ERDC /CERL MP-21-4

US Army Corps
of Engineers®
Engineer Research and
Development Center

Solid-Phase Microextraction (SPME) for Determination of Geosmin and 2-Methylisoborneol in Volatile Emissions from Soil Disturbance

Morgan W. Conrady, Markus Bauer, Kyoo D. Jo,
Donald M. Cropek, and Ryan R. Busby

October 2021

Construction Engineering
Research Laboratory

The U.S. Army Engineer Research and Development Center (ERDC) solves the nation's toughest engineering and environmental challenges. ERDC develops innovative solutions in civil and military engineering, geospatial sciences, water resources, and environmental sciences for the Army, the Department of Defense, civilian agencies, and our nation's public good. Find out more at www.erdc.usace.army.mil.

To search for other technical reports published by ERDC, visit the ERDC online library at https://erdclibrary.on.worldcat.org/discovery.

ERDC/CERL MP-21-4
October 2021

Solid-Phase Microextraction (SPME) for Determination of Geosmin and 2-Methylisoborneol in Volatile Emissions from Soil Disturbance

Morgan W. Conrady, Kyoo D. Jo, Donald M. Cropek, and Ryan R. Busby

Construction Engineering Research Laboratory
U.S. Army Engineer Research and Development Center
2902 Newmark Drive
Champaign, IL 61822

Markus Bauer

Education Center of the German Armed Forces,
Mannheim, DE

Final report

Prepared for U.S. Army Corps of Engineers
Washington, DC 20314

Under Program Element 601102, Project Number AB2, Task 4

Preface

This research was conducted for the U.S. Army Corps of Engineers under the U.S. Army Engineer Research and Development Center (ERDC) Basic Research Program, Program Element 601102, Project Number AB2, Task 4.

The work was performed by the U.S. Army Engineer Research and Development Center, Construction Engineering Research Laboratory (ERDC-CERL). At the time of publication, the Deputy Director of ERDC-CERL was Ms. Michelle Hanson and the Director was Dr. Andrew Nelson.

This article was originally published online in *Chemosphere* on 26 June 2021.

The Commander of ERDC was COL Teresa A. Schlosser and the Director was Dr. David W. Pittman.

Solid-phase microextraction (SPME) for determination of geosmin and 2-methylisoborneol in volatile emissions from soil disturbance

A B S T R A C T

A method is described here for the concentration and determination of geosmin and 2-methylisoborneol (2-MIB) from the gaseous phase, with translation to field collection and quantification from soil disturbances *in situ*. The method is based on the use of solid-phase microextraction (SPME) fibers for adsorption of volatile chemicals from the vapor phase, followed by desorption into a gas chromatograph-mass spectrometer (GC-MS) for analysis. The use of a SPME fiber allows simple introduction to the GC-MS without further sample preparation. Several fiber sorbent types were studied and the 50/30 μm DVB/CAR/PDMS was the best performer to maximize the detected peak areas of both analytes combined. Factors such as extraction temperature and time along with desorption temperature and time were explored with respect to analyte recovery. An extraction temperature of 30 °C for 10 min, with a desorption temperature of 230 °C for 4 min was best for the simultaneous analysis of both geosmin and 2-MIB without complete loss of either one. The developed method was used successfully to measure geosmin and 2-MIB emission from just above disturbed and undisturbed soils, indicating that this method detects both compounds readily from atmospheric samples. Both geosmin and 2-MIB were present as background concentrations in the open air, while disturbed soils emitted much higher concentrations of both compounds. Surprisingly, 2-MIB was always detected at higher concentrations than geosmin, indicating that a focus on its detection may be more useful for soil emission monitoring and more sensitive to low levels of soil disturbance.

1. Introduction

Geosmin and 2-methylisoborneol (2-MIB) are alcohols produced by multiple soil organisms, giving soil its characteristic "earthy" smell (chemical structures shown in Fig. S1). Dozens of cyanobacteria and actinobacteria species have been and are still being documented to produce geosmin and/or 2-MIB (Alghanmi et al., 2018; Krishnani et al., 2008), as well as multiple species of common soil fungi (Breheret et al., 1999; Schnürer et al., 1999), some plants (Freidig and Goldman, 2014; Spörle et al., 1991), and even amoebae (Hayes et al., 1991). Therefore, the likelihood of a soil containing geosmin and/or 2-MIB producers is very high.

Current research on geosmin and 2-MIB is almost exclusively focused on detection of these volatiles in drinking water and aquaculture, as they are the primary contaminant sources of off-taste and unpleasant odors in freshwater and associated food products globally (Conte et al., 1996; Hanson et al., 2003; Son et al., 2015; Watson et al., 2000; Yu et al., 2014). However, it is known that geosmin and 2-MIB are also released from disturbed soils (Metting and Metting, 1992; Watson et al., 2000) but isolation, quantification, and the relationship of volatile chemical emission with soil mechanical disturbance has never been examined *in situ*. Therefore, development of a method that enables *in situ*, rapid, simple collection of these volatile analytes, referred to as the soil volatilome, in proximity to soil disruption in the field would be invaluable. In past research, volatile emissions from intact soils were studied holistically, or in focused studies of geosmin and 2-MIB, soils were removed from natural conditions and extracted in laboratory settings that likely altered the volatilome (Buttery and Garibaldi, 1976; Fabre et al., 2002; Jüttner, 1990; Rinnan et al., 2013; Stahl and Parkin, 1994, 1996). *In situ* field investigation of volatile emissions from disturbed soils will allow a more accurate understanding of the soil volatilome and will provide important information to understand the relationships that control and regulate its composition. Geosmin and 2-MIB are expected to be major components of the soil volatilome. Almost nothing is known regarding production and volatilization of geosmin, 2-MIB and other volatiles from soils, especially *in situ*. The soil volatilome may be a rich

source of information on soil health, fertility, microbial activity, and other useful edaphic properties. Research to isolate and quantify soil volatiles would be invaluable to understand the factors that control and regulate their production, turnover, and emission from the soil into the atmosphere, such as relationships between emissions and soil biological, chemical, and physical properties and climate dynamics.

