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Design and Assessment of a Low-Cost, Autonomous, Methane-Ebullition Measurement Apparatus (MEMA)

by

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An undergraduate honors thesis submitted in partial fulfillment of the requirements for the degree of Bachelor of Science in University Honors and Mechanical Engineering.

Thesis Adviser: Dr. Elliott Gall



Portland State University

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ABSTRACT

Water reservoirs are increasingly recognized as a significant anthropogenic source of methane (CH_4) production and emissions, CH_4 being the second most prevalent greenhouse gas (GHG) after CO_2 . The dominant emission pathway for CH_4 in lacustrine environments is ebullition (bubbling). A survey of current ebullition measurement methods reveals a technology gap; the ability to measure ebullition rates and CH_4 content simultaneously and affordably with high temporal and spatial resolution is not currently available. Characterizing and modeling methane ebullition in water reservoirs is key to quantifying lacustrine methane emissions and providing a basis for potential mitigation efforts. This report documents the development and assessment of a Methane Ebullition Measurement Apparatus (MEMA) designed for in-situ, autonomous, ebullition-rate and methane-concentration measurement in lacustrine environments. MEMA is designed to be affordable and easily replicable in-house by environmental research scientists with limited manufacturing resources, emphasizing low per-unit cost for maximum unit replication and spatial coverage. Documentation of the device's build materials, supplier list, physical design, and control code have all been made publicly available to aid in replication efforts.

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1 Introduction

1.1 Methane: The Greenhouse Gas

Methane gas (CH_4), the most abundant greenhouse-gas (GHG) after carbon dioxide, accounts for 16% of all anthropogenic, GHG emissions worldwide [1]. Recent estimates place the Global Warming Potential of CH_4 , its effective warming impact over a hundred year span, at twenty-eight times that of CO_2 [2]. Although CH_4 's short-term, per-pound global-warming impact is arguably worse than carbon dioxide's (CO_2), its manageability is potentially greater— CH_4 's atmospheric lifetime is 12.4 years, compared to CO_2 which, once emitted, can live in the atmosphere for up to 1000 years—meaning that a reduction in CH_4 emissions would more quickly influence the average quantity of GHGs in the atmosphere [3]. This combination of high environmental impact and potential manageability would suggest that sources of CH_4 emissions would be extensively tracked and documented for climate change mitigation purposes, however, there are significant gaps in the measurement and documentation of anthropogenic CH_4 emissions [4]. Annual atmospheric measurements of methane are used to calculate total, global, CH_4 emissions, but there is limited data regarding how and where these emissions are produced locally [5]. Consequently, analysis of the specific mechanisms and sources of CH_4 production is likewise limited, hindering potential mitigation efforts [4].

1.2 Reservoirs as Methane Emitters

One major anthropogenic source of CH_4 emissions that has been given relatively little attention, until recently, is water-reservoirs. Man-made reservoirs are not represented in the current EPA GHG budget [6] or identified as a significant CH_4 emission source in the Intergovernmental Panel on Climate Change's (IPCC) 2014 Assessment report [2].

Despite this fact, natural lakes, wetlands, and man-made reservoirs have been known sites of CH_4 production and emissions for over 20 years [7]. A recent large-scale study of reservoir emissions in the American Northwest, conducted by Washington State University researchers, places their annual CH_4 contributions on par with major agricultural sources such as rice production [8]. The same study conservatively estimated that methane emissions from water reservoirs make up 1.3% of all GHG emissions worldwide.

In lakes and reservoirs, CH_4 is produced by methanogens—microorganisms which thrive in anoxic conditions and produce CH_4 as a byproduct of their metabolism. CH_4 is produced in the sediment layers,

particularly during the summer months, and is primarily emitted via two pathways: *diffusion* of dissolved CH_4 through the water column and across the water-air boundary layer, and via *ebullition* in which gas bubbles in the sediment rise to the water's surface and burst, releasing their contents into the atmosphere. A significant percentage of these lacustrine CH_4 emissions, particularly in shallow waters, occur via the ebullition pathway [9].

Ebullition rates vary seasonally and are highest during the Summer when CH_4 production increases and water levels are reduced. This reduction in water levels is often a result of intentional 'draw-downs' in which the water level is rapidly lowered by reservoir management, reducing the hydrostatic pressure on CH_4 gas trapped in the sediment and triggering ebullition events. These events, lasting as little as two to four weeks in duration, can account for the majority of a reservoir's annual CH_4 emissions [10]. While ebullition generates the majority of reservoir emissions, diffusion studies dominate lacustrine CH_4 emission research [11]; part of this imbalance may be attributed to the relative difficulty of collecting ebullition data.

1.3 Ebullition Measurement Technologies & their Limitations

Emissions via diffusion can be approximated by direct sampling of the dissolved CH_4 content, combined with local wind and temperature data and application of transport theory [12]. The approximation of CH_4 emissions via ebullition is substantially more difficult; lacustrine ebullition events have high spatial and temporal variability that makes emission estimations from infrequent, local sampling an ineffective measurement method [11][12][13][14].

Adding to that challenge is the fact that the chemical composition of the bubbles being emitted is heterogeneous, with CH_4 concentrations ranging from 30 to 80% of bubble volume and Nitrogen and CO_2 making up the rest [12].

There are a number of pre-existing technologies that attempt to measure CH_4 ebullition in lacustrine environments, each with corresponding advantages and limitations (See Table 1). Based on the various capabilities displayed by available technologies, a set of seven major performance criteria were developed to evaluate and compare the desirability of particular measurement devices or methods, including the method developed in this report:

1. Direct measurement of gas volume.
2. Direct measurement of CH_4 concentration.

Table 1: Comparison of CH₄ Ebullition Measurement Methods

Method	Bubble Volume?	CH ₄ Concentration?	Ebullition Rate?	Continuous?	Measurement Area	Device Cost ¹	Labor Cost ²
Acoustic	Yes	No	Yes	No	Large	\$10k+	High
Autonomous Surface Vehicle	Total Vol.	Yes	Yes	Yes	Med.	\$1k+	Med.
Funnel Trap, Passive	Total Vol.	Yes	No	Yes	Small	\$100+	High
Funnel Trap, Active	Total Vol.	Yes	Yes	Yes	Small	\$100+	High
Funnel Trap, Active + ICOS	Total Vol.	Yes	Yes	Yes	Small	\$10k+	Low.
MEMA	Total Vol.	Yes	Yes	Yes	Small	\$100+	Low

¹Where specific pricing was not available, device costs were estimated based off of major component costs and grouped into three brackets– High (+\$10k), Med. (\$1k+), Low (\$100+).

²Labor costs were grouped into three brackets: High (requires active user or post-processing of samples), Medium (requires intermittent user operation), Low (requires neither active user operation nor post-processing of samples).

3. Direct measurement of ebullition rate.
4. Continuous measurement of emissions.
5. Large area of measurement (reducing number of needed devices).
6. Low device cost (cost of single device).
7. Low labor cost (factoring in device deployment cost as well as cost of processing collected samples).

The first three criteria pertain to the kind of data that is collected. There are some devices that claim to be CH₄ ebullition measurement devices which only measure the volume and rate of bubbles emitted from a lake, either via multiple, high-resolution, in-situ devices [15] or from expensive, labor-intensive, larger-area, acoustic scans [16][17][18]. These methods couple models of bubble diffusion with measurements of atmospheric CH₄ concentration at the surface to estimate the concentration of CH₄ in the measured bubbles once they breach [17]. These devices are therefore an incomplete, or at least indirect, method of CH₄ ebullition measurement.

