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Adaptation of Groundwater Evaluation and Sampling Tools for Underwater Deployment

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Abstract

The EPA-Region 10 Dive Team (Seattle, WA) and the Environmental Response Team Dive Team (Edison, NJ) have adapted groundwater evaluation and sampling tools for use by divers underwater. These tools can be used to collect groundwater/surfacewater transition-zone information to delineate the extent of contamination and define migration pathways for risk assessments and/or to make cleanup decisions. The tools, which include visual surveys, diver deployed probes, minipiezometers, seepage meters, and diffusion samplers, have been used in a variety of ecosystems (estuarine tidal rivers, bays, lakes, etc.) and at depths ranging from shallow subtidal to over 10 m (33 ft). This paper illustrates how divers use the tools, and describes the methods and results of contaminated groundwater evaluations in several industrial waterways in Puget Sound and the Upper Traverse Bay of Lake Michigan. If water clarity allows, divers can conduct surveys for evidence of active or past seeps using visual indicators, such as the presence of precipitate, or deploy real time in situ water quality probes to detect discharging plumes of groundwater that differ from surface water with respect to easily measured parameters. Poor visibility or the absence of visual evidence can negate the effectiveness of this approach. When quantification of seep characteristics is needed, intrusive methods and monitoring instruments can be used to obtain additional information or to collect groundwater samples. Minipiezometers can be used to collect water samples from the transition zone. They are most effectively placed by first using a probe to determine the sediment type, ease of minipiezometer insertion, and thickness of any fine cohesive sediment layer that could prevent successful collection of a sample. Flexible minipiezometers are installed by pounding a steel pipe into the sediment to the desired depth, threading the piezometer into the pipe, and then removing the pipe from the sediment while leaving the piezometer in place. Stainless-steel piezometers are simply pushed into the sediment to the desired installation depth. Tubing is attached to the protruding end of the piezometer and routed to the surface. Seepage meters are devices that enclose a portion of sediment and the overlying water. Typically, five gallon buckets are trimmed to size and valves and bags are attached to the enclosure to collect discharging groundwater and measure flux. Diffusion samplers are devices that are deployed for a predetermined period of time and passively accumulate contaminants from the surrounding environment into a media. Glass vials, filled with distilled water and sealed with polyethylene membranes are commonly used and can be placed by hand to the desired depth in soft sediment.

Keywords: transition zone, minipiezometers, seepage meters, diffusion samplers, Puget Sound, Little Traverse Bay, Superfund, sediment characterization technology, scientific diving

Introduction

Evaluating the connection between groundwater, sediment, and surface water is important to environmental scientists, especially those concerned with 1) loading of contaminants in groundwater entering or discharging into nearby surface water (*e.g.*, Conant *et al.*, 2004); or 2) the effects of contaminants on sediment and benthic inhabitants (*e.g.*, Greenberg *et al.*, 2002). This connection has been the subject of an international workshop (USEPA, 2000a) and is a contaminant pathway of great interest to regulatory agencies (Winter *et al.*, 1998; Ford, 2005; USEPA, 2005b).

Investigation of the transition zone pathway from groundwater to surface water is important for risk assessment, to identify contaminant sources and evaluate source control strategies, to make cleanup decisions (*e.g.*, Biksey and Gross, 2001), and to evaluate the effectiveness of cleanup actions taken.

Many tools have been developed that characterize the pathways, flux, and effects of contaminants in discharging groundwater and these are discussed in USEPA (2000a). In this paper, we present an evaluation of several of these techniques as well as our adaptations of a variety of tools so they can be effectively deployed by divers. The evaluation techniques and tools include visual surveys, probes, minipiezometers, seepage meters, and diffusion samplers.

USEPA (2000a) provides a discussion of visual indicators of groundwater discharge. Some of these include biological clues such as the presence of high biomass benthic algal mats in areas with enhanced nutrient discharge, or dead zones where anaerobic, metal-rich groundwaters are discharging. On a larger scale, certain patterns such as localized plankton blooms may be indicators of discharging groundwater.

Lee (2000) describes the use of a benthic sled, equipped with sensors (usually temperature and conductivity), that is towed along the sediment surface. Changes in sensor readings are indicators of groundwater discharge zones. This approach has been used for at least 20 years to characterize discharge zones in larger water bodies (*e.g.*, Eagle Harbor, WA; Lee, 1990). More recently, techniques have been developed to focus on discharges at a larger scale. These include the use of thermal infrared remote sensors deployed from aircraft to detect cooler groundwater discharges (*e.g.*, USEPA, 2005a).

Piezometers are hollow tubes with a short screened section on the lower portion. They are inserted into the substrate to the desired depth and groundwater is drawn into the tube to collect a representative sample or to measure hydraulic pressure. These measures require only a single deployment. Minipiezometers are smaller versions of piezometers. They vary in diameter, installation technique, depth of deployment and have been used successfully under water up to 30 m (98 ft) in depth (*e.g.*, Lee and Harvey, 1996). To measure hydraulic pressure, the piezometer or minipiezometer can be connected to a manometer (USEPA, 2000a; Greenberg *et al.*, 2002) that simultaneously measures the hydrostatic pressure exerted by the groundwater at the piezometer screen relative to that of the adjacent surface water column. This comparison indicates whether there is an upward vertical gradient (*i.e.*, a discharge or upwelling) or downward vertical gradient (*i.e.*, a recharge or downwelling).

