DEVELOPMENT OF A NOVEL PASSIVE SAMPLING APPROACH FOR MONITORING GEOSMIN AND 2-MIB IN WATER

by

Afi, Theresa Owokor

Submitted in partial fulfilment of the requirements

for the degree of Master of Applied Science

at

Dalhousie University

Halifax, Nova Scotia

December 2022

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

The increased eutrophication of freshwater sources has led to a rise in taste and odour events notoriously caused by geosmin and 2-methylisoborneol (2-MIB). This places more pressure on current monitoring methods due to increased sampling frequency. Unfortunately, conventional grab sampling methods and the required sample preparation steps are laborious, time-consuming and provide only a single-time snapshot of geosmin and 2-MIB levels in the water. An alternative sampling approach for water quality monitoring is passive sampling, which extracts and allows the accumulation of the target analytes directly from the water. The simplicity and robustness of passive sampling makes it more suitable for routine monitoring. The goal of this study was to develop a simple passive sampling protocol for the detection of geosmin and 2-MIB in drinking water source lakes. In bench scale experiments, various passive sampling parameters (adsorbent, elution solvent, sorbent mass to elution volume ratio and elution method) were optimized prior to accessing the method's performance characteristics (i.e., linearity, precision, accuracy, matrix effects, limits of detection and quantitation). Recoveries of 50 and 53% for geosmin and 2-MIB, respectively were obtained with excellent intra and inter day precision (≤15% RSD). Semi-quantitative detection limits of 0.014 and 0.044 μg L^{-1} for geosmin and 2-MIB, respectively, were obtained. The validated passive sampling method was used to conduct a field study at eight lake water sites in Atlantic Canada within a three-month period. The study demonstrated that the developed passive sampling method could be utilized for the reliable detection of geosmin and 2-MIB in source water as well as provide improved resolution for its early detection in drinking water supplies.

LIST OF ABREVIATIONS USED

2-MIB	2-methylisoborneal
CLSA	closed loop stripping analysis
COSCa	COVID-19 Sewer Cage
DH	dynamic headspace
ELISA	enzyme linked immunoabsorbent assay
GC/FID	gas chromatography - flame ionization detector
GC/MS	gas chromatography- mass spectrometry
GC/CI	gas chromatography- positive chemical ionization
GC-DMS	gas Chromatography–differential ion mobility spectrometry
GSM	geosmin
LOQ	limit of quantitation
LLE	liquid Liquid Extraction
LLME	liquid-liquid micro-extraction
LDPE	low-density polyethylene
PEx	matrix post-extraction spiked control
PE (%)	process efficiency
MDL	method detection limit
MAAs	mycosporine-like aminoacids
ME	matrix effect
OTL	odour threshold limit
POCIS	polar organic chemical integrative sampler
PES	polyethersoulfone
PExs	matrix post-extraction spiked control sample.
PGHF	polypropylene glycol coated hollow fibre
PS	polysulphone
PTFE	polytetrafluoroethylene

P&T	purge and trap
QCPR	qualitative polymerase chain reaction
RE (%)	recovery efficiency
SPMD	semi-permeable membrane device
SPE	solid phase extraction
SPME	solid phase micro extraction
SH	static headspace
SBSE	stir-bar sorptive extraction
TWA	time weighted average
T&O	taste and odour
VOCs	volatile organic compounds

AKNOWLEDGEMENTS

I am grateful to God who makes all things possible. This work is a product of the guidance, support and encouragement of Dr. Graham Gagnon, Dr. Amina Stoddart, Dr. Crystal Sweeney, Dr. Margaret Walsh, Dr. Stefanie Colombo, Heather Daurie, Lindsay Anderson, Dave Redden, Clarke Brown, Tobi Oshikoya, Nice Uwitonze, Dallys Serracin-Pitti, Martin Earle, Manda Tchonlla, George Quinn, the CWRS team, my friends and family. Thank you, Dr. Gagnon, for your endless faith in me. You and Dr. Stoddart's vision for water and wastewater research inspires me daily. I am exceedingly grateful to you both for giving me the opportunity to present this research at conferences and webinars. Indeed, I have learnt a lot under your supervision. I would also like to thank Dr. Margaret Walsh and Dr. Stefanie Colombo for being a part of my committee, for your patience throughout this process and for reviewing my thesis. Thank you, Heather Daurie and Jessica Bennet, for your laboratory expertise and helpfulness. To Dr. Crystal Sweeney, I am eternally grateful, your knowledge and contribution to this work is invaluable. Thank you for being my biggest cheerleader! Thank you, Lindsay Anderson for always rooting for me, for your feedback on this paper and for the work you do for the team! To Dave Redden, Clarke Brown, George Quinn, Tobi Oshikoya and Nice Uwitonze, field sampling and laboratory analysis was made easier with your help. Thank you, Manda Tchonlla, Martin Earle and Jorginea Bonang for the water samples you made available during bench scale experiments. I am thankful to Dallys Serracin-Pitti whose research on geosmin contributed significantly to this work. Thanks to everyone at the CWRS, it is always a fun time with you! Thank you, Tarra Chartrand for making my transition into Halifax an easier one. Thank you, Javier Augusto for your feedback on this paper and your help with R programming! To Mr. and Mrs Afi Titus, Blessing, Eunice, Titus and Gabriel, words are not enough to describe how grateful I am that you are family. Thank you for your support throughout this journey. Finally, I would also like to thank the Halifax Regional Municipality (HRM) for their assistance in this sampling study.

CHAPTER 1: INTRODUCTION

1.1 PROJECT RATIONALE

The major source of municipal water supply in many countries is surface water, including Canada, Japan, the United States, Australia, East and Southeast Asia (Dzialowski et al., 2009; Kamata et al., 2020; Rivera, 2018). Eutrophication of surface waters as a result of climate and anthropogenic pressures including increased temperature and precipitation, lake recovery, and pollution has led to an increase in the frequency, duration, severity, and diversity of harmful algal blooms (HABs) (Chapra et al., 2017; Paerl & Huisman, 2009; Woolway et al., 2021; Anderson et al., 2017; DeMont et al., 2021). The proliferation of cyanobacteria in HABs is often associated with an increased occurrence of cyanotoxins and notorious taste and odour (T&O) compounds, such as geosmin and 2-methylisoborneol (2-MIB) as secondary metabolites (Anderson et al., 2017; DeMont et al., 2021; Devi et al., 2021). In freshwater source, geosmin and 2-MIB have been found to contribute significantly to T&O events and is usually affiliated with an undesirable earthy or musty taste and smell in the drinking water (Kim & Park, 2021; Yu et al., 2009). These off-flavour compounds can also be detected in fishes when they accumulate in their lipid tissue (Azaria & van Rijn, 2018). As such, if not adequately managed geosmin and 2-MIB can pose a financial threat both to water utilities and in aquaculture as consumers judge the quality of their drinking water and the organisms they eat by their taste and smell (Azaria & van Rijn, 2018; Dupont, 2005). Amidst the abundant research in detecting and treating these aesthetic concerning contaminants, they remain a global issue due to their increasing frequency and concentrations above human threshold limits (Health Canada, 2005; Perkins et al., 2019; H. Xu et al., 2022).

The human odour threshold level (OTL) for geosmin and 2-MIB is 4 ng L^{-1} and 15 ng L^{-1}, respectively (Pochiraju et al., 2021). Such low thresholds pose a significant monitoring challenge as highly sensitive detection methods are required. Furthermore, the occurrence of geosmin and 2-MIB in source water is dynamic and challenging to predict. Both compounds also require optimized treatment needs that if provided on a year-round basis can quickly become a financial burden (Olsen et al., 2016; Serracin-Pitti, 2017). As

such, frequent monitoring using methods with fast turnaround times is crucial in mitigating T&O events caused by these compounds.

For several decades, grab sampling has been the conventional sample collection method in the analysis of geosmin and 2-MIB in water (Bristow et al., 2019); However, preconditioning steps on grab samples can be time consuming and labour intensive (Marsili, 2000; Tian et al., 2021), making the process unconducive for the achievement of fast turnaround times and high-throughput. Automated processes are also costly and vulnerable to unpredicted power failures and device malfunction. An alternative approach to conventional sampling for water quality monitoring is passive sampling, which vastly simplifies sample collection and preparation by allowing the isolation of target analytes directly from the environmental medium using simple and cost effective devices with low technology and no power requirements (Gomes, 2018).

Passive sampling involves the deployment of a sampler (containing an adsorbent material) into the sample matrix over a specified period. The sample matrix is allowed to flow freely through the sampler during which the target compounds are partitioned into the adsorbent material and concentrated over time(Górecki & Namieśnik, 2002). After the deployment time, the passive sampler is retrieved, and taken for laboratory for analysis. Compared to conventional sampling methods, passive sampling is more representative of actual water conditions as larger water volumes are sampled. This allows one to capture fluctuations in analyte concentrations that grab samples are either likely to miss or overestimate, as grab sampling represents random, discrete volumes of water at single time points that can vary considerably in analyte concentrations over time and location (Gomes, 2018). Since the passive samplers are often easy-to-handle portable devices, they can be deployed at multiple locations over large and remote areas that may be difficult to access or not feasible using conventional sampling methods (Górecki & Namieśnik, 2002; Hayes et al., 2021). Passive sampling also has the advantage of increased sensitivity as it provides the time weighted average concentration of the target analytes (Greenwood et al., 2007). These qualities of passive sampling make it a promising technique for efficient routine monitoring and high throughput analysis. It also shows potentials for the collection of reliable data that can be used in developing region specific predictive models for geosmin

and 2-MIB analysis, which is a useful tool in mitigating T&O events caused by these compounds (Dzialowski et al., 2009).

While studies have applied passive sampling techniques in the recovery of viruses from wastewater (Hayes et al., 2021; Matrajt et al., 2018), pesticides in water (Ibrahim et al., 2013; Kaserzon et al., 2014; Mazzella et al., 2010), volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) in air (Grosse & McKernan, 2014), as well as other target compounds (Alvarez et al., 2004a; Vermeirssen et al., 2009), there remains a limited research in its application for monitoring geosmin and 2-MIB in water, which to the knowledge of the authors has only been explored in one research paper (Liu et al., 2011). As such, this study aims to develop and assess the suitability of a novel passive sampling approach in monitoring geosmin and 2-MIB in aqueous environments.

1.2 RESEARCH OBJECTIVE

The overarching goal of this project was to develop and validate a simple passive sampling protocol for monitoring two notorious drinking water T&O contaminants – geosmin and 2-MIB in source water. To achieve this goal, the following three specific aims were outlined:

1. Design bench-scale experiments for assessing the recovery of geosmin and 2-MIB from spiked lake water using a passive sampling approach that outlines the optimization of the following method parameters: adsorbents (granulated activated carbon (GAC), a solid-phase extraction sorbent (Oasis HLB), and a reversed-phase resin (C18)), elution solvents (ethyl acetate, hexanes, and toluene), elution volume, sorbent mass to elution volume ratio, and elution method parameters (incubation, shaking, and sonication times).
2. Validate the optimized passive sampling method for measuring geosmin and 2-MIB in spiked lake water
3. Conduct field-scale testing in lake water at several sampling sites in Atlantic Canada using this passive sampling protocol to monitor geosmin and 2-MIB.

CHAPTER 2: LITERATURE REVIEW

Geosmin (trans-1,10-dimethyl-trans-9-decalol, GSM), and 2-Methylisoborneol ((IR-exo)-1,2,7,7-tetramethyl-exo-bicyclo-[2.2.21]-heptan-2-ol;2-exo-hydroxy-2-methylbornane, 2-MIB) are naturally occurring volatile organic compounds (VOCs) that can be found in drinking water, soil and recirculating aquaculture systems (Azaria & van Rijn, 2018; Jüttner & Watson, 2007; Mustapha et al., 2021). Both compounds are characterized by their earthy-musty taste and smell and can be detected by humans at trace levels of 4 ng L^{-1} for geosmin and 15 ng L^{-1} for 2-MIB (Pochiraju et al., 2021). The chemical structure of geosmin can be described as a bicyclic sesquiterpenes. It was first isolated from several Streptomyces species (Actinomycetes) in 1965 (Gerber & Lechevalier, 1965). 2-MIB is a monoterpene. It was independently isolated from *Streptomyces iasaliensis NRRL 3382* and *Streptomyces coelicolor A3(2)* in 2008 (Komatsu et al., 2008; C.-M. Wang & Cane, 2008; Yamada et al., 2012). Although actinomycetes produce geosmin and 2-MIB, studies have shown very low correlations between these bacteria and geosmin/ 2-MIB events in raw and portable water (Shugen Pan, 2002).

Over the years, other sources of geosmin and 2-MIB have been identified. Giglio et al., (2011) confirmed the biosynthesis of 2-MIB by *Pseudanabaena limnetica*, a specie of cyanobacteria while geosmin is greatly associated with several distinct taxa of cyanobacteria, namely, multicellular strains of *Oscillatoriales*, *Nostocales* and *Synechococcales* (Churro et al., 2020). Cyanobacteria are considered to be a major source of both geosmin and 2-MIB in aquatic environments where photosynthetic growth is possible (Jüttner & Watson, 2007). They are naturally occurring organisms that exist in nearly every ecosystem, particularly in aqueous environments (Mullineaux & Wilde, 2021). For protection and survival, cyanobacteria produce several secondary metabolites including geosmin and 2-MIB in response to biotic and abiotic stresses in the surrounding environment (Kultschar & Llewellyn, 2018). The environmental stresses that affect the release of geosmin and 2-MIB by cyanobacteria have been shown to vary regionally. Journey et al. (2013) found that increased flushing rate, high water flow, depth of mixing zone (>6m), dissolved oxygen, chloride and

lower nitrogen concentrations were factors that increased the concentration of dissolved geosmin and 2-MIB in a lake and municipal reservoir located at the Piedmont region of Spartanburg County, South Carolina. These findings were analogous to a study on five reservoirs in Kansas, USA in which geosmin was monitored (Dzialowski et al., 2009). Also, cyanobacteria are able to store geosmin and 2-MIB in its cells which can be released upon death or lysing of the cell (Serracin-Pitti, 2017).

Although the release of geosmin and 2-MIB by cyanobacteria has been well documented, their events may not always be correlated with increased eutrophication of water sources. Journey et al., (2013) and Dzialowski et al., (2009) found that in some study sites, geosmin occurrence was uncorrelated with increased nutrient concentrations and peak points were measured in regions with no observable blooms.

These findings show geosmin and 2-MIB events are episodic in nature and concentrations of these T&O compounds are likely to fluctuate throughout the year due to the multiple sources and factors that affect their release in water. And because these compounds cannot be effectively removed (i.e., below human odour threshold limits) using conventional treatment methods of coagulation, sedimentation and filtration, applying their optimized treatment needs on a year-round basis could quickly become a financial burden (Serracin-Pitti, 2017). As such, source monitoring becomes a more cost effective method for the control of geosmin and 2-MIB within a region. Fortunately, these off-flavour compounds have not been found to be of any health concern (Oh et al., 2017).

The current techniques used in monitoring these T&O compounds have been highly focused on grab sampling for water collection followed by sample preparation and analysis. This conventional sampling method as well as its limitations is discussed in more detail below.

2.1 CONVENTIONAL SAMPLING (OVERVIEW AND ADVANTAGES)

Conventional sampling is also known as grab or "spot" sampling. It is the most commonly used method for water collection prior to analyte extraction and analysis (Madrid & Zayas, 2007). Conventional sampling involves the collection of water samples at defined points and times for chemical analysis. Water samples are collected manually using bottles or via automatic samplers. Conventional sampling methods are accepted for regulatory and legislation purposes and have the advantage of standardized procedures and volume quantification of target analytes (Gomes, 2018; Madrid & Zayas, 2007).

2.1.1 Limitations of Conventional Sampling

Data from grab sample analysis may not accurately represent actual water conditions as they describe the water conditions at that moment of sampling. As a result, it may fail to reflect fluctuations and spatial variabilities in contaminant concentrations in the water which could lead to an over or under estimation of the analytes total population load (Gomes, 2018; Madrid & Zayas, 2007). Composite or automated sampling for water collection is usually used to offset these limitations; However, it can easily become time inefficient and more laborious. Another limitation of conventional sampling methods is the difficulty in ensuring effective quality control. The quality of grab sample results is dependent on how well the initial composition of the sample is maintained from sampling through to analysis (Madrid & Zayas, 2007). Considering the multiple steps that require human input (collection, transportation, preservation of samples and extraction of analytes), quality control can easily be impacted which would affect data reliability. Processing methods for grab samples are oftentimes labour intensive, time consuming and require power operated devices that can be expensive (Bristow et al., 2019), although these methods are designed to allow for sensitivity in analyte measurements, the slow turnaround times and low throughput capacity makes grab sampling unconducive particularly for large scale routine monitoring.

2.1.2 Current Sample Preparation Methods for the Extraction of Geosmin and 2-MIB from Water.

Sample preparation is the process of extracting, isolating and concentrating analytes from sample matrices into an analysable format (the final analyte solution) (Choi & Dong, 2005). Different sample preparation techniques following both grab and passively collected samples have been documented (Bristow et al., 2019; Vrana et al., 2005). However, in the analysis of geosmin and 2-MIB, grab sampling has been the most commonly used sample collection method. As such, most current sampling preparation procedures (elucidated below) are tailored for traditionally collected water samples.

2.1.2.1 Solid-phase extraction (SPE)

Solid-phase extraction (SPE) is an efficient and widely used approach that applies the principles of chromatography in the separation of the target analytes from collected samples (Bristow et al., 2019; Keçili et al., 2020). In SPE, a solid sorbent which forms the stationary phase is used to separate target analytes from the sample matrix (mobile phase) through the principle of adsorption. In conventional sampling, SPE on water samples is commonly done using a cartridge packed with stationary solid phase particles (sorbent) (Wells, 2013). Extraction using this device involves four main stages:

a) Conditioning of cartridges: this means using a suitable organic solvent to activate the sorbent by passing it through the cartridge. After which, the activation is removed by passing a liquid similar in composition to the sample matrix but containing no analyte (Berrueta et al., 1995).

b) Loading of water samples: following the conditioning step, the water samples are passed through the cartridges, during which, the target analytes in dissolved state are separated from the sample matrix and retained on the sorbent (Berrueta et al., 1995).

c) Washing the cartridges: this is done by passing through the cartridges, a solvent which does not elute the target analytes for the purpose of removing interfering compounds (Analytical Sciences Digital Library, 2019; Berrueta et al., 1995).

d) Elution: this means removing the compounds retained on the stationary phase using a solvent or a solvent mixture to which the target analytes have a greater affinity to (Berrueta et al., 1995).

Each of these steps along with control variables such as extraction temperature, sample and solvent volume and flowrate must be optimized for maximum analyte recovery.

SPE has the advantage of: 1) simplicity in its use, 2) high analyte selectivity, as there is a wide choice of sorbents, including nonpolar, polar, ion exchange and mixed mode chemistries (Wells, 2013), (e.g., this helps the analyst determine which is most suitable in obtaining clean extracts for analysis of target analytes), and 3) flexibility of design as SPE devices come in different product formats including disks, cartridges, well plates and bulk sorbents to meet the unique experimental designs and goals of the researcher (Agilent, 2022).

Disadvantages of SPE technique include: 1) its dependence on organic solvents and control variables, 2) SPE on grab samples can be time consuming, ranging from 40 (Ikai et al., 2003) to 120 minutes (Abdel Salam, 2007) per sample, and 3) Optimization makes it difficult to manually reproduce results. For improved reproducibility as well as standardization of extraction procedure and reduction of overall cost, automated SPE is usually employed (Zheng, 2020). However, this does not rule out the time and labour constraints of this method. Furthermore, automation is machine dependent and thus susceptible to unpredicted device malfunction or power failure.

2.1.2.2 Liquid Liquid Extraction (LLE)

LLE involves the partitioning of compounds between two immiscible liquids – the sample matrix also known as the diluent and a solvent. The separation occurs due to the difference in the solubility of the target analytes between the two liquid phases. The analyte is transferred from the sample matrix to the organic solvent by direct immersion of the solvent or via headspace sampling (Barroso et al., 2012).Similar to CLSA large sample volumes (0.5 -1 L) and organic solvent (40-400 ml) are required (Bristow et al., 2019). To address this limitation, liquid-liquid micro-extraction (LLME) was developed where solvent volumes of about 1 ml have been used to obtain good recoveries of geosmin and 2-MIB (Lu et al., 2016; Shin & Ahn,

2004). In both LLE and LLME, the choice of solvent used is crucial. Issues of low selectivity and sensitivity using LLE technique have been reported (Rawa-Adkonis et al., 2006).

