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Production and Ebullition of Methane in a Shallow Eutrophic Lake (Lake Elsinore, CA)

A Thesis submitted in partial satisfaction
of the requirements for the degree of

Master of Science

in

Environmental Sciences

by

Denise Nicole Martinez

December 2012

Thesis Committee:

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The Thesis of Denise Nicole Martinez is approved:

Committee Chairperson

University of California, Riverside

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ABSTRACT OF THE THESIS

Production and Ebullition of Methane in a Shallow Eutrophic Lake (Lake Elsinore, CA)

by

Denise Nicole Martinez

Master of Science, Graduate Program in Environmental Sciences
University of California, Riverside, December 2012
Dr. Michael A. Anderson, Chairperson

The volume of methane (CH_4) and other gases in sediments and the rate of CH_4 ebullition were determined for a shallow eutrophic freshwater lake in Southern California. Gas volume, principally as CH_4 , was measured at 28 sites in July 2010, followed by monthly sampling at 7 sites through December 2011. Gas volumes measured in July 2010 at the 28 sites exhibited a complex dependence on sediment properties; the volume of CH_4 and other gases were negligible in very coarse-textured sediment with low water and organic carbon contents. Gas volumes increased strongly with increased silt content, and were highest in sediments with intermediate water contents (60-70%), organic carbon contents (2-3%) and depths (approximately 4 m). Methane was the dominant gas collected from sediment (80 - 90%), while carbon dioxide comprised roughly 2 - 3% of sediment gas in the lake. Gas sampling during cool winter months found very low or undetectable volumes of gas present, while sediment gas volumes increased markedly during the spring and early summer months, and then declined in late

summer and fall. The rate of CH₄ ebullition, quantified with an echosounder, also varied markedly across the lake and seasonally. High rates of ebullition were measured at all 7 sites in July 2011 (up to 96 mmol CH₄ m⁻² d⁻¹), while the rates were more than 50% lower in September and negligible in December 2010. Ebullition rates were inversely correlated with depth and most other sediment properties, but strongly positively correlated with sand content. No simple relationship between ebullition rate and sediment gas volume across the set of sites was found, although ebullition rates at individual sites were positively related to gas volume. Measurements of acoustic target strength of individual bubbles across the sediments and over time were also made. Bubble size and volume varied weakly across the different sediments and depths, with no strong correlation with sediment properties. A statistical characterization of the population of bubbles found broadly normally-distributed bubble size, with kurtosis values of -0.84 to +1.11 and skewness values of -0.23 to 0.62. The ensemble-average weighted mean bubble volume was 0.094±0.023 cm³, although individual bubbles with target strengths as low as -68dB (0.0013 cm³) and as high as -43dB (4.689 cm³) were found. The current understanding of the relative importance of lakes as a source of methane to the atmosphere is limited due to the complexity involved in accurately measuring ebullition episodes, and this work supports the increasing evidence that ebullition may play a dominant role in methane emissions from shallow systems and lakes should be considered as a significant transport mechanism of CH₄ to the atmosphere in GHG emission inventories.

Table of Contents

Chapter 1 – Introduction.....	1
Chapter 2 – Methane Production and Ebullition in a Shallow Eutrophic Lake (Lake Elsinore, CA).....	9
Abstract.....	9
Introduction.....	11
Methods.....	12
Results.....	18
Discussion.....	28
Conclusion.....	34
References.....	36
Chapter 3 – Acoustic Monitoring of Sediment Bubble Volume and Distribution in a Shallow Eutrophic Lake (Lake Elsinore, CA)...	40
Abstract.....	40
Introduction.....	41
Methods.....	42
Results & Discussion.....	45
Conclusion.....	57
References.....	58

List of Tables

Table 2.1 – Sediment properties at the 7 monitoring sites in Lake Elsinore	19
Table 2.2 – Correlation coefficients for linear regressions of sediment properties and measured gas volumes	21
Table 2.3 – Methane concentrations ($\mu\text{mol L}^{-1}$) present in water column at Lake Elsinore on August 23, 2011	23
Table 2.4 – Methane ebullition rates ($\text{mmol m}^{-2} \text{d}^{-1}$) in Lake Elsinore (2010-11).....	25
Table 2.5 – Correlation coefficients for linear regressions of sediment properties and measured CH_4 ebullition rates....	25
Table 3.1 – Descriptive statistics of bubble target strength at the 7 monitoring sites in Lake Elsinore	48
Table 3.2 – R-values of pooled data for sediment properties at relevant monitoring sites in Lake Elsinore for three sampling dates (July 12, August 6, and September 6).....	50

List of Figures

Figure 2.1 – Study site showing sediment and gas sampling Locations at Lake Elsinore, CA	14
Figure 2.2 - Sediment gas volume measured at 28 sites on July 19-26, 2010 as a function of water content, depth, and silt content	20
Figure 2.3 – Seasonal variations in sediment gas volume at sites G1-G7 over the study period of July 2010-December 2011.....	21
Figure 2.4 – Echogram showing bubble tracks from acoustic measurements on July 12, 2012	24
Figure 2.5 – Methane ebullition rates measured on September 6, as a function of sediment depth and sand content.....	26
Figure 2.6 – Methane ebullition rates vs. sediment gas volumes.....	27
Figure 3.1 – Size distribution variations of bubble gas volumes at site G1.....	46
Figure 3.2 - Size distribution variations of bubble gas volumes at site G6.....	47
Figure 3.3 – Average target strength vs. sediment clay content of pooled data	51
Figure 3.4 – Average target strength vs. sediment sand content of	

pooled data 53

Figure 3.5 – Vertical variations in target strength of an individual
gas bubble at site G5 as a function of depth..... 56

Chapter 1: Introduction

The Role of CH₄ in Global Climate Change

Methane (CH₄) is the second largest contributor to global warming, and can be emitted to the atmosphere by natural sources including wetlands and permafrost, as well as anthropogenically, such as through fossil fuel production or rice cultivation. It is a strong greenhouse gas that is more potent than carbon dioxide (CO₂), and has a global warming potential about 23 times greater than that of CO₂ per molecule over a century time horizon (St. Louis et al., 2000). According to measurements made by numerous sources, the concentration of methane in the atmosphere has risen and continues to rise. During the last two hundred years, atmospheric methane concentrations have more than doubled to ~1750 ppbv, and the total annual emission of methane is currently about twice that estimated for the pre-industrial period (Etheridge et al., 1992). Although it is not as heavily focused on in the public media as CO₂, changes in the concentration of CH₄ in the atmosphere can have profound implications in regards to the global methane cycle and global warming, and is thus an important factor when considering the greenhouse gas budget.

Green house gas emission inventories are conducted each year by the EPA and are used to track the contribution of various GHGs from different sources. In response to the recognition of global climate change, many technologies have been implemented to slow down and reduce the addition of GHGs to the atmosphere. Some new techniques involve the capture and utilization of methane from landfills, manure management systems, and coal mines. While these efforts have been successful in slowing the release

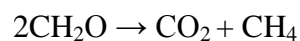
of methane from these particular sources, the current list of methane sources to the atmosphere remains incomplete and thus the contribution of other sources to global warming remains unclear.

The Role of Lakes in CH₄ Emission

Anoxic freshwater sediments can be sites of substantial gas production during the degradation of organic matter. Composition of the gas in the bottom sediments of lakes has been found to consist mainly of methane (>80%), with low amounts of N₂ and CO₂, and trace amounts of other gases such as H₂ and CO (Chau et al., 1977; Poissant et al., 2007).

The process of naturally occurring methane formation occurs primarily via methanogenesis, a form of anaerobic respiration. A variety of microbes that occur naturally in lake sediments symbiotically break down polymers converting organic carbon to carbon dioxide and methane, and use the decomposed organic matter as a source of energy (McCarty, 1982). First, fermentative microbes (acidogens) hydrolyze polymeric materials to monomers that can be converted to higher volatile fatty acids, H₂, and acetic acid. Next the acetogens convert those previously produced higher volatile fatty acids to H₂, CO₂, and acetate. Finally, methanogens take on the last step of methane fermentation by converting the H₂, CO₂, and acetate to CH₄ and CO₂ (McCarty, 1982).

In the absence of oxygen, organic matter is broken down by these methanogenic microbes via the general net reaction:



Carbon is used as the terminal electron acceptor (as opposed to oxygen, in the presence of oxygen) and methanogens reduce CO_2 to produce CH_4 as the final step in the decomposition of organic matter.

Anoxic freshwater sediment is one of the most significant natural sources of CH_4 , and the gas produced here can be exported into the water column through a variety of different pathways, including diffusive flux, plant-mediated flux, bioturbation, sediment disturbances and ebullitive flux (Bastviken, 2004). The rate of gas release from lake sediment can be affected by many factors, including temperature, water depth, and the amount of organic carbon that is available in the sediment for decomposition by bacteria (King & Wiebe, 1978; Schultz et al., 1990; Sorrell & Boon, 1992). Even as early as 1976, scientists proposed that both temperature and supply of organic material to freshwater sediments could have a limiting effect on the activity of methanogenic bacteria based on incubated laboratory experiments (Zeikus & Winfrey, 1976).

Ebullition describes the overall process where gas bubbles that are produced by microorganisms in the sediment are liberated from sediment porewaters and emitted to the atmosphere. It generally occurs in the top 30 centimeters of sediments and is sensitive to changes in water depth (hydrostatic pressure), atmospheric pressure, water temperature, and supply of organic C (Casper et al., 2000; Barabas et al., 2009). Gas bubbles released from the bottom sediment have been found to be composed primarily of CH_4 and generally have low concentrations of CO_2 . The low concentrations of CO_2 relative to the large concentrations of CH_4 in the sediment gas are expected due to the high solubility of CO_2 in water compared to the very low solubility of CH_4 in water

(Chanton & Whiting, 1995). This low solubility of CH₄ relative to CO₂ suggests that CH₄ bubbles can form more readily in the sediment. While bubbles traveling upward through the water column typically have adequate time to dissolve in deep systems, in Lake Elsinore and other shallow waters with depths <50 m, limited dissolution occurs during bubble ascent and thus ebullition is typically the dominant CH₄ emission pathway in these shallow water bodies (Del Sontro et al., 2010).

The process by which methane bubbles emerge from lake sediments as a result of the decomposition of organic matter in the lake bed can generally be described by two distinct bubble emergence modes (Meier et al., 2011). The first involves the escape of small bubbles through the small cracks in the sediment bed, while the second requires growth of a larger bubble until its buoyancy is able to overcome the overlaying surface tension and pressure effects. When the buoyant force of the gas bubble is larger than the restraining force within the sediment (e.g. hydrostatic pressure, viscous and inertial forces), the bubble is able to be released from the sediment into the overlying water column. One major deciding factor between these two modes of bubble escape has been correlated with grain size, and the emergence of bubbles has an effect not only on particle flux, but can also influence mixing processes of nutrients and/or contaminants within the sediment bed (Meier et al., 2011). In both modes of bubble emergence, the gas is vented into the atmosphere once reaching the air/water interface.

Bubbles released from the sediment can serve as a direct conduit of methane from sediments to the atmosphere due to CH₄'s insoluble nature, and ebullition has been recently identified as an important gas transport mechanism that may contribute

significantly to greenhouse gas (GHG) fluxes (Poissant et al., 2007; Huttunen et al., 2001). Studies have shown that the emission of methane from lakes may comprise a considerable portion of non-anthropogenic methane contributions to the atmosphere, and may play a larger role in atmospheric global warming than previously suggested; thus, CH₄ ebullition from lake sediments should be considered in global GHG flux analysis (Poissant et al., 2007; Huttunen et al., 2001, Zheng et al., 2011). Seasonal and temporal variation, temperature, and water depth have all been shown to impact both sediment gas production and rate of bubble ebullition out of the lake sediment, and estimates of the annual contribution of lakes to the overall atmospheric CH₄ emissions have been calculated taking some of these factors into consideration. Smith and Lewis (2000) estimated global emissions of CH₄ from lakes to the atmosphere to be approximately 55 Tg yr⁻¹ assuming that 50% of the surface area of lakes emit methane, while Bastviken et al. (2004) estimated global open water CH₄ flux to be 8-48 Tg CH₄ yr⁻¹, accounting for roughly 6-16% of global non-anthropogenic emissions.