There are other devices which measure CH₄ concentration in addition to bubble volume, such as the passive funnel trap [12] which collects gas from just below the water’s surface and stores it for later manual extraction and processing, or the Varadharajan active funnel trap design [19], which measures bubbling rate in addition to passive gas collection.

Concentration and volume data is a minimum requirement to generate a local ebullition flux estimation for a given reservoir region. Therefore, many CH₄

ebullition studies employ such devices for data collection [10][12][14][20]. Despite their popularity, most funnel trap designs require frequent manual extraction (up to twice a day during high-volume ebullition events) and post-processing of samples via gas chromatography (GC). Some funnel-trap designs are equipped with vent mechanisms, which release built up gas when the trap is full, allowing for extended volume measurement without manual extraction [14], but sacrificing the ability to measure the evacuated gas’ CH₄ concentration.

Ebullition is a spatially-variable emission pathway; CH₄ emission rates may vary greatly between different regions of a lake or reservoir. The usefulness of direct ebullition measurement devices is dependent upon the ability of the researcher to strategically deploy numerous devices for simultaneous data collection [13][14][21]. This need for multiple devices to serve as ‘data points’ for a lacustrine CH₄ emission estimation makes the combined cost of measurement devices and labor a critical experimental constraint. Existing in-situ CH₄ ebullition measurement methods that *do* measure local ebullition rates and CH₄ concentrations simultaneously often employ expensive, high-resolution measurement tools such as Integrated Cavity Output Spectroscopy (ICOS) instruments [22] or portable GC units that process gas samples with an accuracy comparable to their laboratory equivalents and have costs on the order of tens of thousands of dollars³. The high individual cost of such sensor technology limits the number of units that can be deployed simultaneously.

This issue of unit cost vs spatial coverage is bypassed, in part, by Autonomous Surface Vehicle (ASV) devices, such as the Inference or Wivenhoe ASVs [23],

³Measurement equipment estimate prices based on direct quotes from multiple major suppliers.

which are capable of measuring ebullition rates and concentrations across lake transects. These devices are effective at characterizing ebullition rates across large areas and identifying areas of high activity, but are unable to collect detailed data from multiple regions simultaneously and are best complimented by stationary measurement devices in areas of interest. These devices also consume large amounts of energy and are limited by their on-board battery-life, which requires daily chargings, increasing their associated labor costs. [24][23].

There exist additional forms of lacustrine CH₄ flux measurement devices which measure local CH₄ emissions without distinguishing between diffusion and ebullition pathways. Some of these devices possess desirable characteristics, such as low build costs, high accuracy CH₄ concentration measurement, and low maintenance costs [25]. However, their inability to distinguish between ebullition and diffusion limits their ability to be used as a primary source for CH₄ ebullition research.

An additional limitation of existing measurement devices is that there are no low-cost devices (necessary for high-spatial resolution) which measure CH₄ concentration, bubble volume, and ebullition rates concurrently, preventing potential analysis of variable relationships and inhibiting the development of detailed lacustrine CH₄ ebullition models.

1.4 Proposed Methane Ebullition Measurement Apparatus (MEMA)

As has been established, there are a number of pre-existing ebullition measurement methods that meet multiple success criteria, but none meet all of them. It is not uncommon for a CH₄ ebullition researchers to commission or develop their own devices to serve their specific measurement needs, or replicate simple affordable device designs such as the passive funnel trap. A few commercially-available devices have been constructed by sensor design companies for the measurement of CH₄ ebullition [26], but their functionality is limited, and their costs prohibitive, with no product gaining apparent universal popularity as an ebullition measurement device. A survey of CH₄ measurement devices documented in academic journals reveals that authors rarely supply a method for acquiring their devices, or sufficient detail for independent replication, with the exception of the Varadharajan active funnel trap design [19].

This paper proposes an autonomous CH₄ Ebullition Measurement Apparatus (MEMA) designed to measure local CH₄ ebullition rates and concentrations in near-real-time. This design builds upon the Varadharajan

active funnel trap design [19] and seeks to reduce labor costs associated with data collection by automating the CH₄ concentration measurement, eliminating the need for manual CH₄ extraction and costly GC post-processing. The MEMA design also incorporates a venting system, allowing for continuous measurement during high-volume ebullition events. This design seeks to be a feasible and affordable solution for researchers seeking high-temporal-resolution CH₄ ebullition data. During the design phase, material costs and build complexity were reduced as much as possible to increase ease of replication. An accompanying bill of materials, supplier list, design documentation, and control code have all been made publicly available to aid in replication efforts (Appendix A). The MEMA design is functionally unique in that it measures CH₄ concentration and ebullition rate simultaneously, allowing for detailed analysis of the rate-concentration relationship.

2 Methods & Design

2.1 Design Criteria

The initial design criteria for MEMA were informed by discussions with Washington State University Vancouver's (WSUV) Biogeochemistry Laboratory team, headed by Dr. John Harrison, whose ongoing research into methane ebullition in man-made reservoirs serves as a potential application environment for MEMA [10][20]. The Harrison lab employs passive and active funnel traps for the majority of their methane ebullition data collection. Limitations identified in the currently used designs were as follows:

- Lack of paired CH₄-concentration and emission-rate data, preventing the exploration of rate-concentration relationships.
- Lack of automated concentration measurements, requiring additional lab-processing and sample handling.
- Limited gas collection capacity, requiring frequent (daily) sample extractions during high-rate ebullition events.

Identified advantages of the passive and active Varadharajan funnel traps used by the Harrison lab were as follows:

- Low per-unit material cost (<\$300/unit).
- Simple/replicable design (commercially available parts and basic manufacturing processes).
- Long operational period (passive traps may be left to operate indefinitely, active traps remain operational for up to a month without recharging, a suf-

ficiently long monitoring time for a trap that still requires manual extraction).

- High-accuracy, GC concentration measurements from post-processing.

The initial MEMA design sought to resolve the identified limitations of the current CH₄ traps, while retaining the current traps' advantages as much as possible. A set of target requirements were chosen to achieve this goal:

- Automated and simultaneous CH₄ concentration and ebullition rate measurements.
- Infinite gas collection/processing capacity (vent capabilities).
- Low per-unit material cost (\$500/unit).
- Simple/replicable design (commercially available parts and basic manufacturing processes).
- Medium operational period (7 days without recharging).
- Concentration and volume measurements accurate to within $\pm 5\%$ true value (with 95% confidence).

2.2 Material & Component Selection

The primary construction material chosen for the device was PVC. This material was selected for its affordability, machinability, light weight, and its resistance to wear and corrosion in aquatic environments. All fittings, fasteners, wiring, and electronics were selected in standard dimensions and purchased from online retailers who deal in small batch purchases. With the exception of one milled aluminum piece, the only components requiring machine modification were PVC pieces, whose softness permitted all cutting to be performed via readily available hand-tools (drills, saws, and files). All electronics were kept at a breadboard scale, requiring only wire-cutters and a low-budget soldering iron to assemble.

2.2.1 Sensor Selection

Two active sensors are present in MEMA: a differential pressure sensor and a methane concentration sensor. The pressure sensor in MEMA is the same as the pressure transducer and circuit developed for the Varadharajan active funnel trap [19] and serves the same function of measuring the volume of gas in the collection chamber. It's functionality and accuracy for the specific application of ebullition measurement had already been established, and was selected for this reason.