2.1.2.3 Solid phase micro extraction (SPME)

SPME is a solvent free sample preparation technique where the target compounds are partitioned from the sample matrix into a collecting medium known as the receiving phase (Kataoka, 2017). The collecting medium contains a fibre that extracts the target compounds when exposed to the sample matrix for a predetermined period. The fibre is coated with a liquid polymer or a solid sorbent, this part of the device is called the stationary phase. Extracted analytes are then released into an analytical device by thermal or liquid desorption. SPME has the advantage of simplicity, automation, speed, and integration of multiple sample preconditioning steps (extraction and pre-concentration). It was developed to overcome the limitations of the SPE and LLE techniques which require large solvent volumes. SPME has become the most commonly used extraction method for geosmin and 2-MIB analysis (Kataoka, 2017; J. Xu & Ouyang, 2019). The disadvantages of this method include: 1) dependency on control variables such as sampling techniques, extraction temperature and time, Ionic strength, and equilibrium between stationary and liquid phases, 2) SPME sampling by direct immersion increases the risk of fibre contamination, which makes it expensive for routine monitoring. While SPME by headspace sampling has been found to reduce this limitation, it requires more expertise.

2.1.2.4 Closed loop stripping analysis (CLSA)

This extraction method aims to ‘strip’ an analyte from the sample matrix using a ‘purge and trap’ technique. A purge gas is pumped through a large amount of the sample from which it carries the target analytes and retains them on an absorbent trap (often a carbon trap). It is called closed loop because the purge gas moves from the trap back to the pump in a loop fashion. The CLSA technique produces reliable results at trace

levels (i.e., ng/L) but its usage has declined over the years due to time and labour constraints, operational complexity, and large sample volume (0.5 – 2 L) requirements (Bristow et al., 2019).

2.1.2.5 Resin Absorption

In this method, a resin adsorbent is added to a given volume of water sample and rolled at a predetermined speed and time during which the target compounds bind to the resin. The granules are then filtered from the rest of the sample and dried. The attached analytes are then desorbed into a solvent for analysis (Palmentier et al., 1998).

2.1.2.6 Stir-bar sorptive extraction (SBSE)

This extraction method is based on the sorption (absorption and adsorption) of the analyte unto a polymer coated magnetic stir-bar. The adsorption takes place as the coated magnetic rod is stirred in the sample matrix for a given period of time. After which, the analyte is desorbed either thermally or using a liquid. SPSE operates at room temperature and due to its polymer thickness, has a greater enrichment factor compared to SPME. Also, it requires the optimization of enrichment factors such as: sampling techniques, extraction temperature and time. The major drawback of this method is the long extraction time needed for equilibrium between the liquid phases to be reached. Camino-Sánchez et al. (2014) recorded an extraction time of 30 minutes for high precision and reproducibility while Ochiai et al. (2001) recorded extraction times for different sample volumes ranging from 60 – 240 minutes.

2.1.2.7 Purge and Trap (P&T)

This is a solvent free technique that involves the use of an inert gas to purge the target compounds off the water sample. The purge gas passes through the sample matrix and displaces the target compounds from the solution, then moves through a trap to a vent, during this process the target analytes are retained on the trap while the gas leaves through the vent (Deng et al., 2012). Nitrogen or helium has been used as a purge gas

in several papers (Contarini et al., 1997; Ueta et al., 2022; Vogt et al., 2008). Very low detection limits of 0.08ng/L for geosmin and 1.5ng/dm^3 for 2-MIB were recorded by Deng et al. (2012) using this method. Similarly, Bristow et al. (2019) noted that one of the merits of the P&T technique is high extraction efficiency. The demerits of this method are: 1) Contamination of trap from carryover effects, and 2) It can be expensive and time consuming as it frequently utilises a complicated flow path (Bristow et al., 2019).

2.1.2.8 Static headspace (SH) and Dynamic headspace (DH) Sampling

In SH extraction method, the sample is placed in an air-tight container with a region of empty space above the sample (called headspace), the sample is then treated with a dilution solvent or matrix modifier to increase the transfer of volatiles into the headspace. The target compounds are then obtained from the vapour phase held in equilibrium above the sample (Bristow et al., 2019; Restek, 2000). Since analytes are sampled at equilibrium, control variables such as: volume of the sample and volatile fraction, temperature, type of matrix, injection volume and henry's constant of the analyte must be monitored (Wojnowski et al., 2017). A major drawback of this method is its relatively low sensitivity (Bristow et al., 2019; Wojnowski et al., 2017). To offset this limitation high pressure injections have been recommended; However, this makes the process more complicated and expensive (Bristow et al., 2019; Nakamura & Daishima, 2005)

In DH sampling, the volatile substances which enter the headspace are flushed using an inert gas and are trapped in a needle type device (Bristow et al., 2019). It is different from SH method in that the analytes are not sampled at equilibrium and it is more efficient than the P&T technique as the flow of gas is bubbled through the bulk of the sample rather than passed over the matrix, thus increasing volatile recovery (Soria et al., 2015); The major challenge of this method is the preconcentration of the vapour phase prior to analysis, this complicates the extraction process and increases the analysis time (Wojnowski et al., 2017).

Generally, headspace analysis (SH and DH) is time consuming. Also, it is typically used for volatile and semi volatile compounds otherwise, solid residues would be obtained which may not be compatible with

commonly used analytical instruments (Kolb & Ettre, 2006). When non-volatile compounds are being analyzed, pretreatment of the samples prior to sampling might be necessary (Kolb & Ettre, 2006).

The above review demonstrates the need for novel methods which allow for simple, cost effective and fast detection of these off-flavour compounds at environmentally relevant concentration. An alternative approach to conventional sampling for water quality monitoring is passive sampling. This method combines sample preparation and collection as isolation of analytes is done while samplers are deployed in the water (Górecki & Namieśnik, 2002). As such, no human input is required during the extraction process. The technique has the advantages of simplicity, low cost, no power requirement for contaminant extraction, reproducibility and increased sample throughput (Gomes, 2018).

2.2 PASSIVE SAMPLING

Generally, passive samplers are devices made of a solid or liquid sorbent (receiving phase) often contained in an inert perforated casing that allows the sampled medium (air, water, or soil) pass through them entrapping the target analytes in the sorbent. The contaminants are then desorbed from the sorbent for analysis (Grosse & McKernan, 2014; Watson, 2020).

Although there are variabilities as to when the concept of passive sampling began (Burgess, 2012; Górecki & Namieśnik, 2002, 2002), it was first applied in measuring air pollutants and has achieved much recognition in this field. In monitoring aqueous environments passive sampling has become a rapidly growing technique with applications in surface water (International Organization for Standardization, 2011; Mazzella et al., 2010), groundwater (American Society for Testing and Materials, 2014; Auersperger et al., 2022; Soulier et al., 2016), sediments (Burgess, 2012; Fernandez et al., 2009) and wastewater (Hayes et al., 2021; Schang et al., 2021).

The choice of a sampler is based on its affinity to the target analyte, ease of desorption from the sorbent, ease of handling (sample preparation, shipping, deployment, and retrieval), cost of materials, natural and anthropogenic stresses acting on the sampling medium such as presence of wildlife/aquatic organisms, water flow rate, presence of large particulates and expected levels of organic matter. As a result, passive sampling devices must be designed to meet the specific monitoring goals of the investigator which is oftentimes unique to the study region and target analytes. Nevertheless, its operating principle is the same.

2.2.1 Operating Principle of Passive Samplers

In passive sampling, the adsorbent material traps the target compounds using the principle of permeation or diffusion. The material is designed to have high affinity to the target compounds by taking advantage of its chemical properties (Górecki & Namieśnik, 2002). Once deployed in water, passive samplers allow the sampled medium flow freely through it, during which the target compounds present in the dissolved state experience a strong concentration gradient causing it to move from areas of high concentration outside the sampler to the initial low concentration inside the sampler until equilibrium is reached (Burgess, 2012; Harte et al., 2014). While some passive samplers allow most types of chemical constituents through (i.e., permeation through a membrane), others allow the diffusion of only selected groups of compounds/target analytes (i.e., diffusion through a well-defined barrier) (Gomes, 2018).

Passive sampling is a slow process since analytes are allowed to flow freely across the samplers, for this reason samplers are deployed for a predetermined sampling period during which the sorbents are enriched with the target compound(s) and retrieved for laboratory analysis.

The term equilibrium is often used in passive sampling calibration calculations (Grosse & McKernan, 2014; Imbrigiotta & Harte, 2020) and is defined as a condition attained when there is an apparent lack of transfer of target compounds between the collecting and sampling medium. At equilibrium, the change in the concentration of the target compound (s) between both mediums is equivalent to zero. (Burgess, 2012).

2.2.2 Advantages of Passive Sampling

One major advantage of passive sampling over conventional sampling is that it allows for in-situ/on site extraction of target analytes using principles that do not require power or sophisticated technology. Extraction materials are typically in inexpensive, locally available, and easy to handle (Burgess, 2012; Hayes et al., 2021). It combines sample collection and extraction steps which reduces the overall analysis time. Furthermore, its ability to concentrate target analytes in the environmental phase of interest increases the methods sensitivity. Since passive samplers provide time weighted concentration of the target analyte(s), they are more representative of actual water conditions (Gomes, 2018). Due to its high throughput capacity and portability, passive sampling allows for easy multipoint sampling and access to locations where sampling may not be feasible using conventional sampling methods (Hayes et al., 2021). Another advantage of passive sampling is that it allows for high analyte selectively, passive samplers can be designed and optimized to meet the analyst's goals. The simplicity of the method makes it easily reproducible. As a result, different analytes can be targeted based on the adsorbent material chosen.

2.2.3 Application

Passive sampling has been applied in the determination of organic and inorganic compounds in air, water and soil (Górecki & Namieśnik, 2002). It has also been used to understand bioaccumulation in organisms such as benthic invertebrates (Burgess, 2012). With passive sampling, a researcher can determine the time weighted average (TWA) concentration of analyte in the passive sampler - this is the value gotten from the analytical instrument that quantifies the concentration of the target analyte desorbed from the sorbent. The unit of this concentration is reported in terms of analyte concentration per mass of sorbent (e.g., μg/g). One could also determine the time weighted average (TWA) dissolved concentration of target analyte in the sampled medium - this is the concentration of analyte in the dissolved phase around the passive samplers. This information is needed by water utilities to monitor contaminants levels in source water. It is calculated using equation 1.

$$C_{TA_d} = \frac{C_{TA_{PS}}}{K_{PS-d}} \times 1000 \qquad \text{Eq. (1)}$$

Where:

C_{TA_d} = TWA dissolved concentration of target analyte in the sampled medium

$C_{TA_{PS}}$ = TWA concentration of analyte in the passive sampler

K_{PS-d} = The dissolved phase partition coefficient of the passive sampler (L/kg)

Note. values for K_{PS-d} are available in scientific literature (Gomes, 2018; U.S. EPA., 2012) for specific contaminant and passive samplers of which geosmin and 2-MIB is not included. K_{PS-d} values for target analytes can also be calculated from bench scale equilibrium studies using equation 2.

$$K_{PS-d} = \frac{C_p}{C_w} \qquad \text{Eq. (2)}$$

Where C_p is the concentration of the compound in the sampler, usually expressed in ng/g, and C_w is the water phase concentration for the same compound in ng/L. An experimental approach to determine K_{PS-d} values by equilibration, is to maintain constant aqueous concentration (i.e., constant C_w) or to allow these concentrations change over time (single dose design) and evaluate K_{PS-d} from the concentration in both phases (C_p and C_w) at equilibrium (Gomes, 2018).

2.2.4 Passive Sampling Devices

There is a plethora of passive samplers and sorbent materials commercially available and applied in literature but only a limited research on its application in the determination of geosmin and 2-MIB is available (Liu et al., 2011; Tadesse, 2021). Some studies have however evaluated various passive sampling materials and extraction methods for organic and/or odorous compounds with similar chemical properties to geosmin and 2-MIB. These properties include: hydrophobicity and moderate polarity (Young et al., 2014). This section

will attempt to review the passive samplers and sorbent materials used in these studies and potential applications for geosmin and 2-MIB source water monitoring.

Polar Organic Chemical Integrative Sampler (POCIS)

This is a passive sampler that consists of an array of sampling disks mounted on a support rod (Harman et al., 2012). Each disk consists of a solid sorbent sandwiched between two polyethersoulfone (PES) microporous membranes which are then compressed between two stainless steel rings that allow the collecting medium to be exposed to the water (figure 1). Typical sorbents used with POCIS for monitoring organic or polar compounds in aqueous environments have included :triphasic sorbent admixture, a hydrophilic–lipophilic-balanced sorbent (Oasis HLB), a functionalized polymeric sorption material containing N-vinylpyrrolidone (Strata-X), a mixed mode anion-exchange sorbent (Oasis Max), a mixture of ionic liquid and C18-Silica Sorbent (Alvarez et al., 2004b; Brophy, 2019; Godlewska et al., 2021; Mazzella et al., 2010; Soulier et al., 2016; L. Wang et al., 2017).

Figure 1. Polar organic chemical integrative sampler (POCIS) retrieved from a lake after 28 days of exposure time. Adapted from Brophy (2019).

After deployment time, the POCIS is opened, and the sorbent retrieved from the PES membrane. Solvents are used in extracting the target analytes from the sorbent using a solid phase extraction (SPE) technique most suitable and efficient (Ibrahim et al., 2013).

The use of POCIS with suitable sorbent has shown good recoveries and high sensitivity. POCIS also has the advantage of allowing kinetic uptake for a duration ranging from 1week to two months (Wurl, 2009). One limitation of POCIS noted by Soulier et al. (2016) was that the diffusion coefficient of hydrophobic compounds through the PES membrane was low due to a biphasic absorption that occurred in the PES membrane and in some cases, hydrophobic compounds were present in the PES membrane and did not pass into the sorbent.

Chemcatcher

These samplers consist of a 47-mm C-18 Empore disk containing octadecyl silica which acts as a receiving phase in the sampled medium. The disk is covered with a diffusion-limiting membrane material made of polysulphone (PS) for polar analytes and housed in an immobile covering made of polytetrafluoroethylene (PTFE) fibrils (Ahkola et al., 2012; Vrana et al., 2006). Chemcatcher's for polar and non-polar compounds are available. Before deployment, the Empore disks are pretreated with different solvents to form a good interface between the sorbent and the sample matrix. After the deployment time, the Empore disk is removed from the sampler body and extracted using a suitable solvent and SPE technique suitable for the compounds of concern (Ahkola et al., 2012).

Although C18 Empore disk was the solid-phase sorbent material used in the development of the Chemcatcher (Kingston et al., 2000) and has been the most widely used material after, some studies have evaluated the recovery efficiencies of other sorbent materials. For example, Rimayi et al. (2019) used a HLB sorbent as the receiving phase for the Chemcatcher and got good recoveries. Another popular sorbent material used with the Chemcatcher is Styrenedivinylbenzene-reverse phase sulfonated (SDB-RPS) sorbents (Kaserzon et al., 2014; Shaw et al., 2009; Vermeirssen et al., 2009). Figure 2 shows a sample of the chemcatcher deployment kit as well is its general configuration.

Figure 2. General configuration of the chemcatcher and deployment kit. Labelled elements of the chemcatcher (left), adapted from Ahkola et al (2012). Chemcatcher deployment kit (right), adapted from Chemcatcher (2022).

Fibres

Auersperger et al. (2022) used active carbon fibres (ACF- Zorflex® FM10) to detect a wide range of organic compounds from passive sampling in groundwater wells. The adsorbents were contained in stainless steel meshes and lowered into the borehole. After the exposure time (which ranged from 2 weeks to 6 months), the samplers were retrieved, and analysis was done by solid phase extraction of the target analytes from the ACF sorbent.

Similarly, Liu et al. (2011) used polypropylene glycol coated hollow fibre (PGHF) membranes for field sampling of geosmin and 2-MIB. Using equilibrium sampling methods for an exposure time of 1 h, PGHF membranes were used to extract geosmin and 2-MIB from 500mL water samples collected on the field, after which the analytes were extracted from the fibre using liquid desorption and stored in 200 µL glass insert placed into 2 mL brown glass vial with PTFE sealed screw cap. The glass vial containing the solution was then transported to the lab for further analysis using headspace SPME and detection/quantification using GC-MS. The method used in this study could be defined as a combination of passive and grab sampling techniques and while it addresses some of the limitation of conventional sampling methods such as the need to preserve and ship grab samples to the lab for analysis, it does not address labour and cost limitations as

bottles are prepared for on-site sampling, samplers are handled during extraction and a considerable time is needed for equilibrium between both sampling phases to be attained. Furthermore, since samplers are not deployed directly into the water body, the advantage of time weighted concentration and representativeness of actual water conditions linked with passive sampling cannot be confidently attributed to this hybrid method.

Some advantages of this method compared to other passive sampling techniques are its ability to provide results from one field trip and represent them in terms of concentration (mass/volume or concentration/volume). Most passive samplers produce flux results (mass/time or concentration/mass) which is not commonly used and would require kinetic studies and an understanding of the environmental conditions to derive the concentration of dissolved compounds in the sampled medium (Imbrigiotta & Harte, 2020).

Semi-Permeable Membrane Device (SPMD)

This is a type of passive membrane sampler that was developed primarily for sampling hydrophobic, semi-volatile organic compounds and pesticides in surface water but has since then been adapted to measure a wide spectrum of both organic and inorganic compounds (Godlewska et al., 2021). The SPMD is composed of a lay flat, low-density polyethylene (LDPE) tubing containing triolein that is attached to a support as shown in figure 3. Triolein is a pure, high-molecular weight lipid (triglyceride) that is highly sorptive of semi-volatile organic compounds and pesticides (Imbrigiotta & Harte, 2020). When placed in water, SPMDs passively accumulates the target compounds by membrane–lipid–water partitioning. For this reason, the structure of the SPMD sampler is said to simulate the surface and fatty tissues of a fish (Imbrigiotta & Harte, 2020). SPMDs have been used to monitor hydrophobic contaminants that are bioavailable to aquatic organisms (Gourlay et al., 2005). In principle, when these compounds flow past the SPMD they experience a strong concentration gradient to move into it where there are partitioned into the polyethylene membrane

and accumulate in the triolein (Gourlay et al., 2005). After recovery, the sampler is taken to the laboratory where the triolein is removed and extracted with a suitable solvent.

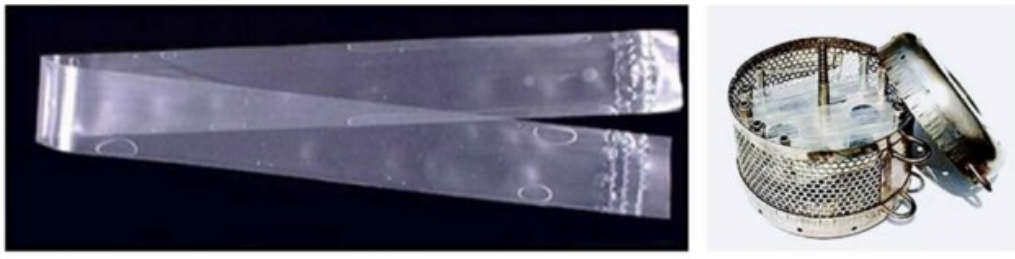

Figure 3. Semi-permeable membrane device (SPMD): a length of low-density polyethylene tubing containing triolein (left) and SPMD casing (right). Adapted from Tadesse (2021).

Innovative Samplers - The Covid-19 Sewer Cage (COSCa)

The flexibility in the design of passive samplers has led to the development of optimized and novel passive samplers for different target compounds (Tadesse, 2021). One of such is the COVID-19 Sewer Cage (COSCa) developed by a PhD student at the Centre of Water Resources Studies (CWRS), Dalhousie University, Halifax for sampling SARS-CoV-2 in wastewater at low prevalence areas (Hayes et al., 2021). This 3D printed passive sampler was built upon the concept of another innovative passive sampling approach in wastewater monitoring -the Moore swab concept (Matrajt et al., 2018). The COSCa (figure 4) was developed to minimize over-saturation of solids on the adsorbent material and to prevent its loss and damage. In the study (Hayes et al., 2021), electronegative filters were selected after an assessment of different absorbent materials for maximum recovery of heat-inactivated SARS-CoV-2 reference material from deionized water and wastewater. In field sampling, after the deployment time, the COSCa is retrieved, and the filters removed for the extraction and analysis of SARS-CoV-2 following an elution - RNA extraction - RT-qPCR analysis procedure explained in the literature.

The COSCa is a 10 cm diameter hollowed sphere with 26 holes, with each hole having a 1.5 cm diameter to foster non-restrictive flow. The COSCa was printed with acrylonitrile butadiene styrene (ABS) plastic, an

engineered thermoplastic with a high melting point that can withstand high autoclave temperatures. The COSCa was printed with solid walls to provide sufficient mass for complete submersion in water (Hayes et al., 2021).