Implications for Water Quality

As indicated previously, gas ebullition is important not only in regards to global GHG emissions, but also has implications for overall water quality in that the emergence of bubbles can also lead to the release of nutrients and other elements stored in the sediments. Ebullition can modify the sediment bed and affect its susceptibility to resuspension as well as its particle mixing rate (Bastviken et al., 2011). Sediment resuspension brought about through ebullition can enhance transport of nutrients into the

water column, and contribute to increased rates of internal loading (nutrient recycling), acting as a memory of past external nutrient inputs into the lake (Bussman, 2005).

Rates of internal loading can be especially high in shallow, eutrophic lakes where mixing that occurs at the sediment–water interface can effectively maintain nutrients in the water column. Bubble ventilation also aids in the diffusive process by carrying pore water to the sediment surface, allowing nutrients to be mixed into the benthic boundary layer via bubble generated diffusion (Bastviken et al., 2011). It has been presumed that only a rather small population of bubble emergence sites is necessary in order to become the dominant mixing process (Del Sontro et al., 2010). Any nutrients contained within the sediments are then carried from the benthic boundary layer into the overlying water column via particle mixing.

In addition to actual ebullition rates, resuspension rates due to ebullition have also been correlated to two distinct time dependent processes: how long a bubbling event lasts and the time interval between successive events (Barabas, 2009). The re-release of nutrients into the water column are made available for primary production, and the amount of organic matter available for degradation subsequently increases. This increase can then lead to an increase in gas ebullition, liberating more nutrients out of the sediments to be used in primary production, creating a positive feedback system of lake eutrophication (Liikanen et al., 2003).

The Need for Further Study

The large variability between lakes and their productivity, water quality, and basin characteristics leads to large uncertainties when estimating overall global CH₄ emission rates. Due to the limited methane emission estimates, the relative importance of lake fluxes on a global basis is not widely understood (Bastviken et al., 2004). While seasonal and temporal variation of flux on a small number of lakes has been studied, an incomplete understanding remains regarding the factors and processes regulating CH₄ ebullition and the amount of CH₄ released to the atmosphere. Ebullition also depends on initial bubble size, depth of bubble release, and initial gas bubble concentrations. A newly formed bubble is not immediately ebullated from the sediment surface as soon as it is formed; it is able to migrate out of the sediment into the water column only when it has reached and surpassed a critical size such that the buoyant force upward is greater than the restraining force within the sediment. Sediment properties are thus important factors that regulate bubble emission. Additionally, since bubble size is a critical factor in determining gas exchange rate and ultimately the terminal fate of ebullated bubbles, it is also important to examine the bubble-size distribution of bubbles at various sites across the lake as well as vertically in the water column (Ostrovsky, 2003).

Objective

My objectives were to investigate CH₄ storage in the sediments, rates of gas ebullition from bottom sediments, and their relationships with sediment properties in a shallow eutrophic lake. I also aimed to investigate the spatial variation of sediment

properties and their relationship to the volume of gas that is released from the sediment, bubble distribution, and ultimately their effect on the overall rates of gas ebullition from bottom sediments in Lake Elsinore, California.

Chapter 2

Methane Production and Ebullition in a Shallow

Eutrophic Lake (Lake Elsinore, CA)

Abstract

The volume of methane (CH₄) and other gases in sediments and the rate of CH₄ ebullition were determined for a shallow eutrophic freshwater lake in Southern California. Gas volume, principally as CH₄, was measured at 28 sites in July 2010, followed by monthly sampling at 7 sites through December 2011. Gas volumes measured in July 2010 at the 28 sites exhibited a complex dependence on sediment properties; the volume of CH₄ and other gases were negligible in very coarse-textured sediment with low water and organic carbon contents. Gas volumes increased strongly with increased silt content, and were highest in sediments with intermediate water contents (60-70%), organic carbon contents (2-3%) and depths (approximately 4 m). Methane was the dominant gas collected from sediment (80 - 90%), while carbon dioxide comprised roughly 2 - 3% of sediment gas in the lake. Gas sampling during cool winter months found very low or undetectable volumes of gas present, while sediment gas volumes increased markedly during the spring and early summer months, and then declined in late summer and fall. The rate of CH₄ ebullition, quantified with an echosounder, also varied markedly across the lake and seasonally. High rates of ebullition were measured at all 7 sites in July 2011 (up to 96 mmol CH₄ m⁻² d⁻¹), while the rates were >50% lower in September and negligible in December 2010. Ebullition rates were inversely correlated

with depth and most other sediment properties, but strongly positively correlated with sand content. No simple relationship between ebullition rate and sediment gas volume across the set of sites was found, although ebullition rates at individual sites were positively related to gas volume.

Key Words: Methane, Sediment, Gas ebullition, Gas storage

1. Introduction

Anoxic freshwater sediments are common sites of substantial gas production during the degradation of organic matter. The gas produced via decomposition is concentrated in the subsurface sediment layers and can then be exported into the water column through different pathways, including diffusive flux, ebullitive flux, plant-mediated flux, and sediment disturbances (Bastviken, 2004). Bubble composition has been found to consist mainly of CH₄, with low amounts of N₂, and CO₂, with trace amounts of other gases such as H₂ and CO (Chau et al., 1977; Poissant et al., 2007). While CO₂ is the most common greenhouse gas (GHG), the global warming potential of CH₄ is 21x larger over a century time horizon, and is thus an important factor when considering the GHG budget (St. Louis et al., 2000).

The production and release of methane from lakes can be affected by many factors, including temperature, water depth, and the amount of organic carbon that is available in the sediment for decomposition by bacteria (King and Wiebe, 1978; Schultz et al., 1990; Sorrell and Boon, 1992). Due to the insoluble nature of CH₄, ebullition has been identified as an important gas transport mechanism that may contribute significantly to greenhouse gas (GHG) fluxes (Poissant et al., 2007; Huttunen et al., 2001). Studies have shown that the emission of methane from lakes may comprise a considerable portion of non-anthropogenic methane contributions to the atmosphere (Zheng et al., 2011). Smith and Lewis (2000) estimated global emissions of CH₄ from lakes to the atmosphere to be approximately 55 Tg yr⁻¹ assuming that 50% of the surface area of lakes emit methane, while Bastviken et al. (2004) estimated global open water CH₄ flux to be

8-48 Tg CH₄ yr⁻¹, accounting for roughly 6-16% of global non-anthropogenic emissions. The large spatial and temporal variability between lakes leads to large uncertainties when estimating overall global CH₄ emission rates. Due to the limited methane emission estimates, the relative importance of lake fluxes on a global basis is not widely understood (Bastviken et al., 2004).

Gas ebullition is not only important in regards to overall global GHG emissions, but can also lead to release of nutrients and other elements stored in the sediments. Sediment resuspension can enhance transport of nutrients into the water column, and contribute to increased rates of internal loading (Bussman, 2005). Through ebullition, increased nutrients are made available for primary production, and the amount of organic matter available for degradation subsequently increases. This increase can lead to an increase in gas ebullition, which again liberates more nutrients out of the sediments to be used in primary production. Gas ebullition, therefore, serves as a type of driving force for a positive feedback system of lake eutrophication (Liikanen et al., 2003).

The current understanding of the relative importance of lakes as a source of methane to the atmosphere is limited due to the complexity involved in accurately measuring ebullition episodes. In this study I investigate the spatial-temporal variation of CH₄ storage in the sediments, rates of gas ebullition from bottom sediments, and their relationships with sediment properties and hypothesize that ebullition can be a particularly effective transport mechanism for CH₄ in Lake Elsinore.

2. Materials and Methods

2.1 Study Site

Lake Elsinore is a shallow eutrophic lake located in Riverside County, CA, and is the largest natural lake in southern California. It has an area of approximately 1,200 ha and is situated at the base of the San Jacinto River watershed with the Santa Ana Mountains to the west. Land use in the 2000 km² watershed includes agriculture, urban and suburban housing, and wild lands. The region has a Mediterranean climate that is characterized by hot dry summers and cool winters with limited rainfall (~25 cm) that falls mostly in the winter. Although the lake level fluctuates widely based on El Niño/La Niña conditions, the lake level also drops each summer-fall by 1 m or more due to evaporative losses (Lawson and Anderson, 2007); at the time of this study, the lake had an average maximum depth near 8 m and an average mean depth of approximately 4.8 m. Axial flow pumps were installed in 2004 to help mix the lake, although they were shown to be largely ineffectual at weakening stability and increasing DO near the sediments (Lawson and Anderson, 2007). A diffused aeration system was installed in 2008 to further enhance mixing processes in the lake, although anoxic surface sediments have persisted over most of the year (Anderson unpublished data, 2008).

2.2 Sediment sampling and characterization

Sediment surface grab samples were collected from 28 sites, on a staggered-start sampling grid, that varied in depth and other properties using an Ekman dredge in late May and early June, 2010 (Anderson and Pacheco, 2011). Samples were homogenized

before being transferred to 500 mL glass wide-mouth jars with Teflon-lined lids and stored on ice for transport back to the laboratory. Sediment was analyzed for a range of properties, including water content, particle size and organic carbon content. Water content was determined in samples by weighing wet samples, oven drying them overnight at 105 °C, and then reweighing them after all of the moisture had been driven off. Particle size was measured using the hydrometer method (Gee and Bauder, 1986). Inorganic C and CaCO₃ were determined manometrically (Loeppert and Suarez, 1996), while total C was measured by high-temperature combustion using a Thermo Flash elemental analyzer. Organic C was determined from the difference between the measured values of total and inorganic C. From this initial survey of 28 sites, 7 sites were selected for more intensive monitoring of gas storage and ebullition rates (Fig. 2.1).

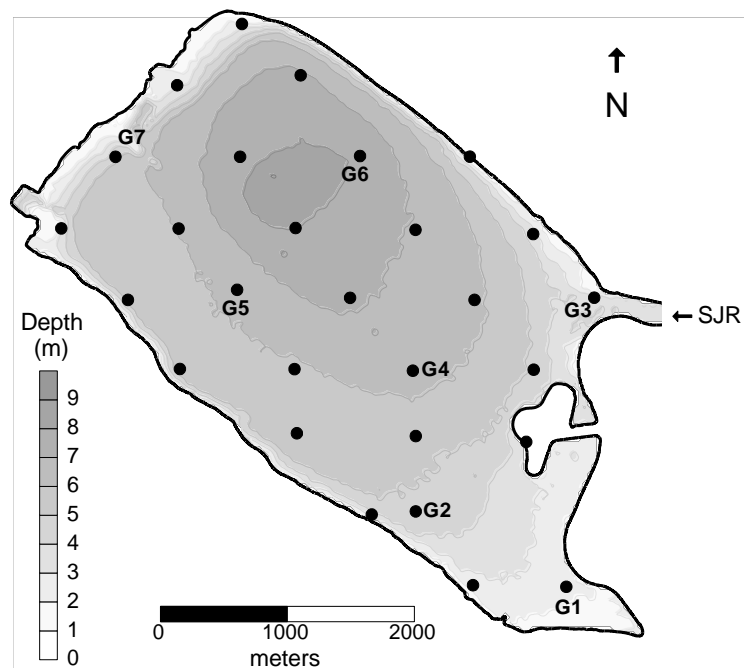


Figure 2.1 - Study site showing sediment and gas sampling locations, Lake Elsinore, CA.