The second sensor is the MQ4 solid-state methane sensor [27]. There are multiple portable methane detection technologies available, primarily optical, microbial,

and solid-state. Optical sensors can operate in high humidity, high concentration environments, but are large and prohibitively expensive (costing thousands of dollars per unit). Microbial sensors are relatively affordable, but are designed for measuring dissolved methane in aqueous environments (not high-humidity gas) and have a low limit of detection of around 100ppm. Solid-state sensors are tolerant to high-humidity environments, are sufficiently precise, and inexpensive (as low as \$5 per element), but also possess a maximum CH₄ detection limit of 10%v. [28]. In ebullition samples from active reservoirs such as Lake Lacamas— one of the Harrison study's primary research reservoirs [10], methane from ebullition samples is regularly recorded in concentrations in excess of 80%. Therefore, the sensor mechanism used needed to be able to tolerate such concentrations as well as maximum relative humidity.

Given that none of the currently available sensor technologies met all the initial requirements, the design of the sensor mechanism needed to accommodate the limitations of one of these sensor technologies. A solid-state, metal-oxide, resistance-based sensor (the MQ4) was selected, as it had the highest concentration tolerance (10% CH₄) and was the most affordable (\$5/unit).

Initially, a relative humidity and temperature sensor was considered, but later dismissed as unnecessary, outside of the calibration process, as the MQ4 sensor signal variability as a function of temperature was within the sensor's noise range for the given temperature variability anticipated in lacustrine sub-surface waters ($\pm 3\text{C}$) and a constant, 100% relative humidity environment [27].

2.3 Dilution Chamber Development

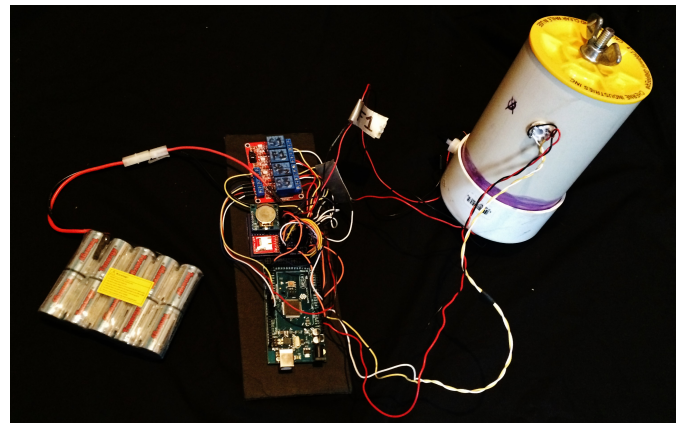


Figure 1: Dilution Chamber Proof-of-Concept Test Setup

To account for the concentration limit of the solid-state sensor, a small dilution chamber was developed (Figure 1), wherein gas samples of known volume are mixed

Table 2: Summary of Initial Dilution Chamber CH₄ Concentration (%v) Calculations and Calibration Results

Initial Dilution Chamber CH ₄ Concentration Calibration							
Injection	CH ₄ Concentration	Base Voltage	Peak Voltage	Rs/R0	Variables and Constants:		
1	0.04%	0.55	0.99	0.500624	Input Voltage (V _{in}):	5	
2	0.08%	0.54	1.37	0.320808	Constant Res. (Ω):	10000	
3	0.12%	0.55	1.52	0.282969	Output Voltage (V _{out}):	variable	
4	0.16%	0.53	2.13	0.159761	Resistance Equation (used to calculate RS and R0 for peak and base voltage):		
5	0.20%	0.52	2.52	0.114229			
Rs/R0:	Resistance at Peak V./ Resistance at Base V.				MQ4(Ω) = (10000Ω*(V _{in} -V _{out}))/V _{out}		
Initial Correlative Function:		Concentration of Methane Gas = -0.001ln(Rs/R0) - 0.0003			R ² = 0.975		

with atmospheric air before being exposed to the MQ4 sensor. The injected sample concentration is determined by measuring the concentration of the diluted gas, then multiplying that concentration by a dilution factor (1) to obtain the original sample concentration value (2).

To ensure that the accuracy of the sensor readings was acceptable (+/-5% true value), given this indirect approach, a preliminary test was performed in a prototype 1-liter test chamber (the final dilution chamber also serves as a self-contained MQ4 sensor calibration environment). The test chamber included a fan, a vent port, an injection port, a MQ4 methane sensor, and an RTH03 Relative humidity and temperature sensor. A range of known concentrations of methane standards, representing a realistic range of methane concentrations (10-100%) were injected in 5mL quantities at an average temperature of 22°C and a relative humidity of 45%. The pre-injection and post-injection sensor voltages (3) were recorded and converted to normalized sensor readings (4) and mapped to their known corresponding CH₄ concentrations (See Table 2).

$$Dilution\ Factor\ (DF) = \frac{Vol_{Chamber}}{Vol_{Gas}} \quad (1)$$

$$\%v\ CH_4 = DF * (Diluted\ \%v\ CH_4) \quad (2)$$

$$\Omega_{sensor} = (\Omega_{constant} * \frac{(V_{in} - V_{out})}{V_{out}}) \quad (3)$$

$$SensorReading(Rs/R0) = \frac{\Omega_{exposed\ sensor}}{\Omega_{baseline\ sensor}} \quad (4)$$

An initial logarithmic relationship between concentration and MQ4 sensor values was found with an R² value of 97.5%. A repeatability test was then performed at a constant sample concentration of 100%, 50%, and 10%, yielding a 95% confidence interval of ±4%. This

placed the sensor's performance within acceptable limits before temperature or humidity variability was factored in. Therefore, the dilution method was determined to be an acceptably accurate mechanism and was included in the MEMA design. A later test confirmed sensor operability at 100% relative humidity.

2.4 Sensor Calibration

Every pressure sensor and methane sensor sensitivity curve is unique to the individual sensor and must be individually calibrated; the following calibration curves represent the behavior of the individual sensors used in the final MEMA prototype and are not to be applied generally.

2.4.1 MQ4 Concentration Curve

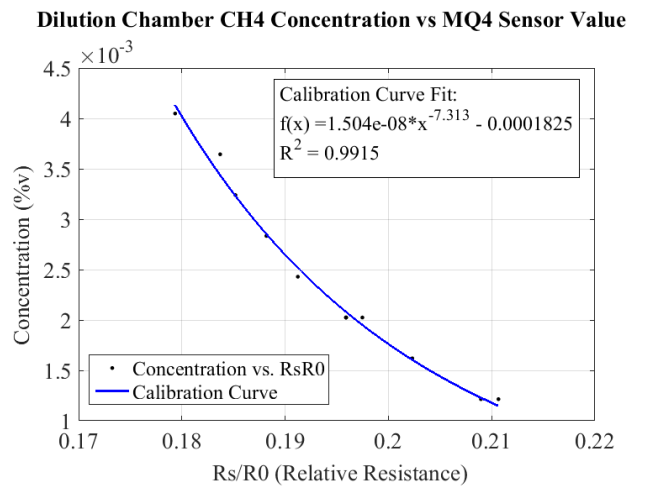


Figure 2: Final MQ4 Sensor to Concentration Calibration

Figure 2 represents true chamber concentration as a function of ten MQ4 Sensor Resistance values. The

maximum true concentration corresponds to a 5ml injection of a 100%v methane standard, while the minimum true concentration corresponds to a 5ml injection of 5% methane standard, representing a realistic range of potential sample concentrations. The resulting power function has an R^2 value of greater than 0.99

