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Michelle Tsuey-Yee Quan
University of Windsor

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Optimization of equilibrated headspace technique for compositional and isotopic analysis of dissolved gases

By

Michelle Tsuey-Yee Quan

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2023

Optimization of equilibrated headspace technique for compositional and isotopic analysis of dissolved gases

By

Michelle Tsuey-Yee Quan

APPROVED BY:

I. Samson

School of the Environment

S. Loeb

Department of Chemistry and Biochemistry

S. Mundle, Advisor

Department of Chemistry and Biochemistry

April 24, 2023

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ABSTRACT

Dissolved gas analysis has been used to quantify concentrations of natural gas and carbon dioxide in solutions for many years, giving insight into bioremediation processes and potential natural gas releases. However, due to the lack of universal dissolved gas methods, there is room for interpretation during sampling, storage, and analysis, causing variation in the data obtained between laboratories, especially as these techniques are often not applicable to stable isotope analysis, which can be used to determine the source of the elevated concentration obtained. Thus, one portion of this thesis aims to gain a greater understanding of the effect of headspace on the resulting concentrations mainly due to the variation in sampling and analysis between techniques used, and through a slight modification in a technique created by an established regulatory organization, the investigation of the validity of stable isotope analysis on dissolved gas samples is also performed to capture the wealth of information that dissolved gases can provide.

From the laboratory and field data obtained throughout this thesis, it was found that the existence of pre-existing headspace within a sample affects the resulting data obtained, mainly elevating concentrations as the volume of headspace increases. As well, it is also advised that consistent sample vessels be used throughout a program or site, to ensure that the data obtained can be comparable as the usage of different sample vessels can cause differing volumetrics, affecting the resulting calculation for concentrations.

DEDICATION

To my parents and brother, who supported me unconditionally, no matter which direction I decide to head.

To my friends that always cheered me on quietly on their own, knowing that I would reach out to them on my own when I needed it.

ACKNOWLEDGEMENTS

I would like to thank MundleLab, who accepted my questions with patience and open arms and were always willing to give me a hand whenever I needed it. Thanks to Kaylee Anagnostopoulos, Meagan Beaton, Julia D’angela, Matthew Day, Karlynne Dominato, Sakshi Khatri, Nadia Tarakki, and Dave Ure, you were the support group and teachers I never knew I needed.

I would like to thank Dr. Scott Mundle, thank you for allowing me to learn and grow under you. The scientist I hope to become one day will hopefully exceed your expectations.

TABLE OF CONTENTS

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LIST OF FIGURES

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CHAPTER I

INTRODUCTION

1.1 Dissolved gases

Dissolved gases (DG) naturally exist in various aqueous solutions such as groundwater, surface waters, and formation waters. As many bodies of water—such as streams and oceans—are in contact with the atmosphere, it allows for gases in the atmosphere, like carbon dioxide (CO_2), nitrogen (N_2), or oxygen (O_2) to be dissolved into the aqueous phase. However, as some of these aqueous solutions are in contact with soils or rocks, other gases including methane (CH_4) and other hydrocarbons could also enter the aqueous phase (Whitehead, 2020). In the dissolved form, many of these DG pose no risk to the environment or the people surrounding the body of water (Coleman, & Coleman, 2013). However, once these gases exit the aqueous phase as bubbles due to the variable temperature and pressure present, these gases become potentially hazardous.

1.2 Hydrostatic Pressure

DG mainly exits the aqueous phase into the gas phase due to hydrostatic pressure. Since hydrostatic pressure increases as the depth increases due to the pressure exerted by a solution at equilibrium due to the force of gravity, the concentration of DG in a solution can increase until the sum of the partial pressure of all gases within the solution exceeds this hydrostatic pressure. Once this sum surpasses this hydrostatic pressure, the gas will leave the aqueous phase as bubbles (Coleman, & Coleman, 2013). Since these gases are no longer in the aqueous phase, they can potentially be hazardous once in the gas phase. For example, if CO_2 and CH_4 were to exit the aqueous phase, gaseous CO_2 can cause death by suffocation while CH_4 can be highly explosive (CCOHS, 2023). Therefore, by determining the concentration of DG in the aqueous phase, the hazards surrounding this aqueous solution based on their DG concentrations can be assessed.

1.3 Application of Compositional Dissolved Gas Analysis in the Literature

Due to the increase in natural gas extraction, the utilization of DG to detect the presence of natural gases in shallow groundwater is of interest. While their specific compositions may vary based on sources, CH_4 is the main component of natural gases along with ethane (C_2), propane (C_3), and other trace gases (Schoell, 1980). These releases can usually be related to well integrity issues and therefore the detection of DG concentrations is important in remediation. In 2017, a controlled release of natural gas into the Borden Research Aquifer was performed to explore fugitive gas releases in groundwater. Cahill et al. (2018) were able to observe elevated concentrations of CH_4 (> 30 mg/L) in comparison to baseline concentrations of < 0.2 mg/L from these fugitive gas releases and were able to detect the release of natural gas into the groundwater through compositional analysis of DG (Cahill et al., 2018). However, not all cases of fugitive gas releases have a detectable or elevated CH_4 concentration to infer a natural gas release. Alongside the variability of baseline shallow groundwater CH_4 concentrations formed from microbial methanogenesis, and the variability of dissolved CH_4 spatially and temporally, compositional analysis of DG is not sufficient to detect natural gas releases (Gorody, 2012). Thus, an integrated approach with more than just compositional analysis of DG samples is important in further solidifying the potential release of natural gases.

1.4 Application of Stable Isotopic Analysis to Dissolved Gas Analysis

The analysis of stable isotopes has been used in many areas of geochemistry, from determining groundwater quality in hydrology to diet assessment in paleontology. By using the differences in the isotope ratios, conclusions can be made about the natural systems involved based on the preferential fractionation of isotopes, where the reactions involved favour the heavy or lighter isotope due to the mass and thermodynamic properties that one isotope may have over another (Sharp, 2017). **Figure 1** is a depiction of some of the geochemical areas in which stable isotope analysis can be applied.

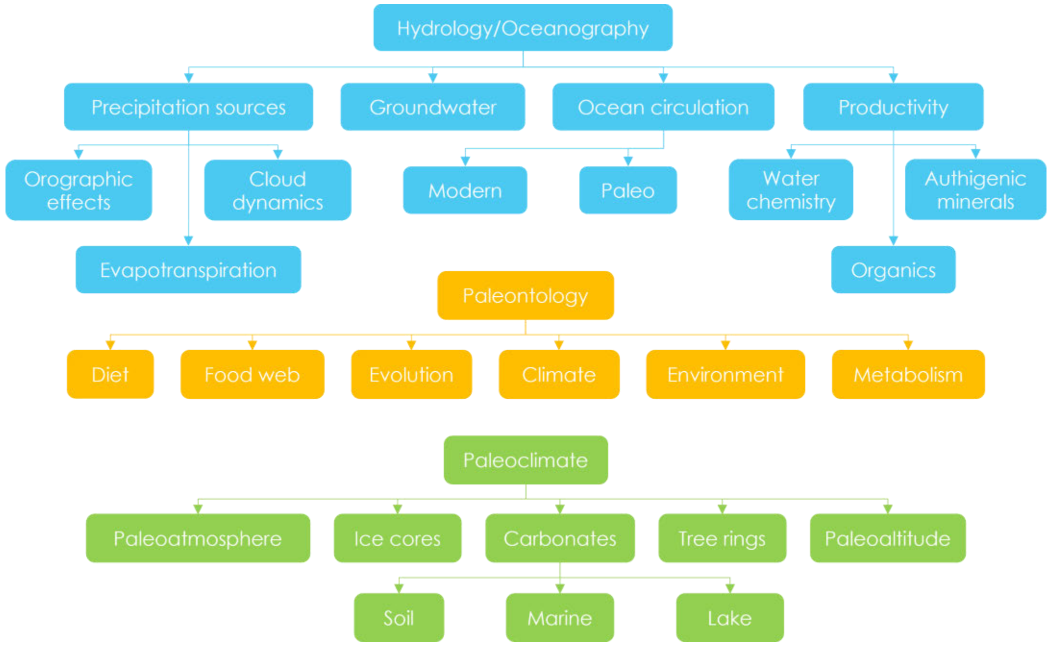

Figure 1: Examples of the types of fields that are studied using stable isotopes, adapted from (Sharp, 2017)

1.4.1 Isotope Notation

When stable isotope analysis is performed, the isotope ratio of a sample is the common notation used to express the value obtained. The isotope ratio, or the delta (δ) value, is first found using the ratio of the heavier isotope to the lighter isotope within a sample. The isotope value of the sample is then compared to a standard that has an unchanging ratio. Since the values only alter slightly, calculations are applied to the ratios to make the difference in the values obtained more apparent (Shoemaker, 2010). **Equation 1** depicts the equation used to determine the isotope ratio of a sample for carbon.

$$\delta^{13}C = [\left(\frac{\left[\frac{^{13}C}{^{12}C}\right]_{sample}}{\left[\frac{^{13}C}{^{12}C}\right]_{standard}}\right) - 1] \times 1000 \qquad \textbf{Equation 1}$$

^{13}C specifically, has been used in hydrocarbon exploration as a tracer to investigate the source, generation, migration, and alteration of these hydrocarbons. This analysis can give insight into the gas type present—whether it originates from microbial or thermogenic processes—as well as the maturity and nature of the parent material (Fuex, 1977).

