered a 'crossover' work, in that *in situ* data acquisition by temperature profiling and GPR provided vital contextual data for the interpretation of the samples collected. However, the study was a major exercise undertaken over three or more years for a PhD thesis (Conant Jr., 2001). Clearly, the methodology could not be repeated on a routine basis. On the other hand, though, the study shows that the degree of heterogeneity across even a small area of the hyporheic zone is sufficient to raise the question of how to ensure that less comprehensive studies represent the wider hyporheic zone. What if a high-resolution *in situ* study at the sediment scale fails to capture (or exclusively captures) a 'hot spot' of activity? This question applies equally to studies of the natural biogeochemistry of the hyporheic zone and to assessments of biodegradation capacity and pollution attenuation.

High-resolution *in situ* measurement techniques have the potential to greatly improve sediment-scale sampling of the hyporheic zone by increasing both spatial and temporal resolution while maintaining analytical resolution. This improvement, however, becomes meaningless without an appropriate characterisation of the local hyporheic zone environment at larger scales, recalling that the specification of high resolution is scale dependent. This fact, as well as economic and logistical considerations, must be taken into account in the design and application of high-resolution *in situ* investigations using any of the tools discussed hereafter.

2.3 *In situ* experimental chambers

By enclosing an area of the sediment–stream interface, *in situ* experimental chambers and microcosms can be used to create a more controlled measurement environment, which can nevertheless respond to changing conditions in the benthic and/or hyporheic zone that surround it. Experimental chambers generally aim to preserve their contents in a natural state with minimal disturbance, while microcosms may typically be filled with a prepared substrate that is left *in situ* to react with the hyporheic environment over a set period of time (e.g., microbial colonisation experiments).

In situ chambers of a fairly standard design (after, e.g., Bott et al., 1978; McIntire and Phinney, 1965) have been widely used in studies of streambed and hyporheic metabolism in streams and lakes, but their most technically advanced forms are found in marine research, where they have become a routine research tool (see Tengberg et al., 1995; Viollier et al., 2003). Such chambers may be subject to sampling for *ex situ* analysis, but have also been used to carry *in situ* measurement devices to measure O_2, pH, H_2S and other metabolic indicators (e.g., Forster et al., 1999; Glud et al., 1994; Gundersen and Jorgensen, 1990; Uzarski et al., 2001; Uzarski et al., 2004). There is great potential for such chambers to be used in conjunction with other *in situ* probes.

Dodds and Brock (1998) provide a useful introduction to the design considerations that surround *in situ* chambers for the measurement of *in situ* metabolism. Uncertainties relate to the small area of streambed (or volume of hyporheic sediment) enclosed by a chamber, its inability to account for heterogeneity in the streambed on a larger or much smaller scale, nutrient limitation as the chamber is closed, alteration of the flow regime, change in the light incident with the streambed, change in temperature profiles and supersaturation of metabolic products (Bott et al., 1997; Dodds and Brock, 1998). These may lead to overestimation of autotrophy and underestimation of hyporheic respiration (Grimm and Fisher, 1984; Pusch and Schwoerbel, 1994). Uzarski *et al*. (2001) present a recent design that attempts to account for many of these factors and employs *in*

situ measurement of DO. This chamber (*Figure 2.3*) considers hyporheic metabolism explicitly and has recently been used to demonstrate the importance of this factor in the accurate estimation of stream primary productivity and community respiration (Uzarski et al., 2004).

2.4 High-resolution *in situ* measurement devices

Compact, reliable probes able to make direct repeated measurements of the hyporheic environment at a fine spatial scale offer the best prospect of achieving the spatial and temporal resolutions needed for high-resolution *in situ* biogeochemical studies. Temperature, oxygen, electrical conductivity (EC) and pH are already commonly measured *in situ* using commercial electrochemical probes that are widely available. Several studies have used these to profile up- and down-welling exchange across the hyporheic zone at high resolution (e.g., Conant Jr., 2004; e.g., Constantz and Thomas, 1997). This section outlines the range of probes available to measure other important chemical species and physical variables.

2.4.1 Electrochemical microsensors

In their simplest form, electrochemical microsensors used to detect chemical concentrations measure the electrical current or electrical potential between indicator electrode(s) and an internal reference. This signal varies proportionally with the presence and/or activity of the target chemical. Electrical probes for the *in situ* measurement of environmental chemical species can operate at detection limits down to parts per trillion (Pei et al., 2001) and spatial resolutions of less than 1 mm. Numerous variations on the theme have been devised and built, often as bespoke units for specific research projects. Bakker and Telting-Diaz (2002) provide an excellent recent overview of the often bewildering array of sensor designs and methodologies. This review looks at three major types that may be of use in hyporheic studies: ion-selective (selective membrane) electrodes (ISEs), voltammetric stripping electrodes and GIME arrays.

2.4.1.1 Ion-selective electrodes

ISEs employ an ion-selective polymeric membrane across which the ionic species of interest diffuse to create a chemical gradient that is measured using a high-impedance voltmeter relative to a reference electrode (*Figure 2.4*). The standard pH electrode is a simple example of an ISE. Since this selection process necessarily 'samples' only free ions, the resulting potentiometric measurement represents the activity of the chemical species in question, rather than its direct concentration at the point of measurement. When coupled with interference that results from the non-optimal selectivity of the membrane, the correct interpretation of the results gathered from ISEs is assisted by an accurate prior knowledge of the expected chemical environment provided by sound theory, valid reference or other, possible *ex situ*, analytical techniques. Probes are designed such that they can be inserted into sediments to varying depths, thus enabling vertical profiling over short timescales.

ISEs have been developed and used to detect an enormous range of ionic species, including O_2, NO_3^-, NH_4^+, Ca^{2+}, CO_3^{2-}, NO_2^-, pH, lead, boron, chloroaromatic acids and anionic surfactants (Lahav et al., 2001; Marki et al., 2002; Muller et al., 1998; Muller et al., 2003; Sanchez and del Valle, 2001; Sanchez and del Valle, 2001; Wilson and Gaffare, 1986; Zhang, 1988). *In situ* measurements of ions involved in nitrogen turnover enabled Marki *et al*. (2002) to resolve fluxes of 2-55 mmol/m^3/d at a vertical spatial resolution of <0.1 mm. Extensive tests in sampled lake sediments and porewaters were carried out by Muller *et al*. (1998), who reported detection resolutions equivalent to 1 μmol (Ca^{2+}, CO_3^{2-}, NH_4^+, NO_3^-) and 10 μmol (NO_2^-) with a reproducibility of ±0.2-0.6 mV. At low concentrations, however, interference from other ionic species, such as K^+, SO_4^{2-} and HCO_3^-, was a problem. Bakker and Pretsch (2001) report the detection of lead in tap water samples at concentrations of 10^{-9} M with an accuracy and precision equivalent to that of inductively coupled plasma–mass spectrometry (ICP-MS). However, this may be reduced to micromolar levels in complex, uncontrolled measurement environments.

Detection limits are dependent on the selectivity and characterisation of the ion-selective membrane and the level of background noise in the environment being measured.

Recent developments in polymer technology have improved electrode durability and enabled the lifetime of ISEs to be extended (e.g., Beltran et al., 2002; e.g., Kolytcheva et al., 1998) to several months *in situ*. Muller *et al*. (2003) recently deployed a nitrogen-selective ISE in an agricultural drainage pipes for 1 year, recording inorganic nitrogen load at 10 minute intervals to create a high-resolution temporal dataset that outperformed alternate-day random sampling, the latter underestimating cumulative loads by up to 5.5 times. Other workers have developed alternative, non-polymer membranes using materials such as chalcogenide glasses in an attempt to improve selectivity and sensitivity – this is a complete branch of the technology in its own right (Kloock et al., 2002; Legin et al., 1995; Miloshova et al., 2003; Tomova et al., 2004; Vlasov et al., 1994). Recent reviews of ISE technology can be found in Bakker *et al*. (1997), Buhlmann *et al*. (1998), Hanrahan *et al*. (2004), in a number of textbooks (e.g., Buffle and Horvai, 2000; Taillefert and Rozan, 2002) and online (e.g., Rundle, 2000).

2.4.1.2 Voltammetric and potentiometric stripping electrodes

One limitation of ISEs is that the probe, once assembled with a particular ion-selective membrane, can be used to target only one chemical species. Voltammetric stripping electrodes, in contrast, are able to sample numerous electrochemically active ions almost simultaneously. The target analytes of stripping voltammetry are typically trace metals (e.g., Locatelli and Torsi, 2001), but also include O_2, S species, $S_2O_3^{2-}$ and I^-.

The principle behind anodic (or cathodic) stripping voltammetry (ASV, CSV) is that an electrode placed in a saturated medium acts as an electron acceptor or donor and thus undergoes redox reactions with ions present in the aqueous solution. These ions aggregate on the electrode. Different species react at different applied voltages according to their redox characteristic. Hence, by 'scanning' across a range of voltages, a combined aggregate of many dissolved species can be collected. The potential within the electrode is then reversed and once again 'scanned' or 'ramped' across a voltage range. The effect of this is the sequential 'stripping' of ions of different chemical species built up on the electrode, and as each species is lost a step in the current signal indicates the quantity of ions removed (*Figure 2.5*). Their chemical species can be inferred from the voltage at which the ions are removed (by comparison with known redox characteristics of different ionic species). In the potentiometric mode, the duration of the stripping procedure is measured and the time spent at each characteristic stripping potential equated with the quantity of analyte.

Variations on the basic ASV and/or CSV principle date back more than two decades (e.g., Nurnberg, 1984), using different voltage signals – square waveform (SWASV), linear waveform (LWASV) and differential pulse ASV (DPASV) – to improve the signal. As long as the species of interest have well-known and clearly differentiable 'stripping voltages', their free ionic concentrations in the solute can be determined simultaneously by one scanning cycle. Data processing methodologies have been developed to better resolve close or interfering stripping signals (e.g., Locatelli, 2000).

ASV and/or CSV has been used to detect Cd, Cu, Fe, Hg, Ar, Se, Pb, Zn, Mn and U in aqueous environments and samples (Banks et al., 2004; Banks et al., 2005; Beni et al., 2004; Croot and Johansson, 2000; Daniele et al., 2000; Greulach and Henze, 1995; Kadara et al., 2003; Locatelli et al., 1999; Locatelli and Torsi, 2001; Olsen et al., 1994; Wang et al., 1995; Wang et al., 1994). Locatelli and Torsi (2001) reported analyses of Ar (III), Se(IV), Cu(II), Pb(II), Cd(II), Zn(II) and Mn(II) in seawater and estuarine samples and standard reference materials. Minimum detection limits in the analytical standards were 10^{-9} mol/l[1], while in the environmental matrices trace metals were detected at $\mu g/l^{-1}$ levels with relative errors of <5%.

