Chemical Transport by Methane Ebullition in a Freshwater Lake

by

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Submitted to the Department of Civil and Environmental Engineering in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
in Environmental Engineering

at the
Massachusetts Institute of Technology

June 2018

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ABSTRACT

Methane bubbling from lakes contributes significantly to atmospheric methane levels, and methane is second only to carbon dioxide in global warming potential. Microorganisms in aquatic sediments produce methane while consuming organic matter, and the majority of this methane is released via bubbling. Bubbles dissolve as they rise, and the fraction of original methane that dissolves versus escapes to the atmosphere is strongly influenced by bubble size. While bubble sizes are critical to methane fate, traditional methods of measuring bubbles sizes in situ are resource intensive (i.e. sonar or video cameras).

In this work we design, build, and deploy a fleet of novel optical bubble size sensors capable of measuring methane bubbles in situ for long periods of time. Data from our field campaign on Upper Mystic Lake, MA illuminate spatial differences in bubble size distributions and provide an estimate of the contribution from methane bubble dissolution to dissolved methane accumulation. These results improve our understanding of processes governing the emission of this important greenhouse gas.

In addition to transporting gas, bubbles effectively transport particles in water columns. This process has been used extensively in industry since the 1900s to separate chemicals of interest from bulk solutions. While bubbles also transport particulate matter in marine systems, to date very little work has focused on the possibility that methane bubbles transport particles in freshwater systems. We use laboratory and field experiments on Upper Mystic Lake to show that bubbles can transport arsenic-containing sediment particles to the surface of the lake from depths exceeding 15 m. While we estimate that arsenic transport is insignificant at the relatively modest methane bubbling levels in Upper Mystic Lake, other water bodies experience an order of magnitude more ebullition and bubbling may therefore constitute a significant contaminant flux in these systems. Furthermore, bubbles may also transport organisms (or pathogens) from the sediment to the water surface.

Thesis Supervisor: Harold F. Hemond
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Acknowledgments

I am very grateful for the expertise, guidance, and intellectual freedom Harry Hemond has given me during my six years at MIT. He has been a truly excellent advisor, both by offering me spot-on suggestions and advice when I need it, and also by giving me the time and space to explore the research ideas that excite me. It has been a true pleasure to work with him. I would also like to thank the rest of my committee, Phil Gschwend and Heidi Nepf, for their suggestions that helped guide and improve my research.

I owe a debt of gratitude to the scientific and social community of Parsons. I have benefitted enormously from the diversity of scientific expertise within the building, and the collegial atmosphere that encourages people to share their time and knowledge. Much of my field work depended on recruiting volunteers, and it is a testament to the giving nature of Parsons that I never struggled to recruit a willing helper. I will miss the lively lunches, Friday breakfasts, Halloween parties, and innumerable daily conversations that have made working here so much fun.

Scientifically, the Supergroup meetings have been an invaluable learning experience. Supergroup has sharpened my critical thinking skills and gotten me used to a barrage of pointed and helpful questions when I present. Presenting is much less intimidating when you are used to having Phil Gschwend in your audience (thank you, Phil)!

Ben Scandella, my fellow bubble chaser, taught me everything I know about boat-based field work, was an excellent sounding board for thinking through challenges, kept me company on countless visits to Upper Mystic Lake, and his sunny and goofy personality always made me smile. Irene Hu has been an excellent labmate, friend, and willing field work helper. I would like to thank Carolyn Ruppel and Amy Mueller for sharing their career advice and life experiences.

My favorite place on campus is the Edgerton machine shop, and this is thanks in large part to Mark Belanger’s genius. He is a superb teacher, and I am constantly amazed by his technical skill, patience, and crystal-clear explanations. My research would not have been possible without the skills he taught me. John MacFarlane has been my go-to person for all lab and safety questions, and I am very grateful for his help and instruction over the years. Vicky Murphy has cheerfully and expertly guided me through the tangle of University operating policies, making my work easier in the process. I also thank my excellent summer UROPs William Popov, Tim Manganello, and Elise Bickford who each spent many days out on the lake with me.

I thank my Mom for being my emotional rock, particularly in the last few years as I have navigated my own transition to motherhood. I thank my Dad for his career wisdom and advice over the years as I have worked to carve my own career path (and for doing the hard and dirty work of helping me haul bubble traps out of the lake every November).

Above all, I would like to thank my husband, Joe, and my two precious children, Eli and Noa. Joe, thank you for always being excited to hear my bubble stories, for being a pillar of support, love, and patience in my life, and for being an outstanding partner in this crazy juggling game of dual careers and parenting. Eli and Noa, you two are the light of my life. You motivate me to work efficiently so I can come home and play, you give me a sense of perspective when work is challenging, and the earnest joy in your little faces makes my heart sing.
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Chapter 1: Introduction

Methane is a potent greenhouse gas with critical implications for current and future climate change. Methane is second only to carbon dioxide in contribution to atmospheric radiative forcing, and represents around 30% of total radiative forcing from greenhouse gases (Forster et al. 2007). Atmospheric methane levels have been rising for at least the last 100 years, and are far above levels from pre-industrial times. Methane levels are expected to continue rising in a warming climate, and studies of methane sources and fates are considered critical to improving climate change projections (Bastviken et al. 2011, Kirschke et al. 2013).

Methane gas comes from a variety of natural sources (including wetlands, termites, freshwaters, and hydrates) and anthropogenic sources (including ruminants, rice paddies, biomass burning, natural gas production, and landfills) (Wuebbles and Hayhoe 2002). Methane is produced either biotically or abiotically. Biotic methane production proceeds via methanogenesis, a form of anaerobic respiration whereby microorganisms living in anoxic environments consume organic matter and produce methane (Borrel et al. 2011). This methanogenesis usually proceeds via CO$_2$ reduction or acetate fermentation (Walter et al. 2008). The remainder of the methane is thermogenically produced when organic molecules are broken down under the high temperatures and pressures at depths exceeding 1 km beneath the Earth’s surface (Judd et al. 2002). Isotopic signatures can distinguish between methane sources, with lighter methane being indicative of a biogenic source (Flores et al. 2008).

Aquatic systems are large methane producers because sediments are typically anaerobic and rich in organic matter. Methane accumulates in the sediment until being released by diffusion, ebullition (bubbling), or transport through plant vascular tissue, although ebullition is often considered the dominant emission pathway (Walter et al. 2006, Bastviken et al. 2011).
Ebullition rates presented in the literature vary widely based on factors such as organic matter input, nutrient loading, and temperature (DelSontro et al. 2010, Deemer et al. 2016). Studies have shown that increased temperature and nutrient loading cause a synergistic effect to greatly increase methane ebullition (Davidson et al. 2018). The link between temperature increases and more methane ebullition raise concerns that climate change will create a positive feedback loop for methane generation (Aben et al. 2017).

Methane ebullition is often triggered by drops in hydrostatic pressure caused either by changes in air pressure due to meteorological events, or changes in water level from tidal action or reservoir draw-down (Chanton and Martens 1988, Joyce and Jewell 2003, Varadharajan and Hemond 2012, Maeck et al. 2014). Ebullition can also occur spontaneously when gas generation exceeds sediment storage capacity (Liu et al. 2016). Bubbles rising through the water column are subject to dissolution, with methane evading the bubble and dissolved gases present in the water column (such as nitrogen) entering the bubble. This dissolution reduces the amount of methane emitted to the atmosphere, and contributes to dissolved methane which can be biologically incorporated into the lake food web (Kankaala et al. 2006, Bastviken et al. 2013, Sanseverino et al. 2012). Existing dissolution models are of the form:

\[
\frac{dM_i}{dz} = -K_{Li}(H_i P_i - C_i) \frac{4\pi r^2}{v_p}
\]

where \(i\) is the gas, \(M\) is the number of moles of gas \(i\) in the bubble, \(z\) is vertical distance (m), \(K_i\) is the gas transfer coefficient (m/s), \(H\) is the Henry's constant (mol/m³/bar), \(P\) is the partial gas pressure within the bubble (bar), \(C\) is the dissolved gas content in the water (mol/m³), \(r\) is bubble radius (m), and \(v_b\) is the bubble rise velocity (m/s). The model adaptation presented in McGinnis et al. 2006 is widely used in freshwater methane literature, and provides empirical estimates for the gas transfer coefficient based on bubble diameter as a function of gas
diffusivity, rise velocity, and/or diameter. The bubble rise velocity is also determined for a range of bubble sizes, and is based on factors such as drag coefficient, Reynolds number, gas density, bubble diameter, and surface tension. We note that numerous parameters in this model have temperature dependencies, including Henry’s constant, gas diffusivity, and water viscosity. We also note that the HiP product in Equation 1 is very high, and therefore dissolved methane levels would have to be several orders of magnitude higher than those typically seen in natural systems for bubble dissolution to be affected.

As seen in Equation 1, bubble dissolution is heavily dependent on bubble size. Small bubbles can dissolve completely as they rise, whereas slower dissolution rates and faster rise velocities mean that larger bubbles contribute a larger fraction of their initial methane to the atmosphere. Despite the importance of bubble size to the fate of methane in rising bubbles, existing methods to estimate bubble size are typically resource-intensive and therefore only used for limited deployments (Greinert and Nützel 2004, Ostrovsky et al. 2008, DelSontro et al. 2014). These methods include hydroacoustic studies with calibrated sonar devices that can be mounted on boats to generate bubble size measurements over multiple lake transects. Video equipment can also gather bubble size information, though this technique is primarily used in deep-water marine seeps (Sauter et al. 2006, Romer et al. 2012, Wang and Socolofsky 2015). Given the episodic and heterogeneous natural of methane ebullition, single-day measurement campaigns may not accurately capture typical bubble size distributions at a given location within a water body. The ability to measure bubble sizes over longer time periods may therefore improve estimates of atmospheric methane emissions from ebullition.

Given the importance of methane bubble sizes to dissolution rates and the partitioning of methane between dissolved and atmospheric pools, Chapters 2 and 3 of this dissertation present
the design, construction, and testing of a new optical bubble size sensor. This sensor will be a valuable addition to current bubble-size measurement techniques, and for the first time will allow for the long-term study of bubble size distributions in situ. Data from this sensor will also allow us to quantify the spatial and temporal heterogeneity in bubble sizes, as well as the importance of methane bubble dissolution to methane cycling in Upper Mystic Lake near Boston, MA (presented in Chapter 4). This work will provide valuable insights into the role bubbles play in transporting methane from aquatic sediments to the atmosphere.

While bubbles are an effective methane conduit in natural systems, bubbles are also used as particle transporters in industrial systems. During bubble particle flotation, surface-active particles form a stable three-phase contact line with a bubble’s gas/water interface and are transported upward during bubble rise. The flotation process is used extensively in industries such as mining, where flotation separates valuable minerals from gangue (Rodrigues and Rubio 2007, Min et al. 2008). Bubble particle flotation also occurs in the ocean, where wave-injected bubbles scavenge a range of organic and inorganic particles and deposit them in a concentrated surface microlayer (Wallace 1972, Blanchard 1975, and Aller et al. 2005).

Despite the abundant evidence that bubbles are effective particle transporters in industrial and open-ocean conditions, very few studies have looked at the importance of bubble particle transport by methane bubbles in freshwater systems. The few existing studies have found evidence that methane bubbles can transport polycyclic aromatic hydrocarbons (Viana et al. 2012) and manufactured gas plant tar (McLinn and Stolzenburg 2009) from the sediment, but the full extent of methane bubble particle flotation in aquatic systems remains unknown. Since aquatic sediment contamination by heavy metals and organic pollutants from industry and sewage discharge is a widespread problem (Nriagu et al. 1996, Taylor and Owens 2009, Pan and
Wang 2012), methane bubble particle transport has the potential to increase contaminant flux beyond rates predicted from advection and diffusion alone.

Upper Mystic Lake, the field site we used to study methane transport by bubbles, also has a long history of sediment contamination due to upstream industrial activities. Sediments contain high levels of arsenic, chromium, and lead in a distinct layered structure that reflects variable input rates over time (Splithoff and Hemond 1996). We hypothesize that bubble-particle transport may mobilize sediment contaminants and deposit toxins such as arsenic on the lake surface. We therefore conduct field sampling and laboratory experiments to quantify particle transport rates, identify particle sources, and to estimate the contribution of this transport to overall arsenic cycling within the lake (presented in Chapter 5).

In summary, this work improves estimates of the fate and transport of methane and associated particles in bubbles emitted from the sediments of Upper Mystic Lake, MA. This work has three main goals:

1. Develop a rugged, economical, and low power sensor capable of measuring bubble sizes in situ for long deployment periods (Chapters 2 and 3).

2. Use the new sensor to characterize spatial and temporal variability in methane bubble size distributions, and to estimate the importance of methane dissolution to the dissolved methane budget within the lake (Chapter 4).

3. Quantify bubble-particle transport rates in Upper Mystic Lake, and estimate the importance of this transport to arsenic cycling (Chapter 5).

The findings from this work will improve our understanding of the unique role that ebullition plays in methane and contaminant cycling in freshwater systems.
REFERENCES


A novel optical sensor designed to measure methane bubble sizes in situ

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Running Head: Sensor to measure CH\textsubscript{4} bubble sizes  
Keywords: methane, ebullition, bubble volume distribution, lake, optical sensor


(Publication reformatted to fit this dissertation)
Chapter 2: A novel optical sensor designed to measure methane bubble sizes in situ

ABSTRACT
This work presents a novel design for an optical bubble size sensor that is rugged, economical to build, and capable of accurately measuring methane bubble sizes in aquatic environments over long deployment periods. The sensor intercepts rising gas bubbles, elongates them in a thin glass tube, and routes elongated bubbles past an optical detector. The optical detector records information on bubble rise velocity and travel time, which can be combined with the flow path geometry to calculate bubble volume at flow rates up to 3 bubbles/second. The sensor circuitry is powered by 6-V C alkaline battery packs and is cased in a waterproof housing built from commercially available PVC pipe fittings. Laboratory testing indicates the sensor can accurately measure bubble volumes up to 1 mL in volume. We deployed the sensor in a lake with a history of methane ebullition and gathered data on bubble size distributions (most bubbles were between 0.025 mL and 0.2 mL) as well as the precise timing of bubbling events. The sensor also includes an optional gas collection system to allow for bulk gas sampling.
INTRODUCTION

Methane gas is a key climate change driver due to its high radiative efficiency (Forster et al. 2007). Recent estimates of methane gas emission vary considerably, from 145-260 Tg CH$_4$/yr for natural methane emissions, and from 264-428 Tg CH$_4$/yr for anthropogenic methane emissions (Denman et al. 2007). This uncertainty stems in part from the difficulty in measuring heterogeneous and time-varying natural methane emissions. In particular, lake and reservoir sediments have recently been shown to produce methane via microbially-mediated anaerobic decomposition of organic matter in significant volumes and at higher rates than previously thought (St. Louis et al. 2000; Bastviken et al. 2004).

Methane produced in lake sediments is emitted from sediments by ebullition, diffusion, or transport through plant vascular tissue. Ebullition is thought to often account for the majority of methane lake emissions and in some cases 95% of methane emissions have been attributed to ebullition (Casper et al. 2000; Walter et al. 2006; Bastviken et al. 2011). Although ebullition may contribute the majority of lake-wide methane emissions, not all methane released from the sediment as bubbles reaches the atmosphere. As bubbles rise, some methane dissolves into the surrounding water and is subject to microbial oxidation and thereby can support the lake food web (Kankaala et al. 2006). The rate of bubble dissolution depends on several factors, including initial bubble size, temperature, dissolved gas concentrations, and bubble rise velocity (Leifer and Patro 2002; McGinnis et al. 2006). McGinnis et al. 2006 and Leifer and Patro 2002 have built bubble dissolution models to explain dissolution rates in marine environments, and these models are widely used among ebullition researchers.

These models are particularly sensitive to the initial bubble size. The McGinnis et al. model shows, for example, that bubbles less than 2 mm in diameter may dissolve completely
when rising through a 20 m water column. Large bubbles lose much less methane, and because of the decreasing pressure gradient can actually increase in dimension as they rise. Clearly, accurate estimates of bubble sizes are essential to estimating the fraction of bubble methane emitted to the atmosphere and the fraction dissolved into the water column.

Current methods to quantify bubble size distributions typically require divers, underwater video equipment, or hydroacoustic instruments (Greinert and Nützel 2004; Ostrovsky et al. 2008; Vagle et al. 2010; Salmi et al. 2011; Bussmann et al. 2013; Leblond et al. 2014). These methods usually restrict data-collection opportunities to brief periods in time and/or space. Currently, no feasible method exists to study how bubble size distributions may vary over long periods of time. While numerous studies have looked at spatial heterogeneity in methane emissions (DelSontro et al. 2011; Varadharajan and Hemond 2012; Maeck et al. 2013, Wik et al. 2013), few studies have addressed spatial variability in bubble size distributions (Ostrovsky 2003, DelSontro et al. 2014).

This gap in data-collection abilities points to the need for a simple, autonomous device that can measure bubble size distributions and be deployed unattended over long periods of time. Such a device would allow for a thorough characterization of bubble size distributions over a range of time and space. Detailed information about typical bubble sizes at different water column elevations would make it possible to determine if existing bubble dissolution models accurately predict bubble behavior in lake water columns, and ultimately to better understand the fate of methane bubbles emitted from lake sediments and the role of methane in the lake carbon balance.

We present a novel optical bubble size sensor that is rugged, uses relatively little power, is economical to build, and is capable of accurately measuring bubble sizes over long deployment periods. The bubble-size sensor measures bubble volumes by optically detecting
bubbles passing through a glass tube and recording information needed to calculate bubble rise
time and velocity. The optical sensor uses LEDs and phototransistors attached to a custom
printed circuit board (PCB), and the PCB is cased in a waterproof PVC housing constructed from
standard plumbing parts (Figure 1).

![Diagram of the sensor system](image)

**Figure 1: Schematic of bubble sizer housing and internal electronics.**

The sensor is deployed underwater where rising methane bubbles are intercepted by an
inverted glass funnel. Larger bubbles elongate as they pass through the glass tube (the funnel's
stem), becoming approximately cylindrical in shape, and their volume is calculated from the
elongated bubble length and the cross-sectional area of the glass tube. In order to determine
elongated bubble length, we use a series of 3 optical detectors and record the time when the top
and bottom of each bubble passes each detector. Figure 2 describes the four data points recorded
for each rising bubble, and how this data is combined to yield bubble volume estimates. Bubbles
with diameters smaller than the tube diameter are not substantially elongated, but appropriate
signal processing still produces accurate estimates of their volumes (Section: Sensor calibration).
Figure 2: Schematic of the five steps for detecting a bubble and recording the data necessary to calculate estimated bubble volume.

As shown in Figure 2, the sensor derives 2 velocity estimates - the velocity of the leading edge of the bubble (MinimumVelocity), and the velocity of the trailing edge of the bubble (MaximumVelocity). In the case where bubble acceleration is zero, these estimates would be equal. However, bubbles initially slow down upon reaching the constriction at the base of the funnel stem. Once they elongate to fit inside the funnel stem they begin to accelerate. If the glass tube is not long enough for bubbles to reach a terminal rise velocity before passing the detectors, data from trailing edge of the bubble will produce a higher velocity estimate than the leading edge. In order to account for this acceleration, we average the high and low velocity readings and assume a constant acceleration. We also average the travel time measurements produced by the detectors 2 and 3, though in practice these measurements are very similar.
MATERIALS AND PROCEDURES

Sensor electronics design

During initial electronics design, both optical and electrical conductivity sensors were tested. Sensing bubble size based on conductivity signals produced inconsistent signals, whereas optical sensors placed along the bubble flow path produced reproducible and robust signals. Extensive tests with an oscilloscope (Tektronix DPO 7104) showed that optical sensors had a high signal to noise ratio, allowing for reliable detection of the leading edge and trailing edge of rising bubbles for bubbles of varying sizes (Figure 3).

![Figure 3: Oscilloscope traces for bubble optical sensing for three separate elongated bubbles (a), and 10 bubbles smaller than the tube diameter (b). Elongated bubbles experience a partial increase in light transmittance when the tube is mostly filled with gas, in between the leading and trailing edge of the bubble (a).](image)
Key electric components used in the sensor design are described Table 1. The bubble size sensor uses 3 pairs of infrared LEDs and phototransistors, facing each other along the bubble flow path. The electrical signals from the phototransistors are wired to the analog input pins of an Arduino Pro Mini circuit board. The Arduino’s microcontroller (ATMEGA328) is programmed to record baseline phototransistor output, identify bubbles when the phototransistor output significantly deviates from this baseline, trigger the data gathering sequence shown in Figure 2, and store the resulting data on an EEPROM chip. The Arduino program files are available from the author upon request.

**Table 1: Sensor electronic components.**

<table>
<thead>
<tr>
<th>Component</th>
<th>Manufacturer</th>
<th>Part Number</th>
<th>Description</th>
<th>Price in 2015</th>
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</thead>
<tbody>
<tr>
<td>Data chip</td>
<td>Microchip Technology</td>
<td>24LC1025-I/P</td>
<td>EEPROM 1Mbit 400kHz 8DIP</td>
<td>$3.50</td>
</tr>
<tr>
<td>Microcontroller</td>
<td>Arduino</td>
<td>DEV-11113</td>
<td>Arduino Pro Mini 328-5V/16MHz</td>
<td>$10</td>
</tr>
<tr>
<td>Breakout board</td>
<td>Future Technology Devices</td>
<td>DEV-09716</td>
<td>FTDI basic breakout 5V</td>
<td>$15</td>
</tr>
<tr>
<td>Infrared phototransistor</td>
<td>Everlight Electronics Co. Ltd.</td>
<td>PT928-6B-F</td>
<td>Phototrans 1.5mm side facing</td>
<td>$0.50</td>
</tr>
<tr>
<td>Infrared LED</td>
<td>Everlight Electronics Co. Ltd.</td>
<td>IR928-6C-F</td>
<td>LED IR 1.5mm side facing</td>
<td>$0.50</td>
</tr>
<tr>
<td>PC board</td>
<td>Advanced circuits</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4: Schematic diagram of bubble sizer circuitry showing power, LEDs, phototransistors, Arduino Pro-Mini, and EEPROM data chip connections.

The complete circuit (Figure 4) is fabricated on a custom PCB as shown in Figure 5. Design files for PCB manufacturing are available from the author upon request. PVC shims are used to properly align the LEDs and phototransistors with the bubble flow path at a height of 0.43 cm above the PCB (See Figures S7 and S8 in the Supplemental Information for PVC shim dimensions). The electronic circuitry is powered using 6-volt battery packs, each composed of 4 C-size alkaline batteries placed in series, with three 6-V packs in parallel for each sensor (Figure 5A).
The glass tube routing bubbles past the sensor electronics is the stem of a 6140 Pyrex funnel with a 75mm diameter cone. While more fragile than plastic, preliminary testing showed that the hydrophilic properties of the Pyrex material reduced instances of bubbles sticking either at the constriction point or along the thin travel tube. The PCB was secured to the glass funnel stem using U-bolts for 0.635 cm (0.25 inch) piping. Between the U-bolts and glass tube we wrapped a 1 cm length of slitted 0.635 cm (0.25 inch) plastic tubing for cushioning and proper alignment between the glass tube and optical sensors.

**Sensor body design**

A detailed materials list and construction guide with step-by-step instructions for the construction of the sensor body can be found in the Supplemental Information. Briefly, the sensor body is made from a nominal 4 inch PVC pipe coupling and 2 pipe plugs, as shown in Figure 6. O-ring grooves and EPDM dash size 244 O-rings in the side of each pipe plug allow
for a water-tight seal between the coupling and the pipe plugs. The sensor electronics and batteries are housed inside this PVC coupling. The Pyrex funnel that routes bubbles past the optical sensor is passed through two holes drilled into the center of the top and bottom pipe plugs. To create a water-tight seal between the funnel stem and the pipe plugs, 2 small o-ring grooves are machined in to the holes in the top and bottom pipe plugs. The PCB containing the sensor electronics is mounted on the funnel stem inside the housing.

In order to increase the number of intercepted bubbles and to collect the bubbles for gas sampling, we also designed a detachable extension funnel and a gas collection chamber. Detailed construction guidelines for each of these can also be found in the Supplemental Information. The detachable extension funnel is made from a thin sheet of high-density polyethylene (HDPE), rolled into a conical shape and secured with stainless steel nuts and bolts. The extension funnel is attached to the sensor housing with three lengths of nylon rope running from holes along the base of the cone to D-rings attached to the sensor housing with a hose clamp (as shown in Figure 6). To protect the glass funnel from breaking, the extension funnel is offset from the glass by approximately 1 cm with a short length of 4 inch diameter PVC pipe. The size of this extension funnel can be changed to increase or decrease the number of intercepted rising bubbles. We used a funnel diameter of 0.5 m for the field experiments reported herein.
Figure 6: Bubble size sensor complete assembly.

The gas collection chamber is mounted to the top of the sensor housing body, and collects all gas as it exits the funnel. Flexible PVC tubing runs from the gas collection chamber to a surface buoy (as shown in Figure 7), allowing the user to retrieve the contents of the gas collection chamber at the water's surface. Gas can then be taken back to the lab for analysis. Additionally, the sampled gas volume measurement serves as an independent check on the cumulative volume recorded by the bubble size sensor.
Figure 7: Bubble sizer deployment and sampling set-up.

Sensor calibration

Since the bubble size sensor directly measures bubble geometry, minimal calibration should be required to achieve a 1:1 fit between actual bubble volume and measured bubble volume. To test this, sensor calibrations were carried out in a bench-top water tank. To create bubbles of known sizes, we used calibrated Eppendorf pipettes to release known volumes of air underwater into an overturned beaker. Each air bubble was then manually released below the bubble size sensor. This method allowed for the creation of bubbles with specific, repeatable volumes. We used volumes from 0.01 mL to 1.5 mL. Gas volumes lower than 0.01 mL could not consistently be ejected from the pipette tips, and bubbles larger than 1.5 mL tended to break apart during passage through the inverted glass funnel.

As shown in Figure 2, the data collection sequence produces two velocity estimates and two time estimates for a total of four bubble volume estimates. Since the observed flow times for detectors 2 and 3 are very similar, the largest difference in estimates is due to the velocity measurements. The velocity measurements differ because bubbles are still accelerating when
they pass each optical detector. Assuming a linear acceleration and averaging the two velocities and flow times yields a nearly 1:1 fit between actual and measured bubble volumes between 0.01 mL and 1 mL (Figure 8). Beyond 1 mL the linear fit is less significant, potentially because bubble acceleration becomes non-linear and the average velocity is less accurate.

![Graph showing bubble size sensor measurements](image)

**Figure 8:** Bubble size sensor measurements for bubble volume plotted against actual bubble volume ($n = 3$ for each data point). For clarity, only standard deviation error bars for the 2nd Upper Velocity Estimate are shown. Standard deviations for the 1st Upper Velocity Estimate are similar in magnitude, and error bars for the lower velocity estimates are within the range of symbol size. Plot shows linear range between 0.1 mL and 1.0 mL used for calibration equation, and approximate linear fit between 1.0 mL and 1.5 mL. 1 to 1 line drawn for comparison.

While simply averaging the velocities and flow times yields a nearly 1:1 fit between actual and measured bubble volumes up to 1mL, this fit can be improved by applying a linear calibration equation for bubbles between 0.01 mL and 1 mL (equation given Figure 8, $R^2=$
The fact that a calibration equation improves the volume estimates is not surprising given that the precise moment a rising bubble triggers each detector is determined by the complicated optical interaction between the cone of light emitted by the LEDs and the curved meniscus of a rising bubble.

To estimate the flux contribution from large bubbles we have included a second linear calibration line for bubbles between 1 mL and 1.5 mL (R² = 0.9261, Figure 8). While this curve allows us to approximate large bubble volumes, the lower certainty of the calibration curve between 1 mL and 1.5 mL adds additional uncertainty to the total flux measurement. Future work should focus on improving the measurements for large bubbles.

Field deployment and monitoring

We installed 3 bubble size sensors in Upper Mystic Lake near Boston, MA during the late summer and fall of 2014. Upper Mystic Lake is a dimictic kettle lake with an observed history of methane ebullition (Varadharajan and Hemond 2012). The sensors were installed 1 m above the hypolimnetic sediments at a depth of approximately 16 meters. The sensor deployment setup consists of 0.635 cm (0.25 inch) nylon rope, cinderblock anchors, four 20.32 cm (8 inch) Polyform buoys, a length of elastic cord, and 0.318 cm (0.125 inch) plastic tubing running from each sensor gas collection chamber to the surface buoy (Figure 7). The elastic cord allows the center surface buoy to rise and fall in response to changes in the lake water level without becoming submerged.

The bubble size sensors were left in place for 3 week intervals. After 3 weeks, a 50 mL Luer-Lock syringe was used to sample all gas from the gas collection chambers and record the collected volume. We then pulled the sensors to the surface for data retrieval and battery
replacement. Data retrieved from each sensor was processed to remove any abnormal data points as described in the Data Post-Processing section below.

**Data post-processing**

There are several physical scenarios that in principle can lead to erroneous bubble data, and thus a post-processing step is implemented to remove those events that clearly lead to error. The first scenario addressed in the post-processing step is when detector 2 senses a bubble that the detector 3 does not, or vice versa. This could occur when multiple bubbles coalesce within the tube while traveling between the detectors, or when larger bubbles break apart between the detectors. The second scenario is when detector 1 is triggered by something other than a bubble (e.g. other opaque objects in the water column), and detectors 2 and 3 are not triggered. A custom Matlab program identifies these scenarios based on data points with missing timing information (e.g. Det3StartTime and Det3EndTime are 0) or when the calculated velocity is negative.

For the data presented in the Assessment section, approximately 12% of the initial raw data points were removed during post-processing. Of these removed data points, 82% were removed due to data consistent with multiple bubbles joining together or larger bubbles breaking apart within the tube.

**ASSESSMENT**

Results from our calibration tests demonstrate that the sensor can accurately measure bubble sizes for individual bubbles up to 1 mL in volume. In these controlled experiments, only one bubble at a time passed through the glass tube. However, real-world conditions are likely to
contain a wide range of ebullition flow rates, likely increasing the probability of errors due to bubble coalescence.

In order to determine the sensor accuracy under higher ebullition rates, we ran a range of bubble flow rates through the sensor using a syringe pump. The syringe pump was set up to create a column of rising bubbles by ejecting air through an outlet submerged below the size sensor. Two different outlet sizes were used to test flow rates with bubble volumes of 0.04 ± 0.004 mL and 0.08 ± 0.009 mL. The bubble volume passing through the sensor was collected for flow rate verification. The resulting data were processed (see data post-processing section) and corrected using the calibration curve discussed in the Sensor calibration section. The actual flow rate in mL/min was then compared with the cumulative volume measurements recorded by the size sensor.

Figure 9: Flow rate tests conducted for small bubbles (0.04 ± 0.004 mL) and larger bubbles (0.08 ± 0.009 mL). Tests show that sensor can resolve approximately 3 bubbles per second for both bubble sizes.
For smaller bubbles, the sensor had a nearly linear response between actual flow rate and recorded flow rate for rates below 8 mL/min (approximately 200 bubbles/min, Figure 9). Above 8 mL/min the sensor could not reliably record flow rates. For the larger bubbles, the response rate was nearly linear until 14 mL/min (approximately 175 bubbles/min), after which the sensor began under-predicting the measured flow rate. The onset of under-prediction corresponds with an increase in rejected data points which could be caused by bubbles coalescing inside the tube.

It is important to note that while we are testing flow rates on a mL/min basis, the temporal spacing of the bubbles over short time scales is particularly critical (e.g., 5 mL/min of evenly spaced bubbles may be easier to measure than 5 mL/min of bubbles that are clustered in several groups). Our results indicate that the sensor can resolve approximately 3 bubbles per second for both 0.04 mL and 0.08 mL bubbles. In comparison, a recent study looking at bubbling hot-spots used an echosounder calibrated at a bubbling rate of approximately 1 bubble per second (DelSontro et al. 2014). For field conditions with high bubble fluxes, the detachable extension funnel described above could be made smaller to accommodate the sensor’s flow rate limitations.

The 2014 field campaign yielded several bubble size distribution data sets, the largest of which is presented in Figure 10. Of the 837 raw data points recorded by the sensor, 745 data points were retained after post-processing. While Figure 10 only includes bubbles up to 1 mL in size (the range over which our calibration curve is most robust), approximately 2% of the measured bubbles were larger than 1 mL. While the absolute number of these large bubbles is small (16 out of 735 bubbles), their large size could disproportionately affect the error between measured bubble volume and collected volume. Indeed, applying the secondary calibration curve for bubbles between 1 mL and 1.5 mL shows that these 16 larger bubbles comprise approximately 20% of the total flux, highlighting the importance of large bubbles on atmospheric
methane emissions. More work should be done to appropriately extend the calibration curve beyond 1 mL to allow for more accurate measurement of large but infrequent bubbles.

![Graph](image.png)

**Figure 10:** Bubble size distribution curve from Upper Mystic Lake, 3–11 October 2014 with volume measured in mL (a) and diameter measured in mm (b).

Bubbling in Upper Mystic Lake was so vigorous during the deployment window of October 3rd to the 17th that the sensor data storage chip reached maximum capacity on October 11th. Because of this, the total volume of gas retrieved from the gas collection chamber cannot be compared to the cumulative volume recorded by the sensor.