1.4.2 Application of Isotopic Dissolved Analysis to Delineate Sources

Baseline carbon methane isotopes ($\delta^{13}C-CH_4$) in shallow groundwater usually have a low isotope value of < -50‰ relative to the Vienna Pee Dee Belemnite (VPDB)—which is the international reference standard for carbon isotopes—and an increase from these values (> -50‰ for $\delta^{13}C-CH_4$), can be an indicator of thermogenic gases present. In the study performed by Cahill et al. (2018), they completed both stable isotope analysis and compositional analysis on the DG samples that were collected and obtained $\delta^{13}C-CH_4$ values from -80‰ to -46‰ during their baseline analysis before the release was performed. Although -46‰ is slightly higher than the usual baseline isotope range for $\delta^{13}C-CH_4$, the authors attribute this increase to microbial CH_4 oxidation. Upon controlled natural gas release, the $\delta^{13}C-CH_4$ values obtained increased towards -42‰ (± 2‰), which matched the $\delta^{13}C-CH_4$ value obtained from the controlled hydrocarbon release (Cahill et al., 2018). Since the isotope values of the controlled natural gas release were comparable to the isotope value obtained from the DG samples after injection, isotopic analysis alongside compositional analysis of DG can be used to both detect and identify a natural gas release.

1.5 Literature study of analysis methods

RSKSOP-175, which is the only established technique by a regulatory organization, was developed by the U.S. Environmental Protection Agency for use by the Ground Water and Ecosystems Restoration Division and outlines the preparation of water samples for the determination of DG (CH_4, C_2, O_2, N_2…) using a known equilibrated headspace. In RSKSOP-175, a water sample is collected in a serum bottle and capped with a Teflon faced septum with a crimp cap, ideally with no headspace present and the aqueous sample fills the sample vessel. If headspace is not present initially, then the analyst will create headspace in the bottle by displacing 10% of the serum volume with high-purity helium during analysis, which is known as the helium displacement process. The bottle is then shaken for five minutes before the headspace sample is injected into a gas chromatography (GC) instrument. Since gas standards are used to calibrate the instrument, when analyzing a sample, the concentrations obtained would be representative of what the concentrations would be in a gas sample instead of a sample that consists of an aqueous and gas phase. To consider the aqueous phase present, a post-analysis calculation is performed using Henry's law constant, compositional data from GC analysis, bottle volume, density, and temperature to determine the resulting DG concentrations. These post-analysis calculations use Henry's law constant, where the concentration of gas particles in the solution phase that is in equilibrium with the pressure in the gas phase can be related, while the volume of solution in the sample vessel is used to consider its effect on the concentration of gases in the headspace (Hudson, 2004). These calculations are performed for each component, as Henry's law constant differs for each component. Although this technique is utilized to determine the concentrations of DG samples, this method was not designed to include isotopic analysis.

While it is the only established technique, deviations of RSKSOP-175 have been created and used within the community as well. An example of a method that was created that is a slight change of RSKSOP-175 is PA-DEP 3686. It was developed by the Pennsylvania Department of Environmental Protection and differs in calibration style. Instead of using a gas phase standard, an aqueous phase standard is used to create the calibration curve, thus the post-analysis calculations are no longer needed as the calibration has already factored in the aqueous solution present in the bottle. Like RSKSOP-175, headspace from a sealed sample vessel is injected into the GC, however, PA-DEP 3686 suggests the usage of an autosampler for consistent injections into the instrument (PaDEP, 2012).

Although both techniques are widely used, one technique has not been determined to be favoured over the other. However, Neslund (2015) presented a series of experiments where both RSKSOP-175 and PA-DEP 3686 were compared to determine which technique yielded the least amount of deviation when determining the concentration of DG. A series of standard gases/solutions were used to make a calibration for both techniques and once the calibration was obtained, the analysis of the same gases and solutions that were used to calibrate the instrument was performed to determine the error associated with each technique. From his findings, it was concluded that PA-DEP 3686 had double the average error in comparison to RSKSOP-175, thus, due to the low amount of average error that the calibration of RSKSOP-175 yielded, it was determined that it was more reliable with its gas standards in comparison to PA-DEP 3686 (Neslund, 2015). The error associated with PA-DEP 3686 can be attributed to the instability of the aqueous standard, which was created by bubbling a gas through reagent water for an hour, saturating the fluid. However, as the bubbling of the gas in the reagent halts, equilibrium processes begin affecting the resulting concentrations obtained, thus giving a calibration that is not stable and reliable as gas standards (Neslund, 2015; PaDEP, 2012).

1.6 Lack of Universal Dissolved Gas Analysis Method

Even though the analysis of DG shows great promise to detect natural gas releases, especially using techniques such as RSKSOP-175 and PA-DEP 3686, there is still limited data related to the reliability and reproducibility of DG analysis between laboratories. This is due to a lack of a universal method used to analyze DG samples both compositionally and isotopically. Although RSKSOP-175 is a reliable technique of choice to compositionally analyze a sample (Madison et al., 2022; Wright et al., 2012; Neslund, 2015), stable isotope analysis is not supported with this technique, thus many studies or commercial laboratories still decide to create a method specific for their application, while incorporating stable isotope analysis (Cahill et al., 2018; Isotech Laboratories; McIntosh et al., 2014; University of Calgary), allowing for isotopic signatures to be obtained. However, due to these adjustments from the original technique, oversights can happen when creating their modified techniques, causing issues to arise when compositional data obtained is to be compared (Neslund, 2015). For example, a study aimed to determine the baseline parameters of various bodies of water in southwestern Ontario by evaluating concentrations of dissolved CH_4 and isotope data obtained (McIntosh et al., 2014) was challenged by Ryan et al. (2015) who raised several concerns that eventually caused Ryan et al. (2015) to publish a rebuttal commentary highlighting issues with the “concentration estimates” that McIntosh et al. (2014) obtained. They pointed out that there were various calculation issues, formulaic errors, and concerning decisions made during sampling that may lead to greater uncertainty when determining the DG concentrations and concluded that the study performed by

McIntosh et al. (2014) would have aided from a verified, universal approach to sampling, storage, manipulation, and analysis of DG samples (Ryan, et al. 2015).

1.7 Non-Ideal Conditions that Arise During Sample Collection and Analysis

Due to the lack of well-studied and utilized universal techniques regarding DG analysis, there is room for interpretation during the handling and analysis of DG samples. For example, although RSKSOP-175 recommends that 10% of headspace is created during the helium displacement process, if there is a headspace volume already present upon arrival, then no further action is needed. This headspace volume that is present initially is referred to as “pre-existing headspace” and differs from the “headspace created” during the helium displacement process as this pre-existing headspace originates from the individuals who collected the sample rather than the analysts who created the defined headspace during the analysis process. Although the creation of 10% headspace is ideal, these methods do not address scenarios in which a sample arrives with less than 10% pre-existing headspace where the resulting sample volume from the headspace is not enough for analysis, or if the sample vessel used has a 10% headspace volume created that is too small for analysis. From these non-ideal scenarios that can occur, there is currently a gap in the literature that does not discuss how these changes may affect the resulting data obtained during sampling and analysis.

1.7 Hypothesis and Objectives

This study first aims to gain insight into the analysis of DG samples under non-ideal conditions by evaluating the following hypotheses in Chapter III:

1. A 10% headspace that is created during DG analysis yields the highest concentration

2. Due to the presence of pre-existing headspace, the headspace can affect the concentrations obtained
    a. The composition of this pre-existing headspace can further affect the concentrations obtained
3. Sample vessel size affects resulting concentrations

[redacted]

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CHAPTER II

MATERIALS AND METHODS

2.1 Method Overview

Evacuated 120 mL serum bottles with crimp-top butyl rubber septa were used as the sample vessel of choice to house the DG samples (Cahill et al., 2018; Eby et al. 2015). [redacted] This process is performed by first inverting the bottle and injecting a pre-determined amount of helium in one syringe, while another syringe will draw the same volume of solution as the helium that was introduced, allowing for the volume change in the sample vessel to be zero. **Figure 2** summarizes the process of performing a helium displacement on a DG sample. Once the headspace was created, the sample was shaken for 5 minutes before an aliquot of the headspace is immediately drawn and injected into a GC for the gases in the solution and headspace to equilibrate (Hudson, 2004). An Agilent 7890B gas chromatography instrument was used along with a flame ionizing detector (FID) for the analysis of hydrocarbons (C_1 to hexane) and for the rest of the components (CO_2, O_2/Ar, N_2, H_2 and He), a thermal conductivity detector (TCD) was used.