2.3 Sediment gas volume

The volumes of gas present in the sediments were measured by displacement following Huttenen et al. (2001). Measurements at 28 sites were made July 19-26, 2010; following this initial survey, 7 sites were selected for approximately monthly sampling from July 2010 to December 2011. The volume of gas stored within the sediments per unit area (L m^{-2}) was determined using a sediment bubble gas sampler constructed from an inverted 27 cm diameter funnel attached to a 3 kg stainless steel weight with a cross-sectional area of 62 cm^2 . The gas sampler was designed to disturb the sediment layer, causing the release and capture of any gas stored in the sediments (Huttenen et al., 2001). The gas bubbles were collected through the inverted funnel into a clear plastic measuring tube (1.5 cm diameter) filled with water and marked from 0 to 50 mL. Gas volume within the measurement tube was determined after return to the water surface following 3-5 sample displacements. Five replicates of each measurement were taken at each of the sites during sampling. Water temperature and conductivity profiles were measured at each location using a YSI Cast Away CTD system.

2.4 Sediment gas composition

Gas samples were also collected from the sediment in order to measure the composition of the gas bubbles (Huttunen et al., 2001). Sediment gas samples were collected by attaching a 30 mL glass vial to the top of the sampler tube prior to gas displacement, and capping it while inverted underwater with a gas-sampling Mininert valve. Samples for gas composition analysis were collected from each of the 7 sites on

two different sampling occasions (July 12, 2011 and August 23, 2011). All samples were stored on ice, transported back to the laboratory, and analyzed within 24 hours. Gas was sub-sampled through the Mininert valve using gas-tight syringes fitted with Mininert push button gas valves. Methane gas concentration was measured by using a Hewlett Packard series 5890A gas chromatograph with flame-ionization detector (FID)(GC-FID). The GC-FID was equipped with a packed stainless steel, 1.8 m column. Flow rate of He carrier gas was 20 mL min^{-1} , He makeup + carrier gas was 30 mL min^{-1} , air + He gas was 300 mL min^{-1} , and H_2 + He gas was 60 mL min^{-1} . Oven, injector, and detector temperatures were held at 40, 100, and $250 \text{ }^\circ\text{C}$, respectively. The methane retention time was 1.2 min and an HP 3396 Series 2 integrator was used to integrate peak areas. Carbon dioxide measurements were conducted using an Analytical Development Co. Series 225 CO_2 analyzer. Concentrations of O_2 and N_2 were quantified using a Hewlett Packard 5890 Series 2 GC with MS5971 mass-spectral detector and MS ChemStation software. In each case, before samples of the collected gas were injected, instrument calibration was performed. Known volumes of each gas were used to create a calibration curve. Peak area of each curve was recorded and inserted into the regression equation to calculate the percent of each gas present in the sample.

2.5 Water sampling - dissolved methane concentrations

Water samples were collected on August 23, 2011 to quantify the dissolved methane concentration within the water column. Samples were collected using a 4 L Van Dorn sampler into 250 mL flasks and were rapidly capped with gas tight Teflon-lined

butyl rubber septa at various depths within the water column (ranging from 0.3 m – 7.5 m below the surface). Roughly 50 mL of headspace was left to allow for air/water partitioning of CH₄. Bottles were brought back to the lab and volume of water in each flask was determined gravimetrically. Bottles were agitated briefly and allowed to stand before carrying out headspace analysis. Headspace gas concentrations were measured using gas chromatography equipped with flame ionization detector as described in section 2.4, and all measurements were taken < 4 hours after collection. Known volumes of methane, ranging from 0 – 400 μL in a gas tight syringe, were injected into the GC-FID to create a calibration curve and regression equation. 200 μL of headspace from each sample were then injected into the GC-FID, and the peak area of each sample was inserted into the calibration equation to calculate concentration of methane in the air headspace above the water. After correcting for any dissolved methane that had not partitioned into the measured gas phase, Henry's Law was used to convert the calculated CH₄ gas phase concentration to the concentration of CH₄ dissolved in water, ($K_H = 27$, $T = 298\text{K}$, $P = 0.97\text{atm}$) (Schwarzenbach et al., 2003).

2.6 Ebullition rates

Hydroacoustic measurements were used to detect bubbles released from bottom sediments and rising through the water column (Ostrovsky, 2008). Hydroacoustic measurements were carried out using a BioSonics DT-X echosounder fitted with a 430-kHz single-beam, a 201-kHz split-beam, and a 38-kHz single-beam transducer. Echograms were collected at each of the seven sampling sites on three of the sediment

gas sampling dates (December 15, 2010, July 12, 2011, and September 6, 2011) between 9 a.m. and 3 p.m. Transducers were calibrated using tungsten-carbide spheres of known target strength prior to collection of acoustic data; data were acquired at 5 pings per second (pps) on each of the 3 frequencies at all sampling sites. Bubble streaks on echograms were counted, and the beam half angle (7.0, 6.6 and 10.0° for the 430-, 201- and 38-kHz transducers, respectively), ping rate, and range to the lake bottom were used to calculate the rate of ebullition per unit area from the sediment to water column and atmosphere. The rate of methane released from bottom sediments was calculated from ebullition rate, the measured concentration of methane in the bubbles, and an average bubble volume of 0.097 cm³ (Ostrovsky et al., 2008), with correction for hydrostatic pressure effects using the ideal gas law.

3. Results

3.1 Sediment properties

Sediments collected at the 28 initial sampling sites varied widely in their water content, texture, bulk density, and organic C content (Anderson and Pacheco, 2011). Sediment exhibited a diverse range of textures (from 0 to 88% sand and 3.3 to 65.4% clay), with finer sediments located in the deeper, more central areas of the lake basin (Anderson and Pacheco, 2011). Of the 7 sites chosen to be sampled more comprehensively (Table 1), sites G1 and G7 are the two shallowest sampling sites, and are located on the southeastern and northwestern borders of the lake (Fig. 2.1). These two sites had the lowest concentrations of organic C and the lowest sediment water contents

(Table 2.1). These two sites also had the highest bulk density values (0.925 and 0.950, respectively), which were more than double the next highest reported bulk density value (0.483 at site G2). Sites G2-G5, which had lake depths between 4.1- 6.6 meters, exhibited a general increase in concentrations of all sediment properties, most notably in pore water content (60-80%), silt content (36-72%) and organic C content (2.3-4.9%) (Table 2.2). Water content, organic C content and other properties at the deepest site (G6) did not vary markedly from the sediment properties at the sites of intermediate depths.

Site	Depth (m)	% H ₂ O	% OC	% Sand	% Silt	% Clay	Density (g cm ⁻³)
G1	2.2	43.2	0.27	86.8	8.4	4.8	0.925
G2	4.6	62.5	2.56	16.9	64.0	19.1	0.483
G3	4.1	66.8	2.33	9.1	72.4	18.5	0.455
G4	6.6	79.6	4.77	3.0	36.3	60.7	0.246
G5	6.4	80.1	4.89	4.3	36.0	59.7	0.245
G6	8.4	81.3	4.21	0.0	56.3	43.8	0.225
G7	3.9	35.9	0.73	48.1	45.4	6.5	0.950

3.2 Sediment gas volume

Following sampling and characterization of the bottom sediments, an initial survey of gas volumes present in the bottom sediments at the 28 sites was conducted on July 19-26, 2010. The volumes of gas stored in the sediments were a complex function of sediment physical and chemical properties, with maximum gas volumes found in sediments with intermediate water contents (Fig. 2.2a), organic C contents (closely correlated with water contents; Anderson and Pacheco, 2011) (not shown), and depths (Fig. 2.2b). Maximum storage of methane and other gases was observed in sediments

with water contents of 60-70% and organic C contents near 2.5%; sediments with greater water contents (Fig. 2.2a) and organic C contents (not shown) had much less gas present. Negligible gas was found in the shallowest sediments (that were also the coarsest textured, with the highest bulk densities and lowest water and organic C contents), while gas volumes increased markedly between 3-4 m depth, and reached maximum values near 4 m depth before generally decreasing (Fig. 2.2b). While water content, organic C content, sand content, and depth were all statistically significantly correlated ($p < 0.05$), they accounted for only 22 - 45% of the variance in measured gas volume and failed to adequately capture overall trends (e.g., Fig. 2.2a,b). The volume of gas stored in sediments, however, was more strongly correlated with the amount of silt present (Fig. 2.2c). In fact, % silt content was a stronger correlate than any other sediment characteristic, accounting for 67% of the variance in observed sediment gas volume (Table 2.2). It is recognized that most of these sediment properties are auto correlated, but silt content appears to be the strongest linear predictor of sediment gas volume.

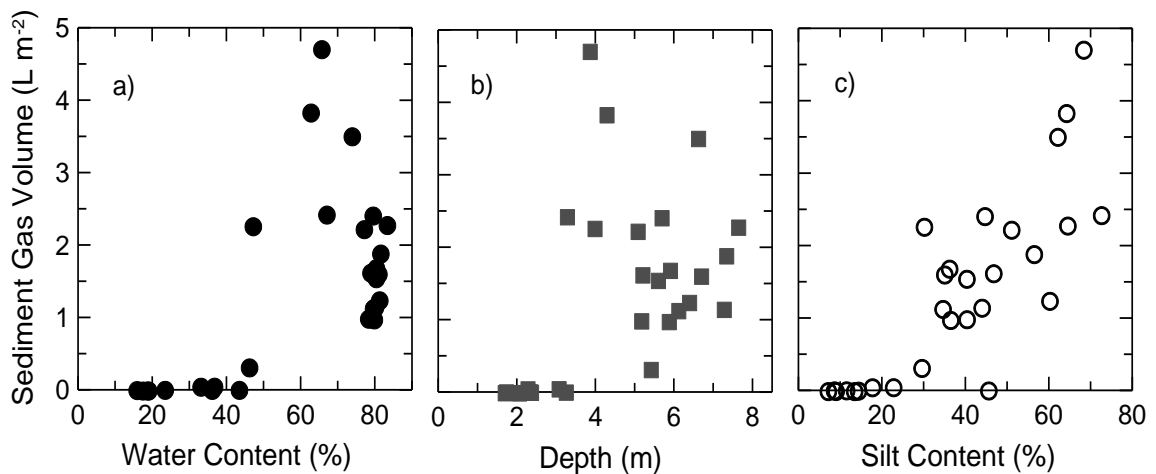


Figure 2.2 - Sediment gas volume measured at 28 sites on July 19-26, 2010 as function of sediment: a) water content, b) depth and c) silt content.

Table 2.2- Correlation coefficients for linear regressions of sediment properties and measured gas volumes (July 2010) (n=28).						
Property ^a	% H ₂ O	% OC	% Clay	% Silt	% Sand	Depth
Gas Volume	0.61***	0.51**	0.36	0.82***	-0.67***	0.47*

*significant at $p < 0.05$; **significant at $p < 0.01$, ***significant at $p < 0.001$

^aAnderson and Pacheco (2011)

Measurements of gas volume made at the 7 sites selected for sampling over the next 18 months demonstrated strong seasonal trends, with the largest volume observed in the summer and negligible volumes present during the cool winter months (Figure 2.3). Measured gas volumes thus tracked water temperatures above the sediments that ranged from about 12°C in the winter to 26 °C in the summer (data not shown).