As shown in Figure 10, most measured bubbles volumes are between 0.025 mL and 0.2 mL (or 1.8 mm to 3.6 mm equivalent radii). This size distribution is remarkably similar to that measured in Lake Kinneret, Israel where 90% of bubble radii were between 1.3 mm and 4.5 mm (Ostroffsky et al. 2008). Our size distribution has 89% of bubble radii between 1.3 mm and 4.5 mm.
mm. These radii are three times larger than those reported for bubbles emitted at 42 m in Sakinaw Lake, British Columbia (Vagle et al. 2010). While determining the factors that govern bubble volume is outside the scope of this work, recent modeling work suggests that bubble size is correlated with sediment characteristics (Katsman 2015).

In addition to the valuable bubble volume data obtained by the sensor, we also record data on the timing of bubble events with millisecond accuracy (Figure 11). Examination of the data shown in Figure 11 indicates that clusters of bubbles tend to be emitted over short time intervals (e.g., 78% of bubbles emitted within 5 minutes of a previous bubble), and that larger bubbles are usually accompanied by a cluster of smaller bubbles. The high level of temporal detail in this data set has the potential to provide important insights into the mechanisms controlling bubble release from sediments.

![Figure 11: Timing of bubbles emitted from Upper Mystic Lake, 8–10 October 2014, a subset of the data shown in Fig. 10.](image-url)
Our efforts in field deployment and data gathering demonstrated that the bubble size sensors are adequately durable, with no noticeable degradation occurring over several months of deployment. Sampling the gas collected in the gas collection chamber from a boat on the surface was straightforward, allowing for a simple method to validate cumulative volume measurements while simultaneously producing gas samples for laboratory analysis. Future sensor improvements will include longer battery life and increased data storage capacity. Additionally, a data and power cable could be run from the sensor to a surface buoy so that battery replacement and data retrieval can happen on the lake surface. This would allow for faster data recovery and long-term deployment above the same patch of sediment with minimal sediment disturbance.

**DISCUSSION**

Knowing the precise size distribution of methane bubbles emitted from lake sediments is critical to predicting methane bubble fate within the water column. As explained earlier, bubble dissolution models that predict the fraction of methane dissolved into the water column and the fraction emitted to the atmosphere depend on knowing initial bubble size. Since current methods to acquire accurate bubble size distributions are usually restricted to brief periods in time and/or space, this relatively simple, low-power bubble size sensor is an important advance to bubble volume measurements in situ. By analyzing gas collected from the gas collection chambers we will also be able to determine average bubble methane concentrations, another important parameter in bubble dissolution models.

In addition to making data collection easier, the sensor enables acquisition of bubble size distributions over a wider temporal and spatial range than current methods allow. The sensor is capable of gathering bubble size information over time periods up to approximately one month.
and future design improvements in battery life and data retrieval techniques will extend this to an entire sampling season. In addition, the sensor is relatively easy and inexpensive to build (see supplemental information for a construction guide), further facilitating the deployment of multiple sensors to study the spatial variability in bubble size distributions throughout a lake.

The sensor also provides detailed information on the precise timing of bubble release. Previous work on improving the temporal resolution of ebullition events has yielded important insights into the mechanisms affecting bubble release (Varadharajan et al. 2010; Scandella et al. 2011), and this bubble size sensor produces time-series much more highly resolved than existing data series.

**COMMENTS AND RECOMMENDATIONS**

The detachable design of both the gas collection chamber and the extension funnel allow for easy customization of the bubble size sensor. The extension funnel could be made larger or smaller to change the number of intercepted bubbles. If the size sensor were deployed in a shallow water environment the gas collection chamber could either be shortened or removed entirely, particularly if independent volume verification is not a priority. In this paper we have presented a simple, efficient field deployment scheme that works well in the calm, low-traffic environment of Upper Mystic Lake. However, the size sensor could be attached to a more robust deployment system suitable for difficult field sites such as those with deeper waters, strong currents, or heavy boat traffic.
ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation under grant number EAR-1045193 and Graduate Research Fellowship Program grant number DGE-0707428, the MIT Martin Family Fellowship to K. Delwiche, the W.E. Leonhard 1941 professorship to H. Hemond, and the Singapore-MIT Alliance for Research and Technology program. Timothy Manganello was funded by the MIT UROP program and assisted with coding, equipment trouble shooting, and field work. The authors thank the personnel at the MIT Edgerton machine shop for their invaluable knowledge and help with sensor housing fabrication. The authors also thank co-PIs on the NSF grant Carolyn Ruppel and Ruben Juanes for their guidance on methane ebullition processes, as well as numerous students in the MIT Parsons laboratory for their help with field work (particularly Benjamin Scandella).

REFERENCES


SUPPLEMENTAL INFORMATION

A novel optical sensor designed to measure methane bubble sizes in situ.
Kyle Delwiche, Schuyler Senft-Grupp, Harold Hemond

Bubble Size Sensor Construction Guide

Sensor Body Materials

- 1 nominal 4 inch PVC coupling*
- 2 nominal 4 inch PVC pipe plugs
- 2 EPDM O-rings, dash size 244
- 2 Buna-N O-rings, 7mm inner diameter, 2.5mm wide
- 4 stainless steel eye bolts, 6-32 thread size and 1.9 cm (0.75 inch) length
- 2 stainless steel hex nuts, 6-32 thread size
- 10 cm long piece of nominal 4 inch PVC pipe
- 2 small zip ties, 10.16 cm (4 inch) in length
- Silicone vacuum grease
- 3 cm thick disc of solid PVC, 7.62 cm (3 inch) diameter
- 1 nominal 1 inch male adapter to male NPT fitting (PVC)
- PVC cement
- Stainless steel hose clamp for pipe sizes 92-165 mm
- 3 stainless steel D-rings for 3.8 cm (1.5 inch) webbing width
- Three 1.5 m lengths of 0.635cm (0.25 inch) diameter twisted nylon rope

*All PVC parts are schedule 40
Sensor Body Construction Directions (Refer to Figures S1, S2, and S3)

Repeat for top and bottom pipe plugs:

1. Using a lathe, cut PVC pipe plug to 3.38 cm in length. SAVE the trimmed ring-shaped portion.

2. Using the lathe, reduce the outer diameter of the trimmed ring from the pipe plug until ring fits inside of PVC coupling. This ring will keep battery packs in place.

3. Cut O-ring groove into side of the pipe plug. Groove should be 0.282 cm deep and 0.475 cm wide, and positioned approximately 0.8 cm from end of pipe plug (Fig S1-B). Make sure that groove is smooth. It may help to reduce the lathe speed.

4. Drill a 0.87 cm (11/32 inch) diameter hole into the center of the pipe plug (Fig S1-A).

5. Use a small, hook-shaped lathe tool to cut an O-ring groove into hole drilled in step 3. Groove should be 0.33 cm wide and 0.154 cm deep. Refer to Figure S4 for example of hook-shaped tool.


7. Grease the large O-ring with silicone vacuum grease and insert into the large O-ring groove.

Instructions for top pipe plug only, Fig S1:

8. On the lathe, machine the flat top of top pipe plug to a smooth finish (Fig S1-C).

9. Drill a 3.33 cm diameter hole in the solid PVC disc. On the lathe, this can be achieved by drilling a 3.175 cm (1.25) inch diameter hole and widening the hole to 3.33 cm diameter using a boring bar.
10. Using PVC cement, glue the nominal 1 inch male adaptor to male NPT in to the hole in the PVC disc (Fig S1-C).

11. Using PVC cement, glue the PVC disc and adaptor onto the flat top of the pipe plug, approximately centered on the small O-ring hole (Fig S1-D).

**Instructions for bottom pipe plug only, Fig S2:**

12. Drill 2 small pilot holes horizontally into two opposite sides of the pipe plug top, being careful not to puncture the pipe plug (for upper pair of eyebolts shown in Fig S2-B).

13. Screw two of the 6-32 stainless steel eyebolts into the pilot holes.

14. Drill 2 small pilot holes into 10 cm long piece of nominal 4 inch PVC, approximately 1 cm from the top edge and equidistant from each other.

15. Screw the remaining 2 eyebolts horizontally into the side of the 10 cm long piece of PVC. Secure with the hex nuts.

16. Use the 2 small zip ties to securely fasten the 10 cm piece of PVC to the bottom pipe plug. This removable piece will protect the glass funnel during deployment (Fig S1-B).

**Instructions on Sensor Body Assembly (Fig S3):**

17. Slide the 3 D-rings on to the hose clamp.

18. Slip the hose clamp around the mid-point of the nominal 4 inch coupling, and begin to tighten the clamp.

19. Slide the D-rings around until they are equidistant from each other. Tighten the hose clamp until rings are firmly in place and hose clamp is very snug (Fig S3). To facilitate the placement of the D-rings around the hose clamp, 2 small zip ties can be used to secure each D-ring to the appropriate location on the hose-clamp.
20. Tie the 3 lengths of nylon rope to the 3 D-rings.

Gas Collection Chamber Materials

- 90 cm of nominal 1 inch clear PVC pipe
- 1 nominal 1 inch PVC coupling
- 1 nominal 1 inch socket female to NPT female PVC adapter
- 1 nominal 1 inch male to 0.25 inch NPT female hex bushing (PVC)
- One nominal 0.25 inch NPT male to 1/8 inch barbed nylon tube fitting
- Teflon tape
- 3 stainless steel eyebolts, 0.25 inch-20 thread size with eye diameter of 0.375 inches.
- PVC cement

Gas Collection Chamber Construction Directions (Refer to Figure S5)

21. Using PVC cement, glue the nominal 1 inch unthreaded female to NPT female adapter on to one end of the 90 cm clear PVC pipe (Fig. S5-B).

22. Using PVC cement, glue the nominal 1 inch coupling to the other end of the clear PVC pipe, and then glue the nominal 1 inch male to 0.25 inch NPT female hex bushing in to the other end of the coupling (Fig. S5-A).

23. Wrap Teflon tape around the barbed tube fitting and screw it in to the nominal 0.25 inch hex bushing.

24. Cut eyebolt threads to 0.63 cm in length and polish the cut ends on a grinder.

25. Carefully drill three shallow pilot holes horizontally into the pipe coupling, equidistant from each other and near the top edge of the coupling (Fig S5-A). Be careful not to break through the wall of the gas collection chamber. Holes should be approximately 0.7 cm
deep, or until drill bit first starts cutting in to hex bushing underneath coupling. Tap the holes.

26. Screw the trimmed eyebolts into the pilot holes, being careful not to puncture the gas collection chamber. The eyebolts will serve as guides for 3 nylon ropes connecting the sensor housing to the deployment structure.

27. Drill four 0.637 cm (0.25 inch) holes through the base of the gas collection chamber. Holes should penetrate the top of the female pipe adapter and the clear PVC tube. These holes will allow water to exit the chamber as bubbles enter (Fig S5-B).

**Detachable Funnel Materials**

- 1 sheet of HDPE, 0.16 cm (1/16 inch) thick and 1 m by 0.55 m
- 3 stainless steel bolts, thread size 0.25 inch-20
- 3 stainless steel nuts, thread size 0.25 inch-20
- Three stainless steel washers, 0.25 inch
- Three 1 m lengths of 0.635 cm (0.25 inch) nylon rope
- 4 zipper-top plastic sandwich bags
- 1200 g of small gravel
- 8 long zip ties

**Detachable Funnel Construction Directions (Refer to Figure S6)**

27. Cut a semi-circular pattern from the sheet of HDPE using Figure S6-A as a guide.

28. Drill three 0.66 cm (0.261 inch) holes equidistant along connection flap (Fig S6-A).

29. Drill holes for nylon rope and rock weight attachment as shown in Figure S6-A. Ropes and weights should be equidistant from each other when cone is assembled.
30. Pull HDPE into a conical shape and secure with the bolts, nuts, and washers.

31. Add 300g of small gravel to each of the 4 sandwich bags. Roll each bag into a cylindrical shape.

32. Attach rock weights to the cone using the zip ties (Fig S6-B).

33. Tie the 3 nylon ropes on to the 3 rope holes (Fig S6-B).

**Electronics Materials**

- Custom printed circuit board (PCB) as described in the main text, section titled Sensor electronics design. Eagle files available from author upon request.
- Four 2 mm machine screws, 12 mm in length
- Four 2 mm nuts
- 2 PVC bars, minimum dimensions 0.9 cm by 1 cm by 3.1 cm
- Electronic parts as described in Figure 5 and Table 1 of main text, and PCB Eagle files
- 2 lengths of straight female headers, 12 pins long
- 1 length of straight female headers, 2 pins long
- 2 lengths of straight male headers, 12 pins long
- 1 length of straight male headers, 2 pins long
- 1 length of right-angle male headers, 6 pins long
- 3 6-V alkaline battery packs, size C. Packs should be assembled front to back in 2 rows of 2 cells (such as Digikey item P644-L022-ND).
- 2 position Molex Micro-Fit 3.0™ connector with female terminals

**Electronics Construction Directions**

34. Using a mill, cut the PVC bars to the specifications shown in Figures S7 and S8.

These shims will properly align the LED and photocells on the PCB.
35. Attach PVC shims to PCB using the 2 mm machine screws and nuts.

36. Solder all electronics and female headers for Arduino attachment to PCB. The 2-pin length of female headers should be soldered to analog pins A4 and A5.

37. Solder straight male headers to Arduino Pro Mini with pins protruding from back side. The 2-pin length of male headers should be soldered to analog pins A4 and A5.

38. Solder right-angle male headers to Arduino Pro Mini with pins protruding from the front side.

39. Slide Arduino Pro Mini into female headers on PCB.

40. Slide EEPROM data chip into IC socket.

41. Wire battery packs so they are connected in parallel and all 3 are connected to the Molex fitting. Use sufficient wire lengths to allow for battery pack placement inside the sensor housing.

**Complete Sensor Assembly Materials**

- Two 0.635 cm (0.25 inch) U-bolts
- Four 0.635 cm (0.25 inch) nuts
- Two 1 cm lengths of 0.635 cm (0.25 inch) flexible plastic tubing, slit down the length of the tube
- 1-6140 Pyrex glass funnel
- Trimmed ring-shaped portion of the pipe plugs made in step 2
- 10 cm length of 0.635 cm (0.25 inch) inner diameter plastic tubing
Complete Sensor Assembly Instructions (See Figure 6 in main text for final product)

42. Push the stem of the Pyrex glass funnel through o-ring hole in the bottom pipe plug.

43. Wrap the two 1 cm lengths of 0.25 inch flexible plastic tubing around the funnel stem, 5 cm apart and approximately centered along the length of the stem.

44. Using the u-bolts, attach the PCB to the funnel stem at the locations of the flexible tubing.

45. Push the 4 inch coupling on to the pipe plug (make sure the large o-ring is greased).

46. Slide the trimmed portion of the pipe plug in to the coupling. This will keep the battery packs from moving around too much.

47. Arrange the 3 battery packs around the PCB, and connect batteries to PCB.

48. Slide the top pipe plug on to the coupling (make sure large o-ring is greased). To accomplish this, temporarily pull the glass funnel downwards to release pressurized air from the housing. Once the top pipe plug is snug on the coupling, push the funnel stem back through the top pipe plug.

49. Push the 10 cm length of plastic tubing on to the top of the funnel stem. This tube will route bubbles past the 4 holes drilled in to the bottom of the gas collection chamber, ensuring that all gas is trapped within the gas collection chamber.

50. Tie the nylon ropes from the extension cone to the D-rings on the sensor housing.

51. Screw the gas collection chamber on to the top pipe plug.

52. Take the 3 nylon ropes tied to the D-rings and pass them through the 3 eye-bolts at the top of the gas collection chamber.
These 3 nylon ropes can then be tied to a stainless steel s-hook for attachment to the deployment structure shown in Figure 8 of the main text.

SUPPLEMENTAL INFORMATION FIGURES

**Figure S1** – Top pipe plug

**Figure S2** – Bottom pipe plug
Side View

Stainless steel hose clamp

D-ring for 3.8 cm (1.5 inch) webbing

Optional zip ties to position D-rings

Figure S3 – Assembled sensor housing

Figure S4 – Hook-shaped lathe tool
Figure S5 – Gas collection chamber

Figure S6 – Detachable extension funnel
a – Right PVC shim

b – Top view

* Figure not drawn to scale

0.206 cm diameter (0.081 inches)
0.102 cm diameter (0.04 inches)

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Figure S7 – Right PVC shim
Figure S8 – Left PVC Shim

* Figure not drawn to scale
An enhanced bubble size sensor for long-term ebullition studies
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Running Head: Bubble size sensor for long-term studies

Keywords: methane, ebullition, bubble volume distribution, lake, optical sensor


doi: 10.1002/lom3.10201

/Publication reformatted to fit this dissertation/
Chapter 3: An enhanced bubble size sensor for long-term ebullition studies

ABSTRACT

Methane ebullition from freshwater sediments is a significant source of greenhouse gas to the atmosphere. Methane bubble size determines the fraction of methane that dissolves into the water column instead of entering the atmosphere, but current methods to measure bubble sizes in situ are limited. Previously we reported the design for a novel optical bubble size sensor capable of measuring methane bubble sizes in situ. Here we report sensor enhancements to allow for continuous long-term sensor deployment, uninterrupted data collection under high ebullition flux, and improved bubble volume measurement accuracy. The enhanced design includes a data and power cable running from the sensor to a custom data buoy housing batteries and an SD memory card. Batteries and SD cards are replaced every 2-4 weeks through the data buoy, allowing for continuous, undisturbed sensor deployment. In addition, sensor parameters have been tuned to reduce error from particle intrusion and fluctuations in raw signals that were observed during transit of some bubbles through the sensor. Field data show that on average the sensor measures cumulative bubble volumes equaling approximately 86% of collected gas volumes. We discuss potential mechanisms of remaining error, some of which may be due to zooplankton intrusion, and suggest directions for future sensor enhancements.

INTRODUCTION

Atmospheric methane currently contributes about 30% as much radiative forcing as carbon dioxide to the globe (Forster et al. 2007). Recent bottom-up estimates of global methane
emissions suggest that approximately 50% of methane comes from non-anthropogenic sources, 11% of which comes from fresh water lakes and rivers (Kirschke et al. 2013). Man-made reservoirs may be even more prolific methane generators than natural lakes (Deemer et al. 2016). Methane is generated in lake and river sediments by anaerobic decomposition of organic matter and enters the atmosphere by diffusion, ebullition, or transport through plant tissue, although ebullition is often thought to be the dominant emission pathway (Casper et al. 2000, Walter et al. 2006, Bastviken et al. 2011). Significant uncertainty remains with respect to both quantifying current ebullition flux and predicting future ebullition flux in a warming climate (Walter et al. 2007, Bastviken et al. 2011, Wik et al. 2016a). This uncertainty arises largely from the difficulty in accurately measuring highly heterogeneous spatial and temporal ebullition patterns (Wik et al. 2016b).

Methane ebullition is often triggered by drops in hydrostatic pressure, either from changes in air pressure, tide, or water level, or from wind-induced shear stress in sediments, although such forcing is not required for bubble release (Joyce and Jewell et al. 2003, Chanton and Martens 1988, Varadharajan and Hemon 2012, Maek et al. 2014). Importantly, bubbles rising through the water column are subject to dissolution and invasion by dissolved gases from the surrounding water, and these processes are highly dependent on the initial size of the bubble (Leifer and Patro 2002, McGinnis et al. 2006). Small bubbles can dissolve completely into the water column, thereby contributing via a microbial loop to the lake food web (Kankaala et al. 2006). Larger bubbles have both a lower relative dissolution rate and faster rise velocities, and therefore contribute a larger fraction of their initial methane content to the atmosphere.

Despite the importance of bubble size to bubble fate in the water, relatively few techniques are available to measure individual methane bubble volume in situ. Some
hydroacoustic studies use calibrated sonar devices to estimate methane bubble size distributions, and these techniques can provide an estimation of bubble sizes over multiple transects in a lake (Greinert and Nützel. 2004, Ostrovsky et al. 2008, DelSontro et al. 2015). However, most hydroacoustic studies are limited to relatively short deployment windows in part because long-term hydroacoustic equipment deployment requires additional infrastructure for power delivery and data storage (Scandella et al. 2015). Video equipment can also aid in bubble size determination, although this technique is primarily used in deep water marine environments (Sauter et al. 2006, Römer et al. 2012, Wang and Socolofsky. 2015).

Recently our research group developed an optical bubble sizing sensor capable of measuring bubble sizes in situ (Delwiche et al. 2015). This device is inexpensive to build and rugged, and the first generation sensor design was capable of continuously measuring bubbles in one location for deployment periods of up to 2 weeks. The bubble sensor routes bubbles upwards through a glass tube (the tube is the stem of a glass funnel that intercepts rising bubbles) and past a series of three infrared beams that are attenuated during bubble passage, providing optical signals from which bubble numbers and volumes are determined. A microcontroller records signals from the detectors, and bubble volumes are calculated from these data. Optional sensor attachments include an external funnel to increase the sampled area, and a gas collection chamber to provide gas samples as well as an independent verification of cumulative gas volume passing through the sensor.

This initial sensor design is described in Delwiche et al. 2015. Based on subsequent design modifications, software improvements, and field deployments in 2015 and 2016, we describe here a number of hardware and software enhancements. These enhancements greatly increase the sensor’s maximum deployment period and provide increased sensor accuracy,
particularly in high bubble flux environments. We also present procedural steps for processing anomalies in field data, as well as a discussion of potential causes for anomalous field data. In summary, we present:

1. Design and testing of a companion power supply and data storage buoy to greatly simplify battery replacement and data downloading while avoiding sediment disturbance, and to increase data storage capacity for uninterrupted data collection in high flux areas. We also describe an improved external funnel to increase sampled area (see Materials and Procedures).

2. Hardware and software modifications to improve sensor accuracy and precision (see Materials and Procedures).

3. Detailed data post-processing steps to properly handle anomalies in field data (see Materials and Procedures).

4. Field data demonstrating that the sensor works well and measures, on average, 86% of the cumulative gas volume collected from the gas collection chamber. We include a detailed analysis of potential sources of missing data, and an assessment of the relative importance of each (see Assessment).

MATERIALS AND PROCEDURES

Introduction to sensor hardware

The bubble sensor routes bubbles upwards through a glass tube and past a series of infrared beams that are interrupted by bubble passage, providing optical signals from which bubble numbers and volumes are determined. The glass tube is the stem of an inverted glass funnel which is cased in a waterproof PVC housing. A circuit board contains three pairs of
infrared LEDs and phototransistors facing each other across the glass funnel stem. We will henceforth refer to each pair of infrared LEDs and phototransistors as individual detectors, with detector 1 being on the bottom, detector 2 in the middle, and detector 3 being at the top. The glass funnel protrudes from the bottom of the waterproof PVC housing to intercept rising bubbles. An Arduino Pro-Mini microcontroller records and stores signals from the detectors, and the data are used to calculate bubble volumes (detailed calculations provided in Delwiche et al. 2015). Additional sensor attachments include an expansion funnel to increase the sampled area if desired, and a gas collection chamber to allow for independent volume verification of the amount of gas passing through the sensor between sampling periods. Full sensor schematic, detailed description of bubble volume calculations, and a step-by-step design guide for the first generation sensor are provided in Delwiche et al. 2015.

Introduction to bubble detection algorithm

The sensor detects the top of a rising bubble by comparing real-time phototransistor analog to digital converter (ADC) readings with background values. Background ADC measurements are taken from the phototransistors approximately every second, and the rolling average of eight consecutive background measurements is used to calculate the threshold to which the sensor compares future ADC readings. Each sensor records separate background readings for each detector to accommodate differences in individual LEDs and phototransistors, or their respective alignment. Bubbles substantially decrease the amount of light reaching each phototransistor, causing a precipitous drop in ADC readings from background levels. The sensor will assume a detector is seeing a bubble while ADC readings are 0.15V below the average background reading. The microcontroller records the times detectors 2 and 3 each see
the beginning and end of a bubble, and combining this information with the space between detectors and the flow path cross sectional area yields volume estimates. If an incoming bubble reaches detector 1 before the previous bubble clears detector 3, the microcontroller will record a multi-bubble event with the corresponding timing information for each bubble. The microcontroller can keep track of up to 12 bubbles per bubbling event, and writes the bubble data to memory in 4-bubble increments.

Hardware upgrades

Custom service buoy and data/power cable for long-term deployment

Sensor battery replacement and data downloading for the first generation sensor described in Delwiche et al. 2015 required the entire sensor to be pulled to the water surface, thus limiting the undisturbed deployment interval to the battery life of 1-2 weeks, or significantly less in high bubble flux locations (due to data storage restrictions). In order to continuously operate the bubble size sensor without disturbing sediments, we designed a custom service buoy so all routine service functions can be carried out easily from the water surface. The service buoy holds 7.4 V lithium ion batteries to power the sensor, and a SD card data storage system. The PVC service buoy is built with a polyurethane float cast around the buoy body using a modified angel food cake pan (as was done in Gardner et al. 2009). The float is coated with epoxy to increase durability. A four-stranded waterproof neoprene-insulated cable carries power to, and data from, the bubble sensor. A tube for gas sample retrieval is also provided. The buoy contains a waterproof bulkhead fitting that the data cable connects to, an air release valve, and a
cap sealed with an O-ring. Buoy is shown in Figure 1 and detailed instructions on buoy construction can be found in the Supplementary Information.

![Diagram of Custom Data Buoy](image)

**Figure 1:** (a) Bubble sizer deployment and sampling set-up with the new data cable. (b) Custom service buoy containing batteries and data storage circuit board for long-term sensor deployment.

The data system on the buoy contains an Arduino Pro-Mini microcontroller which periodically communicates with the bubble size sensor, typically every 12 hours. During communication the bubble sizing sensor transmits all data stored on its EEPROM and then clears the chip. These data are transmitted serially using USB protocol to the buoy’s microcontroller which stores the data on a micro SD card (using an Adafruit MicroSD card breakout board (Figure 2)). In instances of high bubble flux the microcontroller could be programmed to transmit data more frequently to ensure that the EEPROM chip on the bubble size sensor does not reach its maximum capacity of 1023 events. To minimize power consumption, the service buoy's microcontroller can be programmed to sleep when it is not retrieving data. The service buoy circuit board contains a real-time clock to record the precise time of data transmission. Design files for the data buoy PCB and the sensor PCB are available from the author upon request.
PCBs connected through neoprene data cable with bulkhead fittings

MicroFit 3.0 4 position connector Battery clip MicroFit 3.0 4 position connector

7.4V Li-ion rechargeable battery Arduino Pro-Mini

Jumper 5.0V

Battery clip 7.4V Li-ion rechargeable battery Arduino Pro-Mini

7.4V Li-ion rechargeable battery Arduino Pro-Mini

MicroSD card breakout board

Figure 2: Circuit diagram for bubble sizing sensor circuit board and data buoy circuit board.

The service buoy circuit board also contains two surface mounted battery clips for 7.4V, 8800mAh rechargeable lithium-ion battery packs (Tenergy product #31010). One battery pack powers the bubble sizing sensor, and one pack powers the data buoy circuit board. One battery can power the bubble size sensor for 2-3 weeks, but this time can be doubled by using two battery packs in parallel, for a total of 3 battery packs in the buoy.

Upgraded Extension Funnel

In addition to the data cable modifications, we also updated the first generation detachable extension funnel described in Delwiche et al. 2015 to improve performance in the field (Figure 3). The new extension funnel is constructed from a 0.25 m² commercial plastic funnel and secured to the bubble sensor housing with stainless steel rope and carabiners (commercial plastic funnel originally used by the Global Change and Watershed Biogeochemistry research group at
The steel rope connection to the bubble sensor body is more robust and easier to attach than the ropes included in the original design. More detailed instructions on funnel construction can be found in the construction guide in the Supplementary Information. While this funnel is easier to deploy in the field, it has a fixed collection area. The original funnel design presented in Delwiche et al. 2015 has a variable collection area and works well as long as the ropes connecting the funnel to the sensor housing are tightly secured with appropriate knots.

Figure 3: Bubble size sensor complete assembly.

Field Deployment Procedure

We deployed eight sensors in Upper Mystic Lake, MA during the summers of 2015 and 2016. The sensor deployment structure is shown in Figure 1 and consists of a “W” shaped rope structure suspended between ropes and buoys. The structure contains the data cable as well as the PVC tubing necessary for gas sampling. The minimum sensor depth with this deployment
structure is around 2 meters which is beneficial in a lake with significant public recreation, but sensors could also be placed closer to the water surface with a different deployment structure. Specific instructions for deploying sensors on the structure shown in Figure 1 are provided in the Supplemental Information. We visited deployed sensors every 2 weeks to replace batteries, download data, and remove collected gas. In sufficiently high bubble flux environments the gas collection chamber will need to be emptied more often. If using two batteries in parallel to power the bubble size sensor, the sensor could operate for at least 4 weeks between maintenance visits. Specific instructions for servicing the sensor and buoy are also provided in the Supplemental Information. Field data allowed us to analyze bubble sensor performance in the more challenging environment of a natural lake where the sensor is subject to physical stressors, contact with micro and macro organisms, and other environmental factors. We also compared gas volumes collected from the gas collection chambers to the cumulative bubble volume as measured by the sensor for a further assessment of sensor performance.

**Hardware and software modifications to improve sensor accuracy and precision**

Data gathered during 2015 and early 2016 field campaigns pointed to the need for a deeper understanding of sensor functioning under challenging heterogeneous field conditions such as particle or zooplankton intrusion into the bubble flow path, or during high-flux bubble events. To understand and improve sensor performance we developed two methods of measuring detector waveforms and logic levels within the sensor under a range of bubble conditions in the laboratory and field, as described below.
Laboratory oscilloscope monitoring procedure

To directly observe sensor functioning under high-flux bubble conditions, we retrofitted a bubble sensor cap to include a bundle of wires running directly from individual output pins on the sensor circuit board to an oscilloscope. The sensor was deployed underwater in a benchtop fish tank in a stream of bubbles, and the oscilloscope was connected to directly observe raw signal output from two of the three phototransistors at a time. Figure 4 shows the oscilloscope traces for the phototransistors on detectors 2 and 3, respectively the yellow and pink traces. The signal is high when no bubbles are present, and drops when a bubble passes. The signals are plotted against time, so bubbles are detected by the 2nd detector (yellow trace) slightly before detection by the 3rd detector (pink trace).

![Oscilloscope traces](image)

**Figure 4:** An example of oscilloscope traces with a description of each trace. The blue and green traces in Figure 4 represent the microcontroller's response to the passing bubble.
Incoming ADC readings from each detector are compared to background ADC values as described in Materials and Procedures. When an ADC reading drops below the background threshold the microcontroller records the start of the bubble, and the blue and green traces jump high. The blue and green traces remain high while the ADC readings remain low, and once ADC readings recover towards background at the end of the bubble the blue and green traces drop low again.

**Field raw data collection procedure**

After using the oscilloscope to record raw sensor waveforms in the laboratory, we acquired similar data in the field by programming one bubble size sensor to record full time series of all of the raw phototransistor readings taken during a bubble event from detectors one, two, and three. The field data resolution was lower than the laboratory oscilloscope raw data due to timing limitations of the microcontroller. However, even with more coarse data resolution, field raw data show clear bubble traces similar to those observed in the laboratory with the oscilloscope (Figure 5). These raw field data allow us to confirm whether sensor behavior seen in laboratory oscilloscope traces are also observed in the field.
Sensor hardware and software improvements based on oscilloscope and field data

The laboratory oscilloscope work and field raw data collection allowed us to determine that, in general, the phototransistor signal drops sharply as a bubble passes, and recovers rapidly once the bubble is past. This clear delineation between background signal and bubble events makes for robust bubble detection (refer to Materials and Procedures for algorithm description). However, oscilloscope work revealed that while the body of the bubble passes each phototransistor, the ADC signal can fluctuate as shown in Figure 6. The frequency and amplitude of the fluctuations vary based on bubble size and bubble spacing, which indicates that this is a physical effect as opposed to an electrical phenomenon. Signal fluctuations were also observed in raw field data (Figure 7).
Figure 6: Fluctuations apparent in laboratory oscilloscope data (see Fig. 4 for trace descriptions). Fluctuation frequency and amplitude appears to intensify as bubbles become closer together and have correspondingly higher rise velocities.

Figure 7: An example of raw field data showing a signal fluctuation at the trailing edge of the bubble (right hand side).
Interestingly, signal fluctuations seem to increase with decreased bubble spacing and this phenomenon can also be seen in Figure 6. Bubbles that are closer together have higher rise velocities, and comparing bubble rise velocity in the tube to a manual classification of the number of fluctuations observed in the bubble signal yields a significant, positive correlation. We hypothesize that these signal fluctuations are the product of a complex optical interaction between the upper and lower menisci of the rising bubble, as well as changes in the thickness of the water film coating the glass funnel stem during bubble passage. More work is needed to elucidate the precise physical mechanisms underlying these fluctuations.

These fluctuations present a potential problem if the amplitude becomes high enough for the sensor to mistake a fluctuation for the termination of one bubble and beginning of a new bubble. This could lead the sensor to falsely report one bubble event as two bubble events, or for detectors 1, 2, and 3 to record a different number of bubbles for the same bubble event. Indeed, field data from 2015 and early 2016 show significant occurrence of events where detectors 2 and 3 saw a different number of bubbles. While we note that there are multiple potential causes for this data mismatch (as discussed in Assessment), we designed a data smoothing algorithm to mitigate the contribution of signal fluctuations to anomalous field data.

