USE OF AN OXYGEN-REGULATED ULTRASONIC SEEPAGE METER FOR DIRECT MEASUREMENT OF THE PHYSICS AND CHEMISTRY OF SUBMARINE GROUNDWATER DISCHARGE

by

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ABSTRACT

An oxygen-and-light-regulated seepage meter (RSM) was developed to directly measure fluxes of redox-sensitive elements and compounds across the sediment-water interface in estuaries and other water bodies. Submarine groundwater discharge (SGD) is measured manually by the bag-method, or in high temporal (1 s) resolution by an ultrasonic flow sensor. Results from field tests in Guinea Creek, Rehoboth Bay, DE indicate the RSM can effectively maintain ambient estuarine redox and light conditions, and accurately measure chemical fluxes across the sedimentwater interface. By calculating an endmember-based advective chemical flux from the aquifer, the biogeochemical flux of an element or compound to or from the estuarine sediments due to biogeochemical processing can be calculated. During three seepage meter deployments in June and August, simultaneous recharge of brackish surface water and discharge of fresh or nearly fresh groundwater was measured during higher stages of the tide against upward groundwater advection. Mechanisms including (sub)tidal pumping, convection, and bioirrigation could be possible explanations for the observed exchange.

Chapter 1

INTRODUCTION

Groundwater derived nutrient loading has been linked to ecosystem change and eutrophication of coastal water bodies (Valiela et al, 1990; Howarth, 2008). Much of the available information to date regarding SGD-derived nutrient fluxes is based on nutrient concentrations measured a considerable distance from the seepage face, such as in monitoring wells. Biogeochemical processing in the freshwater aquifer, in the salinity transition zone of the coastal aquifer, and at the sediment-water interface can significantly alter the chemistry of the groundwater along its flowpath.

One approach to address these uncertainties, and to more accurately estimate nutrient concentration at the actual point of discharge has been to measure nutrient concentrations across the deep salinity transition zone and within the seepage zone at the coast with precision drive-point sampling devices (e.g. Kroeger et al, 2007; Kroeger and Charette, 2008). Although such sampling is a significant improvement, in many coastal settings it may not fully capture the chemistry of water at the point of discharge, as evidence is increasing that biogeochemical processes occurring in the upper few centimeters of sediment can significantly alter the composition of the groundwater prior to discharge (e.g. Sawyer et al, 2014). Important biogeochemical processes affecting the magnitude of chemical fluxes may include adsorption/desorption to sediments and particles, oxidation-reduction reactions involving nitrogen, trace metals, carbon, and other compounds and elements, removal of N by denitrification and other N₂-producing reactions, fixation, remineralization, and assimilation/ regeneration by benthic microbes. Hence, it is important to accurately quantify *in situ* fluxes by direct measurement at the sediment-water interface.

Traditional seepage meters, such as those described in Lee 1977, and automated seepage meters (e.g. Taniguchi et al, 2001; Paulsen et al, 2001; Charette and Sholkovitz, 2003; Rosenberry et al, 2004) have been used successfully to study the magnitude and spatial and temporal variability of groundwater discharge in lakes in estuaries. However, isolating the enclosed water column and benthic zone below a traditional seepage meter eliminates renewal of oxygen from the surrounding water body, prevents transmission of photosynthetically active radiation (PAR), and can result in artificially reducing and anoxic conditions. As we demonstrate in this study, those experimental artifacts can lead to significant overestimation of chemical fluxes of redox-sensitive and biogeochemically reactive solutes across the sediment-water interface.

To address this problem, we developed a novel oxygen- and light-regulated seepage meter. Flow measurements can be made manually by the bag-method (Lee, 1977), or automatically using an ultrasonic flow sensor (Paulsen et al, 2001). Combining features used in past studies for oxygen regulation (Morford et al, 2007) and light regulation (Krupa et al, 1998), our new device was tested in a eutrophic estuary and performed reliably and reproducibly. In addition, the high sensitivity and high temporal resolution flow measurements enable the study of physical aspects of submarine groundwater discharge that vary over small temporal scales. Using an advective chemical flux estimate derived from fresh and saline endmember concentrations in the shallow aquifer, and the directly measured chemical flux across the sediment-water interface, the net geochemical budgets of redox sensitive-elements and compounds in the upper ~10 cm of estuarine sediments can be quantified.

Chapter 2

METHODS

Development and Testing of the Regulated Seepage Meter

The regulated seepage meter (RSM) consists of a 5 mm thick stainless steel cylindrical base with cross sectional area of 0.46 m^2 , with an opening on its side for attachment of a flow tube via a water-tight nylon cord-grip fitting (Figures 1 and 2). Sections of 3 mm stainless steel angle stock bolted to the inside walls of the cylinder allow for deployment at a constant head height of 30 cm above the sediment surface, and aid in ease of deployment into the sediment. The internal volume of the RSM when deployed in the field, including its flow and sampling system, is 78 L.

The lid is constructed of 9.5 mm thick clear polycarbonate sheet to allow light penetration (Krupa et al, 1998; Point et al, 2007), and is easily detachable from and sealable to the steel base in the field. This feature allows for ample hydraulic equilibration times to be achieved following installation of the base, without the lid attached, so that ambient estuarine chemical conditions can be maintained within the seepage meter during the equilibration period. During deployment, the lid is sealed to the base with bolts and wing nuts via a 2.5 cm outward extending flange lined with a silicone gasket. A section of 3 mm angle stock is installed across the lid top to overcome wave-induced flexing, and through-ports allowed for attachment of the circulation system in the field via quick-connect fittings (described below), (Figure 2).



Figure 1 Schematic diagram of the RSM and flow system components. The water is transported through the sampling tee, to a YSI sonde flow cell, and then through the gas permeable tubing by means of a battery-powered pump. Flow direction is shown with solid black arrows. Groundwater discharge from sediment (SGD), and recharge into sediment (SGR) are shown with grey arrows. Net groundwater discharge or recharge rate, Q_{net}, is measured ultrasonically or manually through the flow tube.