2.4.1.3 Gel-integrated electrodes

ASV-type electrodes suffer from fouling with repeated use. This affects their reliability and longevity and thus reduces their attractiveness for use in hyporheic zone monitoring. One response to this has been to encase the electrode in an aqueous agarose gel (*Figure 2.6*), which allows ions to diffuse from the environment to the electrode, but protects the electrode itself from fouling by colloids or giant molecular material (Pei et al., 2001; Tercier-Waeber et al., 1998; Tercier-Waeber et al., 1999). Like standard stripping electrodes, gel-integrated electrodes become more sensitive the longer the time period of the deposition stage during which the analyte is accumulated on the probe surface. Depending on the length of the deposition stage used, Tercier-Waeber *et al*. (1998) report detection limits for Mn(II) of 0.1 μmol (30 s deposition stage) and 0.5 μmol (5 s deposition stage). Measurement times as long as 30 minutes have been used for high-resolution environmental profiling (Tercier-Waeber et al., 1999).

2.4.1.4 Ultramicroelectrode arrays

A further development was the introduction of arrays of small electrodes, less than 200 μm apart, in place of a single electrode (Feeney and Kounaves, 2000; Herdan et al., 1998; Tercier-Waeber et al., 1998; Wittstock, 2002; Zoski, 2002), a substitution that results in significant improvements in sensitivity and signal-to-noise ratios (*Figure 2.7*; (Xie et al., 2004). Although ultramicroelectrode array (UMEA) technology dates back to the 1970s, an important recent advance in this field was the creation of individually addressable arrays, in which each ultramicroelectrode can be scanned individually, and thus return a simultaneous measurement profile at better than 200 μm spatial resolution. This greatly improves the temporal resolution of data profiling and avoids potential disturbances through movement of the electrode during extended sequential profiling using a spatially integrated UMEA or single electrode probe (Bakker and Telting-Diaz, 2002; Pei et al., 2001; Tercier-Waeber et al., 1999).

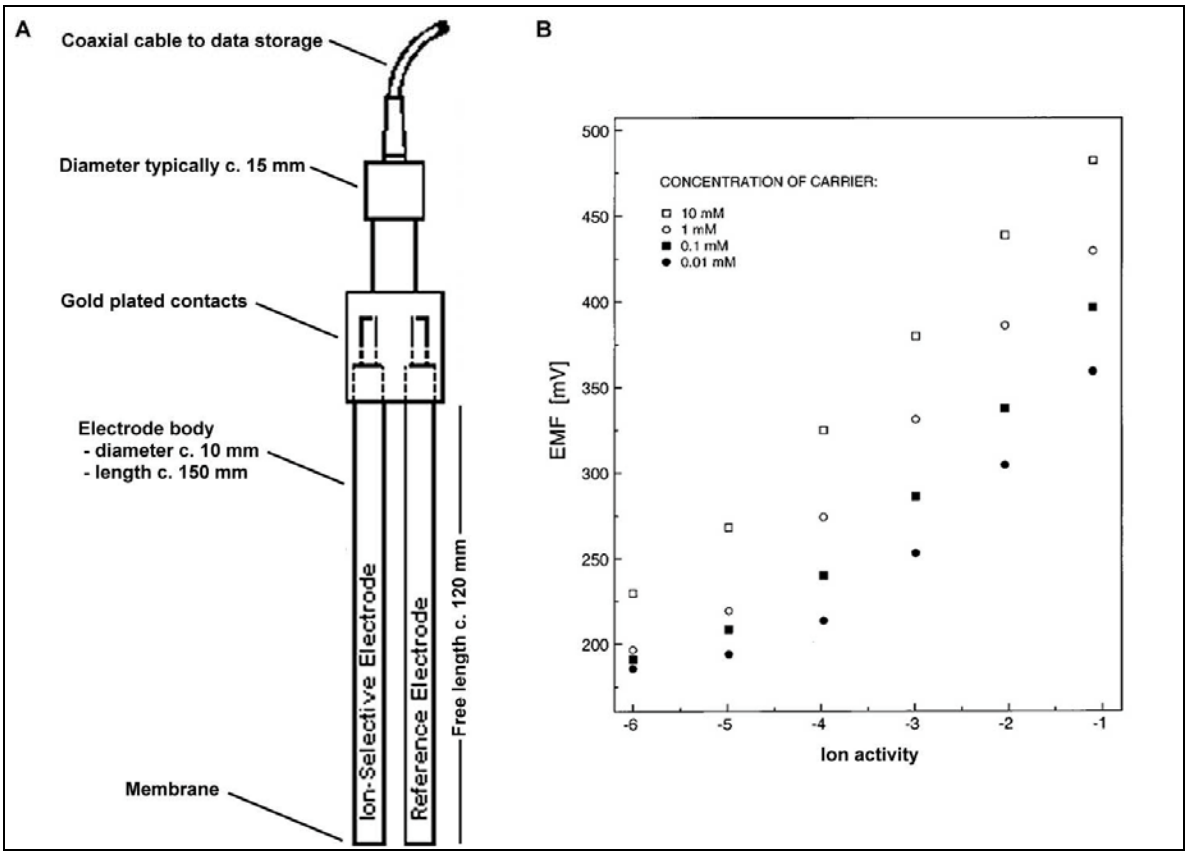

Figure 2.4 Main components (A) and typical response curves (B) for an ion-selective electrode. Note the measured electromagnetic field (EMF) from an analyte at any concentration is dependent upon ion activity (i.e., presence as free ions available to interact with the probe). Diagram adapted from an original in Rundle (2000).

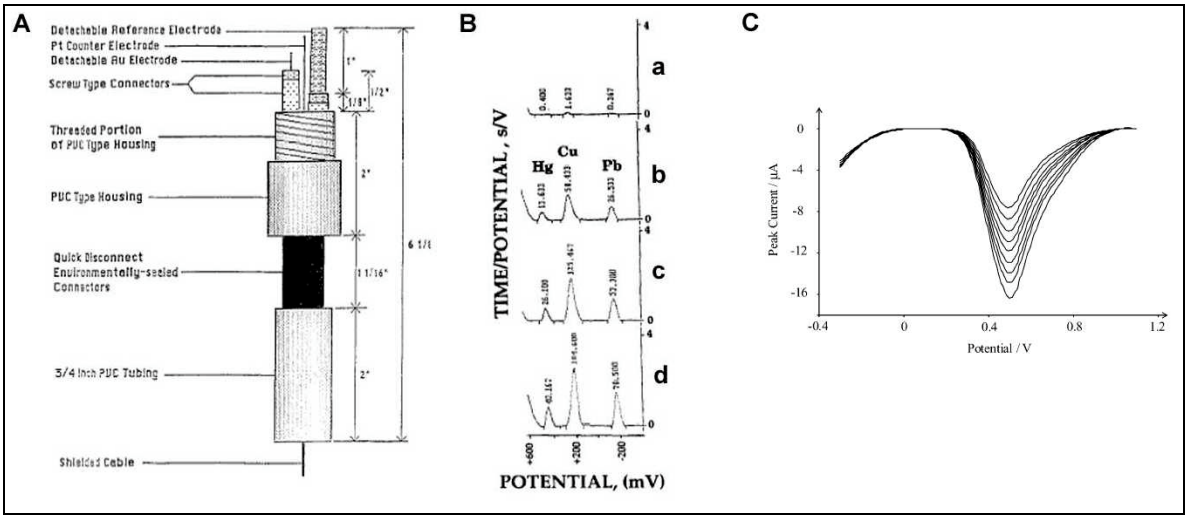

Figure 2.5 (A) A three-electrode potentiometric sensor for the *in situ* measurement of Cu, Pb and Hg in marine sediments. (B) Potentiometric measurements of seawater solutions that contain 0 (a), 5 (b), 10 (c) and 15 (d) μg/l of the three metals. Figures taken from Wang *et al*. (1995) Copyright 1995 Elsevier Science B.V. (C) Curves for several increasing concentrations of Mn added to marine sediment samples and measured using cathodic stripping voltammetry. As the analyte concentration increases, the peak current at the characteristic detection potential for Mn increases. Figure taken from Banks *et al*. (2005) Copyright 2004 Elsevier B.V.

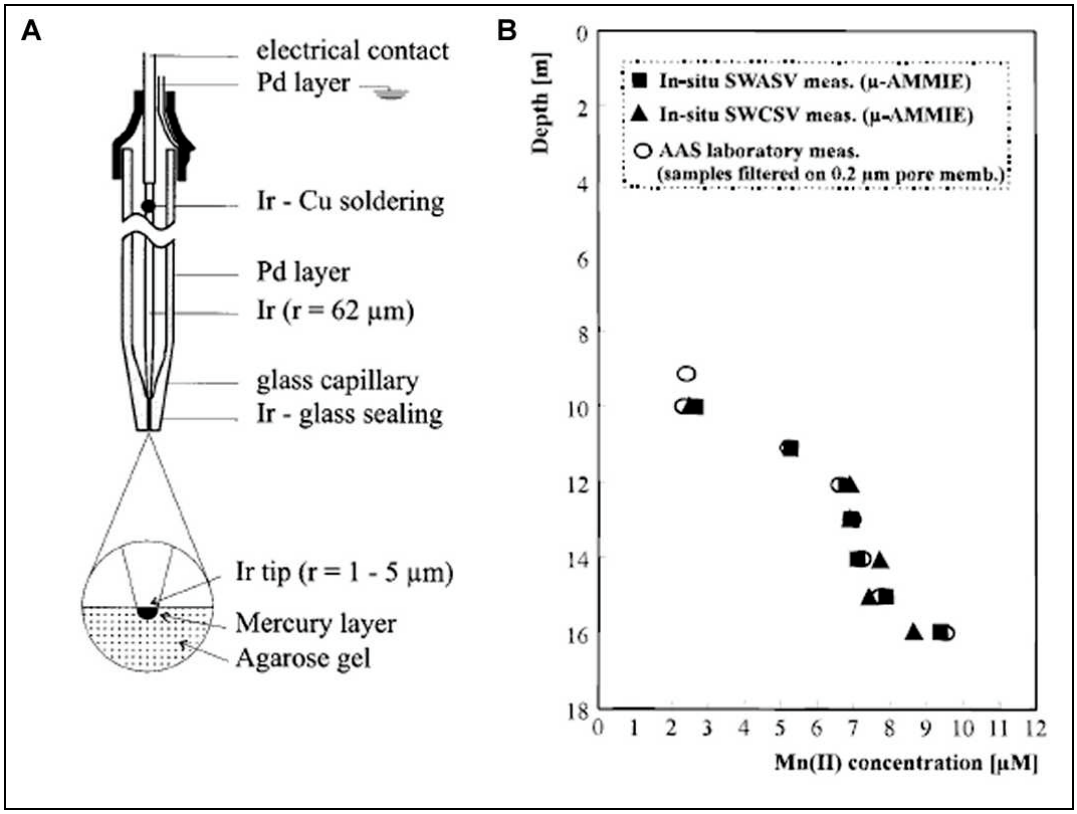

Figure 2.6 (A) Schematic showing components of a gel-integrated iridium electrode used for *in situ* measurements of Mn in lake sediments. (B) Depth profile in lake sediments of Mn, measured using a gel-integrated electrode with square-wave anodic and cathodic stripping voltammetry, compared with *ex situ* atomic absorption spectrometry analysis (AAS) of samples. Figures taken from Tercier-Waeber *et al*. (1998) Copyright 1998 American Chemical Society**.**