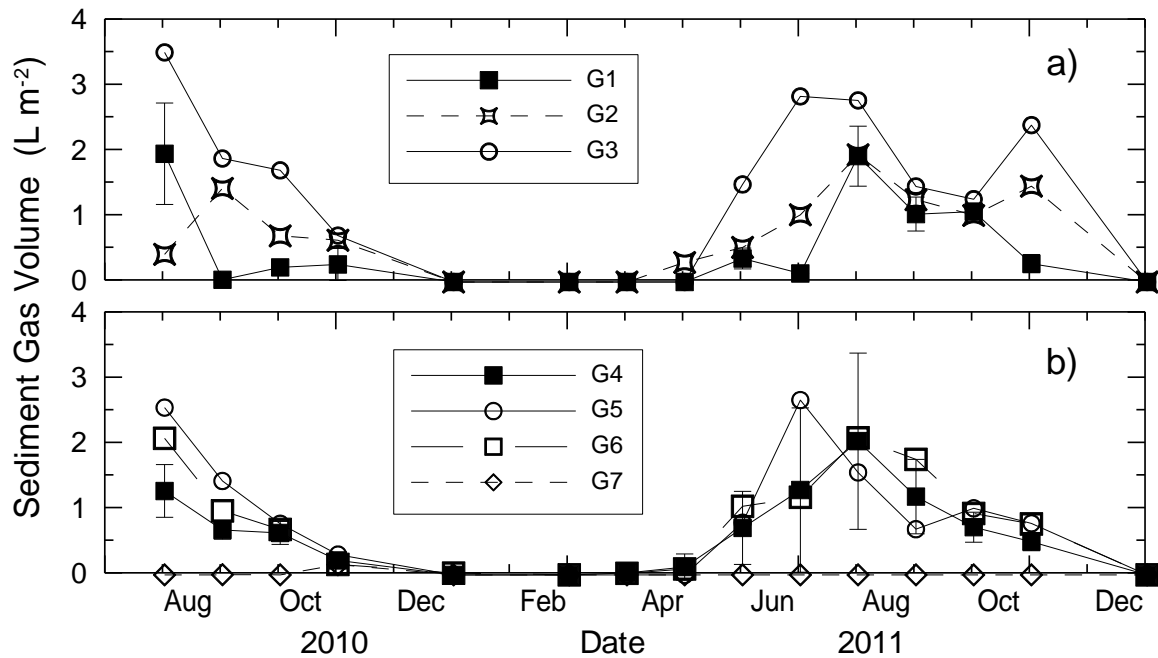


Figure 2.3 - Seasonal variations in sediment gas volume at: (a) sites G1-G3, and (b) at sites G4-G7 over the study period of July 2010-December 2011 (plotted gas volume for site G3 was rescaled to one-half measured value to better demonstrate trends at other sites).

Correlation coefficients for gas volumes vs. temperature for each of the sites (omitting site G7, where negligible gas volumes were found, Fig. 2.3b) ranged from 0.59 to 0.79 and all were statistically significant at $p < 0.05$ ($n=15$). Nonetheless, sediment gas volumes generally reached their highest values in July or early August and then declined later in August or early September (Fig. 2.3), when water temperatures were generally still at or near their summer maximum values (Lawson and Anderson, 2007). Site G3 (average water depth = 4.3 m) consistently yielded the largest gas volumes on each sampling date (note that gas volumes have been rescaled to 50% to more conveniently show trends at other sites) (Fig. 2.3a), and had the highest silt content of any of the 7 sites (72%). It is located at the southeast end of the lake (Fig. 2.1) near the mouth of the channel for San Jacinto River discharge to the lake. This site thus differed from other sites on the lake owing to potential fluvial inputs of suspended solids and apparent deposition of silt. As a result, the relationships it displayed with sediment properties of the lake were quite distinctive from the other sites (Figure 2.3). Gas volume found in sediment at this site were 2x that of the other sites and varied from over 6 L m^{-2} (rescaled) during the warm summer months to $<0.02 \text{ L m}^{-2}$ during the cool winter months. Between June - July of 2011, site G3 had an average gas volume of $5.6 \pm 1.9 \text{ L m}^{-2}$. This value was substantially higher than that of the other 6 sites during this measurement period, which ranged from $2.06 \pm 0.46 \text{ L m}^{-2}$ (site G1) to $4.25 \pm 1.41 \text{ L m}^{-2}$ (site G5). Noteworthy too is the observation that site G7, on a relatively steeper bottom slope than the other sites (Fig. 2.1), generally had very low or undetectable amounts of gas throughout the entire study period.

3.3 Gas composition & methane concentration in water

Gas samples collected and returned to the lab for compositional analysis indicated no substantial difference in composition across the sites during the July 12 and August 23, 2011 sampling events. Methane was the dominant constituent of the gas recovered from the sediments (80-90%) at each site, although N₂ (1-7%), CO₂ (2-3%) and O₂ (0.2-3%) were also found. O₂ most likely entered the gas phase during the sampling procedure. The sum of the measured gases (methane, dinitrogen, carbon dioxide, and oxygen) was 85-105% in most cases.

Water samples collected on August 23, 2011 had low concentrations of dissolved methane, consistent with its limited solubility in water (Table 2.3). Concentrations ranged from 0.07 µmol L⁻¹ CH₄ at site G7 to 4.4 µmol L⁻¹ above the sediments at site G5 (Table 2.3).

Depth (m)	G1	G2	G3	G4	G5	G6	G7
0.3	0.32	0.18	0.88	0.12	0.82	0.33	0.67
2.5	0.42	0.11	0.14	0.13	0.29	1.96	0.07
5		0.82		0.09	4.43	0.95	0.78
6				1.28		0.70	
7.5						1.39	

3.4 Ebullition rates

Echograms clearly show release of gas bubbles from sediments within the lake (Figure 2.4). Gas bubbles rising vertically from the lakebed are seen as off-axis linear

streaks, reflecting the ping rate, advective water currents and any boat movements (Ostrovsky et al., 2008).

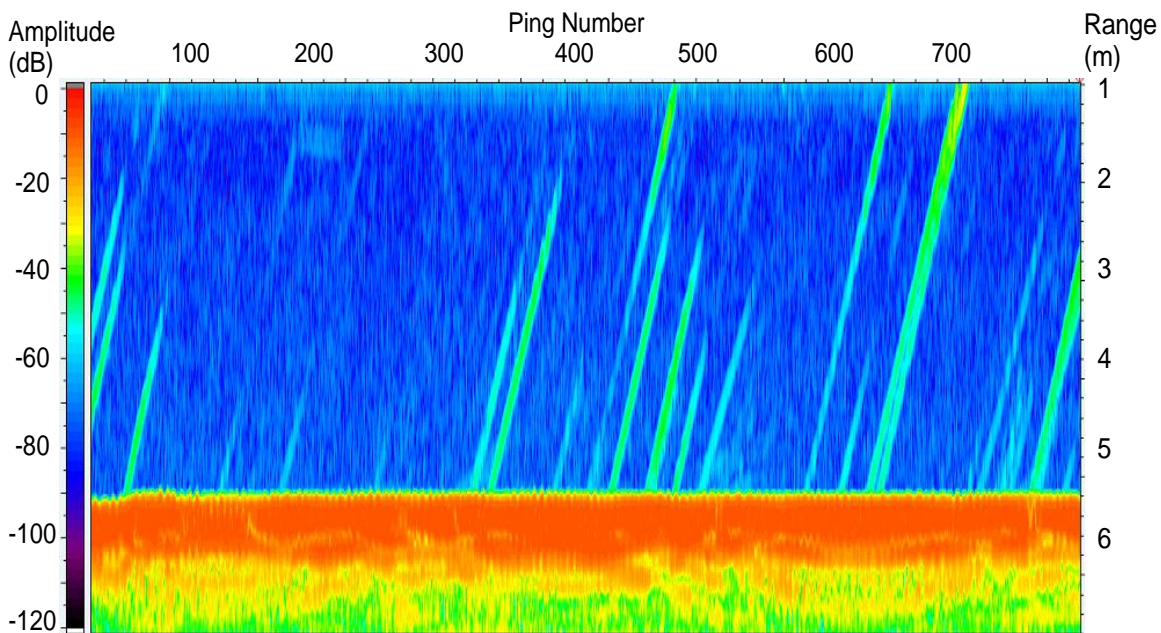


Figure 2.4 - Echogram showing bubble tracks from acoustic measurements on July 12, 2012.

The strength of backscatter in the echogram is a function of the object size and density contrast with water; the bottom sediments are the dominant source of acoustic backscatter within the lake, reaching strengths of -10 dB. Gas bubbles are prominent features in the echogram as well, with well-defined linear bubble tracks resulting from ebullition of CH_4 from bottom sediments (Fig. 2.4).

As noted with gas volumes present in bottom sediments (Fig. 2.3), rates of ebullition were also found to vary across the sampling sites and seasonally (Table 2.4). Ebullition rates on July 12, 2011 ranged from $13.4 - 96.2 \text{ mmol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$, while lower rates were measured on September 6, 2011 ($3.7 - 27.1 \text{ mmol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$). Methane

ebullition was below detection at all sites in December. The release of gas from the sediments was significantly higher at the shallowest site, site G1 (96.2 ± 1.6 and 27.1 ± 7.1 mmol CH₄ m⁻² d⁻¹ in July and September 2011, respectively), than at any of the other sites (13.4 - 27.7 mol m⁻² d⁻¹ in July and 3.7 - 9.5 mol m⁻² d⁻¹ in September, 2011) (Table 2.4).

Date	G1	G2	G3	G4	G5	G6	G7
Dec 15, '10	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Jul 12, '11	96.2±1.6	15.7±3.1	27.7±5.5	13.4±5.7	17.8±7.0	13.4±3.6	21.9±6.8
Sep 6, '11	27.1±7.1	5.1±3.1	8.0±2.4	3.7±0.9	6.6±1.0	3.8±1.2	9.5±2.4

Regression analyses of CH₄ ebullition rates across the 7 sites versus sediment properties found no correlation with volume of gas present in the sediments, and inverse correlations with % H₂O, % organic carbon, % silt, % clay and depth, although CH₄ ebullition was statistically significantly correlated only with depth ($p < 0.05$) (and only for the September 6, 2011 measurement) (Table 2.5; Fig. 2.5a). Rates of CH₄ ebullition were highly positively correlated with % sand, however (Table 2.5; Fig. 2.5b). Correlations with depth and % sand were improved somewhat when data were fitted to exponential functions, although the physicochemical basis for the improved fits are not clear.

Date 2011	% H ₂ O	% OC	% Clay	% Silt	% Sand	Depth	Gas Volume
Jul 12	-0.57	-0.68	-0.56	-0.70	0.88**	-0.72	0.02
Sep 6	-0.66	-0.74	-0.61	-0.72	0.93**	-0.77*	0.03

*significant at $p < 0.05$; **significant at $p < 0.01$

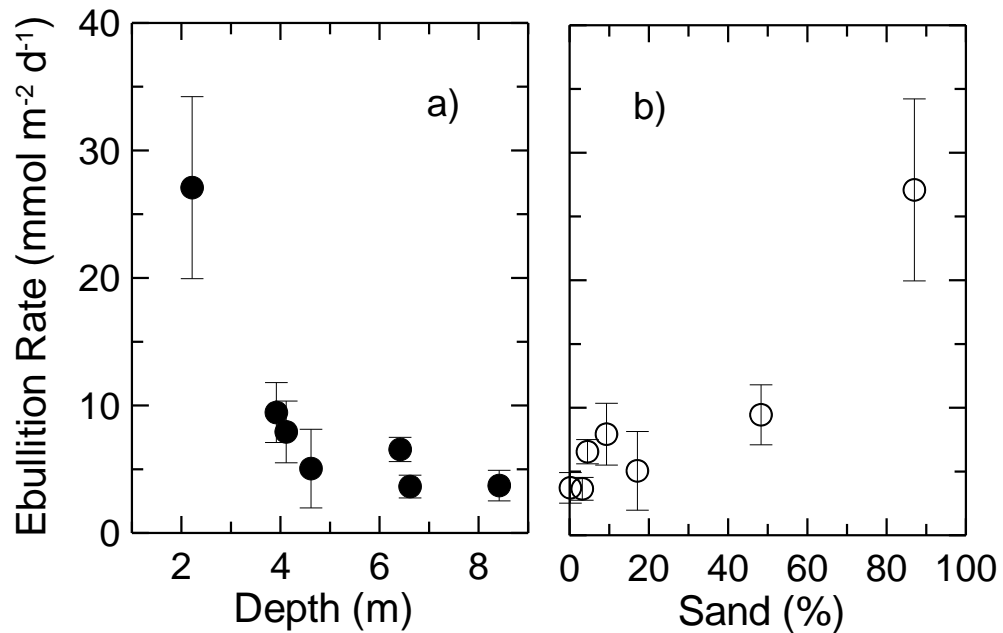


Figure 2.5 - Methane ebullition rates measured on September 6, 2011 as function of sediment: a) depth and b) sand content.