The flow system consists of a 91.4 meter length of thin walled (1.6 mm) gaspermeable silicone tubing, positioned just below the water's surface during deployment to allow diffusion of oxygen across its membrane, and achieve equilibration of dissolved oxygen and other dissolved gases within the seepage meter with that of the surrounding water body (modified from Morford et al, 2007). The diffusivity of the silicone tubing was tested in the lab by pumping N₂-sparged water through a closed loop of the tubing and into a YSI flow-through cell and oxygen sensor. The rate of O₂ diffusion from ambient air into the water filled tube was 11 μ mol O₂ min⁻¹ m⁻¹. During field deployment, the gas-permeable tubing is coiled and placed in a protective floating "cradle" constructed of plastic mesh and plastic foam floats. Water is transported to and from the seepage meter via two sections of more durable (3 mm wall) tygon tubing which are connected to through-ports on the lid. The input port has a 90 degree elbow fitting to direct the flow away from the sediment and to promote thorough mixing. Water is pumped through the system with a submersible DC-powered pump at a rate of 4 L min⁻¹. Results from a field pH tracer test at this circulation rate indicated that the time to reach a new stable pH is ~1 min. This time is assumed to be approximately equivalent to the time required to fully mix the volume of water contained in the RSM and its circulation system.



Figure 2 Photograph of the RSM deployed in the shallow subtidal zone. Components shown are: 1. transparent removable lid, 2-3. inflow and outflow tubes for circulation/ sampling system, 4. Stainless steel base, 5. ultrasonic flow transducers/ transducer assembly.

The sampling platform, consisting of scaffolding, is located a sufficient distance away (~8 m) to avoid hydraulic disturbance, since it has been shown that foot traffic can influence groundwater discharge measurements (Rosenberry et al, 2004). At the sampling platform, a sampling tee with 3-way stopcock, and a YSI 600XLM sonde (YSI Inc., Yellow Springs, OH) contained in a flow-through cell allow for collection of discrete chemistry samples and for continuous measurement (1 min frequency) of salinity, temperature, DO, pH, and ORP from the seepage meter.

The ultrasonic flow sensor used in this study, a FLEXIM F7407 unit (FLEXIM Corp., Edgewood, NY), utilizes ultrasonic transducers externally mounted to a 36 cm long, 9.5 mm ID, 13 mm OD titanium flow tube, as recommended by the factory for optimal precision in flow measurements. The flow transducers measure bidirectional flow, enabling measurement of both recharge and discharge of groundwater. The ultrasonic meter and transducers are intended for indoor applications and therefore had to be waterproofed/ weatherproofed to be deployed in an aquatic setting. This was achieved by first sheathing the transducer cables in 9.5 mm ID flexible PVC tubing. The entire transducer assembly was then sealed in a water-tight PVC enclosure, which consisted of a 10 cm diameter clear PVC tube and flat PVC end caps, with cord grip fittings installed on the end caps functioning as through-ports for the transducer cables. Silicone sealant was used on all through-ports. Dive weights were used to achieve neutral buoyancy of the transducer assembly during deployment, and the transducer assembly was successfully deployed at a depth of up to 1 m for up to 24 h. During deployment, the transducer cables are connected to the ultrasonic flow meter on the sampling platform which is powered by 2 12V marine batteries connected in parallel. Results from a laboratory bench test of ultrasonic flows vs manually controlled flows shows excellent linearity both within and outside of the range of discharges observed in this study (Figure 3, $R^2 = 1.00$, P < 0.001).

A Lee-type seepage meter (Lee, 1977) constructed from a 208 L steel drum end was modified to have a circulation system, discrete sampling port, and flow cell for continuous YSI measurements as described above for the RSM. Its internal volume including circulation system when deployed in the field at a constant head height of 10 cm is 21 L, and its cross-sectional area is 0.26 m^2 . Flow measurements from the standard seepage meter (SSM) were made by the bag method (Lee, 1977), procedure described separately below. The flow tubing diameter for the SSM and the RSM is 9.5 mm, as resistance to flow is minimal with this design (Koopmans and Berg, 2011). This modified standard seepage meter (SSM) lacks gas-permeable tubing for oxygen regulation or clear lid for light penetration; therefore, it serves as a reference for evaluating the combined effect of O_2 and light regulation in the RSM on internal water chemistry and measured net benthic fluxes.



Figure 3 Comparison of ultrasonically measured flow (y-axis) and gravimetrically measured flow reported in volumetric units (x-axis) from laboratory bench test.

Experimental Setup

The RSM and SSM were deployed at two locations in Guinea Creek, a tributary of Rehoboth Bay, Millsboro, DE, USA in June, August, and October 2015. To demonstrate the device's functionality I present results from the June and August deployments at one of the locations. In every case, the RSM and SSM were deployed simultaneously and adjacent to one another separated by a distance of ~1 m in a shoreline-parallel orientation in an attempt to sample the same portion of the subtidal discharge zone directly offshore of the intertidal zone and inshore of the offshore recirculation zone. Experiment duration was ~10 h for June deployments, and ~13 h for August deployments. In all cases, experiments began in the early morning and ended shortly before dark.

Installation of the base of the RSM occurred the day prior to the experiments, and the lid was left detached until immediately before start. The SSM was deployed 30-60 min prior to the first measurements to prevent premature oxygen drawdown within the SSM and underlying sediment, and to allow ample time for hydraulic equilibration. It has been shown that for permeable sediments, most of the recovery from disturbed to steady state occurs within 10-30 min following a seepage meter installation (Rosenberry et al, 2004). Extreme caution was taken to not perturb the sediment prior to or during the experiments.

Preceding the start of the experiments, the seepage meter circulation systems were primed with bay water to remove air. The drawing ends of the tubes were then connected to both the SSM and the unattached RSM lid with quick-connect fittings

underwater (Figure 2). With the other tube ends left unattached, the SSM was installed into the sediment, and the RSM lid was attached and sealed to the base underwater with bolts and wing nuts. Both seepage meters were thus open on the inflow end and were allowed to flush with bay water for >1 system volume equivalent at operating flow rates. This step ensured *in situ* estuarine chemical conditions, including salinity, DO, and other parameters, were achieved within the seepage meters prior to attaching the remaining tube ends and starting the experiments. While our design regulates gases such as DO, as well as redox, and light, it does not regulate other dissolved chemical parameters, including salinity, alkalinity, nutrients and redox-cycled elements, and influences on pH other than carbon dioxide, all of which may affect biogeochemical transformations and transport through the sediment beneath the seepage meter. To avoid potential effects discussed above, we suggest that water within the RSM is reequilibrated with the surrounding water body by disconnecting the inflow tube end of the seepage meter for a period of time equivalent to > 1 system volume before resuming chemistry and flow measurements. Experiment duration for the June and August experiments presented here did not result in a large enough volume of turnover to require this step, but we present this as something to be taken into consideration for longer experiments when significant volume of turnover, and associated changes in unregulated chemical parameters may occur.