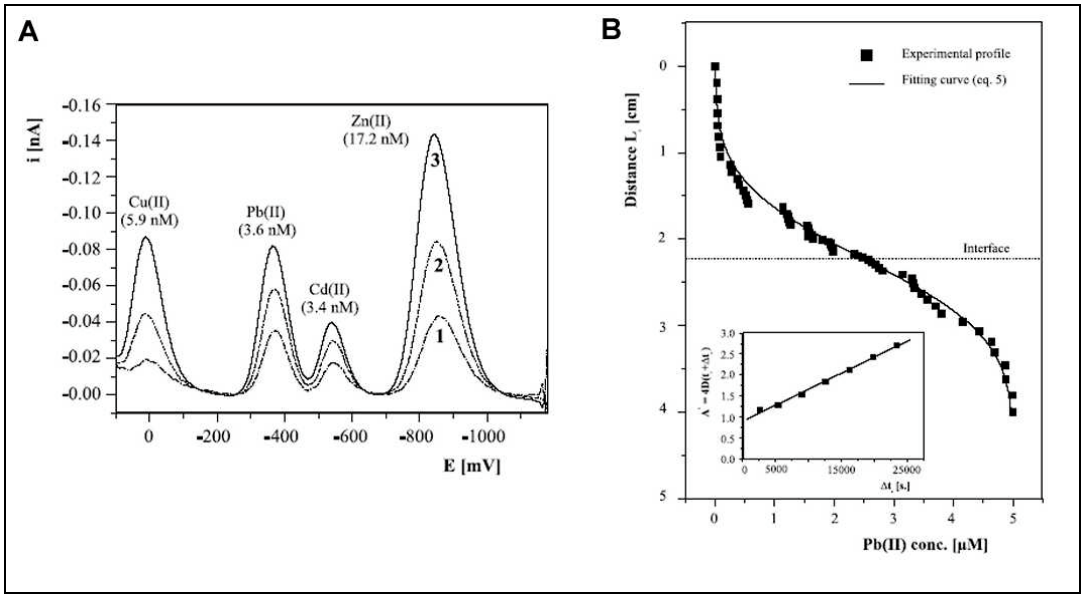

Figure 2.7 (A) Simultaneous voltammetric measurements of Cu, Pb, Cd and Zn in prepared samples using an ultramicroelectrode array (UMEA). Compare the scales with those in *Figure 2.5*(C). (B) Measurements of a small-scale concentration gradient in Pb(II) at <5 µmol. Figures taken from Tercier-Waeber *et al*. (1999) Copyright 1999 IOP Publishing Ltd.

2.4.2 Reactive surface probes

Reactive surface probes present a conceptual difficulty for the strict definition of *in situ* measurement. All probes of this type involve a surface that, in contact with stream or porewater, reacts with or collects ions in proportion with the quantity present in the immediate environment. In this respect, they provide a direct measurement of the *in situ* chemistry. However, for the measurement to be recorded, the probes must be removed and subject to laboratory analyses, a process more akin to sampling than to *in situ* methodologies. Nevertheless, the high spatial resolution of microprofiles achievable through these methods makes them worthy of consideration.

2.4.2.1 Diffusive equilibration in thin films

DET probes employ a thin (0.4 or 0.8 mm) strip of aqueous polyacrylamide gel mounted in an open-fronted frame (*Figure 2.8*). When placed in a saturated environment ions diffuse into the initially ultra-pure gel until equilibrium with the local environment is reached and no further exchange can take place (Davison et al., 1991; Fones et al., 1998; Krom et al., 1994; Mortimer et al., 1998; Zhang and Davison, 1999). The time taken to reach 99 percent equilibrium is typically 12 hours or more, depending on the amount of resupply of solutes to porewater from the solid phase (Harper et al., 1997). On extraction from the system, the gel strip is sectioned horizontally into strips that represent increasing depth intervals. Each strip is back-equilibrated in the laboratory and can be analysed using standard laboratory techniques (e.g., ICP-MS, X-ray spectroscopy) to identify the concentrations of chemical species in the original environment at that depth.

DET probes have been used to measure profiles of a wide variety of analytes at the sub-millimetre vertical scale in both fresh and marine porewaters. These analytes include chloride, sulphate, calcium, alkalinity, ammonia, total CO_2, cadmium, copper, manganese, bromide, nitrate and iron at mmol or μmol concentrations (e.g., Davison et al., 1991; e.g., Mortimer et al., 1998). Docekalova *et al*. (2002) used DET for the simultaneous analysis of 19 elements (Ag, As, Ba, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sr, Tl, V and Zn) and their report is a useful introduction to the practical issues that surround the DET method. The limits to vertical resolution of the profiles are enforced by the width of the sectioning made after the probe is recovered. Alternatively, some probes have been designed with the gel film pre-sectioned, to avoid intra-film vertical diffusion (termed 'profile relaxation'). The minimum section width attempted is 200 μm, which likely represents an absolute limit to spatial profile resolution with DET (Harper et al., 1997).

2.4.2.2 Diffusive gradients in thin films

DGT probes are physically similar but conceptually different to DET devices. DGT incorporates a second layer of gel that contain an ion-exchange resin (*Figure 2.9*), which traps and accumulates ions that cross the diffusive aqueous gel (Davison and Zhang, 1994; Harper et al., 1998; Zhang and Davison, 1995; Zhang et al., 1995). Thus, they may not reach equilibrium with their surroundings, but instead measure the flux of analytes at any point within the profile – i.e. the quantity incident with the probe per unit area per measurement time (time spent by the probe in the aqueous environment). Since there is no lateral diffusion within the probe, a very high two-dimensional spatial resolution is possible.

DGT probes have been widely used in the past 10 years in the fields of soil, lake, river and marine science to measure high-resolution profiles of fluxes and concentrations of Pb, Ni, Cu, Fe, Mn, Zn, Cd, Cs, Cr, Sr, dissolved P, inorganic and organically-complexed metals, trace metal mobilisation and speciation, bioaccumulation and bioavailability of trace metals (among others, Chang et al., 1998; Denney et al., 1999; Downard et al., 2003; Ernstberger et al., 2002; Ernstberger et al., 2002; Fones et al., 2001; Garofalo et al., 2004; Gimpel et al., 2003; Hooda et al., 1999; Luider et al., 2004; Murdock et al., 2001; Naylor et al., 2004; Scally et al., 2003; Scally

et al., 2004; Webb and Keough, 2002; Zhang, 2004; Zhang and Davison, 2001; Zhang et al., 1998; among others, Zhang et al., 1995). Concentrations of Zn and Cu can be recovered at ppm and ppb levels, respectively (Zhang et al., 1998) and fluxes at better than $\mu mol/cm^2/s$ using standard laboratory analytical techniques (e.g., Zhang et al., 1995).

Although DGT probes can be sectioned and analysed in the same manner as DET probes, the properties of the ion-exchange resin make them amenable to measurement by high-resolution image analysis. The resin changes shade (becomes darker) with increasing ion concentration. The colour change is directly proportional to the ion concentration. DeVries and Wang (2003) exploited this by imaging the 'exposed' probe surface using a high-resolution digital camera, and comparing pixel brightness intensity values against a known calibration curve to produce an ion-flux 'map' in the vertical and horizontal dimensions over the area of the probe surface. The relative detail, speed and simplicity of this data recovery method appeals both to the spirit and practice of *in situ* high-resolution measurement.

2.4.2.3 Redox gel probes

Redox gel probes are a variant on the DET and/or DGT theme, developed by Edenborn *et al*. (2002) and Edenborn and Brickett (2002). Redox-sensitive particulate compounds are immobilised within an agar gel, which is then mounted in a cylindrical probe and deployed by insertion into the sediment or environmental sample (*Figure 2.10*). During the period of deployment, all redox-active processes that occur within the probe environment are able to act on the redox-sensitive compound within the probe. Upon retrieval, the probe therefore presents a measurement of non-specific redox activity along its profile. This can be used to make rapid, semi-quantitative measurements of the stability of redox-sensitive materials at different depths within a sediment profile. By using a spatial array of such probes, a three-dimensional map of redox conditions over a sediment volume can be readily obtained (Edenborn and Brickett, 2002).

2.4.2.4 Semi-permeable membrane devices

SPMDs use a narrow strip of low-density polyethylene tubing that contains a thin film of a neutral lipid (e.g., triolein) as the reactive surface in place of aqueous gel (*Figure 2.11*). When placed in water, the SPMD accumulates hydrophobic lipophilic compounds and can therefore be used to study a variety of dissolved organic compounds (DOC), including important pollutants such as PCBs, organochlorine pesticides and PAHs (McCarthy and Gale, 2001). Their strength lies in their selectivity for bioavailable species, which are of most interest to those people attempting to manage pollutants, and their extremely good detection limits over typical deployment periods of several weeks – sub parts-per-quadrillion (Lebo et al., 1995; Lebo et al., 1992). However, it is unclear from current studies as to their suitability for emplacement within sediment profiles in the hyporheic zone.

Like other reactive surface probes, SPMDs provide a time-integrated measurement of the concentration of analytes present in the water during the deployment period of the probe. These deployment periods range from hours (DET and DGT) to days (redox gel probes) or weeks (SPMD) and clearly compromise the ability of these devices to achieve high temporal resolution data. However, their relative ease of use, low cost, versatility and high spatial resolution combined with low detection limits make them a very attractive option for use in hyporheic zone studies. A question mark remains over their deployment at depth beneath the streambed (see section 3.2).

2.4.3 Optical microsensors, planar optodes and spectrometry

Optical sensors are based on the principle of a luminescent chemical (lumophore), the luminescence of which is 'quenched' in the presence of its target analyte. A typical lumophore for detecting oxygen might be a transition metal organic complex that readily fluoresces through the

presence of free electrons. The electrons bind to oxygen if it is present, and thus make a proportion unavailable to fluoresce in proportion to the amount of oxygen present. A light-sensitive receptor can be used to measure this quenching and hence determine the quantity of analyte present using a calibration relationship.

There is a very close relationship between ISEs and these 'optodes', as demonstrated by the extremely detailed technical reviews of Bakker *et al*. (1997), Buhlmann *et al*. (1998) and, more recently, Johnson and Bachas (2003). The main advantage of optical methods over electrodes is that none of the analyte is destroyed or degraded during the measurement, which reduces the long-term calibration drift of optical sensors. Optical methods lay further claim to the high ground of simplicity, disposability and low cost. The optode principle has been used in two types of device, micro-optodes and planar optodes, also known as 'optrodes' (Glud et al., 1996). An alternative optical method is the excitation and natural fluorescence of target molecules by IR light supplied by optical fibres and resolved using spectrometric methods.