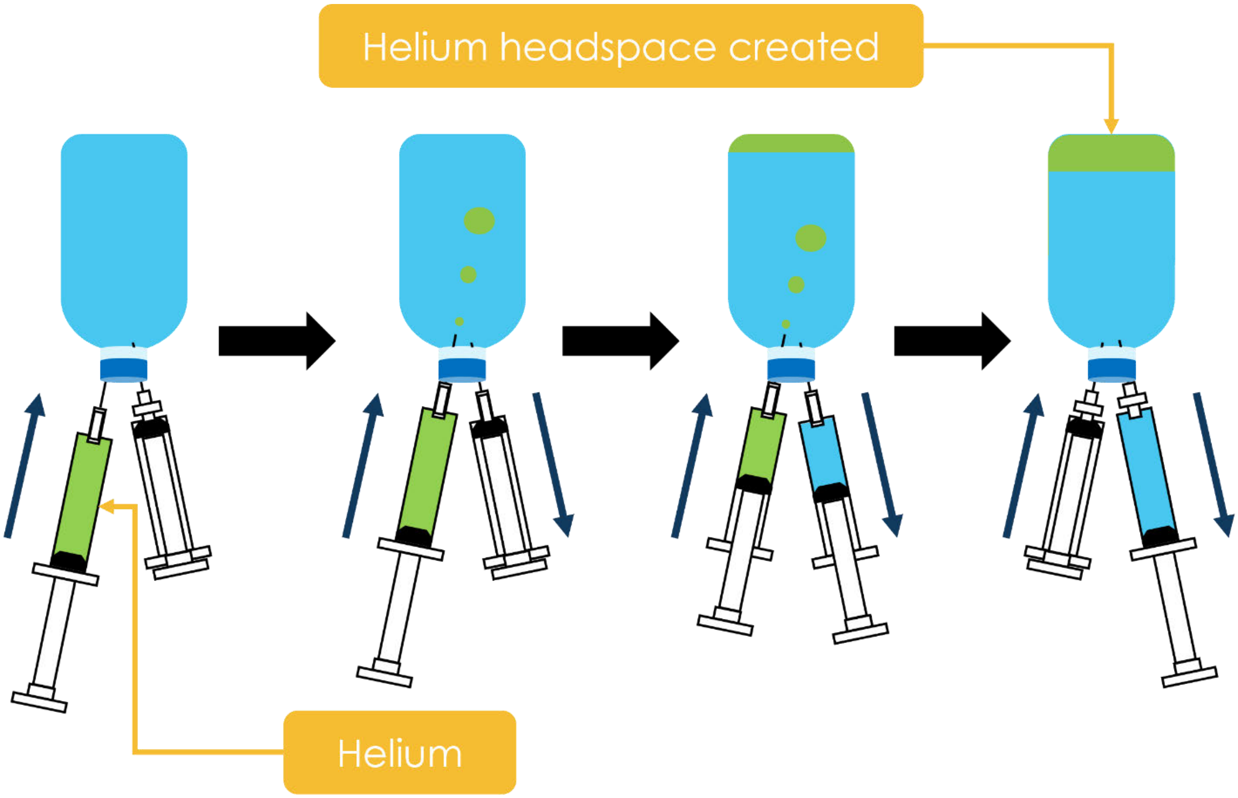

Figure 2: Summary of helium headspace technique to create a headspace for analysis

2.1.1 Post-Analysis Calculations

Throughout the analysis process, the temperature was taken before, during, and after analysis and the weight was also taken before and after the helium displacement process. These variables were recorded and used in the post-analysis calculations. The general equation for DG using this method is displayed in **Equation 2**. C_T is the total DG concentration while C_W and C_H are the concentration of DG in the aqueous phase and the headspace respectively.

$$C_T = C_W + C_H \qquad \textbf{Equation 2}$$

To calculate the DG concentration in the aqueous phase (C_W), the concentration of the headspace obtained from the GC instrument (C_G), the molar concentration of water (55.5 mol/L), the molecular weight of the species, and Henry's constant are needed as shown in **Equation 3**.

This equation was derived from the mole fractions of water and their relationship to the molar concentration of both the water and analyte.

$$C_W = \frac{C_G \times Molar\ concentration\ of\ water \times MW}{Henry's\ Constant \times 1000} \qquad \textbf{Equation 3}$$

Henry's constant can also be calculated for a species based on **Equation 4**. In this equation, A, B, C, and D are coefficients for gaseous solubility while the R is 1.98719 cal/(K×mol). For a more accurate analysis, Henry's Constant for each analysis must be calculated so that it is specific to each temperature condition during the time of assessment.

$$Henry's\ constant = 1/(\exp\left(\frac{A + \frac{B}{T} + ClnT + DT}{R}\right)) \qquad \textbf{Equation 4}$$

Equation 5 describes the calculations for the DG concentration in the headspace, using the concentration of the headspace obtained from the GC instrument (C_G), the density (ρ), the volume of the headspace (V_H), and the volume of the solution present in the glass serum bottle (V_W).

$$C_h = \frac{C_G \times \rho \times V_H}{(V_W - V_H) \times 1000} \qquad \textbf{Equation 5}$$

The volume of solution (V_W) contained in the bottle was determined by taking the mass of the bottle with headspace (m_H) and subtracting the mass of the bottle, septum, and aluminum seal, which was already predetermined to be 93.784 g as shown in **Equation 6**. This mass was determined by taking the average mass of three different sample vessel sets that encompass all the parts involved in one sample vessel. The density of the solution was used to relate the masses obtained to the volumes in the sample vessel and was assumed to be 1 g/mL (ρ_W). A VWR-403B2 analytical balance was used to measure the weight of the samples.

$$V_w = \rho_W(m_H - 93.784g) \qquad \textbf{Equation 6}$$

From **Equation 7**, the volume of the headspace (V_H) in a glass serum bottle can be determined using the mass of the bottle upon arrival (m_A) subtracted by the mass of the bottle with headspace (m_H) once the helium displacement has been performed, assuming the density of the solution is 1 g/mL (ρ_W). However, if the sample vessel used differed from the usual 120 mL bottle used, then the mass of the empty vessel was recorded post-analysis and used instead during calculations.

$$V_H = \rho_W(m_A - m_H) \qquad \textbf{Equation 7}$$

With the concentrations of the DG determined, isotopic analysis was performed on hydrocarbons and CO_2 if they had concentrations above 0.3 v/v% due to the detection limits of the GC front end of the isotope ratio mass spectrometer (IRMS). The sample was first brought to room temperature and then shaken for 5 minutes once again before sampling and injection into the IRMS. A Thermo Scientific TRACE ULTRA GC was used as the front end that connected to an EA IsoLink and Thermofisher CONFLOW IV interface, followed by a Thermofisher Finnigan DELTAplus XP isotope mass spectrometer. Another instrument used was Thermofisher TRACE 1310 connected to another EA IsoLink and CONFLOW IV interface, before connecting to a Thermofisher DELTA V PLUS. Depending on the component of interest, an HP-PLOTU or GS-Q column can be used in the GC for analysis.

2.2 Headspace Volumes Created Experiments

2.2.1 Laboratory Sample Preparation

Figure 3 depicts the laboratory samples that were created in triplicate using Perrier® Sparkling Natural Mineral Water to investigate if the 10% headspace volume created yielded the highest concentration. The evacuated 120 mL serum bottles that were topped with a butyl rubber septum were first filled with the Perrier® Water using a syringe. A series of laboratory samples that ranged from 5 to 20% headspace created during the helium displacement process were produced. The average weight of a filled 120 mL serum bottle, including the serum bottle, butyl rubber septa, and aluminum seal was found to be 212.339 g, after taking the masses of five different filled sample vessels. By using this weight, the volumes to be removed can be determined based on the targeted percentage of headspace, assuming that the density of the solution was 1 g/mL. For example, if a 15% headspace was desired and 15% of 120 mL is 18 mL, then the weight of the sample including the mass of bottle, septa and aluminum seal after displacement should be 212.339 g – 18 g = 194.339 g for the sample to have a 15% headspace.

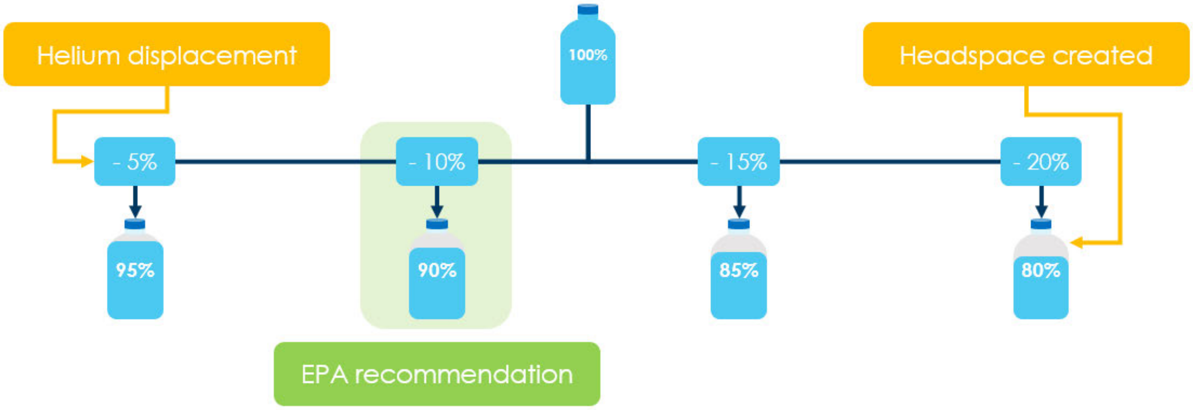

Figure 3: Laboratory samples with various headspace percentages created

2.3 Pre-existing Headspace Experiments

2.3.1 Laboratory Sample Preparation

To investigate the effect of pre-existing headspace, six sample sets (created in triplicate) were prepared using Perrier® Sparkling Natural Mineral Water with different pre-existing headspace volumes according to a similar concept based on **2.2.1**, where the sample vessels were partially filled instead using a syringe, to the targeted pre-existing headspace based on the weight of the bottle. The amount of pre-existing headspace ranges from 0 to 24 mL (0 to 17%) and a helium displacement was performed based on the headspace percentage present initially so each sample vessel would have a minimum of 10% headspace in the bottle for analysis to take place. For example, if a sample vessel had 3% of pre-existing headspace, or 97% solution inside the sample vessel, then a 7% helium displacement is performed to consequently get 10% headspace in the sample vessel before analysis. If the pre-existing headspace amount was less than 12 mL or 10%, then a reduced helium displacement was performed to create a headspace volume of 10% to obtain enough sample volume for analysis. However, if the headspace volume is $\geq$ 12 mL initially, then no helium displacement was performed as indicated in **Figure 4**.