The smoothing algorithm is designed to minimize the possibility that a short-term fluctuation could be mistaken for the termination of a bubble. Instead of comparing each individual phototransistor reading to the bubble detection threshold, the microcontroller uses the average of 8 successive phototransistor readings. This smoothing algorithm decreases the likelihood that a short-term fluctuation in the bubble signal will be interpreted as the end of a bubble. We also increased the sensor sensitivity by increasing LED output by changing the resistors associated with the LEDs from 15k ohms to 12k ohms, a change that increased the
difference between background and bubble readings. Data gathered after the implementation of the smoothing code and enhanced sensitivity show a 45% decrease in the times detectors 2 and 3 recorded different bubble quantities, indicating that the smoothing code improved sensor measurement accuracy. We note that even with the smoothing code, 10% of unprocessed field data contain a mismatch between the number of bubbles seen by detectors 2 and 3, and the possible causes of this mismatch are more numerous than signal fluctuation alone (see Table 2).

Calibration curve

The sensor improvements described above necessitated an update of the original calibration curve presented in Delwiche et al. 2015. The sensor was calibrated in a benchtop fish tank with a range of gas volumes released by an Eppendorf pipette. Each bubble volume generated four distinct volume estimates as described in Delwiche et al. 2015, and all four estimates are plotted in Figure 8. The calibrations for bubbles from 0.01 mL to 1.0 mL (0.26 cm to 1.24 cm equivalent diameter) and 1.0 mL to 1.8 mL (1.24 cm to 1.51 cm equivalent diameter) were linear with low variability between repetitions. Bubbles below 0.01 mL (0.26 cm equivalent diameter) were difficult to accurately produce with the pipettes, and sensor measurement accuracy decreased substantially for bubbles over 1.8 mL (1.51 cm equivalent diameter). The positive intercept on the small bubble linear fit means tiny bubbles cannot be calibrated for, as discussed in the Assessment.
Figure 8: Bubble size sensor measurements for bubble volume plotted against actual bubble volume (n = 4 for each data point). Plot includes the four volume estimates generated during each bubble event, as well as the average of these estimates. Plot shows linear ranges from 0.01 mL to 1.0 mL (0.26 cm to 1.24 cm equivalent diameter) and 1.0 mL to 1.8 mL (1.24 cm to 1.51 cm equivalent diameter) used for calibration equations. The 1 : 1 line is drawn for comparison.

We note that in Delwiche et al. 2015 we attributed the sensor’s inability to accurately measure large bubble sizes to the tendency for large bubbles to break apart within the glass funnel stem. However, further analysis of the data showed that typically at least 97% of the original gas volume is contained in a single large bubble, followed by 1-3 small bubbles, and therefore bubble decomposition is likely an insignificant contributor to sensor inaccuracy. We surmise that sensor inaccuracy for large bubbles stems from the complicated effect on bubble velocity of the bubble exiting the top of the funnel stem, and the fact that large bubbles will exit the funnel stem before the trailing edge velocity is measured. This aspect of the sensor functioning warrants further investigation.
Field data post-processing steps

Unprocessed field data description

After bubble sensor deployment and data collection, field data must be processed to remove incomplete data, or data that do not accurately measure bubble volumes. The potential causes of incomplete or inaccurate data are numerous and will be described in detail in the Assessment, but could include issues such as zooplankton intrusion, sensor confusion during high flux bubble events, or noisy background signals. While there is no way to tell from the field data which physical or electronic mechanism may be contributing to erroneous data, specific data post-processing guidelines can distill reliable bubble data from the un-processed data stream.

Table 2: Possible error codes for each bubble event (summed if more than one occurs for a given bubble event)

<table>
<thead>
<tr>
<th>Error Code</th>
<th>Error Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Data collection time exceeds maximum timeout threshold of 5 seconds</td>
</tr>
<tr>
<td>10</td>
<td>Detector 2 saw more bubbles than detector 3</td>
</tr>
<tr>
<td>100</td>
<td>Detector 3 saw more bubbles than detector 2</td>
</tr>
<tr>
<td>1000</td>
<td>Detector 1 still looking for the end of a bubble</td>
</tr>
<tr>
<td>10000</td>
<td>Detector 2 still looking for the end of a bubble</td>
</tr>
<tr>
<td>100000</td>
<td>Detector 3 still looking for the end of a bubble</td>
</tr>
<tr>
<td>1000000</td>
<td>Detectors 2 and 3 do not see a bubble</td>
</tr>
</tbody>
</table>

The microcontroller is programmed to record the precise timing of each bubble event, as well as specific raw analog signals from each detector. Figure 9 presents an example of the data
stream for one bubble with no errors, along with a description of each number stored during a bubble event. Unprocessed data also contain bubble data with errors, and error codes are described in Table 1. Depending on the error code the bubble event may still contain enough information to calculate bubble volume, but often these data must be discarded because some of the values shown in Figure 9 will be zero.

Typical raw data for a single bubble event:

6530759, 1, 0, 525, 460, 641, 2236042908, 398, 2236125676, 463, 2236123268, 580, 2236208916, 648

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
<th>L</th>
<th>M</th>
<th>N</th>
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<td></td>
</tr>
</tbody>
</table>

A: Time of bubble event (in milliseconds since Arduino power was connected)
B: Number of bubbles in this event (0 to 4)
C: Error code (see Table 1 for error code descriptions)
D, E, F: Background ADC values for detectors 1, 2, and 3, respectively
G, I: Time detector 2 sees beginning and end of bubble, respectively (microseconds)
H, J: Detector 2 ADC value at start and end of bubble, respectively
K, M: Time detector 3 sees beginning and end of bubble, respectively (microseconds)
L, N: Detector 3 ADC value at start and end of bubble, respectively

Figure 9: Example of raw bubble sizer data and description of each entry in the data stream.

Description of data types removed during post-processing

There are four categories of bubble data that must be rejected during post-processing. Table 2 presents each category, includes references to explain potential causes for each data type, and provides an estimate of data category prevalence in field data. The first two categories are composed of incomplete bubble event data where some or all of the data points associated with detectors 2 and 3 are zero. The third category of data to be rejected includes large bubbles outside of the calibration range described in the Assessment.
The fourth data type to be rejected includes data where the four volume estimates acquired for each bubble event do not follow the pattern observed in a controlled laboratory setting, and therefore bubble volume estimates are not reliable. As shown in Figure 8, laboratory work demonstrates that the two lower bubble volume estimates should be similar, and we can quantify this similarity using the coefficient of variation (the ratio of the standard deviation to the mean). We have calculated the coefficient of variation for a range of bubble sizes measured in a controlled laboratory setting, yielding a clear threshold for accepting or rejecting field bubble data (Figure 10). Coefficients of variation increase as bubble volumes decrease, and bubbles smaller than the internal diameter of the funnel stem have much higher coefficients, likely because these bubbles are subject to lateral movement within the flow path (see Assessment for details). Bubble volume estimates with coefficients of variation outside of the acceptable range have unknown accuracy, and are therefore discarded during post-processing. While this approach will result in under-counting cumulative volume measurements, it will improve accuracy of individual measured bubble sizes. Possible bias to the total bubble size distribution from under-counting bubbles is discussed below in the Assessment.
Figure 10: CV between the two lower volume estimates plotted against bubble volume for a series of bubbles created in a laboratory tank. The shaded area delineates acceptable CV values based on bubble volume, as used by the data processing algorithm.
Table 3: Description of different types of data removed during post-processing.

<table>
<thead>
<tr>
<th>Data Type</th>
<th>Description</th>
<th>Potential Causes</th>
<th>Frequency of occurrence in field data</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type 1 – Non-bubble events</strong></td>
<td>Detector 1 sees something, but detectors 2 and 3 see nothing.</td>
<td>See Potential</td>
<td>64% of summer</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mechanism #5 in Assessment.</td>
<td>2016 field data</td>
</tr>
<tr>
<td><strong>Type 2 – Bubble number mismatch</strong></td>
<td>Detector 2 sees a different number of events than detector 3.</td>
<td>See Potential</td>
<td>10% of summer</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mechanisms #2, 3, 5 and 6 in Assessment</td>
<td>2016 field data</td>
</tr>
<tr>
<td><strong>Type 3 – Large bubbles outside of calibration range</strong></td>
<td>Uncalibrated volume measurement falls outside calibration range described in Materials and Procedures.</td>
<td>See Potential</td>
<td>0.26% of summer</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mechanism #8 in Assessment.</td>
<td>field data after removing Types 1, 2, and 4 data</td>
</tr>
<tr>
<td><strong>Type 4 – High coefficient of variation (CV) between volume estimates</strong></td>
<td>CV between the two lower volume estimates* falls above the acceptable range shown in Figure 10.</td>
<td>See Potential</td>
<td>8.5% of summer</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mechanism #6 in Assessment.</td>
<td>2016 field data after removing Type 1 and Type 2 data.</td>
</tr>
</tbody>
</table>

*As described in Delwiche et al. 2015, each bubble event produces 4 volume estimates. See Figure 8 for typical relationship between volume estimates.
ASSESSMENT

Sensor field performance

Sensor ease of installation and maintenance, and a field data example

Sensor deployment at Upper Mystic Lake in 2015 and 2016 showed that the deployment rope structure shown in Figure 1 was straightforward to install in low wind conditions. Replacing SD cards, changing batteries, and sampling the gas was all done from the custom service buoy with minimal effort. Battery life with one battery pack powering the bubble sizing sensor and one battery pack powering the data buoy circuit board was approximately 2 weeks, and this could be doubled by adding an additional battery for the bubble size sensor. Figure 11 shows an example of the data acquired from one of the bubble size sensors. These data were taken in 2016 after sensor hardware and electronic upgrades described in Materials and Procedures were implemented. The figure demonstrates the sensor’s unique ability to measure bubble volume and event timing over long deployment periods. Bubble volume data can also be used to calculate the Sauter Mean Diameter, the diameter of a sphere having the same volume-to-surface area ratio as the complete bubble size distribution (Orsat et al. 1993). The Sauter Mean Diameter can be used in discrete bubble dissolution models to simulate dissolution of the complete bubble size distribution (McGinnis et al. 2002).
Assessing sensor performance using collected gas volumes

In order to assess the sensor’s ability to accurately measure total bubble volumes, we downloaded bubble data and collected the bulk gas samples every 1 to 2 weeks from mid-July to mid-November 2016 and compared measured versus sampled gas volumes. On average, our sensor measured 86% of the total gas collected in the trap (Figure 12). While a small portion of the data points are significantly below the 1:1 line, the majority of points show only a small under-measurement of collected gas. Some under-measurement is expected, and potential reasons for this under-measurement will be discussed later in the Assessment section. While the sensor appears to miss a portion of the ebullition flux (particularly during a smaller number of sampling windows), the relative consistency between measured and collected volumes and the
fact that measured volumes do not exceed collected volumes suggests that collected bubble size
distributions are reasonable. We also note that due to dissolution inside the gas collection
chamber, collected gas volumes are likely lower than total gas volumes. In situ incubation trials
suggest that total gas volumes may be up to 5-10% higher than the reported collected gas
volumes for this reason alone.

Figure 12: Cumulative measured gas volumes as a percentage of the corresponding
collected gas volume. The 1:1 line is drawn for comparison.

Correlation between low measured/collected ratio and Types 2, 3, and 4 data

While many of the data points shown in Figure 12 show relatively close agreement
between measured and collected gas volumes, several points fall far from the 1:1 line. Time
periods with large discrepancies are likely caused by a combination of factors. The occurrence
of Types 2, 3, and 4 data are all correlated with a decreased measured to collected ratio (refer to
Table 2 for data types). Discarding large bubbles outside of the calibration range therefore has a
negative impact on the sensor’s ability to measure total cumulative volume. However, most data sets only had two or fewer discarded large bubbles and the highest number of discarded bubbles was six, indicating that the extent of this effect is likely limited. While we do not know what causes higher occurrences of Types 2 and 4 data, one possible explanation would be the temporary presence of a large particle or zooplankter in the flow path obstructing smooth bubble flow.

To understand if bubble under-measurement biases the bubble size distribution, we looked at the correlation between the bubble size and the ratio of the cumulative measured gas volume to the collected gas volume for each individual sensor. While excluding large bubbles will undoubtedly affect the bubble size distribution, we expect this effect to be minimal because only 0.26% of the data are from these large bubbles (after removing Types 1, 2, and 4 data). By contrast, Types 2 and 4 data represent 10% and 8.5% of the data set, respectively, and it is therefore important to understand if removing these two types of data bias the overall distribution. We found no correlation for 7 of the 8 sensors, and for the 8th sensor the correlation effect was a 0.03 mm decrease in bubble size per 1 percentage point drop in the measured to collected ratio. This correlation could serve as grounds for rejecting bubble size distribution data from this particular sensor during periods of low agreement between measured and collected cumulative gas volumes.

**Potential mechanisms for missing or rejecting bubble data**

To understand the potential causes behind the bubble volume under-measurement reported above, we assess here several physical and electronic effects that could lead the sensor to miss a bubble completely, record insufficient data for bubble volume calculations, or record
data that are discarded in post-processing. Where possible we assessed the likely importance of each effect by analyzing field data or by examining oscilloscope or raw field data traces. Some of the outstanding issues that could lead to missing bubble data might be mitigated by additional sensor modifications beyond the scope of this work, while others are a product of the heterogeneous nature of aquatic ecosystems and would be difficult to mitigate.

**Potential mechanism #1: Bubbles not accelerating smoothly through tube, leading to Type 4 data**

**Issue Summary:** Accurate bubble volume estimates depend on a smooth bubble acceleration through the glass funnel stem, so any obstruction to smooth bubble flow will result in inaccurate bubble volume estimates.

**Implication:** Bubble event data sets may be complete, but the coefficient of variation between the two lower volume estimates will be outside of the acceptable range described in Materials and Procedures, and data will be rejected in post-processing.

**Relevance:** Likely significant because 8.6% of summer 2016 field data were discarded due to high coefficients of variation, and prevalence of high CV data correlates with lower measured/collected ratios. However, we cannot separate the contribution of inconsistent bubble flow to high CVs from other potential sources of high CVs, and future work could include adding a camera to distinguish between physical flow restrictions and sensor measurement artifacts.

**Detailed discussion:** Accurate bubble volume estimates depend on smooth bubble acceleration through the glass funnel stem because the sensor indirectly measures the velocity of the leading and trailing edge of each bubble. To accurately estimate volume, the true average bubble velocity must be a predictable function of the average velocity of the leading and trailing bubble
edge. In a controlled laboratory setting, bubbles are observed to move smoothly up the funnel stem. However, in a field setting bubble flow through the funnel stem could be temporarily restricted by the presence of particulate matter or zooplankton.

Bubbles that do not accelerate smoothly will lead to data with high coefficients of variation between lower volume estimates (described in Materials and Procedures). If the coefficient of variation is higher than the acceptable threshold for that particular bubble volume (as shown in Figure 10), the bubble event data will be rejected during post-processing. These rejected data points are a significant source of missing bubble data because 8.6% of field data were discarded due to high coefficients of variation. Additionally, we found a positive correlation between increased frequency of high CV data and a decreased measured to collected volume ratio.

It is important to note that circumstances other than unsmooth bubble flow can contribute to high coefficients of variation among volume estimates. High coefficients of variation could also be caused by the sensor not properly recognizing the leading and/or trailing edge of each bubble. This could occur if the signal fluctuations discussed in Materials and Procedures cause one detector to prematurely record the trailing edge of a bubble, resulting in higher variability between volume estimates. Different volume estimates would also occur if detector 2 only records part of a passing bubble because of the 'dead-time' issue discussed under Potential Mechanism #3. Additionally, high CVs could also occur if detectors 2 and 3 record a different number of bubbles in a stream, which causes bubble data between the two detectors to be mis-paired. At present there is no way to determine the cause behind individual high CV data points, but redesigning the sensor to include a small camera may help distinguish between physical flow restrictions and sensor measurement artifacts. Camera data could also provide a means of
corroborating sensor volume estimates, thereby improving sensor accuracy and reducing the number of data points rejected in post-processing. We note that we do not think sensor measurement frequency is an important contributor to high coefficients of variation because the measurement frequency is approximately an order of magnitude higher than bubble rise velocity within the funnel stem.

Potential mechanism #2: Background readings too noisy for bubble detection

Issue Summary: If background sensor readings are noisy the detectors will be unable to detect incoming bubbles.

Implication: If detector 1 is put offline due to noisy background readings, the sensor will be unable to record any new bubble events until readings stabilize. If detectors 2 and/or 3 are offline, the sensor will only be able to record incomplete bubble event data.

Relevance: Likely insignificant because field data showed that detectors 2 and 3 were only offline due to background noise 0.05% of the time, though the instances of all three detectors being offline is likely somewhat higher.

Detailed discussion: As is typical of environmental sensors, the bubble size sensor relies on relatively stable background readings to record accurate data (a description of the bubble detection algorithm can be found in Materials and Procedures). If background reading variability exceeds a predefined threshold (two times the difference between the maximum and minimum background values) the sensor will be unable to detect bubbles until subsequent background readings establish a less noisy baseline. If detector 1 is offline due to noise, no field data will be gathered even if detectors 2 and 3 are not offline. We cannot assess the frequency of this scenario because it does not result in any recorded data. As in-lab measurements invariably show
stable backgrounds, it seems likely that noise in the background during field deployment arises from particulate material in the water, although we have not confirmed this. However, a subset of the field data from 2016 includes detection thresholds for detectors 2 and 3, allowing us to determine that 0.05% of unprocessed field data are gathered during times when either detectors 2 or 3 are offline but detector 1 is online. While the occurrence of all three detectors being offline due to noisy background is likely somewhat higher than 0.05%, we still assume that noisy background levels are likely not a large source of missing bubble data. If the sensor were deployed in a more heterogeneous environment the noise requirements could be made less stringent to reduce the number of times the sensor is offline to bubble detection.

Potential mechanism #3: Sensor 'dead-time' during data writing

Issue Summary: The sensor requires a finite amount of time to record bubble event data, during which time the sensor will be unable to detect the arrival of new bubbles.

Implication: Bubbles rising through the flow path during sensor ‘dead-time’ (while the sensor is recording data from previous bubble events) will be missed entirely. If the sensor comes back online while the bubble is already partially in front of the detectors, incomplete bubble event data will be recorded.

Relevance: Likely unimportant in Upper Mystic Lake because dead-time comprises only approximately 0.2% of total time during a high-flux bubble events.

Detailed discussion: The Arduino Pro-Mini microcontroller used in this sensor requires a minimum data storage time of approximately $7ms + 8ms \times (# \text{ of bubbles per event})$. For
example, if three bubbles pass through the sensor during a bubble event, the sensor will be offline to new bubbles for 31 ms during data storage, plus a few additional milliseconds for code completion. If another bubble passes the first detector during this 'dead-time' window it will be completely missed by the sensor, as shown in Figure 13. This 'dead-time' limitation means that during high bubble flux events the sensor will under-count total cumulative bubble volumes.

To assess the significance of this dead-time, we used field data to estimate that only 0.2% of time during high-flux bubble periods is comprised of 'dead-time'. This indicates that data loss to dead-time is likely minor. If reducing dead-time were still a concern (for example if the sensor were to be used in a much higher bubble-flux environment), the sensor could be redesigned to use a faster microcontroller.

![Diagram showing sensor dead-time](image)

Figure 13: Dead-time demonstration for closely spaced bubbles.

*Potential mechanism #4: Bubbles coalescing or breaking apart within flow path*

**Issue Summary:** Proper sensor functioning relies on individual bubbles passing each detector intact. If bubbles coalesce or break apart within the flow path the sensor will be unable to record sufficient data for volume estimation.
Implication: This could lead to a mis-match in the number of bubbles seen by detectors 1, 2, and 3, resulting in incomplete bubble event data sets.

Relevance: Appears minimally important within the glass funnel stem, but bubble coalescence could be occurring at funnel stem constriction which would impact the measured bubble size distribution. More work would be needed to assess the importance of this effect.

Detailed Discussion: Two bubbles entering the glass funnel stem in close succession and then merging in to one bubble as they pass the detectors would make it impossible for the sensor to estimate their volume using the existing algorithm. Fortunately, our laboratory oscilloscope work provided no evidence that bubble coalescence within the flow path was a significant issue. Smaller bubbles separated by even a thin lens of water overwhelmingly remained separated as they rose past detectors two and three. However, a rapid burst of bubbles emitted underneath the glass funnel did tend to coalesce into a larger bubble at the funnel constriction point. One way to reduce this coalescence would be to decrease the total funnel area and thus decrease the possibility of numerous bubbles approaching the funnel at once. However, the merit of this approach must be weighed against the resulting decrease in the amount of data gathered during a given field campaign.

Similar to bubble coalescence, a large bubble breaking into smaller bubbles inside the glass funnel stem would lead to incomplete bubble event data. Oscilloscope data demonstrated that large bubbles passing detector 1 remained intact past detectors 2 and 3. Very large bubbles (over 2 mL or 1.6 cm equivalent diameter) often shed smaller bubbles (typically below 0.05 mL or 0.46 cm equivalent diameter), but this cleavage occurs prior to the bubble passing detector 1 and therefore should not affect cumulative volume measurements.
Potential mechanism #5: False triggering of sensor by particles or organisms

Issue Summary: Zooplankton or other opaque particles passing detector 1 may trigger a bubble detection sequence, but detectors 2 and 3 will not record any data (a “false-start”). If 3 false-starts are recorded within 10 seconds the microcontroller resets the background values, during which time the sensor will be unable to detect incoming bubbles.

Implication: This results in incomplete bubble event data, as well as potential sensor dead-time if background levels are reset after 3 consecutive false-starts.

Relevance: 64% of unprocessed field data consist of events where detector 1 sees something but detectors 2 and 3 see nothing. The frequent occurrence of these data points increase the required data storage capacity, but do not impact cumulative volume measurements because sensors are not offline to bubble detection during these events. While 3 consecutive false-starts that trigger background resets do occur, they only put the sensors offline for approximately 0.03% of the sampling time.

Detailed Discussion: One type of data inconsistency frequently observed in field data is when detector 1 sees a bubble and initiates a data collection sequence, but detectors 2 and 3 fail to see a bubble. This false triggering could be due to opaque particles such as organic matter or zooplankton obstructing light transmittance at detector 1. Particles or zooplankton settling downwards through the glass tube will trigger a data collection sequence, but if the particle is moving downwards detectors 2 and 3 will not record a bubble start and stop. Likewise, if zooplankton travel slowly upwards past detector 1 but fail to reach detectors 2 and 3 before the data collection sequence times out (5 seconds), the bubble event data will be missing values. These "false-start" data points are quite common in field data, accounting for 64% of all raw data recorded during the second half of the 2016 sampling season. However, these data points can
easily be removed during post-processing and the SD card data storage system in the service buoy means that even large numbers of false-start data points will not exceed the sensor data storage capacity.

False-start data will only affect cumulative volume measurements if they trigger a background reset within the sensor. This reset happens if 3 consecutive false-starts occur, and the sensor is offline to new bubble detection during the approximately 8 seconds it takes to re-establish the background detection thresholds. Data gathered in the first half of 2016 included enough information to calculate that background reset put sensors offline only 0.03% of the time. While the sensors could miss passing bubbles during this time, it is unlikely to significantly affect cumulative volume measurements.

While the sensor data stream does not provide sufficient information to determine the cause of these false-start data events, one potential contributor to this type of data is the phantom midge (the larvae of a small fly, Chaoborus). Phantom midges migrate vertically through the water column at night to feed and down during the day to escape predation (Stratton 2011). We routinely find phantom midges in our gas collection chambers, indicating that midges are likely traveling through the sensor. In addition, false-start data more commonly occur during the nighttime hours, consistent with the prime vertical travel time for midges. There is also a positive correlation between the date and the occurrence of “false-start” data, which has numerous possible explanations including zooplankton discovery of sensors over time, seasonal increases in zooplankton abundance, or biofilm build-up on the glass funnel stem.
Potential mechanism #6: Small bubbles wobbling during rise through tube

**Issue Summary:** Bubbles smaller than 4 mm diameter are not elongated as they rise past the detectors, and may therefore be subject to lateral migration within the flow path.

**Implication:** This lateral migration could lead to the detectors missing small bubbles entirely, or to different volume estimates from detectors 2 and 3. Additionally, bubbles with average volume below 0.002 mL (0.16 cm equivalent diameter) are outside the calibration range and are therefore discarded as described under Potential Mechanism #7.

**Relevance:** Twenty-seven percent of bubbles from Upper Mystic Lake are smaller than 4 mm in diameter. The possibility of detectors 2 and 3 recording different volume estimates has been mitigated by the lenient coefficient of variation threshold for smaller bubbles shown in Figure 10. While some smaller bubbles could be missing the sensor entirely or generating incomplete data, this is likely to be a small percentage of the total bubble volume.

**Detailed discussion:** Bubbles smaller than the glass funnel stem (4 mm) will not be elongated as they rise past the detectors. Rather, they will remain spherical and be subject to lateral migration within the tube during rise. This lateral migration could result in data from detectors 2 and 3 yielding slightly different bubble lengths, resulting in higher coefficients of variation between volume estimates. Indeed, laboratory results show that small bubbles have substantially higher coefficients of variation (Figure 10), and we mitigate this effect by using a higher coefficient of variation threshold for small bubbles. This issue could be addressed directly by using a more narrow glass funnel stem that would elongate a greater percentage of rising bubbles, but care would be necessary to ensure the funnel stem was still wide enough to prevent bubbles from becoming stuck. Small bubbles may also be missed entirely by one or more detectors, as shown...
in Figure 14. Field data show that 27% of processed bubbles in Upper Mystic Lake are below the 4 mm threshold.

![Diagram](image)

**Figure 14:** Small bubble traces showing significant variability in signal between detectors 2 and 3, likely because bubbles are smaller than flow path diameter and their position relative to the detectors is not constant (bubbles are approximately 3–4 mm diameter, tube diameter is 4 mm). In some cases, bubbles are not seen at all.

*Potential mechanism #7: Tiny bubbles (smaller than 0.002 mL or 0.15 cm equivalent diameter)* are outside of calibrated sensor range

**Issue Summary:** Due to the positive intercept on the small bubble calibration curve presented in Figure 8, bubbles below a certain lower threshold do not lie in the physically-meaningful portion of the best-fit calibration curve.

**Implication:** Data points for tiny bubbles are not reliable, so data must either be rejected or included with only approximate volume estimates.

**Relevance:** In Mystic Lake, tiny bubbles represent 3% of total unprocessed data (10% of data after removing Type 1 non-bubble event data). Although this represents a substantial occurrence
of tiny bubbles in terms of bubble event count, the impact on cumulative measured volumes is negligible since these bubbles are below 0.002 mL.

**Detailed discussion:** We have not been able to calibrate the sensor for tiny bubbles due to the difficulty in forming accurate tiny bubbles in a laboratory tank. The existing calibration curve presented in Figure 8 was generated for bubbles as small as 0.01 mL (0.27 cm equivalent diameter). Additional calibration attempts for bubbles smaller than 0.01 mL showed that sensor performance was still roughly linear from 0.002 mL to 0.01 mL with a similar calibration equation, but volume estimates lacked precision. This variability could be due to sensor measurement error or variability in actual bubble size. Since 0.002 mL was the smallest gas volume we could dispense, we were unable to verify the sensor’s lower detection limit or the shape of the calibration curve below 0.002 mL. However, even though 3% of total unprocessed field data consist of tiny bubbles, the impact on cumulative volume estimates by discarding these data will be negligible.

It is also possible that modification of the bubble flow path could optimize measurements for tiny bubbles. The present geometry provides both robustness and simplicity, but a noncircular bubble channel geometry and additional optical elements, such as a cylindrical lens to create a light source more nearly approximating a line source, could be worth exploring.

*Potential mechanism #8: Large bubble volumes*

**Issue Summary:** Bubbles larger than 1.8 mL (1.51 cm equivalent diameter) cannot accurately be measured by the sensor, so any data exceeding the 1.8 mL threshold must be discarded.

**Implication:** Discarding data from larger bubbles may disproportionately affect the measured to collected ratios.
Relevance: Only 0.26% of field data were from bubbles over 1.8 mL (after removing Types 1, 2, and 4 data as described in Table 2). If we add 0.26% more bubbles to the data set shown in Figure 11 of volumes 2mL, 3mL, or 4mL (1.56 cm, 1.79 cm or 1.97 cm equivalent diameters), the Sauter Mean Diameter increases by 4%, 7%, or 10%.

Detailed Discussion: The calibration curve presented in Materials and Procedures shows that the sensor can accurately measure bubbles up to 1.8 mL (1.51 cm diameter). Beyond this volume the sensor measurement accuracy breaks down. In practice, this means we reject any field data for bubbles larger than 1.8 mL and in 2016 this comprised only 0.26% of field data (after removing Types 1, 2, and 4 data as described in Table 2). If we artificially add 0.26% more bubbles to the size distribution presented in Figure 11 and recalculate the Sauter Mean Diameter, we find bubble volumes of 2mL, 3mL, or 4mL (1.56 cm, 1.79 cm or 1.97 cm equivalent diameters) raise the Sauter Mean Diameter by 4%, 7%, or 10%. Since the Sauter Mean Diameter has been shown to be useful for estimating bubble dissolution rates for an entire bubble size distribution, the potential increase in Sauter Mean Diameter compared to measured data could be taken into consideration in dissolution calculations. For sites such as the one described in DelSontro 2015 where bubbles over 2 mL (1.56 cm equivalent diameter) are found to contribute significantly to total ebullition flux, the sensor could be altered to contain a wider glass funnel stem which may improve large volume estimates. However, a larger funnel stem means fewer rising bubbles would be elongated, potentially reducing sensor accuracy as described under Potential Mechanism #6.
DISCUSSION

The long-term data from the bubble size sensor, with the upgrades described here, give the unique ability to study temporal trends in ebullition flux and bubble size over long time intervals with minimal sensor servicing and sediment disturbance. These trends are otherwise impossible to detect in short-duration campaigns. For example, the field data show that on average 70% of the total cumulative flux occurred on only 32% of the sampling days, indicating that bubble events tend to be temporally clustered. Temporal clustering means that limited duration sampling campaigns could artificially bias data used to estimate long-term ebullition flux. Recent work to quantify this artificial bias has found that short sampling campaigns are likely to underestimate ebullition (Wik et al. 2016b).

While some existing ebullition measurement techniques also have the ability to estimate daily heterogeneity in flux (Varadharajan and Hemond 2012, Maeck et al. 2014), our sensor has the unique ability to measure variations in bubble flux on the time scale of seconds, as well as individual bubble volumes. These data could be important to estimating bubble dissolution rates because previous studies have found that bubbles emitted less than 3 seconds apart have significantly faster rise times, though the increase in rise velocity is variable and dependent on bubble size (Garner and Hammerton 1954). Current single-bubble dissolution models do not account for potential inter-bubble interactions (McGinnis et al. 2006, Leifer and Patro 2002), and prior to the availability of data from this sensor there was no way to measure the distribution of temporal spacing between bubble events.

This sensor will also allow us to compare size distributions from different locations within a water body. While bubble-sizing sonar devices can be moved to multiple locations within a water body, the relatively short time duration of these sampling campaigns means that
observed differences in bubble size distributions could be an artifact of limited sampling windows. Our sensor is cost-effective enough for multiple sensors to be deployed for long periods of time, thus discerning the spatial variability in bubble size distributions.

In addition to studying spatial heterogeneity in bubble size, the ability to measure bubble sizes for long time periods also allows us for the first time to track changes in bubble size with time and ebullition flux. Previous studies have found seasonal variability in ebullition flux (DelSontro et al. 2010, Maeck et al. 2013). However, since traditional bubble sizing techniques are limited to short campaigns we do not currently know if these changes in ebullition flux are correlated with a change in average bubble size. Since a change in mean bubble size would lead to a change in bubble dissolution rate, it is important to understand if bubble size distributions are constant or variable throughout the year.

**COMMENTS AND RECOMMENDATIONS**

We have presented critical upgrades to our first generation bubble sizing sensor. These upgrades allow for long-term uninterrupted bubble size and ebullition flux measurements. If sensors were to be deployed in a remote field location where bi-monthly or monthly field campaigns to replace batteries were infeasible, the sensor could be modified to run on solar power. The data buoy could also be enhanced with Bluetooth capability, as was done in the original buoy design described in Gardner et al. 2009. Additionally, the sensor could be equipped with a small camera to image bubbles rising through the funnel stem. Camera images could be used to further investigate potential causes of missing or rejected bubble data.
ACKNOWLEDGMENTS

This material is based on work supported by the National Science Foundation under grant number EAR-1045193 and Graduate Research Fellowship Program grant number DGE-0707428, the MIT Martin Family Fellowship to K. Delwiche, the W.E. Leonhard 1941 professorship to H. Hemond, and the Singapore-MIT Alliance for Research and Technology program. Authors thank many people in the MIT Parsons laboratory for their help with field work, particularly Benjamin Scandella and Irene Hu.

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An enhanced bubble size sensor for long-term ebullition studies

Kyle Delwiche, Harold Hemond

SUPPLEMENTAL INFORMATION

SENSOR DEPLOYMENT INSTRUCTIONS

1. Measure rope, cable, and tubing lengths according to the water depth and desired sensor deployment depth. Excess data cable length can be coiled and secured with zip ties.

2. Tie a stainless steel hook on the rope where the sensor will be attached.

3. Tie the rope, PCV tubing, and data cable structure together every 1-2 meters using zip ties. To ensure the rope bears the cable weight during deployment, include a small amount of slack in the cable and tubing between each zip-tie.