Figure 4. COVID-19 sewer cage (COSCa) passive sampler (external and internal view). Adapted from Hayes et al (2021).

2.2.5 Limitations of Passive Sampling

Passive sampling may require two field trips for the deployment and retrieval of samplers. When a long deployment period (i.e. over 24 hours) is required before sample analysis, it may become a limiting factor if immediate results are needed. For example, during a pollution episode that occurs when no prior monitoring strategies for the contaminant have been in place. Another limitation of passive sampling is the use of flux measurements (mass/time). In water quality monitoring and regulation, communication of results in mass/volume measurements is more commonly used (Imbrigiotta & Harte, 2020). As such, further calculations and calibration is required to obtain a similar concentration measurement from the passive samplers (Burgess, 2012). Another factor to consider when using a passive sampling approach is the relatively high solvent volumes that may be required for analyte extraction due to the large surface area of most adsorbent materials used (Harte et al., 2014). Also, passive samplers are usually designed for high selectivity of target compounds. Although this can be viewed in the positive, there is a wide range of parameters for water quality monitoring, as such, there is need to develop passive sampling approaches that

allow for the detection of multiple target compounds otherwise there will remain a dependence on conventional sampling even with simultaneously collected passive samples.

2.3 ANALYTICAL APPROACHES FOR THE DETECTION OF GEOSMIN AND 2-MIB

Detection and/or quantification of the target analytes follows the sampling and extraction steps. Detection methods are usually similar regardless of the sampling or analyte extraction method used (Bristow et al., 2019). The analyst is to ensure the sample preparation method adopted allows for the detection of the target analytes and produces a final solution that is compatible with the instrument, sample preparation methods that improve the sensitivity of analytical instrument are desirable. The following detection methods have been used in the analysis of geosmin and 2-MIB:

- Gas chromatography- Mass spectrometry (GC/MS) (Elliot Wright et al., 2014; Ikai et al., 2003)
- Qualitative Polymerase Chain Reaction (QCPR) (Devi et al., 2021; Su et al., 2013)
- Gas chromatography- positive chemical ionization (GC/CI) (Lu et al., 2016)
- Gas chromatography - Flame ionization detector (GC/FID) (Lloyd et al., 1998)
- Gas Chromatography–Differential Ion Mobility Spectrometry (GC-DMS) (Camara et al., 2013)
- Enzyme Linked Immunoabsorbent Assay (ELISA) (Chung, 1992; Chung et al., 2002)
- Bioelectronic nose (Son et al., 2015)
- Electronic tongue (Migliorini et al., 2020; Son & Park, 2018)
- Bromine reaction (Hensarling & Waage, 2002)

The most common detection method used is a combination of Gas chromatography for analyte separation and Mass spectrometry for detection (Bristow et al., 2019). This combination provides for sensitivity and trace analysis of target compounds. For this study, Geosmin and 2-MIB was detected using GC-MS. This method is explained below:

2.3.1 Gas Chromatography (GC)

In chromatography, the separation of individual compounds in a mixture is achieved when the mobile phase is passed over a stationary phase. The differences in their affinities to these phases results in their separation (ACS Reagent Chemicals, 2017).

Gas chromatography is principally used to separate volatile and thermally stable materials from a sample by distributing its components between a mobile and stationary phase. The mobile phase consists of an inert gas while the stationary phase is found in the column and consist of non-volatile liquid phase coated on a porous solid support. After the sample is injected into the GC instrument, it is vaporized in a vaporization chamber containing an inert gas and attached to a chromatographic column. The inert gas in the vaporization chamber helps to move the sample into the column. Once in the column, various components of the sample are separated by virtue of their partition coefficient. For example, components which are more soluble in the liquid stationary phase are carried more quickly through the column by the inert gas. A gas chromatograph is mainly a separation tool and requires a detection instrument for the identification of sample components or measurement of target compounds (ACS Reagent Chemicals, 2017; Kaur & Sharma, 2018). A wide variety of detectors (listed above) are used to quantify and/or identify the components in the eluent from the column.

2.3.2 Gas Chromatography - Mass Spectrometry (GC-MS)

Gas chromatography–mass spectrometry (GC–MS) is one of the most common techniques used in the analysis of many compounds including VOCs, moderately and non-polar compounds (Falaki, 2019; Reber, 2014; Rockwood et al., 2018). Mass spectrometers are used to separate ions of various compounds according to their charge to mass ratio. After the compounds of a sample have been separated by the chromatograph, Gas phase ions of each compound is produced using electron ionization. These ions provide information concerning the nature and the structure of their precursor molecule. The ions produced are passed into mass analyzers which separate the various ions. The abundance each kind of ion is measured using detectors and

finally a data processing system helps to develop a unique spectrum for each ion based off a comparison between the abundance of the ion and its charge to mass ratio (Hoffmann & Stroobant, 2007). In Tandem mass spectrometry (GC-MS/MS), two mass analyzers are coupled with each other using a collision cell. It differs from MS as it performs mass analysis on the gaseous ions at least twice. From MS, the molecular weight of the parent compound is determined. In MS/MS the parent compound is fragmented further to improve specificity and provide insight into structure elucidation and identifying elementary (Spencer et al., 2021).

CHAPTER 3: MATERIALS AND METHODS

3.1 METHOD DEVELOPMENT

3.1.1 Chemicals, Reagents, Standards, and Adsorbents

Preparation of solutions

Ultra-pure deionized (DI) water with total organic carbon (TOC) concentration of < 2 µg L^{-1} and a resistivity of 18.2 MΩ cm produced from a Milli-Q® purification system (Reference A+, Millipore) was used to prepare the positive control sample (a sample spiked with the same concentration and undergoes the same analysis as the test samples) for each experiment. A geosmin and 2-MIB working solution containing 1500 µg L^{-1} of each analyte was prepared by spiking 9850 µL of MeOH (optima grade, Fisher Scientific, Ottawa, ON, CA) with 150 µL of a geosmin and 2-MIB mix stock containing 100 µg mL^{-1} of each analyte (Sigma-Aldrich Canada, Oakville, ON, Canada) in a 10-mL volumetric flask.

Five calibration standards for geosmin and 2-MIB analysis were prepared using the 1500 µg L^{-1} working solution at concentrations of 1, 1.5, 3, 6, 12, 24, and 48 µg L^{-1}. Calibration standards were prepared in a 10 mL volumetric flask using 9500 µL of ethyl acetate (HPLC grade, Fisher Scientific, Ottawa, ON, CA)) spiked with 500 µL Camphor Internal Standard which was prepared to a concentration of 200 µg L^{-1} In MeOH (camphor 96% from Sigma-Aldrich Canada, Oakville, ON, Canada).

Ethyl Acetate (EA, HPLC Grade), hexanes and toluene (99%) purchased from Fisher Scientific (Ottawa, ON, CA) were used as elution solvents.

Preparation of Adsorbents for bench scale studies

C18 bulk sorbent (SELECTRASORB™ endcapped, Chromatographic Specialties Incorporation, Brockville, ON, CA), granulated activated carbon (GAC, FILTRASORB 300, Calgon Carbon, Moon Township, PA)

and Oasis HLB bulk sorbent (Waters Limited, Stamford Ave., Altrincham, UK) were used as passive sampling adsorbents. Depending on the bench-scale experiment, different masses of adsorbents (500, 1000 or 1500 mg) were measured into 25-µm pore size nylon mesh bags, which were then heat-sealed using a Tabletop Impulse Sealer-8" and placed into stainless-steel casings (9.7 × 6.6 × 5.6 cm) (Figure 4).

Preparation of Adsorbents for field experiments

C18 bulk sorbent was measured into 25-µm pore size nylon mesh bags and placed into the cyanobacterial and algal toxin sampling cage (CATSCa). The CATSCa (Figure 9) is a 3D printed passive sampling device, it is 90-mm in diameter and designed to hold the adsorbents in place during field deployment. The holes at the top, bottom, and sides of the CATSCa allows water to flow freely through it and contact the material inside. The device was printed with acrylonitrile butadiene styrene (ABS) plastic and solid walls for sufficient mass to enable its complete submersion in the aqueous environment. The CATSCa is a modification of the COVID-19 sewer cage (COSCa) developed by Hayes et al. (2021), with the major design change being the incorporation of six chambers to allow for more cyanobacterial targets. During deployment, the CATSCa was secured with a nylon rope and attached to trees on the shoreline to ensure feasible deployment and retrieval.

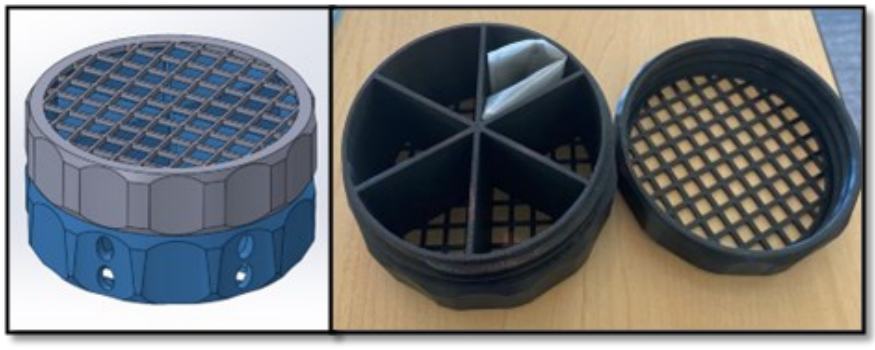

Figure 5. The 3D-desinged (left) and printed (right) cyanobacterial and algal toxin sampling cage (CATSCa) containing the adsorbent prepared in a heat-sealed nylon bag.

Source water collection for method development and validation

Seven 19-L buckets were used to collect lake water from Pockwock and Bennery lake in Halifax, Nova Scotia, Canada on separate calendar days between February and June 2022. The water samples were transported to Dalhousie University and stored at 4 ºC to preserve samples prior to analysis. Water samples suspected of containing the target compounds were left open for at least 24 h to allow evaporation of geosmin and 2-MIB.

3.1.2 Bench-Scale Experimental Design

To develop a passive sampling technique for the determination of geosmin and 2-MIB in source water, a series of bench-scale experiments was performed and has been summarized using a flowchart presented in figure 8. Each experiment involved three stages of analysis: passive sampling of target compounds in spiked water samples, elution of target compounds from adsorbent, and geosmin and 2-MIB analysis via GC-MS. Experiments for the optimization of each method parameter was carried out using these three stages of analysis.

3.1.2.1 Passive Sampling of Target Compounds in Spiked Water Samples

Glass jars (533 mL) were filled with 500 mL DI or lake water and spiked with geosmin and 2-MIB to a concentration of 0.25 µg L^{-1}. To achieve uniform mixing of the spiked water samples and minimize analyte loss due to volatilization, the jars were sealed tightly, placed on an orbital shaker, and stirred for 30 min. Following the 30-min incubation, the shaker was stopped, and the prepared adsorbents (contained in the heat sealed nylon bags) were placed into perforated stainless-steel casings for complete submersion in the spiked samples. The casings were secured with a thin thread and suspended in the spiked water samples by tightly sealing the thread against the lid of the jar. The samples were mixed at 150 rpm for 24 h at room temperature (21 ± 2 ºC). Figure 5 shows the bench scale setup and specific materials for the passive sampling of geosmin and 2-MIB in spiked water samples.

Figure 6. A bench scale setup for the extraction of geosmin and 2-MIB from spiked DI and lake water matrices. A. a batch of samples stirring on an orbital shaker; B. a stainless-steel casing contained an adsorbent immersed in the spiked sample; C. a pre-measured mass of adsorbent inside a heat sealed nylon bag

3.1.2.2 Elution of Target Compounds from Adsorbent

After the 24-h stirring period, the adsorbents were removed from the jars and placed into plastic centrifuge tubes containing an elution solvent. The centrifuge tubes were then sealed, shaken vigorously for 1 min, and allowed to separate into aqueous and organic phases. From the organic supernatant, a 1425-µL volume was transferred into a 2-mL autosampler vial, and 75 µL of the 200-µg L^{-1} camphor internal standard was added to each sample. The vials were then covered using the autosampler caps having PTFE liner (figure 7).

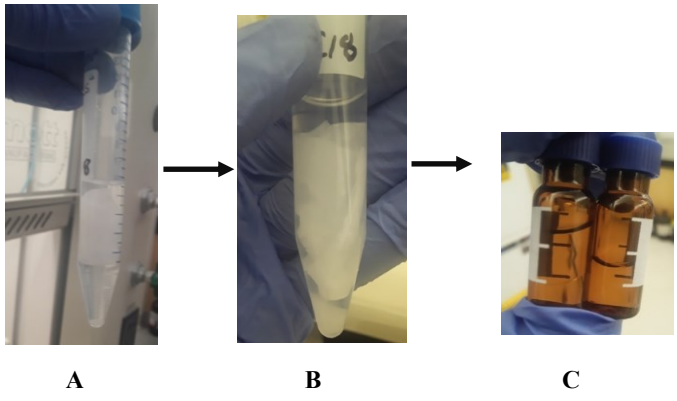

Figure 7. Elution of target compounds from adsorbent and sample preparation for analysis. A. adsorbent transferred into centrifuge tubes containing an elution solvent; B. separation of layers after shaking; C. eluate transferred into 2mL autosampler vials and spiked with camphor internal standard.

3.1.2.3 Geosmin and 2-MIB Analysis by GC-MS

Separation and detection of analytes was done by gas chromatography–mass spectrometry (GC-MS) utilizing parameters outlined in Wright et al., (2014). A volume of 1 µL was injected on a Varian CP-3800 Gas Chromatograph with a capillary column of 30 m × 0.25 mm × 0.25 mm (length(L) × internal diameter (D) × film thickness (FT)). The sample was injected by a CP-8400 autosampler, equipped with an Agilent Ultra inert 4-mm gooseneck liner containing glass wool, at an injector temperature of 200°C. Pure helium was used as the carrier gas at a constant flow rate of 0.7 mL min^{-1}. The GC oven temperature started at 60 °C, held for 0.5 min, then ramped to 300 °C at a rate of 20.0 °C min^{-1} with no hold. An ISQ Single Quadrupole Mass Spectrometer purchased from Fisher Scientific, Ottawa, ON, CA, was used for detection. The parent ion masses for geosmin and 2-MIB were 112 and 95 (Da), respectively, while the product ion masses were 97 and 125 (Da) for geosmin and 67 and 108 (Da) for 2-MIB.

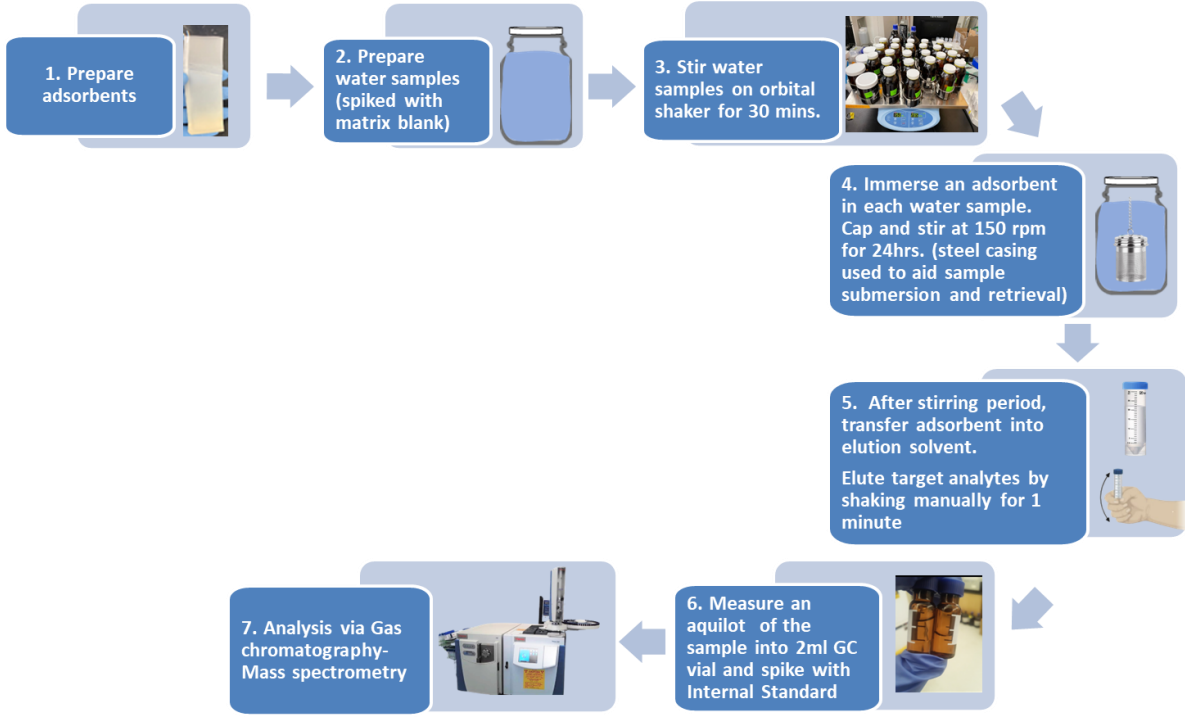

Figure 8. A flow chart of the sample preparation method for the passive sampling of geosmin and 2-MIB from lake water matrix

3.1.3 Optimization of Parameters for Geosmin and 2-MIB Extraction and Recovery

To optimize geosmin and 2-MIB recovery from passive sampling materials, the described bench-scale experiments were conducted to access the following parameters: 1) adsorbent material, 2) elution solvent, 3) elution volume, 4) adsorbent mass and 5) elution methods (i.e., incubation, shaking, and sonication times). All parameters were tested in batches comprised of three spiked sample replicates, a lake water matrix blank (MB), and a spiked DI water sample (positive control). A summary of all parameters optimized is presented in figure 9.

Adsorbent material: The efficiency of GAC, Oasis HLB, and C18 bulk adsorbents in recovering geosmin and 2-MIB from source water was assessed. GAC was chosen as it has been shown to have high geosmin and 2-MIB removal efficiencies (Mustapha et al., 2021) while Oasis HLB and C18 have been used in several studies as adsorbent materials for passive sampling of organic pollutants (Alvarez et al., 2004b; Harman et al., 2012; Mazzella et al., 2010; Vrana et al., 2006). In this experiment, 500 mg of each adsorbent material was submerged into 500-mL lake water samples spiked to 0.25 µg L^{-1} and stirred for 24 h on an orbital shaker. After the stirring period, the target compounds were eluted from each adsorbent using 5 mL of ethyl acetate and analyzed via GC-MS.

Elution Solvent: The experiments in this section were used to assess the elution efficacy of three solvents (ethyl acetate, toluene, and hexane) in extracting the target analytes from the passive sampling adsorbent. All three solvents were selected due to their miscibility with water, making them GC-amenable. Each solvent was used to extract geosmin and 2-MIB from 500 mg C18 that had been stirred for 24 h on an orbital shaker in 500 mL lake water samples spiked to 0.25 µg L^{-1}. Extraction was performed using 5 mL of elution solvent resulting in a 100-fold concentration of the target analytes. Eluted samples were analyzed via GC-MS.

Absorbent Mass-to-Elution Volume Ratio: To optimize the elution volume, 500 mg C18 immersed into 500 mL lake water samples spiked to 0.25 µg L^{-1} and stirred on an orbital shaker for 24 h were eluted with three different volumes of toluene (5, 7.5 and 10 mL) and analyzed via GC-MS. The different volumes had concentration factors of 100, 66.7, and 50 respectively. Recovery efficiency for samples of each elution volume was calculated based on expected analyte concentration in the eluate. At this point of the study, a reduction in the GC-MS sensitivity for geosmin and 2-MIB was observed while using toluene as an elution/injection solvent. As such, the suitability of ethyl acetate as a substitute elution solvent for toluene was assessed in the following experiment (optimization of Adsorbent mass).

Adsorbent Mass: The next optimization step involved experiments to assess different masses (500, 1000, and 1500 mg) of C18 for the recovery of geosmin and 2-MIB from 500 mL lake water samples spiked to 0.25 µg L^{-1}. After the 24-h stirring period, the adsorbents were retrieved for analyte extraction. The 500-mg C18 adsorbents were eluted with 7.5 mL of toluene. To maintain this sorbent mass-to-elution volume ratio, 15 and 22.5 mL was used to elute the 1000- and 1500- mg C18 masses, respectively. Eluted samples were analyzed via GC-MS. Experiments in this section were repeated but using ethyl acetate as the elution solvent.

Incubation time: To assess the impact of incubation time on analyte recovery, geosmin and 2-MIB were extracted from 1500 mg C18 after a 24-h stirring period in 500-mL lake water samples spiked to 0.25 µg L^{-1}. The C18 was eluted in 50-mL centrifuge tubes containing 22.5 mL of ethyl acetate. After vigorous shaking for 1 min, the samples were allowed to incubate for 5 min at room temperature, then analyzed via GC-MS.