2.4.2 MQ4 Repeatability Test

Repeatability tests, in which the same concentration of gas was injected 9 times, were performed at the 10%v, 50%v and 100%v 5ml CH₄ injection concentrations, to determine the noise associated with a constant concentration reading. The 100%v CH₄ repeatability test is shown below in Figure 3:

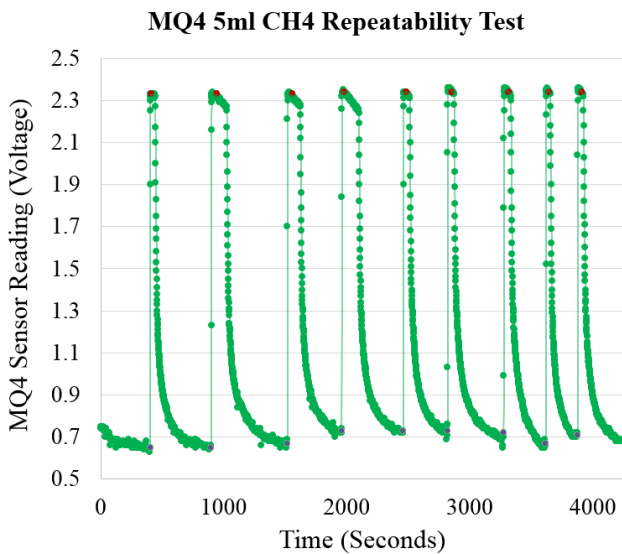


Figure 3: Final 100%v MQ4 5ml Repeatability Test

The maximum standard deviation between final sensor values (4) was found to be 0.0091, which translates to a 4% error in concentration readings, given a confidence of 95%

2.4.3 MQ4 Baseline Drift Test

Baseline drift from a burned-in sensor (MQ4 sensors require 48 hour continuous 'burn-in' operation after extended storage or before initial use to reach a stable base voltage output) is shown in Figure 4.

After running the MQ4 continuously for 48 hours under field conditions, the MEMA logged a positive MQ4 sensor drift at the rate of 0.005 volts an hour, or approximately 0.007% an hour. This continuous running of the MQ4 does not reflect normal run-times of five to

ten minutes and is meant to represent behavior over extended use. To account for this drift, logged sensor values are evaluated against pre-injection baseline values for every concentration measurement. A small change in overall sensor sensitivity should not alter these relative sensor values.

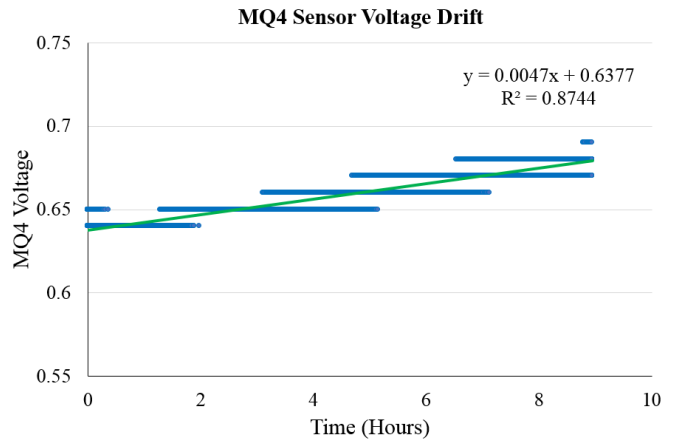


Figure 4: Final MQ4 Drift Test: 10 hour excerpt from Lacomas Field Test

2.4.4 Vent Time after Injection

Figure 5 shows the the change in MQ4 sensor readings during a dilution chamber vent after a methane sample is injected and measured.

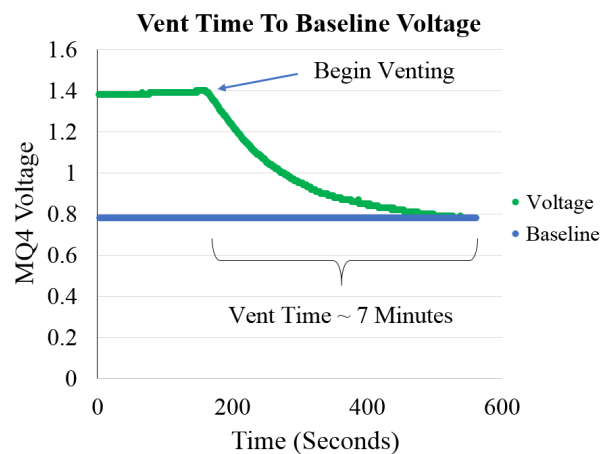


Figure 5: MQ4 Reading Returning to Baseline After Vent

The time required to clear dilution chamber of 5ml of 100% CH₄ gas (maximum sample volume and concentration) and return to baseline after vent process begins is seven minutes. This vent time is the limiting factor in possible concentration measurement frequency.

2.4.5 Varadharajan Pressure Sensor Calibration

The pressure sensor was calibrated using a basic manometer setup, with measurements taken at every inch of water column height, from 2 to 27 inches. This represents the minimum and maximum water displacement height anticipated in the collection chamber at time of concentration measurement. The high pressure sensor accuracy reported in the Varadharajan paper was reflected in this calibration, with a linear fit achieved with an R^2 value of greater than 0.99 (see Figure 6).

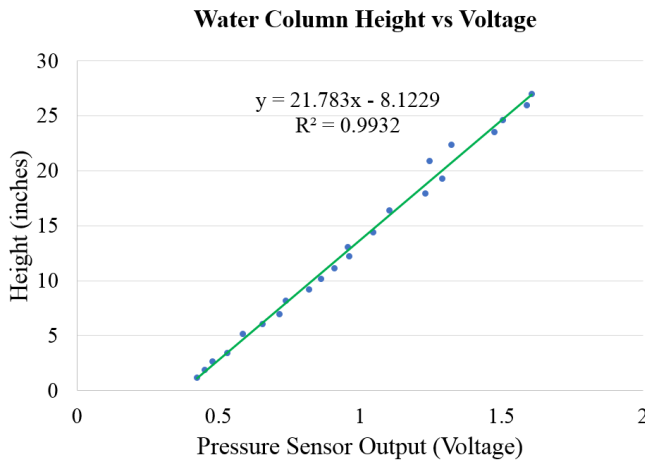


Figure 6: Water Height vs Pressure Voltage Calibration

There are two separate equations to convert from gas column height to total volume, based on the two different tube diameters present in the system. The smaller 3/16" diameter tubing, closest to the dilution chamber, registers smaller changes in volume—beneficial for low ebullition rate situations, while the larger 1/2" diameter pipe allows for up to 75ml of gas to be collected before concentration sampling. A piece-wise function was created to relate pressure reading to volume, taking variable pipe size into account (see Figure 7)

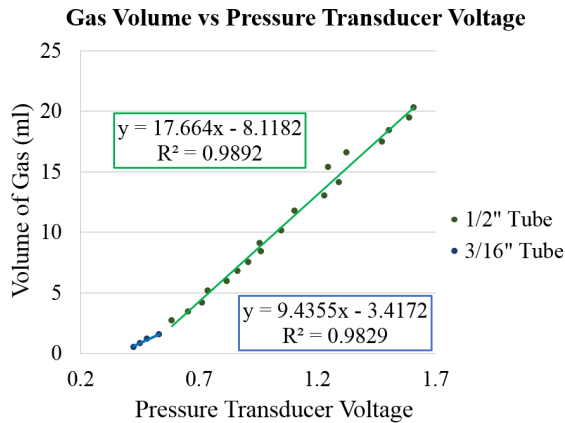


Figure 7: Pressure Voltage to Gas Volume Relationship

There is a 3.5" length of horizontal tubing which connects the pressure sensor to the vertical collection chamber. Gas in this volume is not accurately registered by the pressure sensor as it does not significantly displace water in the vertical direction. This unregistered volume is 1.5mL and defines the lower limit of registerable volume. Once the collected gas fills this gap and the pressure sensor begins to accurately register gas collection, this unmeasured volume can be added to the volume total.