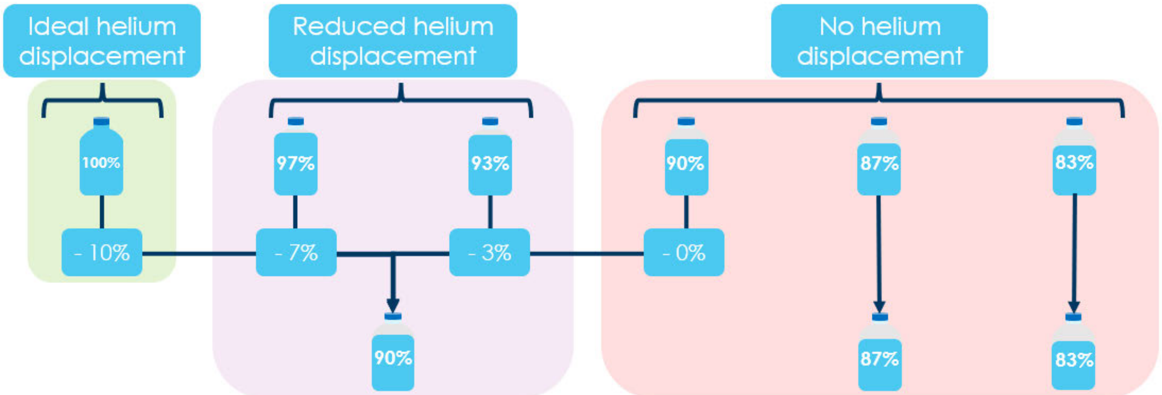

Figure 4: Laboratory samples with various pre-existing headspace created and the resulting weights if helium displacement was performed

For the laboratory samples prepared for intended atmospheric contamination in the headspace, the same concept was used as in **2.3.1**, however, a needle was used to introduce the atmosphere into the headspace for five seconds after the headspace created resulted in a 10% headspace or the pre-existing headspace present upon arrival was greater than 10%. The needle was then removed once the five seconds were over.

[redacted]

CHAPTER III

ANALYSIS OF LABORATORY AND FIELD SAMPLES

3.1 Laboratory Experiments

The method used in this thesis is based on RSKSOP-175 with slight variations to the technique to perform both isotopic and compositional analysis. This method was chosen since it is an established technique created by a regulatory agency that produced a lower error in comparison to the other technique, and it is accessible to most laboratories with a GC, without needing to invest in a headspace autosampler. 120 mL evacuated serum bottles were used with crimp-top butyl rubber septa as the sample vessel of choice during the laboratory experiments. Since the sample vessel was evacuated, the bottle was able to draw the water inside without much pressure applied to the syringe. In a previous study, it was shown that serum bottles with butyl rubber septa had minimal fractionation and the butyl rubber septa used were less permeable than natural rubber septa. It was also noted that serum bottles performed better in comparison to other sample vessels such as Tedlar or FlexFoil bags, where fractionation was present during hold times greater than a month (Eby et al. 2015). Laboratory DG samples were created in the laboratory using Perrier® Sparkling Natural Mineral Water as it is commercially available, reliable, and carbonated. This beverage has been used by laboratories as a diluent for water samples as it contains no organics and saved a lot of time in comparison to preparing deionized water as the diluent of choice (Borman, 1990). Since the beverage is also carbonated, CO_2 concentrations are expected to be relatively high in comparison to the other components obtained. [redacted]

3.1.1 Investigation of the percentage of headspace created

For a sample that arrives with no pre-existing headspace present, the documents pertaining to RSKSOP-175 do not give reasoning behind the 10% helium displacement that is to be performed to create the headspace. Not only does RSKSOP-175 not give a rationale as to why that specific percentage of volume was used, but other studies that analyze DG compositions using a headspace equilibrium technique also chose to use various amounts of headspace during analysis. This specific volume was not consistent percentage-wise nor amount-wise, consequently highlighting an inconsistency with DG analysis throughout the various studies reviewed. To explore the importance of using 10% helium displacement, or if 10% is needed at all, a series of laboratory samples were created in triplicate with various headspaces created ranging from 5-20% using Perrier® Sparkling Natural Mineral Water.

Figure 5 depicts the CO_2 results obtained from the DG analysis performed. Each percentage was performed in triplicate where three separate laboratory samples were created for each percentage and the samples were run on the same day. The highest concentrations were observed at 10% headspace with little variation (SD = ± 21.71 mg/L) in comparison to other headspace percentages. This suggests that a higher percentage of headspace was not chosen since the variation and concentrations were lower and were not as reliable. It is important to note that a 5% headspace could not be analyzed since 6 mL of headspace present would not be sufficient for the 10 mL volume needed for compositional analysis. From these experiments, the percentage of headspace that is displaced during DG analysis affects the resulting concentration obtained, with 10% headspace yielding the highest concentration and lowest variation from the percentages chosen.

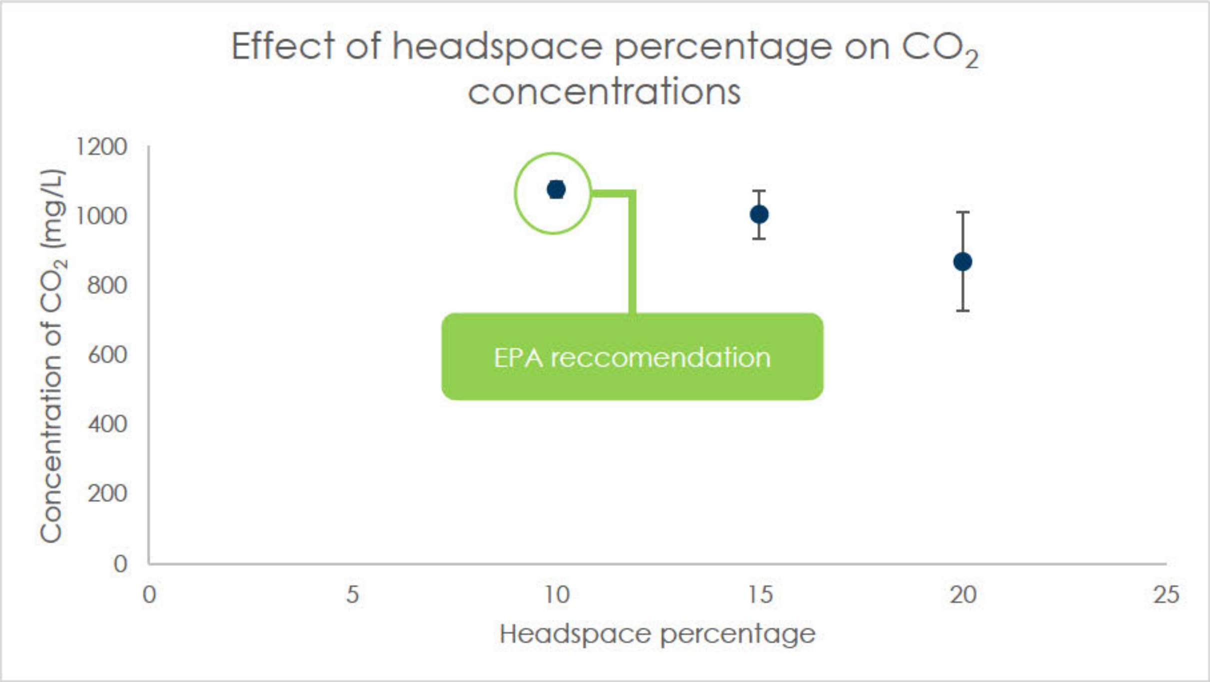

Figure 5: Plot of headspace percentage versus CO_2 concentrations (mg/L)

The decrease in concentration can be explained by the increase in volume in the headspace, as it allows for the same amount of DG molecules to enter a larger headspace volume to equilibrate the system, thus decreasing the resulting concentration obtained. For example, if we compared two systems with the same amount of moles that theoretically enter a headspace, and one system has a headspace volume of 12 mL, while the other has a headspace volume of 18 mL, then the subsequent concentration of the system with a headspace of 18 mL will yield a lower concentration based on **Equation 8**, where the concentration is equal to the number of moles of a gas over the volume of the container.

$$C = \frac{X}{V} \qquad \textbf{Equation 8}$$

3.1.2 Investigation of the effect of pre-existing headspace

Although it is recommended that DG samples arrive with no pre-existing headspace, due to sampling processes, there are cases where significant amounts of pre-existing headspace are unavoidable. At this point, RSKSOP-175 proposes that no displacement is performed when there is a headspace already present upon arrival. These laboratory samples were created to mimic scenarios in which sample vessels are not filled completely, thus containing this “pre-existing headspace”. While these laboratory samples are treated the same after analysis begins, the effect of this pre-existing headspace is not known and as a result, a series of laboratory samples were prepared using Perrier® Sparkling Natural Mineral Water to investigate the effect of pre-existing headspace on the resulting concentrations.