Shaking Time: Experiments were conducted to evaluate 2- and 3- min elution shaking times for maximum geosmin and 2-MIB recovery. C18 adsorbents (1500 mg) were retrieved from 500 mL lake water samples spiked to 0.25 µg L^{-1} after a stirring period of 24 h and eluted in 50-mL centrifuge tubes containing 22.5 mL of ethyl acetate. Samples from each elution shaking time were analyzed via GC-MS.

Sonication Time: These experiments were conducted to evaluate geosmin and 2-MIB recoveries obtained with the inclusion of a sonication step after samples have been shaken in an elution solvent for 1 min. After the extraction of geosmin and 2-MIB from 500-mL lake water samples spiked to 0.25 µg L^{-1}, the retrieved 1500-mg C18 adsorbents were eluted in 50-mL centrifuge tubes containing 22.5 mL of ethyl acetate. The samples were then then sonicated at either 5, 10 or 15 min using a Fisher Scientific FS30D (Waltham, MA, US). After each sonication, the samples were retrieved for analysis via GC-MS.

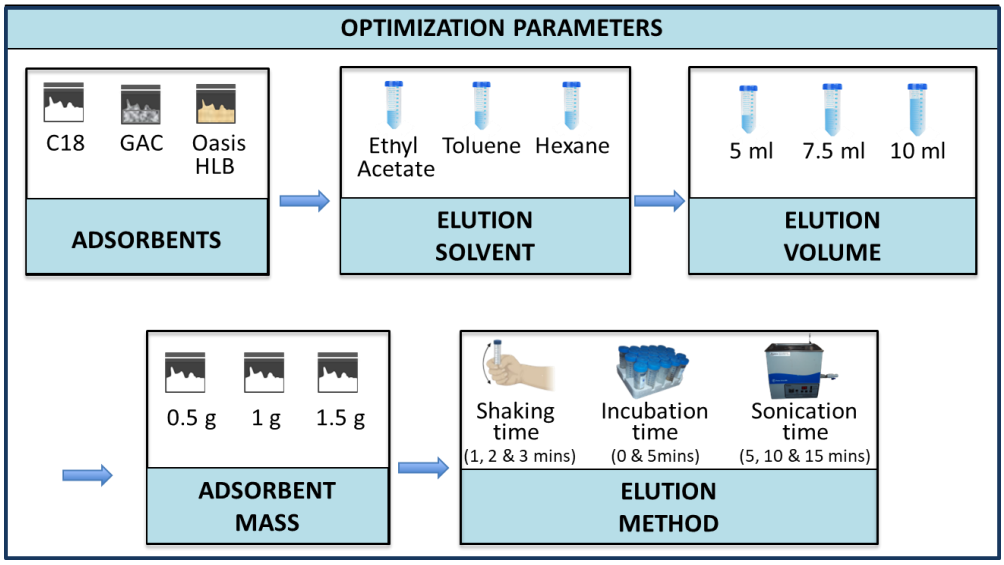

Figure 9. Flowchart of parameters optimized for the passive sampling of geosmin and 2-MIB in water.

3.1.4 Geosmin and 2-MIB Recovery Calculations

All experiments conducted to assess different parameters for geosmin and 2-MIB recovery efficiency were carried out in triplicate. Mean recovery values with standard deviation (SD) and %RSD were calculated. The analyte percent recovery was calculated using Equation 3:

$$\text{Analyte recovery}(\%) = \frac{\text{mean concentration of analyte measured}}{\text{expected analyte concentration in eluate}} \times 100 \qquad \text{Eq. (3)}$$

While the total geosmin/2-MIB concentration expected at the end of analysis (i.e., the expected concentration in the final sample extract/sample eluate) was calculated using Equation 4:

$$\text{Expected analyte concentration in sample eluate} = \frac{C_s \times V_W}{V_s} \qquad \text{Eq. (4)}$$

Where:

C_s = concentration of geosmin/2-MIB spiked into the water sample at the beginning of the experiment

V_W = volume of the water sample containing C_s

V_s = Volume of solvent used to elute C_s from the adsorbent material

3.2 METHOD VALIDATION PARAMETERS

Method validation can be defined as the determination of the suitability of a test method for a given application based upon several data quality parameters, such as precision, accuracy, matrix effect, sensitivity, limits of reliable measurement, and ruggedness of the method (Brian, 2003). New methods must be validated before they can be used for routine monitoring in the environmental phase of interest (US EPA, 1999). In this work, a passive sampling method for the determination of geosmin and 2-MIB in source water was developed. Different adsorbent materials, elution solvents, sorbent mass-to-elution volume ratio and additional elution method parameters have been optimized for improved analyte recovery. This method was further validated for the following analytical performance characteristics also described in Sweeney et al. (2021): accuracy (recovery and process efficiencies, RE (%) and PE (%), respectively), precision (intra and inter-day precision), linearity, matrix effects (ME (%)), method detection limit (MDL), and limit of quantitation (LOQ).

The accuracy of the method was evaluated through the determination of RE (%) and PE (%). Both parameters were evaluated by assessing analyte (geosmin and 2-MIB) recoveries of five test sample replicates at two spiked concentrations (0.27 and 0.54 µg L^{-1} initial spike concentration, which corresponded to 6 and 12 µg L^{-1}, respectively, following the 22.2-fold concentration step). RE (%) was determined using Equation (5).

$$\text{RE (\%)} = \frac{\text{mean concentration of analyte measured}}{\text{mean PExs concentration}} \times 100 \qquad \text{Eq. (5)}$$

The matrix post-extraction spiked control sample (PExs) concentration refers to samples spiked with geosmin and 2-MIB only after the elution process (prior to GC-MS analysis). PExs samples represent analyte concentrations at 100% recovery efficiency while incorporating any matrix effects. PExs samples were spiked at the expected analyte concentration in the final sample extract (i.e., 6 and 12 µg L^{-1}).

PE (%) was evaluated using Equation (6). Here, the mean recovery of the test samples (n=5) was compared to the concentration of the analyte in pure solvent which was prepared using ethyl acetate spiked with geosmin and 2-MIB to a concentration of 6 and 12 µg L^{-1} representing the expected analyte concentration in the sample eluate (final sample extract). PE (%) compares the recovery efficiency of test samples to that of samples that are not impacted by analyte loss due to matrix effect and during sample processing.

$$\text{PE (\%)} = \frac{\text{mean concentration of analyte measured}}{\text{concentration of analyte in pure solvent}} \times 100 \qquad \text{Eq. (6)}$$

Matrix effect is described as a phenomenon where interfering compounds cause a bias (suppression or enhancement) in analyte recoveries. ME(%) can significantly affect the quality of results hence its evaluation should be included in the development and validation of an analytical method (Bienvenu et al., 2017; Sweeney et al., 2021). In this study, the ME (%) was determined using Equation (7).

$$\text{ME (\%)} = \frac{\text{mean PExs concentration}}{\text{concentration of analyte in pure solvent}} \times 100 \qquad \text{Eq. (7)}$$

Where PExs concentration is defined above (Equation 5). This calculation (ME(%)) isolates the effects of the matrix on analyte recovery by comparing the recovery of analytes from test samples that are impacted by matrix effects alone (PExs) to samples that are neither impacted by matrix effects nor sample processing (samples prepared in pure solvent).

Method precision was evaluated through determination of RE (%) and expressed as %RSD. Intra-day precision was evaluated at 0.54 μg L^{-1} (n = 5) by repeating the extraction procedure twice within a 24-h period, while inter-day precision was assessed at 0.54 μg L^{-1} (n = 5) by repeating the extraction procedure on three different calendar days.

Linearity was assessed using five sample replicates at three spiked concentrations (0.045, 0.27, and 0.54 μg L^{-1} which corresponded to 1, 6 and 12 μg L^{-1}, respectively, following the 22.2-fold concentration step). A regression line for each analyte was generated and linearity was evaluated using the correlation coefficient (R^2 value).

The MDL for the extraction of target compounds from lake water matrix was determined based on the procedures outlined in Definition and Procedure for the Determination of the Method Detection Limit, Revision 2 (US EPA, 2016). Using the developed passive sampling method, ten samples spiked with geosmin and 2-MIB to a concentration of 0.045 μg L^{-1} (which resulted in a final concentration of 1 μg L^{-1} following the 22.2-fold concentration step) and 10 MBs were processed on three separate calendar days. The MDL for both the spiked samples and MBs was calculated and the higher MDL value of the two was reported.

The LOQ was calculated as ten times the SD of the 10 replicate spiked sample measurements used in the MDL study.

3.3 FIELD DEPLOYMENT FOR THE PASSIVE SAMPLING OF GEOSMIN AND 2-MIB IN SOURCE WATER (PROOF OF CONCEPT STUDY)

The developed passive sampling method was field-tested in six lakes in Nova Scotia, Canada: Lake Banook, Shubie, Penhorn, Oakfield, Cunard, and Kearney lakes. Eight sampling events were conducted at each location between late May and July 2022. These sites were selected as they are recreational lakes that have been issued a "no swim" advisory due to potential blooms of cyanobacteria - organisms that produce geosmin

and 2-MIB. Samples were collected from two separate locations at Lake Banook and Shubie (marked as A and B for each site) while only one location was sampled at the other four lakes.

For each passive sampling event, 1500 mg of C18 was prepared in a heat-sealed nylon bag, placed into a CATSCa, and deployed for 7 days. Following the deployment period, the CATSCa was retrieved and placed into a plastic bag containing water from the sampling site during transportation to the laboratory (Dalhousie University) on ice. This ensured the adsorbent remained wet until analysis to avoid volatilization of target analytes from the adsorbent. The samples were refrigerated at 4^0C and analyzed within 24 h. Adsorbents were eluted in 50-mL centrifuge tubes containing 22.5 mL ethyl acetate following the procedures outlined in the bench scale experimental design for the elution of target compounds. Some adsorbents had large amounts of particulates covering the surface of the nylon bags used to hold the C18. These samples were either gently rinsed with ultra-pure water or cleaned with Kim wipes prior to sample elution. Both measures were shown to have no impact on analyte recoveries. Before placement of new adsorbent and redeployment, the CATSCa's were first disinfected with chlorine (10% by vol) with a minimum contact time of 30 min.

As the volume of water to which the passive sampler was exposed during each 7-day deployment remains unknown, semi-quantitative analysis was performed using the concentration of target analytes eluted from the passive sampling adsorbent and reported in ng g^{-1}. This value was equal to the analyte concentration measured in the sample eluate (ng L^{-1}), multiplied by the elution volume (0.0225 L) and divided by the adsorbent mass (1.5 g) and recovery efficiency determined in the validation study (Equation 8).

$$\text{Conc.}_{\text{PS}}\ (\text{ng/g}) = \frac{\text{Analyte concentration in final extract (ng L}^{-1}) \times \text{Elution Volume(L)}}{\text{Recovery factor} \times \text{Mass of Absorbent (g)}} \qquad \text{Eq. (8)}$$

Where Conc._{PS} = Concentration of analyte in the passive sampler.

Following each passive sampling deployment period, grab samples were collected at all sampling sites using 1-L amber glass bottles and transported to the laboratory (Dalhousie University) on ice where they were

preserved at 4^0C. Collected grab samples were prepared using SPE method and analyzed via GC-MS following parameters described in Elliot Wright et al. (2014). In this work, an automated SPE and precise handling system (GX-271 ASPEC obtained from GILSON, Middleton, USA) was used. Each sample was loaded onto an SPE cartridge (Waters Sep-Pak tC18 3cc 500 mg, 37–55 µm cartridges obtained from Waters, Mississauga, ON, Canada) and allowed to pass through it at a constant flowrate. Ethyl acetate – an elution solvent was passed through the cartridge to elute the target analytes from the solid phase sorbent. Using this method, the analyte detection limit for grab sample analysis was determined with seven samples spiked to 1 ng L^{-1}. MDLs were 0.6 ng L^{-1} and 0.7 ng L^{-1} for 2-MIB and geosmin, respectively.

Detection rates for both the passive and grab sampling events were calculated using Equation 9:

$$\text{Detection rate (\%)} = \frac{\text{Number of detections per analyte}}{\text{Number of sampling events}} \times 100 \qquad \text{Eq. (9)}$$

3.4 STATISTICAL ANALYSIS AND CALCULATIONS

Recovery experiments to assess the performance of different parameters for the determination of geosmin and 2-MIB were carried out in triplicate measurements. For each passive sampling parameter tested, the mean recovery values with standard deviation (SD) and percent relative standard deviation (%RSD) were calculated. Significant differences in means were determined using either Welch two-sample t-test (two-tailed, $\alpha = 0.05$) programmed on R (version 4.1.3) or single factor ANOVA test ($\alpha = 0.05$) in Excel (version 2207) when comparing three test samples. The variability was expressed as %RSD and used to determine error bars. The regression line to assess linearity was generated using Excel (version 2207).

CHAPTER 4: RESULTS AND DISCUSSION

4.1 COMPARISON OF DIFFERENT ADSORBENTS FOR THE RECOVERY OF GEOSMIN AND 2-MIB FROM SOURCE WATER

Controlled bench-scale experiments were conducted to evaluate recovery efficiencies of three adsorbents (C18, GAC and Oasis HLB) in the passive sampling of geosmin and 2-MIB from lake water. Target analytes were recovered from all three materials although at varying efficiencies (Figure 10). C18 resulted in the highest mean concentrations for both geosmin (11.8 ± 0.74 µg L^{-1}) and 2-MIB (9.5 ± 1.1 µg L^{-1}) with recoveries of 47 and 38% respectively. This adsorbent also showed the lowest variability among the three adsorbents tested for both geosmin and 2-MIB demonstrated by RSD of 6 and 12%, respectively.

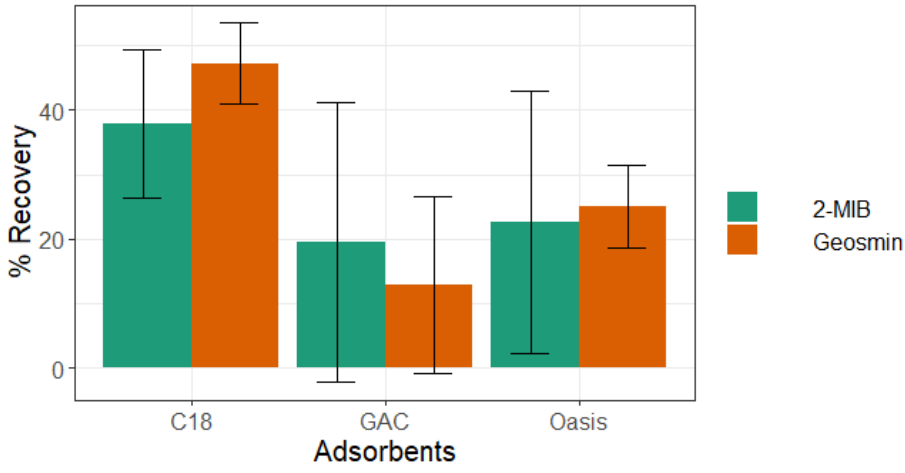

Figure 10. Mean recovery (%) of target analytes extracted from spiked lake water samples using three different passive sampling adsorbents: C18, GAC and Oasis HLB, in bench-scale experiments. Each adsorbent was tested in triplicate and error bars represented standard deviation.

Oasis HLB had a mean geosmin concentration of 6.3 ± 0.4 µg L^{-1} and a recovery of 25% while its mean 2-MIB concentration was 5.6 ± 1.1 µg L^{-1} with a recovery of 23%. Compared with C18, this adsorbent showed a similar variability in geosmin recoveries (RSD = 6%) but higher variability in 2-MIB recoveries (RSD = 20%). GAC resulted in the lowest recovery efficiencies (13% for geosmin and 22% for 2-MIB), with mean

concentrations of 3.2 ± 0.5 µg L^{-1} and 4.9 ± 1.1 µg L^{-1}, for geosmin and 2-MIB, respectively. Concentrations of analyte recovered from GAC also showed the highest variability among all the adsorbents (RSD = 14 and 22 %, for geosmin and 2-MIB, respectively). Interestingly, GAC had the highest percent recoveries (53% for geosmin and 40% for 2-MIB) in the DI water sample which was used as a positive control. This observation might mean that the performance of GAC is impacted by the presence of organic matter in the lake water samples. Such observations have been shown in Hayes et al. (2021). Furthermore, studies have shown that GAC is excellent in the removal of organic matter (Pham et al., 2013; Zhang, 2009). This advantage of GAC might be a limitation in geosmin and 2-MIB lake water monitoring as high selectivity for these compounds is crucial in this water source. This observation also shows some potential for GAC in the detection of geosmin and 2-MIB in treated water using this method since this source should have less or no organic matter content.

The concentrations of geosmin and 2-MIB recovered using C18 was significantly different from that using Oasis HLB with *p*-values of 0.001 and 0.013 (welch t-test) respectively. Moreover, from a procedural standpoint, C18 showed effective dissolution of adsorbed target compounds and suitability for deployment in lake water. Given the extraction performance of C18 and its relatively low variability in recovered concentrations of target analytes among all three adsorbents in this experiment, it was selected for further method development.

4.2 COMPARISON OF THREE ELUTION SOLVENTS IN THE ANALYSIS OF GEOSMIN AND 2-MIB

The efficacy of three elution solvents (ethyl acetate, toluene, and hexane) in eluting geosmin and 2-MIB from C18 as a passive sampling adsorbent in spiked lake water was assessed (Figure 11). The 2-MIB mean recovery concentration measured using samples eluted with toluene (9.7 ± 1.3 µg L^{-1}, 39% recovery) was similar to that eluted with ethyl acetate (9.7 ± 1 µg L^{-1}, 39% recovery). For geosmin, higher recoveries were obtained in samples eluted with toluene (15.4 ± 0.3 µg L^{-1}, 61% recovery) compared to those eluted with

ethyl acetate (11.8 ± 1.3 µg L^{-1}, 47% recovery). Percent recovery of geosmin and 2-MIB using both ethyl acetate and toluene resulted in RSD values <14%.

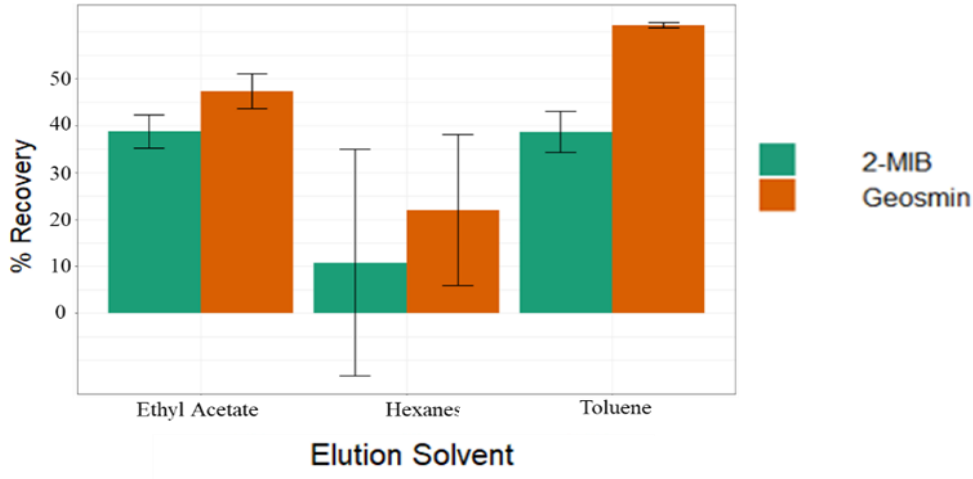

Figure 11. Mean recovery (%) of target analytes extracted from C18 (500 mg) deployed as a passive sampling adsorbent in spiked lake water samples and eluted with three different solvents (ethyl acetate, hexane, and toluene) in bench-scale experiments. Each elution solvent was tested in triplicate and error bars represent standard deviation.

Hexane resulted in the lowest geosmin and 2-MIB mean recoveries (5.5 ± 2.7 µg L^{-1} and 2.7 ± 1.9 µg L^{-1} , respectively) with high variability (RSD = 48% for geosmin and 73% for 2-MIB).

The two best performing solvents were compared statistically using welch t-test. Results showed that the mean geosmin concentrations of samples eluted with toluene was significantly greater than that of samples eluted with ethyl acetate (p = 0.038) while mean 2-MIB concentrations using the two elution solvents were not significantly different (p = 0.983). Since higher geosmin recoveries could be obtained using toluene, it was selected for subsequent experiments.