2.5 MEMA Design Iteration 1.0

The initial MEMA design borrowed heavily from the Varadharajan active funnel trap design (see Figure 8). The funnel, PVC collection chamber, differential pressure sensor, and PVC housing design were largely preserved with minor modifications (see Figure 9).

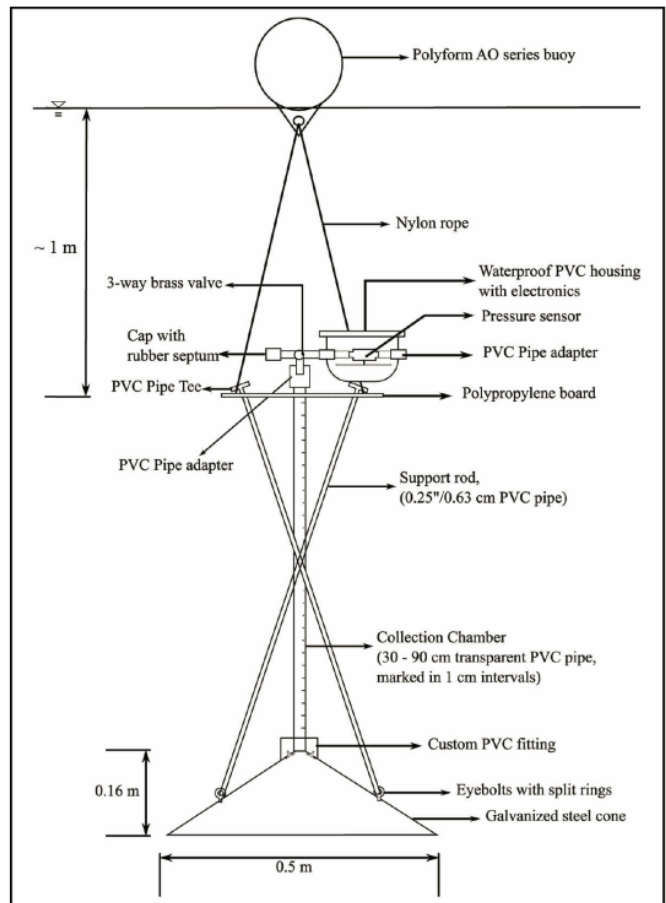


Figure 8: Varadharajan Active Funnel Trap Design (Source: Varadharajan, 2010)

The PVC housing was expanded and modified to accommodate the dilution chamber, its intake and vent valves, as well as an Arduino micro-controller, circuit,

and power-supply. Two additional ports and PVC chimneys were added for air circulation to the inner dilution chamber, along with a floating frame to keep the chimneys above the water's surface.

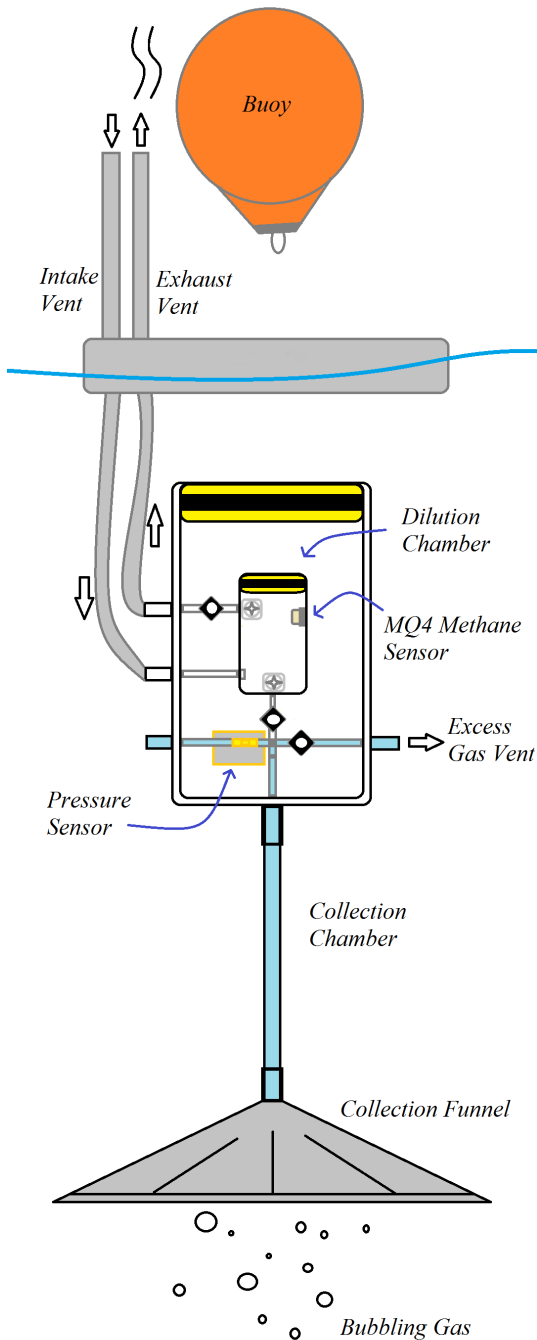


Figure 9: Functional Diagram of MEMA 1.0

The addition of the methane sensor and associated components allows for in-situ measurements of methane concentrations to be paired with real-time ebullition volume and rate data provided by the pres-

sure sensor. The additional exhaust port allows for venting of excess gas in the collection chamber, preventing the trap from filling up during high-rate ebullition events.

2.5.1 MEMA Operational Cycle

The control hardware of MEMA consists of a user-programmable Arduino MEGA microcontroller, an SD card writer for data storage, a real-time clock with an independent battery supply to ensure reliable time-stamping, a series of four 12V power relays for the solenoids and fans, and two NiMH 12V 4200mAh rechargeable batteries connected in parallel and configured to allow for additional batteries to be added for increased operation time. Hookups and programming are also included for the optional addition of a relative temperature and humidity sensor, should the user be operating in more extreme environments and desire additional factors to correct for sensor drift due to environmental variances.

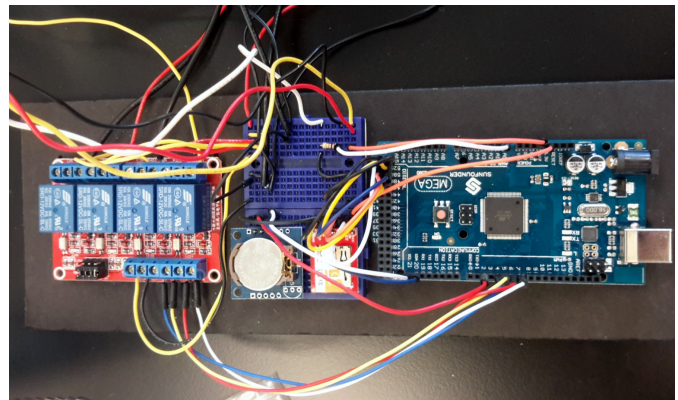


Figure 10: MEMA 1.0 Controls

The device is controlled by an Arduino code designed to be easily modifiable by the user to allow for changes in concentration measurement frequency based on desired data resolution versus operation time (a common trade-off).