Figure 6 depicts the CO_2 concentration obtained from the DG analysis performed on the laboratory sample series created. A sample that is filled without any pre-existing headspace is known as our “ideal sample” and is used as our basis of comparison. As the pre-existing headspace percentage increases, there is an increase in the resulting CO_2 concentration, as indicated by the R^2 of 0.85. Since this value is quite high; it implies a relationship between the amount of pre-existing headspace present and the resulting CO_2 concentration. The elevated CO_2 concentrations are attributed to the nature of the aqueous solution used. As carbonated beverages such as Perrier® Sparkling Natural Mineral Water are exposed to the atmosphere when opened, the saturated solution can now equilibrate with the atmosphere and off-gas the excess CO_2. However, due to the increase in pre-existing headspace present, the off-gassed CO_2 is trapped in the bottle since the Perrier® Water is continuously off-gassing as the solution did not reach equilibrium with the atmosphere before it was sampled, thus resulting in elevated amounts of CO_2. This suggests that the characteristics of the aqueous solution present, and the composition of the headspace in the bottle itself can play a role in the resulting concentrations obtained.

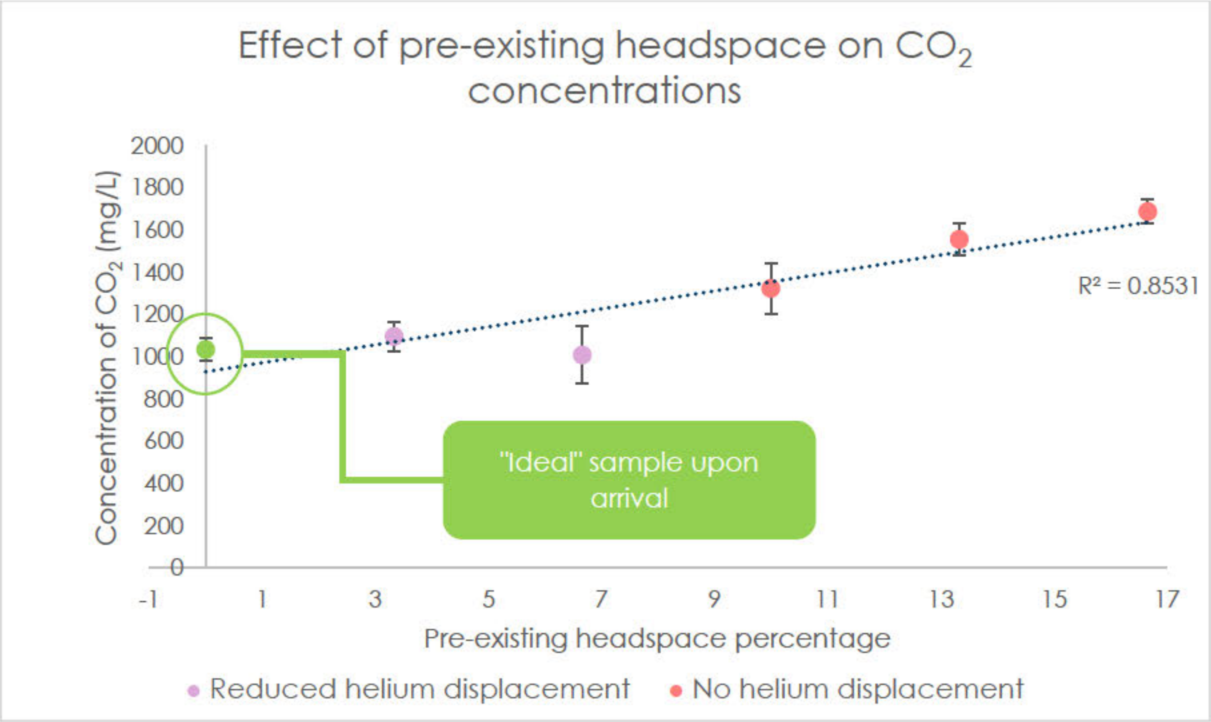

Figure 6: Plot of increasing pre-existing headspace percentage versus CO_2 concentrations (mg/L)

Observing the trendline in **Figure 6**, the data suggests a horizontal relationship (within standard deviation) from 0 to 7% of pre-existing headspace while the pre-existing headspace volume from 8 to 20 mL indicates an increase linearly. By isolating this subset of data from 0 to 7% and 7 to 17% of pre-existing headspace present, the coefficient of determination reinforces these observations made from **Figure 6** where there seems to be both a horizontal and linear relationship within the data obtained. **Figure 7**, which isolates the data from 0 to 7% (0 to 8 mL) of pre-existing headspace present, has a low R^2 of 0.09, implying that there is no linear relationship between the amount of pre-existing headspace present and the resulting CO_2 concentration obtained. On the other hand, laboratory samples that contain 7 to 17% (8 to 20 mL) of pre-existing headspace as shown in **Figure 8**, had a linear correlation with an R^2 of 0.97, suggesting that there is a relationship between pre-existing headspace present and resulting CO_2 concentrations as there is a significant amount of pre-existing headspace present. It is also implied that the samples that did not have a helium displacement were the samples that trended higher in comparison to our ideal sample, thus suggesting that the addition of helium to make said headspace, plays a role in the resulting concentration as well. However, increased sample density with a wider range of pre-existing headspace percentages is needed to confirm these observations.

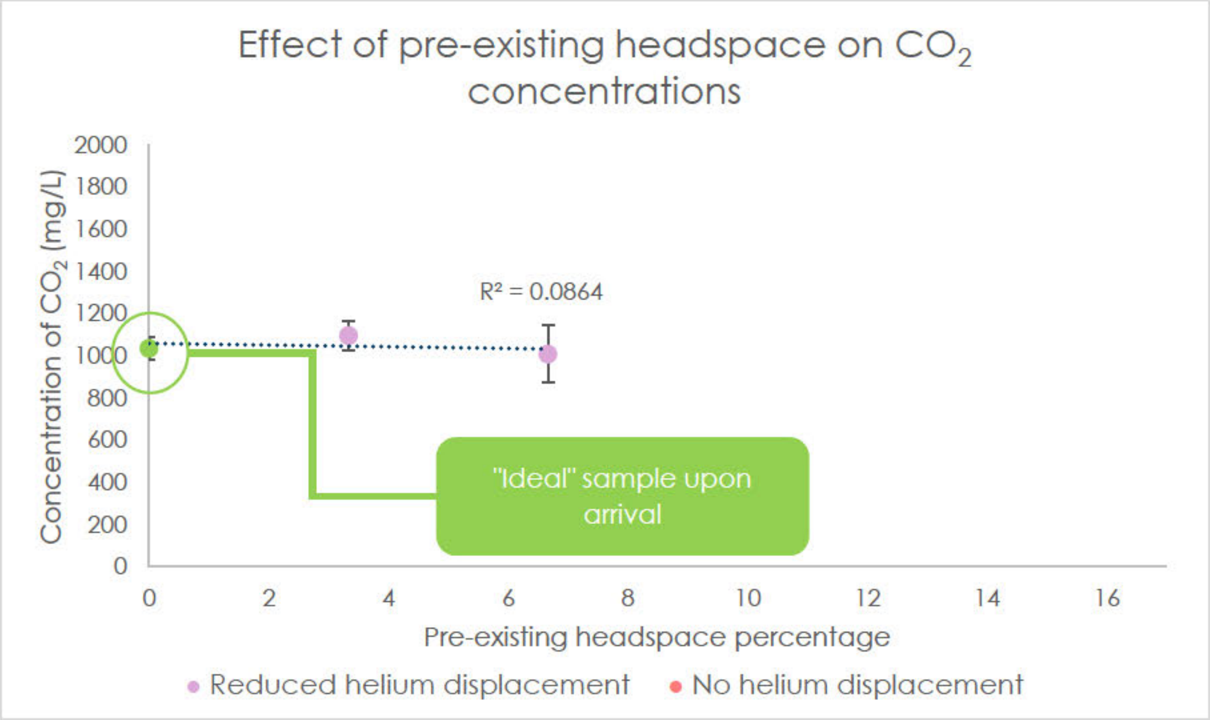

Figure 7: Plot of increasing pre-existing headspace percentage versus CO_2 concentrations (mg/L) (0 to 7%)