Like minipiezometers, a variety of seepage meters designs are used, but all follow a basic design. An inverted container is pushed into the sediment in suspected discharge areas to enclose a portion of the sediment and overlying surface water. Various tubes, collection devices, and instruments can be attached to the seepage meter to capture discharging groundwater, evaluate the characteristics of the discharge, and estimate the discharge rates (Lee and Cherry, 1978; Shaw and Prepas, 1990; Rosenberry and Morin, 2004). Recharge rates can be estimated if a bag with known initial volume of water is attached for a predetermined amount of time.

Diffusion samplers are devices used to accumulate contaminants from the surrounding environment via passive transport. They can be used to estimate the relative spatial differences in the concentration of contaminants in sediment and sediment pore water. Diffusion samplers are often constructed from simple materials such as glass vials sealed with membranes (Divine and McCray, 2004), or they can be more complicated (Church *et al.*, 2002). Diffusion samplers are placed into the medium of interest and allowed to equilibrate for periods ranging from several days to several weeks depending on the study objectives and contaminants of interest. As long as they are compared with tissue concentrations in organisms sampled synoptically, they can be cautiously used as surrogates of what might bioaccumulate in organisms. As such, diffusion samplers give decision makers another way to measure exposure point concentrations where they are highest (porewater) before the dilution that will occur after discharge into a water body. The sampler can be filled with almost any substance of interest to the investigator, and can be used to mimic tissues, or to capture metals, volatiles, or organics. Divers have installed samplers in freshwater and marine systems at depths exceeding 10 m (33 ft) (Savoie *et al.*, 2000; Duncan *et al.*, 2007).

In this paper, we discuss the pros and cons of adapting each of these techniques and tools based on our experience at contaminated sites in the Pacific Northwest and Little Traverse Bay, Lake Michigan. We present the discussion of methods and results together as the purpose of this paper is to foster development of methods to determine actual contaminants concentrations at this important interface.

Methods & Results

Most of our adaptations were made by building on the successful use of the techniques and tools deployed while wading in shallow water bodies. Typically, we first try a given tool 'as is' underwater and then adapt the design or use based on ease of use by divers, site-specific characteristics, project objectives, and management decisions at hand. Our method adaptations and results are summarized in Table 1. In all instances, hard-wired or wireless communication between the divers and the surface crew is very useful to insure effective data collection, device installation, and sample collection.

Table 1. Summary of adaptation of groundwater monitoring tools for deployment and use by divers and results

Tool & Citations	Results	Recommendation
Visual survey[2] *Lee, 2000; USEPA, 2000a-p 50-51* **Adaptation**[1] None needed	Moderately successful; depends very much on visibility in water column and whether bottom sediments become resuspended	Useful to recon to understand substrate. Take a probe to determine the depth of any fine sediment layer. Follow a transect line so locations are known, even in low visibility
Probes recording field parameters (T, cond, etc.) *Lee, 1990, 2000; USFWS, 2006b* **Adaptation**[1] Diver-held probe	Used pH and conductivity measurements to document the extent and effect of cement kiln dust leachate discharge in Lake Michigan.	Probably most useful when visual discharges are noted. Need to have effective communication with surface to record exact location of probes in the water column

Minipiezometers *Lee & Harvey, 1996* **Adaptation**[1] <u>Stainless steel</u> - sturdier probe <u>Plastic</u> - none	Continually evolving design Did not work in some fine sediments; did work when screened/slotted section placed in sandier sediments	Use with sediment probes as indicator of thickness of fine sediment and depth to bearing zone.
Seepage meters *Lee & Cherry, 1978* **Adaptation**[1] Small bucket, tubing and clamping system to allow purging and easy seal for bag collection	Universally successful. Useful in demonstrating hydraulic connection and estimating flux rates and variability in space	Diver intensive tool, requiring minimum of two to three visits. Streamline installation and retrieval by attaching to transect lines. Suggest further use with in-situ probes especially in complex estuarine tidal locations
Diffusion Samplers *Divine & McCray, 2004; Church et al., 2002; Savoie et al., 2000* **Adaptation**[1] None needed	Useful for comparison with piezometer data since can be placed at desired depth in sediments	Most useful for estimating averaged exposure point concentrations
Manometer *USEPA, 2000a, p 48; Greenberg et al., 2002* **Adaptation**[1] Simple tube with air bubble	Tested only once – worked in concept (could hook up and read levels but unsure whether tested in an area with differential hydraulic head)	Further testing is needed

[1] See Duncan *et al.*, 2007 for case study example illustrating adaptation of all tools except the manometer
[2] Including visual observation of discharge during piezometer installation

Visual Surveys

Visual surveys for evidence of groundwater discharge can be successful underwater but are often limited by poor visibility in the water column (*e.g.*, from blooms or resuspension of fine sediments) or by lack of any visible clues. Visual clues can include actual observations of discharging groundwater, stained sediment, the presence of a precipitate or residue on the sediment surface, and biological indicators such as dense localized algal blooms, dead organisms, and behavioral abnormalities.