While no correlation between ebullition rate and sediment gas volume was observed across the 7 sites on any given sampling day, they were correlated for individual sites across the 3 sampling dates (Fig. 2.6). Thus, we see that the shallow sandy sediment at site G1 had the greatest ebullition rate at the lowest corresponding sediment gas volume, while the slightly deeper silty sediment at site G3 yielded the lowest rate of ebullition for a given sediment gas volume (Fig. 2.6). Sediments at sites G2, G4-G6 with intermediate properties (Table 2.1) yielded intermediate rates of ebullition. Site G7 was found to release some methane as gas bubbles even though no gas was measured in the sediments (Fig. 2.6); as previously noted, this site was located near shore at a relatively steep part of the lake basin (Fig. 2.1).

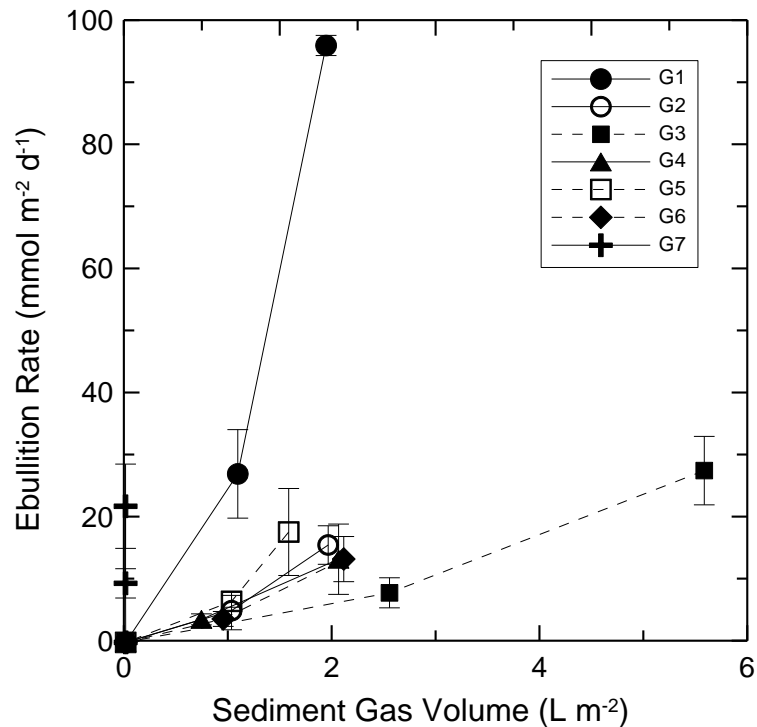


Figure 2.6 - Methane ebullition rates vs. sediment gas volumes measured on December 15, 2010, July 12, 2011 and September 6, 2011.

It appears that echosounder measurements, made off the bow of the boat and oriented toward the center of the lake, may have been sufficiently offset from gas volume measurements (made outside of the ensonified area off the port side) that different sediments were sampled by the 2 techniques at this site. Sediment properties are known to vary strongly over short distances near sloping basin topography (Hakanson & Jansson, 1983).

4. Discussion

Significant volumes of gas were present in the sediments of Lake Elsinore in July 2010, with an average gas volume across the 28 sites of 1.36 L m^{-2} and a maximum measured sediment gas volume of 4.71 L m^{-2} (all values normalized to lake surface, i.e., with no hydrostatic pressure). Areal flux rate corresponds to only the top few cm of sediment disturbed by the gas sampler and thus reported values may be an underestimation of true gas volumes present. Gas volumes were significantly correlated with sediment water content, organic carbon content, silt content and depth, and inversely correlated with sand content (Table 2.2). Relationships generally proved to be much more complicated than simple linear functions, however (Fig. 2.2). Sediments with intermediate values of organic carbon content, water content, and depth demonstrated the highest gas volumes present in the sediments, and at higher or lower values the stored gas volumes were substantially reduced. Gas volumes measured in sediments were most strongly linearly correlated with silt content (Fig. 2.2c).

Gas present in the sediments averaged 85% CH_4 , with low concentrations of CO_2 (2-3%), N_2 and other gases. Assuming the 28 sites reasonably capture the lake-wide distribution of gas with the sediments, we can use the average gas volume of 1.36 L m^{-2} , the lake (and sediment) surface area of approximately 1200 ha, and the mean CH_4 content of the sediment gas (85%) to estimate a total CH_4 volume of $1.4 \times 10^7 \text{ L}$ stored in the sediments in July 2010.

Based on approximately monthly sampling from July 2010 – December 2011 at 7 of the initial 28 sites on Lake Elsinore, gas storage within the sediments was found to

exhibit well-defined seasonal trends, with generally little to no gas present during winter, and much higher gas volumes present during summer. The high gas volumes occurring during summer and negligible amounts during winter indicates a very strong seasonality in CH₄ production. The increase in gas volume could result from active methanogenesis associated with increased rates of microbial activity and decomposition in the anaerobic sediments as water temperature increases; when temperatures drop, the decomposition process begins to slow, and less gas is produced (Kelly and Chynoweth, 1981; Huttunen et al., 2001). Varying levels of dissolved oxygen (DO) in the water column and changes in redox potential can alter sediment microbial activity and therefore may also influence rates of methanogenesis and gas volume production. Increases in gas volume can also result from increases in sedimentation, which supplies fresh organic material for CH₄ production (Matthews et al., 2005).

Gas produced and stored in the sediments was released from the sediments through the processes of ebullition, at rates that were also found to vary seasonally. Ebullitive flux was substantial in July, showed a strong decrease by September, and was generally below detection in December. These findings are consistent with other studies, which have reported that ebullition rates were markedly higher during summer than during winter (Mattson and Likens, 1990; Sorrell and Boon, 1992). While gas storage in sediments demonstrated strong positive correlations with H₂O content, organic C content, silt content and depth (Table 2.2), negative correlations for ebullition rates were found for these sediment properties. Sand content, which was strongly negatively correlated with gas volumes present in sediments (Table 2.2), was very strongly positively correlated

with measured ebullition rates (Table 2.5). Moreover, ebullition was not related to volume of gas present in sediments (Table 2.5). An important, if not also intuitive, finding of our work is that the sediment properties that promote accumulation of gas in Lake Elsinore tend to inhibit the process of ebullition. Sediments with a large quantity of silt-sized material and intermediate water content and related properties thus provide the greatest impedance to ebullition. Such sediment would have intermediate size pores with greater overburden pressure than finer organic rich sediments; conversely, sandy sediment apparently has sufficient pore size and pore connectivity to limit CH₄ accumulation and facilitate bubble release. This would be enhanced by the shallower depth, reduced hydrostatic pressure, and correspondingly greater buoyant forces acting on a given bubble.

The gas bubbles released from the bottom sediment were composed primarily of CH₄ and had only small concentrations of CO₂, despite having a relatively well-mixed water column. The low concentrations of CO₂ (<3%) relative to the large concentrations of CH₄ (80-90%) in the sediment gas were expected due to the high solubility of CO₂ in water compared to the low solubility of CH₄ (Chanton and Whiting, 1995). Methane is the dominant constituent of gas bubbles across many studies; the concentrations of CH₄ found in sediment gas at Lake Elsinore were higher than concentrations of 66-69% measured in some water column studies due to CH₄ dissolution out of the bubble and N₂ and O₂ volatilization into the bubble during its ascent through the water column (e.g., Huttunen et al., 2001; Casper et al., 2000).

The opportunity for dissolution of CH₄ from a bubble is low for Lake Elsinore, however, owing to its shallow depth and short residence time in the water column. Based upon known ping rate (5 pps) and depth in the water column at each ping, we estimate an average rise velocity of 0.22 m s⁻¹, a value that is the same as that reported by Ostrovsky (2003) for bubble ascent in Lake Kinneret. Similar target strength values, generally -53 to -57 dB, were also found. At an average mean depth near 4.8 m, a rise velocity of 0.22 m s⁻¹ corresponds to an average bubble lifetime in the water column of about 22 s (up to about 40 s at the deepest region of the lake over this study period). Calculations by McGinnis et al. (2006) using a bubble gas exchange model indicate that only bubbles released from relatively shallow sites play a significant role in CH₄ emission to the atmosphere, as much of the CH₄ in bubbles from sites deeper than 10-20 m (depending upon bubble size) would be replaced by O₂ and N₂ as CH₄ is dissolved in the water column. Similarly, Zheng et al. (2011) reported that 51-80% of the CH₄ produced in deep water sediments is oxidized in the water column, whereas the majority of the CH₄ released from shallow lake sediments is able to evade oxidation and reach the atmosphere.

Overall, relatively low concentrations of CH₄ were found dissolved in the water column of Lake Elsinore (0.07 - 4.43 μmol L⁻¹), with highest concentrations found above the bottom sediments (Table 2.3). Casper et al. (2000) found similar results for methane concentrations in the water column, also noting that the CH₄ was highest at the deepest points. Bussman (2005) found low CH₄ concentrations in the water column (0.3 μmol L⁻¹), but observed concentrations to increase to 1.11 μmol L⁻¹ when he simulated sediment

resuspension in a microcosm experiment. Sediment resuspension could result from extensive ebullition that would hasten the flux of dissolved CH₄ from sediment pore water to the overlying water in Lake Elsinore. The general relationship between CH₄ concentration in the water and depth below the water surface, then, most likely reflects the greater rate of methane dissolution out of the bubble (following a linear driving force model), combined with aqueous phase diffusive flux from bottom sediments, enhanced release due to ebullition-induced sediment resuspension (Bussman, 2005), potential for some methane oxidation in the better oxygenated upper part of the water column (Zheng et al., 2011; Bastviken et al., 2004; Bastviken et al., 2011), and volatilization flux of CH₄ across the air-water interface.

While it is not possible to quantify all of the processes described above, the volatilization flux of CH₄ from Lake Elsinore can be calculated using the two-layer model for gas exchange, where resistance to mass transport is attributed to diffusional processes within air and water phase interfacial layers (Liss and Slater, 1974). The two-layer model was solved using an average dissolved surface CH₄ concentration of 0.47 μmol L⁻¹ (0.3 m depth on August 23, 2011), surface temperature of 25°C, average daily windspeed (u_{10}) of 2.1 m s⁻¹ (Lawson and Anderson, 2007), nondimensional Schmidt number of 480, and a nondimensional Henry's constant of 27 (Schwarzenbach et al. 2003). Subject to these conditions, we estimate a volatilization flux of CH₄ of 0.31 mmol m⁻² d⁻¹. This value can be compared with the average ebullitive CH₄ flux from the 7 sites on July 12, 2011 of 29.4 mmol m⁻² d⁻¹ and 9.1 mmol m⁻² d⁻¹ on September 6, 2011 (Table 2.4). Allowing, e.g., for an average CH₄ loss of approximately 10% to the water column,

based upon the ~5 m mean depth of the lake and a 3 mm radius bubble (McGinnis et al., 2006), we estimate that ebullitive flux to the atmosphere accounts for >90% of the total CH₄ flux to the atmosphere (during the summer).

The high rates of ebullitive flux from the bottom sediments of Lake Elsinore are consistent with the highly eutrophic conditions present there, and exceed values reported for shallow unproductive Mirror Lake (<1-4 mmol m⁻² d⁻¹) (Mattson and Likens, 1990), a shallow flood plain lake near the River Murray (4-7 mmol m⁻² d⁻¹) (Sorrel and Boon, 1992) and for Lake Postilampi (summer average of 2.9 mmol m⁻² d⁻¹, maximum of 6.1 mmol m⁻² d⁻¹) (Huttunen et al., 2001). Summer ebullitive flux rates were similar, however, to summer values reported for Lake Kinneret (generally 10-20 mmol m⁻² d⁻¹) (Ostrovsky et al., 2008) and the seasonal maximum ebullition rate of 35-37 mmol m⁻² d⁻¹ reported for hypereutrophic Wintergreen Lake (Strayer and Tiedje, 1978), but below values reported for a large tropical reservoir in Zambia/Zimbabwe (Del Sontro et al., 2011), a sub-tropical freshwater storage in Australia (Grinham et al., 2001), and a Swiss hydropower reservoir (Del Sontro et al., 2010). The very high rate of ebullition measured at the shallowest site in our study (96.2±1.6 mmol m⁻² d⁻¹) is quite similar to the maximum CH₄ ebullition rate of 95 mmol m⁻² d⁻¹ reported by Thebrath et al. (1993) for the shallow (2 m depth) littoral sediment in Lake Constance.