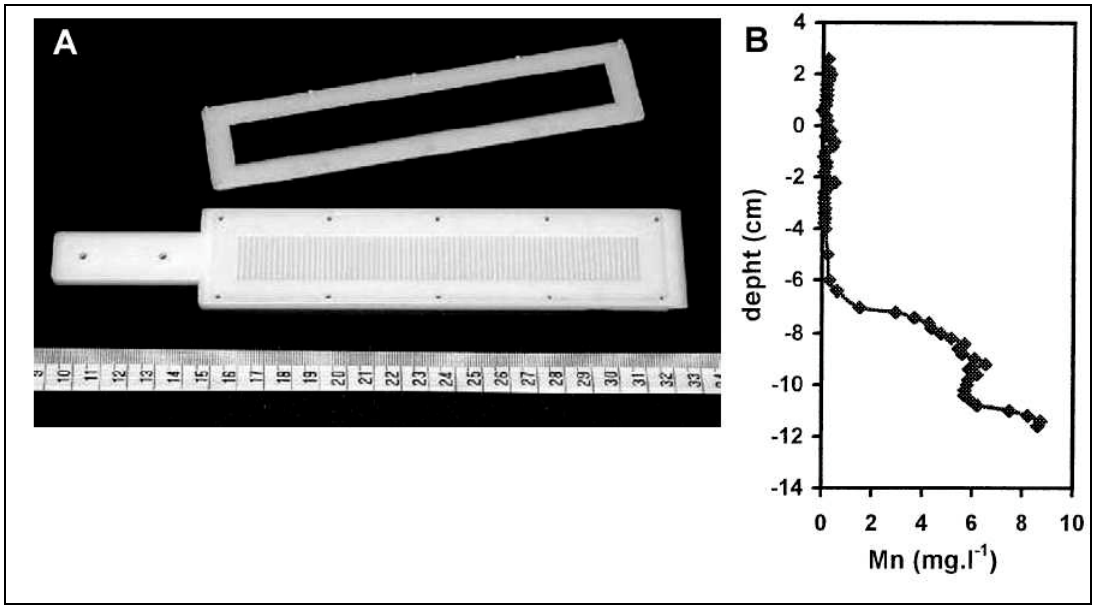

Figure 2.8 Diffusive equilibration in thin films (DET). (A) Standard apparatus is a gel strip attached to a plastic paddle-shaped backing plate and held in place by a retaining plate. The strip can be obtained pre-sectioned, as in this image. (B) Typical vertical profile for Mn within shallow estuarine sediments. High spatial resolution can be obtained. Taken from Docekalova *et al*. (2002) Copyright 2002 Elsevier Science B.V.

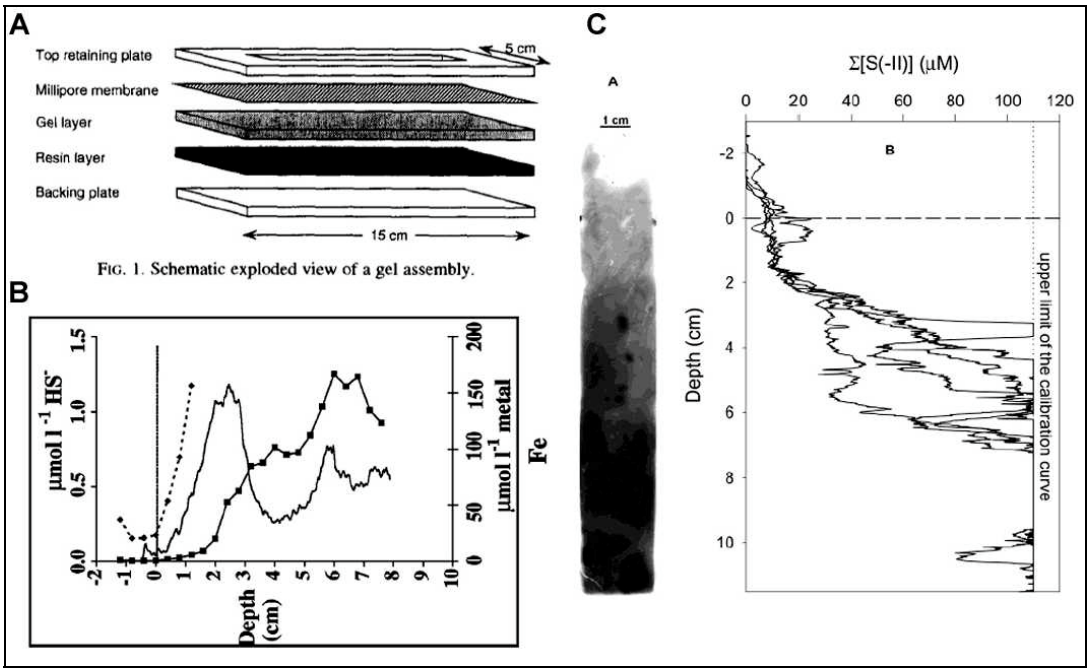

Figure 2.9 Diffusive gradients in thin films (DGT). (A) Schematic showing component layers of the DGT probe. The resin layer, which traps analyte ions, is the essential difference between DGT and DET. Figure taken from Zhang *et al*. (1995) Copyright 1995 Elsevier Science Ltd. (B) Typical vertical profiles for Fe and sulphide obtained simultaneously using DGT analysed by sectioning. Figure taken from Naylor *et al*. (2004) Copyright 2004 Elsevier B.V. (C) DGT strip analysed by computer image processing and vertical sectioning to obtain high-resolution two-dimensional mapping and vertical profiling of S(II) in a lacustrine wetland. Figure taken from DeVries and Wang (2003) Copyright 2003 American Chemical Society.

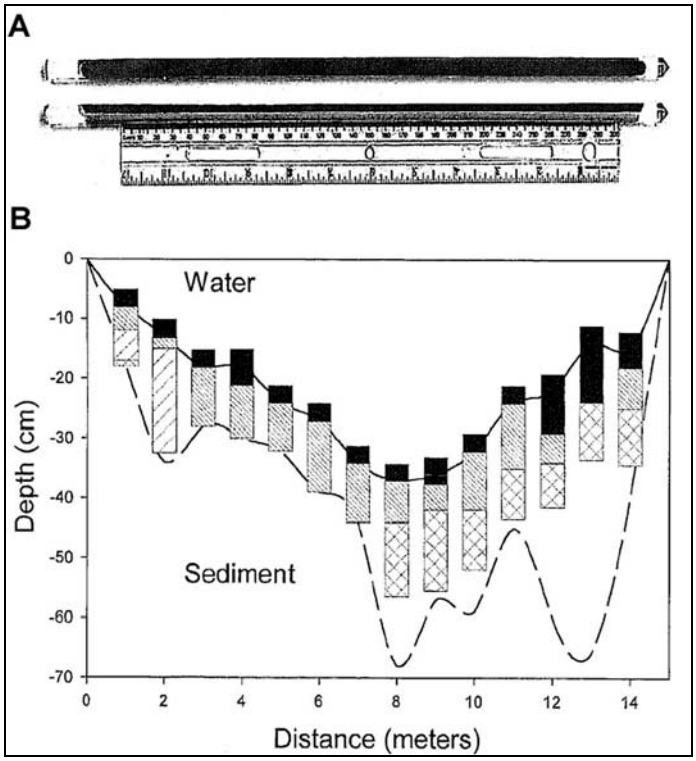

Figure 2.10 Redox gel probe developed by Edenborn *et al*. (2002). (A) Redox-sensitive MnO_2 is incorporated into an agar gel and encased in rigid tubing of total length approximately 35 cm. (B) Numerous probes emplaced in a section across a lacustrine and wetland environment and left for 21 days record broad distribution of redox conditions with depth, based on degree of alteration of the MnO_2 in the probe (black – no alteration; slanting downward right hatching – incomplete dissolution; slanting downward left hatching – complete dissolution; cross hatching – precipitation reaction). Figures taken from Edenborn *et al*. (2002) Copyright 2002 Taylor & Francis Group Plc.

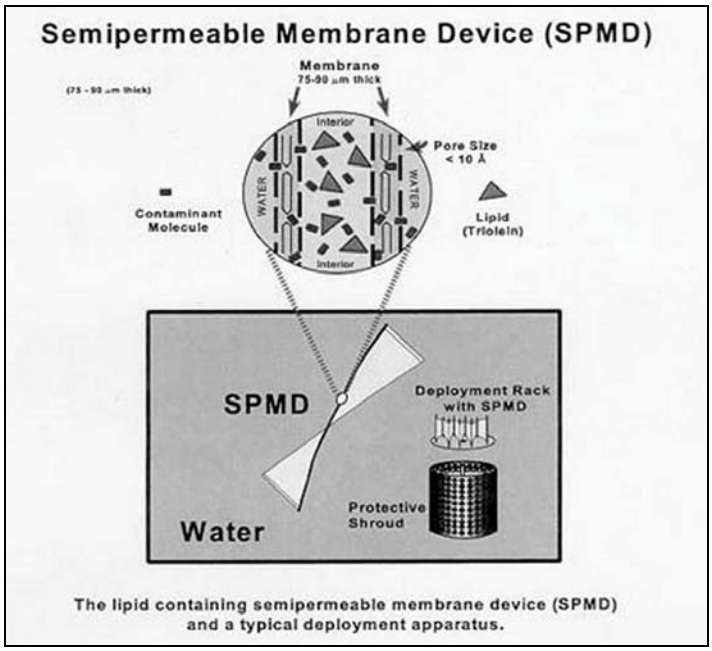

Figure 2.11 A semi-permeable membrane device consists of a flat plastic tube with lipid sealed inside. This membrane allows bioavailable contaminants to pass through and concentrate in the lipid. Figure taken from website http://wwwaux.cerc.cr.usgs.gov/spmd/, accessed 15th March 2005.

2.4.3.1 Micro-optodes

Optical microsensors, or micro-optodes (Viollier et al., 2003), are the direct equivalent of single microelectrodes. The probe tip is coated with the lumophore, which is connected to an excitation source and a fluorescence detector via a fibreoptic cable that carries both the excitation and fluorescence light. Optodes have been developed for a large range of analytes, although many of these have not been tested *in situ* in the environment. Among these are H^+, Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ag^+, Zn^{2+}, Hg^{2+}, Pb^{2+}, U(IV), NH_4^+, CO_3^{2-}, NO_2^-, sulphite, Cl^-, I^-, NH_3, SO_2, ethanol and O_2 (Antico et al., 1999; Bakker et al., 1997). Of all these, oxygen has been the most widely addressed in environmental contexts. Glazer *et al*. (2004) report, in a recent comparison of optical and voltammetric oxygen sensors, the detection of oxygen at concentrations of the order 1-100 μmol, but warn that the response time to dynamic changes in O_2 content is poor (*Figure 2.12*). Ag has been measured in drinking water samples to nanomolar levels (Lerchi et al., 1996). Klimant *et al*. (1997) demonstrate that micro-optodes for oxygen and temperature measurements can achieve a spatial resolution of <50 μm.

2.4.3.2 Planar optodes

Planar optodes are more similar to reactive surface probes in that they employ a two-dimensional surface coated with the lumophore (Glud et al., 1996). This technique appears to have been almost exclusively applied to the study of two-dimensional heterogeneous oxygen flux (Glud et al., 2001; Holst and Grunwald, 2001; Hulth et al., 2002; Liebsch et al., 2000; Roy et al., 2002). Using a charge-coupled device (CCD) array, an image is obtained *in situ* and hence oxygen concentrations mapped in two dimensions at a spatial resolution of as little as 26 μm per pixel (Glud et al., 1996). An optically transparent planar optode permits an image of the sediment structures associated with the oxygen map to be simultaneously obtained (*Figure 2.13*;) (Holst and Grunwald, 2001).