Discrete samples for later analysis of nitrate (NO_3^-), ammonium (NH_4^+), total dissolved nitrogen (TDN), dissolved organic carbon (DOC), chloride (Cl^-), sulfate ($SO4^{3-}$), and trace metals manganese, iron, copper, strontium, barium, and uranium

(Mn, Fe, Cu, Sr, Ba, and U) were collected from the sampling tees on each seepage meter (Figure 1), with acid-cleaned HDPE syringes at the start of the experiment and every 30-60 min for the duration. Samples were filtered through 0.45 μ m polyethersulfone disc filters into combusted glass vials (for DOC and TDN) or acid cleaned HDPE scintillation vials (for remainder of analytes). Samples for DOC and trace metals were preserved with either hydrochloric or nitric acid, respectively, to pH<2, and refrigerated until analysis. Samples for nitrate, ammonium and TDN were frozen until analysis. The sample fraction for Cl⁻ and SO₄³⁻ was preserved with 1M zinc acetate to prevent oxidation of sulfide to SO₄³⁻ and refrigerated until analysis. Sample volume was minimized (<150 mL at each time point) to avoid the need for dilution corrections due to displacement of seepage meter water with bay water during sample collection.

For the entire duration of the experiments, calibrated YSI 600XLM sondes in flow-through cells recorded salinity, temperature, pH, ORP, and DO in the RSM and the SSM at 1 min frequency. Periodically, bubbles of gas, presumably oxygen generated by photosynthesis, accumulated within the RSM and collected on the YSI DO probe. To prevent interference with DO measurement, the bubbles were periodically removed by tapping the flow-through cell. Small sections of noisy DO data corresponding to these instances were filtered out of the data set. A YSI 600XLM V2 sonde installed ~10 cm above the bay floor at the study site recorded the same parameters as well as tidal elevation in the estuary. Tidal elevation recorded by the therefore is relative to the bay floor elevation adjacent to the seepage meter. Thus, tidal elevation data is not relative to a temporally constant datum, and cannot be compared across deployments. In all cases, the instruments were calibrated one day prior to start of the experiment following manufacturer protocols, and were crosschecked immediately before and after the experiments in a bucket of circulating bay water. ORP values were later converted to values of Eh in mV by adding 200 to the values (YSI Inc., Yellow Springs, OH).

Submarine Groundwater Discharge

During the time period between collection of chemistry samples, groundwater discharge was quantified either ultrasonically (Paulsen et al, 2001, 2003; Smith et al, 2005) or by the traditional bag method (Lee, 1977). The ultrasonic sensor was employed in the RSM in June for a period of ~24 hours which included the ~10 daylight hours during which the water chemistry measurements were made. Before the start of the experiment, the flow transducer assembly was attached and sealed to the base of the RSM and the sensor was set to log data at 1 s frequency. Data were later converted to units of L h⁻¹ or cm d⁻¹ based on flow tube and seepage meter geometry. Chemistry sampling from the seepage meter results in short periods of erroneous ultrasonic flow data, so flow data from such time periods was removed from the dataset.

Manual measurement of flow by the bag method was used in all other experiments presented in this manuscript. Procedures used in this study are modified

from Russoniello et al (2013). 40 L bags made of thin-walled plastic were pre-filled with ~2 L of bay water to allow measurement of groundwater recharge into the aquifer in addition to groundwater discharge from the aquifer, and to overcome bag resistance to flow (Rosenberry et al, 2008). Bags were weighed to the nearest 0.05 kg with a digital scale before and after deployment to quantify the change in water mass. Assuming negligible dispersive mixing between the bag and the seepage meter during bag deployment (Russoniello, 2012), the final salinity in the bag could be calculated as a weighted average based on the percent contribution of the change in bag mass to final bag mass:

$$S_{final} = w'S_{initial} + w'S_{sm}$$

Where $S_{initial}$, S_{sm} and S_{final} are initial salinity, average salinity in the seepage meter, and final salinity; and w' is the percent contribution of the change in bag mass to final bag mass. Knowing the temperatures of initial and final bag water, their densities could be calculated (Fofonoff and Millard, 1983), and the masses converted to volumes to obtain volumetric flow rate in L h⁻¹.

Using a temporally varying endmember for salinity equal to the instantaneous salinity measured in the seepage meter, the volumetric rate of recharge or discharge of ambient salinity water across the sediment-water interface, Q_s , can be calculated at each sampling interval *i*, or as a time-weighted mean for each deployment based on the following mass balance relationship:

$$Q_{s(i)} = \frac{\frac{\delta S_i}{\delta t_i} V + S_i Q_i}{S_i}$$
$$Q_{s(avg)} = \frac{\sum_{i=1}^n w_i' \left(\frac{\delta S_i}{\delta t_i} V + S_i Q_i\right)}{S_i}$$

Where, for each sampling interval *i*, δS is the change in salinity within the seepage meter, δt is the change in time, *S* is the measured salinity in the seepage meter, *Q* is the volumetric discharge or recharge rate, V is the volume of the seepage meter and circulation system, and *w*' is the percent weight of sampling interval duration to total experiment duration. The difference between Q_{net} and Q_s is Q_f , or the fraction of Q_{net} that is fresh or nearly fresh, is determined as follows:

$$Q_f = Q_{net} - Q_s$$

For calculation of net benthic fluxes (described separately below), volumetric flow units of L h⁻¹ are used. For comparison of net groundwater discharge rates among the two seepage meters in this study and to other studies, flow units are converted to units of specific discharge in cm d⁻¹ based on their cross-sectional areas. These terms are respectively referred to as either Q or q in this manuscript.