At several sites we have visually observed groundwater discharge. For example, at the ASARCO, Ruston, WA site (USEPA, 2000b), hydrogeologists predicted the discharge location on the basis of onshore wells (B. Zavala, USEPA-R10 pers. com.). Divers were able to see groundwater discharge mixing with the surface water at the predicted location due to changing refractive indices. The mixing was similar to the freshwater/saltwater interface that can be observed visually in estuarine systems with salt-wedge dynamics (pers. obs.). At a site in Little Traverse Bay, Lake Michigan, the discharging groundwater was ice-tea colored and was plainly visible relative to the clear surface water. In this relatively low-energy environment, darker colored groundwater accumulated and concentrated in pockets and depressions in the sediment, creating microhabitats very different than the surrounding surface water.

Dissolution reactions can occur when discharging groundwater, carrying a high burden of dissolved materials, encounters and reacts with surface water forming a precipitate or residue on the sediment surface. At one site (Duncan *et al.*, 2007) the groundwater discharge in the shallow subtidal zone created a white precipitate that was easy for divers to locate and document. In Little Traverse

Bay, a grey to white colored crust was present as a thick veneer over the native sediment (USFWS, 2006a – see reference to posted video). In actively discharging areas, a dark colored fluid was associated with the precipitate. Areas of precipitate where this dark fluid was not observed were not actively discharging, suggesting that the pattern of groundwater seepage was variable over time and space. In Eagle Harbor, WA, we have observed creosote discharging from beneath the sediment and pooling on the seafloor (Figure 1A). Saltwater has been observed discharging to the Willamette River from a Portland, OR, facility, where salt was used as a raw material for manufacturing (ERM, 2005). When divers inserted minipiezometers into the sediment and before they attached the sampling tube, they noted a visual stream discharging from the protruding end of the piezometer.

In Little Traverse Bay, dead crayfish and dead round goby (*Neogobius melanostomus*) were observed in areas of concentrated groundwater discharge (Figure 1B). In addition, goby respiratory and swimming behaviors were altered in these areas. Gobies flared their opercula, exposing the fill arch and filaments, and pumped water forcibly out of their mouth through a rapid adduction of the gill covers. Additionally, while in the groundwater discharge area, they swam in rapid semicircular bursts rather than in controlled forward movements (USFWS, 2006b).

Probes

As an adaptation to the visual survey, divers have been deployed equipped with communications gear and the probe end of a water quality monitoring device. The probe is attached to a cable which relays data to display and a datalogger. The diver swims along transects in the suspected area of a groundwater discharge while the surface support team monitors the instrument and the diver communicates visual descriptions of bottom conditions. As mentioned above, similar equipment has been used very successfully when deployed from boats (Lee, 2000; USFWS, 2006b). The advantage of a diver-held sensor is that the exact location of the seep or anomaly can be determined and characterized. If the diver is using a communication device, the physical characteristics of the discharge and surrounding area can be described and relayed to the surface team as they monitor the data display. Further, the diver can easily adjust the sensor distance from the sediment surface and relay that distance to the boat to determine the extent of the discharging plume.

At a groundwater discharge site in Little Traverse Bay (USFWS, 2006b), a diver on surface-supplied air carried an In Situ Troll 9000 Professional® multi-sensor water quality monitoring instrument (Figure 1C) that was hard wired through a 300 ft (91 m) cable to a display and datalogging unit. The probe cable was attached to the diver's air supply and communications umbilical using cable ties and electrical tape. Parameters measured included pH, conductivity, depth, temperature, oxidation-reduction potential, and dissolved oxygen. The surface team was able to observe pH and other water quality parameters on the display unit with respect to the diver's verbal description of the subsurface conditions. The verbal descriptions and pH evaluations were documented in field log books and using the still and video cameras, and all data were stored in the instrument's data logger.

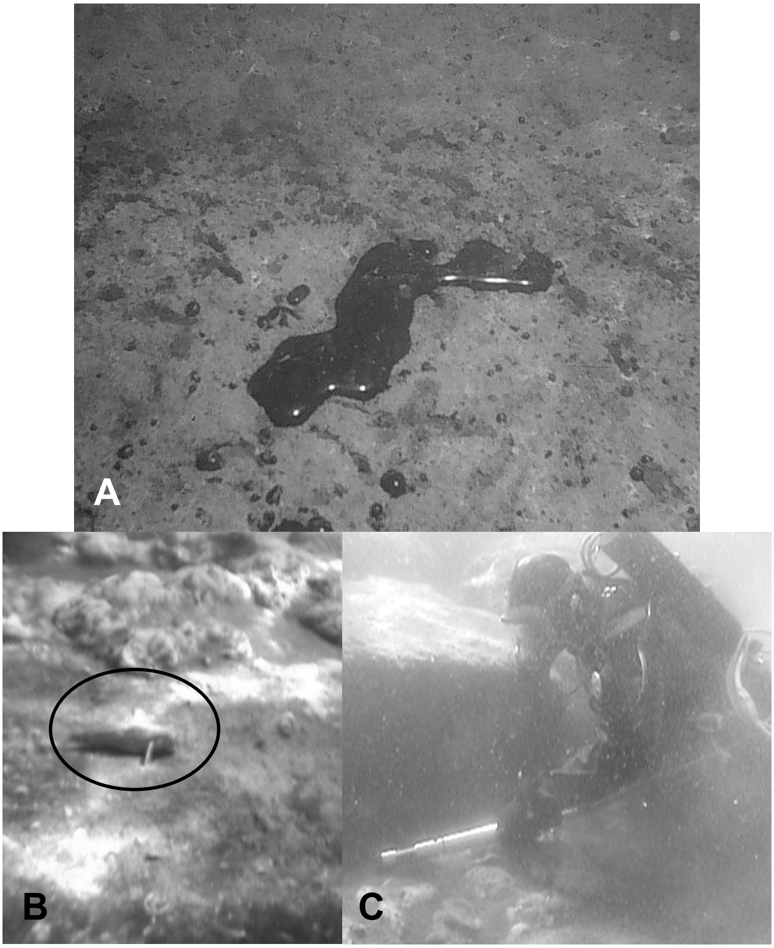

Figure 1. Example of the utility of visual survey. A. Creosote, from subsurface, pooling on seafloor in Eagle Harbor, Bainbridge, WA. B. Dead round goby (*Neogobius melanostomus*) in area of concentrated groundwater discharge (Little Traverse Bay, MI). C. Diver measuring pH in discharge zone in Little Traverse Bay.