A fundamental requirement for *in situ* investigations of the soil volatilome is a highly reliable field collection mechanism at the point of generation, followed by a sensitive analytical method for the volatile compounds from collected samples. The available analytical instrumentation for measuring VOCs in air samples, usually gas chromatography (GC) combined with mass spectrometry (MS), flame ionization detector (FID) or headspace flame ionization detector (HSGC-FID), are well-served by pre-concentration to lower the detection limits. Although other analytical methods are available for measuring VOCs in air, for instance, proton transfer reaction mass spectrometry, GC-MS is more mature and far more widely used, which opens the door for broad use of our technique. Most of the pre-concentration techniques that have been developed for VOCs from air samples involve sorbents and resins fol-lowed by thermal desorption or solvent extraction (Lord et al., 2002; Oliver et al., 1996). The desorbed VOCs are then carried with an inert gas into the analytical instrument for quantification and identification. From its introduction by Pawliszyn (Arthur and Pawliszyn, 1990; Belardi and Pawliszyn, 1989), solid-phase microextraction (SPME) has grown into a well-known and trusted technique for analyte collection and concentration from air. SPME relies on the adsorption of analytes from air or water onto chemically modified silica fibers. The fibers can concentrate and retain the analytes until thermal desorption directly into the injection port of the GC. SPME fiber coatings can be chosen for sensitivity and selectivity of target analytes and can provide extremely low detection limits with the requisite resolution and identification power (Shirey, 2007). While mature SPME-GC-MS methods for deter-mination of geosmin and 2-MIB from water samples exist (Jeleń et al., 2003; Watson et al., 2000), including from headspace samples (Lloyd and Grimm, 1999), the use of SPME for field collection of the volatilome with respect to soil disturbance is unexplored.

The purpose of this paper is to explore the use of SPME for collection of geosmin and 2-MIB from air immediately above a soil disturbance and provide initial evidence for a relationship between the volatilome and the soil disturbance. This work provides proof of concept for a technique that enables *in situ* field collection and study of these compounds arising from the soil. Since we expect both geosmin and 2-MIB to be present, and perhaps the major contributors to the soil volatilome, our research attempts to find conditions that are suitable for both compounds concurrently, without the complete loss of either analyte.

2. Materials and methods

2.1. Chemicals and reagents

Geosmin (99.0%) and 2-MIB (99.3%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Standards were dissolved in hexane (99.9% purity, Fisher, Waltham, MA, USA) to prepare 1 mg L^{-1} stock solutions of both compounds. Liquid calibration standards were prepared in the range of 0.05 μg L^{-1} - 20 μg L^{-1} for each compound by diluting different amounts of the standard stock solution with hexane. The stock solution was good for six months when stored at −20 °C and the calibration standards were prepared weekly and stored in the dark at 4 °C.

2.2. Gas chromatography-mass spectrometry (GC-MS) instrumentation

The analyses were performed on an Agilent 7890B/5977A GC-MS system (Agilent Technologies, Inc., Santa Clara, CA, USA) equipped with a PAL3 RSI 85 autosampler (CTC Analytics AG, Zwingen, Switzerland). The target compounds were separated using a HP-5MS (30 m × 0.25 mm, 0.25 μm film thickness) capillary column (Agilent). The GC-MS parameters for liquid injection and SPME analyses were initially chosen based on previous studies (Jeleń et al., 2003). Helium was used as the carrier gas and was maintained at a constant flow rate of 1.2 mL min^{-1}.

2.3. Liquid injection

Liquid injection analysis was conducted to determine the detection limits of the GC-MS system for 2-MIB and geosmin and to evaluate sensitivity and recovery of the SPME-GC-MS method. The inlet temperature for direct liquid injection was 250 °C. The oven temperature program was held at 60 °C for 3 min, ramped at 15 °C min^{-1} to 180 °C and held for 1 min, and finally ramped at 30 °C min^{-1} to 250 °C. The temperature of the transfer line was 250 °C and ion source was set at 230 °C. The mass spectrometer was operated in the EI positive mode (70 eV). The solvent delay was set to 7.5 min, and the gain factor was 1.00. The mass spectrometer was operated in either the full scan acquisition (SCAN) mode from 40 to 400 amu with 4.0 scans sec^{-1} to identify the mass fragmentation pattern and the retention time of the compounds, or in the selected ion monitoring (SIM) mode for refined calibration and quantification of 2-MIB and geosmin. The selected ion mass-to-charge ratios (m/z) for 2-MIB and geosmin (±1.0) are listed in Table S1 in the Supplemental Information (Jeleń et al., 2003; Lloyd et al., 1998). After retention time determination of these compounds in SCAN mode, 9.0 min was selected as the transition point from 2-MIB ions (before 9.0 min) to geosmin ions (after 9.0 min).

The calibration of the GC-MS system for liquid injection was performed using nine different concentrations between 0.05 μg L^{-1} and 20 μg L^{-1} (equivalent to 0.1 pg–40 pg loaded onto the column) for each analyte. Each concentration was analyzed in triplicate. A volume of 2 μL was injected into the GC-MS with a 4 mm i. d. single taper inlet liner (Agilent) using the PAL3 liquid injection tool equipped with a 10 μL syringe (Agilent). Injections were carried out in splitless mode and the split valve was closed for 5 min. The ion fragments obtained from this study (2-MIB (95.0, 108.0, and 135.0 m/z) and geosmin (97.0, 112.0, and 125.0 m/z)) agree well with the values (±1.0) obtained from previous work as shown in Table S1. The method detection limit (MDL) for each compound was determined by analyzing the 0.2 μg L^{-1} concentration standard eight times and multiplying the standard deviation (SD) with the one-sided 99% t-value of the student's t-distribution with a degree of freedom of 7 (2.998). The method quantification limit (MQL) was defined as three times MDL (40 CFR 136, 1984).

2.4. SPME analysis

Four different SPME fibers: 50/30 μm DVB/Carboxen (CAR)/PDMS (Supelco, Inc. Bellefonte, PA, USA), 65 μm PDMS/DVB (Supelco), 85 μm Polyacrylate (Restek Corporation, Bellefonte, PA, USA), and 100 μm PDMS (Restek) were studied to determine geosmin and 2-MIB sorption properties based on their general ability to adsorb semi-volatile and volatile compounds according the manufacturer's fiber selection guides (Kong and Cao, 2018; Watson et al., 2000).

The PAL3 autosampler, equipped with a SPME fiber conditioning module and a sample agitation module, was used for automatic fiber conditioning. Fiber conditioning temperatures and times were chosen according to the manufacturer's instructions (Table S2). During laboratory assessment, the PAL3 was responsible for sample concentration onto the SPME fiber from the headspace of vials in the sample agitation module, as well as injection into GC-MS inlet for thermal desorption. The inlet port of the GC was equipped with a 0.75 mm i. d. inlet liner (Supelco) for SPME sample analysis and was operated in splitless mode to increase linear flow rates around the fiber.

The Total Vaporization Technique (TVT) (Rainey et al., 2014) was used to prepare vapor standards of geosmin and 2-MIB using the previously prepared liquid calibration standards. A 10 μL aliquot of a

geosmin or 2-MIB standard in hexane (0.05 μg L^{-1} to 20 μg L^{-1}) was injected through the septum of a 20 mL screw top vial (Agilent) using a 10 μL syringe (Hamilton Company, Reno, NV, USA). The small 10 μL volume was chosen to ensure fast and total vaporization of both standard and solvent within the vial, keep the resulting pressure inside the vial low, and allow determination of chemical recovery. The use of TVT was efficient because it allowed for the extraction of the target analytes straight from the vapor phase to a fiber placed in the headspace (Rainey et al., 2014). Sorption onto SPME fibers from TVT vials occurred in the sample agitation module under temperature control.