An example operation cycle is as follows:

1. MEMA is turned on.
2. Excess gas vent is opened for 15 minutes to allow for deployment of MEMA and flushing of collection chamber.
3. Evacuation vent is closed and pressure measurement baseline is recorded. Pressure measurements begin to be recorded.
4. Waits for critical volume of gas (10ml, or other defined by user) to be collected by funnel (as determined by offset from pressure sensor baseline and pressure calibration curve 6).

5. Intake fan turns on, MQ4 sensor turns on.
6. Wait 90 seconds to 5 minutes (warm-up time for sensor scaled to a time since last concentration measurement: 10 minutes to 2+ hours)
7. Check for stable MQ4 reading (± 0.02 Volts/second), store unique baseline MQ4 reading once stable.
8. Re-measure initial pressure measurement for collected gas and store value (initial volume).
9. Open Gas Injection solenoid to dilution chamber for under 1 second (time user adjustable, regulates injection volume), releasing a portion of collected gas and then close again.
10. Re-measure gas volume collected and store as post-injection pressure value (subtract new value from previous value to verify actual volume of gas injected). Store measured gas volume.
11. Open Excess Gas Vent Solenoid to water for approx. 10 seconds (until pressure sensor reading returns to baseline) to vent excess gas and then close again.
12. Log MQ4 values for 1 minute. Store MQ4 sensor value (maximum value defined at 10 seconds after injection, when dilution chamber is fully mixed) as final sensor reading, along with corresponding pressure value.
13. Turn on Outtake Fan and Air Outtake Solenoid.
14. Wait for MQ4 readings to return to predefined baseline, then turn off (alternatively, to save power, turn off MQ4 immediately and wait 7 minutes – calculated max time to baseline)
15. Turn off Intake and Outtake Fans and Air Solenoid.
16. Repeat from step 3.

This operational loop allows for methane measurements to be taken as long as there is battery power, with a maximum volume sampling rate of one sample a second and a concentration sampling rate of one sample every 15 minutes.

2.5.2 MEMA 1.0 Usability Testing

The intent is for MEMA to be financially and practically feasible for researchers with limited resources to construct. In line with this goal, MEMA must also be feasible to operate with limited resources. MEMA is intended to be deployed from and retrieved using small motor boats occupied by one to two people. To represent a realistic field scenario, MEMA 1.0 was deployed in Lake Lacamas by a single individual off of a narrow dock (see Figure 11).

Based off of this usability test, flaws were identified in the initial design:

- Floating frame makes handling and moving of MEMA as a single unit difficult.
- Inability to orient MEMA upright on land requires large area to store and maneuver device before deployment.
- Retrieval of MEMA difficult due to added weight of collection chamber full of water, generating moment about base of PVC housing chamber during extraction, cracking stiff PVC collection chamber.



Figure 11: MEMA 1.0 Initial Field Test

2.6 MEMA Design Iteration 2.0

Considering the failings of MEMA 1.0, structural changes were made to the device to improve portability, maneuverability, and prevent failure during the retrieval process. Improvements included a soft-plastic collection chamber, support legs for the PVC housing, elimination of the floating frame, and extension of the exhaust chimneys, which were affixed directly to the housing (see Figure 12).



Figure 12: MEMA 2.0

MEMA 2.0 was successfully deployed and extracted under the same conditions as MEMA 1.0, with no mechanical failure or additional challenges noted.

3 Results & Discussion

The MEMA 2.0 volume and concentration measurement subsystems were re-calibrated and tested individually, before being re-integrated into the final assembly and undergoing a full 3-day field test on Lake Lacamas. Low ebullition rates in the field required additional in-lab performance testing to verify functionality of MEMA's methane ebullition measurement capabilities.

3.1 Full-Immersion Validation Testing

Pressure data from field test was collected over the course of 48 hours (see Figure 13). Anticipating high-ebullition rates, critical volume rating was set to 20ml. Critical volume was not reached over the course of 48 hours, so no concentration measurements were taken.

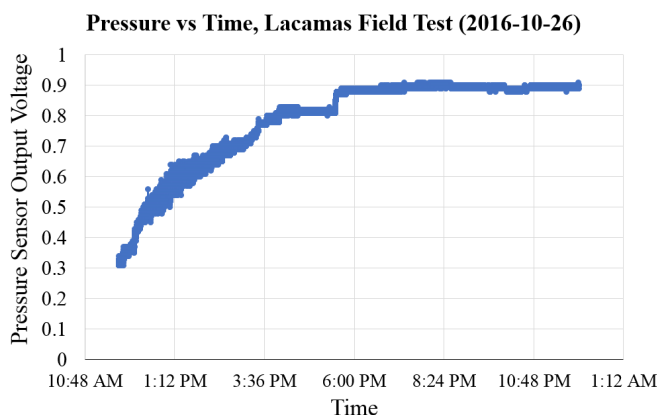


Figure 13: Pressure vs Time Data Collected Over Course of First 12 Hours of Lacamas Field Test

The pressure logs documented low ebullition activity and established the electrical and mechanical functionality of the device after prolonged exposure to field conditions. Figure 14 provides an example of raw data collected during the field test.

V:	0.67 P:	0.88	Time:	7:02:07 PM	Date:	26/10/2016
V:	0.68 P:	0.89	Time:	7:02:09 PM	Date:	26/10/2016
V:	0.68 P:	0.89	Time:	7:02:10 PM	Date:	26/10/2016
V:	0.67 P:	0.89	Time:	7:02:11 PM	Date:	26/10/2016
V:	0.66 P:	0.88	Time:	7:02:12 PM	Date:	26/10/2016
V:	0.67 P:	0.89	Time:	7:02:13 PM	Date:	26/10/2016
V:	0.67 P:	0.89	Time:	7:02:14 PM	Date:	26/10/2016
V:	0.67 P:	0.89	Time:	7:02:15 PM	Date:	26/10/2016
V:	0.68 P:	0.89	Time:	7:02:16 PM	Date:	26/10/2016
V:	0.67 P:	0.89	Time:	7:02:17 PM	Date:	26/10/2016
V:	0.67 P:	0.89	Time:	7:02:18 PM	Date:	26/10/2016
V:	0.68 P:	0.89	Time:	7:02:19 PM	Date:	26/10/2016
V:	0.67 P:	0.89	Time:	7:02:20 PM	Date:	26/10/2016
V:	0.67 P:	0.89	Time:	7:02:21 PM	Date:	26/10/2016
V:	0.67 P:	0.89	Time:	7:02:22 PM	Date:	26/10/2016

Figure 14: Excerpt of Raw Data Logs

Table 3: Summary of Error and Sources

CH4 Concentration Error (Diluted):	Value	Gas Volume Error: (Undiluted):	Value
MQ4 Sensor Noise (95% Conf. Int.):	4%	Pressure Sensor Resolution:	0.21 ml
MQ4 Measurement Resolution:	0.56%	Pressure Sensor Noise:	0.65ml
Solenoid Injection Uncertainty:	0.009 ml	Pressure Model Uncertainty (95% Conf. Int.):	1.1%
Calibration Curve Error (95% Conf. Int.)	1.10%	Total Concentration Test Error (Undiluted, Confidence Interval 95%):	4.44%

During the field test, there was more noise from the pressure sensor than was reflected in lab tests. This noise corresponded to times of more active ebullition and daylight hours. It is suspected that waves and other disturbances are to blame. Pressure values also appeared to spike after an incoming bubble, then settle down to a new pressure baseline. Logging code was modified to delay storing critical pressure values until just after a spike in pressure.