Minipiezometers

Design

We have used two basic minipiezometer designs. The first design uses a pipe as the means of inserting a flexible tubing piezometer into the sediments (Figure 2A; Figure 3A, B, C). The second basic design is a small diameter minipiezometer with inner supporting rod (Figure 2B). We have used two sizes of stainless steel piezometers, a small version (1/8 inch Outside diameter; 18 inch length) (USEPA, 2000a) and a more robust version (1/4 inch OD; 5 ft long) with 3/8 inch diameter supporting rod ('Doc Thompson' design; Figure 3D, E). The supporting rods protect the screened end (that is weakened somewhat by the cuts made to allow the groundwater to enter the piezometer) and prevent sediment from entering the piezometer during installation.

Deployment

The tubing-type piezometer is installed using a steel pipe (Figure 2A; Figure 3A). The pipe is driven into the sediment with a bolt placed loosely on the sediment-end to provide a drive point and to prevent sediment from entering the pipe. Once the pipe is driven in to the desired depth, the piezometer (Figure 3B & C) is fed down through the pipe until it contacts the bolt. While holding the piezometer in place, the pipe is then carefully removed while tamping up and down on the pipe so that sediment packs in around the piezometer. A coil of tubing is then connected to the protruding end of the piezometer. The coil is released and it floats to the surface, where it is recovered by the surface team and connected to a peristaltic pump used to sample the groundwater (Figure 3F). This piezometer installation method has been used very successfully by EPA divers in intertidal zones. Our attempts thus far (one site) to use these underwater have not been as successful. After the supporting rod has been removed (Figure 2B-3), divers find it difficult to attach tubing for sample collection without disturbing the piezometer, or to reinsert the support rod to move the sampler if the initial attempt is unsuccessful.

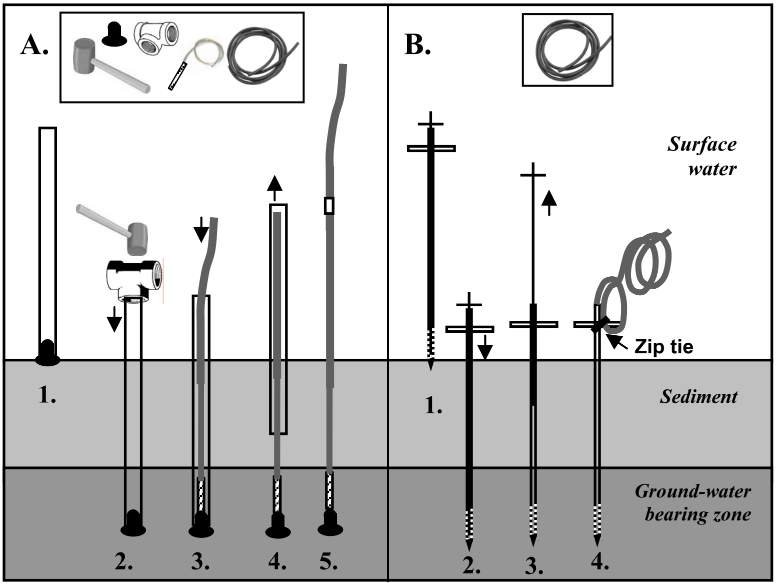

Figure 2. Illustration of piezometer installation. A. Non-rigid (tubing) piezometer: Inset-diver carries down hammer, spare bolts, pipe tee, piezometer, and coil of tubing (in addition to 4 ft steel pipe with bolt taped lightly to one end). 1. Place pipe and bolt on sediment surface, 2. Push then hammer in pipe and bolt, 3. Insert piezometer. 4. Remove pipe while tamping sediments around piezometer while holding it in place 5. Connect piezometer to coil of tubing and release to surface. (After Duncan *et al.*, 2007; Fig. 3B. Copyright © 2007 Society of Environmental Toxicology and Chemistry. From *Integrated Environmental Assessment and Management*. Reprinted by permission of Alliance Communications Group, a division of Allen Press, Inc.)

B. Stainless steel piezometer, either 18 inches or 5 ft in length: Insets - diver carries down coil of tubing and piezometer with rod inserted to support slotted end. 1. Place vertical on surface, 2. Insert, 3. Remove inner supporting rod, 4. Attach tubing, zip-tie a loop to prevent kinking and release or bring bitter end to surface support personnel to begin purging procedures.