Calibration curves for each fiber were prepared by analyzing TVT vials prepared with a combined geosmin and 2-MIB gas standard at nine different concentrations between 0.25 and 10 μg m^{-3}. Common SPME extraction and desorption parameters were used for all fibers based on a previous study (Jeleń et al., 2003). Extraction of the sample vial was performed at a temperature of 30 °C for 30 min with desorption in the GC-MS injection port at 260 °C for 5 min. Injections were carried out in splitless mode and the split valve was closed for 5 min. The oven tem-perature program was held at 50 °C for 1 min, ramped at 10 °C min^{-1} to 200 °C and held for 1 min, and finally ramped at 20 °C min^{-1} to 220 °C. The MS parameters were the same as previously listed in Section 2.3 for SIM mode, except 9.5 min was chosen as the time point to switch from 2-MIB ions to geosmin ions. The selection of the best fiber was made based on a combination of GC-MS responses for both analytes in addi-tion to a prediction of expected relative importance of these analytes from field soil disruption.

2.5. SPME method optimization

SPME extraction and desorption parameters were systematically altered to determine effects on the GC-MS peak area of both geosmin and 2-MIB using only the best fiber type identified in Section 2.4. All opti-mization studies described below used a single solution that contained both geosmin (5.0 μg L^{-1}) and 2-MIB (5.0 μg L^{-1}) in hexane. MDL and MQL of the SPME method were determined for both compounds ac-cording to the procedure described above for liquid injection calibration analysis using the SIM mode.

The following extraction and desorption parameters were tested to determine the effect on extraction efficiency: extraction temperature, extraction time, desorption temperature, and desorption time. Five different temperatures: 30, 40, 50, 60, and 70 °C were tested with a constant extraction time of 30 min to determine the optimal extraction temperature of the fiber. The effect of extraction time of the fiber was examined at 10, 20, 30, 40, and 50 min at the optimal extraction temperature. Desorption was conducted at 260 °C for 5 min for both experiments. Fiber desorption was tested at five different inlet temperatures: 230, 240, 250, 260, and 270 °C with a constant desorption time of 5 min. Finally, the fiber was desorbed at five different desorption times: 1, 2, 3, 4, and 5 min at the optimal desorption temperature. The MS parameters remained the same as previously listed for SIM mode in Section 2.3, and the GC oven temperature program remained the same as previously listed in Section 2.4. All SPME method optimization ex-periments were conducted in triplicate. Carryover was also tested after every three samples by running a fiber blank that was not exposed to the samples using the optimized parameters to confirm that our conditions removed all analytes prior to further analysis.

As a final evaluation, nine different geosmin and 2-MIB gas calibration standards at concentrations between 0.05 μg L^{-1} and 20 μg L^{-1} were evaluated using the optimized SPME method. The calibration standards were analyzed three times each. The sensitivity, linearity, and detection limit of this SPME method was compared to the liquid injec-tion calibration method.

2.6. Open-air field collection of geosmin and 2-MIB from disturbed soils

Five different open-air field trials were conducted for collection of geosmin and 2-MIB using exposed DVB/CAR/PDMS fibers. Fibers were immediately retracted following exposure, stored in their storage boxes at room temperature, and analyzed within 24 h of exposure. A Drummer silty clay loam soil (fine-silty, mixed, superactive, mesic Typic Endoaquoll) was selected on the campus of the Construction Engineering Research Laboratory (Champaign, IL, USA) in an area with perennial turfgrass cover. Soil percent moisture and temperature data were collected at the time of each sample collection using a ΔT W.E.T soil temperature and moisture probe (ΔT Devices, Cambridge, UK) with three replicate samples collected and averaged around each sampling point. Air temperature and humidity levels were obtained with a Fisherbrand Traceable digital thermometer (ThermoFisher Scientific, Waltham, MA, USA) at the time of sample collection. In Trial 1 (air temperature of 24 °C, 74% relative humidity; no soil data), a single fiber was placed 2 cm above the soil surface and exposed to ambient air for 20 min to obtain a background sample. The soil at this immediate location was then disturbed by pressing a Corona SoilRIPPER (Corona Tools, Corona, CA, USA) into the soil completely, twisting 180°, and lifting to pull the disturbed soil plug loose. The plunger was then pressed to release the plug and the process was repeated for three additional rotations to fully disrupt the soil plug in a replicable manner, giving a soil disturbance 18.4 cm in diameter and 13.3 cm deep (3.5 L volume). A single DVB/CAR/PDMS fiber was immediately placed 2 cm over the disturbed soil and exposed for 20 min. Figs. S2 and S3 show undisturbed and disturbed sampling in the field using SPME. Both fibers were analyzed for geosmin and 2-MIB using SIM mode.

For Trial 2 (air temperature of 24 °C, 74% relative humidity; soil temperature of 30.5 °C, 28.8% moisture), immediately after disturbing the soil in a manner similar to Trial 1, individual DVB/CAR/PDMS fibers were placed over the disturbed area 2 cm above the original soil surface and exposed for 1, 2, 5, 10, or 20 min and analyzed using SIM mode for geosmin and 2-MIB detection. In Trial 3 (air temperature of 21 °C, 71% relative humidity; soil temperature of 22.9 °C, 29.1% moisture), five DVB/CAR/PDMS fibers were placed 2 cm over the disturbed soil and exposed for 1, 2, 5, 10, and 20 min, identical to Trial 2, with the exception that SCAN mode was utilized for analysis. In Trial 4 (air temperature of 23.0 °C, 67% relative humidity; soil temperature of 30.3 °C, 32.9% moisture), eight DVB/CAR/PDMS fibers were used in the field. A single blank fiber was initially exposed in its box for 30 min at a distance of 4 m from the other fibers, a second fiber was exposed 2 cm above an undisturbed soil surface for 30 min, and 6 fibers were exposed 2 cm above the disturbed soil surface for 10, 20, 30, 40, 50, or 60 min and analyzed using SIM mode. In Trial 5 (air temperature of 19.8 °C, 44% relative humidity; soil temperature of 23.2 °C, 15.0% moisture), eight DVB/CAR/PDMS fibers were exposed 2 cm above the surface of a similarly disturbed area of the soil and three replicates were exposed for 20 and 40 min each and 2 replicates were exposed for 30 min each. Fibers were analyzed using SIM mode for detection of geosmin and 2-MIB. Means of replicate geosmin and 2-MIB concentrations were compared to identify the optimal exposure times in Trial 5 for both compounds.