4.3 OPTIMIZATION OF SORBENT MASS-TO-ELUTION VOLUME RATIO

The sorbent mass-to-elution volume ratio was assessed using different volumes of toluene (5, 7.5, and 10 mL) to elute geosmin and 2-MIB from 500 mg C18 deployed as a passive sampling adsorbent in spiked lake water (Figure 12). For geosmin, the highest mean percent recovery was obtained from samples eluted with

7.5 mL of elution solvent (39%), followed by samples eluted with 10 mL (30%). The 5 mL volume resulted in the lowest percent recovery (27%). An RSD of 5% was obtained using the 7.5-mL elution volume which was lower than other volumes tested (17% for 5 mL and 34% for the 10 mL).

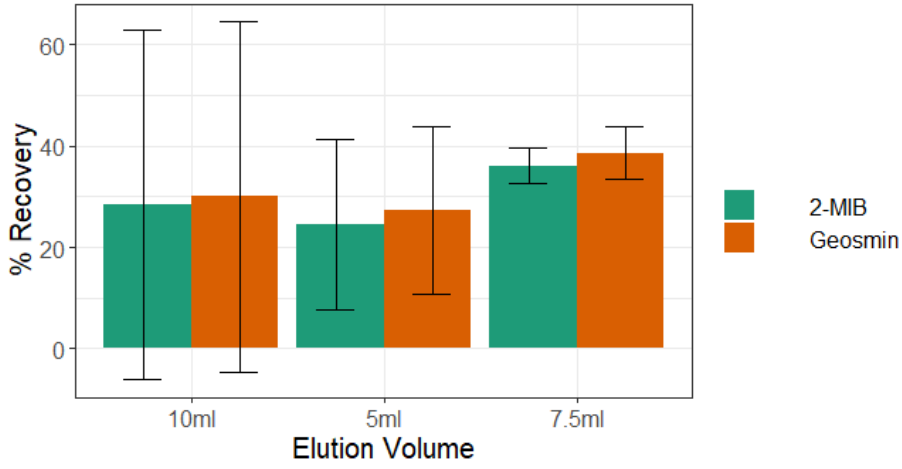

Figure 12. Mean recovery (%) of target analytes extracted from C18 (500mg) deployed as a passive sampling adsorbent in spiked lake water samples eluted with three different elution volumes (5, 7.5, and 10 mL) of toluene in bench-scale experiments. Each volume was tested in triplicate and error bars represent standard deviation.

Similar to geosmin, mean 2-MIB percent recovery was highest using the 7.5-mL elution volume (36 ± 4%) followed by the 10-mL (28 ± 35%), while the 5-mL elution volume had the lowest recovery (25 ± 17%).

Percent recoveries (n=3) using these different elution volumes showed no significant difference for geosmin (p = 0.172, ANOVA) and 2-MIB (p = 0.145, ANOVA); However, since the 7.5-mL elution volume demonstrated a higher mean percent recovery with the lowest variability, it was selected for further optimization experiments.

4.4 OPTIMIZATION OF ADSORBENT MASS

This bench-scale passive sampling experiment assessed the geosmin and 2-MIB recoveries from spiked lake water using three C18 masses: 500, 1000 and 1500 mg (Figure 13). Recovery analysis to optimize this parameter also assessed the elution of these three masses using two different solvents – ethyl acetate and

toluene. Due to an observed decrease in analyte response over time with the use of toluene and the greater environmental impact of the solvent, ethyl acetate (which, from previous experiments, had a 2-MIB recovery performance comparable with that of toluene) was assessed in parallel with toluene as a potential alternative elution solvent.

In general, higher adsorbent masses showed increased analyte recoveries and reduced variabilities as demonstrated by their %RSD. This observation was the same for both toluene and ethyl acetate (Figure 13).

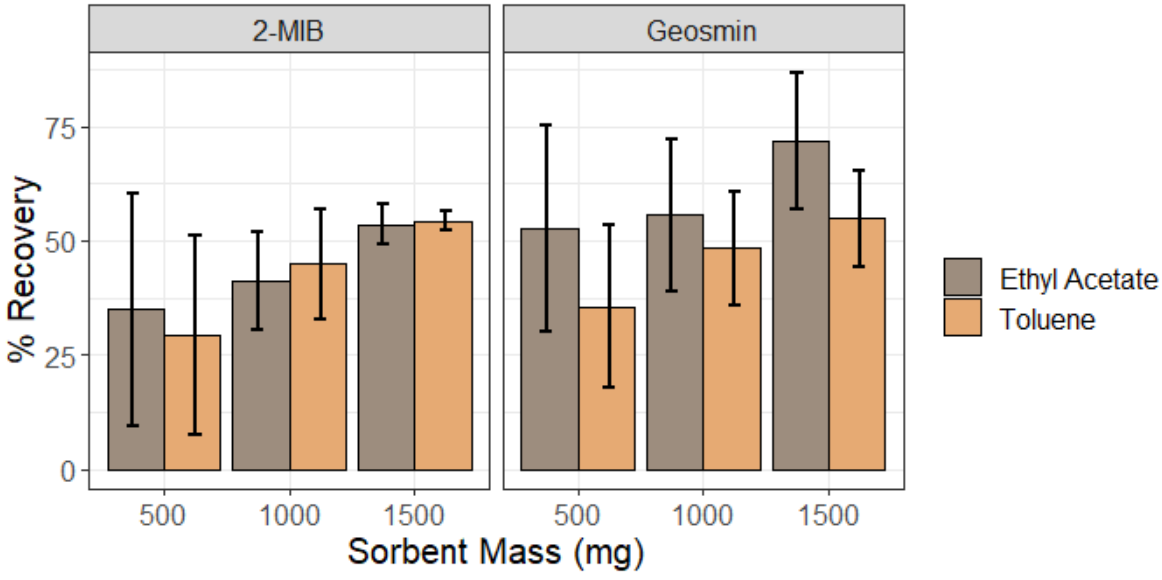

Figure 13. Mean recovery (%) of target analytes extracted from three different masses of C18 deployed as a passive sampling adsorbent in spiked lake water samples and eluted with ethyl acetate and toluene in bench-scale experiments. Each C18 mass was tested in triplicate and error bars represent standard deviation.

In the experiments using ethyl acetate, the differences in mean geosmin recoveries from 500, 1000 and 1500 mg of C18 were not significant (p = 0.142, ANOVA). However, the 1500-mg samples showed the highest mean percent recovery and lowest RSD (72 ± 15%). C18 masses of 500 and 1000 mg had mean percent recoveries of 53 ± 23% and 56 ± 17%, respectively. For 2-MIB, the three masses were shown to be significantly different (p = 0.021, ANOVA) and had mean percent recoveries and corresponding RSD value as follows: 500 mg (35 ± 26%), 1000 mg (41 ± 19%), and 1500 mg (54 ± 5%). These results show that

samples eluted from 1500 mg of C18 had the highest 2-MIB recovery efficiency and the lowest variability. The significance test for geosmin suggests that any of the three masses can be used; however, in situations where both compounds are analyzed, extracting geosmin and 2-MIB separately may increase the total analysis time and extraction material needed. To accommodate co-extraction of both compounds of interest, the 1500 mg mass of C18 was chosen for subsequent experiments as it provided optimal results for both geosmin and 2-MIB recovery.

In the experiments using toluene, the recoveries of both target analytes using the different C18 masses (500, 1000 and 1500 mg) were significantly different (*p*-values of 0.021 and 0.002 for geosmin and 2-MIB, respectively, ANOVA) and indicated that the 1500-mg C18 mass produced the highest recovery for both geosmin (54.8 ± 11%) and 2-MIB (54.3 ± 2%) while having the lowest variability among the three masses tested. The percent recovery of geosmin from samples eluted from 1000 and 500 mg of C18 were: 48.3% (12% RSD) and 35.6% (18% RSD) respectively, while the 2-MIB recoveries from the same respective adsorbent masses were 45% (12% RSD) and 29.3 % (22% RSD).

Comparing the recoveries obtained at the 1500 mg mass using both solvents, ethyl acetate resulted in higher geosmin and 2-MIB recoveries compared to toluene. RSD values were ≤ 15% for both target analytes using either toluene or ethyl acetate. Although the difference in the analyte recoveries from both solvents was not significant (2-MIB ($p = 0.641$) and geosmin ($p = 0.095$), welch t-test), ethyl acetate was chosen over toluene due to its reduced environmental impact compared to toluene (US National Library of Medicine, 2017).

4.5 EVALUATION OF DIFFERENT ELUTION METHOD PARAMETERS: INCUBATION, SHAKING AND SONICATION TIMES

Maximum recoveries of 72% for geosmin and 54% for 2-MIB have been obtained from optimization experiments using 1500 mg C18 as a passive sampling adsorbent, ethyl acetate as an elution solvent and an elution shaking time of 1 min. Further optimization involved assessing the impact of additional elution

method parameters on analyte recoveries: elution sample incubation, shaking and sonication times were assessed. Samples for each parameter were analyzed in triplicate.

To test the impact of elution sample incubation on analyte recoveries, a 5-min incubation time was selected to provide more contact time between the target analytes and extraction solvent. This step resulted in a geosmin recovery efficiency of 60% (RSD = 5%) and 2-MIB recovery of 40% (RSD = 5%). These results show that the incubation of elution samples for 5 min did not improve the recovery of target compounds. Rather, a decrease in recovery concentrations was observed; hence, this elution method parameter was not carried forward in subsequent experiments.

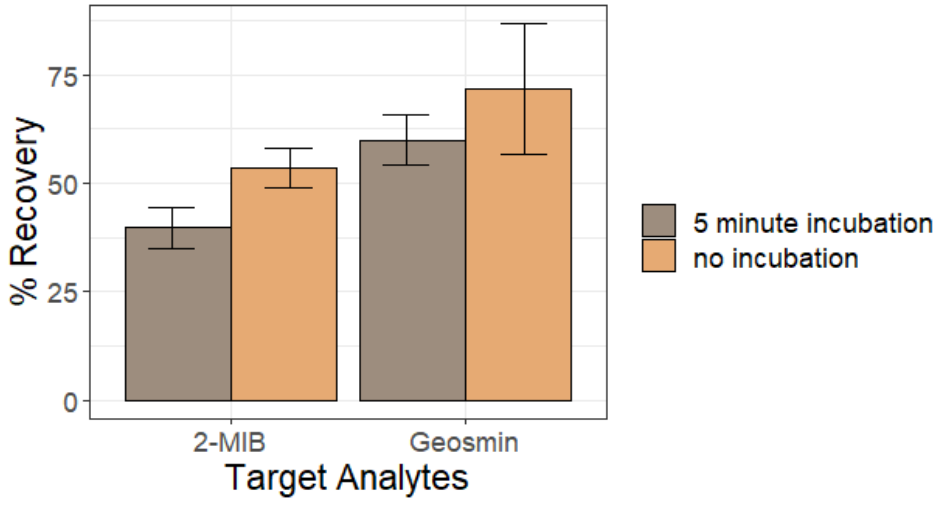

Figure 14. The effect of a 5-min incubation time on the mean recovery (%) of target analytes extracted from 1500 mg C18 deployed as a passive sampling adsorbent in spiked lake water samples and eluted with ethyl acetate in bench-scale experiments. Samples were analyzed in triplicate and error bars represent standard deviation.

The next parameter evaluated for geosmin and 2-MIB recovery optimization was the elution shaking time (2 and 3 min). Samples shaken for 2 min produced mean recoveries of 66.8 and 41.9% for geosmin and 2-MIB, respectively, while samples shaken for 3 min resulted in a mean geosmin and 2-MIB recovery of 61.8% and 43.6%, respectively. RSD values for all tests were <9% for both analytes. These results show that increasing

the elution shaking time did not increase percent recoveries for either geosmin or 2-MIB (Figure 15A). Hence, the 1-min shaking time was maintained.

The final optimization parameter evaluated was sonication. Brief exposure to ultrasonic energy at low temperatures has been used to cause cell lysing in geosmin and 2-MIB producing organisms for the purpose of measuring total analyte concentrations in water samples (Oh et al., 2017; Wu & Duirk, 2013). Therefore, the effect of sonication in extracting geosmin and 2-MIB adsorbed onto the sorbent was assessed as a function of time (5, 10, and 15 min) (Figure 15B).

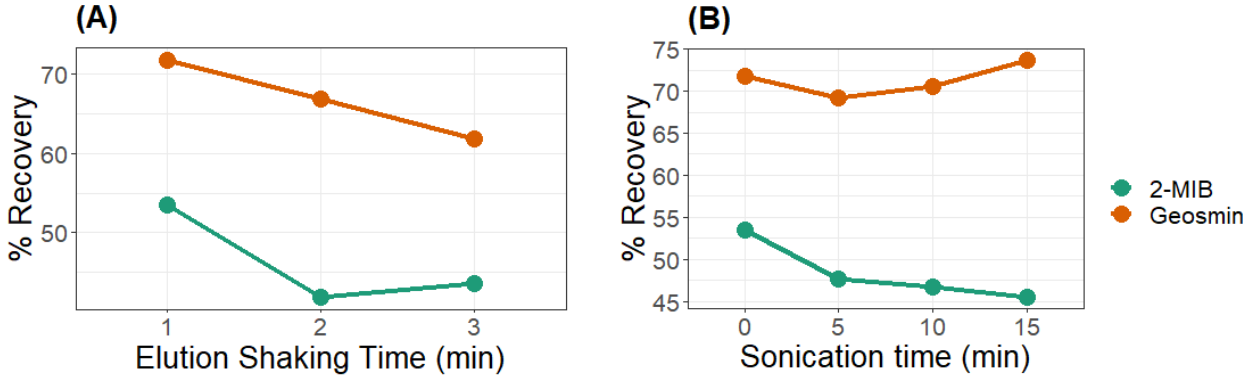

Figure 15. The effect of elution shaking time (A) and sonication time (B) on the mean recovery (%) of target analytes extracted from 1500 mg C18 deployed as a passive sampling adsorbent in spiked lake water samples and eluted with ethyl acetate in bench-scale experiments. Samples were analyzed in triplicate and error bars represent standard deviation.

There was no statistical difference in analyte recoveries among the three sonication times tested for both geosmin ($p = 0.575$, ANOVA) and 2-MIB ($p = 0.624$, ANOVA). As such, recoveries of target analytes from samples that were not sonicated were compared to those from samples sonicated for the least amount of time (5 min). With the 5-min sonication, mean recoveries of 69% for geosmin and 48% for 2-MIB (RSD = 9% and 5%, respectively) were achieved, which were lower than the recoveries obtained from samples that were not sonicated (72% for geosmin and 54% for 2-MIB). These results indicate that sonication did not improve

geosmin and 2-MIB recoveries from C18. Hence, sonication was not included as an elution method parameter in this passive sampling protocol.

4.6 METHOD VALIDATION

A series of bench-scale experiments in the development of a passive sampling approach for geosmin and 2-MIB monitoring in lake water resulted in the following optimized method parameters: 1500 mg C18 as adsorbent, ethyl acetate as elution solvent, a 500 mg mass-to-7.5 mL elution volume ratio, and an elution shaking time of 1 min.

Accuracy of the optimized method was measured in terms of recovery and process efficiencies (RE% and PE%, respectively) at spiked analyte concentrations of 0.27 and 0.54 µg L^{-1} (6 and 12 µg L^{-1}, respectively, in sample extract after the 22.2 fold concentration step). For 2-MIB, RE% at the 0.27 µg L^{-1} spike level was 38% and 45% at the 0.54 µg L^{-1} spiked level, while for geosmin, an RE of 53% was obtained at both spiked levels. PE% for 2-MIB were 38 and 45% at the 0.27 and 0.54 µg L^{-1} spike levels, respectively, while for geosmin, PE% at the lower spike level was 52% and at the higher spike level was 48%. In both geosmin and 2-MIB analysis, values for the RE% and PE% were consistent at both spiked levels and %RSD values ranged from 6 to 15%, which are below the generally accepted maximum value of 20% (American Public Health Association, 2005). Since the PE% measures the overall analyte loss (i.e. from matrix interferences and during sample preparation) while the RE% evaluates analyte loss during sample preparation only, the similarity in RE% and PE% for both target analytes indicates that analyte loss is mostly due to the assay itself rather than matrix interferences and that this analyte extraction technique was successful in removing interferences from the lake water matrix.

In an additional measure of accuracy, mean analyte recovery (n=10) was calculated for samples analyzed at the lowest spike concentration (0.045 µg L^{-1} which corresponds to 1 µg L^{-1} in the final sample extract). This was done to determine whether analyte recovery efficiency was impacted by the spiked concentration.

Interestingly, while mean percent recovery at the two higher spike concentrations (0.27 and 0.54 µg L^{-1}) was consistent, mean percent recovery at the 0.045 µg L^{-1} spike concentration was observed to be significantly greater (85% for 2-MIB and 120% for geosmin with RSD values of 12 and 9%, respectively). A possible reason could be that analyte recovery concentrations at the 0.045 µg L^{-1} spike level may be approaching the LOQ, thus affecting the methods quantitation accuracy at this spike level. Nevertheless, it cannot be ruled out that recovery efficiencies for both geosmin and 2-MIB may be improved at concentrations below 0.045 µg L^{-1} in water, using this passive sampling approach. Future studies may involve kinetic experiments to show uptake rate and adsorption capacity at concentrations near the 0.045 µg L^{-1} spike level as well as improvements in assay sensitivity.

In a conservative approach, overall recovery efficiency of the passive sampling method was determined as the analyte mean percent recovery obtained from 20 replicates at the 0.54 µg L^{-1} spike level processed on three separate calendar days. Recoveries for 2-MIB and geosmin were 53 and 50%, respectively, with RSD values of 15 and 10%.

Precision was analyzed at the 0.54 µg L^{-1} spiked level. Excellent intra-day precision (RSD ≤ 11%) was observed for both geosmin and 2-MIB. Inter-day precision between the three days tested was demonstrated by a 10% RSD for geosmin and a 15% RSD for 2-MIB.

Matrix effects were evaluated using Equation (7). Values below 100% indicate ion suppression while those above 100% indicate ion enhancement, and ME (%) of 100% denotes no observable matrix effects (Sweeney et al., 2021). At the 0.27 µg L^{-1} spike level, ME (%) for geosmin and 2-MIB were 108 and 109%, respectively showing very minimal interferences in analyte response. At the 0.54 µg L^{-1} spike level, an ME value of 98% was obtained for 2-MIB, and there was no observable matrix effect in geosmin recovery at this spike level (i.e., ME = 100%). Results for ME (%) are in-line with accuracy measurements where similarities in RE (%) and PE (%) were observed.

To test the method for linearity, five sample replicates spiked at concentrations of 0.045, 0.27 and 0.54 µg L^{-1} (which corresponds to 1, 6 and 12 µg L^{-1}, respectively, following the 22.2-fold concentration step) were analyzed. Linearity was observed for both geosmin ($R^2 = 0.9965$) and 2-MIB ($R^2 = 0.9775$) (Figure 16).

The MDL for the novel passive sampling method was determined following the procedures outlined in US EPA (2016) using both spiked samples (n=10) and method blanks (n=9). MDLs for 2-MIB and geosmin were 0.044 and 0.014 µg L^{-1} (which corresponds to 0.98 and 0.32 µg L^{-1} in the final sample extracts), respectively (Table 2). These MDLs were experimentally determined values based on 500-mL lake water samples spiked to an initial concentration of 0.045 µg L^{-1} and passively sampled with 1500 mg C18 over a 24-h period. The calculated LOQ was 0.046 µg L^{-1} for 2-MIB and 0.051 µg L^{-1} for geosmin (which corresponds respectively to 1.02 and 1.13 µg L^{-1} in the final sample extracts). As the volume of water to which the passive sampler is exposed during deployment in the field remains unknown, the determined MDL and LOQ values are semi-quantitative. As such they were converted to their concentration per gram of the passive sampling adsorbent using Equation 8 and are presented in Table 2.

Overall, the performance characteristics of this method met all validation criteria. Given that the passive sampling method demonstrated acceptable precision (RSD values below 20%), linearity, and minimal matrix effects (ranging between 98 and 109%) for both analytes, recoveries of at least 50% are deemed acceptable by the Environmental Protection Act (2021).