4. To counteract the weight of the data cable, attach multiple small floats to the data cable.

5. Once assembled, the cable, tubing, and rope structure can be coiled on to a large wooden spool to facilitate field deployment.

6. In the field, lower the anchor farthest from the bubble sensor while uncoiling one diagonal leg of the rope structure. Once the anchor is on the bottom, move the boat in the desired deployment direction while uncoiling the other diagonal leg with the attached data cable and PVC tubing.
7. At the pre-determined sensor deployment location, stop uncoiling the rope. Attach the detachable expansion funnel and gas collection chamber to the properly assembled and sealed sensor housing. Connect the data cable and PVC tubing to the sensor, clip the sensor to the hook on the rope, and put the sensor in the water.

8. Uncoil the remainder of the rope, and lower the second anchor. If the underwater center buoy is not submerged, move the anchors farther apart.

9. Attach the data buoy to the data cable, empty the PVC tubing of any gas, make sure data buoy circuit board has an SD card and a desiccant pack, connect the batteries, and record time of battery connection.

**SERVICE BUOY MAINTENANCE INSTRUCTIONS**

1. Pull buoy in to boat, open air-release valve at buoy base, and remove buoy cap.

2. Unplug batteries from printed circuit board, noting which battery powered which Arduino microcontroller.

3. Remove SD card and replace with blank SD card (**do not remove SD card while batteries are still connected**).

4. Plug fresh batteries in to printed circuit board. If using two batteries in parallel, batteries should be of equal voltage rating, chemistry, and charge state.

5. Record time batteries were connected. Replace cap on buoy, shut air-release valve, and return buoy to the water.
BUBBLE SIZE SENSOR CONSTRUCTION GUIDE

**Sensor Body Materials**

- 1 nominal 4 inch PVC coupling*
- 2 nominal 4 inch PVC pipe plugs
- 2 EPDM O-rings, dash size 244
- 2 Buna-N O-rings, 7 mm inner diameter, 2.5 mm wide
- 4 stainless steel eye bolts, 6-32 thread size and 1.9 cm (0.75 inch) length
- 2 stainless steel hex nuts, 6-32 thread size
- 11.5 cm long piece of 5 inch diameter acrylic pipe
- 2 small zip ties, 10.16 cm (4 inch) in length
- Silicone vacuum grease
- 3 cm thick disc of solid PVC, 8.9 cm (3.5 inch) diameter
- 1 nominal 1 inch male adapter to male NPT fitting (PVC)
- PVC cement
- Stainless steel hose clamp for pipe sizes 92-165 mm
- 3 stainless steel D-rings for 3.8 cm (1.5 inch) webbing width
- Three 1.5 m lengths of 0.635 cm (0.25 inch) diameter twisted nylon rope
- 1 four pin bulkhead fitting, MacArtney Underwater Technology part MCBH4F
- 1 7/16”-20 hex nut
- 1 7/16” washer
- 4 Molex Micro-Fit 3.0™ female sockets for 24 gauge wire (Digikey WM7082CT-ND)
- 1 Molex 4 pin housing connector receptacle (Digikey WM1847-ND)
*All PVC parts are schedule 40

**Sensor Body Construction Directions (Refer to Figures S1, S2, and S3)**

**Repeat for sensor housing top and base:**

28. Using a lathe, cut PVC pipe plug to 3.38 cm in length.

29. Cut O-ring groove into side of the pipe plug. Groove should be 0.282 cm deep and 0.475 cm wide, and positioned approximately 0.8 cm from end of pipe plug (Fig S1-B). Make sure that groove is smooth. It may help to reduce the lathe speed.

30. Drill a 0.87 cm (11/32 inch) diameter hole into the center of the pipe plug (Fig S1-A).

31. Use a small, hook-shaped lathe tool to cut an O-ring groove into hole drilled in step 3. Groove should be 0.33 cm wide and 0.154 cm deep. Refer to Figure S4 for example of hook-shaped tool.

32. Insert small O-ring in to the small O-ring groove. Do not grease O-ring.

**Instructions for sensor housing top only, Fig S1:**

33. On the lathe, machine the flat top of top pipe plug to a smooth finish (Fig S1-C).

34. Drill a 3.33 cm diameter hole in the solid PVC disc. On the lathe, this can be achieved by drilling a 3.175 cm (1.25) inch diameter hole and widening the hole to 3.33 cm diameter using a boring bar.

35. Drill a 7/16” hole (0.4375 cm) in the top pipe plug 2.5 cm from one edge.

36. Using an end mill, cut a slight indentation centered on the 7/16” hole to the outer diameter of the 7/16” washer. Indentation must be cut on the under-side of the pipe plug. Washer needs to sit in this indentation, flush against the pipe plug (Fig S1-A).
37. Measure 2.5 cm from one edge of the solid PVC disc towards the center of the disc. Draw a chord through this point, perpendicular to the diameter of the disc. Remove this crescent-shaped segment of PVC material, either by cutting with a band saw or milling.

38. Using PVC cement, glue the nominal 1 inch male adaptor to male NPT in to the hole in the PVC disc (Fig S1-C).

39. Using PVC cement, glue the PVC disc and adaptor onto the flat top of the pipe plug, centered on the small O-ring hole (Fig S1-D) and positioned to maximize clearance around the 7/16” hole.

40. Pass the bulkhead fitting through the 7/16” hole in the top of the pipe plug, and secure with the washer and nut.

41. Crimp the female Molex sockets on to the ends of the bulkhead wires. Insert sockets into the 4-prong male Molex clip. Hold Molex clip such that you are looking in to holes where you will insert the sockets, and the plastic latch is facing upwards. From left to right, insert black, red, green, and white wires.

42. Grease the large O-ring with silicone vacuum grease and insert into the large O-ring groove.

**Instructions for sensor base only, Fig S2:**

43. Drill 2 small pilot holes horizontally into two opposite sides of the pipe plug top, being careful not to puncture the pipe plug (for upper pair of eyebolts shown in Fig S2-B).

44. Screw two of the 6-32 stainless steel eyebolts into the pilot holes.

45. Use a 0.635 cm (0.25 inch) end mill to cut 3 notches into the 11.5 cm long piece of acrylic. Notches should be equidistant to each other, and 4.42 cm (1.75 inches) deep. Check that this piece fits onto funnel with the hex standoff(s) (Fig S2-B).
46. Drill and tap two 6-32 holes into the piece of acrylic, approximately 1 cm from the top edge and equidistant from each other. Holes should be on the opposite end of the pipe from the notches.

47. Screw the remaining 2 eyebolts horizontally into the side of the 10 cm long piece of acrylic, using Teflon tape as necessary to keep eyebolts snug. Secure with the hex nuts.

48. Use the 2 small zip ties to securely fasten the acrylic piece to the bottom pipe plug. This removable piece will protect the glass funnel during deployment (Fig S1-B).

49. Grease the large O-ring with silicone vacuum grease and insert into the large O-ring groove.

**Instructions on Sensor Body Assembly (Fig S3):**

50. Slide the 3 D-rings on to the hose clamp.

51. Slip the hose clamp around the mid-point of the nominal 4 inch coupling, and begin to tighten the clamp.

52. Slide the D-rings around until they are equidistant from each other. Tighten the hose clamp until rings are firmly in place and hose clamp is very snug. To facilitate the placement of the D-rings around the hose clamp, 2 small zip ties can be used to secure each D-ring to the appropriate location on the hose-clamp.

53. Tie the 3 nylon ropes to the 3 D-rings

**Gas Collection Chamber Materials**

- 90 cm of nominal 1 inch clear PVC pipe
- 1 nominal 1 inch PVC coupling
- 1 nominal 1 inch socket female to NPT female PVC adapter
- 1 nominal 1 inch male to 0.25 inch NPT female hex bushing (PVC)
- One nominal 0.25 inch NPT male to 1/8 inch barbed nylon tube fitting
- Teflon tape
- 3 stainless steel eyebolts, 0.25 inch-20 thread size with eye diameter of 0.375 inches.
- PVC cement

**Gas Collection Chamber Construction Directions (Refer to Figure S5)**

54. Using PVC cement, glue the nominal 1 inch unthreaded female to NPT female adapter on to one end of the 90 cm clear PVC pipe (Fig. S5-B).
55. Using PVC cement, glue the nominal 1 inch coupling to the other end of the clear PVC pipe, and then glue the nominal 1 inch male to 0.25 inch NPT female hex bushing in to the other end of the coupling (Fig. S5-A).
56. Wrap Teflon tape around the barbed tube fitting and screw it in to the nominal 0.25 inch hex bushing.
57. Cut eyebolt threads to 0.63 cm in length and polish the cut ends on a grinder.
58. Carefully drill three shallow pilot holes horizontally into the pipe coupling, equidistant from each other and near the top edge of the coupling (Fig S5-A). Be careful not to break through the wall of the gas collection chamber. Holes should be approximately 0.7 cm deep, or until drill bit first starts cutting in to hex bushing underneath coupling. Tap the holes.
59. Screw the trimmed eyebolts into the pilot holes, being careful not to puncture the gas collection chamber. The eyebolts will serve as guides for 3 nylon ropes connecting the sensor housing to the deployment structure.
60. Drill four 0.637 cm (0.25 inch) holes through the base of the gas collection chamber.

Holes should penetrate the top of the female pipe adapter and the clear PVC tube. These holes will allow water to exit the chamber as bubbles enter (Fig S5-B).

**Detachable Funnel Materials**

- 1 commercial funnel designed for 55 gallon barrel deer feeders (Texas Hunter, LFBF)
- 3 stainless steel female hex standoffs, ½” length and 6-32 thread size
- 3 stainless steel screws, ½” length and 6-32 thread size
- 3 stainless steel washers, #6 screw size
- 3 stainless steel ¼”-20 eyebolts with a 1 inch shank
- 3 stainless steel ¼”-20 locknuts
- 3 stainless steel ¼”-20 nuts
- 6 stainless steel washers for the ¼”-20 eyebolts
- 3 stainless steel split rings, approximately 1 inch diameter
- 3 12oz lead cannonball sinkers (Cabela's IK-118098)
- 3 lengths of stainless steel wire rope, 1/16” diameter and 24 cm long
- 6 stainless steel rope compression sleeves for 1/16” diameter wire rope
- 3 stainless steel carabiners (McMaster 3716T51)

**Detachable Funnel Construction Directions (Refer to Figure S6)**

61. Drill a 0.635 cm (0.25 inch) hole 4 cm up from the base of each funnel ridge.

62. Thread the regular ¼”-20 nut on one eyebolt, add a washer, and pass the eyebolt through the top of the hole. Add another washer, and secure with the ¼”-20 lock nut. Make sure to align eyebolt such that it is parallel with the funnel ridge. Repeat 3 times.

63. Drill a 0.35 cm (0.138 inch) hole 18.5 cm up from the base of each funnel ridge.
64. Place a washer on the 6-32 screw and pass the screw upwards through the hole. Screw on the standoff.

65. Attach one 12 oz cannonball sinker to each eyebolt using the split rings.

66. Pass the wire rope through the eyebolt, and use the compression sleeve to form a small loop around the eyebolt. Crimp sleeve with appropriate crimping tool.

67. Pass the remaining end of the wire rope through the carabiner and use the compression sleeve to form another small loop. All three wire ropes should be the same length after crimping. Crimp sleeve with appropriate crimping tool.

**Sensor Electronics Materials**

- Custom printed circuit board (PCB) for bubble size sensor (Eagle files available from author upon request).
- Four 2M machine screws, 12 mm in length
- Four 2M nuts
- 2 PVC bars, minimum dimensions 0.9 cm by 1 cm by 3.1 cm
- Electronic parts described in Table 1 in Delwiche et al., 2015.
- 2 lengths of straight female headers, 12 pins long
- 1 length of straight female headers, 6 pins long
- 1 length of straight female headers, 2 pins long
- 2 lengths of straight male headers, 12 pins long
- 1 length of straight male headers, 6 pins long
- 1 length of straight male headers, 2 pins long
- 1 four position Molex Micro-Fit 3.0™ connector (Molex product #43650-0413)
- 2 2kΩ surface mount resistors, size 0603
- 3 10kΩ surface mount resistors, size 0603
- 3 12kΩ surface mount resistors, size 0603
- 1 eight pin (4 x 2) IC socket with 0.1 inch pitch and 0.3 inch row spacing
- 1 0.1µF surface mount capacitor, size 0603
- 1 10µF surface mount capacitor, size 1210

Sensor Electronics Construction Directions

68. Using a mill, cut the PVC bars to the specifications shown in Figures S7 and S8. These shims will properly align the LED and photocells on the PCB.

69. Attach PVC shims to PCB using the 2 mm machine screws and nuts. Shims are on opposite side of board from surface mount components.

70. Solder all electronics and female headers for Arduino attachment to PCB. Female Arduino headers are on same side of board as surface mount components.

71. Solder the two 2k resistors to the back of the Arduino near the A4 and A5 pins. Solder straight male headers to Arduino Pro Mini with pins protruding from back side. The 2-pin length of male headers should be soldered to analog pins A4 and A5.

72. Slide Arduino Pro Mini into female headers on PCB.

73. Slide EEPROM data chip into IC socket.

Complete Sensor Assembly Materials

- Two 0.635 cm (0.25 inch) U-bolts
- Four 0.635 cm (0.25 inch) nuts
- Two 1 cm lengths of 0.635 cm (0.25 inch) flexible plastic tubing, slit down the length of the tube
- 1 6140 Pyrex glass funnel
- 10 cm length of 0.635 cm (0.25 inch) inner diameter plastic tubing
- 1 Silica Gel desiccant bag

**Complete Sensor Assembly Instructions (See Figure 3 in main text for final product)**

74. Push the stem of the Pyrex glass funnel through o-ring hole in the bottom pipe plug.
75. Wrap the two 1 cm lengths of 0.635 cm (0.25 inch) flexible plastic tubing around the funnel stem, 5 cm apart and approximately centered along the length of the stem.
76. Using the u-bolts, attach the PCB to the funnel stem at the locations of the flexible tubing.
77. Push the 4 inch coupling on to the pipe plug (make sure the large o-ring is greased).
78. Attach bulkhead fitting wire clip to sensor PCB.
79. Add desiccant bag to housing.
80. Slide the top pipe plug on to the coupling (make sure large o-ring is greased). To accomplish this, temporarily pull the glass funnel downwards to release pressurized air from the housing. Once the top pipe plug is snug on the coupling, push the funnel stem back through the top pipe plug.
81. Push the 10 cm length of plastic tubing on to the top of the funnel stem. This tube will route bubbles past the 4 holes drilled in to the bottom of the gas collection chamber, ensuring that all gas is trapped within the gas collection chamber.
82. Place the assembled sensor housing on top of the extension funnel, making sure to line up the standoffs with the grooves in the sensor housing.
83. Loosen the hose clamp holding the D-rings to the sensor housing. Lower the hose clamp until the carabiners on the funnel can be clipped on to the D-rings. Once the carabiners are attached, raise the hose clamp until the metal wires are taught and tighten hose clamp.
Make sure the metal wires are tight enough that the extension funnel is securely fastened to the sensor housing.

84. Screw the gas collection chamber on to the top pipe plug.

85. Take the 3 nylon ropes tied to the D-rings and pass them through the 3 eye-bolts at the top of the gas collection chamber.

86. Tie the 3 nylon ropes to a stainless steel s-hook for attachment to the deployment structure shown in Figure 1 of the main text.

**Data Buoy Materials**

- 30 cm length of nominal 3 inch PVC pipe
- 3 nominal 3 inch PVC couplings
- 2 nominal 3 inch PVC pipe plugs
- 1 EPDM O-ring, dash size 236
- 1 Angel food cake pan
- Par-Tall #2 mold release paste
- Dow Corning high vacuum grease
- US Composites 2-part expanding polyurethane foam, 8lb density
- West Marine 105 epoxy resin
- West Marine 207 epoxy hardener
- 1 7/16”-20 thread size nut
- 1 7/16” washer
- 1 1/8” stainless steel NPTF male straight connector
- 1 PVC ball valve, 1/8” NPT female (such as McMaster 4757K11)
- Stainless steel hose clamp for pipe sizes 80–150 mm
- 2 stainless steel D-rings for 3.8 cm (1.5 inch) webbing width
- 3 Li-ion battery packs, 18650 7.4V 8800mAh (Tenergy #31010)
- 1 30 cm length each of black, red, green, and white 24 gauge stranded wire
- 2 four pin male Molex wire receptacle housings (Molex #43645-0400)
- 8 female Molex connecting sockets (Molex #0462350001)
- 1 four pin female Molex housing connector plug (Molex #0436400401)
- 4 male Molex connecting sockets (Molex #0430310002)
- Sandpaper
- Disposable paintbrush

Data Buoy Assembly Instructions

Instructions for buoy end plugs (refer to Fig S9):

87. On the lathe, machine the top of the first pipe plug to a flat, smooth finish.

88. Drill a 7/16” diameter hole in the center of the first plug.

89. Drill and tap a hole for the 1/8” straight connector. Hole should be 1.5 cm from one flat edge of the PVC pipe plug. Screw the connector into the hole using Teflon tape to form a tight seal.

90. Screw the PVC ball valve onto the 1/8” straight connector such that valve handle points downwards when in open position.

91. Insert the bulkhead fitting in to the 7/16” hole and secure with the nut and washer.

92. Crimp the female Molex sockets on to the ends of the bulkhead wires. Insert sockets into the 4-prong male Molex clip. Hold Molex clip such that you are looking in to holes where you will insert the sockets, and the plastic latch is facing upwards. From left to right, insert black, red, green, and white wires.
93. Make a 4-stranded 30 cm extension cable using the black, red, green, and white wires. Place a female Molex clip on one end and a male Molex clip on the other, making sure to keep the wire colors consistent. Connect this extension cable to the bulkhead fitting Molex clip.

94. On the lathe, trim the second pipe plug to 3 cm in length.

95. Cut O-ring groove into side of the second pipe plug. Groove should be 0.282 cm deep and 0.475 cm wide, and positioned approximately 0.6 cm from end of pipe plug (Fig S9 – C). Make sure that groove is smooth. It may help to reduce the lathe speed.

96. Grease the O-ring with silicone vacuum grease and insert into the O-ring groove.

**Instructions for buoy body (refer to Fig S9):**

97. Cut a 1 cm ring from one of the pipe couplings. Using the PVC cement, glue this ring 7.5 cm from one edge of the PVC pipe.

98. Cut an 8.9 cm (3.5 inch) diameter hole in the center of the angel food cake pan.

99. Coat the inside of the angel food cake pan with the mold release paste.

100. Spread a thin ring of vacuum grease right around the hole in the angel food cake pan, on the inside of the pan.

101. Pass the short end of the PVC pipe through the hole on the inside of the angel food cake pan. Let the wider ring formed by the pipe coupling rest on the base of the angel food cake pan, on top of the ring of vacuum grease (grease will keep the polyurethane foam from seeping through this crack). Support the angel food cake pan from below with the pipe resting in the center.
102. Following the instructions on the polyurethane foam container, mix 300-350 total milliliters of foam mix. To achieve consistent mixing, we mounted a disposable paddle on to a hand-held drill.

103. Quickly pour the foam mixture into the angel food cake pan and let it rise. After foam is fully risen and cooled, remove the angel food cake pan.

104. Use the sandpaper to roughen the surface of the foam and remove the mold release paste.

105. Following the instructions on the epoxy container, mix a small batch of epoxy. Paint the foam with the epoxy, using multiple batches and layers until foam is fully coated in a thick shell of epoxy.

106. Using the PVC cement, glue the first pipe plug in to one of the couplings (make sure it already has the extension cable built in step 66). Glue this coupling on to the long end of the buoy.

107. Use the PCV cement to glue the remaining coupling to the short end of the buoy.

108. Use the hose clamp to secure the D-rings towards the base of the buoy body. D-rings should be on opposite sides of the buoy (Fig S9 – A).

**Buoy Electronics Materials**

- Arduino Pro Mini 328 – 5V/16MHz
- MicroSD card breakout board (Adafruit product #254)
- DS3231 precision RTC breakout (Adafruit product #3013)
- 1 four position Molex Micro-Fit 3.0™ connector (Molex product #43650-0413)
- 2 two position through-hole Molex connector (Molex product #0432550059)
- 2 two position connector plug (Molex product #0050841025)
- 2 0.1\mu F surface mount capacitor, size 0603
- 1 10\mu F surface mount capacitor, size 1210
- 2 lengths of straight male headers, 8 pins long
- 2 lengths of straight female headers, 8 pins long
- 2 length of straight female headers, 12 pins long
- 2 length of straight female headers, 6 pins long
- 1 length of straight female headers, 2 pins long
- Two 0.437” nylon spacers, unthreaded #2
- Two 2M machine screws, 12 mm in length
- Two 2M nuts
- Two 2-56 nylon machine screws, 7/16” length
- Two 2-56 female hex standoffs, 7/16” in length

**Buoy Electronics Construction Directions**

109. Repeat step 44 for the buoy PCB Arduino.

110. Solder the 8 pin male headers to the MicroSD breakout board and the DS3231 clock.

111. Solder all female headers and remaining electronic components to PCB.

112. Pass the 2-56 nylon screws through the holes in the DS3231 clock, and screw in to the 2-56 nylon standoffs. DS3231 can now be installed on the PCB.

113. Place the MicroSD breakout board on the PCB. Pass the 2 mm machine screws through the holes on the breakout board, through the 0.437” nylon spacers, and through the holes on the buoy PCB. Secure the screws with the 2 mm nuts.

**Optional Battery Sled Materials**
- 1 37 cm long piece of schedule 80 PVC pipe, nominal 2 ½” diameter

**Optional Battery Sled Instructions (refer to Fig S10)**

114. Cut the PVC pipe in half length-wise.

115. Use CNC mill programming software such as Mastercam to create a program for the cuts shown in Figure S10.

116. Mount the half-pipe on the mill and run the program.

117. Drill a 1.27 cm (0.5 inch) diameter hole 1.9 cm from the top edge of the half-pipe.
SUPPLEMENTARY INFORMATION FIGURES

Figure S1 - Top pipe plug

Figure S2 - Bottom pipe plug
Figure S3 – Assembled sensor housing

Figure S4 – Hook-shaped lathe tool
Figure S5 - Gas collection chamber

Figure S6 - Detachable extension funnel
**Figure S7** – Right PVC shim

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**Figure S8** – Left PVC Shim

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Figure S9 - Custom data buoy

Figure S10 - Optional battery sled
Methane bubble size distributions, flux, and dissolution in a freshwater lake

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/Publication reformatted to fit this dissertation/
Section 4: Methane bubble size distributions, flux, and dissolution in a freshwater lake

ABSTRACT

The majority of methane produced in many anoxic sediments is released via ebullition. These bubbles are subject to dissolution as they rise, and dissolution rates are strongly influenced by bubble size. Current understanding of natural methane bubble size distributions are limited by the difficulty in measuring bubble sizes over wide spatial or temporal scales. Our custom optical bubble size sensors recorded bubble sizes and release timing at 8 locations in Upper Mystic Lake, MA continuously for 3 months. Bubble size distributions were spatially heterogeneous even over relatively small areas experiencing similar flux, suggesting that localized sediment conditions are important to controlling bubble size. There was no change in bubble size distributions over the 3 month sampling period, but mean bubble size was positively correlated with daily ebullition flux. Bubble data was used to verify the performance of a widely-used bubble dissolution model, and the model was then used to estimate that bubble dissolution accounts for approximately 10% of methane accumulated in the hypolimnion during summer stratification, and at most 15% of the air-water methane flux from the epilimnion.
INTRODUCTION

Freshwater lakes and reservoirs are a significant source of methane to the atmosphere, and methane is a potent greenhouse gas with large implications for future climate change\(^1\text{-}^4\). Ebullition is often the dominant methane transport pathway compared with dissolution from sediments and transport through plant vascular tissue, and can represent up to 95% of lake methane emissions\(^4\). Since rising bubbles are subject to dissolution, only a portion of the methane released from the sediment as bubbles is emitted to the atmosphere. The remainder dissolves into the water column where it is available for biological incorporation into the lake food web\(^5\text{-}^7\).

Bubble dissolution rates depend strongly on bubble size and to a lesser extent on water chemistry, temperature, and dissolved gas concentrations\(^8\text{-}^{10}\). Despite the importance of methane bubble size to dissolution and atmospheric emissions, relatively few estimates of lacustrine methane bubble size distributions exist\(^11\text{-}^{13}\). Existing bubble size distribution measurements are typically limited to short periods in time or space, and therefore little is known about the spatial and temporal changes in methane bubble size distributions within a water body.
Given the limited knowledge about bubble size distributions, it is difficult to estimate the importance of bubble dissolution to the dissolved carbon budget in a lake. Some data suggest that dissolution may contribute significantly to methane in the hypolimnion, and insignificantly to methane in the epilimnion. Recent modeling work suggests that bubble dissolution can be important to both hypolimnetic and epilimnetic methane accumulations at sufficiently high ebullition flux. In all cases the bubble dissolution equations used to calculate contributions to dissolved methane were developed for deep marine environments and have not been independently verified for shallow, freshwater conditions.

The purpose of this work is to characterize the temporal and spatial variability of methane bubble size distributions in a dimictic kettle lake, to test the performance of a widely-used bubble dissolution model under relatively shallow freshwater conditions, and to quantify the importance of dissolving bubbles to dissolved methane levels within both the hypolimnion and epilimnion. Detailed bubble size distribution data were gathered using our recently-developed bubble size sensors which can measure in situ bubble volumes over long time periods. By deploying multiple bubble size sensors at 2 depths within the lake for a multi-month period we are able to address the following questions:

1. What is the distribution of bubble sizes in this lake and how spatially and temporally variable are these sizes?
2. Do existing methane dissolution models accurately predict the evolution in bubble size distribution as bubbles rise through a water column?
3. How important is bubble dissolution to accumulated methane in the hypolimnion, or to the air-water flux of dissolved methane from the epilimnion?
MATERIALS AND METHODS

Bubble size distributions were measured using a bubble size sensor and data processing algorithms described in Delwiche et al.\textsuperscript{16} and Delwiche and Hemond\textsuperscript{17}. Briefly, the sensor uses infrared LEDs, phototransistors, and a microcontroller to optically detect and measure bubbles rising through an inverted glass funnel stem. The sensor electronics are encased in a custom water-proof housing, and a custom surface data buoy holds batteries and electronics capable of powering the sensor via a data cable for up to 4 weeks between battery replacements. Raw sensor data is downloaded at the data buoy and post-processing algorithms convert the data to estimated bubble volumes. The sensor also includes optional attachments to increase the number of intercepted bubbles and to sample their bulk methane content.

Sensor deployment

Eight bubble size sensors were deployed at two different depths in Upper Mystic Lake, MA from July-November of 2016. Upper Mystic Lake is a dimictic, eutrophic kettle lake near Boston, MA with a history of methane ebullition\textsuperscript{18-19}. The sensor deployment site shown in Figure 1 was chosen because of its mild bathymetry gradients and observed history of ebullition in preliminary field work. Four sensors were deployed at 16m depth (sensors T1, T2, T3, and T4), and four sensors were deployed at 3m depth (sensors T6, T7, T8, and T9) using the deployment system described in Delwiche and Hemond\textsuperscript{17}. Initial deployments prior to July had more sensors in the vicinity of T3, but field results showed that collected bubble volumes were consistently lower around T3 and much higher around T7, so in July sensors T1, T6, and T4 were moved southward to capture more bubble data. Sensor T3 remained in place and continued to see negligible ebullition for the remainder of the deployment window. We believe the lack of
measured ebullition represents a real phenomenon because the sensor continued to record data consistent with particulate matter floating past the detectors (indicating the sensor was working), and we did not collect gas in the gas collection chamber. The lack of ebullition in a location with similar bathymetry and expected organic matter deposition to a bubbling area has intriguing implications for controls on ebullition flux, although this topic was outside the scope of the present study.

Figure 1: Upper Mystic Lake field site showing the sensor deployment locations (sensor IDs visible in inlay). Bathymetric lines drawn at 3.05 m (10 foot) increments.
Data collection and sampling

We visited sensors every 1-2 weeks to download data and collect gas accumulated in the gas collection chambers. Collected gas was stored in wetted glass syringes and analyzed within 24 hours on a thermal conductivity gas chromatograph. Methane results were calibrated using commercial standards of 10%, 50%, and 100% methane, and nitrogen results were calibrated against 10%, 50% and atmospheric nitrogen concentrations. We periodically measured temperature and dissolved oxygen using a Hydrolab MiniSonde probe, and gathered water samples for dissolved methane analysis using a sampling device described in Peterson. Dissolved gases were extracted into a helium-filled headspace by shaking samples for 20 minutes and then analyzing the headspace gas on a Shimadzu 2014 gas chromatograph using a flame ionization detector.

To quantify potential changes in bulk methane content within the gas collection chambers in between sampling intervals, we incubated a known quantity of methane in a trap modified to block any incoming bubbles and deployed at 3 m depth. Multiple measurements of the change in gas volume and methane content over 1-2 week periods allowed us to modify measured methane contents in the other traps to account for this modest in-trap dissolution. In addition to the modified trap at 3 m, we also ran incubation trials in T3 (at 16 m) when it became apparent that T3 was deployed in a location with negligible ebullition flux.

Bubble dissolution model

Bubble dissolution rates are calculated using the following mass transfer equation:
\[
\frac{dM_i}{dz} = -K_L(H_iP_i - C_i) \frac{4\pi r^2}{v_b}
\]

(1)

where \(i\) is the gas, \(M\) is the number of moles of gas \(i\) in the bubble, \(z\) is vertical distance, \(K_L\) is the gas transfer coefficient, \(H\) is the Henry's constant, \(P\) is the partial gas pressure within the bubble, \(C\) is the dissolved gas content in the water, \(r\) is bubble radius, and \(v_b\) is the bubble rise velocity. Many approximations for the bubble gas transfer coefficient and the bubble rise velocity exist\(^{21}\), and the equations used in this study are those included in the model from McGinnis et al.\(^9\) The bubble dissolution model was written in Matlab, integrated using the Euler method, and run with Upper Mystic Lake dissolved oxygen, dissolved methane, and temperature profiles (profiles in S.I.). Nitrogen was assumed to be in equilibrium with the atmosphere.

**RESULTS AND DISCUSSION**

**Bubble size and flux characteristics**

**Spatial heterogeneity in bubble size distributions**

During the 2016 field season sensors were fully operational from August through mid-November, excluding times during power loss or sensor malfunction. Of the 8 sensors deployed, 7 recorded a substantial number of ebullition events throughout the season. We believe that sensor T3, which only recorded 4 bubbles all season, was deployed in a low flux area as described in Materials and Methods.

Previous studies of methane bubble size distributions have either included distributions at a single location in a water body, or distributions measured over a short period of time. These previous studies have therefore left open the question of spatial heterogeneity in bubble size distributions within a water body. The 2016 field data shows that there are statistical differences
between some distributions even over the relatively small and bathymetrically homogeneous sampling area chosen for this study (Figure 2), implying that localized sediment structure may play an important role in determining bubble size distributions. We also note that several size distributions had a double-peak structure with one peak between 3-4 mm diameter, and a peak around the mean bubble diameter. Further work is necessary to determine prevalence and cause of this double peak distribution structure.

Dissolution modeling using data from sensors T1, T2, and T4 to predict distributions at T6, T7, and T9 yields size distributions that are consistent with distributions measured at T6, T7, and T9 (modeled results of 5.77 mm, 5.50 mm, and 5.46 mm, respectively, compared to measured results of 5.6 mm, 5.7 mm, and 5.7 mm, respectively). Sensor T8 appears to have a significantly larger bubble size distribution, and it therefore may not be appropriate to use one bubble size distribution to calculate dissolution rates over an entire water body.
Figure 2: Bubble size distributions from each sensor deployed during 2016, including mean bubble diameters and Sauter Mean Diameters (SMD). Letter in the top left corner shows statistically different distributions (comparisons are only made between sensors at the same deployment depth, 16m or 3m). Sensor 3 only saw 4 bubbles during the 2016 season.
Temporal heterogeneity in bubble size

As shown in Figure 2, bubble size distributions vary spatially even over relatively short distances. The question remains as to whether size distributions vary temporally. Although our bubble size data only span 3 months, within this limited context we saw no evidence of systematic changes to the bubble size distributions. However, we did find that average daily bubble size was positively (though non-linearly) correlated with daily ebullition flux (Figure 3). This indicates that higher ebullition flux is attributed both to more bubbles and to increased bubble size. The natural logarithm of daily ebullition flux was a significant predictor for average daily bubble size (p<0.05, excluding days with fewer than 10 bubbles), and the regression coefficient of 0.46 indicates that, for example, a 50% increase in daily ebullition flux yields a 0.08 mm increase in daily average bubble size. To determine whether this would have an appreciable impact on net methane dissolution, we modeled the amount of methane dissolution per mL gas emitted from all bubbles on days when flux was 40 – 60 mg CH₄/m²/day. We then modeled the effect of the predicted increase in bubble size distribution due to a 100% and 200% increase in flux and found that this resulted in a 3% and 5% decrease, respectively, in the amount of methane dissolved per mL gas emitted to atmosphere. Therefore, bubble dissolution volumes calculated with size distributions gathered on relatively low flux days may mildly over-represent in situ dissolution rates.
Figure 3: Relationship between average daily bubble diameter (mm) and daily ebullition flux (mg CH₄/m²/day). Best fit lines drawn for data sets with significant correlation between ebullition flux and daily average bubble diameter. To improve accuracy of the daily bubble diameter, days with fewer than 10 bubbles are not included.