3. Results and discussion

3.1. Liquid injection

The retention times (RT) for geosmin and 2-MIB from liquid injections were identified using standard stock solutions for each compound alone and then together in the same solution. Samples were analyzed using both SCAN and SIM modes. A typical chromatogram is shown in Fig. S1 for SCAN mode. The MassHunter Program Library identified the 2-MIB peak at 8.24 min and the geosmin peak at 10.50 min. As expected with our system, geosmin has a longer elution time than 2-MIB with this HP-5MS capillary column, as also noted by others who used the same column type (Jeleń et al., 2003). The mass spectra for these two compounds are shown in Figs. S4 and S5. We recognize that

since geosmin elutes at 10.5 min, it is not necessary to ramp to 250 °C; however, heating to this elevated temperature ensured that we minimized any potential carryover of compounds. If minimization of analysis time is critical, this oven profile can be altered.

The combined standard stock solutions were also analyzed using the SIM mode (for example, see Fig. S6) using the circled masses in the spectra for these compounds, which agreed with the literature values (Table S1). Use of the SIM mode eliminates nearly all background peaks. The calibration curves for geosmin and 2-MIB using liquid injection in the SIM mode is shown in Fig. 1. The best fit lines for the data display excellent linearity over almost four orders of magnitude and illustrate a slightly higher response for 2-MIB over geosmin.

Eight samples of the 0.2 μg L^{-1} concentration were analyzed for each compound and the SD was determined. The MDL and MQL values were calculated using the SD for each target analyte as previously described in Section 2.3. The MDL and MQL values for a 2 μL direct injection of 2-MIB in hexane solution were 0.042 μg L^{-1} (0.084 pg injected) and 0.126 μg L^{-1}, respectively (Table S3). The MDL and MQL values for a 2 μL direct injection of geosmin in hexane solution were 0.054 μg L^{-1} (0.108 pg injected) and 0.162 μg L^{-1}.

3.2. SPME

3.2.1. Analysis of 2-MIB and geosmin by SPME

The retention times of each compound were investigated using TVT with a 50/30 μm DVB/CAR/PDMS fiber for a set of standard solutions at nine different concentrations. This three-component fiber was chosen based on success in previous SPME-GC-MS studies (Jeleń et al., 2003). Initially, we performed a blank analysis with the fiber inserted into the headspace of a 20 mL vial with ambient air. Fig. S7 illustrates an example chromatogram of a blank run in SCAN mode. Potential interferences were noted by appreciable peaks at 10.67 (a siloxane peak), 13.79 (a phthalate peak), and 15.67 (96% match with isobutyl laurate) min originating from volatile compounds in the ambient air, or off-gassing from vial, septum, or the fiber itself, despite the SPME fiber conditioning step. The retention times of these background peaks did not interfere with our analyte peaks (*vide infra*) as denoted on the chromatogram. Minor column bleed and instrument noise are also noted in the background.

Using TVT, a standard solution containing 1 mg L^{-1} geosmin and 1 mg L^{-1} 2-MIB was analyzed via SPME using the SCAN mode (Fig. S8). The 10.67 min background peak is observed but 2-MIB (8.74 min) and geosmin (11.86 min) both elute in regions unobscured by interferents present in the blank (Fig. S7). The DVB/CAR/PDMS fiber is therefore a reasonable choice for analysis of these two compounds. While the liquid injection analysis above noted a similar but slightly higher MS response for 2-MIB over geosmin (Figs. S1 and 1), the DVB/CAR/PDMS fiber preferentially sorbs and releases the geosmin component as evidenced by its larger peak area compared to 2-MIB. Using pure hexane as the TVT sample, Fig. S9 demonstrates the presence of the ubiquitous 10.67 min background peak, and the lack of either 2-MIB or geosmin as a contaminant in the solvent and no carryover of these compounds on conditioned fibers.

The same combined 1 mg L^{-1} standard solution with TVT and DVB/CAR/PDMS fibers was used to detect 2-MIB and geosmin in SIM mode (Fig. S10). As expected, this mode clearly shows both peaks at the same retention times as the SCAN mode, while eliminating nearly all contaminant peaks. The retention times of both compounds are slightly longer than those of the liquid injection for geosmin and 2-MIB primarily due to the additional time needed for analyte desorption from the fiber. Based on the complete baseline separation, the peak symmetry, and the absence of degradation products, use of an extraction temperature of 30 °C for 30 min and a desorption temperature of 260 °C for 5 min is a valid set of initial analysis conditions for SPME collection from the headspace samples.

3.2.2. Comparison of different fiber types

The four different fiber types were compared to determine which fiber is best to collect and detect 2-MIB and geosmin. The 2-MIB and geosmin calibration curves for each fiber type can be found in Figs. S11–S14. Multicomponent coatings with different thicknesses can be compared with respect to relative adsorption of 2-MIB and geosmin (Shirey, 2007). PDMS is a good general purpose sorbent for hydrophobic molecules. The DVB coating is usually suitable for larger molecules as well as single matrices with multiple target analytes, while CAR is aimed at lower molecular weight molecules (Shirey, 2007). The polyacrylate coating is suitable for polar analytes found in polar matrices (Shirey, 2007).

The peak area results from the 20 μg L^{-1} geosmin and 20 μg L^{-1} 2-MIB standard stock solution for each of the fiber types are compared in Fig. S15, where a lower peak area indicates the inability of the analyte to either adsorb onto or release from the fiber. Despite the presence of hydroxyl groups in both molecules, neither analyte performed well with the polyacrylate fiber. The other three fibers had much better sorption properties with these small analytes.

From the liquid calibration curve above (Fig. 1), we expect a slightly larger peak area for 2-MIB over that of geosmin at the same concentration. All fibers, however, show a preference for geosmin over 2-MIB using these extraction and desorption conditions. PDMS and PDMS/DVB were very similar in performance for both compounds and may be the best fibers to keep the performance of both analytes consistent. If 2-MIB is the only analyte of interest, the PDMS fiber had the best properties for this compound. The 50/30 μm DVB/CAR/PDMS fiber had the single best response for either compound with a large peak area for the geosmin. It also had the highest response when totalling both peak areas. Since we were unsure which of these two compounds would be dominant in the field soil disruption studies, and we were uncertain as to the amount of analytes emitted, we chose the three-component fiber for further experiments due to its superior geosmin performance and total capacity.

3.2.3. SPME parameter optimization

Our goal was to maximize the analyte peak areas with respect to changing the SPME extraction and desorption conditions from the TVT

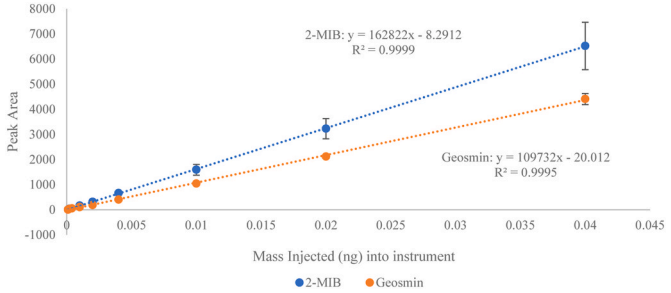

Fig. 1. Liquid calibration curves for 2-MIB and geosmin in SIM mode.