3.2 Error analysis

A number of potential error sources were identified as significant to investigate:

- Pressure Sensor Noise
- Pressure Sensor to Volume Model Uncertainty
- Solenoid Injection Volume Variability
- MQ4 CH₄ Sensor Noise
- MQ4 CH₄ Sensor to Concentration Model Uncertainty

Potential sources of error that were neglected included the following:

- Pressure Sensor Drift (Neglected due to time constraints).
- Pressure Sensor Noise in Varying Environmental Conditions ((Neglected due to time constraints).
- MQ4 CH₄ Sensor Humidity and Temperature Effects (Literature shows these factors may bias system, but do not significantly effect trends or sensitivity, expected device will be calibrated to fit application conditions).
- Atmospheric Methane Content (Sensitivity of MQ4 sensor significantly below required sensitivity for atmospheric CH₄ concentration measurement [27]).
- Changes in dilution chamber volume (unable to quantify).

Random, measurement, and calibration error values, given a confidence interval of 95%, were calculated for both concentration and volume measurements (see Table 3). Errors associated with curve-fit equations scale to the sensor value, while random and measurement error remain constant regardless of sensor value. Therefore, there is not one single theoretical error percentage. Con-

centration measurements possess a constant associated error rate, with a relatively constant injection volume, while error associated with the total gas volume varies with collected gas volume.

To clarify, volume error applies to total gas volume in the collection chamber, not injection volume which is regulated by solenoid timing and further verified by pressure sensor readings. Testing of solenoid injection method yielded consistently repeatable volume injections for a given time setting. Error for injection volume was defined by the precision of measurement, not by an identified inconsistency in values.

Final Tests of the dilution chamber, in which a range of known quantities (5-100%v) of CH₄ were injected into the chamber via the solenoid valve, yielded an average error rate of 4.44%. with a noted bias toward under-estimation of concentrations (confidence interval of 95%). This places the accuracy of the concentration measurement mechanism within the target range of $\pm 5\%$. However, the aggregation of theoretical error sources for concentration measurement suggest the error rate greater than 5% (further analysis and testing needed).

The total gas volume error is a minimum of 1.1%, as defined by the calibration curve, with field tests suggesting a larger noise range than those present in lab conditions (further analysis and testing needed).

3.3 Fulfillment of Design Goals

Of the six design goals established at the beginning of the MEMA design process, four of those goals were met:

- Automated and simultaneous CH₄ concentration and ebullition rate measurements.
- Infinite gas collection/processing capacity.
- Simple/replicable design (commercially available parts and basic manufacturing processes).
- Concentration and volume measurements accurate to within $\pm 5\%$ true value.

The two goals that were not successfully met were as follows:

- Low per-unit material cost (\$500/unit).

Table 4: MEMA 2.0 Performance Overview

CH ₄ Concentration Range and Accuracy	5-100% ±5%
Maximum Volume Measurement Rate	1 Sample/Sec.
Maximum CH ₄ Sampling Rate	1 Sample/ 15 Min.
Volume Measurement Only Battery Life	5 Days
Maximum Sampling Rate Battery Life	48 Hours
Hourly CH ₄ Sampling Battery Life	4 Days
Material Cost	\$823/Unit

- Medium operational period (7 days without recharging).

The final material cost for MEMA is \$823, 323 dollars past the target unit price, though still in the 'Low' price bracket when compared to thousand or ten thousand dollar instruments which are currently available.

The final operational battery time is three days shorter than the target 7 days, but MEMA is equipped to accommodate additional battery packs, so the initial operation time goal could be easily met, but would increase the final material cost of the device.

The high-frequency measurement capabilities of MEMA coupled with its currently limited operational time makes the device best suited to documenting high-rate ebullition events that occur over the course of weeks rather than months.

4 Conclusion

A functional, in-situ, autonomous methane ebullition measurement device was successfully designed and constructed using affordable materials and accessible tools, with field and laboratory tests demonstrating its integrity and accuracy (a summary of MEMA functionality is presented in Table 4).

MEMA constitutes a novel ebullition measurement device, in terms of its dual ebullition-rate and CH₄-concentration measurement capabilities and its relative affordability and replicability. Resources pertaining to MEMA's materials, construction, programming, and data interpretation are all publicly available (Appendix A) to aid in further design replication, improvement, and testing.

4.1 Future Research and Improvements

Further research relating to MEMA should include extended field tests in lakes and/or reservoirs during times of high ebullition rates or drawdown events - to better establish the device's performance under maximum stress and further assess the mechanical integrity of the device over time. Performing such field tests with

a neighboring passive funnel trap or active Varadharajan funnel trap could serve to confirm MEMA concentration and volume measurements. Additionally, in-lab testing should be continued to ensure results are repeatable and consistent over time and a range of temperature and humidity conditions.

The unit cost of MEMA could be reduced through further research into part suppliers, larger batch purchases, or redesigns that sacrifice ease of replication for more affordable initial materials. For example, if a user possessed sufficient understanding of electrical circuits and programming and had access to PCB technology, the control system could be assembled on a single board out of more affordable sub-components, instead of relying on a generic micro-controller (Arduino) and attachments.

MEMA could also be improved if cost was increased. Additions that expand the functionality of MEMA such as solar-power, additional in-line safety valves, and more effective vent fans, for example, could be added at a cost. Additionally, the bulkiness of MEMA could be reduced, and reliability of construction could be increased with the development of custom parts or use of higher-strength materials which require more sophisticated machining techniques. Investing in more expensive, more reliable custom part construction might be of value to researchers that are predominantly interested in the performance of the device and are less concerned with cost constraints.

References

- [1] C. C. D. US EPA, "Global Emissions," 2014. [Online]. Available: <http://www.epa.gov/climatechange/ghgemissions/gwps.html> 1
- [2] O. Edenhofer, R. Pichs-Madruga, Y. Sokona, J. C. Minx, E. Farahani, K. Susanne, K. Seyboth, A. Adler, I. Baum, S. Brunner, P. Eickemeier, B. Kriemann, J. Savolainen, S. Schlomer, C. von Stechow, and T. Zwickel, *Climate Change 2014: Mitigation of Climate Change*, 2014. [Online]. Available: <http://www.ipcc.ch/report/ar5/wg3/> 1