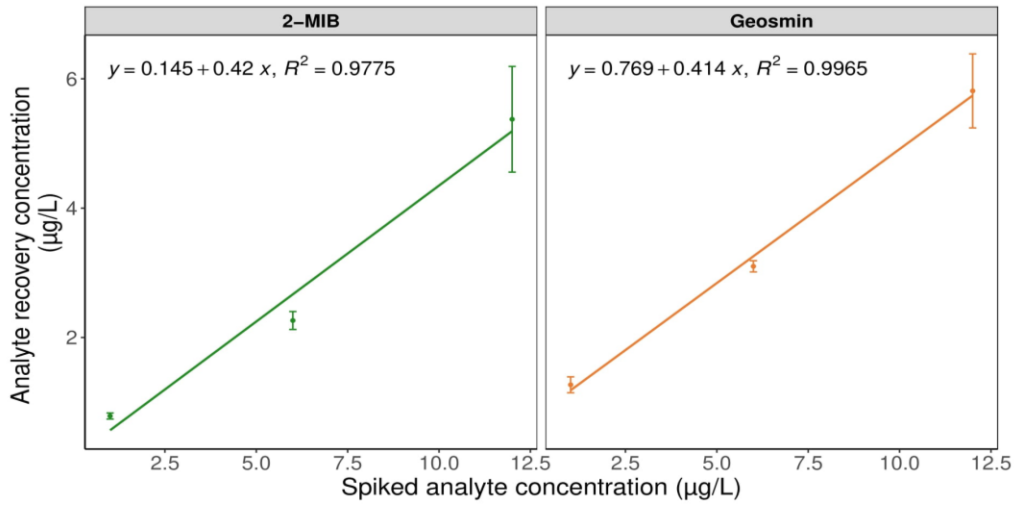

Figure 16. Regression lines showing mean analyte concentrations for 2-MIB (A) and geosmin (B) recovered at spiked concentrations of 1, 6, and 12 µg L^{-1} in final extracts. These values correspond respectively to initial spike levels of 0.045, 0.27, and 0.54 µg L^{-1} in water samples. Samples were analyzed in replicates of five at each spike concentration and error bars represent standard deviation.

Table 1. Process and recovery efficiencies, %RSD, matrix effects, and intra- and inter-day precision of an analytical method for extracting taste and odour compounds from lake water through passive sampling (n = 5).

Analyte	Initial spike level (µg L^{-1})[a]	PE[b] (%)	RE[c] (%)	RSD (%)	ME[d] (%)	Intra-day precision (%RSD)	Inter-day precision (%RSD)
2-MIB	0.045	85	N/A	12	N/A	N/A	N/A
	0.27	38	38	9	109	N/A	N/A
	0.54	45	45	15	98	9	15
Geosmin	0.045	120	N/A	9	N/A	N/A	N/A
	0.27	52	53	6	108	N/A	N/A
	0.54	48	53	10	100	10	10

[a] Initial spike level concentrations: 0.045, 0.27, and 0.54 µg L^{-1} corresponds to final extract concentrations of 1, 6, and 12 µg L^{-1}

[b] PE = process efficiency (absolute recovery)

[c] RE = recovery efficiency (relative recovery)

[d] ME = matrix effects

Table 2. Linearity and detection limit data

Analyte	Parent ion (m/z)	Product ions (m/z)	t_r[a] (min)	R^2 value (analytical standards)	R^2 value (test samples)	MDL[b] (ng g^{-1})	LOQ[c] (ng g^{-1})	Recovery Factor (%)
2-MIB	95	67, 108	8.211	0.9967	0.9775	27.7	28.9	53
Geosmin	112	97, 125	9.990	0.9986	0.9965	9.6	33.8	50

[a] t_r = analyte retention time

[b] MDL = method detection limit represented by the analyte concentration in the extracted eluate per gram of passive sampling adsorbent

[c] LOQ = limit of quantitation represented by the analyte concentration in the extracted eluate per gram of passive sampling adsorbent

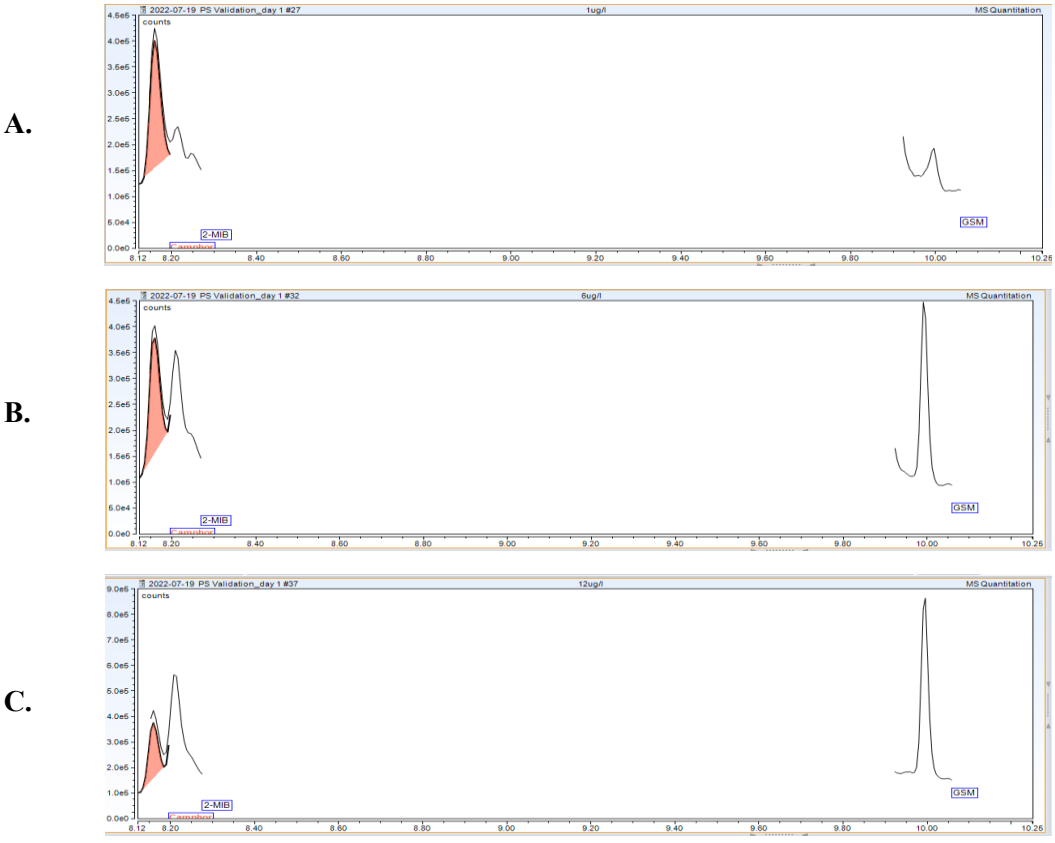

Figure 17. Chromatogram of a standard mixture of 2-MIB and geosmin (GSM) in sample eluate spiked at final concentrations of (A) 1 µg L^{-1}, (B) 6 µg L^{-1}, and (C) 12 µg L^{-1} with IS (camphor). Peaks were detected at *m/z* values for the quantitation (parent) and confirming ions (product) (Table 2).

4.7 DETERMINATION OF GEOSMIN AND 2-MIB IN LAKE WATER AT SEVERAL SITES IN ATLANTIC CANADA (PROOF OF CONCEPT STUDY)

In a proof-of-concept study to assess the performance of this novel passive sampling approach under real environmental conditions, the validated method was implemented in the field for the detection of geosmin and 2-MIB in lake water collected from six lakes in Atlantic Canada. The monitoring program was conducted from May to July 2022 and compared the new passive sampling method to a traditional grab sampling technique. The two target taste and odour compounds were measured at eight locations: Banook (sites A and B), Shubie (sites A and B), Penhorn, Oakfield, Kearney, and Cunard. The passive samplers were deployed for seven days. During retrieval of the passive samplers, grab samples were also collected and transported to the Dalhousie University laboratory for analysis.

Eight sampling events were conducted at each location. At five locations and on five separate sampling events, the deployed passive samplers were not found on site. To achieve a non-bias comparison of the methods (passive and grab), samples from 59 paired sampling events were analyzed.

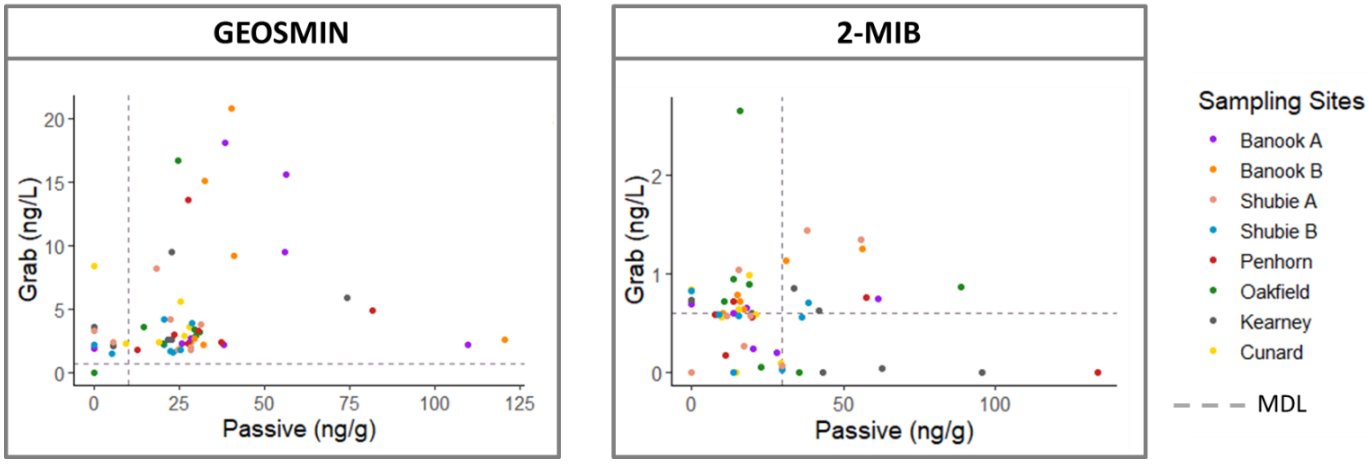

Figure 18. Geosmin and 2-MIB concentration plot using grab and passive sampling methods

Both compounds were successfully detected using the passive samplers. Concentration up to 125 ng g^{-1} of geosmin accumulated in the passive samplers were measured (Figure 18). Using the passive sampling

method, at two locations (Banook B and Oakfield), geosmin was detected on all sampling events (Figure 19). The detection rates based on the total number of detections from all sampling events at each of the other locations were: 88% (Banook A), 75% (Shubie A), 57% (Shubie B), 71% (Penhorn), 86% (Kearney) and 75% (Cunard). Results from grab sampling analysis also showed that geosmin concentrations were relatively high, reaching up to 20 ng L^{-1} (Figure 18). Using the grab sampling method, geosmin was detected on all sampling events at seven locations and on six sampling events at Penhorn (Figure 19). Cumulative geosmin detection rates for the grab and passive sampling methods were 98 and 81% respectively.

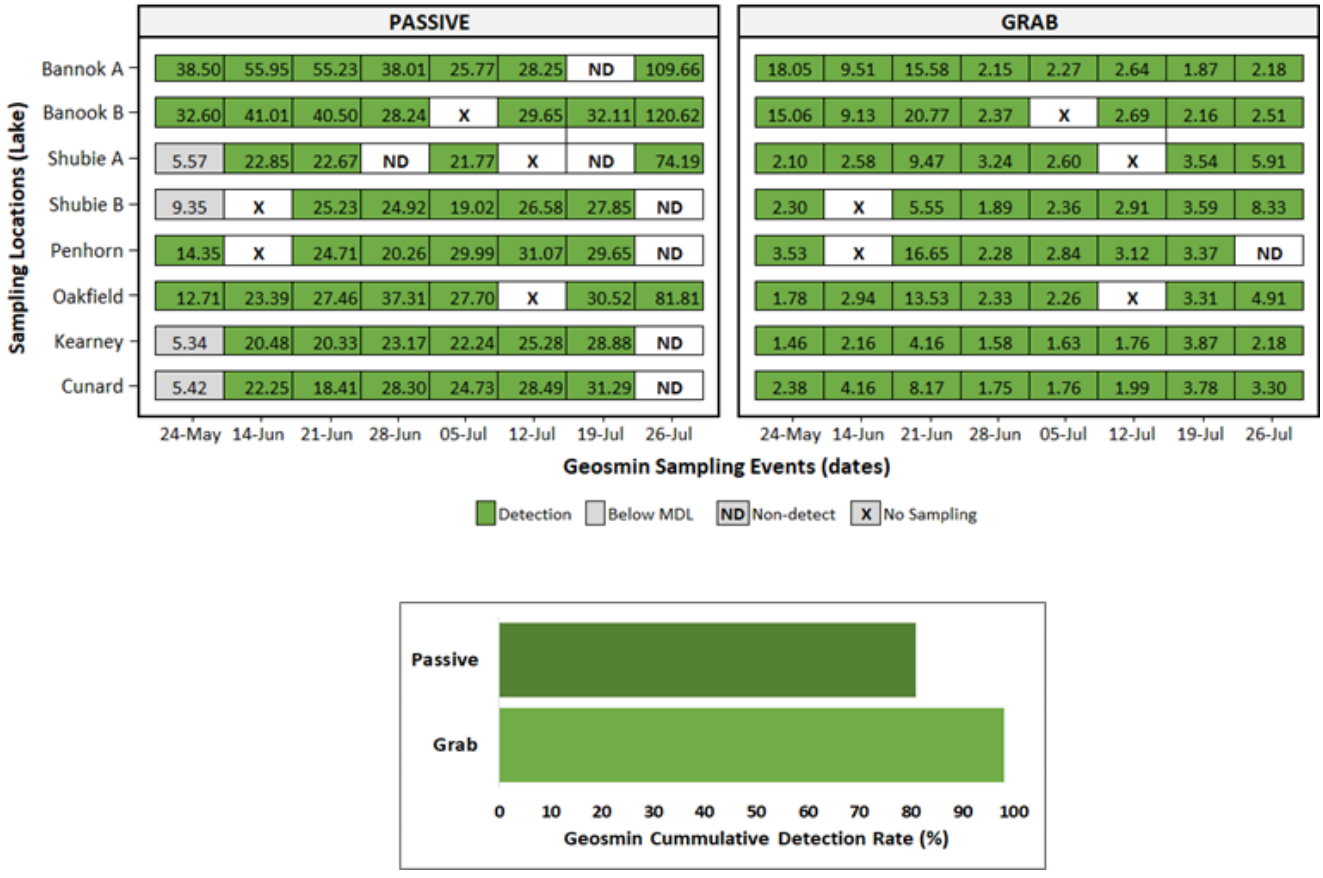

Figure 19. Geosmin monitoring data for 59 sampling events from eight lake water sampling sites using the validated passive sampling approach and the conventional grab sampling method (May- July 2022). Cumulative detection rates for both sampling methods are presented.

2-MIB detection rates for both methods were significantly lower compared to geosmin (Figure 20). From the passive samplers, 2-MIB had a cumulative detection rate of 34% and individual detection rates ranging from 14 to 71% for each location. While, using the grab sampling method, 2-MIB was detected in all sampling locations and at detection rates ranging from 25 to 71%. The cumulative detection rate for 2-MIB via grab sampling analysis was 44%. These results indicate that concentrations of 2-MIB might be lower in the sampled medium compared to geosmin, but more interestingly, that the occurrence of analytes using both methods are in correlation.

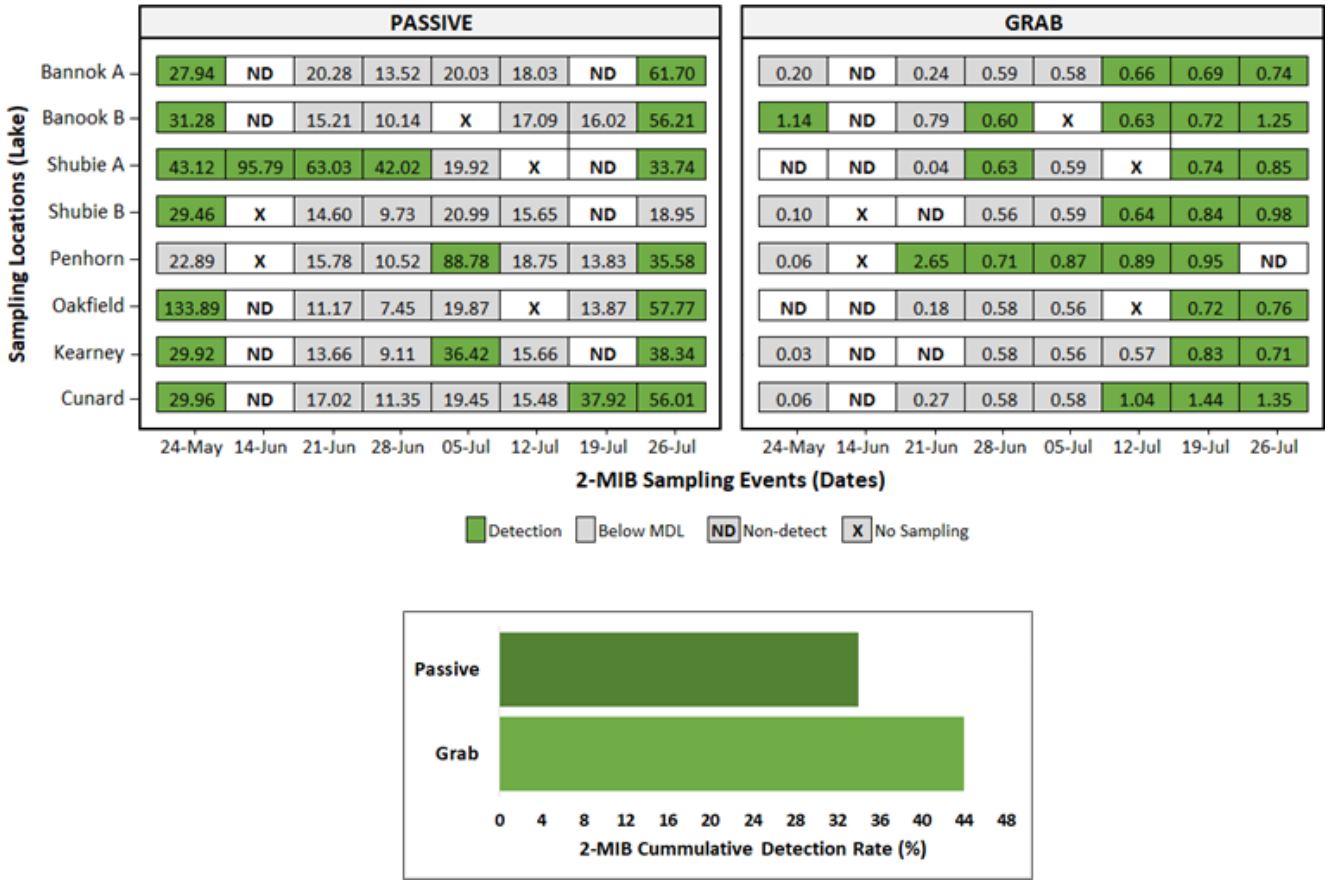

Figure 20. 2-MIB monitoring data for 59 sampling events from eight lake water sampling sites using the validated passive sampling approach and the conventional grab sampling method (May- July 2022). Cumulative detection rates for both sampling methods are presented.

Out of the 59 sampling events, 18% of the 2-MIB detections in the grab samples were below the detection limit of the passive samplers (27.7 ng g^{-1}) and 4% grab sample detections for 2-MIB where non-detects in the passive. Similarly, out of the 59 sampling events for geosmin, 7% of grab sample detections were below the passive sampling detection limit (9.6 ng g^{-1}) while 10% of geosmin detections in the grab were not detected using the passive sampling method. Future research may involve optimization experiments to improve method recovery efficiency.

Another observation made in this field study was the early detection of 2-MIB from the passive samplers which was not captured in the grab samples. The bulk of the grab sampling detections were from concentrations measured between late June to July. Before this, 2-MIB had been detected via passive sampling conducted at seven locations in May, and at Shubie A, detections for 2-MIB were seen until late June during which, its concentration in paired grab samples were either below the detection limit or not detected (Figure 20). For this work, the determined grab sampling MDL (0.6 and 0.7 ng L^{-1} for 2-MIB and geosmin, respectively) is below detection limits attainable by most commercial labs. As such, the developed passive sampling method also demonstrates the ability to concentrate and detect geosmin and 2-MIB in source waters when conventional grab samples result in concentrations below the detection limits of these laboratories.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

Taste and odour impedes drinking water quality especially from a consumer standpoint. It is thus important to monitor T&O compounds to ensure concentrations remain below human threshold limits. Among these compounds are geosmin and 2-MIB, notoriously known for their earthy taste and smell in water. Rise in geosmin and 2-MIB events has led to more frequent monitoring of these compounds. However, the current sampling techniques are labour intensive and costly. Moreover, the need for more representative samples is highlighted by the limitations of conventional grab sampling methods. Alternative sampling approaches such as passive sampling have been employed in the detection of analytes from various matrixes. In this work, a novel passive sampling approach for the detection of geosmin and 2-MIB in source water was developed, validated and applied in a field study (along with paired grab samples) at six lakes in Atlantic Canada.