Table 1
SPME method optimization parameter determination showing mean peak area comparison for 2-MIB using 50/30 μm DVB/CAR/PDMS fiber.

Extraction			Desorption		
Temperature (°C)	Mean peak area[a]	Standard deviation	Temperature (°C)	Mean peak area[a]	Standard deviation
30	109.79	14.36	230	87.80	3.39
40	64.67	2.39	240	79.79	8.46
50	45.04	10.30	250	110.15	11.65
60	38.58	8.56	260	106.60	7.62
70	34.71	9.24	270	116.10	8.20
Time (min.)	Mean peak area[a]	Standard deviation	Time (min.)	Mean peak area[a]	Standard deviation
10	123.63	6.64	1	52.28	7.18
20	91.29	10.54	2	61.51	17.59
30	80.50	4.79	3	63.47	3.46
40	64.63	6.70	4	66.63	16.89
50	47.73	6.03	5	45.28	13.53

[a] Average of three samples.

Table 2
SPME method optimization parameter determination showing mean peak area comparison for geosmin using 50/30 μm DVB/CAR/PDMS fiber.

Extraction			Desorption		
Temperature (°C)	Mean peak area[a]	Standard deviation	Temperature (°C)	Mean peak area[a]	Standard deviation
30	860.43	83.12	230	752.74	21.10
40	941.39	47.80	240	527.42	15.42
50	1021.69	28.26	250	635.89	78.22
60	918.81	92.02	260	380.42	16.82
70	759.46	39.05	270	295.51	19.32
Time (min.)	Mean peak area[a]	Standard deviation	Time (min.)	Mean peak area[a]	Standard deviation
10	663.10	35.00	1	483.52	14.59
20	718.17	67.57	2	509.38	140.53
30	738.11	30.83	3	473.04	83.43
40	655.71	45.59	4	471.57	119.54
50	560.30	53.40	5	330.46	17.71

[a] Average of three samples.

headspace, indicating maximum recovery of the two analytes, to derive a single fieldable analysis method. Extraction temperature is an important parameter when analyzing compounds via headspace-SPME (HS-SPME) because it influences the mass transfer rates and partitioning of analytes between the solution, sorbent, and gas phases. Higher temperatures increase the vapor pressure of volatile analytes in the headspace, however, higher temperatures may also negatively impact sorption efficiency of the different SPME fiber coatings. To determine the best extraction temperature to maximize 2-MIB and geosmin combined, 10 μL standard stock solution containing 5 μg L^{-1} of both 2-MIB and geosmin was injected into three separate 20 mL headspace vials. For each sample set analysis, a DVB/CAR/PDMS SPME fiber was used to extract the samples in the vials at 30, 40, 50, 60, and 70 °C. Tables 1 and 2 show the 2-MIB and geosmin peak area as a function of extraction temperature. The best extraction temperature for 2-MIB (Table 1) was 30 °C, and the best extraction temperature for geosmin (Table 2) was 50 °C. It is evident in Table 1 that, as extraction temperature increases, 2-MIB partitions back into the gas phase at relatively low temperature (>30 °C) while geosmin begins this process above 50 °C. Therefore, 30 °C was chosen as the optimal extraction temperature for 2-MIB and geosmin combined to avoid substantial loss of 2-MIB at higher temperatures.

The duration of fiber exposure to the headspace can strongly influence the analyte adsorption into the stationary phase of the fiber coating. Previous work indicates extraction yield increases over relatively long exposure times (Watson et al., 2000). It was found that 2-MIB and geosmin reached an apparent equilibrium after 1–2 h in an enclosed headspace (Watson et al., 2000). Here, shorter extraction times of 10 through 50 min were investigated at 30 °C to determine 2-MIB and geosmin recoveries. The collection of 2-MIB quickly dropped off after 10 min of extraction (Table 1) while most efficient recovery of geosmin was found to occur at 30 min extraction time (Table 2). According to a water extraction study in which geosmin and 2-MIB were analyzed using SPME, a peak decrease for 2-MIB and geosmin occurred between 4 and 20 min for sample collection time on the SPME fiber and 5 min was the optimal time between sensitivity and sample time (Lloyd et al., 1998). Therefore, a longer extraction time is not necessarily better. The extraction conditions of 10 min at 30 °C provides a reasonable balance in the simultaneous extractions of 2-MIB and geosmin. These happen to be the best for extraction of 2-MIB but the determination (peak area) of this analyte drops off rapidly when not optimized. The ideal extraction conditions for geosmin are 30 min at 50 °C but it is less sensitive to sub-optimal settings.

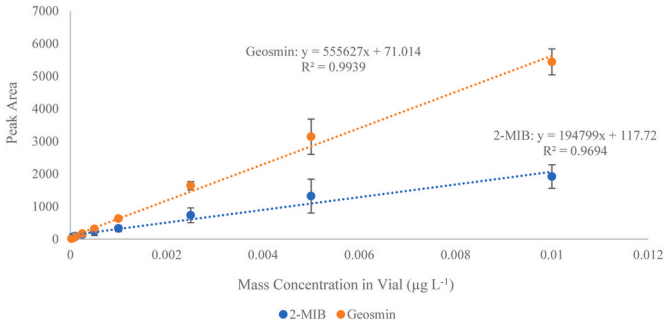

Fig. 2. Calibration curves for 2-MIB and geosmin using a combined TVT and DVB/CAR/PDMS fiber method.

To determine the optimal desorption temperature of the fiber in the injection port, TVT and the DVB/CAR/PDMS fiber was used with a 5 μg L^{-1} geosmin and 5 μg L^{-1} 2-MIB sample, extracted at 30 °C for 10 min. Each of the different fibers were desorbed into the GCMS at a series of inlet temperatures: 230, 240, 250, 260, and 270 °C at a constant desorption time of 5 min. The peak area of 2-MIB increased with increasing desorption temperature and was maximized at 270 °C (Table 1). Geosmin was very sensitive to the desorption temperature and decreased rapidly with increasing temperature above 230 °C (Table 2). A desorption temperature of 230 °C provides the best balance for determination of both analytes. Although 2-MIB enjoys a higher desorption temperature, geosmin is substantially lost or degraded as the temperature increases from 230 °C to 270 °C. It is known that if adesorption temperature is too high for a specific analyte, decomposition of the analyte and damage to the fiber can occur (Dong et al., 2005).