Groundwater Sampling

Twenty-five Groundwater samples were collected between 12 and 45 cm below the sediment-water interface at the site location in June and August of 2015 to characterize the shallow groundwater chemistry and define the fresh and saline groundwater endmembers in the upper seepage zone near the seepage meters. Samples were collected before, during, and after the experiments to measure spatially and temporally representative endmembers in the shallow aquifer. Groundwater was collected with a stainless steel push-point sampler (M.H.E. Products, East Tawas, Michigan) and transported with a peristaltic pump to a YSI Pro-Plus and flow-through cell for field measurement of salinity, DO, pH, and ORP. Discrete samples were collected and preserved as described above for collection of samples from seepage meters.

Laboratory Analyses

DOC and TDN samples were analyzed on an O.I. Analytical Aurora 1030C auto-analyzer. DOC was analyzed by high temperature catalytic oxidation and nondispersive infrared detection, and TDN was analyzed by high temperature catalytic oxidation and chemiluminescence detection. Nitrate and ammonium were analyzed on a Seal AA3 auto-analyzer by the cadmium reduction method, and the phenol hypochlorite method, respectively (Strickland and Parsons, 1972). Nitrate concentrations measured in seepage meters were highly erratic and difficult to interpret. I do not have reason to suspect that the analyses were in error, and so the rapidly varying concentrations might suggest that biogeochemical cycling in the sediments is the dominant driver, while advective fluxes due to groundwater flow were relatively unimportant. This in itself is an important finding, but further attempts to interpret the patterns were not fruitful. Therefore nitrate data are not discussed further in this manuscript. Trace metals were measured by inductively-coupled plasma mass spectrometry (ICP-MS) at the Woods Hole Oceanographic Institution in Woods Hole, MA following standard protocols (dissolved Fe data from the SSM is excluded due to risk of potential contamination from the standard seepage meter walls). Chloride and sulfate were measured on a Metrohm 850 Ion Chromatograph following standard protocols.

Net Benthic Fluxes

Net benthic chemical fluxes were calculated per unit area of bay floor for manual and ultrasonic applications. The flux is expressed either as an instantaneous flux at each time interval *i*, or as a time-weighted mean for the entire experiment, using the following mass balance relationship:

$$J_{net(i)} = \frac{\frac{\delta C_i}{\delta t_i} V + C_i Q_i}{A}$$

$$J_{net(avg)} = \frac{\sum_{i=1}^{n} w_i' \left(\frac{\delta C_i}{\delta t_i} V + C_i Q_i \right)}{A}$$

Where, for a given sampling interval *i*, δC is the change in concentration of the solute within the seepage meter, δt is the change in time, Q is the volumetric rate of groundwater discharge or recharge, C is the concentration of the solute in the seepage meter, V is the total volume of the seepage meter and circulation system, A is the area of the bay floor covered by the seepage meter, w' is the percent weight of sampling interval duration to total experiment duration, and J_{net} is the net flux of the solute across the sediment-water interface. The flux is expressed either per unit area per unit time as shown above (e.g. μ mol m⁻² h⁻¹), or as a ratio to q_{net} (e.g. J_{net}/q_{net} , units of μ mol cm⁻¹ of seepage). The latter is necessary for direct comparison of results from adjacent seepage meters having different values of q_{net} , and is therefore used in this manuscript when comparing fluxes measured from the adjacent devices.

In all cases, standard errors and standard deviations for the derived variables presented in this study were propagated based on the standard errors and standard deviations of the independent variables (Meyer, 1975). Analytical precisions were determined for each analyte based on repeated analysis (n>10 in all cases) of standard natural reference materials or primary calibration standards in the concentration range of field observations. Using R base statistical software (R Core Team, 2013), significant differences in time-weighted mean fluxes of the various analytes per cm of seepage among the adjacent standard and regulated seepage meters in June and August were tested for using 2-sample student's t-tests.

Advective Chemical Fluxes to the Upper Seepage Zone

Saline groundwater endmember concentrations of TDN, NH₄⁺, DOC, and Mn in June and August were defined as the concentration corresponding to the highest salinity measured in groundwater samples (salinity=27.6, Figure 4). The fresh groundwater endmember concentrations for these solutes were defined as the average concentration for the five water samples with lowest salinities measured in this study (average salinity for five samples =0.09, Figure 4). At times, secondary analytes such as DOC and trace metals were not collected at every sample point due to sampling difficulties, therefore there are fewer sample points for these analytes (Figure 4).



Figure 4 Concentration of TDN, NH₄⁺, DOC, and Mn vs salinity in the shallow portion of the aquifer at the site location in June (blue diamonds) and August (black diamonds). Samples were collected between 12 and 45 cm depth.

Having determined spatially representative fresh and saline shallow groundwater endmember concentrations, and fresh and saline fractions of volumetric SGD flux, a theoretical average advective solute flux estimate from the aquifer to the overlying estuarine sediments can be calculated per deployment (Officer, 1979; Officer and Lynch, 1981; Ullman et al, 2003). The below equation is modified to include freshwater and saline components of flow:

$$J_t = \frac{EM_fQ_f + EM_sQ_s}{A}$$

Where EM_f and EM_s are the fresh and saline shallow groundwater endmember concentrations, Q_f and Q_s are volumetric fresh and saline SGD flux. Throughout this manuscript I refer to J_t as the "theoretical" advective flux that would occur if solutes were transported conservatively through sediment within the upper seepage zone.

Using this flux estimate and the directly measured net benthic flux, the flux of an element or compound to or from the estuarine sediments overlying the aquifer, J_b , can be calculated.

$$J_b = J_{net} - J_t$$

This term represents the loss or gain due to the net effect of a suite of undifferentiated biogeochemical processes and reactions that may include adsorption/ desorption to sediments and particles, biogeochemical transformations/ reactions, and assimilation/ regeneration by microbes). A negative value of J_b indicates removal from solution as the element or compound is advected upwards from the aquifer below, a positive value of J_b indicates a realease into the receiving water body that exceeds the input from the aquifer, and a value of zero would indicate the flux across the sediment water interface equals that of the flux in from the aquifer (i.e. neither removed nor released, conservative transport).