Our current 5.0 ft (1.5 m) stainless steel piezometer has been used at several sites in Puget Sound (Lower Duwamish River estuary; *e.g.*, Windward, 2006) at depths ranging from 20 to 40 ft (6 to 12 m). To reduce the chance of the tubing kinking, we zip-tie a loop of tubing to the handle of the piezometer (Figure 2B-4). Also, we can choose to have the diver remain at the location while preliminary sampling is conducted so the diver can reposition the unit if necessary. If the piezometer is moved, backflushing from the boat via the peristaltic pump is effective in preparing the unit for relocation.

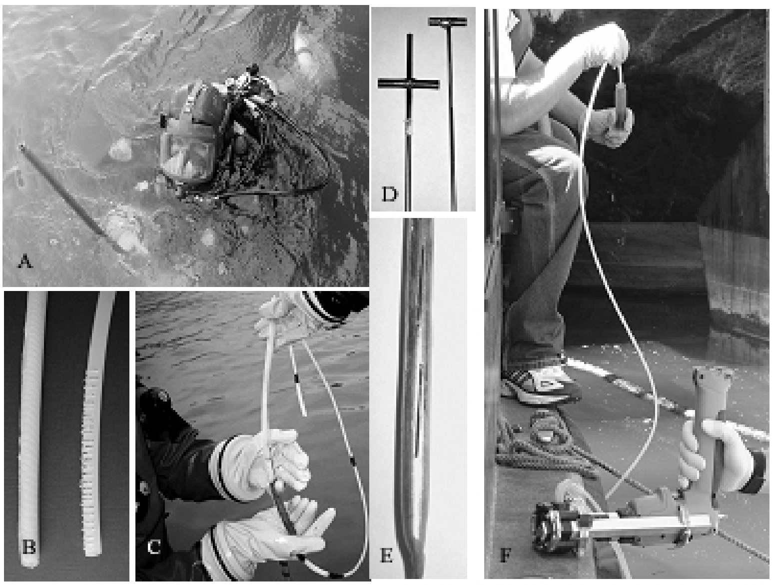

Figure 3. Piezometers and sampling. A. Diver with steel pipe through which the tubing-type piezometer is threaded (see Figure 2 A.1.). B. Screened end of piezometer showing cuts into tubing and mesh wrap (From Duncan *et al.*, 2007; Fig. 3A. Copyright © 2007 Society of Environmental Toxicology and Chemistry. From *Integrated Environmental Assessment and Management*. Reprinted by permission of Alliance Communications Group, a division of Allen Press, Inc.). C. Diver in personal protective equipment holding piezometer following removal from sediments. Dark area is where sediment is entrained on the screening material. D. Top end of 'Doc Thompson' piezometer (stainless steel, 1/4 inch OD, 5 ft long) and supporting rod. E. Close-up of slotted end of 'Doc Thompson' piezometer. F. Sampling.

In general, for a successful deployment, a piezometer must be installed into a sufficiently coarse sediment to allow water movement into the piezometer; if the screened interval of the piezometer is in very fine textured sediment (*e.g.*, mud), it will be much less successful in collecting a sample (Duncan *et al.*, 2007). We learned from working near the shoreline, that probing muddy sediments and feeling and listening for the scrape of coarser grains on the small diameter minipiezometer can give a good indication where sampling within a small area might be successful. Therefore, we have a variety of probes available that divers can carry and test sediments before installing a piezometer.

Sampling

To determine if the minipiezometer is successfully collecting a groundwater sample or if surface water is migrating down the side of the tube and entering the minipiezometer, we evaluate samples in conjunction with field water quality measures (*e.g.*, dissolved oxygen, pH, conductivity, etc.). These measures are compared to surface water values. Once the field parameters stabilize (particularly dissolved oxygen, which is generally much lower in groundwater), sample containers are filled for analysis. In addition, we measure head differential with respect to the surrounding surface water by connecting a manometer to the piezometer. We have designed and deployed an underwater version (Figure 4) but not yet tested it in a known discharge area. In this design, the diver carries a closed loop (containing an air pocket) attached to a meter stick and places it vertically on a supporting structure (*e.g.*, a rod inserted next to the piezometer, or the handle of a seepage meter as illustrated in the photograph in Figure 4B). Even if the tubing collapses with depth, it will re-expand when the loop is opened. One end of the loop is connected to the piezometer while the other end is left open to surface water.