Five different desorption times: 1, 2, 3, 4, and 5 min, were investigated to determine the optimal desorption time for the analytes when in the GC inlet. All parameters for the GC-MS were kept the same as in the previous sections, with an extraction temperature of 30 °C for 10 min, and a desorption temperature of 230 °C. Each desorption time was tested in triplicate with TVT analysis of a 5 μg L^{-1} geosmin and 5 μg L^{-1} 2-MIB sample. Tables 1 and 2 illustrate 2-MIB and geosmin peak areas as a function of desorption time. The peak area of 2-MIB slightly increased with increasing desorption time, reaching a maximum at 4 min, while the peak area of geosmin appears consistent across the 1–4 min desorption time. Peak areas for both analytes decreased at 5 min; therefore, 4 min was chosen as the best sample desorption time.

Our parametric selections above were chosen so that we do not completely lose one of the analytes as we attempt to maximize both. Once the characteristics of the soil volatilome are known, re-evaluation of the parameters in future research may be necessary to maximize one species to the likely detriment of the other.

Table 3
2-MIB and geosmin detection from DVB/CAR/PDMS SPME fibers exposed to undisturbed and disturbed soils.

Trial	Mode	Exposure time (min)	2-MIB Concentration (μg/L)	Geosmin concentration (μg/L)
1	SIM	20 (Undisturbed)	0.156	0.011
1	SIM	20	1.179	0.121
2	SIM	1	0	0
2	SIM	2	0.638	0.054
2	SIM	5	0.6	0.1
2	SIM	10	0.868	0.1
2	SIM	20	2.656	0.09
3	SCAN	1	0	0
3	SCAN	2	0	0
3	SCAN	5	0	0
3	SCAN	10	0	0
3	SCAN	20	0	0
4	SIM	0 (Blank)	0	0
4	SIM	30 (Undisturbed)	0.312	0.025
4	SIM	10	2.624	0.27
4	SIM	20	3.958	0.247
4	SIM	30	8.128	0.591
4	SIM	40	20.328	2.738
4	SIM	50	5.329	0.921
4	SIM	60	12.046	1.988
5	SIM	20	9.179	0.723
5	SIM	20	5.933	0.244
5	SIM	20	3.041	0.119
5	SIM	30	3.844	0.286
5	SIM	30	9.203	0.564
5	SIM	40	6.56	0.385
5	SIM	40	12.872	1.081
5	SIM	40	3.798	0.414

3.2.4. SPME calibration curve

Using the parameters uncovered above, the DVB/CAR/PDMS fiber and the TVT method were utilized to construct and re-evaluate calibration curves for both 2-MIB and geosmin as presented in Fig. 2. The R^2 values using this set of method parameters were 0.9694 for 2-MIB and 0.9939 for geosmin, representing good linearity. In a previous study in which water samples were analyzed for geosmin and 2-MIB using HS-SPME, the R^2 values were 0.984 for 2-MIB and 0.993 for geosmin (Watson et al., 2000). Since we expected the concentration of these analytes to fall within this smaller range, the upper range of the calibration curve was 0.01 μg L^{-1} in the vial headspace. We also, however, analyzed 0.1 and 0.2 μg L^{-1} (10 and 20 times greater) vial concentrations. These samples had 2-MIB average peak areas of 72,882.16 and 118,591.30 and geosmin average peak areas of 107,171.70 and 196, 741.80, respectively, indicating that our calibration curve is far from the saturation point of these fibers.

Since the amount of geosmin or 2-MIB injected into the TVT vial and the response of the GC-MS from mass directly injected into the instrument are known (Fig. 1), the % recovery of these compounds by the fiber from within the TVT vial can be calculated. Using the highest concentration standard, 200 pg of both analytes injected into the vial resulted in peak areas that approximate 50 pg of geosmin and 13 pg of 2-MIB. This corresponds to a 25.5% recovery of geosmin and 6.5% recovery of 2-MIB from the total in the TVT vial. Since both compounds are present in equal amounts in the vial, geosmin is outcompeting 2-MIB for sorption sites on the fiber even though some parameters are biased toward 2-MIB.

Injection of 10 μL of a 20 μg L^{-1} standard into the 20 mL vial creates a 10 ng L^{-1} internal concentration. Analysis of eight different 1 ng L^{-1} standards allows calculation of an MDL in the vapor phase for geosmin and 2-MIB of 0.16 ng L^{-1} (3.2 pg in the vial) and 0.72 ng L^{-1} (14.4 pg in the vial), respectively. Similarly, the MQL in the vapor phase for geosmin and 2-MIB are 0.47 ng L^{-1} and 2.2 ng L^{-1}, respectively (Table S3). Our method uses standards containing both compounds and a SPME method that is not completely optimized for either compound. While this method will be used for analysis of field samples as we expect both compounds to be present, the data will inform us whether future research requires a refinement of the method to focus on a single compound.

3.3. Open-air collection of geosmin and 2-MIB from disturbed soils

In Trial 1, both fibers placed at the soil surface detected concentrations of geosmin and 2-MIB (Table 3). However, the fiber placed over the soil surface after soil disruption detected much higher concentrations of both compounds, with a 2-MIB concentration more than 7 and geosmin concentration 11 times higher when exposed to the disturbed soil compared to the undisturbed soil.

Trials 2 and 3 utilized identical exposure intervals for geosmin and 2-MIB, with the only difference being the use of SCAN (Trial 2) and SIM (Trial 3) modes. All fibers exposed for 2 min or more in Trial 2 SIM mode detected both 2-MIB and geosmin, while neither 2-MIB nor geosmin were detected in any of the exposed fibers in Trial 3 SCAN mode (Table 3). This difference indicates that SIM mode must be utilized in studies with small soil disturbances where low concentrations of both compounds are expected. Although we did not determine the MDL of our method in SCAN mode, higher concentrations of these compounds would certainly be observable in SCAN mode (Fig. S1). Trial 3 in SCAN mode did, however, confirm that no other volatile chemicals were emitted from the same disturbed soil with any consistency and geosmin and 2-MIB are the primary species of interest for studies of disturbed soils. The Trial 2 SIM mode concentrations further indicated that increased exposure times for both 2-MIB and geosmin generally resulted in higher collection efficiencies. Since the highest concentrations were observed at the greatest exposure times, we studied longer exposure times for effect on analyte collection.

Trial 4 indicated that 40 min exposure was optimal for detection of both geosmin and 2-MIB compared to 10, 20, 30, 50, and 60 min in SIM mode (Table 3). The blank fiber sample did not detect either geosmin or 2-MIB, while the fiber placed directly over undisturbed soil detected low background concentrations of both (Table 3). Comparing the undisturbed sample to the 30 min exposure of disturbed soil clearly demonstrates the substantial release of these compounds due to soil disturbance in agreement with Trial 1. In Trial 4, exposure to disturbed soil yielded concentrations of both 2-MIB and geosmin over 20 times higher than the fiber exposed to undisturbed soil, depending on field exposure time (Table 3). The difference between disturbed and undisturbed at 30 min, for example, is (8.13–0.31 =) 7.8 μg L^{-1} additional 2-MIB in the immediate atmosphere due to disruption of 3.5 L of soil. As a rough approximation, a soil disruption of just 0.1 L would double the amount of 2-MIB present in the atmosphere, well above the SPME MQL for this compound.