Extrapolating from our average measured ebullition rates, we estimate up to 668 tonnes of CH₄ emitted to the atmosphere from Lake Elsinore each year. This is larger than annual CH₄ flux reported from a hydroelectric reservoir in southwest China (50.9 tonnes yr⁻¹) (Zheng et al., 2011) and significantly larger than mean CH₄ emissions from a

small freshwater eutrophied lake in Finland, Lake Postilampi ($0.19 \text{ tonnes yr}^{-1}$) (Huttunen et al., 2000).

At individual sediment sites, the rate of ebullition was strongly related to the volume of gas stored in the sediment (Fig. 2.6). If we consider the gas volume stored in the sediment as the driving force for ebullition, then the silt-rich sediment at site G3 exhibits the greatest impedance to ebullition, while the shallow sandy sediment at site G1 provides the least resistance (Fig. 2.6). Sediments with greater % H₂O and other properties provide intermediate levels of impedance to ebullition. A simple linear driving force model would suggest that the ratio of ebullition rate to sediment gas volume provides a measure of the impedance to gas transfer within the sediments. Such an analysis suggests that impedance to gas transfer varies by a factor of 8 across the sediment sites.

5. Conclusions

Considerable variability exists in measured rates of methane ebullition and release from lakes in different hydrogeologic and climatic settings, and with different basin characteristics and water quality. An incomplete understanding remains concerning the properties and processes governing methane production and ebullition in lakes. Our measurements are perhaps the first to systematically quantify gas storage in bottom sediments as a function of sediment properties and over time, and relate these properties to methane ebullition. The storage of gas in bottom sediments of Lake Elsinore in July 2010 was found to be statistically significantly correlated with water content, organic C

content, depth and, most strongly correlated with silt content, while gas content was significantly inversely correlated with sand content. Gas volumes present in bottom sediment exhibited strong seasonal trends, reaching maximum values in late spring and early summer (up to $>6 \text{ L m}^{-2}$, corrected for hydrostatic pressure), declining through late summer and fall to reach minimum values (generally below detection) in the cool winter months. Properties that were positively correlated with gas storage in sediments were found to be inversely correlated with CH_4 ebullition, while sand content of the bottom sediments (inversely correlated with sediment gas content) was found to be strongly ($r=0.88-0.93$, $p<0.01$) positively correlated with ebullition rate. Moreover, volume of gas stored in the sediments was uncorrelated with ebullition rate across the sites on a given sampling day, although ebullition rates at each of the site were strongly related to gas volume retained within the bottom sediment.

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Chapter 3

Acoustic Monitoring of Sediment Bubble Volume and Distribution in a Shallow Eutrophic Lake (Lake Elsinore, CA)

Abstract

Measurements of acoustic target strength of individual bubbles above the sediments and over time were made at a shallow eutrophic freshwater lake in Southern California. Hydroacoustic measurements were made at 7 sites on July 12, 2011, September 6, 2011, and August 1, 2012 to study bubbles as they were released from sediments and rose through the water column. Echograms were analyzed for target strength and the weighted average bubble volume of methane (CH₄) and other gases ebullated from sediments were determined. Bubble size and volume varied weakly across the different sediments and depths, with no strong correlation with sediment properties. A statistical characterization of the population of bubbles found broadly normally-distributed bubble sizes, with an ensemble-average weighted mean bubble volume of $0.094 \pm 0.023 \text{ cm}^3$, kurtosis values of -0.84 to +1.11, and skewness values of -0.23 to 0.62, although individual bubbles with target strengths as low as -68dB (0.0013 cm^3) and as high as -43dB (1.69 cm^3) were found.

Key Words: Methane, Sediment, Bubble Volume, Gas Ebullition

1. Introduction

Bubble ebullition describes the process that liberates gas produced by methanogens as a result of the breakdown of organic material in bottom sediments. Methane has been found to be the main constituent (>80%) of the bubbles being emitted from the bottom of lakes, and due to the low solubility of CH₄, ebullition has been recently identified as an important gas transport mechanism. Recent research efforts suggest that ebullition may have a much greater contribution than other transport mechanisms that are considered in current GHG analyses, and thus may play a bigger role in atmospheric global warming than previously suggested (Poissant et al., 2007; Huttunen et al., 2001). As the process of bubble formation and emergence remains poorly understood, methane emissions from natural lakes and man-made reservoirs are often neglected as significant sources of methane and have not yet been included in global GHG budgets (Bastviken et al., 2011).

Temperature and water depth have been shown to impact sediment gas production and rate of bubble ebullition out of lake sediments, and recent estimates of the annual contribution of lakes to the overall atmospheric CH₄ emissions have been calculated. Research conducted at Lake Elsinore (Chapter 2) have concluded that gas volumes present in bottom sediment exhibit strong seasonal trends that reach maximum values in late spring and early summer (up to >6 L m⁻², corrected to zero hydrostatic pressure) and reach minimum values generally below detection limits in the cool winter months. We estimated a summer (July) ebullition rate of 29.4 mmol m⁻² d⁻¹ and a much lower volatilization flux of CH₄ of 0.31 mmol m⁻² d⁻¹; as a result, ebullitive flux from Lake

Elsinore accounts for >90% of the total CH₄ flux to the atmosphere (Chapter 2).

Questions remain, however, about the details of the ebullition process.

While CH₄ has been established as the main constituent of gas within sediments and bubbles released from bottom sediment, a newly formed bubble is not immediately released from the sediment surface as soon as it is formed. It is able to migrate out of the sediment into the water column only when it has reached a critical size such that the upward buoyant force is greater than the restraining force within the sediments. Sediment properties are thus thought to influence gas storage and ebullition (Chapter 2).

Additionally, since bubble size is a critical factor in ebullition and ultimately the fate of bubbles, it is also important to understand the size distribution of bubbles at various sites across the lake as well as vertically in the water column.

In this study, we use a 201-kHz split-beam echosounder to investigate the acoustical target strength and physical size of gas bubbles released from the sediment, bubble size distribution, critical buoyant force, and ultimately their effect on the overall rates of gas ebullition from bottom sediments in Lake Elsinore.

2. Materials and Methods

2.1 Study site

Studies were conducted at Lake Elsinore, a shallow lake with a maximum depth of about 9 m at the time of this study. Located in Riverside County, Lake Elsinore is the largest natural lake in southern California (approximately 1,200 ha) and is highly eutrophic with frequent algal blooms. Due to frequent drought and occasional El Nino

conditions, the lake has varied widely in water quality and has undergone various management actions including a reconfiguration of the lake basin in 1995, occasional inputs of recycled water since 2003, and installation of mechanical surface mixers in 2005 and a diffused aeration system in 2008 (Anderson, 2010). A detailed study based on gas sampling and hydroacoustic surveying showed that gas volumes present in bottom sediment of Lake Elsinore exhibit strong seasonal trends, reaching maximum values in early summer up to $>6 \text{ L m}^{-2}$ and that $>90\%$ of the summer CH_4 emission to the atmosphere is attributable to ebullitive flux (Chapter 2).

2.2 Hydroacoustic measurements and analysis of gas bubbles

Hydroacoustic measurements were used to detect bubbles released from bottom sediments and rising through the water column (Ostrovsky et al., 2008). Hydroacoustic measurements were carried out using a BioSonics DT-X echosounder fitted with a 201-kHz split-beam transducer. Echograms were collected between 9 a.m. and 3 p.m. at each of the seven sampling sites (Ch.2; Fig 2.1) on July 12, 2011 and September 6, 2011, and during a 24-hr study on August 1, 2012. The transducer was calibrated using a 37-mm tungsten-carbide sphere of known target strength prior to collection of acoustic data; data were acquired at 5 pings per second (pps) at all sampling sites.

Echograms were analyzed by Biosonics Visual Analyzer software which quantified target strengths of bubbles within $\sim 0.5 \text{ m}$ of the lake bottom at each sampling site and on each sampling date. Quantified targets were separated into 1 dB TS bins within the -69 to -40 dB range. Using methods similar to that of Ostrovsky et al. (2008),

target strengths were used to assess the physical size of bubbles. The average target strengths (calculated by the Biosonics software) were used to calculate the backscattering cross section (σ_{bs}) through the equation

$$TS = 10\log(\sigma_{bs}) \quad (1)$$

where σ_{bs} is the backscattering cross section (m^2). Ostrovsky et al. (2008) previously found σ_{bs} and bubble volume (V_B) to be related through the empirical equation:

$$V_B = 995600\sigma_{bs}^{1.3426} \quad (2)$$

such that we are able to accurately quantify the volume of the ebullated bubbles.

The buoyant force (F_b) associated with each bubble volume (V_B) was calculated using the equation

$$F_b = \rho g V_B \quad (3)$$

where ρ = density of water (1000 kg/m^3), g = acceleration due to gravity (9.8 m/s^2) and V_B = volume of bubble (m^3), uncorrected for hydrostatic pressure.

Since bottom sediments are present at a wide range of depths in the lake (0 – 9 m), the size and volume of bubbles released from bottom sediments will also be dependent upon depth. Bubble volumes were corrected for hydrostatic pressure (P_{hyd}), where P_{hyd} ($N \text{ m}^{-2}$) is given by the equation:

$$P_{hyd} = \rho_{H_2O} g z \quad (4)$$

Addition of P_{hyd} to P_{atm} (0.97 bar atm) obtains the total pressure (P_{tot}) at any depth, z . While simple ideal gas law calculations allow one to estimate how bubble volume would vary as a function of hydrostatic pressure, such calculations would not

consider gas dissolution into aqueous phase. As a result, bubble target strength and size were experimentally evaluated by tracking individual bubbles as they rose through the water column. From the three initial surveys of all 7 sites, ten individual echograms were selected for more intensive analysis. Echograms with minimal interference from fish or zooplankton were used to evaluate bubble size distributions based on target strength. Echograms were analyzed using Biosonics Visual Analyzer software and the echo threshold was adjusted to -65 dB in order to better distinguish between fish and bubbles and avoid the inclusion of targets other than bubbles in our echogram analysis. Target strengths were quantified for individual bubbles (between -65 to -40 dB) from the lake bottom to the lake surface, and were separated into bins representing 0.5 m depth intervals of the water column.

3. Results & Discussion

3.1 Bubble size distribution above sediments

Probability distribution functions were plotted to show the % of total targets sampled at each dB (sampling analysis ranged from -69 to -40 dB). Bubbles emitted from the shallowest site G1 (2 m depth in Table 3.1) exhibited the narrowest range of target strength values and volumes when compared to all other sampling sites, with TS values ranging from -59 to -48 dB (bubble volume 0.012 to 0.358 cm³), with 22% of the population exhibiting a median TS of -55 dB and volume of 0.041 cm³ upon release from bottom sediment (Figure 3.1).