2.4.3.3 Chalcogenide-glass fibreoptic IR spectroscopy

Recent developments in fibreoptic technology have resulted in a wide variety of applications for the *in situ* sensing of chemicals at IR wavelengths (MacDonald et al., 2004; Saito and Kikuchi, 1997; Sanghera et al., 2002; Sanghera et al., 2000). Based on this fibreoptic technology, Michel *et al*. (2004) developed a novel *in situ* probe to detect volatile organic pollutants and applied it in groundwater beneath a landfill. Fibre evanescent wave spectroscopy (FEWS) uses a chalcogenide-glass optical fibre to transmit IR excitation radiation to a location in the sub-surface, and transmits any emission response back to a Fourier transform spectrometer (*Figure 2.14*). The system has been tested in standard groundwater wells and can detect dichlorobenzene ($C_6H_4Cl_2$) and tetrachloroethylene (C_2Cl_4) at resolutions of parts per million (1 mg/l; (Michel et al., 2004). The broad bandwidth of transmission of chalcogenide glasses in the mid-IR wavelengths (800-4000 cm^{-1}) means that a wide variety of organic molecules can potentially be targeted *in situ* in combination with newly developed portable spectrometers (e.g., Beyer et al., 2003).

2.4.4 Biosensors

In modern environmental technology, a biosensor is generally defined as an analytical device that uses biological macromolecules to recognise an analyte and subsequently activate a signal that is detected with a transducer. The transducer converts the biological response into an electrical signal. The biological recognition of the analyte affords biosensors excellent sensitivity (typically μg/l to mg/l) and selectivity for the detection of an individual compound, a group of similar molecules (typically based on similar functionality and molecular shape) or a general toxic effect. Biological entities that have been employed in this way include immunochemicals, enzymes, complete bacteria, human oestrogen receptors and DNA hybridisation (Rodriguez-Mozaz et al., 2005). Genetic modification has greatly improved biosensor technology, as genes that promote fluorescence or other electrochemical response can be grafted onto organisms or

other biological materials that are responsive to target chemicals (e.g., Paitan et al., 2003). Rodriguez-Mozaz *et al*. (2005) provide a useful short review of the current state of biosensors for environmental analysis, including details of some major research programmes and details of commercially available probes. However, it is not made clear how these probes have been, or may be, deployed *in situ*. A biosensor for cadmium based on the genetic modification of *Escherichia coli*, which can be used online in waste streams and potentially *in situ* in the environment, was reported by Biran *et al*. (2000). Similarly, Nivens *et al*. (2004) recently described efforts to create a rugged field-deployable *in situ* bioluminescent probe (*Figure 2.15*) and give an excellent account of the technical considerations that must be overcome to achieve this goal.

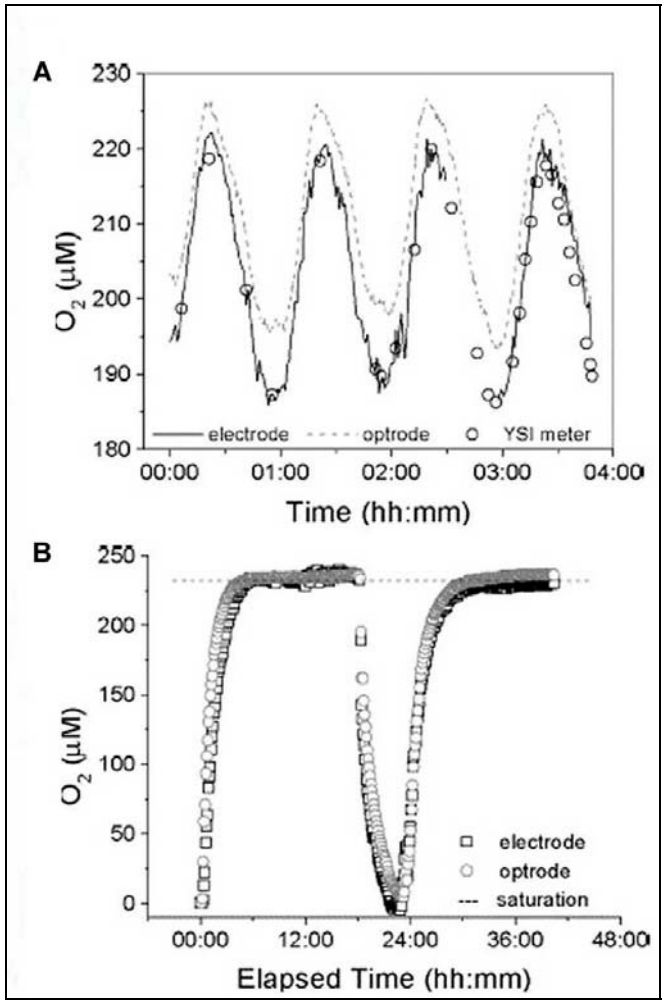

Figure 2.12 Comparison of O_2 measurements by micro-optode and ion-selective electrode. (A) Higher frequency changes in oxygen concentration result in a poor fit of the optode data. (B) In less dynamic environments, the performance of the optode closely matches that of the electrode. Figures taken from Glazer *et al*. (2004) Copyright 2004 Elsevier B.V.

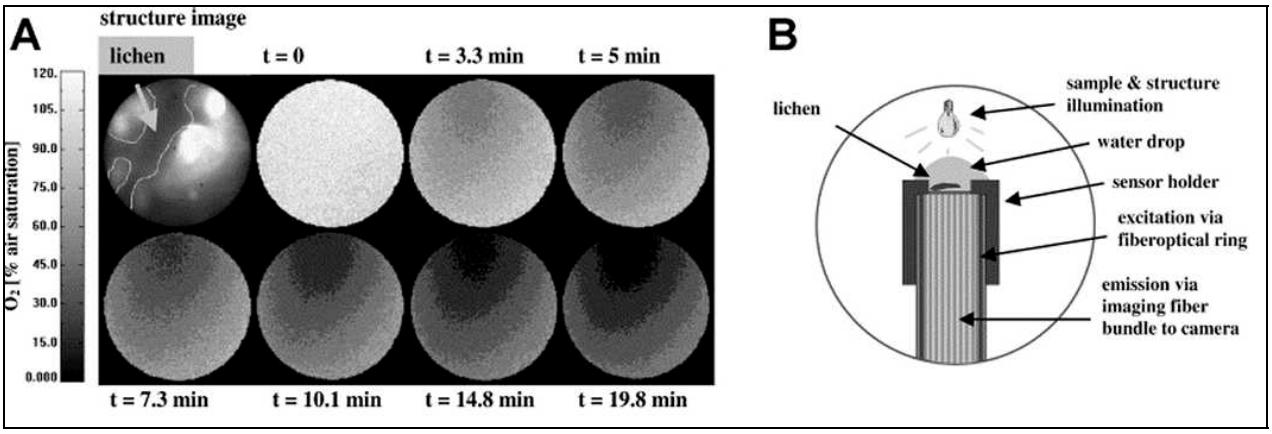

Figure 2.13 (A) A transparent planar optode deployed with a fibreoptic endoscope to measure respiration by means of O_2 luminescence lifetime. The fibreoptic bundle carries both excitation and emission light for the optode. (B) An external light source allows the structures related to the oxygen signal to be imaged through the transparent optode. Figures taken from Holst and Grunwald (2001) Copyright 2001 Elsevier Science B.V.

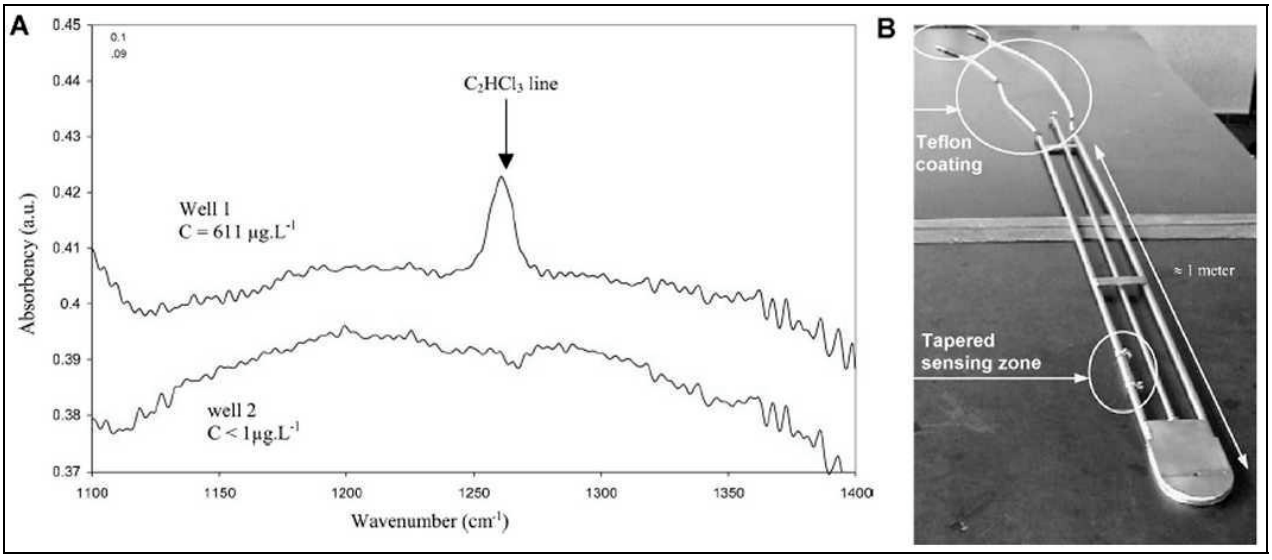

Figure 2.14 Fibre evanescent wave spectroscopy (FEWS) probe employing chalcogenide-glass optic fibre to transmit IR excitation radiation to detect organochloride pollutants in groundwater. (A) C_2HCl_3 can be clearly detected at a concentration of 611 µg/l, but it is not detectable when present in trace quantities. (B) The probe is simple and light in construction and relatively rugged. Figures taken from Michel *et al*. (2004) Copyright 2004 Elsevier B.V.