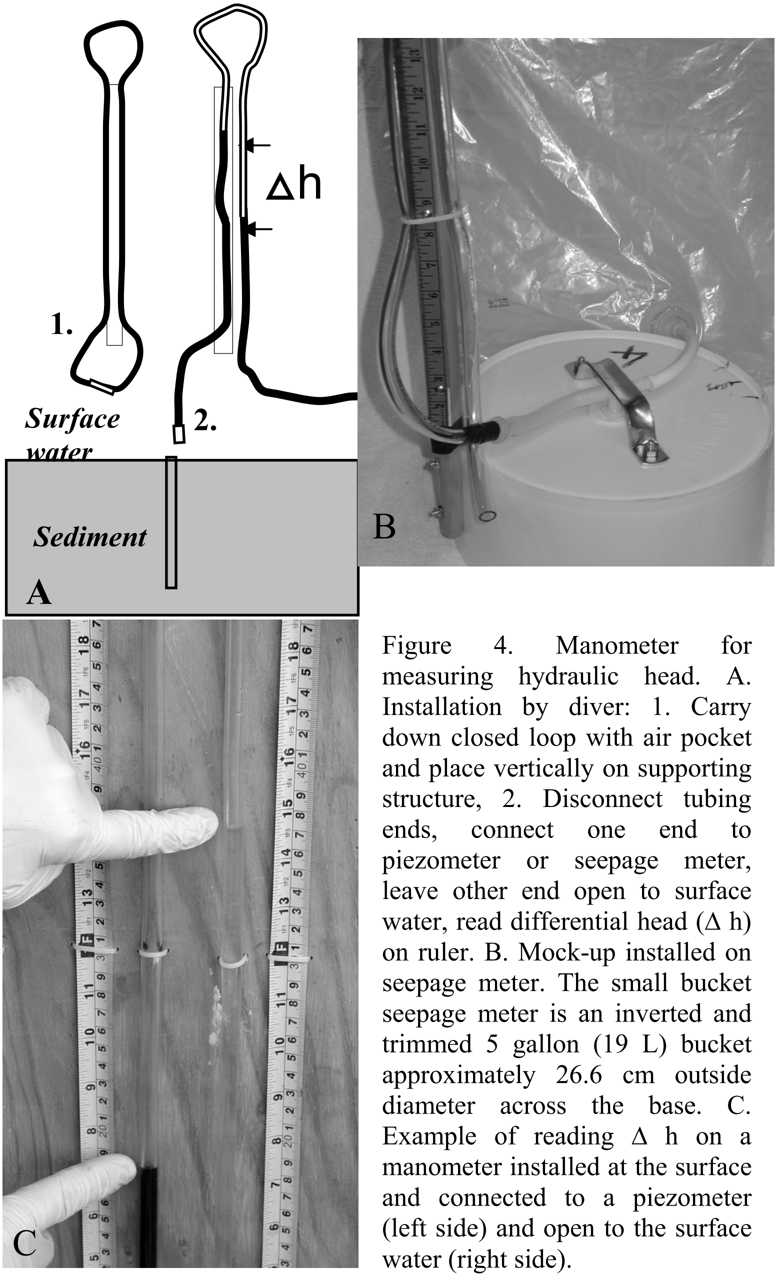

Figure 4. Manometer for measuring hydraulic head. A. Installation by diver: 1. Carry down closed loop with air pocket and place vertically on supporting structure, 2. Disconnect tubing ends, connect one end to piezometer or seepage meter, leave other end open to surface water, read differential head (Δ h) on ruler. B. Mock-up installed on seepage meter. The small bucket seepage meter is an inverted and trimmed 5 gallon (19 L) bucket approximately 26.6 cm outside diameter across the base. C. Example of reading Δ h on a manometer installed at the surface and connected to a piezometer (left side) and open to the surface water (right side).

Seepage Meters

Design:
There is a long history of seepage meters usage (Lee and Cherry, 1978). The first design we tested underwater was the trimmed end of a 55 gallon (208 L) drum into which we inserted a stopper with a tube connecting to a bag. Because of its utility in detecting flux and estimating groundwater discharge rate over a large area, this unit has been very useful in demonstrating a hydrologic connection between the ground and surface-water systems. The unit is fairly heavy and bulky, so we have switched to using smaller plastic buckets (Figure 4B). Our standard seepage meter is a trimmed 10 gallon (38 L) bucket that is easy for divers to deploy. These have a T connection so that one side can be opened for purging while the other side remains connected to a sampling bag. In addition, they have a 'handle' to accommodate a manometer (Figure 4B) as well as assist with installation.

Deployment
In general, seepage meters are diver-intensive tools. When deploying the meters, a diver must minimize and note the head space (*i.e.*, depth of insertion) and ensure that there is a good seal around the meter to prevent surface water from entering the meter. We have found it useful to prepare and deploy seepage meters first thing in the morning with all tubing, clamps, and sampling bags (rolled up) attached. We clip them loosely to a transect line, deploy the line plus meters from a boat, then have a diver follow the line and install each meter (*i.e.*, open the purge and push the meter into sediments). The second dive may be toward the end of the day or even the next day and the bags may be repeatedly changed out as needed. Usually we conduct only three dives with the third dive done mid to end of the second day. During the final dive, divers close and collect

the bags. Optionally, divers can then remove the meters and place them on the sediment surface. Because the meters are clipped into transect lines, they can be removed by boat as the boat moves down the transect line and the line is hauled aboard. If the divers have not removed the meters from the sediment, a vertical pull on the transect line is generally sufficient to loosen and retrieve the meters.

Sampling

If only discharge rate information is needed, the divers connect a bag at the same time as the meter is deployed. If a sample will be collected for analysis and is intended to be representative of groundwater, the meter must be allowed to discharge a volume sufficient to purge the head space. This purging time requires some estimate of groundwater flux and head space. After the purge time, the diver returns to direct the groundwater discharge into a collection bag. After the bag is left in place the desired length of time, the diver returns again to collect the bag. Often, it is advantageous at this time to replace the bag and collect a second sample.

Because purging is necessary if the samples are to be analyzed for contaminants, in addition to estimating head space in the meter and time needed to purge that volume, we have also tested a quantitative method to evaluate the water quality in the seepage meter relative to the ambient bottom water. To do this we placed two in-situ continuously recording units (Datasonde®; Hach Environmental, CO) on our large seepage meter, one that records ambient bottom water quality and the other that records the water quality inside the meter. Figure 5 shows an example of results from one study we conducted over the course of six days where we were able to record divergence in measurements of oxidation/reduction potential over time (USEPA, 2005d).