Temporal heterogeneity in ebullition flux

In addition to measuring bubble size, the sensors provide detailed data on the timing of bubble release. Figure 4 shows the complete time series for bubbles measured by each sensor. As has been found with previous studies¹⁹,²², ebullition events often coincided with drops in hydrostatic pressure (see S.I.), and high flux events often occurred simultaneously at multiple sensor locations.
Figure 4: Time series of individual bubble emissions as recorded by each sensor, with corresponding diameter measurement (mm). Grey bars correspond to times sensors were offline. Blue circles correspond to data previously published in Delwiche and Hemond. Plots are ordered based on deployment location from North to South as shown in Figure 1.
In contrast with earlier studies, temporal resolution for data shown in Figure 4 is exceptionally high (on the sub-second scale) which provides a powerful tool for studying fine-scale temporal dynamics of methane bubble release. Bubbles in Upper Mystic Lake are often tightly clustered in time. For example, 25% of bubbles are found to enter the sensor within 1 second of a previous bubble (Figure 5). While it cannot be shown from these data that bubble clusters are emitted from the exact same bubble vent, visual observations of bubble events within Upper Mystic Lake show that several bubbles in quick succession often break the surface in the same location. The degree of temporal clustering observed in this data set is similar to that found using Upper Mystic Lake ebullition data gathered using a sonar device\textsuperscript{18}. Temporal clustering on the daily scale (see S.I.) corroborated previous findings that to accurately estimate ebullition rates, bubble flux must be measured for many days\textsuperscript{23}.

![Cumulative Frequency Percentage of the Time Between Bubble Arrivals](image)

**Figure 5:** Cumulative frequency percentage of the time between bubble arrivals (in seconds). The horizontal and vertical lines show that 25\% of the bubble data is recorded within 1 second of the previous bubble.

The close temporal spacing of rising bubbles could be significant to bubble dissolution. Previous studies suggest that bubbles rising within a few seconds of each other may experience
higher velocities\textsuperscript{24-26}. While an increase in velocity would by itself reduce the bubble travel time and therefore reduce total dissolution, this effect is partially compensated for by the fact that increased velocity will keep bubbles larger, and larger bubbles have higher rates of dissolution (see equation 1). For example, a 5 mm diameter bubble released at 16 m and subjected to a 30% velocity increase (30% being an upper bound based on existing literature\textsuperscript{24-26}) will experience 5% less dissolution (by volume) than a 5 mm bubble with no velocity increase. The effect is larger for smaller bubbles, and a 1 mm diameter bubble will experience 25% less dissolution by volume.

Close bubble spacing could also contribute to bubble coalescence. Because dissolution rates are highly dependent on bubble size, coalescence has the potential to significantly impact dissolution. The physical and chemical mechanisms of bubble coalescence are complex, and changes with water chemistry, bubble size, and bubble rise trajectory\textsuperscript{27-29}, so more work would be needed to quantify the significance of methane bubble coalescence in freshwater environments.

**Bubble dissolution and contribution to dissolved methane in lake**

**Comparing bubble dissolution model to field data**

The bubble dissolution model introduced by McGinnis et al.\textsuperscript{9} is often used to estimate bubble dissolution rates, but bubble dissolution rates vary based on water chemistry and the model has not previously been tested for performance in shallow, freshwater environments. To test the model under these conditions, we modeled the dissolution of bubbles measured at 16 m and compared the results to bubbles measured at 3 m (using data from August to minimize temperature changes, and bubble data from all sensors to limit the impact of variability in bubble sizes between deployment locations), as shown in Figure 6. Bubbles were assumed to be 80%
methane and 20% at 16 m depth based on the bulk gas samples, taking into consideration in situ dissolution as discussed in Materials and Procedures. We found the results were statistically equivalent when the diffusion exponent $n$ presented in Equations S2-S3 in the Supporting Information was 0.55, which is between the values used for clean and dirty water (0.5 vs 0.67, respectively). For a sensitivity analysis of the impact of clean versus dirty water and the variable exponent $n$, please see the Supporting Information. The weighted methane fraction for the bubble size distribution was 74% which is within the range expected based on field bulk gas samples (corrected for in situ dissolution). We therefore conclude that the model adequately represents bubble dissolution for the eutrophic freshwater conditions present in Upper Mystic Lake.

![Figure 6: Using field data to verify the bubble dissolution model. The dashed line represents the combined bubble size distribution measured at 3 m. The solid line is the predicted size distribution at 3 m based on bubble sizes measured at 16 m, as calculated by the bubble dissolution model. Distributions are statistically similar, indicating that the model performs well.](image)
Contribution from dissolving bubbles to hypolimnetic methane accumulation

Dissolved methane profiles taken in August 2016 and November 2016 show an accumulation of approximately 300 mmol CH₄/m² in the bottom 3 meters of the sampling area (Figure S1 in S.I.). We use the aforementioned bubble dissolution model with bubble data gathered at 16 m to estimate that approximately 32 mmol CH₄/m² of this accumulation was due to bubble dissolution (similar estimation achieved using the Sauter Mean Diameter approximation discussed in McGinnis et al.⁳⁰, equation included in SI). Methane bubble dissolution therefore represents a significant but modest contribution to methane input to the hypolimnion in this lake at the observed ebullition flux rates. Diffusion from porewater likely contributes the majority of the remainder of the dissolved methane in the hypolimnion, though sources such as lateral inflow, in situ production, and sediment disturbance (e.g.: by internal waves or biota) may play a role given their importance elsewhere.⁳¹-⁴³

Contribution from dissolving bubbles to epilimnetic methane flux across air/water interface

Methane in epilimnetic waters is subject to biological oxidation and therefore does not accumulative significantly. Therefore, we estimated the importance of bubble dissolution to the methane budget in the epilimnion by comparing it to dissolved methane flux across the air/water interface:

\[ F_{a/w} = k \times (C_{a/w} - p_a K_H) \]  

(2)

where k is the gas transfer velocity (calculation method presented in the Supporting Information), C is the dissolved gas concentration, p is the gas partial pressure, and K is Henry’s constant. The estimated diffusive flux of methane to the atmosphere during August was 0.8 mmol/m²/day, although this may be an underestimate given the recently reported importance of
micro-bubbles in enhancing the air/water diffusive flux of methane\textsuperscript{35-36}. The estimated bubble dissolution into the epilimnion calculated using the model was approximately 0.1 mmol/m\textsuperscript{2}/day. Since this is at most 13\% of the total estimated diffusion flux from the epilimnion, there must be other sources of methane to the epilimnion to account for dissolved methane levels. This conclusion is supported by previous studies showing that littoral sediments and in situ methane production are of primary importance to epilimnetic methane\textsuperscript{14,31,37-38}. These findings are also in line with recent modeling work suggesting that at the ebullition levels observed in Upper Mystic Lake, the contribution from dissolving bubbles to the lacustrine carbon balance is likely to be minor\textsuperscript{15}.

**Supporting Information**

Calculation for the Sauter Mean Diameter (eq S1), the gas transfer rate equations used in the bubble dissolution model (eqs S2-S4), the method for approximating epilimnetic air/water methane flux (eqs S5-S9), profiles for temperature, dissolved oxygen, and dissolved methane (Fig S1), the relationship between flux and hydrostatic pressure (Fig S2), a discussion of the daily temporal heterogeneity in ebullition flux (Fig S3), and a discussion of the diffusion exponent $n$ in the bubble dissolution model (Fig S4).

**Acknowledgements**

We would like to thank students of the Parsons lab for their fieldwork assistance, and Mark Belanger for his help in the machine shop. This material is based on work supported by the National Science Foundation under grant number EAR-1045193 and Graduate Research Fellowship Program grant number DGE-0707428, the MIT Martin Family Fellowship to K. Delwiche, the W.E. Leonhard 1941 professorship to H. Hemond, and the Singapore-MIT Alliance for Research and Technology program.
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SUPPLEMENTAL INFORMATION

Methane bubble size distributions, flux, and dissolution in a freshwater lake

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A. Methods

1. Calculating sauter mean diameter

Previous research has demonstrated that the Sauter Mean Diameter (SMD) can be used to simulate dissolution of an entire bubble size distribution. The Sauter Mean Diameter is the equivalent diameter of a bubble with the same volume to surface area ratio as the entire bubble size distribution:

\[ SMD = \frac{\sum d^3}{\sum d^2} \]  

where \( d \) is the diameter of each bubble in the bubble size distribution.

2. Calculating epilimnetic methane flux across air/water interface

The total dissolved methane flux across the air/water interface is:

\[ F_{a/w} = k_i \times (C - p_a K_H) \]  

where \( C \) is the dissolved gas concentration, \( p_a \) is the gas partial pressure (1803 ppb methane), and \( K_H \) is Henry’s constant. The \( k_i \) represents the piston velocity, calculated as:

\[ k_i = \left( \frac{Sc(T)}{600} \right)^a \times k_{600} \]  

Where \( a = -0.67 \) when \( u_{10} < 5 \text{ m/s} \) (from Liss et al., 1986), \( u_{10} \) is the wind speed 10 m above the earth’s surface, \( Sc(T) \) is the Schmidt number for methane at the surface water temperature and \( k_{600} = 2.07 + 0.215 u_{10}^{1.7} \text{ (cm/hr)} \). From Cole and Caraco. The \( u_{10} \) is estimated using Mackay and Yuen:

\[ u_{10} = \left( \frac{10.4}{\ln(z)+8.1} \right) \times u_z \]
The Cole and Caraco relationship for \( k_{600} \) was developed based on data from a lake with relatively low wind speeds. While other studies have highlighted the superiority of site-specific \( k_{600} \) measurements\(^8\), their results are in good agreement with the Cole and Caraco relationship above 1.0 m/s. Local wind data is available through the Turkey Hill weather station in nearby Arlington, MA, and the average wind speed in August 2016 was 1.3 m/s. Though the anemometer height at Turkey Hill is unknown, previous work at Upper Mystic Lake comparing Turkey Hill wind data to anemometer readings from a buoy on the lake estimated that the relationship between these wind speeds is approximately\(^9\):

\[
u_{UML,1m}(\text{m/s}) = u_{station(\text{m/s})} + 0.5
\]

The methane concentration in the epilimnion was approximately 1.2 \( \mu \text{M} \) at 1 m depth, yielding an air/water methane flux of approximately 0.8 mmol/m\(^2\)/day. This flux calculation method was used previously on Upper Mystic Lake by Varadharajan\(^9\). We note that the average ebullition flux was also 0.8 mmol/m\(^2\)/day, and the similar magnitude between diffusion and ebullition reflects the fact that ebullition in the deep part of Upper Mystic Lake is relatively low compared to other lakes where ebullition flux dominates\(^{10-11}\).

**B. Results and Discussion**

**1. Temperature, dissolved oxygen, and dissolved CH\(_4\) profiles**

The temperature, dissolved oxygen, and dissolved methane profiles presented in Figure S1 were used in the bubble dissolution model. The profiles presented here are in line with data from previous sampling campaigns at Upper Mystic Lake measuring dissolved oxygen and temperature more frequently (e.g.: Varadharajan 2009\(^9\) and Peterson 2005\(^{12}\)). The dissolved methane profile was also used to calculate that approximately 0.3 mol CH\(_4\)/m\(^2\) of dissolved
methane accumulated in the bottom 3 meters of the water column between August 5th and November 13th, 2016.

2. Hydrostatic pressure drops trigger ebullition

As has been widely demonstrated before\textsuperscript{13-14}, drops in hydrostatic pressure at Upper Mystic Lake tend to trigger ebullition events. We monitored hydrostatic pressure using a commercial sensor (the Solinst Model 3001 Levelogger Gold) that is permanently installed at Upper Mystic Lake. As can be seen in Figure S2, large ebullition events are typically preceded by large drops in pressure. Flux peaks also tend to occur simultaneously in multiple traps.

3. Daily temporal heterogeneity

Methane ebullition from natural waters is widely known to be a temporally heterogeneous process, with emissions concentrated over short time intervals\textsuperscript{14-15}. Ebullition at Upper Mystic Lake is also temporally clustered, as is visible in Figure 4 of the main text. To quantify the temporal variability in methane ebullition, we calculate daily ebullition flux and compared this to the cumulative ebullition flux and the number of days contributing to this cumulative flux (Figure S3). The separation between the two lines in Figure S3 demonstrates that the majority of the ebullition flux occurs on a small number of days (for reference, note that in the hypothetical case of constant flux the two lines would be the same). For example, the dotted line indicates that 60% of the sampled days only account for about 22% of the total flux. This corroborates previous findings\textsuperscript{16} that short-duration sampling campaigns may underestimate ebullition flux unless they happen to coincide with higher-flux time periods.
C. Figures

**Figure S1:** Temperature profile in degrees C (left), dissolved oxygen profile in mg/L (middle), and dissolved methane in μM (right) taken in August, October, and November of 2016.

**Figure S2:** Hydrostatic pressure in m of water relative to the low point on Sept. 1\textsuperscript{st}, 2016 (left axis), and daily ebullition flux in mg CH\textsubscript{4}/m\textsuperscript{2}/day (right axis). Vertical dashed grey lines show that ebullition peaks often coincide with dropping hydrostatic pressure. Daily ebullition is plotted for sensor 1 and other sensors show similar event timing.
Figure S3: Cumulative sum of daily ebullition flux (dashed line) and the number of days contributing to the cumulative flux (solid line), plotted against the daily ebullition flux in mg CH$_4$/m$^2$/day. The separation between the Flux Volume and Number of Days demonstrates that ebullition flux is not homogeneous, but rather occurs in bursts over a smaller subset of days. For example, dotted vertical line shows that 60% of the sampled days only account for 22% of the total observed flux.

D. References


Chapter 5: Methane bubbles transport sediment and arsenic to a lake surface

ABSTRACT

Bubbles effectively adsorb and transport particulate matter both in industrial and marine systems. While methane bubbles emitted from anoxic sediments are found extensively in aquatic ecosystems, relatively little attention has been paid to the possibility of methane bubble particle transport. We quantified methane bubble-facilitated particle transport on Upper Mystic Lake, MA, and microscope-based evidence demonstrated that transported particles were likely from the sediment. Concentrations of arsenic, chromium, and lead in the particulate matter were similar to bulk sediment measurements, further indicating that bubbles are transporting sediment particles from depths exceeding 15 m. Testing in a 15 m tall laboratory bubble column showed that over 90% of bubble particulate matter originated in the sediment instead of being scavenged from the water column. We conclude that bubbles transport particles upwards through a stratified water column through which significant movement of sedimentary material would otherwise not be expected. This could have important implications for chemical or biological cycling in natural ecosystems, although we found that bubble-facilitated arsenic transport on Upper Mystic Lake is likely a minor component of total arsenic cycling.

INTRODUCTION

Bubble particle flotation is a process by which amphiphilic particles attach to a bubble’s gas-water interface and are transported upwards during bubble rise. This phenomenon is used extensively in industry for applications such as separating valuable minerals from gangue
(Rodrigues et al. 2007, Min et al. 2008), removing ink during paper recycling (Vashisth et al. 2011), recovering desirable proteins and microorganisms from industrial bioreactors (Schügerl 2000), and treating wastewaters (Lin and Lo 1996, Aldrich and Feng 2000, Rubio et al. 2002).

Bubble-mediated particle transport also occurs in the open ocean and contributes to an accumulation of surface-active particles at the surface of the ocean (Wallace et al. 1972, Blanchard 1975, Aller et al. 2005). The ocean surface microlayer (operationally defined based on sampling protocol, with sampling thickness ranging from 50-400 um (Cunliffe et al. 2013)) has been found to contain microorganisms, pesticides, heavy metals, organic contaminants, and other chemicals far in excess of concentrations in underlying waters (Wurl and Obbard 2004). The bubbles responsible for transporting particulate matter are injected into the ocean surface by breaking waves and scavenge particles as they rise (Liss 1975).

Despite the abundant evidence that bubbles are effective particle transporters in industrial and open-ocean conditions, very little is known about the importance of bubble particle transport in freshwater systems. Although smaller freshwater systems may lack the white-cap waves necessary to inject bubbles into the water column, methane bubbles produced in anoxic sediments are prevalent in these systems. These bubbles originate in the sediment as a product of microbial organic matter decomposition, and are released to the surface during drops in hydrostatic pressure, sediment disturbance, or upon sufficient gas accumulation (Chanton et al. 1988, Joyce and Jewell 2003, Varadharajan and Hemond 2012, Maeck et al. 2014, Liu et al. 2016).

Since methane bubbles can rise from great depths through density-stratified waters, bubble flotation could provide a chemical link from deep water to surface waters that would otherwise not occur through diffusion alone. This potential transport could have important
implications for aquatic chemical and biological cycles. Since aquatic sediments are often contaminated with heavy metals and organic pollutants (Nriagu et al. 1996, Taylor and Owens 2009, Pan and Wang 2012), methane bubbles have the potential to transport contaminated particles to the water surface. To date, very few studies have addressed the particle-transport capability of methane bubbles generated in aquatic sediments. While the few existing studies have found evidence that methane bubbles can transport polycyclic aromatic hydrocarbons (Viana et al. 2012) and manufactured gas plant tar (McLinn and Stolzenburg 2009), the full extent of methane bubble particle flotation in aquatic systems remains unknown.

To begin addressing the many questions related to methane bubble particle flotation in freshwater systems, we have quantified bubble-particle transport under field conditions in Upper Mystic Lake, MA, an urban lake with a history of sediment contamination. We also used laboratory bubble columns to further study the potential for bubble-particle transport. Given the importance of bubble size to particle flotation, we used a previously-designed bubble size sensor (Delwiche et al. 2015, Delwiche and Hemond 2017) to measure bubble diameter distributions both in the lake and in the laboratory. We address the following questions:

1. Can bubbles emitted from lake sediment transport particles to the lake surface?
2. Where do particles originate? Do bubbles shed or scavenge particles as they rise?
3. How does bubble volume affect particle transport?
4. What implications does this transport pathway have for arsenic cycling in Upper Mystic Lake?

**Brief introduction to flotation theory**

Rising bubbles collide with particles and under the right conditions the particle and bubble will form a stable three-phase contact line. Bubble-particle flotation efficiency is highly
dependent on bubble-particle interactions, and particle capture efficiency ($E_{\text{cap}}$) is determined by the effectiveness of three sub-steps:

$$E_{\text{cap}} = E_c E_a E_s$$

where $E_c$, $E_a$, and $E_s$ are the particle collision, attachment, and stability efficiencies, respectively (Yoon and Lutrell 1989, Dai et al. 2000).

*Particle-bubble collision efficiency, $E_c$*

Bubbles collide with particles as they rise through the water column. Particles move along streamlines around the bubble, and collision occurs if the particle radius is greater than the smallest distance between the fluid streamline and the bubble interface. Many models exist to predict $E_c$, the collision efficiency (Dai et al. 2000). Earlier models focused only on hydrodynamic effects, and found that the probability of collision was proportional to particle diameter and inversely proportional to bubble diameter (Yoon and Lutrell 1989). However, recent efforts have demonstrated that particle inertia also affects collision efficiency: initially, inertia propels a particle toward the bubble interface, but later the centrifugal force generated as the particle is swept outwards along the bubble interface decreases collision efficiency (Dai et al. 1998). A thorough review of collision models has been presented in Dai et al. 2000, and the Generalized Sutherland Equation has been shown to predict bubble particle collision well for particles between 1 – 100um in size and bubble diameters between 0.08 and 0.15 cm (Hassanzadeh et al. 2017).
**Particle-bubble adhesion efficiency, $E_a$**

After a particle collides with a bubble, a stable three-phase contact line between particle, gas, and water must develop for stable particle adhesion. For this to occur, the liquid film between the particle and bubble must thin and rupture in less time than it takes the particle to be swept past the bubble interface (Tao 2005). Film thinning and rupturing depend on particle factors such as roughness, hydrophobicity, and electric charge. The more hydrophobic a particle is, the less stable the thin film separating bubble and particle is likely to be. Rougher particle surfaces are able to pierce the bubble interface more readily, and to hold micro gas bubbles that can increase attachment efficiency (Krasowska and Malysa 2007, Hassas et al. 2016). Evidence also suggests that adhesion increases for smaller particles and smaller bubbles, up to a lower size limit (Yoon and Lutrell, 1989).

**Particle-bubble detachment efficiency, $E_d$**

Particles detach from the interface if a collision between the bubble and another particle imparts enough kinetic energy to overcome the particle attachment forces (Ralston et al. 1999). The forces acting on the particle when it is attached to the bubble include the capillary force acting along the three-phase contact line, the particle weight in the liquid, and the hydrodynamic drag force (Tao 2005). Additionally, when a rising bubble collides with a particle in solution it induces a vibration in the bubble. This vibration causes the adhered particles to move in a circulatory pattern, thus generating centrifugal force which, if strong enough, can detach the particles (Cheng and Holtham 1995).
**Role of bubble and particle size in flotation**

In general, flotation rates per unit of gas volume increase as particle size increases and bubble diameter decreases. Smaller bubbles increase the particle collision probability and will therefore increase flotation as long as bubbles maintain sufficient buoyancy to rise (Tao 2005). Larger particles are more likely to collide with a rising bubble which increases collision efficiency. Due to the complexity of the physics and dependence on particle characteristics, different studies offer different optimum bubble and particle sizes (Ahmed and Jameson 1985, Yoon and Lutrell 1989, Feng and Aldrich 1999). Although the range of optimum bubble volumes reported in the literature varies, industrial flotation systems typically use bubble diameters much smaller than the 2mm and larger bubble diameters often seen in natural aquatic systems (DelSontro et al. 2005, Ostrovsky et al. 2008, Bussman et al. 2013). Since very large bubbles have mobile interfaces (Clift et al. 1978), and bubble interface vibrations are known to increase the particle detachment probability, we expect particles on very large bubbles to have a higher probability of detachment. However, since we could find no literature on flotation with large bubbles, further work is needed to understand the physics of particle detachment for bubbles of large diameters. Another difference between flotation systems and natural aquatic systems is that aquatic systems can be quite deep, and therefore bubble volumes change due to hydrostatic pressure changes across the water column. We could not find literature discussing the effect of bubble volume change on flotation, but we surmise that as bubbles grow and their interfaces become more mobile, the detachment probability may increase.
METHODS

Upper Mystic Lake field site history

Upper Mystic Lake in Arlington, MA is an urban, dimictic kettle lake with an average depth of 15 m, a maximum depth of 24 m, and a surface area of 0.5 km². The lake is used extensively for recreational and scientific purposes, and previous studies have focused on methane ebullition on the lake (Varadharajan and Hemond 2012, Scandella et al. 2016, Delwiche and Hemond 2017). Chemical manufacturing and leather tanning industries during the late 1800s and 1900s produced toxins such as arsenic, chromium, and lead and deposited them in waste piles and settling ponds along the Aberjona River which feeds Upper Mystic Lake. These toxins flowed into the lake during manufacturing and later during earth-moving activities. Arsenic, lead, and chromium were deposited in layers in the Upper Mystic Lake sediments, and sediment cores reveal a distinct layered pattern with peak metal/metalloid concentrations traceable to years of peak manufacturing or earth-moving (Spliethoff and Hemond 1996).

Materials and supplies

Sample digestions were done with nitric acid from Fisher Scientific (Optima grade for ultra-trace elemental analysis). All plastic ware was soaked in 5-10% HNO₃ for 24 hours and rinsed with Milli-Q water prior to use.

Field sampling and analysis

We ran field tests in an area of the lake previously found to have relatively high ebullition rates (Delwiche and Hemond 2017). To efficiently collect multiple samples in a single visit and minimize algae build-up in our sampling containers, we triggered bubble events by dropping an anchor into the sediment (calculations showed that the resulting bubble diameter distributions
were statistically similar to those of un-triggered bubbles). We then manually positioned a custom bubble size sensor above the rising bubble plume (sensor described previously in Delwiche et al. 2015 and Delwiche and Hemond 2017). Bubbles exiting the sensor, and any particles adhered to the bubble/water interface, were collected in a removable sample cup attached to the top of the funnel stem. Several anchor drops within an area of roughly 10 m by 10 m were required to intercept a sufficient number of bubbles, and we intentionally collected samples with different total gas volumes. We also collected a blank water sample to correct for background contributions of particulate matter and arsenic concentrations in bubble-transported particle data.

We filtered samples within 24 hours with pre-weighed Whatman Grade 41 quantitative cotton filters (nominal pore size 20 μm, 25 mm diameter). Due to filter clogging, we typically used multiple filters for each sample. After filtering we air-dried filters, weighed them, transferred each to microwave digestion vessels, and added 10 mL of nitric acid. Samples were digested in a MARS6 microwave oven, diluted with 30 mLs of Milli-Q water, and then filtered with a 0.2 um polyethersulfone membrane syringe filter. For analysis, we diluted samples to 2 % nitric acid, added a rhodium internal standard, and analyzed on an Agilent 7900 ICP-MS with a 5 point calibration curve from 0.05 - 10 ppb. Blank analysis to determine background arsenic concentrations in the Whatman cotton filter paper found levels at least two orders of magnitude below sample concentrations.

**Laboratory column design and operation**

*Large Column*

To study bubble particle shedding and scavenging, we built a 15 m tall bubble column in the laboratory stairwell. The column is comprised of four sections of 6 inch (15.3 cm) nominal
diameter transparent polyvinyl chloride (PVC) pipe joined by threaded unions with o-ring seals. The base of the column is a reducing tee fitting with a removable spigot for drainage, and the column was filled at the top. We built a sediment container connected to 1/8 inch copper tubing that could be lowered into the column and secured at any depth. We used a syringe pump to push air into the sediment through the tubing at a controlled rate. Sediment was originally collected with an Ekman dredge from the same place in Upper Mystic Lake used for field sampling.

For experimental runs, we injected 50 mL of air at 0.7 mL/min. Prior to the start of each run we took background water samples to correct for background contributions to particulate matter and arsenic concentrations in bubble-transported particle data. Bubbles passed through a customized bubble size sensor fitted with the same sample collection cup design used in the field setting. We filtered bubble column samples using pre-weighed 5.0 µm and 0.2 µm Whatman Nuclepore membrane filters with 47mm diameter which allowed us to use only one of each filter per sample. Filters were dried, weighted, digested, diluted, and analyzed as described above. Blank analysis on Nuclepore membranes and lab filtering procedures found arsenic contamination levels approximately two orders of magnitude below total (total being the sum of results from the 5 µmol filter and 0.2 µmol filter) sample concentrations.

**Small column**

To study the effect of water pH we constructed a 1.5 m tall column from 7.4 cm diameter transparent PVC pipe. The column base was fitted with an o-ring sealed port for gas injection into the sediment via a syringe pump. For the first two trials comparing pH, we placed approximately 500 mL of thoroughly mixed Upper Mystic Lake sediment into the column and
filled with tap water (with pH = 9 prior to equilibration with carbon dioxide in atmosphere). We injected 50 mL of air at 0.7 mL/min, and measured bubble volumes using a custom-built bubble size sensor built with a smaller-diameter waterproof housing to fit the smaller width of the bubble column. We conducted three replicate experiments with the same water and sediment and tracked water pH. We then removed the water from the column (leaving the original sediment in place) and replaced it with tap water that had been acidified to pH = 6.5 with trace metal grade HNO₃ and ran three replicate experiments. The second set of trials comparing pH were conducted similarly, except we replaced the sediment along with the water before beginning the pH = 6.5 experiments. Sampling and analysis details were the same as those for the large bubble column.

**Bubble volume normalization**

For both field and laboratory data, we measured bubble volumes at the top of the water column. However, bubble volumes at the surface differ from those at the sediment because rising bubbles undergo both gas dissolution and expansion due to pressure reduction (Leifer and Patro 2002). In order to effectively compare data gathered from different systems, we used the bubble dissolution model of McGinnis et al. 2006 to estimate initial bubble volumes based on surface measurements. This model requires water temperature and dissolved gas concentration profiles, which we estimated from profiles collected in October 2016 for field bubble volumes (Delwiche and Hemond 2017). The laboratory column was assumed to be 21 degrees C, in equilibrium with the atmosphere with respect to oxygen and nitrogen, with negligible dissolved methane.
RESULTS AND DISCUSSION

Particle transport

Figure 1: Picture of the lake surface after a triggered bubble event showing an accumulation of particulate matter (visible as light specs on the water surface, though in reality particles are black).

Field data shows bubbles transport particles

During field tests we observed particles accumulating on the water surface during bubble triggering events (Figure 1), and individual bursting bubbles often left particles distributed in a ring pattern. This visual evidence of bubble-particle transport was further supported by the sample data showing a clear upwards trend between total particle mass and gas volume (Figure 2). Higher gas volumes led to significantly more particle mass transport ($r^2 = 0.79$, $p<0.05$), with some minor spread in the data indicating that other factors in addition to total gas volume affect particle transport rates. Some of this variability may have arisen because samples were collected in an area of tens of square meters and localized sediment characteristics may impact
particle transport rates. Variability could also come from a difference in bubble volumes since bubble volumes affect flotation rates (Yoon and Luttrell 1989), although we found no statistical trend between particle mass transport and average bubble diameter (see discussion below). We also note that triggering bubbles by dropping an anchor undoubtedly disturbed the sediments, and this artificial perturbation may have affected particle transport rates.

![Graph showing total particle mass per sample mg vs total bubble volume mL]

**Figure 2:** Total particle mass (in mg) associated with the bubbles captured during each bubble triggering event. Triggering events yielded different bubble volumes (given in mL).

*Particles may be from the sediment*

Field mass transport data demonstrate that bubbles are capable of transporting particles to a lake surface, but do not determine the particle origins. Microscope images of the particles show biological material as well as material that may be inorganic (Figure 3). Many of the biological structures in the particles appear to be the carapaces and head shields of *Bosmina spp*, which have been found extensively in other freshwater lake sediments (Kerfoot 1995). To further characterize the particulate matter, we compared metal concentrations to concentration
ratios from sediment samples and found that the ratios of arsenic, chromium, and lead to the bulk sediment mass were within the range (but on average only 70%) of the ratios measured for bubble-transported particulate matter (Figure 4). The fact that the average metals content per particle mass for the particulate matter are lower than the sediment ratios could suggest that bubbles preferentially transport fractions of the sediment that have lower metals concentrations (e.g. organic matter such as the *Bosmina spp* remains).

![Figure 3: Light microscope images of bubble-transported particulate matter showing many apparent *Bosmina spp* carapaces and head shields, along with material that may be primarily inorganic in nature.](image)

Our data strongly suggest that bubbles transport sediment directly from the bottom of the lake to the water surface. This direct transport occurs over a 15 m deep water column, (and does not preclude the possibility that bubbles can transport particles over significantly larger depths.) This transport provides a direct chemical link between the sediment and surface waters, a link that otherwise would not occur during months of stratification (sediment transport to the lake surface could theoretically occur during unstratified periods, but transport would likely not be as rapid as bubble transport). Furthermore, the rapid rise of bubbles limits the time available for
oxidation reactions, and suggests that sediment particulate matter may reach the lake surface in a reduced state, with possible consequences for both toxicity and reactivity.

Figure 4: Comparing mass of arsenic, chromium, and lead per kg of sediment (open triangles) and bubble-transported particulate matter (solid circles). Standard deviation scale similar to point size and therefore omitted for figure clarity.

**Bubble column data indicates minimal particle shedding and scavenging**

While field sampling data indicate that bubbles transport particles for distances in excess of 15 m from sediments to the lake surface, field data do not indicate whether bubbles shed particles as they rise. Particle shedding would contribute to more sediment mass mobilization per bubble than would be predicted based on measurements from surface samples alone. To quantify the importance of particle shedding, we conducted experiments in a 15 m tall bubble column in our laboratory stairwell (as described in Methods). Bubble tests showed significant particle transport even in the absence of the disturbance caused by dropping the anchor in field
experiments (though fluxes were approximately 4 times lower than field data, see discussion below). Bubbling tests conducted at 5 m, 10 m, and 15 m showed no significant difference in total particle transport rates (Figure 5). Data also showed that on average, greater than 98% of particle mass transport was composed of particles larger than 5 μm, and less than 2% was between 0.2 μm and 5 μm.

The lack of a trend between mass transport and depth indicates that particle shedding is insignificant, though the large degree of variability between replicates could have masked underlying physical processes. In particular, we note that samples taken after raising or lowering the sediment bed had markedly higher particle mass transport rates (noted by the extra black circles around data points in Figure 5). This could be because transportable particles get depleted during replicate bubbling events, and moving the sediment bed mixes the sediment. This surmised influence of localized sediment conditions also supports our hypothesis based on field data that heterogeneous sediment conditions contribute to variability in particle mass transport.
Figure 5: Transferred particle mass per L of gas bubbled in the large bubble column, as a function of bubble release depth. Solid circles represent samples where bubbles were emitted from the sediment bed, diamonds represent samples where gas was bubbled directly above the sediment bed. Hollow circles around solid circles denote samples with recently-disturbed sediments.

Another possible explanation for the relative similarity of particulate mass transported from different depths is that bubbles also scavenge particles as they rise, and shedding and scavenging rates are similar. To quantify the bubble scavenging capacity, we compared the data from 5 m and 10 m to samples gathered when gas was bubbled several centimeters above the sediment. Particle mass scavenging represented approximately 10% of the mean particle transport for 5 m and 10 m (Figure 5), indicating that while scavenging rates are non-zero, the large majority of the particulate matter in these experiments was from the sediment.