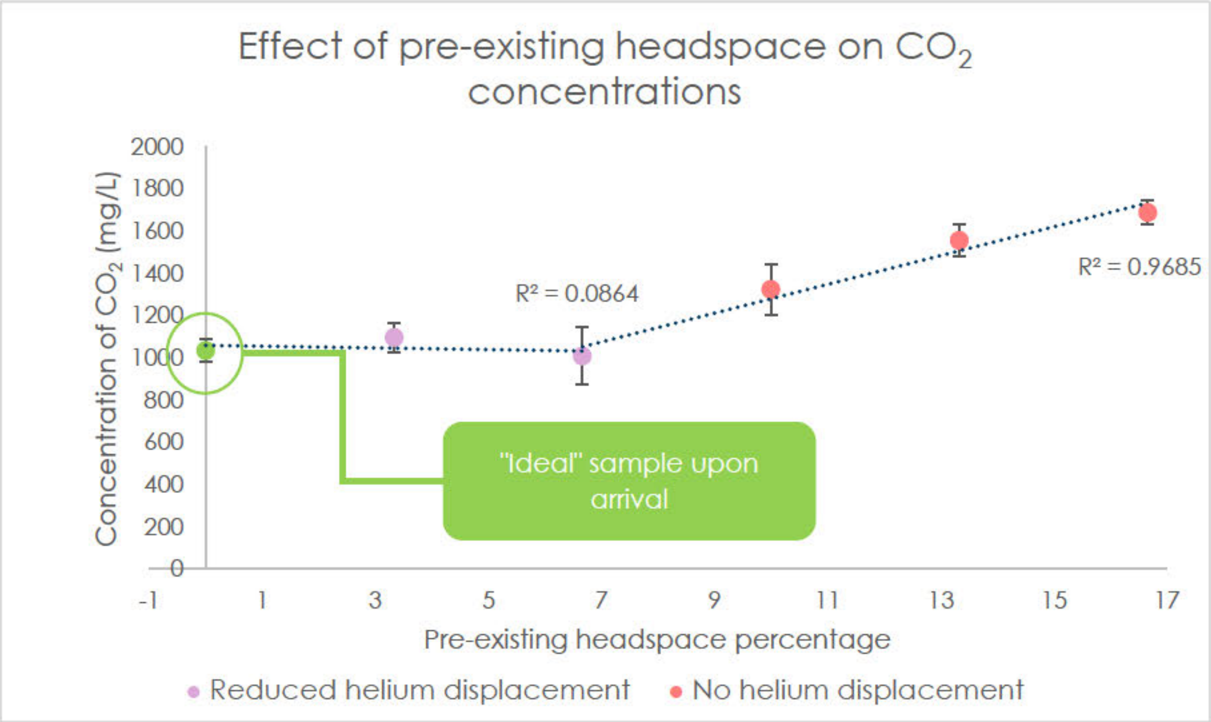

Figure 8: Plot of increasing pre-existing headspace percentage versus CO_2 concentrations (mg/L) (7 to17%)

From these experiments, it can be concluded that if there is less than 8 mL of pre-existing headspace in the serum bottle, the effect on the resulting concentrations is minimal; however, if there was more than 8 mL of pre-existing headspace present, then this unwanted headspace will produce concentrations that are elevated from the true value.

3.1.3 Investigation of contaminated pre-existing headspace

As indicated beforehand, the elevated concentration of CO_2 is attributed to the increase of pre-existing headspace and the nature of the solution used as Perrier® Sparkling Natural Mineral Water is saturated with CO_2. To further investigate the effect of pre-existing headspace and the composition of the headspace, a series of experiments were designed with deliberately contaminated headspace to determine the effect of the headspace composition on the resulting concentrations. Three laboratory sample sets created in triplicate, ranging from 4 to 20 mL of pre-existing headspace were prepared similarly to the samples in **3.1.2**, but instead of analyzing them immediately after helium displacement was performed (if needed), the laboratory samples were exposed to the atmosphere for five seconds before closing the system once again by puncturing a needle through the septum before removing it once the five seconds were over.

By exposing the system to the atmosphere, the elevated concentrations of CO_2 present in the headspace had an opportunity to mix with the atmosphere, thus lowering the concentration of CO_2. As shown in **Figure 9**, when the laboratory samples are exposed to the atmosphere, the resulting CO_2 values were depleted, although still in a linear fashion with an R^2 of 0.94. This series of laboratory samples shows that the initial concentration of the headspace, and whether the solution was equilibrated beforehand, greatly affects the resulting concentrations obtained.

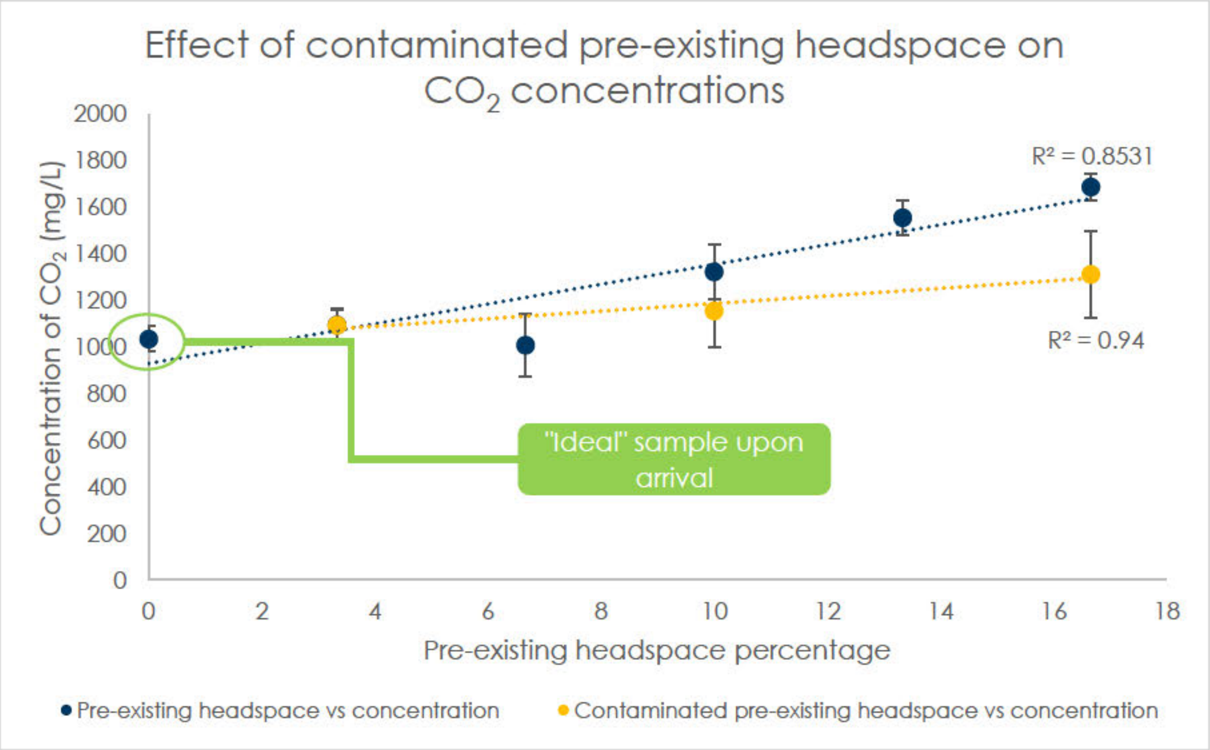

Figure 9: Increasing contaminated and non-contaminated pre-existed headspace percentage versus CO_2 concentrations (mg/L)

Through the experiments that were performed in this section, the role of the percentage of headspace created, presence of pre-existing headspace and atmospheric contaminated pre-existing headspace was investigated and determined to play a role in the resulting compositional data obtained. By filling a sample vessel to the point at which little to no headspace is present, the effects of differing headspace percentages and pre-existing headspace can be minimized.