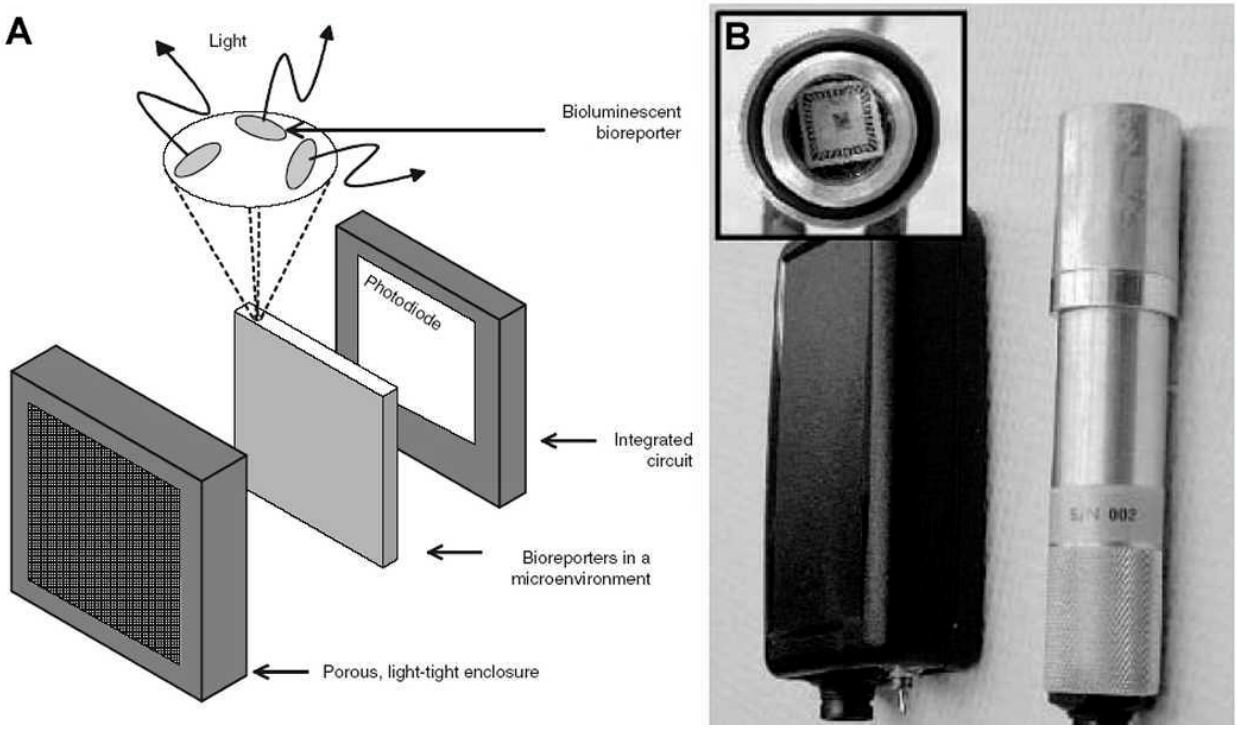

Figure 2.15 Principle of a rugged field-deployable bioluminescence biosensor. (A) Target-specific bioluminescent bacteria are cultured in a microenvironment with a controlled diffusion connection to the measurement environment. Their luminescence in the presence of the target analyte is detected by photodiodes in an integrated circuit and the electric signal transmitted to data storage. (B) This demonstrates a rugged aluminium probe casing (length 9 cm) and integrated chip housing (inset) developed for field deployment by Nivens *et al*. (2004) Copyright 2004 The Society for Applied Microbiology**.**

Chee *et al*. (2000) recently developed a biosensor based on immobilised *Pseudomonas putida* bacteria, which fluoresce in the presence of oxygen. These were coupled to an optical detector via an optical fibre and used to measure BOD at low levels in river water. The device could measure BOD down to 0.5 mg/l with a rather large relative error of +/– 20 percent at 1 mg/l (Chee et al., 2000). Overall, however, the results compared well with standard BOD analysis for the same samples. Other BOD biosensors have been in development for many years, using electrodes to measure respiration of immobilised microbes (for a review see Liu and Mattiasson, 2002).

2.4.5 Geophysical techniques

The relevance of geophysics to hyporheic zone biogeochemistry is its ability to provide detailed, dynamic contextual information about the environment in which biogeochemical processes are expected to act. Geophysical surveys are widely used in geology, oceanography and other earth sciences to determine sub-surface structures at a wide range of scales from sub-centimetre up to tens or hundreds of metres. A preliminary survey could guide subsequent deployment of high-resolution *in situ* probes, or repeated surveys could aid the interpretation of temporal trends in biogeochemical data. Three types of geophysical measurement have potential uses in the hyporheic zone: acoustic imaging and/or profiling, electric resistivity and tomography, and GPR (***Figure 2.16***).

2.4.5.1 Acoustic imaging and/or profiling

Acoustic survey technology is based on the principle of reflected sound waves emitted from a source at known velocity and received at a receptor. Velocity and phase differences between emitted and received waves provide information regarding the physical nature and relative position of the reflecting body.

Betteridge *et al*. (2003) describe the application of acoustic devices in the profiling of near-bed water characteristics and bed profiles in marine environments. They used acoustic backscatter and Doppler velocity profiling techniques, in which the signal reflected (‘scattered’) back to the receiver is used to determine sediment load and water flow velocity profiles to within 0.04 m of the bed. They also employed an acoustic ripple profiler and high-resolution sonar scanning system to map structures on the bed with a vertical and horizontal resolution of 0.005 m at a repeat time of 1 minute. This enabled rates of dynamic change in the physical environment of a sediment–water interface to be measured rapidly.

2.4.5.2 Electrical resistivity and tomography

The EC of sediment porewater is strongly dependent on its salinity, which also has significant impacts on biogeochemical processes. Electrical resistivity imaging measures the bulk resistivity of sediment that lies between arrays of electrodes arranged across the section to be measured, while borehole tomography involves measurements between paired electrodes placed in separate boreholes on either side of the profile section. While the acoustic technology described above concentrates on the in-stream, near-bed environment, electrical imaging techniques generate maps of the sub-surface environment in terms of electrical properties, from which proxies for porewater ionic strength can be determined. These techniques are necessarily limited to environments in which the various water bodies that mix within the hyporheic zone have distinctly different saline characteristics. As such, it may be of use in numerous coastal plain, estuarine or deltaic settings, as Acworth and Dasey (2003) have demonstrated.

2.4.5.3 Ground-penetrating radar

GPR uses reflected microwave radiation to detect structural and compositional (including porewater content) boundaries in sub-surface sediments. Although widely used in other

disciplines, very few studies have used GPR to probe the hyporheic zone, those of Naegeli *et al*. (1996) and Conant Jr *et al*. (2004) being notable exceptions. They showed that GPR in conjunction with sediment coring could be used to map hyporheic zone sediment structures at a vertical resolution of up to 0.2 m over continuous horizontal profiles of tens of metres. The radar data enables fine sedimentary units to be traced continuously throughout the area of interest, while the cores allow these units to be characterised and those characteristics applied as environmental variables in biogeochemical or flow-transport models, or as high-resolution contextual data for point measurements of biogeochemical variables. An extremely detailed and comprehensive technical review of the use of GPR in sedimentary environments, including fluvial and lacustrine contexts, is found in the recent paper by Neal (2004).

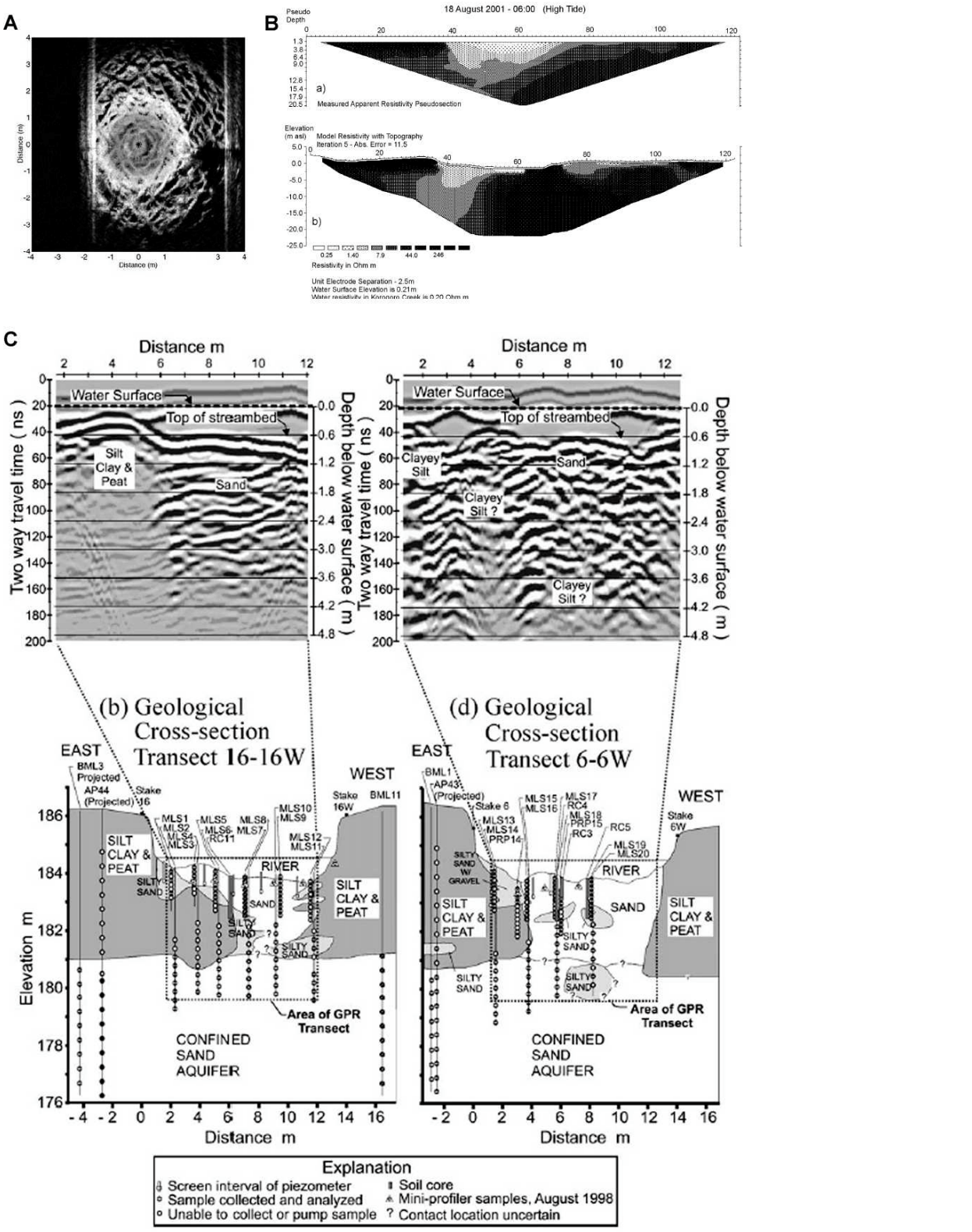

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Figure 2.16 Geophysical techniques of interest to hyporheic zone biogeochemistry. (A) Acoustic imaging can provide detailed streambed topography. Figure from Betteridge *et al*. (2003) Copyright 2003 Elsevier B.V. (B) Cross-stream electrical imaging provides two-dimensional mapping of porewater conductivity from which mass transport and mixing can be monitored, especially in coastal aquifer hyporheic studies. Figure from Acworth and Dasey (2003) Copyright 2003 Springer-Verlag. (C) Ground-penetrating radar in conjunction with sediment cores provides high-resolution data on the lateral extent and relations of hyporheic zone sediment units and structures which may significantly affect porewater flow patterns, residence times and biogeochemical activity. Figure taken from Conant Jr *et al*. (2004) Copyright 2004 Elsevier B.V.

3 Practical considerations

3.1 Site and data logistics

The limitations of *in situ* high-resolution technologies – the barriers to their application in the hyporheic zone – may be environmental, logistical or instrument-specific. To some extent these are inter-related. A large, deep or fast-flowing stream or one with a deep and extensive hyporheic zone exerts severe environmental conditions on delicate probes or those that require regular calibration; while the problem of deploying, monitoring and retrieving *in situ* probes from such locations is a considerable logistical one. However, if the stream is small, shallow and slow, with a small hyporheic zone, probes can be deployed and collected by hand on a regular basis, and so both environmental and logistical barriers to *in situ* monitoring are reduced.