Results from bench-scale method validation experiments and a proof-of-concept field study show that this passive sampling approach was successful at detecting both target compounds at environmentally relevant concentrations. The method also allowed for the detection of 2-MIB at concentrations that were below the detection limit of the conventional sampling method. Future research to investigate the adsorption kinetics of the passive sampling materials as well as improvements to the methods recovery efficiency for both compounds is recommended. As such, factors to consider based on observations made in this study include the analyte enrichment factor, type of adsorbent packaging, the design of the passive sampling device, and the analyte extraction mode which are further elucidated below.

Assessment of Analyte Enrichment Factor

In bench scale experiments, the optimal mass-to-elution volume ratio for the elution of target analyte from C18 resulted in a 22.2-fold concentration of the target analytes. To ensure analyte recovery, the method was developed using high analyte spike concentrations. However, from validation study, it was observed that recovery efficiencies for both geosmin and 2-MIB may be improved at low concentrations. Following adsorption studies at concentrations near the 0.045 $\mu g\ L^{-1}$ spike level, optimization experiments to access

different elution volumes may allow for an improved enrichment factor while reducing the volume of elution solvent required.

Assessing Adsorbent Packaging Type

For this work, C18 bulk sorbent was utilized and due to the nature of this packaging type, the optimized C18 mass was measured into a nylon mesh bag for deployment in the passing sampling case. Although analyte recovery analysis from bench scale experiments showed satisfactory performance using this adsorbent preparation technique. During retrieval of field deployed passive samplers, we observed that the surfaces of some nylon mesh bags used to hold the C18 were particulate-laden, while the surface of the C18 itself was visibly clear. Assessing other packaging types that allow the direct elution of analyte from the C18 (i.e. no contact with the external holding material) may improve recovery and assay selectivity while allowing for high-throughput analysis. An alternative C18 packaging that may reduce solid retention on adsorbent material are the C18 disks, this sorbent form may not require the use of the nylon mesh bag and could be positioned in the CATSCa using a perforated solid membrane.

Assessing Passive Sampler Design

The design of the passive sampling device may also be impacting analyte recovery in the field. The passive sampler (CATSCa) used in this study allows a non-restrictive flow of water through the adsorbent material. While this passive sampling device has been successful in wastewater monitoring (Hayes et al., 2021) and has demonstrated potential in this field study, frontiers for improvements in source water monitoring may be explored. Some passive samplers used to monitor volatile organic compounds (VOC) in air have been configured either by its morphology or the introduction of a diffusive barrier to control the rate of VOC collection by the adsorbent media (Grosse & McKernan, 2014). This helps in reporting concentrations by

volume of air sampled. Although both matrices are different, the principle of the technology is the same. As such, lessons can be applied for an optimized water quality monitoring of target analytes.

Assessing Analyte Extraction Mode

Experiments to access different extraction modes in the elution of geosmin and 2-MIB from C18 might provide insight for improved analyte recovery. In this work, elution of analyte was done using static extraction mode, where the adsorbent is exposed to a fixed volume of the elution solvent over a predetermined time period. Another extraction mode to consider in the elution of target analytes is dynamic extraction where determined elution solvent volumes flow through the sample allowing the target analytes to come in contact with fresh solvent continuously (Luque-García, 2005). However, if the dynamic extraction mode is to be applied, the adsorbent form or the morphology of the adsorbent casing must be considered as sorbent are often placed in tube like materials during extractions.

In conclusion, passive sampling provided an easier, cost effective, fast and robust method for sample processing. It also allowed for high sample throughput analysis. During this summer monitoring program, grab sampling was halted temporarily on two occasions due to broken parts of the SPE device. Whereas the passive samplers were shown to be more robust as they are simple devices with no power requirements. Also, materials for passive sampling were easy to prepare, deploy and retrieve from the field. Retrieved samplers required approximately 2 hrs for the preparation of each sample batch ($\approx$ 20 samples). This allowed for fast turnaround times compared to the grab sampling method were an equal amount of processing time ($\approx$ 2 hrs) was required per sample. This study also contributes to the limited research on the passive sampling of these volatile organic compounds (geosmin and 2-MIB).

REFERENCES

Abdel Salam, M. (2007). *Chemical modification of multi-walled carbon nanotubes and their potential applications as new adsorbents for solid phase extraction from aqueous solutions* [Carleton University]. https://curve.carleton.ca/24af5b00-85fd-45e8-bb12-97eea390dcf2

ACS Reagent Chemicals. (2017). Chromatography. In *ACS Reagent Chemicals* (Vol. 1–0). American Chemical Society. https://doi.org/10.1021/acsreagents.2007

Agilent. (2022). *Solid Phase Extraction (SPE) | Cartridges, Well Plate, Sorbents | Agilent*. https://www.agilent.com/en/product/sample-preparation/solid-phase-extraction-spe

Ahkola, H., Herve, S., & Knuutinen, J. (2012). Overview of passive Chemcatcher sampling with SPE pretreatment suitable for the analysis of NPEOs and NPs. *Environmental Science and Pollution Research International*, *20*. https://doi.org/10.1007/s11356-012-1153-0

Alvarez, D. A., Petty, J. D., Huckins, J. N., Jones-Lepp, T. L., Getting, D. T., Goddard, J. P., & Manahan, S. E. (2004). Development of a passive, in situ, integrative sampler for hydrophilic organic contaminants in aquatic environments. *Environmental Toxicology and Chemistry*, *23*(7), 1640–1648. https://doi.org/10.1897/03-603

Alvarez, D. A., Petty, J. D., Huckins, J. N., Jones-Lepp, T. L., Getting, D. T., Goddard, J. P., & Manahan, S. E. (2004b). Development of a passive, in situ, integrative sampler for hydrophilic organic contaminants in aquatic environments. *Environmental Toxicology and Chemistry*, *23*(7), 1640–1648. https://doi.org/10.1897/03-603

American Public Health Association. (2005). American Water Works Association and Water Environmental Federation. *Standard Method for Examination of Water and Wastewater.*

American Society for Testing and Materials. (2014). *Standard Guide for Selection of Passive Techniques for Sampling Groundwater Monitoring Wells (ASTM Standard No. D7929-14)*. https://www.astm.org/d7929-14.html

Analytical Sciences Digital Library. (2019, June 10). *Solid-Phase Extraction*. Chemistry LibreTexts. https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_(Analytical_Chemistry)/Analytical_Sciences_Digital_Library/Active_Learning/Contextual_Modules/Sample_Preparation/03_Solid-Phase_Extraction

Anderson, L. E., Krkošek, W. H., Stoddart, A. K., Trueman, B. F., & Gagnon, G. A. (2017). Lake Recovery Through Reduced Sulfate Deposition: A New Paradigm for Drinking Water Treatment. *Environmental Science & Technology*, *51*(3), 1414–1422. https://doi.org/10.1021/acs.est.6b04889

Auersperger, P., Koroša, A., Mali, N., & Jamnik, B. (2022). Passive Sampling with Active Carbon Fibres in the Determination of Organic Pollutants in Groundwater. *Water*, *14*(4), Article 4. https://doi.org/10.3390/w14040585

Azaria, S., & van Rijn, J. (2018). Off-flavor compounds in recirculating aquaculture systems (RAS): Production and removal processes. *Aquacultural Engineering*, *83*, 57–64. https://doi.org/10.1016/j.aquaeng.2018.09.004

Barroso, M., Moreno, I., da Fonseca, B., Queiroz, J. A., & Gallardo, E. (2012). Role of microextraction sampling procedures in forensic toxicology. *Bioanalysis*, *4*(14), 1805–1826. https://doi.org/10.4155/bio.12.139

Berrueta, L. A., Gallo, B., & Vicente, F. (1995). A review of solid phase extraction: Basic principles and new developments. *Chromatographia*, *40*(7), 474–483. https://doi.org/10.1007/BF02269916

Bienvenu, J.-F., Provencher, G., Bélanger, P., Bérubé, R., Dumas, P., Gagné, S., Gaudreau, É., & Fleury, N. (2017). Standardized Procedure for the Simultaneous Determination of the Matrix Effect, Recovery, Process Efficiency, and Internal Standard Association. *Analytical Chemistry*, *89*(14), 7560–7568. https://doi.org/10.1021/acs.analchem.7b01383

Bristow, R. L., Young, I. S., Pemberton, A., Williams, J., & Maher, S. (2019). An extensive review of the extraction techniques and detection methods for the taste and odour compound geosmin (trans-1, 10-dimethyl-trans-9-decalol) in water. *TrAC Trends in Analytical Chemistry*, *110*, 233–248. https://doi.org/10.1016/j.trac.2018.10.032

Brophy, M. (2019). *Understanding Water Quality and the Presence of Microcystin-Lr in a Small Drinking Water Supply*. https://DalSpace.library.dal.ca//handle/10222/76669

Burgess, R. M. (2012). Guidelines for Using Passive Samplers to Monitor Organic Contaminants at Superfund Sediment Sites. *Environmental Protection*, 32.

Camara, M., Gharbi, N., Lenouvel, A., Behr, M., Guignard, C., Orlewski, P., & Evers, D. (2013). Detection and Quantification of Natural Contaminants of Wine by Gas Chromatography–Differential Ion Mobility Spectrometry (GC-DMS). *Journal of Agricultural and Food Chemistry*, *61*(5), 1036–1043. https://doi.org/10.1021/jf303418q

Camino-Sánchez, F. J., Rodríguez-Gómez, R., Zafra-Gómez, A., Santos-Fandila, A., & Vílchez, J. L. (2014). Stir bar sorptive extraction: Recent applications, limitations and future trends. *Talanta*, *130*, 388–399. https://doi.org/10.1016/j.talanta.2014.07.022

Chapra, S. C., Boehlert, B., Fant, C., Bierman, V. J., Henderson, J., Mills, D., Mas, D. M. L., Rennels, L., Jantarasami, L., Martinich, J., Strzepek, K. M., & Paerl, H. W. (2017). Climate Change Impacts on Harmful Algal Blooms in U.S. Freshwaters: A Screening-Level Assessment. *Environmental Science & Technology*, *51*(16), 8933–8943. https://doi.org/10.1021/acs.est.7b01498

Chemcatcher. (2022). *Chemcatcher—Passive Water Quality Sampler for Micropollutants*. https://chemcatcher.ie/

Choi, C. K., & Dong, M. W. (2005). 5—Sample Preparation for HPLC Analysis of Drug Products. In S. Ahuja & M. W. Dong (Eds.), *Separation Science and Technology* (Vol. 6, pp. 123–144). Academic Press. https://doi.org/10.1016/S0149-6395(05)80049-2

Chung, S. Y. (1992). Attempts to Improve the Sensitivity of an Enzyme-Linked Immunosorbent Assay for 2-Methylisoborneol. *Water Science and Technology*, *25*(2), 89–95. https://doi.org/10.2166/wst.1992.0039

Chung, S. Y., Vercellotti, J. R., Johnsen, P. B., & Klesius, P. H. (2002, May 1). *Development of an enzyme-linked immunosorbent assay for geosmin* (world). ACS Publications; American Chemical Society. https://doi.org/10.1021/jf00004a030

Churro, C., Semedo-Aguiar, A. P., Silva, A. D., Pereira-Leal, J. B., & Leite, R. B. (2020). A novel cyanobacterial geosmin producer, revising GeoA distribution and dispersion patterns in Bacteria. *Scientific Reports*, *10*(1), Article 1. https://doi.org/10.1038/s41598-020-64774-y

Contarini, G., Povolo, M., Leardi, R., & Toppino, P. M. (1997). Influence of Heat Treatment on the Volatile Compounds of Milk. *Journal of Agricultural and Food Chemistry*, *45*(8), 3171–3177. https://doi.org/10.1021/jf960849s

DeMont, I., Stoddart, A. K., & Gagnon, G. A. (2021). Assessing strategies to improve the efficacy and efficiency of direct filtration plants facing changes in source water quality from anthropogenic and climatic pressures. *Journal of Water Process Engineering*, *39*, 101689. https://doi.org/10.1016/j.jwpe.2020.101689

Deng, X., Xie, P., Qi, M., Liang, G., Chen, J., Ma, Z., & Jiang, Y. (2012). Microwave-assisted purge-and-trap extraction device coupled with gas chromatography and mass spectrometry for the determination of five predominant odors in sediment, fish tissues, and algal cells. *Journal of Chromatography A*, *1219*, 75–82. https://doi.org/10.1016/j.chroma.2011.11.031

Devi, A., Chiu, Y.-T., Hsueh, H.-T., & Lin, T.-F. (2021). Quantitative PCR based detection system for cyanobacterial geosmin/2-methylisoborneol (2-MIB) events in drinking water sources: Current status and challenges. *Water Research*, *188*, 116478. https://doi.org/10.1016/j.watres.2020.116478

Dupont, D. P. (2005). Tapping into Consumers' Perceptions of Drinking Water Quality in Canada: Capturing Customer Demand to Assist in Better Management of Water Resources. *Canadian Water Resources Journal / Revue Canadienne Des Ressources Hydriques*, *30*(1), 11–20. https://doi.org/10.4296/cwrj300111

Dzialowski, A. R., Smith, V. H., Huggins, D. G., Denoyelles, F., Lim, N.-C., Baker, D. S., & Beury, J. H. (2009). Development of predictive models for geosmin-related taste and odor in Kansas, USA, drinking water reservoirs. *Water Research*, *43*(11), 2829–2840. https://doi.org/10.1016/j.watres.2009.04.001

Elliot Wright, Heather Daurie, & Graham A. Gagnon. (2014). *Full article: Development and validation of an SPE-GC-MS/MS taste and odour method for analysis in surface water*. https://www.tandfonline.com/doi/full/10.1080/03067319.2014.974586

Environmental Protection Act. (2021). *Protocol for analytical methods used in the assessment of properties under Part XV.1 of the Environmental Protection Act and excess soil quality (Ontario Regulation 153/04)*. Ontario.Ca. http://www.ontario.ca/page/updated-protocol-analytical-methods-used-assessment-properties-under-part-xv1-environmental

Falaki, F. (2019). Sample Preparation Techniques for Gas Chromatography. In *Gas Chromatography—Derivatization, Sample Preparation, Application*. IntechOpen. https://doi.org/10.5772/intechopen.84259

Fernandez, L. A., MacFarlane, J. K., Tcaciuc, A. P., & Gschwend, P. M. (2009). Measurement of Freely Dissolved PAH Concentrations in Sediment Beds Using Passive Sampling with Low-Density Polyethylene Strips. *Environmental Science & Technology*, *43*(5), 1430–1436. https://doi.org/10.1021/es802288w

Gerber, N. N., & Lechevalier, H. A. (1965). Geosmin, an Earthy-Smelling Substance Isolated from Actinomycetes. *Applied Microbiology*, *13*(6), 935. https://doi.org/10.1128/am.13.6.935-938.1965

Giglio, S., Chou, W. K. W., Ikeda, H., Cane, D. E., & Monis, P. T. (2011). Biosynthesis of 2-methylisoborneol in cyanobacteria. *Environmental Science & Technology*, *45*(3), 992–998. https://doi.org/10.1021/es102992p

Godlewska, K., Stepnowski, P., & Paszkiewicz, M. (2021). Pollutant analysis using passive samplers: Principles, sorbents, calibration and applications. A review. *Environmental Chemistry Letters*, *19*(1), 465–520. https://doi.org/10.1007/s10311-020-01079-6

Gomes, L. G. B. (2018). *Determination of partition coefficients between passive samplers and the aquatic environment for trace levels of organic pollutants*. https://repositorio.ul.pt/handle/10451/35568

Górecki, T., & Namieśnik, J. (2002). Passive sampling. *TrAC Trends in Analytical Chemistry*, *21*(4), 276–291. https://doi.org/10.1016/S0165-9936(02)00407-7

Gourlay, C., Miège, C., Noir, A., Ravelet, C., Garric, J., & Mouchel, J.-M. (2005). How accurately do semi-permeable membrane devices measure the bioavailability of polycyclic aromatic hydrocarbons to Daphnia magna? *Chemosphere*, *61*(11), 1734–1739. https://doi.org/10.1016/j.chemosphere.2005.04.039

Greenwood, R., Mills, G., & Vrana, B. (2007). *Passive Sampling Techniques in Environmental Monitoring*. Elsevier.

Grosse, D., & McKernan, J. (2014). *Passive Samplers for Investigations of Air Quality: Method Description, Implementation, and Comparison to Alternative Sampling Methods*. Https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NRMRL&direntryid=308311&simplesearch=1&searchall=etsc

Harman, C., Allan, I. J., & Vermeirssen, E. L. M. (2012). Calibration and use of the polar organic chemical integrative sampler—A critical review. *Environmental Toxicology and Chemistry*, *31*(12), 2724–2738. https://doi.org/10.1002/etc.2011

Harte, P., Brayton, M., & Ives, W. (2014). *Use of passive diffusion samplers for monitoring volatile organic compounds in ground water*. https://pubs.usgs.gov/fs/fs-088-00/

Hayes, E. K., Sweeney, C. L., Anderson, L. E., Li, B., Erjavec, G. B., Gouthro, M. T., Krkošek, W. H., Stoddart, A. K., & Gagnon, G. A. (2021). *A Novel Passive Sampling Approach For Sars-Cov-2 In Wastewater in a Canadian Province with Low Prevalence Of Covid-19*. Https://Doi.Org/10.1039/D1ew00207d

Health Canada. (2005, May 19). *Guidelines for Canadian Drinking Water Quality: Guideline Technical Document – Taste*. https://www.canada.ca/en/health-canada/services/publications/healthy-living/guidelines-canadian-drinking-water-quality-guideline-technical-document-taste.html

Hensarling, T. P., & Waage, S. K. (2002, May 1). *A bromine-based color reaction for the detection of geosmin* (world). ACS Publications; American Chemical Society. https://doi.org/10.1021/jf00095a017

Hoffmann, E. de, & Stroobant, V. (2007). *Mass Spectrometry: Principles and Applications*. John Wiley & Sons.