Based on mean comparisons, Trial 5 confirmed the Trial 4 finding that 40 min exposure for both geosmin and 2-MIB using DVB/CAR/PDMS fibers is the most effective exposure time. Mean 2-MIB concentrations were 6.05, 6.52, and 7.74 μg L^{-1} at 20, 30, and 40 min exposure, respectively, while geosmin concentrations were 0.36, 0.43, and 0.63 μg L^{-1} at 20, 30, and 40 min exposure, respectively (Table 3). Concentration variability, however, was high between samples, but this is not unanticipated due to high variation of biochemical processes in any given soil and the possibility that individual fibers vary in their affinity for binding of specific compounds.

Geosmin and 2-MIB were detected far above background levels in all disturbed soil samples exposed for at least 2 min from all trials and experimental conditions using DVB/CAR/PDMS fibers in SIM mode. In addition, since both 2-MIB and geosmin were detected just above undisturbed soils and not in the fiber blank, these compounds are continuously percolating from the soil and are most prevalent at the soil surface. Further, because only a very small volume of soil was disturbed (3.5 L), larger or multiple soil disturbances could yield more information regarding the concentration, duration, diffusion, and other properties associated with their emission from disturbed soils.

It was expected that both geosmin and 2-MIB would be detected near disturbed soil. The total origin of these compounds, however, remains unknown. As Actinomycetes, filament forming bacteria, are a primary producer of these compounds, soil disruption that destroys these filaments could initiate an immediate release of 2-MIB and geosmin. Alternatively, prior release of these compounds that accumulate in soil pore spaces and are released upon pore destruction could also result in increased concentrations. What is known is that the release of these compounds from disturbed soils is immediate and seems to continue at elevated levels for at least the time duration studied here.

Mean concentrations for 2-MIB and geosmin from exposure to disturbed soil samples across all trials analyzed using SIM mode were 5.64 μg L^{-1} and 0.55 μg L^{-1}, respectively (Table 3). The 2-MIB concentration was consistently higher (on average 10 times) than geosmin under any condition, which agrees with previous research detecting higher concentrations of 2-MIB compared to geosmin in soils directly (Buttery and Garibaldi, 1976; Stahl and Parkin, 1994, 1996) and is likely influenced by the microbial ecology of producers, biochemical production of the compounds, and sorption chemistry with soil constituents. Recovery rates of geosmin and 2-MIB in soils using wet purging are documented at 15% and 24%, respectively, indicating likely soil adsorption, particularly with geosmin (Stahl and Parkin, 1994). Both geosmin and 2-MIB are produced by a number of soil organisms (Alghanmi et al., 2018; Breheret et al., 1999; Krishnani et al., 2008; Schnürer et al., 1999); however, most organisms only appear to be biochemically equipped to produce one or the other of these compounds (Anuar et al., 2017). This may be due to the specific biosynthetic pathways, molecular properties, or other factors possessed by individual genera, species, and isolates of the compound producers. Geosmin biosynthesis occurs from conversion of farnesyl diphosphate (the universal C_{15} sesquiterpene precursor) via a single enzyme, geosmin synthase (Giglio et al., 2011; Jiang et al., 2006). 2-MIB biosynthesis occurs from conversion of geranyl diphosphate (the universal C_{10} sesquiterpene precursor) via two enzymes, geranyl diphosphate 2-methyltransferase and MIB synthase (Giglio et al., 2011; Komatsu et al., 2008). Given that soil organisms are responsible for production of 2-MIB and geosmin and the variation in concentrations measured from the same soil over time, it is likely that numerous environmental variables influence the production and subsequent emission of 2-MIB and geosmin from disturbed soils, and may at least partially explain the discrepancy between emitted concentrations of the two compounds. The influence of variation in microbial populations on geosmin and 2-MIB production has been previously reported (Stahl and Parkin, 1996). As other variables such as soil moisture, temperature, texture, pH, and vegetation influence the soil microbial community, they too will likely influence emission of 2-MIB and geosmin.

Based on the above results, we can make multiple recommendation for further investigation. First, while the DVB/CAR/PDMS fiber was best for geosmin analysis, the collection and analysis method should be tailored for geosmin to maximize its response. This is the lower concentration analyte in all cases studied here and conclusions based on its presence requires more attention to an optimized method. Second, in the soils investigated here, use of a PDMS fiber and a 2-MIB optimized method may be preferable if correlating soil disruption to concentration as its greater concentration will increase sensitivity. Third, use of multiple fibers of both types is best when the relative amounts of these two species in the volatilome is unknown. As stated above, other variables could change the ratio of these compounds and an initial screen may be required until a more comprehensive correlation between volatilome and soil parameters is established. In addition, this work does point out a SPME drawback where a fiber sample is available for only a single analysis. Each desired replicate requires an additional fiber. Finally, increased utilization of this method under variable disturbance scenarios and environmental conditions will provide additional information to develop further analyses of these compounds and its potential applications.

4. Conclusion

The purpose of this study was to develop and evaluate a SPME method that would allow for the simultaneous collection and analysis of two soil volatiles, 2-MIB and geosmin, from the air near a soil disturbance. Direct liquid injection of hexane standards of these two analytes provided initial information on elution time, fragment masses for SIM analysis, and detector response for recovery calculations when using SPME fibers. Among tested fibers, a PDMS fiber was determined to be best for 2-MIB. If either geosmin alone or the maximum mass of total analytes sorbed on the fiber is the analytical focus, a DVB/CAR/PDMS SPME fiber coating is most effective. Multiple parameters were tested to determine the effect on the mass introduced on-column with the DVB/CAR/PDMS SPME fiber, but these parameters should be regarded as guidelines for optimization with other systems, fibers, and analytes in mind. MDL and MQL for the SPME method for both 2-MIB and geosmin were calculated and were determined to be low enough to detect concentration changes of the analytes in the air over much smaller soil disruption events than employed here. Both geosmin and 2-MIB were detected at low background concentrations just above undisturbed soil, but emissions from over a disturbed soil quickly exceeded background levels at fiber exposures greater than 2 min. In the soil types studied here, 2-MIB emission from a minor soil disturbance was ten-fold higher than the accompanying geosmin concentration, indicating that 2-MIB is the more valuable marker for monitoring soil disruption.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was funded under the U.S. Army Engineer Research and Development Center (ERDC) Basic Research Program through Program Element 601102/Project AB2/Task 4. Opinions, interpretations, conclusions and recommendations are those of the authors and are not necessarily endorsed by the U.S. Army.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2021.131333.

References

Alghanmi, H.A., Alkam, F.M., Al-Taee, M.M., 2018. Effect of light and temperature on new cyanobacteria producers for geosmin and 2-methylisoborneol. J. Appl. Phycol. 30, 319–328. https://doi.org/10.1007/s10811-017-1233-0.