Furthermore, as with the field samples, bubble column particulate matter element concentrations
are similar to the bulk sediment (see Figure S1 in S.I.). Interestingly, contaminant concentrations in the scavenged particulate matter follow a different trend (discussed in S.I.) and suggest that lead, chromium, and arsenic are not evenly distributed among sediment particulate matter. Contaminant levels in regular bubble column samples support our conclusion that bubbles are primarily transporting sediment matter to the lake surface, despite the relatively deep water column, and particle shedding appears to be minimal. Since particle shedding rates appear to be minimal, particle transport measured at the surface of the lake are likely representative of total bubble-facilitated particle transport rates.

*Explaining differences between field and bubble column data*

While both field data and bubble column data clearly demonstrate that bubbles are capable of transporting particulate matter, average transport rates in the field were approximately 4 times higher than average transport rates in the large bubble column (0.07 ± 0.03 mg/L for the columns vs 0.26 ± 0.2 mg/L for the field). While bubble diameters were different between the two sample sets (see Figure 6), as we discuss below there did not appear to be a trend between bubble diameter and particle transport over our data sets. Given the observed relationship between recent sediment disturbance and higher particle transport rates, we think the higher field transport rates can be explained (at least in part) by physical sediment disturbance from the dropped anchor. Another possibility is that the sediment sample we used for the bubble column happened to contain particulate matter less conducive to bubble transport. Yet another possibility is that the dissolved and particulate matter present in Upper Mystic Lake water enhances bubble particle flotation. Future work should focus on trapping naturally-emitted
methane bubbles from the lake to determine whether sediment disturbance caused the increased transport rates in the field, or if observed rates are indeed typical of in situ lake conditions.

One further experimental factor to consider was that the city tap water used to fill the bubble column is maintained around pH = 9 to minimize pipe corrosion. Typical pH levels in the lake are between pH 6-7 (Senn 2001), and previous work on bubble particle flotation has shown that increasing the pH can inhibit natural organic matter particle transport (Shi et al. 2017). To test the effect of pH on sediment flotation, we ran experiments in our small bubble column with water pH starting at 9 (and dropping from 8.5 – 8.0 during the course of the experiment due to atmospheric equilibration), and water pH starting at 6.5 (and remaining close to 6.5 during the experiments). These experiments did not show a statistically significant difference related to water pH (0.084 ± 0.03 mg/mL for pH = 8-8.5 versus 0.062 ± 0.02 mg/mL for pH = 6.5). See Supplemental Information for figures.

**Effect of bubble diameter**

Despite the documented importance of bubble diameter in flotation systems (Yoon and Luttrell 1989), we found no trend between average bubble diameter and particle mass transport (Figure 6, note that we only have bubble diameter distributions for 5 of the field data points). However, we do note that bubble diameter is not a static measurement and in deep water columns bubbles will change volume significantly as they rise, which complicates the search for a trend. Average bubble diameter varies between data sets, and we attribute the variation between the small and large laboratory columns to differences between the sediment height above the gas injection point (preliminary work suggested that sediment depth influenced bubble volume). It is also important to note that while we are reporting average bubble diameters, the
sensor only measured on average 35% of the total flux due to a combination of flow anomalies caused by the sample cup attached to the bubble sensor outflow and to previously-documented limitations in sensor data storage and measurement capability at high bubble flux (Delwiche et al. 2015a). Anecdotally, we did observe that large bubbles entering the sampling cup carried no perceptible particles, whereas smaller bubbles had visible attached particles. Thus we conclude that sediment particle transport rates are likely significantly lower for very large bubbles, but more work is needed to characterize transport rates for the range of bubble diameters observed in natural aquatic systems.

![Graph](image)

**Figure 6: Bubble-transported particle mass (g/L) versus the average bubble diameter (mm).**

**Implications for arsenic cycling**

Our finding that methane bubbles transport particulate matter over depths of at least 15 m could have important implications for chemical and biological cycles in natural systems. Aquatic sediments are often contaminated with heavy metals and organic pollutants, so bubble particle flotation could resuspend contaminants and thereby increase human exposure to legacy contaminants. Upper Mystic Lake sediments contain high levels of arsenic, and ICP data from
our field samples shows that bubble transported particles contain arsenic at an average ratio of 100 µg/kg particle, and 8 µg arsenic per liter of gas bubbled (Figure 7). Bubble column arsenic data showed similar ratios of particulate matter arsenic to sediment (Figure S1), and the pH effect on arsenic transport appeared to be insignificant (though more information may be needed, see Supplemental Information for more details). Given the average daily gas flux of 45 mL/m²/day estimated in a 2016 field campaign for this general sampling area, this corresponds to an estimated arsenic flux of 0.005 µmol/m²/day. This estimate likely represents the high end of transport, because as discussed earlier the bubble-particle transport rates in the field may have been artificially enhanced by the anchor disturbing the sediments.

Figure 7: Arsenic, chromium, and lead mass (in µg) transported versus the volume of each sample (in mL, as measured at the lake surface). Error bars represent standard deviation and are mostly smaller than marker size.

This estimate of expected daily arsenic flux can be compared with historical measurements of arsenic cycling in Upper Mystic Lake. In 2000, Knauer et al. 2000 measured
approximate arsenic accumulations on the order of 0.5 µmol/m²/day in the epilimnion of Upper Mystic Lake. This flux is two orders of magnitude larger than our estimate for bubble transported arsenic of 0.005 µmol/m²/day, indicating that bubble-arsenic transport may not be a major contributor to total arsenic input to the epilimnion of Upper Mystic Lake. However, a significant fraction of the As input to the epilimnetic waters of UML may be due to inflow from the Aberjona River, estimated at 92 kg arsenic/year by Hemond 1995 (though this amount has likely decreased due to ongoing remediation activities upstream from the lake). Similar flux of bubble transported arsenic may therefore represent a larger fraction of epilimnetic input in other lakes. In addition, arsenic-containing particles transported by bubbles are deposited directly at the water surface, which makes it particularly susceptible to direct ingestion by swimmers. The World Health Organization limits for arsenic in drinking water is 10 µg/L, and at the average human water intake of 2.7-3.7 L/day (Dietary reference intakes for water, potassium, sodium, chloride, and sulfate, 2004) this corresponds to a daily arsenic intake of 27-37 µg. In this context, the bubble-transported arsenic flux of 0.4 µg/m²/day is still quite small. This indicates that for Upper Mystic Lake, bubble-facilitated arsenic transport likely does not contribute significantly to total arsenic cycling or to concerning human exposure.

In addition, although bubble-facilitated transport does not appear to dominate arsenic transport in Upper Mystic Lake, much higher ebullition rates have been reported elsewhere in the world. Numerous hydropower reservoirs have been found to experience at least an order of magnitude more methane ebullition than we measure at Upper Mystic Lake (Deemer et al. 2016). Co-occurrence of high ebullition rates and contaminated sediment could lead to significant bubble-facilitated contaminant cycling, and future efforts should be made to quantify contaminant transport rates in contaminated, high bubble flux reservoirs.
Implications for organism cycling

In addition to transporting chemical contaminants, bubbles may also transport organisms (or pathogens) directly from the sediment to the water surface, potentially introducing a novel component to aquatic life cycles. For example, our field and laboratory particulate matter samples contained many small black spheroids on the order of 0.5mm in diameter. Microscopic images of these objects (Figure 8) indicate that they are likely ephippia, the protective cases on diapausing eggs produced by zooplankton such as Daphnia. Ephippia can overwinter in lake sediments or survive periods of desiccation, providing a seed bank to recolonize the water column when favorable conditions return (Hairston 1996, Caceres and Tessier 1998). Diapause termination cues often include physical stimuli such as temperature and photoperiod changes, and more work needs to be done to determine if biological cues (ie: food abundance) also play a role (Gyllström and Hansson 2004).

Figure 8: Microscopic image of potential Daphnia ephippia found in bubble-transported particulate matter. Scale bar is 400 µm.
While the cues that trigger egg hatching from ephippia vary between (and potentially among) species and are not fully understood, it is reasonable to assume that the warmth and light at the top of the lake could provide a favorable hatching environment for ephippia previously stored in the dark, cold, anoxic sediments of the hypolimnia. Bubble transport may therefore provide a previously-unstudied mechanism for diapausing eggs to hatch and contribute to zooplankton growth in the water column. Additionally, we note that a variety of organisms overwinter in lake sediments. For example, the potentially toxic cyanobacterium *Microcystis* can be found in large amounts in the sediments of some lakes (Verspagen et al. 2004). Modeling efforts have found that the absence of *Microcystis* recruitment from the benthos to the water column could reduce the summer bloom by 50% (Verspagen et al. 2005). Recruitment is thought to largely be a passive process caused by wind-induced resuspension, or bioturbation (Verspagen et al. 2004). Bubble transport of *Microcystis* could represent a novel recruitment pathway, though more work would be needed to determine if bubble transport could significantly contribute to algal blooms. Future work could also address the possibility that sediment resuspension triggered by bubble release (as opposed to direct transport by adsorption to the bubble interface) may recruit organisms or pathogens to the water column.

**CONCLUSIONS**

Bubble-particle transport between the sediment and surface of Upper Mystic Lake is a novel transport pathway capable of moving particulate matter upwards in a stratified water column through which significant movement of sedimentary material would otherwise not be expected. Bubbles appear capable of transporting arsenic-containing sediment particles over depths exceeding 15 m. and do not appreciably shed particles as they rise. While bubble-facilitated arsenic transport in Upper Mystic Lake appears minor from both the perspective of
total arsenic accumulation in the epilimnion and of human exposure, lakes with higher ebullition flux may experience more significant chemical transport. Additionally, since bubbles also appear to transport biological material, studies should focus on whether this represents a meaningful transport pathway to aquatic species.

REFERENCES


SUPPLEMENTAL INFORMATION:

Methane bubbles transport sediment and arsenic to a lake surface

Contaminant ratios in bubble column particulate matter and sediment

Ratios of arsenic and chromium to total mass of bubble-transported particulate matter are in line with ratios found in the sediment, while lead levels are lower in the bulk sediment sample (Figure S1). The differences for lead may be because sediment used in the bubble columns was acquired during a different sampling campaign than the sediment used for the digestion. Additionally, Figure S1 shows results for the two scavenged particle samples. Neither sample contained chromium, one sample had arsenic at levels consistent with regular column samples, and both samples had high lead concentrations. The different scavenging rates among contaminants are quite interesting, and suggest that lead, chromium, and arsenic may be associated with particles having different affinities for bubble scavenging. More work should be done to understand contaminant distribution among sediment particulate matter and how this affects transport.
Figure S1: Comparing mass of arsenic, chromium, and lead per kg of particulate matter for laboratory experiments (large bubble column, small column with pH = 8, small column with pH = 6.5) and bulk sediment. Data from trials with the same water pH are lumped together. Open triangles are ratios measured in sediment sample. Open squares are from samples where gas was emitted directly above the sediment and particulate matter was therefore scavenged from the water column. Error bars representing standard deviations are of same approximate size as symbols, and are therefore omitted for clarity.

Arsenic transport in bubble columns

The amount of transported arsenic in the bubble column was independent of bubble release depth (Figure S2), and reflects trends observed in total particulate mass transported with depth (Figure 5 in the main text). Arsenic transport by gas emitted above the sediment rather than into the sediment represented 1% and 12% of arsenic transport from 5m and 10m, respectively. As with particle mass transport, this indicates that the large majority of arsenic in
bubble-transported particulate matter originates in the sediment even in water columns exceeding 15 m depth.

Figure S2: Transported arsenic per L of gas bubbled in the large column, as a function of bubble release depth. Solid triangles represent samples were gas was emitted in to the sediment bed, and diamonds are samples were gas was emitted directly above the sediment bed. Large circles indicate recently mixed sediment conditions. Error bars representing standard deviations are of same approximate size as symbols, and are therefore omitted for clarity.

**pH effect on arsenic transport**

Figure S3 shows the relationship between water pH and bubble-particle transport. The two data sets are statistically equivalent (p>0.05) when considering all values. However, if the data points associated with recently-mixed sediment are excluded, than particle transport at pH
8-8.5 is significantly higher than transport at pH 6.5. Data associated with arsenic transport at different show a similar trend (Figure S3, right panel), with pH having no significant difference except when excluding the recently mixed data points. More work would be needed to determine if these trends continued under repeated sampling, especially since existing literature suggests that particle transport should be lower at higher pH (Shi et al. 2017). We note that after correcting for background concentrations, arsenic transport on particles between 0.2 and 5 µm is negligible, therefore we present arsenic quantities on particles larger than 5 µm.

![Graph](image)

Figure S3: Effect of water pH on total transported particle mass in g/L (left) and arsenic in µg/L (right). Larger black circle around data points indicates recently mixed sediment conditions. Error bars represent standard deviation calculated from ICP data uncertainty.

Supplemental information references
Chapter 6: Summary and future work

SUMMARY

The work presented in these chapters introduces a unique tool to measure methane bubble sizes in situ, increases our understanding of methane bubble emission patterns and dissolution in a freshwater lake, and begins to explore the importance of methane bubble particle transport to contaminant cycling in a lake. Given the importance of methane to global climate change, and the increased recognition that aquatic systems produce significant amounts of methane bubbles, this work represents a meaningful advancement in a critical environmental field.

Bubble size sensor

Methane bubble diameter has a large impact on dissolution rate, which in turn influences the amount of methane entering the Earth’s atmosphere from aquatic systems. Therefore, understanding methane bubble diameter distributions is fundamental to understanding how methane partitions between the water column and the atmosphere. Prior to this work, measuring bubble volumes was resource intensive and only done for short sampling campaigns. The novel optical bubble size sensor we developed makes it more cost effective to measure methane bubble volumes, and for the first time allows us to track methane bubble volumes over long time periods.

The sensor itself is built around an inverted glass funnel that is encased in a waterproof housing. The funnel intercepts rising methane bubbles, and a custom circuit board mounted to the funnel stem uses pairs of LEDs and light detectors and a microprocessor to record timing information associated with each bubble. Timing data combined with channel geometry leads to
accurate bubble volume estimations, and laboratory calibrations further improve the data fit. We also document through extensive laboratory testing the current sensor limitations, including issues related to hardware processing speeds, data storage limitations, data irregularities caused by flow obstructions in the funnel stem, and channel geometry limits that put a lower bound on the detectable bubble size (0.15 cm diameter). Some of these issues could be addressed with future hardware and software improvements, which we will discuss below.

We deployed this sensor in the field with a detachable gas collection chamber, a separate data storage buoy filled with batteries, and an extension funnel to increase the bubble collection area. Four months of data from 8 deployed sensors show that the sensors measure on average 86% of the total ebullition volume passing through the sensor (see Figure 12 in Chapter 2). Given the complexity of field systems and the inherent difficulty with long-term underwater deployments (ie: algae build-up), the sensors perform well and are a valuable addition to bubble volume measurement techniques.

**Ebullition patterns and bubble dissolution**

We deployed eight bubble size sensors at two depths within Upper Mystic Lake near Boston, MA for four months. Collecting bubble size data at two depths allowed us to track the change in bubble diameter distribution between 16 m and the lake surface. We compared this diameter evolution with model results from a popular existing bubble dissolution model, and found that the model adequately predicts our recorded change in bubble diameter. We then used the data, coupled with dissolved methane profiles taken over the course of the season, to estimate that dissolving bubbles contribute approximately 10% of the total dissolved methane.
accumulation in the hypolimnion of Upper Mystic Lake. Dissolving bubbles also represent at most 15% of the diffusive air-water methane flux from the epilimnion of Upper Mystic Lake.

Bubble diameter distributions measured over the course of the season did not appear to change from summer to fall, but there was spatial variability. Two sensors deployed at the northern most extent of the sampling area experienced substantially less ebullition and much larger bubble diameters, pointing to relatively large variability in the ebullition process on the scale of tens of meters within the lake. The other six sensors experienced similar flux, but bubble diameter distributions were still statistically different which indicates that localized sediment conditions are also important in controlling bubble diameter.

**Bubble particle transport**

Bubbles effectively scavenge and transport particles in water columns, a process that has been used extensively in industry since the 1900s to separate chemicals of interest from bulk solutions. While bubbles have also been found to transport particulate matter in marine systems, to date very little work has focused on the possibility of methane bubble particle transport in freshwater systems. Anecdotally, we routinely see that bubbles bursting on the surface of Upper Mystic Lake leave a visible ring of particles, and this observation led us to study methane bubble particle transport. We used a modified bubble size sensor to sample bubbles and their associated particles in Upper Mystic Lake, and found a linear relationship between total bubble volume and mass of associated particles. Particulate matter concentrations of arsenic, chromium, and lead, as well as microscope images strongly indicated that the particulate matter originated in the sediment, even in water depths exceeding 15 m deep. We
therefore conclude that bubbles transport particles upwards through portions of a stratified water column that would not otherwise exchange material.

This sediment particle transport could have important implications for chemical cycling in natural systems, particularly in systems with contaminated sediments. Since Upper Mystic Lake sediments are contaminated with arsenic due to historical upstream chemical manufacturing facilities, we estimated the arsenic cycling due to methane bubbling. We found that potential arsenic transport was two orders of magnitude lower than previously-reported arsenic accumulations in the epilimnion of the lake. While bubble-facilitated arsenic cycling may be minor at the ebullition levels typical for Upper Mystic Lake, many lakes and reservoirs are known to experience an order of magnitude more ebullition. Therefore, there remains a need to study bubble-particle transport in systems with high flux and contaminated sediments. Additionally, bubbles may be transporting organisms or pathogens from the sediment to the surface, and the importance of this potential transport to aquatic life cycles should be studied.

**FUTURE WORK**

Our field work showed that in general, the bubble size sensors accurately measure methane bubble volumes and total cumulative fluxes passing through the sensor. However, on several occasions the sensors measured flux much lower than the actual flux, and in one case a sensor stopped transmitting data. Future work should focus on improvements to sensor hardware and software that will make them more robust and reliable in the challenging conditions of long-term field deployment. Sensors need to be able to handle lake flora growing in the glass funnel stem, lake fauna crawling or swimming through the funnel, and other heterogeneous conditions inherent to natural systems. These conditions can diminish the
sensor’s ability to detect bubbles, or lead to false detection of non-bubble events. The microprocessor code accommodates some of this variability by continually updating background detection thresholds, but more work could be done to improve these algorithms. These improvements could narrow the gap between sensor-measured gas flux and actual gas flux.

We also envision numerous hardware improvements that would make sensor field deployment less labor intensive. Currently the sensor is powered by rechargeable lithium ion battery packs that must be replaced every 2-4 weeks. Future work could include redesigning the buoy to wirelessly transmit data and adding solar panels to eliminate the need for routine field trips. Sensor circuitry could also be modified to contain a small video camera to film bubble passage through the sensor in field conditions. Such footage may contribute to improving bubble sensing algorithms, and may also shed light on the lake fauna that like to traverse the funnel.

Our work on bubble-particle transport in a lake setting presents many interesting questions for future work:

- How much do particle transport rates vary based on different sediment characteristics?
- Do bubbles emitted naturally from the sediment have similar transport rates to artificially triggered bubbles?
- Over what depth can bubbles transport particles?
- What fraction of bubble-transported particles adhere to the air/water interface at the surface of the lake, and how long do the particles remain here?
- In contaminated water bodies with high ebullition flux, does bubble-facilitated particle transport contribute to significant contaminant accumulation at the water surface?
• Do bubbles transport organisms or pathogens, and could this transport represent a meaningful component of life cycles?

Investigating these questions would undoubtedly lead to more interesting unknowns, and we see this as an exciting area for future work.

**BROADER IMPACTS**

Interest in methane ebullition from aquatic systems continues to grow as improved measurement techniques show that methane ebullition comprises a significant (and potentially growing) component of atmospheric methane. Given the importance of methane to climate change and the overwhelming thread that climate change poses to human civilizations, it is critical that we understand the processes affecting methane ebullition flux to the atmosphere. However, the spatial and temporal heterogeneity of methane ebullition makes it a difficult process to study, and extensive field campaigns are necessary to adequately estimate ebullition flux. Measuring bubble sizes in situ traditionally requires even more equipment than simply measuring total flux, so any improvements to bubble measurement techniques will greatly assist future field efforts. Our simple, economical bubble size sensor provides a valuable tool that will allow researchers to expand the understanding of methane fate and transport in aquatic systems. The sensors have already been deployed in projects spanning three continents, and continue to be used by our colleagues in the methane community. We anticipate that data from ongoing international projects will provide valuable insight into the sediment mechanics of bubble release, and may help improve methods to estimate ebullition rates from aquatic systems. These outputs should increase our ability to accurately predict methane emissions, though many unanswered questions about the fate and transport of methane from aquatic systems will remain.
The particle transport work presented here draws on the established fields of industrial foam flotation and marine particle transport, and applies these well-known bubble transport principles to a new system, freshwater lakes. Given the pervasive extent of sediment contamination and high ebullition flux, we believe there is a possibility that bubble particle transport could contribute meaningfully to chemical or organismal transport. However, much work remains to be done to understand the complexities of particle transport by methane bubbles in natural ecosystems.
APPENDIX

A1: Additional information for sensor functioning and calibration

Sensor functioning details

The LEDs on the sensor circuit board emit infrared light at 940 nm to a phototransistor with peak sensitivity at 940 nm (see table A8-1 for specific part numbers). When the bubble passes in front of the LED, the change in refractive index between the water and the gas cause the light to bend away from the phototransistor. This results in a decrease of light, as can be seen in Figure 3 in Chapter 2.

Calibration curve

The calibration curve presented in Figure 8 of Chapter 4 shows that the sensor can estimate bubble volume very well from 0.02 mL to 1 mL. Assessment below 0.02 mL is less accurate, as shown in Figure A1-1 and discussed below. Sensor performance between 1 mL and 1.8 mL is still reasonable, though noise increases as volumes approach 1.8 mL. Anything beyond 1.8 mL is deemed outside the range of the sensor. The larger the bubble, the higher the buoyancy force, and therefore the faster the acceleration through the funnel stem. The trailing meniscus for bubbles beyond 1.8 mL moves so quickly that the sensor is unable to accurately measure the timing of the meniscus passage, and therefore the variability in volume estimates increases. Bubbles accelerate through the glass funnel stem, presumably because their rise velocity is reduced at the constriction where they first enter the funnel stem, and then buoyancy force causes them to accelerate as they rise past the detectors. By averaging the four volume
estimates we are assuming that this acceleration is linear, but as can be seen in Figure 8 of Chapter 4, this assumption appears to break down as bubble volume increases past 1 mL.

![Calibration Curve](image)

**Figure A1-1:** The lower end of the calibration curve presented in Chapter 4, Figure 8, plotted on a log-log scale. Small volume estimates show the increased variability that arises when bubbles are smaller than the funnel stem diameter.

The fact that the raw sensor estimates are slightly larger than the 1:1 line is likely a function of the fact that the radius of the elongated bubble within the funnel stem is actually smaller than the funnel stem itself due to a thin layer of water film between the bubble and glass tube wall. This film of water helps the bubble move upwards within the funnel stem, and we can plot the potential thickness of this film by calculating the internal bubble radius that would be required to produce the volume over-estimates we see for bubbles from 0.05 to 1 mL (Figure A1-
2). This thickness appears to be around 0.2 mm. Above 1 mL we can no longer use this simple method to estimate film thickness because the flow regime has changed. Below 0.05 mL the water film will be thicker because bubbles do not fill the entire glass stem diameter. We also note that an additional explanation for the deviation from the 1:1 line in the mid-volume range could be that the bubbles do not form exact cylinders, and the top of the bubble in particular is likely to have a curved shape. However, these issues are accounted for with the calibration curve.

![Figure A1-2: Estimated wetted perimeter thickness (cm) between bubble and glass funnel stem, plotted against the bubble volume (mL).](image)

**Calibration curve error estimates**

The calibration curve shown in Figure 8 of Chapter 4 has a small amount of associated error. The curve for bubbles below 1.0 mL is $y = (1.17 \pm 0.009)x + 0.02 \pm 0.0038$ ($r^2 = 0.99$, mean square error = $1.9 \times 10^{-4}$). The curve for bubbles between 1.0 mL and 1.8 mL is $y = (0.45 \pm 0.045)x + 0.73 \pm 0.064$ ($r^2 = 0.93$, mean square error = 0.0012). We can use this uncertainty to
estimate uncertainties in the bubble diameters and cumulative volume sums presented throughout this thesis. We use the error propagation formula generically described as:

\[
V_w = \left( \frac{dw}{dx} \right)^2 V_x + \left( \frac{dw}{dy} \right)^2 V_y + \left( \frac{dw}{dz} \right)^2 V_z
\]

where \( w = x + y + z \) and \( x, y, \) and \( z \) are independent variables (Peters et al. 1974).

When we propagate errors for volume and diameter estimates, we find that standard deviation error bars are smaller than the size of points on data plots.

**Small bubble limitations**

To make the sensor’s performance for small bubbles easier to see, we have included the lower end of the calibration curve shown in Figure 8 of Chapter 4 and plotted it on a log-log plot (Figure A1-1). The multiple volume estimates per bubble are relatively similar down to a bubble volume of 0.02 mL (3.4 mm diameter). For bubbles below 0.01 mL (2.6 mm diameter), bubble volume estimates have much larger variability. We assume this is because these very small bubbles can move horizontally within the funnel stem (which has an inner diameter of 4 mm), and this horizontal movement will increase variability in the sensor measurements. While a smaller diameter tube would likely improve these small-volume estimates, it would also increase the likelihood that particulate matter or living organisms in the lake could obstruct the flow path. We also note that while recent studies have highlighted the importance of microbubbles in methane transport from freshwater lakes (McGinnis et al. 2015), these bubbles have a diameter smaller than 1 mm and are therefore below the lowest reliable detection limit of the sensor.
References


A2: Fine scale temporal spacing for bubbling events

One of the major advantages of the bubble size sensor over other existing techniques to measure ebullition flux is the sensor’s ability to capture fine-scale temporal dynamics for bubbling events. For example, Figure A2-1 shows four separate bubble event clusters (chosen approximately randomly from field data) spanning 5-10 seconds each. For these four clusters, the event begins with the largest bubble, followed by numerous smaller bubbles. This pattern has numerous possible explanations. It could a sign that larger bubbles are necessary to open a conduit in the sediment before smaller bubbles can be released. The pattern could be caused because larger bubbles typically rise faster, thus leading to the largest bubble being measured first. Alternatively, several smaller bubbles could be coalescing to form the larger, leading bubble. While more work would be needed to determine if this pattern persists throughout the bubble diameter data and to explore potential causes, this pattern shows the level of fine-scale information the bubble size sensor is capable of capturing.
Figure A2-1: Close temporal spacing on 4 bubble release clusters. Event clusters span 5-10 seconds, and for these 4 events it appears that the largest bubble in a cluster comes first.
A3: Evidence for phantom midge interference in bubble size sensor

As discussed in Chapter 3, we find evidence in our field data that phantom midges pass through the bubble size sensors. These midges collect at the gas/water interface within the gas collection chamber, and during sampling events we remove them from the traps (see Figure A3-1 for midge image). Sensors also record a lot of “falsestart” data that may be attributed (at least in part) to phantom midge migration through the funnel stem. This migration is a nocturnal event, and for many of the sensors we see an increase in “falsestart” events during night hours (Figure A3-2). Future sensor adaptations could involve creating a zooplankton sensor by adding features such as a camera.

Figure A3-1: Microscope image of phantom midge found in bubble size sensor bulk gas trap (picture is a composite of two separate images).
Figure A3-2: Number of “falsestart” events recorded by each bubble size sensor per hour of day (with hour 0 being 12:00 am). Note the different scales for each y-axis.
A4: Spatial heterogeneity in bubble flux

As discussed in Chapter 5, the bubble size sensor deployment location chosen for the 2016 field campaign was chosen in part to increase the amount of gathered data. Preliminary work during the 2015 and 2016 field season demonstrated that a small portion of the lake tended to have relatively homogeneous and high ebulition rates, and we chose this area for bubble sensor deployment to maximize our data collection. However, this area is not reflective of the broader ebulition heterogeneity across the lake. In 2008, Varadharajan deployed 8 bubble traps across the entire lake, and found average daily ebulition fluxes from 1 to 80 ml/m²/day, with an overall average of 28 ml/m²/day. In contrast, aside from sensor 3, the flux range measured in this work was 15 to 49 ml/m²/day, with an overall average of 38 ml/m²/day. Therefore, estimates of methane accumulation attributable to bubble dissolution are likely an overestimate for the anoxic portions of Upper Mystic Lake. This further highlights the relatively minor contribution of dissolving bubbles to methane accumulation that we discussed in Chapter 5.

We note that fluxes per meter squared were determined by dividing the flux measured by each sensor by the collection funnel surface area of 0.2 m². Since bubbles could have experienced lateral advection during rise, the flux measured by one sensor may reflect flux from a sediment patch some distance away. Fricker and Nepf (2000) estimated that seiche-induced bed velocities were on the order of 1 cm/sec. For a typical bubble rise velocity of 20 cm/sec, this would correspond to a potential lateral bubble displacement of 75 cm over 15 m of bubble rise.

References:


A5: Turkey Hill weather station details

The Turkey Hill weather station used for wind speed estimates in Chapter 5 is a personal weather station reporting weather data through the website www.wunderground.com (weather station identification KMAARLIN21). This site is to the west of Upper Mystic Lake, the northwest of Turkey Hill (peak elevation around 107 m), and the self-reported weather station elevation is 78 m. The weather station appears to be in a residential area, and may be affixed to a residence (the exact station location is not provided). The station is approximately 400 m from the Turkey Hill peak.
A6: 2016 field data (including bulk methane and nitrogen content)

Table A6-1: Sensor ID, gas collected per sampling event, approximate midge count per sampling event, and methane/nitrogen contents in bulk gas.

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<th>Days since previous collection</th>
<th>Methane content (%)</th>
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A7. Isotope data from methane bubble samples

During the summer 2016 sampling campaign we sent a subset of bubble sensor bulk gas samples to the UC Davis Stable Isotope Facility. Results are presented in Table A7-1:

Table A7-1: Carbon 13 isotope readings for bulk gas samples.

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<th>Sensor ID</th>
<th>Sensor Depth (m)</th>
<th>$\delta^{13}$C$_{VPDB}$</th>
<th>Methane Fraction (volume %)</th>
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A8. Bubble sensor supply list

Table A8-1: Parts supplier and product numbers for many of the specific products required to build a complete bubble size sensor and data buoy.

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<th>Supplier</th>
<th>Product #</th>
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<td>McMaster</td>
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<td>Gas collection trap</td>
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<td>Gas collection trap</td>
<td>McMaster</td>
<td>8745K65</td>
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<td>Gas collection trap</td>
<td>McMaster</td>
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<td>McMaster</td>
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<td>McMaster</td>
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<td>Texas Hunter</td>
<td>LFBF</td>
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<td>Male headers</td>
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</table>
A9. Bubble sizer assembly instructions

The following instructions were provided to colleagues deploying bubble sensors that I had sent them:

Assembling Sensor Housing for Deployment

1. Push a glass funnel up through the base of the bubble sensor housing. Remove the housing top and side, leaving just the base. Make sure funnel is inserted as far as possible.
2. Wrap the ~1cm pieces of tubing onto the glass funnel stem. Tubing pieces should be as far apart as the holes in the sensor circuit board, and should be positioned around the center of the funnel stem (several centimeters each from top and bottom).
3. Bolt the sensor circuit board onto the funnel stem using the U-bolts. Make sure the plastic tubing is cushioning the funnel stem both where it touches the U-bolt and where it touches the circuit board. **Make sure circuit board is securely attached to funnel stem.**
4. Re-install the pipe coupling that forms the body of the sensor housing. If necessary, spread a little vacuum grease on to the large O-ring before pushing the pipe coupling on.
5. Put a desiccant pack into the sensor housing.
6. Gently pull the glass funnel downwards until the circuit board is resting against the base of the sensor housing. Take the housing top and **attach the wire clip to the circuit board.** Then push the housing top on to the pipe coupling. Gently maneuver the glass funnel until the funnel stem can be pushed up through the small O-ring in the center of the housing top. (Be careful not to get any vacuum grease on the glass funnel while you are handling it).

Assembling Sensor Attachments for Deployment

1. Use a screw driver to loosen the hose clamp on the outside of the sensor housing. Push the hose clamp downwards until it is a few centimeters from the bottom of the pipe coupling.
2. Place the sensor housing on to the black extension funnel, making sure to match the grooves in the sensor housing with the posts on the funnel.
3. Attach the carabiners to the D-rings (adjusting D-rings to align with the eyehooks on the extension funnel).
4. Loosen the hose clamp again, and now pull the hose clamp up as high as possible until the metal rope is taut – tighten hose clamp.
5. Screw the gas collection chamber on to the top of the sensor housing.
6. Take the set of 3 ropes tied together, and pass one rope through each eye-hook at the top of the gas collection chamber. Tie these ropes to the D-rings. Adjust knots so sensor hangs vertically when suspended from hook.
7. When attaching the data cable to the bulkhead fitting on the sensor, make sure to grease the female fitting (spread enough grease on the female fitting to cover the holes, but no need to force more grease into the holes)
Buoy Instructions

1. Plug the buoy circuit board into the wire clip inside the buoy.
2. Make sure there is a blank SD card in the Micro-SD breakout board.
3. Place one battery pack in each of the 3 grooves on the battery sled. The 2 batteries closest together at the base of the sled should be clipped into the small circuit board designed to put the batteries into parallel (these two batteries MUST have similar voltages!). Wires from this board will then plug into the outer-most clip on the main buoy circuit board. The 3rd battery will plug into the inner clip on the main buoy circuit board.