Chapter 3

RESULTS AND DISCUSSION

Submarine Groundwater Discharge

The measurement of SGD in high temporal resolution with the ultrasonic sensor, and in somewhat lower temporal resolution with manual measurements of flow revealed patterns occurring across minute timescales, as well as tidal timescales (Figure 5). Net specific discharge measured at location one in Guinea Creek was anticorrelated with tidal elevation (Figure 5), as has been observed in past seepage meter studies from permeable sediments in coastal unconfined aquifers (e.g. Taniguchi et al, 2001; Michael et al, 2003; Sholkovitz et al, 2003). Although this trend with respect to tide was observed consistently, overall magnitude of discharge differed among seepage meters spaced <1 m apart. This reflects the natural spatial heterogeneity widely observed in coastal systems (e.g. Shaw and Prepas, 1990; Michael et al, 2003), and is not the result of the different geometry of the seepage meters or the different flow measurement approaches used, as indicated by the larger q observed in the RSM in June, versus the larger q observed in the SSM in August (Figure 5).



Figure 5 Time series of specific discharge ± SE and tidal elevation at Guinea Creek in (a) June (b) August of 2015. Specific discharge (q) was measured with the ultrasonic flow sensor in the June regulated seepage meter deployment. For the 3 other deployments shown here, q was measured manually with bags. Section of ultrasonic data highlighted by the vertical blue bar is expanded in Figure 6. Note scales on Y-axes for specific discharge differ in the two panels.

The highly variable ultrasonic data observed during the daytime low tide, left hand side of Figure 5, is likely wave-driven variations in groundwater discharge, and at times, wave driven groundwater/ surface water exchange across the sediment-water interface (e.g. Precht and Huettel, 2004; Sawyer et al, 2013; Russoniello et al, 2018) resulting from observed large boat wakes. There is also a lesser degree of variability in positive q that is present even during times of low wave action, such as during the overnight high tide. This section of data is highlighted by the vertical blue bar (Figure 5).

To examine the fine temporal scale variability in discharge during the overnight period of low wave energy highlighted in Figure 5, a linear regression was fitted to the 20 min span of ultrasonic flow data, and subtracted from the raw field data to obtain adjusted flow data:

$$q_{adj} = q_{raw} - (mt + b)$$

Where q_{raw} is the raw field data; *m* and *b* are the slope and y-intercept of the regression line; *t* is the sample interval duration, and q_{adj} is the adjusted field data (Figure 6). To test whether the variability observed was driven by waves, or reflected instrument noise, comparison was made to ultrasonic "zero-flow" data that were recorded by closing the water-filled flow-tube off entirely to flow with a 2-way valve, both in the laboratory and attached to the submerged seepage meter in the field. Laboratory and field-measured zero-flow data are shown in Figure 6 as the dashed black line and solid red line, respectively. Variability in lab zero-flow data represents

baseline instrument "noise", whereas variability in field zero-flow data represents baseline instrument noise plus *in situ* noise due to influence of variable conditions, such as temperature. The difference between the field-zero line (red) and the field data line (blue) (Figure 6) show the true variation in q in this coupled groundwater/ surface water system. The duration of the peaks is on the order of ~20 s, and are likely small variations in the rate of discharge at the interface resulting from wind-generated or infra-gravity waves (Precht and Huettel, 2004; Bertin et al, 2018). Standard deviations for the normalized field data, the field zero-flow data, and the lab zero-flow data are 0.40, 0.14 and 0.07 cm d⁻¹, respectively across 20 min (1200 observations).



Figure 6 Comparison of field-measured ultrasonic flow data (blue line) against field zero-flow data and laboratory zero-flow data (solid red line, and dashed black lines, respectively). "Zero-flow" data was obtained both in the lab and in the field (attached to the seepage meter in the shallow subtidal zone) by closing the tube off entirely to flow, and measuring the background noise. This graph is a close-up view of the data collected during an overnight high tide which is shown in Figure 5 as the vertical blue bar. Data are adjusted to the arbitrary value of zero for analysis of second-scale variability independent of minute and hour scale trends. Standard deviations of normalized data are 0.40, 0.14, and 0.07 cm d⁻¹ for field data, field zero data, and lab zero data based on 20 min of data recorded at 1 s frequency (n=1200).

The continuous measurement of q_{net} , q_s , and q_f in high temporal resolution in the RSM has revealed patterns and processes occurring over a tidal timescale (Figure 7). Salinity within the seepage meter decreased at a relatively constant rate throughout the entire deployment, including the period of time when a diminished net groundwater discharge occurred during higher a tidal stage (Figure 7). This decrease in salinity during this time period was too large to be explained by the measured rate of positive groundwater advection alone (Figure 7), even if the groundwater was 100 percent fresh. Hence the derived variable q_s , or the component of total net groundwater seepage rate that is equal to the ambient salinity in the meter, must be negative for a period of time; and q_f , the component that is fresh or nearly fresh must exceed q_{net} for an approximately equivalent amount of time in order to explain the observed change in salinity (Figure 7). This pattern, the surface water recharge/ simultaneous freshened groundwater discharge that is in excess of q_{net} , was also observed in the adjacent June SSM deployment, and in the August RSM deployment at location one during high tide, when upward groundwater advection was lowest. Several mechanisms can drive this simultaneous exchange against upward groundwater advection within the subtidal discharge zone which are discussed below.

Groundwater salinity at 20 cm depth below the sediment surface and near the seepage meters was 0.1 PSU based on two measurements made during a mid-flood and a mid-ebb tide on two consecutive days preceding the June experiments, and average salinity within the RSM during the observed surface water recharge/ freshened discharge was ~20 PSU. Assuming groundwater salinity at a depth of 20 cm was negligibly different during our experiment, this corresponds to a salinity gradient of 19.9 g L⁻¹ over 20 cm, or 0.995 g L⁻¹ cm⁻¹. Based on this salinity gradient, a rate of q_s due to 1 dimensional diffusion was calculated to be ~-1x10⁻⁴ cm d⁻¹, which is too small to explain the observed exchange. Although the rate of groundwater discharge varied due to small surface water waves during the nighttime high tide, wave-induced

porewater exchange during this time is zero, since values of q_{net} were always positive (Figure 5), thus wave-pumping is not contributing to the exchange we observed.

Although currents can drive porewater exchange across the sediment water interface, often referred to a shear in the literature (Webster and Taylor, 1992), the depth of exchange is typically on the order of mm, and therefore exchange rates are small in magnitude. We would expect porewater exchange across the bay floor driven by shear under our seepage meter to be small in magnitude, and constant across time owing to a water circulation rate that was constant at 4 L min⁻¹. Also, this would likely not result in the discharge of significantly fresher water due to shallow depth of exchange, thus, it seems unlikely this mechanism could drive the exchange we observed.