- [3] Working Group III of IPCC, "Fifth Assessment Report - Mitigation of Climate Change," Tech. Rep., 2014. [Online]. Available: <http://www.ipcc.ch/pdf/assessment-report/ar5/wg3/ipcc{-}wg3{-}ar5{-}full.pdf> 1
- [4] S. A. Montzka, E. J. Dlugokencky, and J. H. Butler, "Non-CO2 greenhouse gases and climate change," *Nature*, vol. 476, no. 7358, pp. 43–50, 2011. [Online]. Available: <http://dx.doi.org/10.1038/nature10322> 1
- [5] E. J. Dlugokencky, E. G. Nisbet, R. Fisher, and D. Lowry, "Global atmospheric methane: budget, changes and dangers." *Philosophical transactions. Series A, Mathematical, physical, and engineering sciences*, vol. 369, no. 1943, pp. 2058–2072, 2011. 1
- [6] P. A. Matson, *Advancing the Science of Climate Change*, 2010. [Online]. Available: <http://www.nap.edu/catalog/12782.html> 1
- [7] V. L. St. Louis, C. a. Kelly, É. Duchemin, J. W. M. Rudd, and D. M. Rosenberg, "Reservoir Surfaces as Sources of Greenhouse Gases to the Atmosphere: A Global Estimate," *BioScience*, vol. 50, no. 9, p. 766, 2000. 1
- [8] B. R. Deemer, J. A. Harrison, S. Li, J. J. Beaulieu, T. Delsontro, N. Barros, J. F. Bezerra-Neto, S. M. Powers, M. A. Dos Santos, and J. A. Vonk, "Greenhouse Gas Emissions from Reservoir Water Surfaces: A New Global Synthesis Manuscript," *BioScience*, vol. 66, no. 11, pp. 949–964, 2016. 1
- [9] J. Joyce and P. W. Jewell, "Physical controls on methane ebullition from reservoirs and lakes," *Environmental and Engineering Geoscience*, vol. 9, no. 2, pp. 167–178, may 2003. [Online]. Available: <http://eeg.geoscienceworld.org/cgi/doi/10.2113/9.2.167> 1
- [10] J. A. Harrison, B. R. Deemer, M. K. Birchfield, and M. T. O'Malley, "Reservoir Water-Level Drawdowns Accelerate and Amplify Methane Emission," *Environmental Science & Technology*, vol. 51, no. 3, p. acs.est.6b03185, feb 2017. [Online]. Available: <http://pubs.acs.org/doi/abs/10.1021/acs.est.6b03185> 1, 2, 3, 4
- [11] D. Bastviken, L. J. Tranvik, J. Downing, J. a. Crill, P. M, and A. Enrich-prast, "the Continental Carbon Sink," *Science*, vol. 331, no. Table 1, p. 50, 2011. 1
- [12] P. Casper, S. C. Maberly, G. H. Hall, and B. J. Finlay, "Fluxes of methane and carbon dioxide from a small productive lake to the atmosphere," *Biogeochemistry*, vol. 49, no. 1, pp. 1–19, 2000. 1, 2
- [13] M. Wik, B. F. Thornton, D. Bastviken, J. Uhlb??ck, and P. M. Crill, "Biased sampling of methane release from northern lakes: A problem for extrapolation," *Geophysical Research Letters*, vol. 43, no. 3, pp. 1256–1262, feb 2016. [Online]. Available: <http://doi.wiley.com/10.1002/2015GL066501> 1, 2
- [14] A. Maeck, H. Hofmann, and A. Lorke, "Pumping methane out of aquatic sediments – Ebullition forcing mechanisms in an impounded river," *Biogeosciences*, vol. 11, no. 11, pp. 2925–2938, 2014. 1, 2
- [15] K. Delwiche, S. Senft-Grupp, and H. Hemond, "A novel optical sensor designed to measure methane bubble sizes in situ," *Limnology and Oceanography-Methods*, vol. 13, no. 12, pp. 712–721, dec 2015. [Online]. Available: <http://doi.wiley.com/10.1002/lom3.10060> 2
- [16] I. Ostrovsky, D. F. McGinnis, L. Lapidus, and W. Eckert, "Quantifying gas ebullition with echosounder: the role of methane transport by bubbles in a medium-sized lake," *Limnology and Oceanography: Methods*, vol. 6, no. May 2017, pp. 105–118, 2008. 2
- [17] D. F. McGinnis, J. Greinert, Y. Artemov, S. E. Beaubien, and A. Wüest, "Fate of rising methane bubbles in stratified waters: How much methane reaches the atmosphere?" *Journal of Geophysical Research: Oceans*, vol. 111, no. 9, 2006. [Online]. Available: <http://doi.wiley.com/10.1029/2005JC003183> 2
- [18] G. Plant, M. Nikodem, P. Mulhall, R. K. Varner, D. Sonnenfroh, and G. Wysocki, "Field test of a remote multi-path CLaDS methane sensor," *Sensors (Switzerland)*, vol. 15, no. 9, pp. 21 315–21 326, 2015. 2
- [19] C. Varadharajan, R. Hermosillo, and H. F. Hemond, "A low-cost automated trap to measure bubbling gas fluxes," *Limnology and Oceanography: Methods*, vol. 8, no. 7, pp. 363–375, jul 2010. [Online]. Available: <http://doi.wiley.com/10.4319/lom.2010.8.363> 2, 3, 4
- [20] B. R. Deemer, J. A. Harrison, S. Li, J. J. Beaulieu, T. Delsontro, N. Barros, J. F. Bezerra-Neto, S. M. Powers, M. A. Dos Santos, and J. A. Vonk, "Greenhouse gas emissions from reservoir water surfaces: A new global synthesis," pp. 949–964, nov 2016. [Online]. Available: <https://academic.oup.com/bioscience/article-lookup/doi/10.1093/biosci/biw117> 2, 3

- [21] J. J. Beaulieu, M. G. McManus, and C. T. Nietch, "Estimates of reservoir methane emissions based on a spatially balanced probabilistic-survey," *Limnology and Oceanography*, vol. 61, no. Thornton 1990, pp. S27–S40, 2016. 2
- [22] J. P. Goodrich, R. K. Varner, S. Froking, B. N. Duncan, and P. M. Crill, "High-frequency measurements of methane ebullition over a growing season at a temperate peatland site," *Geophysical Research Letters*, vol. 38, no. 7, pp. 1–5, 2011. 2
- [23] M. Dunbabin and A. Grinham, "Quantifying Spatiotemporal Greenhouse Gas Emissions Using Autonomous Surface Vehicles," *Journal of Field Robotics*, vol. 34, no. 1, pp. 151–169, 2016. 2, 3
- [24] A. Grinham, M. Dunbabin, D. Gale, and J. Udy, "Quantification of ebullitive and diffusive methane release to atmosphere from a water storage," *Atmospheric Environment*, vol. 45, no. 39, pp. 7166–7173, 2011. [Online]. Available: <http://dx.doi.org/10.1016/j.atmosenv.2011.09.011> 3
- [25] N. T. Duc, S. Silverstein, L. Lundmark, H. Reyier, P. Crill, and D. Bastviken, "Automated flux chamber for investigating gas flux at water-air interfaces," *Environmental Science and Technology*, vol. 47, no. 2, pp. 968–975, 2013. 3
- [26] Senect, "Die Automated Bubble Trap (ABT) <http://www.senect.de/abt/>," 2016. [Online]. Available: <http://www.senect.de/abt/> 3
- [27] Zhengzhou Winsen, "Flammable Gas Sensor Model: MQ-4) Manual (Version 1.3)," Tech. Rep., 2014. 4, 11
- [28] N. S. Lawrence, "Analytical detection methodologies for methane and related hydrocarbons," *Talanta*, vol. 69, no. 2 SPEC. ISS., pp. 385–392, apr 2006. [Online]. Available: <http://linkinghub.elsevier.com/retrieve/pii/S0039914005006739> 4

Appendices

A Additional Resources

For complete design documentation and control code go to the MEMA Documentation Page:

<https://github.com/FrancescaFr/MEMA>.

The documentation page includes CAD assembly files, Arduino Code, circuit diagrams, bill of materials, a supplier list, additional test results, and calibration/calculation spreadsheets.