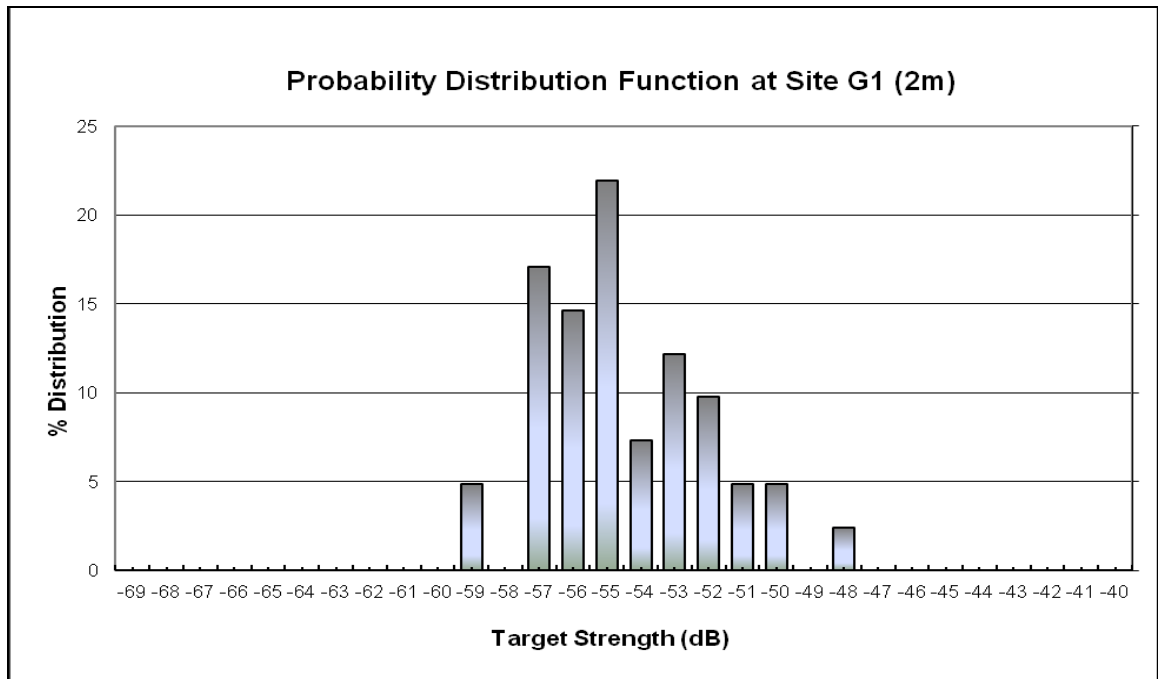


Figure 3.1: Size-distribution variations of bubble gas volume at site G1.

The deepest sampling site G6 (8 m) emitted bubbles much smaller in size than G1, and had the widest range of target strength values (from -65 to -43 dB, volume 0.0019 to 1.68 cm^3) (Table 3.1; Figure 3.2). This site also possessed the most normal and symmetrical distribution of all the sites, and had a median TS of -56 dB (equivalent to a bubble volume of 0.030 cm^3). Sites G3, G5 and G7 also had median TS values of -56 dB. Site G4 had a median bubble TS of -57 dB (volume of 0.022 cm^3), which is only slightly smaller than the majority of the sampling sites.

Del Sontro et al. (2011) observed bubbles at Lake Wohlen in Switzerland showing ranges similar to Lake Elsinore's site G6, with the smallest TS distribution beginning at -65 dB. The range of bubble target strengths in this study, however, was

much narrower, with the largest TS values reaching -51 dB, as opposed to the much larger TS of -43 at Lake Elsinore (Fig. 3.2).

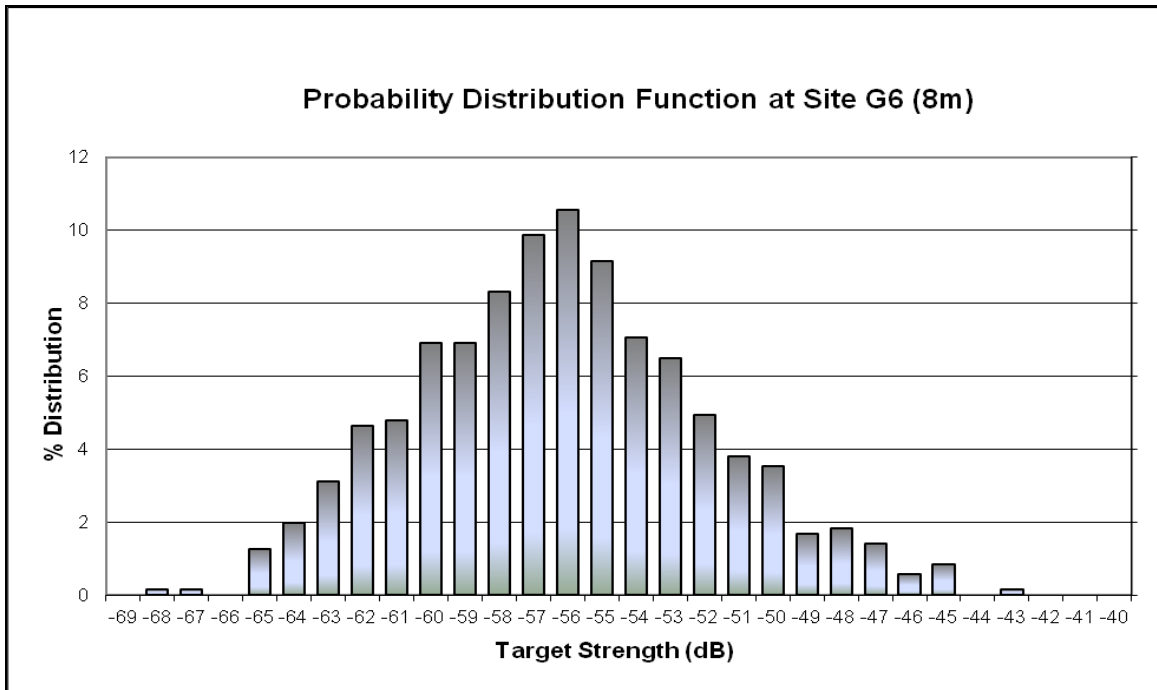


Figure 3.2: Size-distribution variations of bubble gas volume at site G6.

Applying the ideal gas law ($PV=nRT$), bubble volumes were normalized to account for different hydrostatic pressure effects and average weighted bubble volumes were found to range from 0.060 cm^3 to 0.126 cm^3 . The overall mean weighted bubble volume emitted from Lake Elsinore was found to be $0.094 \pm 0.023 \text{ cm}^3$. This is almost exactly the same as the average bubble volume reported by Ostrovsky et al. (2008), who calculated an average bubble volume of 0.097 cm^3 in Lake Kinneret, Israel. Although the target strength distribution range studied by Del Sontro et al. (2011) indicated a smaller

bubble size at Lake Wohlen, the weighted mean TS for all observed bubbles was equivalent to a 0.108 cm^3 , similar to values found in Lake Elsinore and Lake Kinneret. Greinert et al. (2010) also found similar bubble volumes emerging from seeps in the Black Sea. These findings suggest that, despite obvious spatial and geographical heterogeneity, bubbles seem to be emitted at broadly similar sizes from lakes.

Descriptive statistics were developed using Excel to provide information about the central tendency and variability of the bubble target strength at each sampling site (Table 3.1). Kurtosis, which characterizes the relative peakedness or flatness of a distribution compared with the normal distribution, was found to be positive at sites G3 and G7. This indicates that the bubble volume distribution at these sites was less spread out than a normal bell distribution (more peaked, with a higher peak bubble volume and less deviation about that main peak). Sites G1, G2, G4, G5, and G6, on the other hand, had negative kurtosis values, representative of a distribution that is flattened and more spread out than a normal distribution.

Site	Depth (m)	Mean TS (dB)	Kurtosis	Skewness	Minimum	Maximum
G1	2	-55.26 ± 0.64	-0.41	0.62	-59.26	-50.6
G2	5.4	-59.48 ± 0.36	-0.52	0.19	-68.66	-45.77
G3	5	-55.13 ± 0.41	1.11	0.01	-62.73	-45.77
G4	6.3	-56.55 ± 0.32	-0.17	0.08	-67.51	-46.56
G5	6.2	-59.09 ± 0.25	-0.84	0.03	-68.69	-46.19
G6	8	-56.44 ± 0.24	-0.03	-0.23	-69.12	-45.52
G7	4.2	-56.86 ± 0.27	0.54	0.29	-61.54	-52.33

Skewness is a measure of asymmetry around the mean of a distribution, and positive skewness indicates a distribution where any asymmetry extends toward more positive values. Sites G3, G4, and G5 all produced skewness values very close to zero (0.01, 0.08, and 0.03, respectively) which means they are more or less symmetrical and generally report values as would be estimated from a normal distribution. Site G6 (-0.23) was the only sampling site to exhibit negative skewness (distribution favoring smaller bubble volumes than expected) (Fig. 3.2), while sites G1, G2, and G7 demonstrated positive skewness, suggesting the release of larger bubble volumes than a normal distribution.

McGinnis et al. (2006) reported that the initial emerging bubble size is directly indicative of the amount of methane released to the atmosphere since smaller bubbles usually dissolve before reaching the air/water interface, leaving the larger bubbles as the dominant atmospheric CH₄ contributor. Greinert and Nützel (2004) found that larger bubbles (> 7 mm) transported the majority of gas to the atmosphere, even if these larger bubbles represented only a small portion of the total bubble size distribution. Larger bubbles being emitted from Lake Elsinore has important implications for gas flux out of sediments, as larger bubbles contribute much more to the total CH₄ efflux to the atmosphere and thus to the total GHG budget.

3.2 Sediment properties & bubble size

Average TS and bubble volume (equation 2) at each site and on each of the three sampling dates were pooled together and plotted against various sediment properties

(depth, bulk density, % H₂O, organic C, silt, clay, and sand content) in order to examine the role sediment properties play in the size of bubbles at time of ebullition. A thorough sediment compositional analysis was previously conducted on surface grab samples collected from each of the sampling sites at the start of an initial study (Anderson and Pacheco, 2011). Statistically significant relationships were found between bubble volume and water content, organic C content, clay content, sand content, and bulk density measured in that earlier study (n=16, p <0.05) (Table 3.2). It is recognized that most of these sediment properties are auto correlated, but clay content appears to be the most strongly correlated to average bubble target strength.

Table 3.2 - R-values of pooled data for sediment properties at relevant monitoring sites in Lake Elsinore for three sampling dates (July 12, August 1, and September 6).							
	Depth (m)	% H₂O	% Silt	% Organic C	Bulk Density (g/cm³)	% Clay	%Sand
Avg TS (n=16)	-0.407	-0.515*	-0.122	-0.619*	0.538*	-0.639**	0.559*

*significant at $p < 0.05$; **significant at $p < 0.01$, ***significant at $p < 0.001$

Meier et al. (2011) found evidence that sediment type (grain size, porosity) plays a key role in controlling the overall size and shape of bubbles emerging from sediment. Of all of the significant sediment properties, % clay showed the greatest correlation to acoustic bubble size ($r = -0.639$). Sites G4 & G5, which have the highest clay content (60.7 and 59.7%, respectively) emitted the smallest bubbles ($0.013 - 0.022 \text{ cm}^3$), while site G1 (clay content = 4.8%) released the largest bubble ($.052 \text{ cm}^3$) (Figure 3.3).

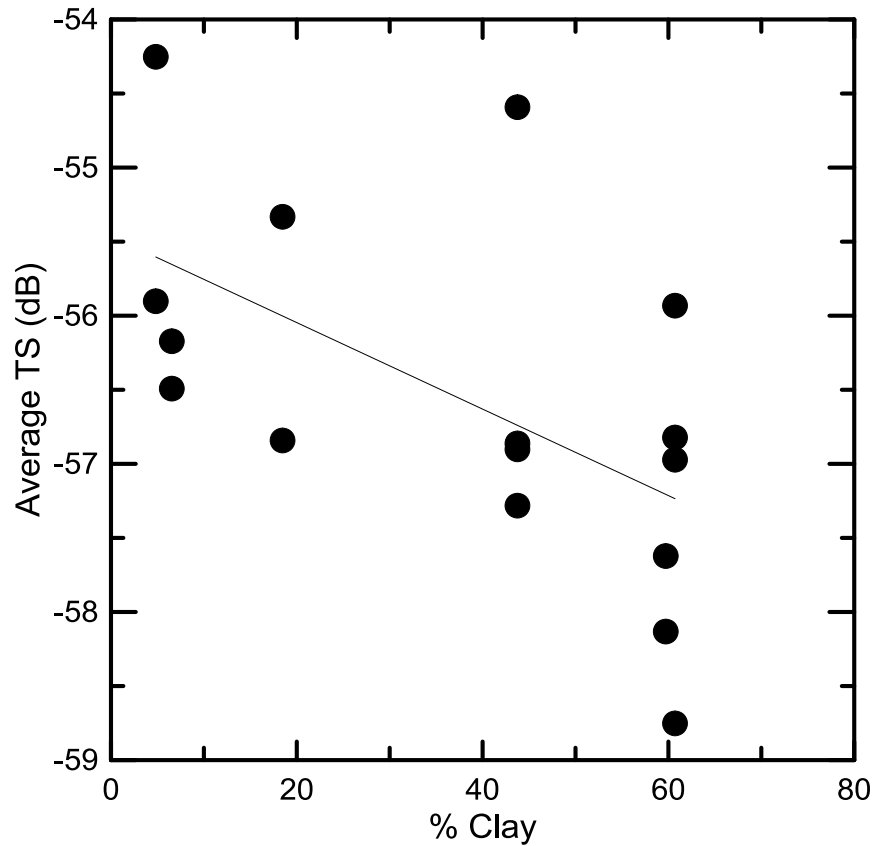


Figure 3.3: Average target strength vs. sediment clay content of pooled data.