In this regard, *in situ* high-resolution methods and sampling methodologies are equivalents. Both are impeded by more challenging environments, and therefore the techniques and infrastructure developed for sampling – installation of boreholes (Carlyle and Hill, 2001), water and sediment profilers (Conant Jr. et al., 2004), piezometer nests (Franken et al., 2001) and protected measurement chambers (Malcolm et al., 2004; Malcolm et al., 2003; Uzarski et al., 2001) – may all be adapted for the deployment of *in situ* measurement devices. In particularly difficult environments, remote semi-autonomous 'rigs', such as the landers developed by marine-sediment scientists, may be worthy of consideration (e.g., Breuer et al., 2002; Nickell et al., 2003; refs. in Viollier et al., 2003). *Table 3.1* outlines important logistical considerations of *in situ* high-resolution techniques. Note that these do not consider deployment using an hyporheic chamber or remote instrument rig.

Table 3.1 Logistical considerations for *in situ* high-resolution technologies.

Probe	Power requirements	Data storage infrastructure	Size/weight/labour requirements
ISEs Stripping voltammetry UMEAs	Low – usually a 12 V supply is sufficient	Permanent during monitoring period; datalogger or computer	Probe small, light; data storage and power supply may be heavy to install and dismantle
DET/DGT/redox gel SPMDs	None	None – laboratory analysis	Small and light
Micro-optodes Planar optodes	Low – supply for excitation light	Permanent during monitoring period; datalogger or computer	Probe small, light; data storage and power supply may be heavy to install and dismantle
Fibreoptic IR spectrometry	Low – supply required for excitation light	Permanent during monitoring period; datalogger or computer	
Biosensors	Low	Permanent during monitoring period; datalogger or computer	
GPR Acoustic imaging/profiling Electrical imaging	High – power for source and receiver	Temporary; datalogger or computer	Survey infrastructure complex and large-scale

3.2 Instrument durability

Instrument durability is important in determining whether a particular environment presents logistical difficulties and whether a probe is able to collect data over the time period and with the accuracy required. The wide range of probe types discussed in this report have a similarly wide range of effective lifetimes, construction methods, optimum operating environments and so on. *Table 3.2* summarises the durability issues characteristic of each probe type.

Table 3.2 Durability considerations of *in situ* high resolution technologies.

Probe	Main durability issues	Typical lifetime	Optimum operating conditions
ISEs	Choice of membrane; damage to membrane	Up to a year in field conditions, dependent on membrane and environment	Minimal ionic 'noise'; minimal dirt (fouling); robust housing required
Stripping voltammetry	Fouling of the electrode over repeat cycles; damage to electrodes	Several stripping cycles; days	Gel integration significantly reduces fouling; otherwise as for ISEs; robust housing required
UMEAs	Fouling; damage to electrode array and connections	Similar to stripping voltammetry; although can make a profile in a single cycle so fewer total cycles required (i.e., longer lifetime)	As for stripping voltammetry; robust housing required
DET/DGT/redox gel	Damage to exposed gel face; replacement gel strips are cheap and readily available; housing simple and robust	12+ hours to days per gel strip	Relatively steady-state environments as probes are time-integrated; silt or sand rather than gravel or cobbles
SPMDs	Simple but delicate; no published usage in sediments	Several days+ per membrane	Relatively steady-state since time-integrated; robust housing required in sediments
Micro-optodes	Deployment in more 'noisy' environments than electrodes since more specific	Reduced long-term drift in measurements compared to electrodes; no reversible transformations of fluorophore so potential for long life	As for ISEs
Planar optodes	Damage to optode; fouling of optode surface	As for micro-optodes	As for ISEs
Fibreoptic IR spectrometry	Simple probe design; potential for damage to fibreoptic	Long and reusable	Minimal noise; sufficient quantity of analyte
Biosensors	Survival in storage and deployment of cell cultures	Depends on survival of biocultures	Sufficient quantity of analyte
Geophysical surveys	n/a	n/a	n/a

3.3 Performance against targets

Table 1.1 sets out a series of targets that define a high-resolution study of various parameters of interest to hyporheic zone biogeochemists. Recall that different processes operate on different scales and the targets used here are a necessarily crude amalgam of the wide range of analytical methods and process targets addressed by the probes described in the preceding sections. However, *Table 3.3* attempts to provide a broad assessment of the performance of each probe type in terms of the high-resolution targets set in Section 1:

A. Conduct general measurement of ambient conditions, physical structures, water flow and chemical gradients at spacing of less than 0.1 m;
B. Conduct specific measurements of chemical species at concentrations of less than 1 mg/l for major ions and/or nutrients and less than 1 μg/l for trace compounds, at a precision of better than ±0.1 mg/l or ±0.1 μg/l, respectively;
C. Conduct specific measurements of sediment pore structures, porewater flow paths, biofilm structures and surface chemistry at a spatial resolution of 10^{-3} m or less (sub-millimetre scale);
D. Repeat measurements at intervals of several minutes, if not continuously, to capture dynamic changes in flow patterns and chemical gradients;
E. Repeat measurements at intervals of weeks or months to capture seasonal changes in time-integrated biogeochemical conditions.

Table 3.3 Performance of *in situ* technologies against high resolution targets set earlier in this document. Brackets indicate partial attainment of a target; for example, sampling using freeze coring can provide better than 0.1 m spatial resolution, but is not performed *in situ* and is not repeatable.

Probe	A	B	C	D	E
Sampling	(✓)	✓			(✓)
ISE	✓	✓	✓	✓	✓
Stripping voltammetry	✓	✓	✓	✓	✓
UMEA	✓	✓	✓	✓	✓
DET	✓	✓	✓		✓
DGT	✓	✓	✓		✓
Redox gel probe	✓	✓			✓
SPMD	✓	✓			✓
Micro-optode	✓	✓	✓	✓	✓
Planar optode		✓	✓	✓	✓
Fibreoptic IR spectrometry		✓		✓	✓
Biosensors		✓	✓	✓	✓
GPR	0.2 m				✓
Acoustic imaging/profiling	✓			✓	✓
Electrical imaging	✓				✓

3.4 Cost and availability

Capital equipment costs are invariably the most important factor in determining the feasibility of research using a particular probe or method. Could the research question be answered using a more cost-effective method? Can the probe be reused and thus costs spread across several research projects? Similarly, the costs of developing a bespoke probe are significant; indeed, probe development is often the main focus of an entire research project in its own right. Therefore, probes that are relatively cheap, ideally reusable and readily available from commercial manufacturers or research partners are the most attractive options. The wide range

of probe types discussed in the literature, often custom-built, means it is difficult to quote exact costs. However, *Table 3.4* lists the relative lifetime costs and general availability of the major types of probes discussed in this report.

Relative cost is necessarily subject to change and highly dependent on experimental scale and design. The following general ranges are used here:

- 'Very low' indicates that a probe could be obtained and used *in situ* at a cost of less than £500;
- 'Low' indicates the cost of acquiring and installing probes and support infrastructure is typically less than £1000;
- 'Medium' indicates that these costs may increase up to £5000;
- 'High' indicates that the apparatus is either expensive or will require design, development and build using non-standard materials.

Table 3.4 General cost and availability considerations for the high-resolution *in situ* probes described here. Relative availability codes: 1 – Good (commercially available); 2 – Good (available in research community); 3 – Poor (few practical designs available); 4 – Poor (custom design required). In several cases, customisation of an existing method may be required and is notated (4). Website references are current at 15th March 2005.

Probe	Relative cost	Relative simplicity	Relative availability	Further information *(suppliers shown for reference only and are **not** recommendations)*
Sampling	Medium	Medium	1, 2, 3, 4	n/a
ISE	Low	Simple	1 (4)	NICO2000, London, UK http://www.nico2000.net/index.htm
Stripping voltammetry	Low–medium	Medium	1, 2 (4)	Tresanton Oceanographic, Hampshire, UK http://www.tresanton.co.uk/
UMEA	High	Complex	3, 4	Feeney and Kounaves (2000)
DET	Very low	Simple	1, 2	University of Lancaster, UK
DGT	Very low	Simple	1, 2	http://www.dgtresearch.com/DGTResearch/Info.html
Redox gel probe	Low	Simple	2	Edenborn *et al*. (2002)
SPMD	Very low	Simple	2 (4)	Environment Agency Passive Monitoring Project, Jon Goddard, SE Area – Thames Region, Camberley.
Micro-optode	Medium–low	Medium	1, 2 (4)	RS Aqua, Hampshire, UK http://www.rsaqua.co.uk/index.asp
Planar optode	Medium–high	Medium	3 (4)	
Fibreoptic IR spectrometry	Medium	Medium	3, 4	Michel *et al*. (2004)
Biosensors	Medium-high	Complex	1, 2 (4)	Susan Alcock, Cranfield University, UK (SENSPOL) http://www.cranfield.ac.uk/biotech/senspol/
GPR	Low–medium	Medium	1, 2	Environmental and Industrial Geophysics Group http://www.geolsoc.org.uk/template.cfm?name=geogroup12
Acoustic imaging/profiling	Medium–high	Complex	2 (4)	
Electrical imaging	Medium	Medium	1, 2	

4 Application to key research areas

This section draws on the preceding discussion of resolution requirements, experimental approaches, *in situ* monitoring devices and practical limitations to provide a series of short 'specifications' for *in situ* high-resolution experiments in three key research areas within hyporheic zone biogeochemistry. In doing this, the aim is to demonstrate potential uses of all the probe types included within this review and to provide inspiration to apply these methods to actual problems. Each research area can be addressed using a different suite of *in situ* measurement techniques, which determine potential costs and logistical constraints.

4.1 Community metabolism and biomass

Target processes	
Energy cycling Aerobic microbial processes Biofilm and bacterial populations	
Target variables and required monitoring resolutions	
Oxygen flux, concentration and/or consumption	<10 mmol/m^3/d^{-1} and/or <1 mg/l
TOC, DOC and carbon/nitrogen ratios	<1 mg/l
Protein concentrations	<1 mg/l
Contextual data	
Sediment structures and characteristics Stream–hyporheic water exchange and hyporheic flow Temperature, pressure, pH	
Applicable probes	
This research area has previously been addressed by sampling controlled environments in benthic or *hyporheic chambers* and *microcosms*. Adaptation of these devices to support *in situ* measurements seems an obvious starting point for *in situ* studies. Uzarski *et al*. (2001) have already employed *DO microelectrodes* to measure oxygen variables *in situ* in a hyporheic chamber. *Optodes* and *DET* can also measure oxygen, the latter offering high-resolution microprofiles in shallow hyporheic sediments. Recent developments in *biosensors* present the possibility of *in situ* protein assay. High-resolution profiling with *temperature, pressure and pH electrodes*, possibly supported by *GPR* and/or coring characterisation of the wider sedimentary environment, will provide ambient contextual information.	
Cost implications	
Use of an established deployment methodology and of oxygen as a primary target (for which probes are widely available and well characterised) keeps the preliminary and initial capital costs relatively low. However, use of biosensors for *in situ* measurement of proteins is an underdeveloped methodology and requires proving. Satisfactory high-resolution profiling of ambient conditions may require either multiple probes and extra data storage, or labour-intensive manual profiling with single probes; either way adds to the expense.	
Essential references	
Glud *et al*. (1996; 2001)	Optodes and planar optodes for O_2
Liu and Mattiasson (2002)	Monitoring of BOD in wastewater treatment
Nivens *et al*. (2004)	Development of a rugged field-deployable biosensor
Thorbergsdottir *et al*. (2004)	Typical 'benthic' chamber for O_2 flux and production
Uzarski *et al*. (2001)	Hyporheic chamber, measurement of hyporheic metabolism
Vanrolleghem and Lee (2003)	Review – new methods for monitoring wastewater
Viollier *et al*. (2003)	Review – current *in situ* methods in marine sediment science