Figure 7 Time-series of q_{net} (1 min averages), q_s , and q_f (10 min running mean) in cm d⁻¹ (grey line, red line, and black line, respectively) measured in the RSM in June. Salinity measured in the RSM, from which q_s , and q_f are derived, is also shown. Dashed line is drawn at zero to differentiate between (+) discharge and (-) recharge. Note the surface water recharge/ simultaneous fresh or nearly fresh discharge at high tide.

Porewater exchange rates due to bioirrigation can be large (Martin et al, 2006). The surface water/ freshened groundwater exchange we observed predominated exclusively at high tide regardless of the time of day, and discharge was predominantly fresh (Figure 7), and the phenomenon was observed not only in the oxygenated RSM, but in the hypoxic SSM (Figure 8). In addition, the sediments in Guinea Creek are primarily compact sand with little evidence of burrows (personal observation). Since bioirrigation would not be isolated to high tidal stages, the organisms responsible would not persist in the sediment beneath a hypoxic chamber, and the associated discharge would expected to be brackish or saline (Martin et al, 2006), we are skeptical that bioirrigation could be the primary driver of the phenomenon observed in Guinea Creek. However, it is possible that the signal due to bioirrigation would be wiped out and by increased rate of saline discharge we typically observed at low tide (Figure 7), and therefore more difficult to detect. Thus we cannot discount bioirrigation as a process potentially contributing to the surface water discharge/ freshened discharge in the RSM.

Due to the prevalence of this feature around high tide, we investigated tidal pumping and density-driven convection as possible drivers, since we would expect these processes to be more tidally dependent than the other mechanisms discussed above. Although tidal pumping is a mechanism driving surface water infiltration at high tide, and subsequent groundwater exfiltration at low tide in the intertidal zone (Robinson et al, 2007), it is also understood as a process that can drive unidirectional surface water infiltration/ subsequent exfiltration across the sediment water interface in the subtidal zone (Sawyer et al, 2013). To our knowledge, it has not been shown whether (sub)tidal pumping can result in simultaneous freshwater discharge, or whether surface water can infiltrate against upward groundwater advection due to this mechanism. Therefore we cannot definitively say whether the observed exchange can be explained by this process.

Density-driven convection in permeable sediments, sometimes termed salt fingering, has been shown in laboratory experiments to form in the presence of an unstable density gradient, (Baker and Osterkamp, 1988; Gosink and Baker; 1990).

This mechanism, in theory, would result in a net zero exchange of ambient surface water and fresh or nearly fresh groundwater in the absence of vertical groundwater transport for a period of time until a stable density configuration is reached due to convective mixing and dispersion. This mechanism has been hypothesized as a potential cause for observed entrainment of saline water in the shallow sediments against moderate to high upward groundwater seepage in Great South Bay, NY (Bokuniewicz, 1992), where a density gradient similar to what we measured in Guinea Creek was observed $(2x10^{-4} \text{ g cm}^{-2} \text{ in Great South Bay versus } 7x10^{-4} \text{ g cm}^{-2} \text{ in Guinea}$ Creek). Although we cannot state with certainty with the data at hand, it seems possible that the minimal wave activity and decreased rate of upward groundwater advection during high tide (Figure 5), and a density gradient such as what we measured could set up a condition conducive to salt fingering. Regardless of the mechanism(s) resulting in freshwater q in excess of net measured q (Figure 7), the observation is significant, because to our knowledge, it has not been directly measured previously.

Groundwater Chemistry

Salinity in groundwater samples at times varied vertically and horizontally over small distances. For example, the highest salinity observed in August (27.6 PSU) was collected at a depth of 27 cm, with fresher water found shallower located a small lateral distance away (3.8 PSU at 18 cm depth). This irregular distribution could be due to the effect of temporally varying drivers of porewater exchange such as waves

and tides, as well as anisotropic conditions in the upper portion of the aquifer with respect to hydraulic conductivity. If conditions were to allow, salt fingering could also result in this type of irregular distribution of salinity in shallow permeable sediments, such as that observed in GSB, NY (Bokuniewicz, 1992; Bokuniewicz et al, 2004) and observed in test tank experiments (Webster et al, 1996).

Concentrations of TDN, NH_4^+ , DOC, and Mn in the shallow groundwater correlated with salinity, and not with depth at this location (Figure 4). In our analyses, therefore, we used groundwater salinity as a proxy to define representative endmembers rather than depth.

Performance Assessment of the Regulated Seepage Meter

We discuss below several lines of evidence that demonstrate the RSM is a novel and effective device for measurement of concentration and net benthic fluxes of redox-sensitive, and biogeochemically reactive elements and compounds. First, the regulation capacity of the RSM was sufficient to closely approximate *in situ* DO, pH, and Eh with that of the surrounding estuary (Figure 8). Dissolved oxygen concentration in Guinea Creek recorded over several days in June and August followed a typical day-night cycle characteristic of eutrophic estuarine tributaries of the Delaware Inland Bays (Tyler et al, 2009), reaching minima and maxima of 14 and 196 % saturation in June, and 10 and 158% in August (data not shown). Ambient DO concentrations at the start of the experiments in June and August were 58 and 37 % saturation, and steadily increased over the course of the daytime (Figure 8). In the

SSM, DO concentration decreased in both experiments, but a more rapid decrease and lower minimum concentration was measured in August (~0%) vs June (~50%), indicating a higher overall oxygen demand during the daytime August experiment vs the daytime June experiment (Figure 8). Overall, DO, pH, and Eh in the RSM matched the estuary during the daytime experiments (Figure 8), demonstrating the utility of the RSM's regulation abilities for closely approximating *in situ* conditions. In June, the experiment ran overnight, but it was discovered that the gas-permeable tubing may have over-oxygenated the water in the seepage meter during this time as values measured 10 cm above the bay floor fell below 15% saturation, while oxygen concentration in the RSM never fell below ~50% saturation. This was attributed to the gas permeable loop resting higher in the water column where oxygen concentrations were presumably higher than near the bay floor during nighttime. Light regulation capacity was inferred by measuring DIC concentration in the RSM and SSM as a proxy for photosynthesis. A rapid decrease in DIC in the RSM in contrast to a gradual increase in the SSM (data not shown) indicated that the polycarbonate lid allowed sufficient transmission of photosynthetically active radiation into the enclosed water column and benthos. I note, however, that these are qualitative observations, since the RSM's gas permeable tubing is expected to exchange carbon dioxide, a component of DIC, with ambient estuarine water.