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CHAPTER IV

CONCLUSION

[redacted] The conclusions obtained can be summarized below:

- 10% headspace displacement is recommended for the lowest variability and greatest concentrations obtained
- Pre-existing headspace > 8 mL in a 120 mL sample vessel can affect resulting compositional data and the initial composition of the headspace plays a role in the resulting compositional data
    - It is recommended that little (≤ 8 mL) to no pre-existing headspace is targeted during the sampling of DG samples to reduce the effects of pre-existing headspace
- Sample vessels with volumes that differ from the recommended can be used and analyzed, however, data between different sample vessels are difficult to compare
    - It is recommended that sample vessels used are kept consistent throughout the sampling program so the resultant data can be compared to each other

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APPENDICES

Appendix A

Data tables from Laboratory Experiments

Sample name	Volumetric data			Headspace gas concentrations (v/v%)															Dissolved gas concentrations (mg/L)					
	Pre-existing headspace (mL)	Amount removed (mL)	Headspace (%)	CH_4	C_2	C_3	iC_4	nC_4	$neoC_5$	iC_5	nC_5	nC_6	CO_2	$Ar + O_2$	N_2	He	H_2	Total	dg-CH_4	dg-C_2	dg-C_3	dg-CO_2	dg-O_2	dg-N_2
Perrier® Sparkling Natural Mineral Water A	0	12	10.0	0.011	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	56.77	0.79	3.83	38.59	<0.01	100.00	0.011	<0.002	<0.003	1095.98	1.58	5.95
Perrier® Sparkling Natural Mineral Water B	0	12	10.0	0.009	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	51.06	0.71	3.57	44.65	<0.01	100.00	0.009	<0.002	<0.003	996.48	1.50	5.85
Perrier® Sparkling Natural Mineral Water C	0	12	10.0	0.009	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	54.07	0.98	4.72	40.22	<0.01	100.00	0.009	<0.002	<0.003	1059.06	1.95	7.28
			Average	0.010									53.97	0.83	4.04	41.15			0.010			1050.51	1.67	6.36
			SD	0.001									2.86	0.14	0.61	3.13			0.001			50.29	0.24	0.80
			SD %	13.811									5.29	16.53	14.99	7.61			12.580			4.79	14.32	12.57

Sample name	Volumetric data			Headspace gas concentrations (v/v%)															Dissolved gas concentrations (mg/L)					
	Pre-existing headspace (mL)	Amount removed (mL)	Headspace (%)	CH_4	C_2	C_3	iC_4	nC_4	$neoC_5$	iC_5	nC_5	nC_6	CO_2	$Ar + O_2$	N_2	He	H_2	Total	dg-CH_4	dg-C_2	dg-C_3	dg-CO_2	dg-O_2	dg-N_2
Perrier® Sparkling Natural Mineral Water A	0	12	10.0	0.008	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	54.56	0.49	2.72	42.22	<0.01	100.00	0.009	<0.002	<0.003	1068.50	1.00	4.32
Perrier® Sparkling Natural Mineral Water B	0	12	10.0	0.009	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	54.07	0.98	4.72	40.22	<0.01	100.00	0.009	<0.002	<0.003	1059.06	1.95	7.28
Perrier® Sparkling Natural Mineral Water C	0	12	10.0	0.009	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	56.46	0.52	2.84	40.18	<0.01	100.00	0.009	<0.002	<0.003	1100.49	0.99	4.16
			Average	0.009									55.03	0.66	3.42	40.87			0.009			1076.02	1.31	5.25
			SD	0.000									1.26	0.27	1.12	1.17			0.000			21.71	0.55	1.76
			SD %	5.542									2.29	41.15	32.83	2.86			2.398			2.02	41.73	33.51

Sample name	Volumetric data			Headspace gas concentrations (v/v%)															Dissolved gas concentrations (mg/L)					
	Pre-existing headspace (mL)	Amount removed (mL)	Headspace (%)	CH_4	C_2	C_3	iC_4	nC_4	$neoC_5$	iC_5	nC_5	nC_6	CO_2	$Ar + O_2$	N_2	He	H_2	Total	dg-CH_4	dg-C_2	dg-C_3	dg-CO_2	dg-O_2	dg-N_2
Perrier® Sparkling Natural Mineral Water A	0	18	15.0	0.007	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	52.30	0.01	1.18	46.50	0.00	100.00	0.009	<0.002	<0.003	1072.33	0.04	2.67
Perrier® Sparkling Natural Mineral Water B	0	18	15.0	0.006	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	51.37	0.01	1.22	47.39	0.00	100.00	0.009	<0.002	<0.003	1005.85	0.03	2.68
Perrier® Sparkling Natural Mineral Water C	0	18	15.0	0.007	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	49.08	0.01	0.61	50.30	0.00	100.00	0.008	<0.002	<0.003	935.06	0.02	1.12
			Average	0.006									50.92	0.01	1.00	48.06			0.009			1004.41	0.03	2.15
			SD	0.000									1.66	0.00	0.34	1.99			0.001			68.64	0.01	0.90
			SD %	2.026									3.26	29.17	34.36	4.14			9.394			6.83	37.23	41.75

Sample name	Volumetric data			Headspace gas concentrations (v/v%)															Dissolved gas concentrations (mg/L)					
	Pre-existing headspace (mL)	Amount removed (mL)	Headspace (%)	CH_4	C_2	C_3	iC_4	nC_4	$neoC_5$	iC_5	nC_5	nC_6	CO_2	$Ar + O_2$	N_2	He	H_2	Total	dg-CH_4	dg-C_2	dg-C_3	dg-CO_2	dg-O_2	dg-N_2
Perrier® Sparkling Natural Mineral Water A	0	24	20.0	0.004	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	39.80	0.00	0.31	59.89	0.00	100.00	0.006	<0.002	<0.003	704.75	0.00	0.79
Perrier® Sparkling Natural Mineral Water B	0	24	20.0	0.005	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	46.37	0.00	0.22	53.40	0.00	100.00	0.009	<0.002	<0.003	953.23	0.00	0.67
Perrier® Sparkling Natural Mineral Water C	0	24	20.0	0.005	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	45.92	0.00	0.16	53.91	0.00	100.00	0.009	<0.002	<0.003	948.62	0.00	0.49
			Average	0.004									44.03	0.00	0.23	55.73			0.008			868.87	0.00	0.65
			SD	0.001									3.67	0.00	0.07	3.61			0.002			142.15	0.00	0.15
			SD %	12.883									8.34	22.74	31.13	6.47			20.701			16.36	19.22	23.07

Sample name	Volumetric data			Headspace gas concentrations (v/v%)															Dissolved gas concentrations (mg/L)					
	Pre-existing headspace (mL)	Amount removed (mL)	Headspace (%)	CH_4	C_2	C_3	iC_4	nC_4	$neoC_5$	iC_5	nC_5	nC_6	CO_2	$Ar + O_2$	N_2	He	H_2	Total	dg-CH_4	dg-C_2	dg-C_3	dg-CO_2	dg-O_2	dg-N_2
Perrier® Sparkling Natural Mineral Water A	20	0	16.7	0.015	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	87.91	2.20	9.51	<0.01	0.36	0.00	0.020	<0.002	<0.003	1665.13	5.74	20.02
Perrier® Sparkling Natural Mineral Water B	20	0	16.7	0.013	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	82.65	3.41	13.92	<0.01	<0.01	0.00	0.019	<0.002	<0.003	1644.55	9.66	31.92
Perrier® Sparkling Natural Mineral Water C	20	0	16.7	0.015	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	87.27	2.48	10.22	<0.01	<0.01	100.00	0.022	<0.002	<0.003	1750.08	7.09	23.63
			Average	0.014									85.95	2.70	11.22				0.020			1686.58	7.50	25.19
			SD	0.001									2.87	0.63	2.37				0.001			55.94	1.99	6.10
			SD %	6.413									3.34	23.45	21.11				5.667			3.32	26.52	24.22

Sample name	Volumetric data			Headspace gas concentrations (v/v%)															Dissolved gas concentrations (mg/L)					
	Pre-existing headspace (mL)	Amount removed (mL)	Headspace (%)	CH_4	C_2	C_3	iC_4	nC_4	neoC_5	iC_5	nC_5	nC_6	CO_2	Ar + O_2	N_2	He	H_2	Total	dg-CH_4	dg-C_2	dg-C_3	dg-CO_2	dg-O_2	dg-N_2
Perrier® Sparkling Natural Mineral Water A	16	0	13.3	0.013	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	79.11	4.20	16.66	0.02	<0.01	0.00	0.014	<0.002	<0.003	1469.20	9.04	28.36
Perrier® Sparkling Natural Mineral Water B	16	0	13.3	0.015	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	84.68	3.00	12.28	0.03	<0.01	0.00	0.018	<0.002	<0.003	1608.00	6.99	22.80
Perrier® Sparkling Natural Mineral Water C	16	0	13.3	0.016	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	85.35	2.88	11.75	<0.01	<0.01	0.00	0.016	<0.002	<0.003	1586.13	5.67	18.05
			Average	0.015									83.05	3.36	13.56	0.03			0.016			1554.44	7.23	23.07
			SD	0.002									3.43	0.73	2.70	0.01			0.002			74.63	1.70	5.16
			SD %	10.611									4.13	21.71	19.87	22.99			10.984			4.80	23.49	22.36

Sample name	Volumetric data			Headspace gas concentrations (v/v%)															Dissolved gas concentrations (mg/L)					
	Pre-existing headspace (mL)	Amount removed (mL)	Headspace (%)	CH_4	C_2	C_3	iC_4	nC_4	neoC_5	iC_5	nC_5	nC_6	CO_2	Ar + O_2	N_2	He	H_2	Total	dg-CH_4	dg-C_2	dg-C_3	dg-CO_2	dg-O_2	dg-N_2
Perrier® Sparkling Natural Mineral Water A	12	0	10.0	0.014	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	73.63	5.38	20.93	0.04	<0.01	100.00	0.013	<0.002	<0.003	1356.83	9.36	27.92
Perrier® Sparkling Natural Mineral Water B	12	0	10.0	0.017	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	76.78	4.76	18.44	<0.01	<0.01	100.00	0.014	<0.002	<0.003	1418.68	7.66	22.51
Perrier® Sparkling Natural Mineral Water C	12	0	10.0	0.014	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	64.46	7.41	28.09	0.02	<0.01	100.00	0.012	<0.002	<0.003	1191.63	12.42	35.89
			Average	0.015									71.62	5.85	22.49	0.03			0.013			1322.38	9.81	28.78
			SD	0.002									6.40	1.39	5.01	0.02			0.001			117.38	2.41	6.73
			SD %	12.288									8.94	23.75	22.28	54.31			9.082			8.88	24.59	23.40