**Note #1**– Only connect the batteries when the buoy is connected to the data cable! Otherwise it would be easy to short the metal pins, potentially making the batteries explode.

**Note #2**– The two battery packs wired in parallel MUST have similar voltages to prevent battery explosion.
4. Slide the battery sled to the bottom of the buoy. Make sure the buoy contains a desiccant pack.
5. Open the air release valve, push the buoy top on, and close the air release valve.
6. When attaching the data cable to the bulkhead fitting on the buoy, make sure to grease the female fitting (spread enough grease on the female fitting to cover the holes, but no need to force more grease into the holes).

Collecting Data

1. Open the air release valve on the buoy and remove the buoy top.
2. Unplug the batteries.
3. Remove the micro-SD card and replace it with a blank micro-SD card.
4. Replace batteries if needed.
5. Reconnect the batteries and **record the time batteries were reconnected.** (Note - Once the batteries have been reconnected, do not remove the SD card! If card is accidentally removed while the batteries are connected, you must reinsert the SD card and push the small reset button on the Arduino.)
6. Put the top back on the buoy and close the air-release valve.

Downloading Data Manually (if this becomes necessary)

1. Install the Arduino software. I have been using version 1.0.6 and had some issues when I tried updating, so use version 1.0.6: [https://www.arduino.cc/en/Main/OldSoftwareReleases#previous](https://www.arduino.cc/en/Main/OldSoftwareReleases#previous)
3. Disconnect the buoy circuit board from the wire clip, and attach the small circuit board for downloading data.
4. Make sure the double-sided 6-pin piece is in the female header on the circuit board. Push the red FTDI breakout board on to the 6 pins with the top of the board pointing towards the battery clip. Connect the red USB cable to the computer and the FTDI board.
5. Open the Arduino program and make sure the proper serial port is selected under Tools>Serial Port.
6. Open the serial monitor by clicking on the magnifying glass icon in the upper right corner.
7. Make sure baud rate is set to 57600 using the pull down menu in the lower right corner of the serial monitor window.
8. Type any letter in to the command line. This should cause Menu text to appear.
9. To download data, type ‘A’. Cut and paste this data into a .txt file. Then delete data from the sensor by typing ‘X’, then ‘Y’.
A10: Bubble size sensor data processing code

Please contact Kyle Delwiche (k.delwiche@alum.mit.edu) for latest version.

%% MATLAB program to process, filter, and plot data from the bubble size sensor described in Delwiche and Hemond, 2017
% Written by Kyle Delwiche

% Please contact Kyle Delwiche for future code improvements
% (k.delwiche@alum.mit.edu)

% Prior to running this program, upload .csv data file using Matlab's "Import Data" tool. Make sure to:
% - upload .csv files only
% - select Numeric Matrix under "Output Type",
% - under column delimeters/more options choose "treat delimeters as one"
% - start selection at first row of numerical data and not above
% - save file after uploading

%%% ****************** PROCESS DATA ******************

clear all; close all; clc;

****************** Import Data*************************

filename = 'filename'; %CHANGE THIS, file to be processed
exportfilename = 'exportfilename'; %CHANGE THIS, place to save the processed file
prompt = 'Enter time batteries were connected (m/d/yyyy hh:mm:ss AM/PM)' ; %prompt user to input sensor start time and date
StartTime = input(prompt,'s'); %this date will be used to determine calendar date/time of bubble events
StartTime = datenum(StartTime);

a = load(filename); %load data (will load as a structure)
b = struct2cell(a); %convert to cell
Fielddata = cell2mat(b); %convert to matrix

%***********Deal with "falsestart" data structure (future Arduino updates could restructure Falsestart data so this bit is unnecessary)***********
%**********Code could likely be improved to make this faster**********

%**************rearrange data set one row at a time**************
if size(Fielddata,2)>14 %If there is "falsestart" data the matrix will have more than 14 columns
jj=0;

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x = 15; %number of data points for each line of data +1
while sum(isfinite(Fielddata(:,x))) > 0 %continue loop as long as there
    is "falsestart" data remaining
        spacer = 0; %starts off at 0, spacer will accomodate table
        referencing as Fielddata grows
        jj=jj+1;
        while isnan(Fielddata(jj,x)) == 0 %for all rows that extend beyond
            the usual #x-1 values, i.e. rows with falsestartdata

                %split the data matrix into rows above and below the current row
                tofloatable = Fielddata(1:jj-1+spacer,:);
                bottomofetable = Fielddata(jj+spacer+1:end,:);

                %pull apart the current row one "falsestart" section at a time
                middleofetablel =
                    [Fielddata(jj+spacer,1:6),zeros(1,8),NaN*ones(1,(size(Fielddata,2)-(x-1)))];
                % pull out the first "falsestart" data point in the set
                middleofetable2 = [Fielddata(jj+spacer,7:end),NaN*ones(1,6)];
                % tack on NaN's to complete the line
                Fielddata =
                    [topofetable,middleofetablel,middleofetable2;bottomofetable]; %put everything
                together in to table with 1 more row
                spacer = spacer+1;
            end
        end
    Fielddata = Fielddata(:,1:x-1); %remove all columns beyond column x,
    these are full of NaNs)
end
Fielddata(isnan(Fielddata)) = 0; %replace remaining NaN's with zeros, just
in case any NaN's remain

%**************Reformat data structure for multi-bubble
%events****************************************************
%First pull out certain rows in data table
ClockTime = Fielddata(:,1); %Time of event (in msec
since sensor was powered on)
Bubbles = Fielddata(:,2); %# of bubbles in event
Errors = Fielddata(:,3); %error code associated
with bubble event
Det2Startime = Fielddata(:,7); %time (in usec) that
detector 2 saw start of bubble
Det2Endtime = Fielddata(:,9); %time (in usec) that
detector 2 saw end of bubble
Det3Startime = Fielddata(:,11); %time (in usec) that
detector 3 saw start of bubble
Det3Endtime = Fielddata(:,13); %time (in usec) that
detector 3 saw end of bubble

%Add missing data for multi-bubble events (Time, bubble #, and error code
%are only stored for the first bubble in an "event").

for k=1:size(Fielddata,1) %Fielddata_rows

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if ClockTime(k) == 0
    ClockTime(k) = ClockTime(k-1);
    Bubbles(k) = Bubbles(k-1);
    Errors(k) = Errors(k-1);
end
end

index = find(Errors(:)==0);  %Find all bubble events with error code "0"
Errors(index,:) = 9;  %convert these to "9" so I can delete rows
with zeros later on

%Remove all bubble events with incomplete information
combinedtable = horzcat(ClockTime,Bubbles,Errors,Det2StartTime,Det2EndTime,Det3StartTime,Det3EndTime);
combinedtable(any(~combinedtable,2), :) = [];  %remove any row in table
containing a zero. These correspond to events with incomplete info (ie;,
det2endtime' wasn't detected)

%***************Calculate bubble volume
ClockTime = combinedtable(:,1);
Bubbles = combinedtable(:,2);
Errors = combinedtable(:,3);
Det2StartTime = combinedtable(:,4);
Det2EndTime = combinedtable(:,5);
Det3StartTime = combinedtable(:,6);
Det3EndTime = combinedtable(:,7);

StartStart = Det3StartTime - Det2StartTime;  %Time between detectors 2 and
3 each seeing start of bubble (usec)
EndEnd = Det3EndTime - Det2EndTime;  %Time between detectors 2 and
3 each seeing end of bubble (usec)
Det2Time = Det2EndTime - Det2StartTime;  %length of time bubble was in
front of detector 2 (usec)
Det3Time = Det3EndTime - Det3StartTime;  %length of time bubble was in
front of detector 3 (usec)

spacing = 0.5588;  %detector spacing in cm

VelStartStart = spacing./(StartStart./1000000);  %velocity (lower estimate)
in cm/sec
VelEndEnd = spacing./(EndEnd./1000000);  %velocity (upper estimate)
in cm/sec

%Bubble length calculations
Length2StartStart = VelStartStart .* Det2Time/1000000;  %bubble length
    calculated using det2 time and start-start velocity, cm
Length2EndEnd = VelEndEnd .* Det2Time/1000000;
Length3StartStart = VelStartStart .* Det3Time/1000000;
Length3EndEnd = VelEndEnd .* Det3Time/1000000;
AverageLength = (1/4)*(Length2StartStart + Length2EndEnd + Length3StartStart + Length3EndEnd);
%Bubble volume calculations
area = 0.1294; %cross-sectional area of funnel stem, cm^2
Volume2StartStart = Length2StartStart * area; %volume in mL
Volume2EndEnd = Length2EndEnd * area;
Volume3StartStart = Length3StartStart * area;
Volume3EndEnd = Length3EndEnd * area;
AverageVolume = (Volume2StartStart+Volume2EndEnd+Volume3StartStart+Volume3EndEnd)/4;

%Implement calibration curve
smallbub = find(AverageVolume < 1.1); %index of volumes below 1.1mL threshold
bigbub = find(AverageVolume >= 1.1); %index of volumes above 1.1mL threshold

%*****Future code versions may use predict() function with regression model
%output******************************
AverageVolume_Calibrated(smallbub,1) = (AverageVolume(smallbub) - 0.0213)./1.174; %calibration parameters published in Delwiche and Hemond, 2017 (DOI: doi: 10.1002/lom3.10201)
AverageVolume_Calibrated(bigbub,1) = (AverageVolume(bigbub) - .4501)./0.7324; %calibration parameters published in Delwiche and Hemond, 2017 (DOI: doi: 10.1002/lom3.10201)

%*************Calculate Coefficients of Variation for start-start measurements and end-end measurements*************
%*************These will be used later to discard data with high CV values**************
stdevSS = std([Volume2StartStart,Volume3StartStart],0,2);
meanSS = mean([Volume2StartStart,Volume3StartStart],2);
stdevEE = std([Volume2EndEnd,Volume3EndEnd],0,2);
meanEE = mean([Volume2EndEnd,Volume3EndEnd],2);
CV_SS = stdevSS./meanSS;
CV_EE = stdevEE./meanEE;

% Create date in string format
DateTime = StartTime + ClockTime./(1000*60*60*24); %ClockTime values are stored in milliseconds and datenum puts things in terms of dates, so divide ClockTime by # of milliseconds in a day
DateTimeStr = datestr(DateTime);

%Combine data, remove any remaining zeros
data = horzcat(DateTime, ClockTime, Bubbles,Errors,
AverageVolume_Calibrated, CV_SS, CV_EE);
data(data<0)=0; %convert all negative values to 0 (tiny bubbles will have negative volume due to calibration equations)
in = find(any(~data,2)); %index of zero values
data(in, :) = [];
DateTimeStr(in,:) = [];
%Save data
column_header = {'Date', 'Matlab DateTime', 'ClockTime (ms since Arduino started)', 'Bubbles (# bubbles in event)', 'Errors (refer to Delwiche and Hemond 2017 for error codes)', 'AverageVolume_Calibrated (mL)', 'CV_SS', 'CV_EE'};

xlswrite(exportfilename, cellstr(column_header), 'Processed','A1');
xlswrite(exportfilename, cellstr(DateTimeStr), 'Processed','A2');
xlswrite(exportfilename, data, 'Processed','B2'); %export processed data to table.
clearvars -Except data exportfilename

%% ****************************FILTER PROCESSED DATA***************************

%filter according to critera in Delwiche and Hemond, 2017 (DOI: 10.1002/lom3.10201)

ClockTime = data(:,2);
DateTime = data(:,1);
Volume = data(:,5);
Diameter = 20 * ((3 * Volume)./(4*3.1415)).^ (1/3);
CV_SS = data(:,6);
NumBubbles = data(:,3);

DataCompilation = [DateTime, ClockTime, Diameter, Volume, CV_SS, NumBubbles];
CV1 = 0.75; % CV cut off for bubbles smaller than 0.02 mL
CV2 = 0.15; % CV cut off for bubbles between 0.02 and 0.06 mL
CV3 = 0.075; % CV cut off for bubbles between 0.06 and 0.15 mL
CV4 = 0.05; % CV cut off for bubbles larger than 0.15 mL
% CV cut offs presented in Delwiche and Hemond, 2017 (DOI: 10.1002/lom3.10201)

% remove large CVs with variable ranges based on bubble volume
delete_CV1 = find(DataCompilation(:,5) > CV1 & DataCompilation(:,4) < 0.02);
DataCompilation(delete_CV1,:) = []; %remove all rows with CV over 0.75 and volume below 0.02 mls

delete_CV2 = find(DataCompilation(:,5) > CV2 & DataCompilation(:,4) >= 0.02 & DataCompilation(:,4) < 0.06);
DataCompilation(delete_CV2,:) = []; %remove all rows with CV over 0.15 and volume between 0.02 and 0.06 mls

delete_CV3 = find(DataCompilation(:,5) > CV3 & DataCompilation(:,4) >= 0.06 & DataCompilation(:,4) < 0.15);
DataCompilation(delete_CV3,:) = []; %remove all rows with CV over 0.075 and volume between 0.06 and 0.15 mls

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delete_CV4 = find(DataCompilation(:,5) > CV4 & DataCompilation(:,4) >= 0.15);
DataCompilation(delete_CV4,:) = []; %remove all rows with CV over 0.05 and volume over 0.15mL

% Remove bubbles over 1.543mLs
Volume_Cutoff = 1.543; %maximum measured bubble size allowed (corresponds with actual value of 1.8mL, see calibration curve for upper limit)
delete_vol = find(DataCompilation(:,4)>Volume_Cutoff); %index for rows to delete
DataCompilation(delete_vol,:) = []; %remove all rows with volumes larger than volume cutoff

volume_sum = sum(DataCompilation(:,4)) %total bubble volume after filters are applied

column_header = {'DateTime (Matlab format)', 'ClockTime (usec since Arduino started)', 'Diameter (mm)', 'Volume (mL)', 'CV_SS', 'NumBubbles (# bubbles in event)'};
xlswrite(exportfilename, cellstr(column_header), 'Processed and trimmed', 'A');
xlswrite(exportfilename, DataCompilation, 'Processed and trimmed','A2');

% ******** PLOT DATA **********************

%******************** Plot histogram*****************************
figure
hold on
realDiameter = hist(DataCompilation(:,3),bins_for_displaying_diameter_data);
%create histogram of bubble sizes
realDiameter = realDiameter./length(DataCompilation).*100; %convert to frequency percentage
bar(bins_for_displaying_diameter_data,realDiameter,l,'FaceColor',[0.8, 0.8, 0.8])
xlabel('Bubble Diameter(mm)', 'FontSize', fontsize, 'FontName', fontname)
ylabel('Normalized Frequency', 'FontSize', fontsize, 'FontName', fontname)
title('Bubble Size Distribution');
xlim([0,13])
ylim([0,15])
set(gca,'XTick', 0:1:13, 'YTick', 0:5:25);

%********* Plot Time Series*******************************

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subplot(1,2,2)

dates = Data_Compilation(:,1); %dates
diameters = Data_Compilation(:,3); %diameters in mm

scatter(dates, diameters, 15, 'filled', 'MarkerEdgeColor', [0 0 0],
'MarkerFaceColor', [0 0.4 0.9], 'LineWidth', 0.7)
ylabel('Bubble Diameter (mm)', 'FontSize', fontsize, 'FontName', fontname)
datetick('x',15)
title('Bubble Release Timing');
ylim([0,15])
xlim([min(dates) max(dates)]); %set x-axis limit to encompass the whole
data set
A11. Arduino code for bubble size sensor

Please contact Kyle Delwiche (k.delwiche@alum.mit.edu) for latest version.

/****************************************************************************
*********** ********* ********* ********* ********* ********* *********
Title: Bubble Sizing Detector Firmware
Version: 1.1
Date Started: 01 December 2015

Description: This code is the firmware for the bubble size detector

Authors: Schuyler Senft-Grupp (skysg@alum.mit.edu) and Kyle Delwiche
         (k.delwiche@alum.mit.edu)

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         4.0 International License. To view a copy of this license, visit
         http://creativecommons.org/licenses/by-nc-sa/4.0/.

******************************************************************************
****************************************************************************/

/****************************************************************************
*********** ********* ********* ********* ********* ********* *********
*********/
#include <Wire.h> // Arduino library for I2C communications
#include <digitalWriteFast.h>
#include <BubbleDetector.h>
#include <BDStorage.h>

******************************************************************************
*********/
* PIN DECLARATIONS

******************************************************************************
*********/
const uint8_t ledOne = 4; // Detector 1 LED
const uint8_t ledTwo = 3; // Detector 2 LED
const uint8_t ledThree = 2; // Detector 3 LED
const uint8_t detOne = A0; // Detector 1 ADC input
const uint8_t detTwo = A1; // Detector 2 ADC input
const uint8_t detThree = A2; // Detector 3 ADC input

/***************************************************************************/
* GLOBAL CONSTANTS
/***************************************************************************/
const uint8_t LOOKFORSTART = 0;
const uint8_t LOOKFOR_END = 1;
const unsigned long MAX_TIMEOUT = 5000000; // Maximum time allowed for data-collection sequence
const uint16_t MIN_THRESHOLD = 30; // The minimum change in ADC value required to trigger data collection sequence
const uint8_t NOISE_MULTIPLIER = 2; // The amount to multiply the difference between max/min background readings
// for estimate of background noise threshold
const uint16_t BKGD_STORAGE = 1000; // Store every BKGD_STORAGE ADC reading in background readings

/***************************************************************************/
* GLOBAL VARIABLE DECLARATIONS
***************************************************************************/
unsigned long timeOfLastTimeout = 0;
uint8_t numberTimeouts = 0;
uint8_t numberFalsestarts = 0;
const uint8_t MAX_NUM_TIMEOUTS = 3;
const uint8_t MAX_NUM_FALSESTARTS = 3;

unsigned long timeoutClockStart = 0;

// Each of the detectors has a state variable. The detector is always either
// waiting to see the start of a bubble (LOOK_FOR_START) or waiting to see
//the end of a bubble (LOOK_FOR_END).
uint8_t detOneState = LOOK_FOR_START;
uint8_t detTwoState = LOOK_FOR_START;
uint8_t detThreeState = LOOK_FOR_START;

//Structures defined in BubbleDetector.h file
//They store estimates of background readings and noise
eventinfo eventInfo; // A struct to store information about bubble event
bubbledata bData[MAX_NUMBER_BUBBLES]; // An array of structs to store bubble data
backgrounddata detOneBkgd; // A struct with information on detector 1 background
ADC value
backgrounddata detTwoBkgd; // A struct with information on detector 2 background
ADC value
backgrounddata detThreeBkgd; // A struct with information on detector 3 background
ADC value
ADCdata detOneADC; // A struct with information on detector 1 ADC values
during bubble event
ADCdata detTwoADC; // A struct with information on detector 1 ADC values
during bubble event
ADCdata detThreeADC; // A struct with information on detector 1 ADC values
during bubble event
uint8_t detOneNumBubbles; // Number of bubbles Detector 2 sees during a bubbling event
uint8_t detTwoNumBubbles; // Number of bubbles Detector 2 sees during a bubbling event
uint8_t detThreeNumBubbles; // Number of bubbles Detector 3 sees during a bubbling event
uint8_t mostBubblesSeen; // The higher of either detTwoNumBubbles or detThreeNumBubbles
uint16_t bkgdCounter; // Variable to keep track of when to record background ADC reading

/* HELPER VARIABLES - these are generic variables but declaring them here gives better estimate of RAM usage*/

uint16_t adcReading = 0;
uint8_t i; // Used for counting in loops
uint8_t numBubblesInTube; // Used to keep track of number of bubbles in tube at once
uint8_t nextState; // Will either be LOOK_FOR_START or LOOK_FOR_END
uint32_t tempTime;
/***/
/***/

* PERFORM SETUP TASKS

*/

void setup()
{

    // Initialize pins
    pinMode(ledOne, OUTPUT);
    pinMode(ledTwo, OUTPUT);
    pinMode(ledThree, OUTPUT);
    pinMode(detOne, INPUT);
    pinMode(detTwo, INPUT);
    pinMode(detThree, INPUT);

    // uncomment if pin 3 on memory chip is not hard wired to 5V
    // pinMode(13, OUTPUT);
    // digitalWrite(13, HIGH);

    //setup serial for debugging purposes
    Serial.begin(57600);      // Baud communication rate

    analogReference(INTERNAL);    // Use the built-in reference voltage
    InitializeBkgdStructs();     // Initialize background data structs.
    InitializeADCData();       // Initialize ring buffers holding ADC values
    bkgdCounter = 0;             // This counter increments every time detector 1 does not sense a bubble.

    bdstorage.begin();         //this may be necessary to begin storing data on chip if I don't have the serial.print statement below
}

/***
* BEGIN LOOKING FOR BUBBLES
***/

void loop()
{
    // Create loop that checks if a bubble has entered glass tube

}
detOneState = LOOK_FOR_START; // Detector 1 is initially looking for start of bubble

//clear start and end time arrays after each detection event

for(i = 0; i < MAX_NUMBER_BUBBLES; i++){ //ABOUT 100 MICROSECONDS TO COMPLETE
  bData[i].d2stime = 0;
  bData[i].d2sval = 0;
  bData[i].d2etime = 0;
  bData[i].d2eval = 0;
  bData[i].d3stime = 0;
  bData[i].d3sval = 0;
  bData[i].d3etime = 0;
  bData[i].d3eval = 0;
}

while(detOneState == LOOK_FOR_START){ // Before the first bubble enters the tube
  if(Serial.available() > 0){ // Allows for communication between Arduino and computer if connected
    talkToComputer(); // talkToComputer defined below
  }

  //Take ADC reading
  digitalWriteFast(ledOne, HIGH); // Turn on the LED for detector 1

  //Check if it is time to take a background reading and if so turn on the other detector LEDs
  if(bkgdCounter == BKGD_STORAGE){
    digitalWriteFast(ledTwo, HIGH); // Turn on the LED for detector 2
    digitalWriteFast(ledThree, HIGH); // Turn on the LED for detector 3
  }
  //this is a throw away reading that takes ~100 microseconds
  analogRead(detOne);

  delayMicroseconds(200); // Delay necessary to allow photocells to stabilize
tempTime = micros(); // record time the ADC reading is going to be taken
  adcReading = analogRead(detOne); // Read the ADC for detector 1
  UpdateADC(&detOneADC, adcReading);

  // Compare ADC reading to background readings. If sensor determines there is a bubble in the tube, detOneState will switch to LOOK_FOR_END which will break while loop
detOneState = CheckForBubble(&detOneBkgd, detOneADC.totalADC, LOOK_FOR_START);

// If no bubble has been detected (detOneState is still LOOK_FOR_START), check if it is
time to store a background reading
if(bkgdCounter >= BKGD_STORAGE && detOneState == LOOK_FOR_START){

    //Read each detector and update its background value
    UpdateBkgd(&detOneBkgd, adcReading);
    adcReading = analogRead(detTwo);
    UpdateBkgd(&detTwoBkgd, adcReading);
    UpdateADC(&detTwoADC, adcReading);

    adcReading = analogRead(detThree);
    UpdateBkgd(&detThreeBkgd, adcReading);
    UpdateADC(&detThreeADC, adcReading);

    bkgdCounter = 0;                      // Reset background counter
    analogRead(detOne);                   // Throw away reading for detector one

}

bkgdCounter = bkgdCounter + 1;        // Increment background counter
delay(1);                             //this used to be at beginning of while loop, I moved it 160708
to try to increase turn-around time between bubble detection events (ie, if det1 is seeing a bubble
as soon as the arduino finishes storing data and enters this while loop
}

 /*******************************************************************************/
 /******************************************************************************
 * A BUBBLE HAS NOW BEEN DETECTED ENTERING THE GLASS TUBE
 /*******************************************************************************/
numBubblesInTube = 1; // Initially set to 1 because the first bubble has been detected

// Initialize detTwo and detThree state and the number
// of bubbles they've seen
detTwoState = LOOK_FOR_START;
detThreeState = LOOK_FOR_START;
detTwoNumBubbles = 0;
detThreeNumBubbles = 0;
mostBubblesSeen = 0;

// Get the current time so that we know when to timeout the operation of looking for a bubble
timeoutClockStart = micros();
tempTime = timeoutClockStart;

analogRead(detOne); // Throw out 1st ADC reading, it tends to be noisy. (also
// adds a small delay for everything to stabilize)
analogRead(detTwo);
analogRead(detThree);

while ((numBubblesInTube > 0) && (tempTime - timeoutClockStart < MAX_TIMEOUT)) {

    // Take ADC reading from detector 1 to keep track of whether more bubbles enter the tube
    tempTime = micros();
    adcReading = analogRead(detOne); // Read the ADC for detector 1
    UpdateADC(&detOneADC, adcReading); // Update the ADC ring buffer with the new
    // value (keeps the past 3 events)
    nextState = CheckForBubble(&detOneBkgd, detOneADC.totalADC, detOneState); //Use
    the 3-point running average to check if a bubble beginning or end is seen

    // If another bubble is detected, update the number of bubbles in the tube
    if(detOneState == LOOK_FOR_START && nextState == LOOK_FOR_END) {
        numBubblesInTube += 1;
    }

    detOneState = nextState; // Update detector 1 status

    // Take ADC reading from detector 2. At this detector we want to capture both the beginning and
    // end of the bubble
    tempTime = micros(); // Record current time
    adcReading = analogRead(detTwo); // Read the ADC for detector 2
UpdateADC(&detTwoADC, adcReading); // Update the ADC ring buffer with the new value (keeps the past 3 events)
nextState = CheckForBubble(&detTwoBkgd, detTwoADC.totalADC, detTwoState);

// If detector 2 sees the start of a bubble, record the current time
if(detTwoState == LOOK_FOR_START && nextState == LOOK_FOR_END) {
    bData[detTwoNumBubbles].d2stime = tempTime;
    bData[detTwoNumBubbles].d2sval = adcReading;
}

// If detector 2 sees the end of a bubble, record the current time
if(detTwoState == LOOK_FOR_END && nextState == LOOK_FOR_START) {
    bData[detTwoNumBubbles].d2etime = tempTime;
    bData[detTwoNumBubbles].d2eval = adcReading;
    detTwoNumBubbles += 1;      // Increment total number of bubbles detector 2 has seen
}
detTwoState = nextState;   // Update detector 2's status

******************************************************************************
Take a measurement for detector 3.  This is almost the same as detector 2.
******************************************************************************

tempTime = micros();       // Record current time
adcReading = analogRead(detThree);  // Read the ADC for detector 3
UpdateADC(&detThreeADC, adcReading); // Update the ADC ring buffer with the new value (keeps the past 3 events)
nextState = CheckForBubble(&detThreeBkgd, detThreeADC.totalADC, detThreeState);

// If detector 3 sees the start of a bubble, record the current time
if(detThreeState == LOOK_FOR_START && nextState == LOOK_FOR_END) {
    bData[detThreeNumBubbles].d3stime = tempTime;
    bData[detThreeNumBubbles].d3sval = adcReading;
}

// If detector 3 sees the end of a bubble, record the current time
if(detThreeState == LOOK_FOR_END && nextState == LOOK_FOR_START) {
    bData[detThreeNumBubbles].d3etime = tempTime;
    bData[detThreeNumBubbles].d3eval = adcReading;
    detThreeNumBubbles += 1;
    numBubblesInTube -= 1;     // Decrease total number of bubbles in the tube
}
detThreeState = nextState;  // Update detector 3's status
/*******************************************************************************************/
Error checking to make sure we don't overflow the maximum number of bubbles that can be counted
*******************************************************************************************/
if(detTwoNumBubbles == MAX_NUMBER_BUBBLES || detThreeNumBubbles == MAX_NUMBER_BUBBLES){
timeoutClockStart = 0; // This will cause while loop to exit
}

//Code to limit # of timeouts //i think this needs to get moved up into while loop
if ((tempTime - timeoutClockStart > MAX_TIMEOUT)){
if ((tempTime - timeOfLastTimeout) < (MAX_TIMEOUT*2)){
    numberTimeouts++;}
else{
    numberTimeouts = 1;
}
timeOfLastTimeout = tempTime;
}
if(numberTimeouts >= MAX_NUM_TIMEOUTS){
    InitializeBkgdStructs();
    numberTimeouts = 0;
}
*******************************************************************************************/
**********
* STORE DATA
*******************************************************************************************/
**********
//No more bubbles in tube, so save the data we have
//or transmit if in debug mode.

// First turn off all LEDs
// digitalWriteFast(ledOne, LOW);
//digitalWriteFast(ledTwo, LOW);
//digitalWriteFast(ledThree, LOW);

// Keep track of errors
eventInfo.errorVal = 0;

// Error: Sensor timed out before finishing data collection sequence, 00000001
if((tempTime - timeoutClockStart > MAX_TIMEOUT)){

225
eventInfo.errorVal = bdeTIMEOUT;
}
// Error: Neither detector 2 or 3 saw a bubble, 01000000
if(detTwoNumBubbles == 0 && detThreeNumBubbles == 0){
    eventInfo.errorVal = eventInfo.errorVal | bdeFALSESTART;
}

// Error: Detector 1 is still looking for the end of a bubble, 00001000
if(detOneState == LOOK_FOR_END){
    eventInfo.errorVal = eventInfo.errorVal | bdeDET1NOEND;
}

// Error: Detector 2 is still looking for the end of a bubble, 00010000
if(detTwoState == LOOK_FOR_END){
    eventInfo.errorVal = eventInfo.errorVal | bdeDET2NOEND;
}

// Error: Detector 3 is still looking for the end of a bubble, 00100000
if(detThreeState == LOOK_FOR_END){
    eventInfo.errorVal = eventInfo.errorVal | bdeDET3NOEND;
}

// Error: Detector 2 saw more bubbles than detector 3, 00000010
if(detTwoNumBubbles > detThreeNumBubbles){
    eventInfo.errorVal = eventInfo.errorVal | bdeDET2MOREBUBBLES;
}

// Error: Detector 3 saw more bubbles than detector 2, 00000100
if(detTwoNumBubbles < detThreeNumBubbles){
    eventInfo.errorVal = eventInfo.errorVal | bdeDET3MOREBUBBLES;
}

eventInfo.numBubbles = max(detTwoNumBubbles, detThreeNumBubbles); // Maximum number of bubbles seen by detectors 2 and 3
eventInfo.det1avg = detOneBkgd.total/NUM_BKGD_POINTS; // Average background ADC reading for detector 2 during bubble event
eventInfo.det1startval = detOneBkgd.startdetvalue; // ADC value that triggered beginning of detector 2 data collection sequence
eventInfo.det1endval = detOneBkgd.enddetvalue; // ADC value that triggered end of detector 2 data collection sequence
eventInfo.det2avg = detTwoBkgd.total/NUM_BKGD_POINTS; // Average background ADC reading for detector 2 during bubble event
eventInfo.det2startval = detTwoBkgd.startdetvalue; // ADC value that triggered beginning of detector 2 data collection sequence
eventInfo.det2endval = detTwoBkgd.enddetvalue; // ADC value that triggered end of detector 2 data collection sequence
eventInfo.det3avg = detThreeBkgd.total/NUM_BKGD_POINTS; // Average background ADC reading for detector 3 during bubble event

eventInfo.det3startval = detThreeBkgd.startdetvalue; // ADC value that triggered beginning of detector 3 data collection sequence

eventInfo.det3endval = detThreeBkgd.enddetvalue; // ADC value that triggered end of detector 3 data collection sequence

//For debugging purposes, data can be printed while the Arduino is connected to a computer.
//For field deployment, keep this commented out.

// PrintData(); // PrintData() defined BELOW

//Save the data to the EEPROM chip

bdstorage.saveBubbleEvent(&eventInfo, bData); //make sure you printdata first so you can see bubbles 1-4 in groups of 4+ bubbles!