4.2 Nutrient and trace metal cycling

Target processes	
Redox reactions	
Metal–organic interactions	
Nitrification and denitrification	
Target variables and required monitoring resolutions	
Free ionic concentration	<1 mg/l
Bioaccessible concentration	<1 mg/l
Speciation	<1 mg/l
Contextual data	
Sediment structures and characteristics	
Stream–hyporheic water exchange and hyporheic flow	
Temperature, pressure, pH	
Applicable probes	
Detection of trace metals and other major ions is a well-established application of *ISEs*, *stripping voltammetry* and *UMEAs*, which have been used in some field settings, especially marine and coastal sediments. Typically, they are deployed from a remote rig in these settings. *Temperature*, *pH* and *EC probes*, which are closely related electrochemical probes, are routinely deployed in freshwater environments and similar methodologies may be explored for ***ISEs***. *UMEAs* have the advantage of being able to measure microprofiles without needing to be moved. *DET* and *DGT* are also capable of high-resolution ion profiles in sediments, but cannot achieve temporal resolutions of less than several hours or days. *Redox gel probes* may also provide useful contextual information mapping redox conditions in three dimensions. *Biosensors* have considerable potential in this area, since they can target not only free ions but also specifically bioavailably free ions. An *in situ* high-resolution approach could be based around mapping and profiling on the sediment–reach scale, with DET/DGT and redox gel probes. These lack high temporal resolution, but in conjunction with contextual probes (temperature, pH, geophysics) could be used to target sites for short-term deployments of electrochemical probes or biosensors.	
Cost implications	
ISEs and stripping voltammetric and/or potentiometric processes are fairly readily available at low costs, but customisation for and proving in the field environment, together with the need for data storage infrastructure, may increase costs. However, if this infrastructure is already in place to support temperature or pH probes, the extra costs may be reduced. UMEAs are still in an early stage of development for field applications and require a significant development phase in any project. DET, DGT and redox gel probes, however, are low cost, either commercially available or simple to design and construct. DET and DGT have a well-developed methodological basis and so could be deployed quickly and cheaply. Biosensors carry high development costs at present but, given their potential for high spatial and temporal resolution probing of a large range of targets with high specificity, may generate the greatest rewards if field deployments are made possible.	
Essential references	
Beltran *et al*. (2002)	Durable nitrate-selective membranes for ISEs
Biran *et al*. (2000)	Electrochemical biosensing of cadmium
Downard *et al*. (2003)	Lability of metal ion–fulvic acid complexes by DGT
Edenborn *et al*. (2002)	Design and construction of redox gel probes
Hanrahan *et al*. (2004)	Review – design and application of electrochemical sensors
Marki *et al*. (2002)	Monitoring of nitrogen turnover in lake sediments by ISEs
Muller *et al*. (2003a)	Use of an ISE for high resolution inorganic N in drains
Naylor *et al*. (2004)	Sulphide and metal co-release in marine sediments by DGT
Tercier-Waeber *et al*. (1998, 1999)	Voltammetric probes (single and UMEA) *in situ* in lakes
Viollier *et al*. (2003)	Review – current *in situ* methods in marine sediment science

4.3 Pollutant fate and transport

Target processes	
Attenuation of pollutants in sediments	
Flux of pollutants through sediments	
Effect of pollutants on hyporheic biomass	
Target variables and required monitoring resolutions	
Pollutant species concentration	<1 mg/l
Degradation product species concentration	<1 mg/l
Microbial processes	
Contextual data	
Sediment structures and characteristics	
Stream–hyporheic water exchange and hyporheic flow	
Temperature, pressure, pH	
Applicable probes	
This research area is currently typically monitored by borehole, piezometer or profiler-based sampling and laboratory analysis. However, *ISEs*, *stripping voltammetry*, *SPMDs*, *DGT*, *fibreoptic IR spectrometry*, *optodes* and *biosensors* are all theoretically able to measure major pollutants, especially organics and toxic metals (see Section 4.2) *in situ*. Furthermore, SPMDs, optodes and biosensors can target bioaccessible fractions that are of particular interest in this area of hyporheic zone biogeochemistry. For all these technologies, durable field-deployment infrastructure requires development. The past 10 years have seen considerable support for research into the development of biosensors able to monitor environmental pollution *in situ*, resulting in Europe in collaborative interdisciplinary networks such as SENSPOL (http://www.cranfield.ac.uk/biotech/senspol). An *in situ* high-resolution approach might start with longer-term reach-scale mapping and profiling with SPMDs, DGT and contextual probes (temperature, pH, geophysics) to enable targeted sediment-scale profiling and discrete-time monitoring with an optode or biosensors.	
Cost implications	
SPMDs and DGT are simple, commercially available and require little infrastructure, which makes them a cheap option. Fibreoptic IR spectrometry is a novel method, but has been deployed successfully in boreholes in the field and further development should concentrate on refining detection limits and targets. Costs will lie in constructing the probe and support infrastructure. Numerous biosensors for organic and biological pollutants exist, some of them commercial, but few have been deployed successfully in field conditions and development costs are high in this area. To manage costs, an experiment programme should aim to maximise the efficiency of relatively low-cost contextual data to determine the best sites for more intensive higher cost probes.	
Essential references	
Beyer *et al*. (2003)	Mini spectrometer for field detection of chlorinated organics
Daniele *et al*. (2000)	Estuarine monitoring of Cu, Hg by stripping voltammetry
McCarthy and Gale (2001)	Persistent hydrophobic organic compounds by SPMD
Michel *et al*. (2004)	IR chalcogenide-glass fibreoptic spectroscopy in the field
Paitan *et al*. (2003)	Review – online and *in situ* biosensors for pollution
Rodriguez-Mozaz *et al*. (2005)	Review – biosensors for environmental applications

5 Conclusions and recommendations

Modern hyporheic zone research pursues an understanding of biogeochemical processes at sub-centimetre spatial scales and sub-hour timescales because it is recognised that heterogeneity and dynamism at these scales underlie phenomena at the larger scales. The development of effective, predictive reach- or catchment-scale management models is underpinned by thorough process understanding at the sediment scale. The biogeochemical system in the hyporheic zone of any one stream is a combination of generic processes that operate within a specific context. An accurate description of this system must include both these elements. The goal of high-resolution data is to properly characterise the detail and dynamics of processes, while to make measurements *in situ* ensures that the dynamic environmental context is captured at the same scale, which aids interpretation of the interactions between process and context.

This maxim, 'detail within context', underlies the use of *in situ* high-resolution methods. Only by measuring the two simultaneously and at one site can the unique interactions between them be determined. Starting from this principle, three elements of a practical research framework can be determined.

5.1 Clear process targets

Fundamental to the success of an *in situ* high-resolution experiment is a sound identification and understanding of the process to which it is addressed. This allows:

- Selection of a minimum suite of probes to capture all the *in situ* dynamics of the target process;
- Identification of useful monitoring resolutions and detection limits for the target variable of each probe;
- Better interpretation of the unique effects of the *in situ* context on the target process through *a priori* prediction from models based on ideal conditions.

There is always, in theory at least, a too-high resolution. Essential to the successful development and quick uptake of *in situ* high-resolution methods is efficiency in terms of materials/costs, time and data. The greater the reduction in uncertainty, the greater the power of interpretation in the uncontrolled *in situ* environment and the better the efficiency of the data collected.

5.2 Suites of complementary probes

Different applications each require a different suite of *in situ* probes, perhaps complemented by *ex situ* techniques for data validation and verification. Section 4 highlights the importance of ensuring that the probes within any suite complement each other to reduce the duplication of data and maximise the support provided to each dataset by the others. The definition of a suite of complementary probes should include the required detection limits and monitoring resolutions necessary to enable the efficient interpretation of each dataset in the context of the others, and hence of the target process in the context of its *in situ* environment.

The process of identifying and understanding the target system, defining its variables and designing a suite of probes that can efficiently monitor that system *in situ* is a 'bottom-up' approach, which ensures that the goal of 'detail within context' is achieved. As detail improves, so must the context, since if detail cannot be properly interpreted it loses its purpose and its justification.

5.3 Protocols and standard methods

Sampling methodologies benefit from transferable protocols and standard methodologies – recognised sampling protocols, standard storage and transport routines, and well-established laboratory and field analytical methods (e.g., Keith, 1990). These protocols:

- Aid experimental design;
- Increase confidence in obtaining and achieving results;
- Encourage equipment manufacturers and suppliers to commercialise technologies;
- Reduce costs;
- Set precedent and provide justification for the adoption of a particular methodology.

In situ high-resolution approaches currently lack these established protocols. Partly, this results from the relative lack of development in probe technology, but this review shows that such devices are beginning to 'come of age'. Partly, it results from the relative obscurity, or specialisation, of those areas in which *in situ* high-resolution technique has made advances – marine sediment science, for example, or wastewater technology. If research into biogeochemistry of the hyporheic zone is to embrace *in situ* high-resolution methods as a reliable addition to, let alone a replacement for, standard sampling methodologies, well-defined experiment design, data collection and data processing protocols are vital to aid its critical discourse, continuing development and eventual widespread dissemination. This report concludes with a number of recommendations for future work to develop *in situ* high-resolution technologies for use in hyporheic zone biogeochemistry.

5.4 Recommendations

5.4.1 Technologies ready for use

DET/DGT, stripping electrodes (GIMEs, etc.), optodes, geophysics and temperature profiling are all well-developed and commercially available technologies for many analytes of interest to hyporheic zone biogeochemistry:

- Incorporate these technologies into current (planned) field experiments;
- Develop and disseminate standard methodologies for the use of these technologies.

5.4.2 Most promising developing technologies

Optical methods, such as fibreoptic IR spectroscopy, IA-UMEAs and biosensors, hold great promise for high-resolution, high-specificity *in situ* measurement in the hyporheic zone:

- Conduct 'proof-of-principle' experiments for use of these technologies in the field and hyporheic zone environments;
- Identify strengths and weaknesses and develop solutions for these;
- Propose conceptual *in situ* probe suites that incorporate these technologies;
- Identify and tackle economic barriers to wider production of these technologies.

5.4.3 Deployment infrastructure

To minimise logistical and analytical problems with *in situ* measurements, a sound standard infrastructure for deployment in the hyporheic zone must be developed:

- Methods of borehole, 'lander' and hyporheic chamber deployment of *in situ* probes should be designed, tested and disseminated;
- Standard infrastructure for on-site data collection and storage should be developed;

- The range of technologies for remote data retrieval (telemetry) should be made clear and integrated into future research design.

5.4.4 Gaps in the research

There are still significant areas of interest to hyporheic zone biogeochemistry that do not appear to be readily addressed by the existing *in situ* high-resolution technologies. These areas include microbial community profiling, macrobenthic community survey, biomass assay, pollutant detection and three-dimensional high-resolution microprofiling of both chemical species and sediment structures. Prompt and original research into measurement techniques is required to address these gaps.

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