Ibrahim, I., Togola, A., & Gonzalez, C. (2013). Polar organic chemical integrative sampler (POCIS) uptake rates for 17 polar pesticides and degradation products: Laboratory calibration. *Environmental Science and Pollution Research*, *20*(6), 3679–3687. https://doi.org/10.1007/s11356-012-1284-3

Ikai, Y., Honda, S., Yamada, N., Onuma, S., Tomita, B., Kawamura, N., & Miyazaki, Y. (2003). Determination of Geosmin and 2-Methylisoborneol in Water using Solid Phase Extraction and Headspace-GC/MS. *Journal of the Mass Spectrometry Society of Japan*, *51*(1), 174–178. https://doi.org/10.5702/massspec.51.174

Imbrigiotta, T. E., & Harte, P. T. (2020). Passive sampling of groundwater wells for determination of water chemistry. In *Techniques and Methods* (No. 1-D8). U.S. Geological Survey. https://doi.org/10.3133/tm1D8

International Organization for Standardization. (2011). *Water quality—Sampling: Guidance on passive sampling in surface waters (1SO Standard No. 5667-23:2011)*. https://www.iso.org/cms/render/live/en/sites/isoorg/contents/data/standard/05/06/50679.html

Journey, C. A., Beaulieu, K. M., & Bradley, P. M. (2013). Environmental Factors that Influence Cyanobacteria and Geosmin Occurrence in Reservoirs. In *Current Perspectives in Contaminant Hydrology and Water Resources Sustainability*. IntechOpen. https://doi.org/10.5772/54807

Jüttner, F., & Watson, S. B. (2007). Biochemical and Ecological Control of Geosmin and 2-Methylisoborneol in Source Waters. *Applied and Environmental Microbiology*. https://doi.org/10.1128/AEM.02250-06

Kamata, M., Matsui, Y., & Asami, M. (2020). National trends in pesticides in drinking water and water sources in Japan. *Science of The Total Environment*, *744*, 140930. https://doi.org/10.1016/j.scitotenv.2020.140930

Kaserzon, S. L., Hawker, D. W., Kennedy, K., Bartkow, M., Carter, S., Booij, K., & Mueller, J. F. (2014). Characterisation and comparison of the uptake of ionizable and polar pesticides, pharmaceuticals and personal care products by POCIS and Chemcatchers. *Environmental Science: Processes & Impacts*, *16*(11), 2517–2526. https://doi.org/10.1039/C4EM00392F

Kataoka, H. (2017). Chapter 1—Sample preparation for liquid chromatography. In S. Fanali, P. R. Haddad, C. F. Poole, & M.-L. Riekkola (Eds.), *Liquid Chromatography (Second Edition)* (pp. 1–37). Elsevier. https://doi.org/10.1016/B978-0-12-805392-8.00001-3

Kaur, G., & Sharma, S. (2018). *Gas Chromatography -A Brief Review*. https://www.researchgate.net/publication/344042922_Gas_Chromatography_-A_Brief_Review

Keçili, R., Büyüktiryaki, S., Dolak, İ., & Hussain, C. M. (2020). 5—The use of magnetic nanoparticles in sample preparation devices and tools. In C. Mustansar Hussain (Ed.), *Handbook of Nanomaterials in Analytical Chemistry* (pp. 75–95). Elsevier. https://doi.org/10.1016/B978-0-12-816699-4.00005-0

Kim, K. T., & Park, Y.-G. (2021). Geosmin and 2-MIB Removal by Full-Scale Drinking Water Treatment Processes in the Republic of Korea. *Water*, *13*(5), Article 5. https://doi.org/10.3390/w13050628

Kingston, J. K., Greenwood, R., Mills, G. A., Morrison, G. M., & Persson, L. B. (2000). Development of a novel passive sampling systemfor the time-averaged measurement of a range of organic pollutants inaquatic environments. *Journal of Environmental Monitoring*, *2*(5), 487–495. https://doi.org/10.1039/B003532G

Kolb, B., & Ettre, L. S. (2006). *Static Headspace–Gas Chromatography: Theory and Practice* (1st ed.). Wiley. https://doi.org/10.1002/0471914584

Komatsu, M., Tsuda, M., Ōmura, S., Oikawa, H., & Ikeda, H. (2008). Identification and functional analysis of genes controlling biosynthesis of 2-methylisoborneol. *Proceedings of the National Academy of Sciences*, *105*(21), 7422–7427. https://doi.org/10.1073/pnas.0802312105

Kultschar, B., & Llewellyn, C. (2018). Secondary Metabolites in Cyanobacteria. In *Secondary Metabolites—Sources and Applications*. IntechOpen. https://doi.org/10.5772/intechopen.75648

Liu, J.-F., Tao, Y., Sun, J., & Jiang, G.-B. (2011). Development of polypropylene glycol coated hollow fiber membranes as passive sampler for field equilibrium sampling of odorous compounds in environmental waters. *Analytical Methods*, *3*(3), 696–702. https://doi.org/10.1039/C0AY00670J

Lloyd, S. W., Lea, J. M., Zimba, P. V., & Grimm, C. C. (1998). Rapid analysis of geosmin and 2-methylisoborneol in water using solid phase micro extraction procedures. *Water Research*, *32*(7), 2140–2146. https://doi.org/10.1016/S0043-1354(97)00444-2

Lu, J., Wills, P. S., & Chris Wilson, P. (2016). Trace analysis of off-flavor/odor compounds in water using liquid-liquid microextraction coupled with gas chromatography—Positive chemical ionization-tandem mass spectrometry. *Frontiers of Environmental Science & Engineering*, *10*(3), 477–481. https://doi.org/10.1007/s11783-015-0820-z

Luque-García, J. L. (2005). Extraction | Pressurized Fluid Extraction. In P. Worsfold, A. Townshend, & C. Poole (Eds.), *Encyclopedia of Analytical Science (Second Edition)* (pp. 591–597). Elsevier. https://doi.org/10.1016/B0-12-369397-7/00692-0

Madrid, Y., & Zayas, Z. P. (2007). Water sampling: Traditional methods and new approaches in water sampling strategy. *TrAC Trends in Analytical Chemistry*, *26*(4), 293–299. https://doi.org/10.1016/j.trac.2007.01.002

Marsili, R. (2000). Solid-Phase Microextraction | Food Technology Applications. In I. D. Wilson (Ed.), *Encyclopedia of Separation Science* (pp. 4178–4190). Academic Press. https://doi.org/10.1016/B0-12-226770-2/06791-0

Matrajt, G., Naughton, B., Bandyopadhyay, A. S., & Meschke, J. S. (2018). A Review of the Most Commonly Used Methods for Sample Collection in Environmental Surveillance of Poliovirus. *Clinical Infectious Diseases*, *67*(suppl_1), S90–S97. https://doi.org/10.1093/cid/ciy638

Mazzella, N., Lissalde, S., Moreira, S., Delmas, F., Mazellier, P., & Huckins, J. N. (2010). Evaluation of the Use of Performance Reference Compounds in an Oasis-HLB Adsorbent Based Passive Sampler for Improving Water Concentration Estimates of Polar Herbicides in Freshwater. *Environmental Science & Technology*, *44*(5), 1713–1719. https://doi.org/10.1021/es902256m

Migliorini, F. L., Teodoro, K. B. R., dos Santos, D. M., Fonseca, F. J., Mattoso, L. H. C., & Correa, D. S. (2020). Electrospun nanofibers versus drop casting films for designing an electronic tongue: Comparison of performance for monitoring geosmin and 2-methylisoborneol in water samples. *Polymers for Advanced Technologies*, *31*(9), 2075–2082. https://doi.org/10.1002/pat.4930

Mullineaux, C. W., & Wilde, A. (2021). The social life of cyanobacteria. *ELife*, *10*, e70327. https://doi.org/10.7554/eLife.70327

Mustapha, S., Tijani, J. O., Ndamitso, M., Abdulkareem, A. S., Shuaib, D. T., & Mohammed, A. K. (2021). A critical review on geosmin and 2-methylisoborneol in water: Sources, effects, detection, and removal techniques. *Environmental Monitoring and Assessment*, *193*(4), 204. https://doi.org/10.1007/s10661-021-08980-9

Nakamura, S., & Daishima, S. (2005). Simultaneous determination of 22 volatile organic compounds, methyl-tert-butyl ether, 1,4-dioxane, 2-methylisoborneol and geosmin in water by headspace solid phase microextraction-gas chromatography–mass spectrometry. *Analytica Chimica Acta*, *548*(1), 79–85. https://doi.org/10.1016/j.aca.2005.05.077

Ochiai, N., Sasamoto, K., Takino, M., Yamashita, S., Daishima, S., Heiden, A., & Hoffman, A. (2001). Determination of trace amounts of off-flavor compounds in drinking water by stir bar sorptive extraction and thermal desorption GC-MS. *Analyst*, *126*(10), 1652–1657. https://doi.org/10.1039/B102962M

Oh, H.-S., Lee, C. S., Srivastava, A., & Ahn, H.-M. O. and C.-Y. (2017). *Effects of Environmental Factors on Cyanobacterial Production of Odorous Compounds: Geosmin and 2-Methylisoborneol*. *27*(7), 1316–1323. https://doi.org/10.4014/jmb.1702.02069

Olsen, B. K., Chislock, M. F., & Wilson, A. E. (2016). Eutrophication mediates a common off-flavor compound, 2-methylisoborneol, in a drinking water reservoir. *Water Research*, *92*, 228–234. https://doi.org/10.1016/j.watres.2016.01.058

Paerl, H. W., & Huisman, J. (2009). Climate change: A catalyst for global expansion of harmful cyanobacterial blooms. *Environmental Microbiology Reports*, *1*(1), 27–37. https://doi.org/10.1111/j.1758-2229.2008.00004.x

Palmentier, J.-P. F. P., Taguchi, V. Y., Jenkins, S. W. D., Wang, D. T., Ngo, K.-P., & Robinson, D. (1998). The determination of geosmin and 2-methylisoborneol in water using isotope dilution high resolution mass spectrometry. *Water Research*, *32*(2), 287–294. https://doi.org/10.1016/S0043-1354(97)00280-7

Perkins, R. G., Slavin, E. I., Andrade, T. M. C., Blenkinsopp, C., Pearson, P., Froggatt, T., Godwin, G., Parslow, J., Hurley, S., Luckwell, R., & Wain, D. J. (2019). Managing taste and odour metabolite production in drinking water reservoirs: The importance of ammonium as a key nutrient trigger. *Journal of Environmental Management*, *244*, 276–284. https://doi.org/10.1016/j.jenvman.2019.04.123

Pham, T. T., Nguyen, V.-A., & Van der Bruggen, B. (2013). Pilot-Scale Evaluation of GAC Adsorption Using Low-Cost, High-Performance Materials for Removal of Pesticides and Organic Matter in Drinking Water Production. *Journal of Environmental Engineering*, *139*, 958–965. https://doi.org/10.1061/(ASCE)EE.1943-7870.0000704

Pochiraju, S., Hoppe-Jones, C., Adams, C., & Weinrich, L. (2021). Development and optimization of analytical methods for the detection of 18 taste and odor compounds in drinking water utilities. *Water Research X*, *11*, 100099. https://doi.org/10.1016/j.wroa.2021.100099

Rawa-Adkonis, M., Wolska, L., Przyjazny, A., & Namieśnik, J. (2006). Sources of Errors Associated with the Determination of PAH and PCB Analytes in Water Samples. *Analytical Letters*, *39*(11), 2317–2331. https://doi.org/10.1080/00032710600755793

Reber, E. A. (2014). Gas Chromatography-Mass Spectrometry (GC-MS): Applications in Archaeology. In C. Smith (Ed.), *Encyclopedia of Global Archaeology* (pp. 2953–2959). Springer. https://doi.org/10.1007/978-1-4419-0465-2_340

Restek, A. (2000). Technical guide for static headspace analysis using GC. *Restek Corp*, 11–12.

Rimayi, C., Chimuka, L., Gravell, A., Fones, G. R., & Mills, G. A. (2019). Use of the Chemcatcher® passive sampler and time-of-flight mass spectrometry to screen for emerging pollutants in rivers in Gauteng Province of South Africa. *Environmental Monitoring and Assessment*, *191*(6), 388. https://doi.org/10.1007/s10661-019-7515-z

Rivera, A. (2018). *Transboundary groundwater issues within Canada and between Canada and the U.S.*

Rockwood, A. L., Kushnir, M. M., & Clarke, N. J. (2018). 2—Mass Spectrometry. In N. Rifai, A. R. Horvath, & C. T. Wittwer (Eds.), *Principles and Applications of Clinical Mass Spectrometry* (pp. 33–65). Elsevier. https://doi.org/10.1016/B978-0-12-816063-3.00002-5

Schang, C., Crosbie, N. D., Nolan, M., Poon, R., Wang, M., Jex, A., John, N., Baker, L., Scales, P., Schmidt, J., Thorley, B. R., Hill, K., Zamyadi, A., Tseng, C.-W., Henry, R., Kolotelo, P., Langeveld, J., Schilperoort, R., Shi, B., … McCarthy, D. T. (2021). Passive Sampling of SARS-CoV-2 for Wastewater Surveillance. *Environmental Science & Technology*, *55*(15), 10432–10441. https://doi.org/10.1021/acs.est.1c01530

Serracin-Pitti, E. (2017). *The Effects of Pre-Ozonation on Geosmin and Natural Organic Matter Removal*. Https://www.semanticscholar.org/paper/the-effects-of-pre-ozonation-on-geosmin-and-natural-serracin-pitti/23acb17812a499fae921d0b49798e1fc06c1cee1

Shaw, M., Eaglesham, G., & Mueller, J. F. (2009). Uptake and release of polar compounds in SDB-RPS Empore™ disks; implications for their use as passive samplers. *Chemosphere*, *75*(1), 1–7. https://doi.org/10.1016/j.chemosphere.2008.11.072

Shin, H.-S., & Ahn, H.-S. (2004). Simple, Rapid, and Sensitive Determination of Odorous Compounds in Water by GC–MS. *Chromatographia*, *59*(1), 107–113. https://doi.org/10.1365/s10337-003-0125-4

Shugen Pan. (2002). *Sources and control of geosmin and MIB in midwestern water supply reservoirs* [Ph.D., University of Kansas]. https://www.proquest.com/docview/276285567/abstract/5F33390617CF4007PQ/1

Son, M., Cho, D., Lim, J. H., Park, J., Hong, S., Ko, H. J., & Park, T. H. (2015). Real-time monitoring of geosmin and 2-methylisoborneol, representative odor compounds in water pollution using bioelectronic nose with human-like performance. *Biosensors and Bioelectronics*, *74*, 199–206. https://doi.org/10.1016/j.bios.2015.06.053

Son, M., & Park, T. H. (2018). The bioelectronic nose and tongue using olfactory and taste receptors: Analytical tools for food quality and safety assessment. *Biotechnology Advances*, *36*(2), 371–379. https://doi.org/10.1016/j.biotechadv.2017.12.017

Soria, A. C., García-Sarrió, M. J., & Sanz, M. L. (2015). Volatile sampling by headspace techniques. *TrAC Trends in Analytical Chemistry*, *71*, 85–99. https://doi.org/10.1016/j.trac.2015.04.015

Soulier, C., Coureau, C., & Togola, A. (2016). Environmental forensics in groundwater coupling passive sampling and high resolution mass spectrometry for screening. *Science of The Total Environment*, *563–564*, 845–854. https://doi.org/10.1016/j.scitotenv.2016.01.056

Spencer, C., Zhang, W., & Ouyang, Z. (2021). *Mass Spectrometry and Applications—ClinicalKey*. https://www-clinicalkey-com.ezproxy.library.dal.ca/#!/content/book/3-s2.0-B9780323673204000055

Su, M., Gaget, V., Giglio, S., Burch, M., An, W., & Yang, M. (2013). Establishment of quantitative PCR methods for the quantification of geosmin-producing potential and Anabaena sp. In freshwater systems. *Water Research*, *47*(10), 3444–3454. https://doi.org/10.1016/j.watres.2013.03.043

Sweeney, C. L., Bennett, J. L., Brown, C. A. M., Ross, N. W., & Gagnon, G. A. (2021). Validation of a QuEChERS method for extraction of estrogens from a complex water matrix and quantitation via high-performance liquid chromatography-mass spectrometry. *Chemosphere*, *263*, 128315. https://doi.org/10.1016/j.chemosphere.2020.128315

Tadesse, D. (2021). *Application of Passive Sampling in The State and Regional Water Boards for Water Quality Monitoring Programs*. 39.

Tian, L., Han, F., Fodjo, E. K., Zhai, W., Huang, X.-Y., Kong, C., Shi, Y.-F., & Cai, Y.-Q. (2021). An Effective and Efficient Sample Preparation Method for 2-Methyl-Isoborneol and Geosmin in Fish and Their Analysis by Gas Chromatography-Mass Spectrometry. *International Journal of Analytical Chemistry*, *2021*, 9980212. https://doi.org/10.1155/2021/9980212

Ueta, I., Komatsu, T., Fujimura, K., & Saito, Y. (2022). Porous Membrane-Assisted Purge and Trap Sampling for Determination of VOCs in Gas Chromatography with Needle-Type Extraction Device. *Chromatographia*, *85*(1), 7–12. https://doi.org/10.1007/s10337-021-04103-1

US EPA. (1999). *Protocol for EPA approval of new methods for organic and inorganic analytes in wastewater and drinking water*.

U.S. EPA. (2012). *Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Procedures for the Determination of the Freely Dissolved Interstitial Water Concentrations of Nonionic Organics*. Https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NHEERL&direntryid=237621

US EPA. (2016). Definition and procedure for the determination of the method detection limit, Revision 2. *Environmental Protection Agency EPA*. https://www.epa.gov/sites/default/files/2016-12/documents/mdl-procedure_rev2_12-13-2016.pdf

US National Library of Medicine. (2017). *Ethyl Acetate*. https://webwiser.nlm.nih.gov/substance?substanceId=446&identifier=Ethyl%20Acetate&identifierType=name&menuItemId=70&catId=86

Vermeirssen, E. L. M., Bramaz, N., Hollender, J., Singer, H., & Escher, B. I. (2009). Passive sampling combined with ecotoxicological and chemical analysis of pharmaceuticals and biocides – evaluation of three Chemcatcher^{TM} configurations. *Water Research*, *43*(4), 903–914. https://doi.org/10.1016/j.watres.2008.11.026

Vogt, M., Turner, S., Yassaa, N., Steinke, M., Williams, J., & Liss, P. (2008). Laboratory inter-comparison of dissolved dimethyl sulphide (DMS) measurements using purge-and-trap and solid-phase microextraction techniques during a mesocosm experiment. *Marine Chemistry*, *108*(1), 32–39. https://doi.org/10.1016/j.marchem.2007.10.001

Vrana, B., Allan, I. J., Greenwood, R., Mills, G. A., Dominiak, E., Svensson, K., Knutsson, J., & Morrison, G. (2005). Passive sampling techniques for monitoring pollutants in water. *TrAC Trends in Analytical Chemistry*, *24*(10), 845–868. https://doi.org/10.1016/j.trac.2005.06.006

Vrana, B., Mills, G. A., Dominiak, E., & Greenwood, R. (2006). Calibration of the Chemcatcher passive sampler for the monitoring of priority organic pollutants in water. *Environmental Pollution (Barking, Essex: 1987)*, *142*(2), 333–343. https://doi.org/10.1016/j.envpol.2005.10.033

Wang, C.-M., & Cane, D. E. (2008). Biochemistry and Molecular Genetics of the Biosynthesis of the Earthy Odorant Methylisoborneol in Streptomyces coelicolor. *Journal of the American Chemical Society*, *130*(28), 8908–8909. https://doi.org/10.1021/ja803639g

Wang, L., Gong, X., Wang, R., Gan, Z., Lu, Y., & Sun, H. (2017). Application of an immobilized ionic liquid for the passive sampling of perfluorinated substances in water. *Journal of Chromatography A*, *1515*, 45–53. https://doi.org/10.1016/j.chroma.2017.08.001

Watson, N. (2020). *Passive sampling and its pivotal role in greener sampling of VOCs | Markes International*. https://markes.com/content-hub/blog/passive-sampling-and-its-pivotal-role-in-greener-sampling-of-vocs

Wells, D. A. (2013). Solid-Phase Extraction with Cartridges☆. In *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*. Elsevier. https://doi.org/10.1016/B978-0-12-409547-2.04918-0

Wojnowski, W., Majchrzak, T., Dymerski, T., Gębicki, J., & Namieśnik, J. (2017). Dynamic Headspace Sampling as an Initial Step for Sample Preparation in Chromatographic Analysis. *Journal of AOAC international*, *100*(6), 1599–1606. https://doi.org/10.5740/jaoacint.17-0206

Woolway, R. I., Sharma, S., Weyhenmeyer, G. A., Debolskiy, A., Golub, M., Mercado-Bettín, D., Perroud, M., Stepanenko, V., Tan, Z., Grant, L., Ladwig, R., Mesman, J., Moore, T. N., Shatwell, T., Vanderkelen, I., Austin, J. A., DeGasperi, C. L., Dokulil, M., La Fuente, S., … Jennings, E. (2021). Phenological shifts in lake stratification under climate change. *Nature Communications*, *12*(1), 2318. https://doi.org/10.1038/s41467-021-22657-4

Wu, D., & Duirk, S. E. (2013). Quantitative analysis of earthy and musty odors in drinking water sources impacted by wastewater and algal derived contaminants. *Chemosphere*, *91*(11), 1495–1501. https://doi.org/10.1016/j.chemosphere.2012.12.024

Wurl, O. (2009). *Practical Guidelines for the Analysis of Seawater*. CRC Press.

Xu, H., Zhang, J., Wang, W., Li, Y., & Pei, H. (2022). Moderate pre-ozonation coupled with a post-peroxone process remove filamentous cyanobacteria and 2-MIB efficiently: From bench to pilot-scale study. *Journal of Hazardous Materials*, *424*, 127530. https://doi.org/10.1016/j.jhazmat.2021.127530

Xu, J., & Ouyang, G. (2019). Extraction | Solid-Phase Microextraction☆. In P. Worsfold, C. Poole, A. Townshend, & M. Miró (Eds.), *Encyclopedia of Analytical Science (Third Edition)* (pp. 100–108). Academic Press. https://doi.org/10.1016/B978-0-12-409547-2.14552-4

Yamada, Y., Cane, D. E., & Ikeda, H. (2012). Chapter Seven—Diversity and Analysis of Bacterial Terpene Synthases. In D. A. Hopwood (Ed.), *Methods in Enzymology* (Vol. 515, pp. 123–162). Academic Press. https://doi.org/10.1016/B978-0-12-394290-6.00007-0

Young, S., Park, M., & Snyder, S. (2014). GC-Q-Tof Analysis of Taste and Odor Compounds & Disinfection Byproducts in Water. https://nemc.us/docs/2014/Presentations/Mon-Academic%20Research%20Topics%20in%20Environmental%20Measurement%20and%20Monitoring%20-1.5-Young.pdf

Yu, J. W., Zhao, Y. M., Yang, M., Lin, T.-F., Guo, Z. H., Gu, J. N., Li, S., & Han, W. (2009). Occurrence of odour-causing compounds in different source waters of China. *Journal of Water Supply: Research and Technology-Aqua*, *58*(8), 587–594. https://doi.org/10.2166/aqua.2009.023

Zhang, T. (2009). Application and development of activated carbon for potable water treatment in China. *Biomass Chemical Engineering*, *43*(2), 54–59.

Zheng, N. (2020). 21—Automated and high-throughput extraction approaches. In C. F. Poole (Ed.), *Solid-Phase Extraction* (pp. 573–588). Elsevier. https://doi.org/10.1016/B978-0-12-816906-3.00021-2