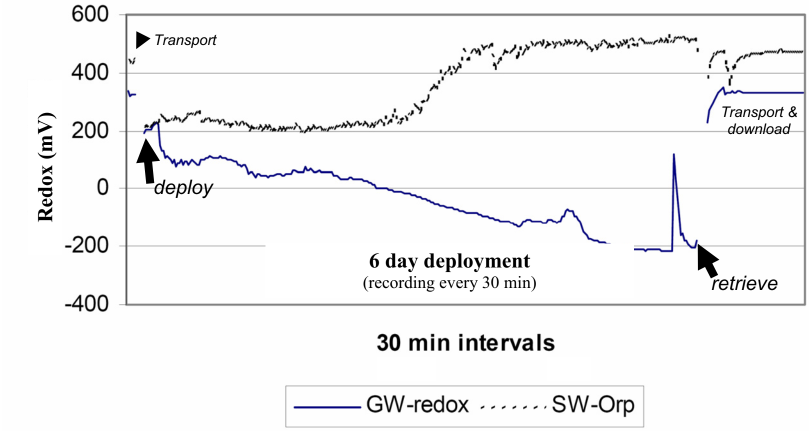

Figure 5. In situ probe (Datasonde®) comparison for Redox (oxidation-reduction potential) in groundwater (GW – probe hooked to seepage meter) and surface water (SW – probe placed on top of seepage meter). GW redox declined through the six days, while SW redox was stable, then increased midway through the deployment period and leveled off. The two units differed by about 100 mV in the lab after retrieval (after USEPA, 2005d; Figure 6). The cause of the spike in GW redox just prior to retrieval is unknown.

This in-situ approach may be particularly useful to understanding variability in groundwater discharges in complex estuarine systems subject to salt-wedge dynamics, tidal ranges, and rainfall events.

We have used seepage meters successfully to estimate groundwater discharge rates. In tidal situations we find it very important to take the tidal stage into consideration when conducting short deployments. For example, variable discharge rates may make more sense when compared with rate of tidal discharge. In one study (USEPA, 2005c), seepage rates (in milliliters/hour) were lower when the rate of tidal change (in ft/hour) was lowest (Figure 6). Even though seepage meter readings can vary over time and space (Corbett *et al.*, 1999), we find that the data collected is an extremely valuable line of evidence for the evaluation of groundwater discharge and exposure. We have noted that seepage meters deployed in contaminated areas have a tendency to become stained, retain odors, or develop rings of contamination on the inside. Figure 7 shows two examples of stains in meters placed in sediments near a site with known volatile organic carbon contaminants in the on-site groundwater wells (USEPA, 2005b). In addition to their central role in estimating discharge rates, we have found that seepage meters will collect discharging groundwater in areas where our minipiezometers may fail. Furthermore, meters offer dramatic visual evidence of discharge when divers bring the bags on board.

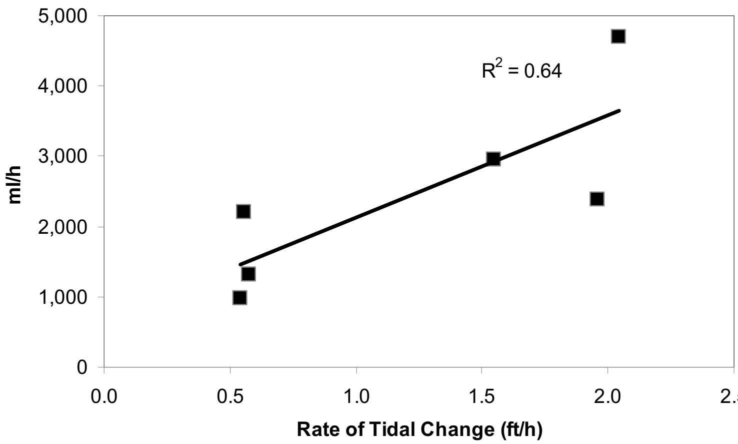

Figure 6. Example of seepage meter data results. Seepage collection rate during a falling tide as a function of the rate of tidal change (after USEPA, 2005c; Figure 6C)

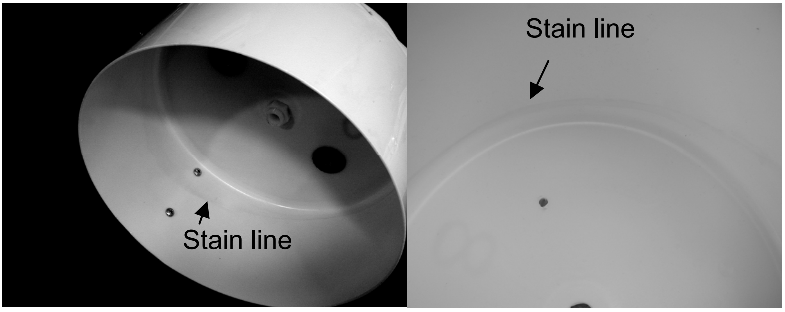

Figure 7. Examples of staining in inside of plastic seepage meter (USEPA, 2005c)

Diffusion Samplers

Design

Like the other tools discussed above, diffusion samplers have a long history of use in waterbodies and in sediment in shallow zones (*e.g.*, Church *et al.*, 2002). We have evaluated the design and deployment of diffusion samplers in the intertidal zone (Windward, 2006). For a subtidal investigation in the Hylebos Waterway, WA (Duncan *et al.*, 2007), we adapted a design from Divine and McCray (2004). We filled 40 milliliter glass vials with distilled deionized water and covered the openings with 15 micron polyethylene membranes held in place by two O-rings. Triplicate sealed vials were placed into a vented, capped tube (Figure 8) that was inserted into the sediment by hand.