Sample name	Volumetric data			Headspace gas concentrations (v/v%)															Dissolved gas concentrations (mg/L)					
	Pre-existing headspace (mL)	Amount removed (mL)	Headspace (%)	CH_4	C_2	C_3	iC_4	nC_4	neoC_5	iC_5	nC_5	nC_6	CO_2	Ar + O_2	N_2	He	H_2	Total	dg-CH_4	dg-C_2	dg-C_3	dg-CO_2	dg-O_2	dg-N_2
Perrier® Sparkling Natural Mineral Water A	8	4	10.0	0.010	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	46.83	6.58	25.35	21.23	<0.01	100.00	0.008	<0.002	<0.003	882.31	10.62	30.94
Perrier® Sparkling Natural Mineral Water B	8	4	10.0	0.012	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	53.12	5.07	19.73	22.07	<0.01	100.00	0.011	<0.002	<0.003	1014.16	9.08	27.08
Perrier® Sparkling Natural Mineral Water C	8	4	10.0	0.012	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	55.37	4.10	16.13	24.39	<0.01	100.00	0.009	<0.002	<0.003	414.77	6.13	19.55
			Average	0.011									51.77	5.25	20.40	22.56			0.010			770.41	8.61	25.86
			SD	0.001									4.43	1.25	4.65	1.64			0.002			314.98	2.28	5.79
			SD %	11.876									8.55	23.76	22.78	7.25			15.834			40.88	26.48	22.39

Sample name	Volumetric data			Headspace gas concentrations (v/v%)															Dissolved gas concentrations (mg/L)					
	Pre-existing headspace (mL)	Amount removed (mL)	Headspace (%)	CH_4	C_2	C_3	iC_4	nC_4	$neoC_5$	iC_5	nC_5	nC_6	CO_2	$Ar + O_2$	N_2	He	H_2	Total	dg-CH_4	dg-C_2	dg-C_3	dg-CO_2	dg-O_2	dg-N_2
Perrier® Sparkling Natural Mineral Water A	4	8	10.0	0.012	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	60.24	2.06	8.67	29.02	<0.01	100.00	0.013	<0.002	<0.003	1169.43	4.17	13.68
Perrier® Sparkling Natural Mineral Water B	4	8	10.0	0.012	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	56.79	2.81	11.49	28.89	<0.01	100.00	0.011	<0.002	<0.003	1082.79	5.04	15.82
Perrier® Sparkling Natural Mineral Water C	4	8	10.0	0.013	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	54.01	3.02	12.21	30.75	<0.01	100.00	0.011	<0.002	<0.003	1032.53	5.28	16.30
			Average	0.012									57.02	2.63	10.79	29.55			0.012			1094.91	4.83	15.27
			SD	0.000									3.12	0.51	1.87	1.04			0.001			69.25	0.58	1.39
			SD %	2.493									5.48	19.19	17.35	3.51			5.449			6.33	12.07	9.13

Sample name	Volumetric data			Headspace gas concentrations (v/v%)															Dissolved gas concentrations (mg/L)					
	Pre-existing headspace (mL)	Amount removed (mL)	Headspace (%)	CH_4	C_2	C_3	iC_4	nC_4	$neoC_5$	iC_5	nC_5	nC_6	CO_2	$Ar + O_2$	N_2	He	H_2	Total	dg-CH_4	dg-C_2	dg-C_3	dg-CO_2	dg-O_2	dg-N_2
Perrier® Sparkling Natural Mineral Water A	0	12	10.0	0.011	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	56.77	0.79	3.83	38.59	<0.01	100.00	0.011	<0.002	<0.003	1095.98	1.58	5.95
Perrier® Sparkling Natural Mineral Water B	0	12	10.0	0.009	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	51.06	0.71	3.57	44.65	<0.01	100.00	0.009	<0.002	<0.003	996.48	1.50	5.85
Perrier® Sparkling Natural Mineral Water C	0	12	10.0	0.010	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	51.76	0.26	1.67	46.30	<0.01	100.00	0.009	<0.002	<0.003	1008.73	0.52	2.59
			Average	0.010									53.20	0.59	3.02	43.18			0.010			1033.73	1.20	4.80
			SD	0.001									3.12	0.29	1.18	4.06			0.001			54.25	0.59	1.91
			SD %	11.843									5.86	48.55	39.00	9.40			13.164			5.25	49.00	39.84

Sample name	Volumetric data			Headspace gas concentrations (v/v%)															Dissolved gas concentrations (mg/L)					
	Pre-existing headspace (mL)	Amount removed (mL)	Headspace (%)	CH_4	C_2	C_3	iC_4	nC_4	$neoC_5$	iC_5	nC_5	nC_6	CO_2	$Ar + O_2$	N_2	He	H_2	Total	dg-CH_4	dg-C_2	dg-C_3	dg-CO_2	dg-O_2	dg-N_2
Perrier® Sparkling Natural Mineral Water A	4	8	10.0	0.010	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	58.88	1.14	5.15	34.82	<0.01	100.00	0.010	<0.002	<0.003	1152.37	2.23	7.80
Perrier® Sparkling Natural Mineral Water B	4	8	10.0	0.011	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	57.97	0.37	2.09	39.56	<0.01	100.00	0.010	<0.002	<0.003	1108.66	0.68	2.95
Perrier® Sparkling Natural Mineral Water C	4	8	10.0	0.010	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	53.42	0.80	3.69	42.08	<0.01	100.00	0.009	<0.002	<0.003	1020.04	1.42	5.01
Contaminated with atmosphere			Average	0.010									56.76	0.77	3.64	38.82			0.010			1093.69	1.44	5.25
			SD	0.000									2.92	0.39	1.53	3.69			0.001			67.42	0.77	2.43
			SD %	4.078									5.15	50.29	42.09	9.49			7.073			6.16	53.72	46.32

Sample name	Volumetric data			Headspace gas concentrations (v/v%)															Dissolved gas concentrations (mg/L)					
	Pre-existing headspace (mL)	Amount removed (mL)	Headspace (%)	CH_4	C_2	C_3	iC_4	nC_4	$neoC_5$	iC_5	nC_5	nC_6	CO_2	$Ar + O_2$	N_2	He	H_2	Total	dg-CH_4	dg-C_2	dg-C_3	dg-CO_2	dg-O_2	dg-N_2
Perrier® Sparkling Natural Mineral Water A	12	0	10.0	0.010	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	55.89	9.22	34.58	0.27	0.03	100.00	0.009	<0.002	<0.003	1056.12	15.57	44.39
Perrier® Sparkling Natural Mineral Water B	12	0	10.0	0.016	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	64.25	7.47	28.25	0.01	<0.01	100.00	0.010	<0.002	<0.003	1199.00	9.44	25.84
Perrier® Sparkling Natural Mineral Water C	12	0	10.0	0.015	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	65.29	7.30	27.37	<0.01	0.03	100.00	0.009	<0.002	<0.003	1209.21	8.26	21.86
Contaminated with atmosphere			Average	0.014									61.81	8.00	30.07	0.14			0.009			1154.78	11.09	30.70
			SD	0.003									5.15	1.06	3.93	0.18			0.001			85.59	3.92	12.03
			SD %	21.461									8.33	13.29	13.08	132.39			7.226			7.41	35.38	39.19

Sample name	Volumetric data			Headspace gas concentrations (v/v%)															Dissolved gas concentrations (mg/L)					
	Pre-existing headspace (mL)	Amount removed (mL)	Headspace (%)	CH_4	C_2	C_3	iC_4	nC_4	$neoC_5$	iC_5	nC_5	nC_6	CO_2	$Ar + O_2$	N_2	He	H_2	Total	dg-CH_4	dg-C_2	dg-C_3	dg-CO_2	dg-O_2	dg-N_2
Perrier® Sparkling Natural Mineral Water A	20	0	16.7	0.012	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	75.07	5.11	19.78	0.03	<0.01	100.00	0.016	<0.002	<0.003	1510.54	13.42	41.78
Perrier® Sparkling Natural Mineral Water B	20	0	16.7	0.010	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	63.56	7.46	28.97	<0.01	<0.01	100.00	0.012	<0.002	<0.003	1279.55	17.57	54.24
Perrier® Sparkling Natural Mineral Water C	20	0	16.7	0.010	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	58.47	8.75	32.76	<0.01	<0.01	100.00	0.012	<0.002	<0.003	1142.71	22.22	66.57
Contaminated with atmosphere			Average	0.011									65.70	7.11	27.17				0.014			1310.93	17.74	54.20
			SD	0.001									8.50	1.85	6.68				0.002			185.91	4.40	12.39
			SD %	11.692									12.94	26.02	24.58				15.518			14.18	24.82	22.86

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VITA AUCTORIS

NAME: Michelle Tsuey-Yee Quan

PLACE OF BIRTH: Windsor, ON

YEAR OF BIRTH: 1998

EDUCATION: Vincent Massey Secondary School,
Windsor, ON, 2016

University of Windsor, B.Sc.,
Windsor, ON, 2021