} // end of loop()

**************************************************************************
**********
* CHECK TO SEE IF DETECTOR SEES THE BEGINNING OR END OF A BUBBLE

**************************************************************************/

uint8_t CheckForBubble(backgrounddata* bkgd, uint16_t newValue, uint8_t state){

if(state == LOOKFOR_START){ // While the detector is looking for the start of a bubble
    if(newValue < bkgd->startdetvalue){
        return LOOKFOR_END; // A new bubble has been detected
    }
    else{
        return LOOKFOR_START; // No bubble has been detected
    }
}

else{ // While the detector is looking for the end of a bubble
    if(newValue > bkgd->enddetvalue){
        return LOOKFOR_START; // End of bubble has been detected
    }
    else{
        return LOOKFOR_END; // Detector still looking for end of bubble
    }
}

}
/*******************************************************************************/

**********
* UPDATE MAX, MIN, AND DETECTION VALUE OF THE BACKGROUNDDATA STRUCT

*******************************************************************************/

void UpdateBkgd(backgrounddata * bkgd, uint16_t newValue) {

    // Update the total value
    bkgd->total = bkgd->total - bkgd->rb[bkgd->pos] + newValue;

    // Store the new value
    bkgd->rb[bkgd->pos] = newValue;

    // Update the pos value
    bkgd->pos = bkgd->pos + 1;
    if(bkgd->pos == NUM_BKGD_POINTS) {
        bkgd->pos = 0;
    }

    // Update max/min and total values of ringbuffer
    bkgd->maxvalue = 0;
    bkgd->minvalue = 1024; // Maximum value of 10 bit ADC

    for (uint8_t j = 0; j < NUM_BKGD_POINTS; j++) {
        if(bkgd->rb[j] > bkgd->maxvalue) {
            bkgd->maxvalue = bkgd->rb[j];
        }
        if(bkgd->rb[j] < bkgd->minvalue) {
            bkgd->minvalue = bkgd->rb[j];
        }
    }

    // Pick the more conservative noise threshold
    uint16_t noiseThreshold = max((bkgd->maxvalue - bkgd->minvalue) *
        NOISE_MULTIPLIER,
        MIN_THRESHOLD);

    // If the threshold is greater than the average value, then detection is impossible
    if((bkgd->total/NUM_BKGD_POINTS) < noiseThreshold) {
        //MAYBE THIS ISN'T EVEN NECESSARY ANY MORE........
        bkgd->startdetvalue = 0;
        bkgd->enddetvalue = 1023; // 2^10-1
    } else {
        // Pick the more conservative detection value

228
bkgd->startdetvalue = (bkgd->total/NUM_BKGD_POINTS) - 30;
bkgd->startdetvalue = bkgd->startdetvalue*8;

// The enddetvalue is arbitrarily larger than the startdetvalue by half the noise threshold.
// This should add significant hysteresis so that a bubble is not instantly detected and then
"undetected"
bkgd->enddetvalue = bkgd->total/NUM_BKGD_POINTS - 20;
bkgd->enddetvalue = bkgd->enddetvalue*8;

void UpdateADC(ADCdata * adc, uint16_t newValue){
  // Update the total value
  adc->totalADC = adc->totalADC - adc->rbADC[adc->posADC] + newValue;

  // Store the new value
  adc->rbADC[adc->posADC] = newValue;

  // Update the pos value
  adc->posADC = adc->posADC + 1;
  if(adc->posADC == NUM_ADC_POINTS){
    adc->posADC = 0;
  }
}

/* INITIALIZE THE BACKGROUNDDATA STRUCTS USED IN THE PROGRAM
**************/
void InitializeBkgdStructs(){
  for (i = 0; i < NUM_BKGD_POINTS; i++){
    detOneBkgd.rb[i] = 0;
    detTwoBkgd.rb[i] = 0;
  }
}
detThreeBkgd.rb[i] = 0;
}
detOneBkgd.pos = 0;
detTwoBkgd.pos = 0;
detThreeBkgd.pos = 0;
detOneBkgd.total = 0;  //new addition
detTwoBkgd.total = 0;  //new addition
detThreeBkgd.total = 0;  //new addition
detOneBkgd.startdetvalue = 0;  //new addition
detTwoBkgd.startdetvalue = 0;  //new addition
detThreeBkgd.startdetvalue = 0;  //new addition
//Why don't I initialize the enddetvalue??
UpdateBkgd(&detOneBkgd, 0);
UpdateBkgd(&detTwoBkgd, 0);
UpdateBkgd(&detThreeBkgd, 0);

/**************************
* INITIALIZE THE ADCDATA STRUCTS USED IN THE PROGRAM
***************************/

//This program must be called in setup()
void InitializeADCData(){
  for (i = 0; i < NUM_ADC_POINTS; i++){
    detOneADC.rbADC[i] = 0;
    detTwoADC.rbADC[i] = 0;
    detThreeADC.rbADC[i] = 0;
  }
detOneADC.posADC = 0;
detTwoADC.posADC = 0;
detThreeADC.posADC = 0;
detOneADC.totalADC = 0;  //new addition
detTwoADC.totalADC = 0;  //new addition
detThreeADC.totalADC = 0;  //new addition

  UpdateADC(&detOneADC, 0);
  UpdateADC(&detTwoADC, 0);
  UpdateADC(&detThreeADC, 0);
}

/*****************
* COMMUNICATION BETWEEN ARDUINO AND COMPUTER
**********
void talkToComputer() {
    char c = Serial.read();
    uint32_t startTime = millis();  // initialize startTime which is used to return to logging after
    // a period of inactivity
    boolean talkingToComputer = true;
    Serial.println("Menu");
    Serial.println(bdstorage.getNumRecords();
    Serial.println(" Events Stored");
    bdstorage.resetRead();  // Reset the data read address when entering menu
    Serial.println("A: All  H: Header  N: Next  R: Reset\nX: Delete  E: Exit");
    while(talkingToComputer) {
        if(Serial.available() > 0) {
            c = Serial.read();
            startTime = millis();
        } else if(millis() - startTime > 60000) {  // Go back to logging after minute of inactivity
            c = 'E';  // E to exit the talking to computer state
        } else {
            c = ' ';  //
        }

        if(c == 'A') {  // If user enters 'A', read the data and print to screen
            bdstorage.resetRead();
            uint16_t numR = bdstorage.getNumRecords();
            for (uint16_t t = 0; t < numR; t++) {
                bdstorage.readEvent(&eventInfo, bData);
                PrintData();  // PrintData() defined below
            }
        } else if(c == 'E') {  // If user enters 'E', exit the talking to computer state and return to
            talkingToComputer = false;
        } else if(c == 'H') {  // If user enters 'H', display data column headers
            Serial.println("ms,Bubbles,Error,D2 Back,D2 Det,D2 End,D3 Back,D3 Det,D3 End,D2s,D2val,D2e,d2val,D3s,D3val,D3e,d3val");
        } else if(c == 'N') {  // If user enters 'N', display next line of data
            int r = bdstorage.readEvent(&eventInfo, bData);
            if(r == 0) {
                Serial.println("A: All  H: Header  N: Next  R: Reset\nX: Delete  E: Exit");
            }
        }
    }
}
else{
    Serial.println("End of Data");
}
}
else if(c == 'R'){
    // If user enters 'R', reset N so it displays first line of data
    bdstorage.resetRead();
}
else if (c == 'X'){
    // If user enters 'X', delete all data upon verification
    Serial.println("Delete?(Y/N)"); // Verify user wants to delete all data, Y = yes and N = no
    while(Serial.available() == 0){
    }
    c = Serial.read();
    if(c == 'Y'){
        Serial.print("Deleting...");
        bdstorage.deleteData();
        Serial.println("Done");
    }
}
else if(c == 'W'){
    Serial.print("WrA: ");
    Serial.println(bdstorage.getWrAddr(), HEX);
    Serial.print("StartAddr: ");
    Serial.println(bdstorage.getDataStartAddr(), HEX);
    Serial.print("RdA: ");
    Serial.println(bdstorage.getRdAddr(), HEX);
} //end else if
} //end while
Serial.println("Logging");
} //end talking to computer

RIENDATADATA() defined farther down

/********************************************************************************
**********
* PRINTING DATA TO COMPUTER DURING SERIAL CONNECTION

********************************************************************************
**********/

void PrintData()
{
    Serial.print(eventInfo.eventTime); // Time in microseconds of bubble event
    Serial.print(".");
    Serial.print(eventInfo.numBubbles); // Number of bubbles recorded during bubble event
    Serial.print(".");
    Serial.print(eventInfo.errorVal, BIN); // All error codes associated with bubbling event
    Serial.print(".");
}
Serial.print(eventInfo.det1avg); // Background ADC value for detector 2 at time of bubble event
Serial.print(",");
Serial.print(eventInfo.det2avg); // Background ADC value for detector 2 at time of bubble event
Serial.print(",");
Serial.print(eventInfo.det3avg); // Background ADC value for detector 3 at time of bubble event
Serial.print(",");
for (i = 0; i < eventInfo.numBubbles; i ++){
  if(i > 0)
    Serial.print(",",");
  Serial.print(bData[i].d2stime); // Bubble start time for detector 2
  Serial.print(",");
  Serial.print(bData[i].d2sval); // ADC value that triggers beginning of detector 2 data collection sequence
  Serial.print(",",");  
  Serial.print(bData[i].d2etime); // Bubble end time for detector 2
  Serial.print(",",");  
  Serial.print(bData[i].d2eval); // ADC value that triggers end of detector 2 data collection sequence
  Serial.print(",",");  
  Serial.print(bData[i].d3stime); // Bubble start time for detector 3
  Serial.print(",",");  
  Serial.print(bData[i].d3sval); // ADC value that triggers beginning of detector 3 data collection sequence
  Serial.print(",",");  
  Serial.print(bData[i].d3etime); // Bubble end time for detector 3
  Serial.print(",",");  
  Serial.println(bData[i].d3eval); // ADC value that triggers end of detector 3 data collection sequence

}
A12. Arduino code for data collection buoy

Please contact Kyle Delwiche (k.delwiche@alum.mit.edu) for latest version.

>Title: Bubble Sizing Data Buoy Firmware
Version: 1.1
Date Completed: 17 October 2016

Description: This code is the firmware for the data buoy Arduino that controls the bubble size detector.

Authors: Kyle Delwiche

The portions of this code that put the Arduino to sleep are from Donal Morrissey - 2011.

```c
#include <avr/sleep.h>
#include <avr/power.h>
#include <avr/wdt.h>
#include <SD.h>

#define LED_PIN (13)

volatile int f_wdt=1;
int counter = 1;  //initialize to 1
int X = 2700;    // of watchdog interrupt cycles between data downloading sequence. Each cycle is ~8 seconds, so 2700 cycles = 6 hours

File myFile;     //File we will be storing on SD card
int byteNumber = 1;   //Incoming serial data
char a[9];        //Placeholder array for serial.readBytes to put data in to
int placeHolder = 1;  //Dummy variable making while loop go continuously
int dummyVar = 1;     //Dummy variable making void loop() go continuously
int tempTimeStart;  //A timing variable that will help us break out of while loop when serial.readbytes stops receiving data
int tempTimeEnd;  //A timing variable that will help us break out of while loop when serial.readbytes stops receiving data
int variable = 3;
```
/** Name: ISR(WDT_vect) ***/
ISR(WDT_vect)
{
  if(f_wdt == 0)
  {
    f_wdt=1;
  }
  else
  {
    //Serial.println("WDT Overrun!!");
  }
}

/*/ Name: enterSleep ***/
void enterSleep(void)
{
  setsleepmode(SLEEP_MODE_PWR_SAVE); /* EDIT: could also use SLEEP_MODE_PWR_DOWN for lowest power consumption. */
  sleep_enable();

  /* Now enter sleep mode. */
  sleep_mode();

  /* The program will continue from here after the WDT timeout*/
  sleep_disable(); /* First thing to do is disable sleep. */

  /* Re-enable the peripherals. */
  power_all_enable();
}

/*/ Name: setup ***/
set_names
ttedm/
Returns: Nothing.
Parameters: None.
Description: Setup for the serial comms and the Watch dog timeout.
void setup()
{
  pinMode(13, OUTPUT);

  /***
  *** Setup the WDT ***/
  
  /* Clear the reset flag. */
  MCUSR &= ~(1<<WDRF);

  /* In order to change WDE or the prescaler, we need to
  * set WDCE (This will allow updates for 4 clock cycles).
  */
  WDTCSR |= (1<<WDCE) | (1<<WDE);

  /* set new watchdog timeout prescaler value */
  WDTCSR = 1<<WDP0 | 1<<WDP3; /* 8.0 seconds */

  /* Enable the WD interrupt (note no reset). */
  WDTCSR |= _BV(WDIE);

  pinMode(10, OUTPUT); //Set this up for serial communication
  a[8] = 0;
  Serial.setTimeout(5000); //make serial.readbytes wait 5 seconds before timing out

  delay(7000); //delay 7 seconds every time battery is restarted so the bottom
  arduino has time to initialize. It can't be more than 8 seconds or the watchdog timer runs over.
  SD.begin(4); //Open communication lines with SD card
}

***************************************************************************
***** Name: enterSleep
***** Returns: Nothing.
***** Parameters: None.
***** Description: Main application loop.
***************************************************************************

void loop()
{
  if(f_wdt == 1) //Every 8 seconds the Arduino will wake. Every X wakeups it will toggle the
    LED
  {
    if(counter == X){ //If the Arduino has woken up X number of times, run through data-
                        gathering sequence
      downloadData();
      counter = 1; //reset the counter variable to 1 for sleep cycle code
    }
  else{


counter = counter + 1; //update counter variable
}

/* Don't forget to clear the flag. */
f_wdt = 0;
/* Re-enter sleep mode. */
enterSleep();
else
{
    /* Do nothing. */
}
}

/**************************************************************
* Name:   downloadData
* Returns: Nothing.
* Parameters: None.
* Description: Enters the arduino into sleep mode.
* 
***************************************************************/

void downloadData(void)
{
    while (dummyVar > 0){
        myfile = SD.open("Sensor_Data.txt", FILE_WRITE); //Open a file called "Sensor Data"
        Serial.begin(57600); //set the Baud rate
delay(1000); //Delay necessary because it might take a while for the serial connection to establish
        Serial.print('k'); //Start the Menu function, this could be any letter
tempTimeStart = millis(); //record temporary time
        while(! Serial.available())
            tempTimeEnd = millis(); //record temporary time

        if ((tempTimeEnd - tempTimeStart) > 5000){ //5 seconds of no serial contact has elapsed, re-start while loop by setting dummyVar to 0.
            dummyVar = 0; //causes while loop to end when Serial.readBytes times out
        }
    } //Wait until there is data in the buffer

    while(Serial.available() > 0){ //As long as there is data in the buffer, keep reading data
        Serial.readBytes(a,8); //Read 8 bits of data from the buffer
delay(1); //Add in small delay here in case it takes longer to send over Menu text
myFile.print(a);  //Send data to SD card
}

Serial.print('A');  //Ask bottom Arduino to send first line of data from EEPROM chip

tempTimeStart = millis();  //record temporary time
while(!Serial.available()){
  tempTimeEnd = millis();  //record temporary time

  if ((tempTimeEnd - tempTimeStart) > 1000){  //1 seconds of no serial contact has elapsed, re-start while loop by setting dummyVar to 0.
    dummyVar = 0;  //causes while loop to end when Serial.readBytes times out
  }
  //Wait until there is data in the buffer
}

tempTimeStart = millis();  //record temporary time
while (placeHolder > 0){  //Keep looping until Serial.readBytes doesn't see any more data in buffer
  byteNumber = Serial.readBytes(a,8);  //read 8 bytes at a time
  tempTimeEnd = millis();  //record temporary time

  if ((tempTimeEnd - tempTimeStart) > 10000){  //once it takes Serial.readBytes longer than XX seconds to get more data, exit while loop
    placeHolder = 0;  //causes while loop to end when Serial.readBytes times out
  }
  myFile.print(a);  //Send data to SD card
}

myFile.print("Bytes available on buffer right NOW: ");
myFile.println(Serial.available());  //Make sure no data remains in the buffer

Serial.print('X');  //delete data
Serial.print('Y');  //confirm delition
Serial.print('E');  //exit from logging mode

myFile.close();  //Close file (otherwise it doesn't save properly)

Serial.end();  //Close serial connection
placeHolder = 1;  //reset placeholder to 1
break;  //end the downloadData function once data has been collected
/*****************************If serial connection doesn't establish, restart loop***************************/

myFile.close(); // Close file (otherwise it doesn't save properly)
Serial.end(); // Close serial connection
dummyVar = 1; // reset dummyVar to 1 to enter while loop again, this way Arduino gets another shot at establishing serial connection

}
A13. Arduino library files for bubble size sensor: BDStorage.cpp

Please contact Kyle Delwiche (k.delwiche@alum.mit.edu) for latest version.

/**
 * Authors: Schuyler Senft-Grupp and Kyle Delwiche
 * Version: 1.
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 * ShareAlike 4.0 International License. To view a copy of this license, visit
 * http://creativecommons.org/licenses/by-nc-sa/4.0/.
 **/
#include "BDStorage.h"

BDStorage bdstorage;

// Public methods
uint16_t BDStorage::begin(){
  //Start 12C communication
  Wire.begin();

  //find data
  rdAddr = 0;
  uint8_t val;

  uint8_t prevHasData;
  rdAddr = 0x00020000 - 128;
  Wire.beginTransmission(DEV_ADDR_HIGH);
  Wire.write((uint8_t) (rdAddr >> 8)); //MSB = most significant bits
  Wire.write((uint8_t) (rdAddr & 0xFF));
  Wire.endTransmission();
  val = Read8bit((uint8_t) true);
  if(val == 0xFF)
    prevHasData = 0;
  else
    prevHasData = 1;

  rdAddr = 0;
  wrAddr = 0xFFFFFFFF;
  dataStartAddr = 0xFFFFFFFF;
  numRecords = 0;

  while(rdAddr < 0x00020000 && (wrAddr == 0xFFFFFFFF || dataStartAddr == 0xFFFFFFFF)){
    if(rdAddr > 0xFFFF){
      Wire.beginTransmission(DEV_ADDR_HIGH);
    }else{
      Wire.beginTransmission(DEV_ADDR_LOW);
    }
    Wire.write((uint8_t)(rdAddr >> 8)); //MSB = most significant bits
    Wire.write((uint8_t)(rdAddr & 0xFF));
  }
Wire.endTransmission();
val = Read8bit((uint8_t) true);
if(prevHasData == 0 && val != 0xFF){
dataStartAddr = rdAddr;
}
if(prevHasData == 1 && val == 0xFF)
wrAddr = rdAddr;
rdAddr += 128;
if(val == 0xFF)
prevHasData = 0;
else{
    numRecords++;
    prevHasData = 1;
}

uint32_t a1, a2, a3;
/**
a1 = analogRead(A6);
a2 = analogRead(A7);
a3 = ((a2 & 0x1) << 16) | ((a1 & 0x1) << 15) | ((a1 & 0x2) << 14) |
   ((a1 & 0x2) << 13) | ((a1 & 0x4) << 12) | ((a2 & 0x4) << 11) | ((a1 & 0x8) <<
10) | ((a1 & 0x8) << 9) ;
/**
if(numRecords == MAX_RECORDS){  //case where memory is full - we
don't know where the actual "start" is.
  //TO DO - look for earliest time stamp
  wrAddr = 0;
  rdAddr = 0;
dataStartAddr = 0;
} else if(numRecords == 0){  //case where there is no data
dataStartAddr = a3;
    //maybe make this a random number
    wrAddr = a3;
    rdAddr = a3;
}/**
else if(wrAddr > dataStartAddr)
numRecords = (wrAddr - dataStartAddr) >> 7;
else
numRecords = ((0x00020000 - dataStartAddr) + wrAddr) >> 7;
/**
return numRecords;
}

uint8_t BDStorage::saveBubbleEvent(struct eventinfo* eventInfo, struct
bubbledata * bdata)
{

  //Check to make sure there is space to write
  if(numRecords >= MAX_RECORDS){
    return 1;
  }

  if(wrAddr > 0xFFFF){
    Wire.beginTransmission(DEV_ADDR_HIGH);
  } else {
    Wire.beginTransmission(DEV_ADDR_LOW);
}
Wire.write((uint8_t) (wrAddr >> 8)); //MSB = most significant bits
Wire.write((uint8_t) (wrAddr & 0xFF)); //LSB = least " "
Write8bit(eventInfo->errorVal);
Write32bit(eventInfo->eventTime);
Write8bit(min(eventInfo->numBubbles, 4));
Write16bit(eventInfo->det2avg);
Write16bit(eventInfo->det2startval);
Write16bit(eventInfo->det2endval);
Write16bit(eventInfo->det3avg);
Write16bit(eventInfo->det3startval);
Write16bit(eventInfo->det3endval);
Write16bit(eventInfo->det3avg);
Write16bit(eventInfo->det3startval);
Write16bit(eventInfo->det3endval);
Wire.endTransmission((uint8_t)true); //do not send a stop signal to the chip
delay(5);
wrAddr += 18;

//total bytes written to chip == 18
//total bytes sent to wire buffer 21
Serial.println(" "); */
for (uint8 t i = 0; i < min(eventInfo->numBubbles, 4); i ++){
    if(wrAddr > 0xFFFF)
        Wire.beginTransmission(DEV_ADDR_HIGH);
    else
        Wire.beginTransmission(DEV_ADDR_LOW);
    Wire.write((uint8_t) (wrAddr >> 8)); //MSB = most significant bits
    Wire.write((uint8_t) (wrAddr & 0xFF)); //LSB = least " "
    Write32bit(bdata[i].d2stime);
    Write16bit(bdata[i].d2sval);
    Write32bit(bdata[i].d2etime);
    Write16bit(bdata[i].d2eval);
    Write32bit(bdata[i].d3stime);
    Write16bit(bdata[i].d3sval);
    Write32bit(bdata[i].d3etime);
    Write16bit(bdata[i].d3eval);
    if(i < min(eventInfo->numBubbles, 4)-1)
        Wire.endTransmission((uint8_t)true);
    else
        Wire.endTransmission((uint8_t)true);
    delay(5);
    wrAddr += 24;
    //24 bytes
}

wrAddr = ((wrAddr >> 7) + 1) << 7;
numRecords += 1;

//wrap the write address around to zero
if(wrAddr >= 0x00020000)
    wrAddr = 0;
if(eventInfo->numBubbles > 4){
    //delay(5); //wait for page to write - can do with polling later
    eventInfo->numBubbles -= 4;
    //save the remaining bubbles on new memory page
    // add something here to manually shift data since fancy method below
doesn't work for some reason.
    for (uint8_t l = 0; l < min(eventInfo->numBubbles, 8); l ++){
        bdata[l].d2stime = bdata[l+4].d2stime;
        bdata[l].d2sval = bdata[l+4].d2sval;
        bdata[l].d2etime = bdata[l+4].d2etime;
        bdata[l].d2eval = bdata[l+4].d2eval;
        bdata[l].d3stime = bdata[l+4].d3stime;
        bdata[l].d3sval = bdata[l+4].d3sval;
        bdata[l].d3etime = bdata[l+4].d3etime;
        bdata[l].d3eval = bdata[l+4].d3eval;
    }
    saveBubbleEvent(eventInfo, bdata);
    //saveBubbleEvent(eventInfo, bdata+sizeof(bubbledata)*4);
}
return 0;
}

uint8_t BDStorage::readEvent(struct eventinfo* eventInfo, struct bubbledata * bdata){
    if(wrAddr > dataStartAddr)
    {
        if(rdAddr >= wrAddr)
        {
            return 1;
        }
    }
    else{
        if(rdAddr < dataStartAddr && rdAddr >=wrAddr)
        {
            return 2;
        }
    }
    if(rdAddr > 0xFFFF){
        Wire.beginTransmission(DEV_ADDR_HIGH);
    }else{
        Wire.beginTransmission(DEV_ADDR_LOW);
    }
    Wire.write((uint8_t) (rdAddr >> 8)); //MSB = most significant bits
    Wire.write((uint8_t) (rdAddr & 0xFF));
    Wire.endTransmission();
    //The value of rdAddr is used (but not changed) in Read_bit()
    //So do not change the value of rdAddr until done
    //reading from this page
    eventInfo->errorVal = Read8bit((uint8_t)false);
    eventInfo->eventTime = Read32bit((uint8_t)false);
    eventInfo->numBubbles = Read8bit((uint8_t)false);
    eventInfo->det2avg = Read16bit((uint8_t)false);
eventInfo->det2startval = Read16bit((uint8_t)false);
eventInfo->det2endval = Read16bit((uint8_t)false);
eventInfo->det3avg = Read16bit((uint8_t)false);
eventInfo->det3startval = Read16bit((uint8_t)false);
eventInfo->det3endval = Read16bit((uint8_t)false);

// Check to make sure we can't overrun memory
if(eventInfo->numBubbles > MAX_NUMBER_BUBBLES){
    eventInfo->numBubbles = 4;
    eventInfo->errorVal = eventInfo->errorVal | bdeMEMORY;
}
for(uint8_t j = 0; j < eventInfo->numBubbles; j++){
    bdata[j].d2stime = Read32bit((uint8_t)false);
    bdata[j].d2sval = Read16bit((uint8_t)false);
    bdata[j].d2etime = Read32bit((uint8_t)false);
    bdata[j].d2eval = Read16bit((uint8_t)false);
    bdata[j].d3stime = Read32bit((uint8_t)false);
    bdata[j].d3sval = Read16bit((uint8_t)false);
    bdata[j].d3etime = Read32bit((uint8_t)false);
    bdata[j].d3eval = Read16bit((uint8_t)false);
}
Read8bit((uint8_t)true); // just do this to send stop bit
rdAddr += 128; // increment read address to next page
// wrap the write address around to zero
if(rdAddr >= 0x00020000){
    rdAddr = 0;
}
return 0;

uint32_t BDStorage::getRdAddr(){
    return rdAddr;
}

uint32_t BDStorage::getWrAddr(){
    return wrAddr;
}

uint32_t BDStorage::getDataStartAddr(){
    return dataStartAddr;
}

uint16_t BDStorage::getNumRecords(){
    return numRecords;
}

void BDStorage::deleteData(){
    uint8_t val;
    rdAddr = 0;
    while(rdAddr < 0x00020000){
        if(rdAddr > 0xFFFF)
            Wire.beginTransmission(DEV_ADDR_HIGH);
        else
            Wire.beginTransmission(DEV_ADDR_LOW);
        // Send data
        Wire.write(val);
        Wire.endTransmission();
    }
}

// More code...
bits

Wire.write((uint8_t) (rdAddr >> 8));  //MSB = most significant bits
Wire.write((uint8_t) (rdAddr & 0xFF));
Wire.endTransmission();
val = Read8bit((uint8_t) true);

if(val != 0xFF){
    if(rdAddr > 0xFFFF)
        Wire.beginTransmission(DEV_ADDR_HIGH);
    else
        Wire.beginTransmission(DEV_ADDR_LOW);
    Wire.write((uint8_t) (rdAddr >> 8));  //MSB = most significant bits
    Wire.write((uint8_t) (rdAddr & 0xFF)); //LSB = least
    Write8bit(0xFF);
    Wire.endTransmission(true);
    delay(5);
}
    rdAddr += 128;
}
dataStartAddr = wrAddr;
numRecords = 0;
}

void BDStorage::resetRead(){
    rdAddr = dataStartAddr;
}

// Private Methods
void BDStorage::Write8bit(uint8_t data)
{
    Wire.write(data);
}

void BDStorage::Write16bit(uint16_t data)
{
    Wire.write(data >> 8);
    Wire.write(data);
}

void BDStorage::Write32bit(uint32_t data)
{
    Wire.write(data >> 24);
    Wire.write(data >> 16);
    Wire.write(data >> 8);
    Wire.write(data);
}

uint8_t BDStorage::Read8bit(uint8_t sendStop)
{
    uint8_t mydata = 0;
    uint8_t bytesReceived = 0;
    uint8_t devAddr;
    if(rdAddr > 0xFFFF)
        devAddr = DEV_ADDR_HIGH;


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else
    devAddr = DEV_ADDR_LOW;
bytesReceived = Wire.requestFrom(devAddr, (uint8_t)1, (sendStop));
while (Wire.available())
{
    mydata = Wire.read();
}  //end of while loop
return mydata;
}

uint16_t BDStorage::Read16bit(uint8_t sendStop)
{
    uint16_t mydata = 0;
    uint8_t bytesReceived = 0;
    uint8_t c = 0;

    uint8_t devAddr;
    if(rdAddr > 0xFFFF)
        devAddr = DEV_ADDR_HIGH;
    else
        devAddr = DEV_ADDR_LOW;

    //read the 2 bytes from eeprom memory
    bytesReceived = Wire.requestFrom(devAddr, (uint8_t)2, sendStop);
    while (Wire.available())
    {
        c = Wire.read();
        mydata = (mydata << 8) + c;
    }  //end of while loop
    return mydata;
}

uint32_t BDStorage::Read32bit(uint8_t sendStop)
{
    uint32_t mydata = 0;
    uint8_t bytesReceived = 0;
    uint8_t c = 0;

    uint8_t devAddr;
    if(rdAddr > 0xFFFF)
        devAddr = DEV_ADDR_HIGH;
    else
        devAddr = DEV_ADDR_LOW;

    //read the 4 bytes from eeprom memory
    bytesReceived = Wire.requestFrom(devAddr, (uint8_t)4, sendStop);
    while (Wire.available())
    {
        c = Wire.read();
        mydata = (mydata << 8) + c;
    }  //end of while loop
    return mydata;
}
A14: Arduino library files for bubble size sensor: BDStorage.h

Please contact Kyle Delwiche (k.delwiche@alum.mit.edu) for latest version.

/**************************************************************************
Author: Schuyler Senft-Grupp
Version: 1.1
License: This work is licensed under the Creative Commons Attribution-NonCommercial-ShareAlike 4.0 International License. To view a copy of this license, visit http://creativecommons.org/licenses/by-nc-sa/4.0/.
**************************************************************************/

#ifndef __BDSTORAGE_H__
#define __BDSTORAGE_H__

#include <stdio.h>
#include "pins_arduino.h"
#include <Wire.h>
#include <BubbleDetector.h>

// constants up here
const uint8_t DEV_ADDR_LOW = 0b01010000; //this is the 7 bit i2C address - the wire library adds in the 8th bit depending on read or write
const uint8_t DEV_ADDR_HIGH = 0b01010100;
const uint8_t EMPTY_PAGE = 0xFF;
const uint16_t MAX_RECORDS = 1024;

class BDStorage{
  public:
    uint16_t begin();
    uint8_t saveBubbleEvent(struct eventinfo* eventInfo, struct bubbledata * bdata);
    uint8_t readEvent(struct eventinfo* eventInfo, struct bubbledata * bdata);
    uint32_t getRdAddr();
    uint32_t getWrAddr();
    uint32_t getDataStartAddr();
    uint16_t getNumRecords();
    void deleteData();
    void resetRead();

  private:
    uint32_t dataStartAddr;
    uint32_t rdAddr;
    uint32_t wrAddr;
    uint16_t numRecords;
    void Write8bit(uint8_t data);

  #if defined(__GNUC__) || defined(__clang__)
    #pragma pack(push, 1)
  #endif

  #if defined(__GNUC__) || defined(__clang__)
    #pragma pack(pop)
  #endif

}
void Write16bit(uint16_t data);
void Write32bit(uint32_t data);
uint8_t Read8bit(uint8_t sendStop);
uint16_t Read16bit(uint8_t sendStop);
uint32_t Read32bit(uint8_t sendStop);

};
extern BDStorage bdstorage;
#endif //__BDSTORAGE_H__
A15: Arduino library files for bubble size sensor: BubbleDetector.h

Please contact Kyle Delwiche at k.delwiche@alum.mit.edu for latest version.

/**
Description: Header file for all constants and definitions for bubble detector code.

Author: Schuyler Senft-Grupp
Version: 1.1
Date: 5/15/2013
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**/

#ifndef __BUBBLE_ONE_DETECTOR__
define __BUBBLE_ONE_DETECTOR__

#include <Arduino.h>

const uint8_t MAX_NUMBER_BUBBLES = 12; // The maximum number of bubbles that can be stored at the same time.
const uint8_t NUM_BKGD_POINTS = 8; // the number of background points to store
const uint8_t NUM_ADC_POINTS = 8; // the number of background points to store

// bde stands for bubble detector error
const uint8_t bdeTIMEOUT = 0b00000001;
const uint8_t bdeDET2MOREBUBBLES = 0b00000010;
const uint8_t bdeDET3MOREBUBBLES = 0b00000100;
const uint8_t bdeDET1NOEND = 0b00001000;
const uint8_t bdeDET2NOEND = 0b00010000;
const uint8_t bdeDET3NOEND = 0b00100000;
const uint8_t bdeFALSESTART = 0b01000000;
const uint8_t bdeMEMORY = 0b10000000;

/****************************
Declare structs to hold background measurements for each sensor
These use continuous ring buffers
*****************************************************************************/

struct backgrounddata{
    uint16_t rb [NUM_BKGD_POINTS]; // ring buffer for data
    uint8_t pos; // pos in the ring buffer - 0 to 7
    uint16_t minvalue; // minimum value in the ring buffer

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uint16_t maxvalue;  //maximum value in the ring buffer
uint32_t total;  //the sum of all values in the ring buffer - divide by NUM_BKGD_POINTS to get avg value
uint16_t startdetvalue;  //the value required to signify a bubble start event
uint16_t enddetvalue;  //the value required to signify a bubble end event

Declare structs to hold ADC measurements for each sensor during a bubble detection event
*****************************************************************************************/
struct ADCdata{
  uint16_t rbADC[NUM_ADC_POINTS];  //ring buffer for data
  uint8_t posADC;  //pos in the ring buffer - 0 to 2
  //uint16_t minvalueADC;  //minimum value in the ring buffer
  //uint16_t maxvalueADC;  //maximum value in the ring buffer
  uint32_t totalADC;  //the sum of all values in the ring buffer - divide by NUM_BKGD_POINTS to get avg value
  //uint16_t startdetvalueADC;  //the value required to signify a bubble start event
  //uint16_t enddetvalueADC;  //the value required to signify a bubble end event
};

declare structs to hold event information
*****************************************************************************************/
struct eventinfo{
  uint32_t eventTime;
  uint8_t numBubbles;
  uint8_t errorVal;
  uint16_t det1avg;
  uint16_t det1startval;
  uint16_t det1endval;
  uint16_t det2avg;
  uint16_t det2startval;
  uint16_t det2endval;
  uint16_t det3avg;
  uint16_t det3startval;
  uint16_t det3endval;
};

declare structs to hold bubble information
*****************************************************************************************/
struct bubbledata{
  uint32_t d1stime;


uint16_t d1sval;
uint32_t d1etime;
uint16_t d1eval;
uint32_t d2stime;
uint16_t d2sval;
uint32_t d2etime;
uint16_t d2eval;
uint32_t d3stime;
uint16_t d3sval;
uint32_t d3etime;
uint16_t d3eval;
};

#endif