Sediment organic carbon content was also found to be closely correlated with acoustic bubble volume ($r=-0.619$). Sampling sites G4 & G5 which have the highest reported organic carbon content values (4.77-4.89%, respectively) emitted the smallest bubbles, while sites G1 & G7 with the lowest % organic C content (<1%) emitted bubbles ranging from 0.052 to .026 cm³, volumes which are in the upper range of all bubble volumes measured. The larger values of % organic C at sites G4 and G5 may be one key attribute contributing to these sites emitting the smallest acoustic bubble sizes

from the lake bed. Additionally, these high clay, high OC sediments would be expected to release the smallest bubbles due to the restricted pore space.

In contrast to the previously discussed properties, bulk density and sediment sand content both showed a positive correlation with bubble volume. That is, as bulk density and % sand increased, bubble volume also increased. Del Sontro et al. (2011) found that gas bubbles in sediment beds consisting of larger particles percolated up through the granular cracks and emerged with a size similar to the grain size. It is suggested that bubbles formed in coarser-textured, high bulk density sediment attain a greater size and exert a greater upward buoyant force before migrating to the sediment surface and being released to the water column. Moreover, the diameter of pores is larger in sands, and the size of the pore space, along with the tendency for these pores to be well connected to each other, may allow larger bubbles to move more easily through sandy sediment than through finer textured muddy sediments, even though these finer-textured clay sediments normally have a higher total porosity overall. Low porosity in sands, however, can inhibit gas movement, and we see here that largest % sand content (~87%) resulted in the largest bubble volume, median % sand content at site (~60%) resulted in intermediate bubble volumes, and sites with small amounts of sand often resulted in the smallest bubble volumes although variability was very high (Figure 3.4).

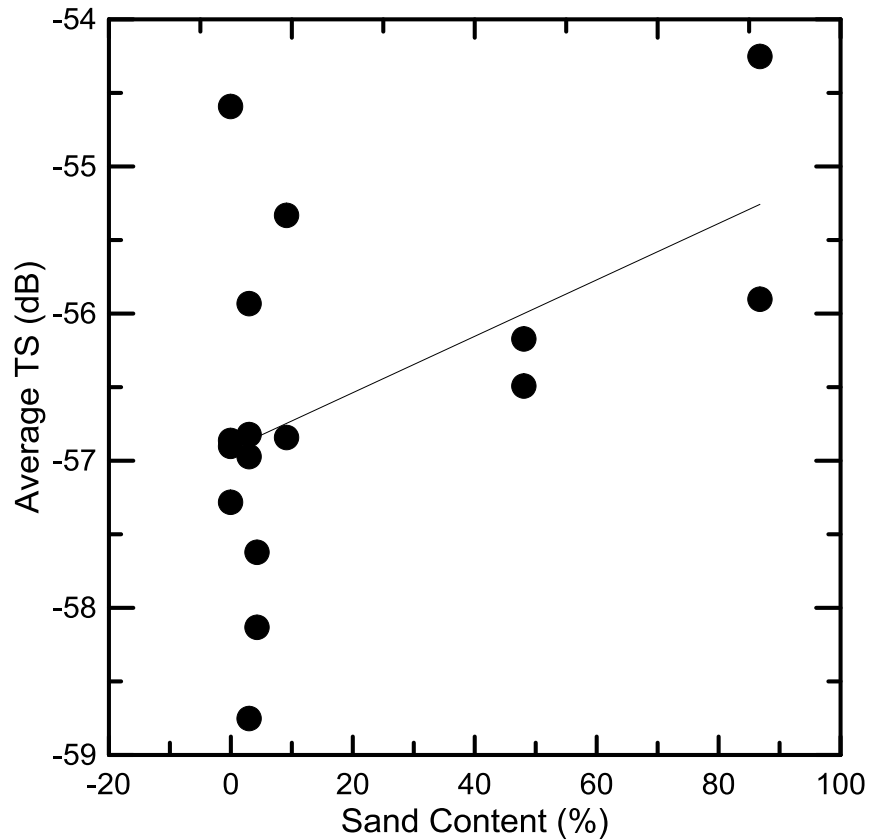


Figure 3.4: Average target strength vs. sediment sand content of pooled data

Acoustical targets from all sampling sites were plotted as histograms to test for normality, and standard Gaussian distributions with respect to number of targets found at each TS were observed at all sampling sites on pooled data except for site G2, which was extremely unsymmetrical, skewed to the right, and unlikely to come from a normal distribution. As a result, site G2 was omitted from (most) statistical analyses. When target strength was plotted against sediment depth for the September sampling date, a statistically-significant correlation was yielded, with a slope equal to -0.49. This slope suggests that there is a decrease in bubble TS of approximately 0.5 dB for every 1m

increase in depth to the bottom of the lake. The relationship between bubble size and sediment depth remains tenuous, however, and clearly depends on a variety of factors and sediment properties. Not unlike the gas volume storage and ebullition findings from previous studies (Chapter 2), a slight trend is discernible, with the smallest average TS (-57.62) and smallest associated bubble volume (0.018 cm^3) emitted at median depths (5-7.5 m). Somewhat surprisingly, the largest sized bubbles were emitted at both the shallowest site G1 (1.8 m, 0.052 cm^3) and the deepest site G6 (8.6m, 0.047 cm^3).

Data thus suggests that depth is playing some role in the TS (size) of bubbles released from bottom sediments, as bubble size decreasing with depth is a result of larger hydrostatic pressure at deeper sites. While sediment properties yielded stronger and more statistically significant R-values than depth, depth remains a covariate to the overall bubble ebullition process and we can conclude that both depth and sediment composition influence overall bubble size.

Critical buoyant force is the upward force that the bubble must achieve in order to overcome viscous and frictional forces and migrate out of the sediment into the water column. These forces are largely due to sediment overburden pressure, although hydrostatic pressure also comes into play here. Overall, the critical buoyant force is able to give us a good indication of the resistance that each sediment type exerts against the occurrence of an ebullition event. Due to the direct relationship between buoyancy and volume, larger bubble volumes result in larger buoyant forces. The critical buoyant force a bubble at 1.8 m depth needs to overcome in order to migrate out of the sediment was found to be 0.00051 N, while a bubble at a depth of 6.5 m requires a much smaller force

(0.00013 N). Further measurements with a larger sampling pool of bubble targets is necessary to corroborate relationships between acoustic bubble size and sediment properties and reduce the chance of any error due to multiple bubbles or possible outliers.

3.3 Bubble size ascending in water column

Eleven individual bubble streaks were analyzed for any changes in size that a gas bubble undergoes as it is ebullated from the lake bottom and makes its way up through the water column. All of the bubbles yielded a relationship such that the bubble had its smallest volume upon initial release relative to values found higher in the water column, which can generally be explained by the decrease in hydrostatic pressure as the bubble rises in the water column, resulting in an increase in bubble volume (Figure 3.5). While most bubbles generally increased in size (lower negative TS values) as they ascended through the water column, others peaked at some point on the bubble's journey through the water column and then began to decrease in volume again, perhaps due to dissolution. Since most of the analyzed bubbles exited the transducer beam angle before reaching the top of the water column, no clear and concise conclusions can be made regarding the overall changes in bubble volume over the full depth range in Lake Elsinore.

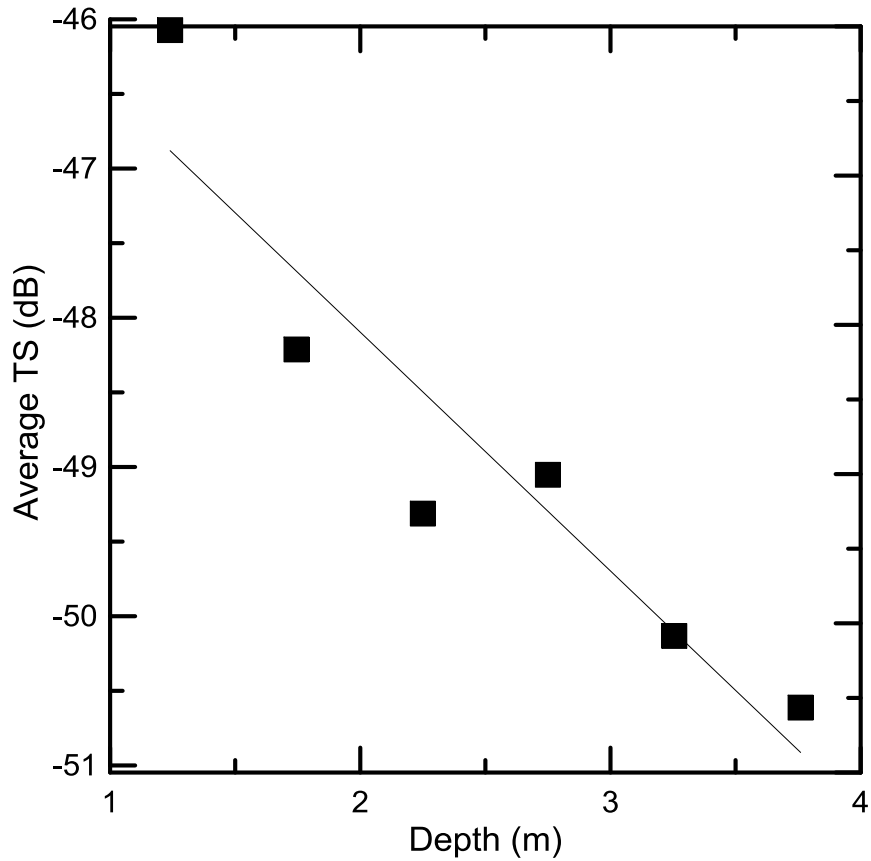


Figure 3.5: Vertical variations in target strength of an individual gas bubble at site G5 as a function of depth.

As bubbles rise through the water column, there is an exchange of gases that may occur to approach equilibrium. While CH_4 may be dissolved out of the rising bubble, this lost gas may be replaced with N_2 and O_2 being transported into the bubble – these two processes occurring simultaneously might offset each other, resulting in no significant net gas gain/loss and thus no apparent trend in the change of bubble volume.

4. Conclusions

Hydroacoustic measurements provide valuable insight into bubble size distribution during the process of ebullition. The size of a bubble is directly related to the σ_{BS} which can be easily calculated from the TS recorded by the echosounder. Using the empirical equation of Ostrovsky et al. (2008), we calculated average weighted bubble volumes in the same size range as Ostrovsky (0.09 cm^3). The majority of the total bubble volume was found in the largest bubbles – these large bubbles, however, constituted a small number of the total bubbles emitted from the sediment. Overall, smaller bubble volumes (lower TS) were found at lake sites with higher clay content, OC content, H_2O content, silt content, and at deeper sites. Larger bubbles (larger values of TS) were mostly associated in sediments with higher bulk density, although variability was substantial across the 3 sampling dates. It is suggested that further hydroacoustic surveying with a larger sampling pool of bubble targets is necessary to validate relationships between target strengths, acoustic bubble size and sediment properties.

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