Deployment

Diffusion samplers are easy for divers to deploy. We use a deployment technique similar to seepage meters, *i.e.*, tie them to a transect line and deploy to the sediment surface by boat for burial by divers. For the Hylebos Waterway investigation (Duncan *et al.*, 2007) divers placed the samplers approximately 60 to 80 cm (24 to 32 in) (arm-length) into fine textured muddy sediment.

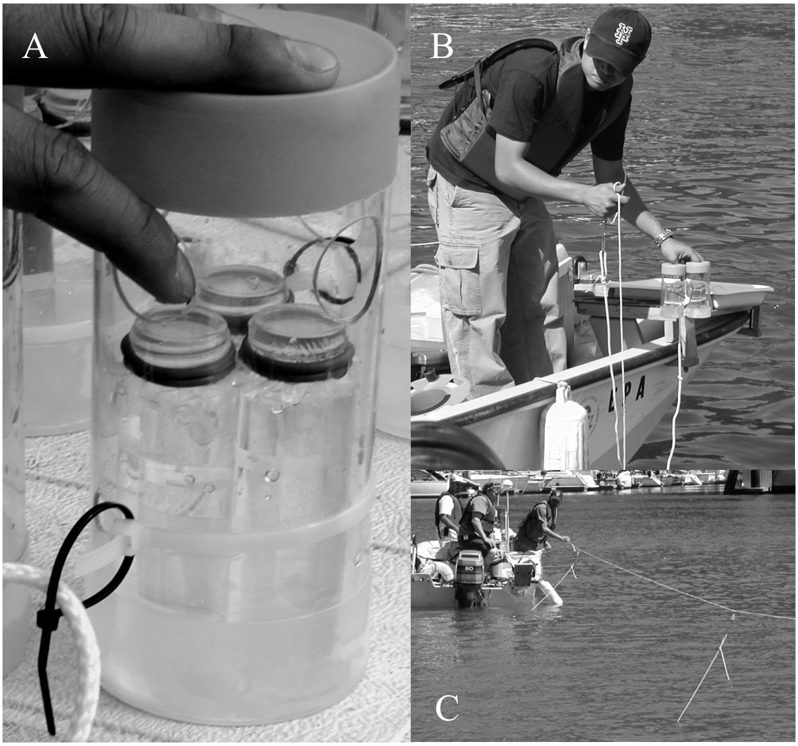

Figure 8. Passive diffusion sampler deployment. A. Triplicate vials within the chamber (chamber is 7.0 cm outside diameter) are covered by a thin polyethylene membrane held in place with two O-rings. (From Duncan *et al.*, 2007; Fig. 5A. Copyright © 2007 Society of Environmental Toxicology and Chemistry. From *Integrated Environmental Assessment and Management*. Reprinted by permission of Alliance Communications Group, a division of Allen Press, Inc.). B. Chamber clipped into transect line. C. Deployment of transect line with chambers clipped in.

Sampling

This is the tool we have the least experience with in producing results that assist with site cleanup decisions. However, diffusion samplers are useful as a line of evidence to determine potential exposure pathways. At the Hylebos Waterway, the contaminants of concern included volatile organics. Vinyl chloride was detected at several locations in the waterway at concentrations ranging from 6.7 to 4,200 ug/L. This compared favorably with the piezometer data which ranged from 4.4 to 8,800 ug/L (Duncan *et al.*, 2007). There was some concern that there might be off gassing and loss of material when divers retrieved the samplers from depths of 30 ft or more. Although this hypothesis deserves more rigorous testing, as a partial test, some vials were capped on the bottom and compared with vials brought to the surface uncapped. The vials showed no evidence of bubbles forming or any effects on the membrane covering the vial opening.

Discussion

The increasing attention given to determining the effects of contaminants in groundwater and transition zone water as it discharges through sediments into surface water has led to improvements in application of simple tools to use underwater. The tools described in this paper are good alternatives to and complementary to traditional hydrogeological approaches such as on-shore wells or, as is occurring more frequently, coring to obtain the sediment, groundwater, and contaminant profile beneath the waterbody itself. Further, the biologically active zone in sediment is increasingly recognized as a key compliance point for meeting relevant standards in site cleanup, and the means to collect representative samples via these sampling techniques in this zone is important. These techniques work equally well in evaluating groundwater in contact with contaminated sediment. The use of multiple tools is an important consideration. Each of the tools discussed provides a different and valuable line of evidence for evaluating effects of contaminants in groundwater. Preliminary direct investigation with these tools can help design more detailed studies of fate and transport of contaminants discharging to surface water. For example, the investigatory work in the Hylebos waterway has led to an intensive evaluation of the contaminated groundwater plume beneath the waterway including: investigatory borings beneath the site to delineate the nature and extent of contaminated groundwater and source material; installation of nested (*i.e.*, multiple depths) piezometer transects perpendicular to the waterway for resolution of hydraulic gradients; deployment of ultrasonic seepage meters for additional characterization of the groundwater flux with respect to tidal stage; and a geophysical suite of continuous resistivity profiling, acoustic imaging of subsurface stratigraphy, and detailed bathymetry based on side scan sonar (Duncan *et al.*, 2007).

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