Variability in concentrations of DOC, TDN, NH₄⁺ and Mn at the hour scale was observed from both types of seepage meters, and likely reflects natural temporal variability due to rapid biogeochemical cycling of these species in the benthic zone

and water column (Figure 8). Aside from substantial hourly variation observed in some analytes, concentration trends of analytes across a tidal timescale differed significantly among the RSM and the SSM.



Figure 8 Concentration time-series of DO, DOC, TDN, NH4⁺, Mn (in μM), pH, and Eh (in mV) measured in the regulated seepage meter (black line), standard seepage meter (red line), and in the estuary (blue line), for June 2015 (top row), and August 2015 (bottom row). Concentrations of redox-sensitive analytes in the RSM and the SSM are also shown (black and red dotted lines, respectively), and exhibit different behavior depending on the type of seepage meter used.

As anticipated, the resulting fluxes derived from the changes in concentration of these chemical species also differed among the two seepage meters (Figure 9). Mean benthic fluxes of TDN, NH_4^+ , DOC, and Mn per cm of seepage from the SSM were in every case significantly greater than mean fluxes from the adjacent RSM (2 sample Student's t-tests: *P*<0.001). Also, in many cases when a positive flux was

indicated by the SSM, the RSM indicated the flux was actually negative (Figure 9). A difference as large as 2 orders of magnitude was observed for NH_4^+ fluxes measured in June, for example.

Results from 2 sample Student's t-tests indicate insignificant difference in mean flux for salt (Figure 9), Cl⁻, SO4³⁻, Cu, Sr, Ba, and U (not shown). For chloride and salt, and to a slightly lesser degree, sulfate, concentration trends as well as benthic fluxes per cm of seepage measured with the different devices were in excellent agreement. This is as expected due to the conservative nature of these species. Insignificant differences in mean fluxes of Cu, Sr and Ba are attributed to insignificant correlation with Eh at site 1 overall (P > 0.05). For Uranium, the relatively large propagated error in the RSM with respect to difference in mean time-weighted flux is responsible for the statistical insignificance, since, unlike the other metals, U was anticorrelated with Eh at site 1 overall (P < 0.001).



Figure 9 Boxplots of time-weighted mean benthic fluxes per cm seepage of (a) salt, (b) ammonium, (c) TDN, (d) DOC, and (e) Mn from the RSM (green boxes) and SSM (grey boxes) by month. Lines, boxes, and whiskers correspond to time-weighted means, standard errors, and standard deviations. Dashed line is drawn at the origin to indicate either positive or negative chemical flux across the sediment-water interface.

The ability of the RSM to closely approximate natural light and chemical conditions provides confidence in the accuracy and representativeness of measured fluxes across the sediment water interface. Since the experiments were carried out during the day, the RSM-measured net benthic fluxes represent daytime fluxes. The absence of photosynthesis during nighttime, and associated development of potentially hypoxic and reducing conditions within the sediments (e.g. Tyler et al, 2009) may result in larger fluxes of redox-sensitive elements and compounds, sometimes involving a shift from negative to positive fluxes. The consistent agreement of chemical conditions within the RSM with *in situ* chemical conditions within a eutrophic estuary provides strong evidence that the device is capable of accurately measuring representative chemistry and fluxes in most environmental settings. The consistent disagreement in concentration trends of redox-sensitive elements and compounds within the RSM and SSM proves that the device offers a significant methodological improvement over traditional seepage meters.



Figure 10 Barplots \pm standard error of theoretical groundwater-driven advective flux to the estuary, net benthic flux across the sediment-water interface (J_{net}) and the difference between them or the biogeochemical flux (J_b) , measured from the RSM in June and August of 2015. A negative value of J_b indicates retention as the element or compound is transported from the aquifer below; a positive value of J_b indicates a release into the receiving water body that exceeds the input from the aquifer (a net gain of material during transport through the shallow estuarine sediments); and a value of zero indicates the flux across the sediment water interface equals that of the flux in from the aquifer (i.e. apparent conservative transport). Note scales on Y-axes are drawn appropriate to each analyte.

Biogeochemical Fluxes of Redox Sensitive Elements and Compounds

Theoretical groundwater solute fluxes to the overlying estuarine sediments, when used in combination with the measured net fluxes across the sediment-water interface from the RSM, provide a way to quantify the biocheochemical flux of an element or compound to or from the upper seepage zone (Figure 10). A measured net flux across the sediment-water interface that is less than groundwater-driven advective chemical flux would indicate removal due to undifferentiated biogeochemical processes and reactions. In contrast, a measured net flux exceeding the input from the aquifer would indicate release (i.e. non-conservative addition) of the element or compound as it passes through the overlying estuarine sediment into the estuary. Both patterns were observed to different degrees in this study and are discussed below.

During the June experiment, only ~10% of the theoretical flux of TDN from the aquifer to the overlying estuarine sediments passed across the sediment-water interface into the overlying estuarine water (Figure 10). In August, the net benthic flux of TDN was negative (-175 ±18 µmol m⁻² h⁻¹) indicating the estuarine sediments were a significant sink for both estuarine and groundwater derived TDN (J_b = -566 ±23 µmol µmol m⁻² h⁻¹, Figure 10). We expect that estuarine sediments are a greater N sink in August than in June since chlorophyll *a* concentrations measured in nearby mesocosms connected to the bay floor were 19.1 mg L⁻¹ in August, and 10.9 mg L⁻¹ in June (Torre, 2016). Based on this observation, we can infer that assimilation rate of N by benthic microalgae due to photosynthesis, would therefore be greater in August than in June.

During the June experiment, a low overall NH_4^+ concentration and small changes in concentration measured in the seepage meter over time with respect to analytical precision resulted in a greater propagated standard error in net benthic flux (6 ±22 µmol m⁻² h⁻¹), Figure 10. The expected flux from the aquifer was 57 ±16, indicating the estuarine sediments were a sink of groundwater derived NH_4^+ . During the August experiment, net NH_4^+ flux across the sediment water interface was significantly negative, indicating the estuarine sediments as a sink to both estuarine

and groundwater derived NH_4^+ . Thus, overall, the biogeochemical fluxes of NH_4^+ exhibited a similar seasonal pattern to that of TDN, as expected, since assimilation rates of NH_4^+ by benthic microalgae can be similar to, and often times greater than assimilation rates for other the other forms of N, such as NO_3^- (York et al, 2007), that comprise the TDN pool.

Net fluxes of Mn across the interface were significantly negative, thus the calculated biogeochemical fluxes to the sediment during the June and August experiments were significant (-11 and -12 μ mol m⁻² h⁻¹) when compared against the expected flux from groundwater, which was ~1 μ mol m⁻² h⁻¹, (Figure 10). This indicates the estuarine sediments as a significant sink to both groundwater-derived and estuary-derived Mn. Flux of Fe into the estuarine sediment from the water column was also observed in June (-4 $\pm 2 \mu$ mol m⁻² h⁻¹), and August (-7 $\pm 1 \mu$ mol m⁻² h⁻¹). Since *in* situ dissolved oxygen in the estuary increased as the experiments progressed over the course of the day during both June and August as the estuary rebounded from nighttime oxygen minima below 15 % saturation (data not shown), it follows that oxygen concentration in the estuarine sediments also decreased overnight, perhaps to an even greater degree, creating conditions under which Mn and Fe oxides could be reduced and released from the sediments into the water column (Stumm and Morgan, 1970). This was likely the source of the large Mn flux measured in the SSM in June (Figure 9), associated with artificially low oxygen concentrations and redox conditions (Figure 8). It is therefore logical that as oxic conditions returned to the estuary and sediments during daytime, the reduced forms would oxidatively precipitate out of

solution (e.g. Charette and Sholkovitz, 2002), and re-enter the sediments This is indeed what we observed with both Mn and Fe during the RSM flux experiments.

Contrary to the observed behavior of TDN, NH₄⁺, and Mn, the net flux of DOC across the sediment water interface greatly exceeded the theoretical advective chemical flux to the overlying estuarine sediments in the June experiment, but theoretical and observed did not differ for the August experiment (Figure 10). This indicates that the estuarine sediments are the principal source of DOC to the estuary in June, but that in August, DOC behaves approximately conservatively during transport (e.g. Beck et al, 2007), from the shallow groundwater to the estuary. Although we cannot state with certainty due to impossibly shallow porewater sampling depths, a biogeochemical flux of DOC ~one order of magnitude greater in June than in August in the presence of similar rate of upward groundwater advection, as we observed, would suggest significantly greater porewater DOC concentration in the upper seepage zone in June. Rate of removal of particulate organic carbon (POC) from the water column and subsequent burial in estuarine sediments may be substantially greater over the winter as primary producers die off. Some portion of that buried POC enters the dissolved phase, resulting in elevated porewater DOC concentrations in the upper seepage zone. This may be a mechanism for the apparent elevated porewater DOC concentrations, and large measured benthic DOC flux observed in June.

Chapter 4

CONCLUSIONS

During three deployments in June in August at location one in Guinea Creek, simultaneous recharge of brackish surface water and discharge of fresh or nearly fresh groundwater was measured during higher stages of the tide against upward groundwater advection. Mechanisms including (sub)tidal pumping, convection, and bioirrigation could be possible explanations. Regardless of the responsible driver(s), the fresh or nearly fresh discharge in excess of net measured discharge at high tide is significant, since to our knowledge, this occurrence has not been measured in the field previously. It is also of potential ecological importance, as it may enable groundwater derived chemical loads, including N, to bypass the biogeochemically reactive salinity transition zone (e.g. Webster et al, 1996), and have a greater chance of entering the waterbody having undergone less biogeochemical alteration. Understanding the mechanisms controlling this occurrence, and the linkage between it and benthic chemical fluxes is something we hope to better understand through future deployments.

Chemical conditions measured in the RSM during the June and August experiments closely matched ambient estuarine conditions, thus demonstrating that the RSM as configured is capable of effectively regulating oxygen and light under the eutrophic conditions found in our study area. This provides confidence that the device could be effectively used in most environmental settings. Over-oxygenation occurred in the seepage meter overnight as oxygen concentrations near the bay floor reached

values below 15% saturation. Future deployments of this system should take this into consideration. Anchoring the tubing closer to the bay floor may be necessary to match extreme diurnal fluctuations in dissolved oxygen found in some water bodies.

As anticipated, chemistry and fluxes measured in the adjacent SSM differed significantly from ambient estuarine conditions during the experiments. Evaluating the performance of the standard seepage meter in such a setting is a worthwhile and valuable field test, because it confirms that such a device should not be used to directly measure chemical fluxes under such conditions. In many cases, such as for NH₄⁺, TDN, DOC, and Mn, use of a SSM would lead to a significant overestimation of net benthic flux. It is possible that a light-only regulated seepage meter or device such as the modified standard seepage meter used in this study would be suitable for measuring fluxes under oligotrophic conditions, from organic-poor sediment with low oxygen demand, or during times of year with lower average surface water temperatures, lower respiration rate, and therefore reduced sediment oxygen demand.

Our field tests have demonstrated that this novel tool enables the unprecedented direct measurement of ecologically representative chemical fluxes across the sediment-water interface; and when coupled to already-available tools, enables the measurement of the biogeochemical dynamics and chemical budgets of ecologically important elements and compounds within the upper few centimeters of estuarine sediment. Demonstrating the significance of the upper few centimeters of estuarine sediment in acting both as a sink to groundwater-derived and estuary-derived N, and a source of DOC to the overlying water column, has added to existing

knowledge of the ecological importance of this zone. It is possible that elements and compounds retained in the estuarine sediments during the summer months, as we have observed, would be released in colder months. Similarly, we might expect biogeochemical and redox cycling of ecologically important elements and compounds to occur across a day-night cycle, particularly in the warm season in eutrophic estuaries, where temporally transient periods of hypoxia have been shown to occur. The measurement of geochemical budgets in shallow estuarine sediments, and chemical fluxes to estuaries across diurnal and seasonal timescales are important research questions that could be addressed with future deployments.

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