Anuar, N.S.S., Kassim, A.A., Utsumi, M., Iwamoto, K., Goto, M., Shimizu, K., Othman, N. A., Zakaria, Z., Sugiura, N., Hara, H., 2017. Characterization of musty odor-producing actinomycetes from tropics and effects of temperature on the production of musty odor compounds. Microb. Environ. 32, 352–357.

Arthur, C.L., Pawliszyn, J., 1990. Solid phase microextraction with thermal desorption used fused silica optical fibers. Anal. Chem. 62 (19), 2145–2148. https://doi.org/10.1021/ac002181019.

Belardi, R.P., Pawliszyn, J.B., 1989. The application of chemically modified fused silica fibers in the extraction of organics from water matrix samples and their rapid transfer to capillary columns. Water Qual. Res. J. 24 (1), 179–191. https://doi.org/10.2166/wqrj.1989.010.

Breheret, S., Talou, T., Rapior, S., Bessière, J.M., 1999. Geosmin, a sesquiterpenoid compound responsible for the musty-earthy odor of *Cortinarius herculeus, Cystoderma amianthinum*, and *Cy. carcharias*. Mycologia 91 (1), 117–120. https://doi.org/10.1080/00275514.1999.12060999.

Buttery, R.G., Garibaldi, J.A., 1976. Geosmin and methylisoborneol in garden soil. J. Agric. Food Chem. 24 (6), 1246–1247.

CFR 136, 1984. Definition and Procedure for the Determination of the Method Detection Limit. United States Code of Federal Regulations Title 40 Part 136 Appendix B. Office of the Federal Register, College Park, MD, USA.

Conte, E.D., Shen, C.Y., Miller, D.W., Perschbacher, P.W., 1996. Microwave distillation-solid phase absorbent trapping device for the determination of off-flavors geosmin and methylisoborneol in catfish tissue below their rejection levels. Anal. Chem. 68, 2713–2716.

Dong, C., Zeng, Z., Yang, M., 2005. Determination of organochlorine pesticides and their derivatives in water after HS-SPME using polymethylphenylvinylsiloxane-coated fiber by GC-ECD. Water Res. 39 (17), 4204–4210. https://doi.org/10.1016/j.watres.2005.08.004.

Fabre, M., Aubry, V., Guichard, E., 2002. Comparison of different methods: static and dynamic headspace and solid-phase microextraction for the measurement of interactions between milk proteins and flavor compounds with an application to emulsions. J. Agric. Food Chem. 50 (6), 1497–1501. https://doi.org/10.1021/jf0107065.

Freidig, A.K., Goldman, I.L., 2014. Geosmin (2β,6α-Dimethylbicyclo[4.4.0]decan-1β-ol) production associated with *Beta vulgaris* ssp. *vulgaris* is cultivar specific. J. Agric. Food Chem. 62 (9), 2031–2036. https://doi.org/10.1021/jf4047336.

Giglio, S., Chou, W.K.W., Ikeda, H., Crane, D.E., Monis, P.T., 2011. Biosynthesis of 2-methylisoborneol in cyanobacteria. Environ. Sci. Technol. 45, 992–998.

Hanson, T.R., 2003. Economic impact of off-flavor to the U.S. catfish industry. In: Rimando, A.M., Schrader, K.K. (Eds.), Off-flavors in Aquaculture. American Chemical Society, Washington, D.C., pp. 13–29

Hayes, S.J., Hayes, K.P., Robinson, B.S., 1991. Geosmin as an odorous metabolite in cultures of a free-living amoeba, *Vannella* species (Gymnoamoebia, Vannellidae). J. Protozool. 38 (1), 44–47. https://doi.org/10.1111/j.1550-7408.1991.tb04798.x.

Jeleń, H.H., Majcher, M., Zawirska-Wojtasiak, R., Wiewiórowska, M., Wąsowicz, E., 2003. Determination of geosmin, 2-methylisoborneol, and a musty-earthy odor in wheat grain by SPME-GC-MS, profiling volatiles, and sensory analysis. J. Agric. Food Chem. 51 (24), 7079–7085. https://doi.org/10.1021/jf030228g.

Jiang, J., He, X., Cane, D.E., 2006. Geosmin biosynthesis. *Streptomyces coelicolor* germacradienol/germacrene D synthase converts farnesyl diphosphate to geosmin. J. Am. Chem. Soc. 128, 8128–8129.

Jüttner, F., 1990. Monoterpenes and microbial metabolites in the soil. Environ. Pollut. 68 (3–4), 377–382. https://doi.org/10.1016/0269-7491(90)90039-F.

Komatsu, M., Tsuda, M., Ōmura, S., Oikawa, H., Ikeda, H., 2008. Identification and functional analysis of genes controlling biosynthesis of 2-methylisoborneol. Proc. Natl. Acad. Sci. U.S.A. 105, 7422–7427.

Kong, Y., Cao, Z., 2018. Determination of Off-Odor Compounds in Drinking Water Using an SPME Device with Gas Chromatography and Mass Spectrometry. Agilent Technologies, Inc.. Application Note 5994-0626EN, retrieved from website: https://www.agilent.com/cs/library/applications/application-spme-arrow-gc-ms-ms-water-analysis-5994-0626en-agilent.pdf.

Krishnani, K.K., Ravichandran, P., Ayyappan, S., 2008. Microbially derived off-flavor from geosmin and 2-methylisoborneol: sources and remediation. In: Whitacre, D.M. (Ed.), Reviews of Environmental Contamination and Toxicology, vol. 194. Springer, New York, NY, pp. 1–27. https://doi.org/10.1007/978-0-387-74816-0_1.

Lloyd, S.W., Grimm, C.C., 1999. Analysis of 2-methylisoborneol and geosmin in catfish by microwave distillation-solid-phase microextraction. J. Agric. Food Chem. 47 (1), 164–169. https://doi.org/10.1021/jf980419x.

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 Res. 32 (7), 2140–2146. https://doi.org/10.1016/S0043-1354(97)00444-2.

Lord, H., Yu, Y., Segal, A., Pawliszyn, J., 2002. Breath analysis and monitoring by membrane extraction with sorbent interface. Anal. Chem. 74 (21), 5650–5657. https://doi.org/10.1021/ac025863k.

Metting Jr., F.B., 1992. Structure and physiological ecology of soil microbial communities. In: Metting, F.B. (Ed.), Soil Microbial Ecology: Applications in Agricultural and Environmental Management. Marcel Dekker, Inc., New York, NY, pp. 3–25.

Oliver, K.D., Adams, J.R., Daughtrey Jr., E.H., McClenney, W.A., Yoong, M.J., Pardee, M. A., Almasi, E.B., Kirshen, N.A., 1996. Technique for monitoring toxic VOCs in air: sorbent preconcentration, closed-cycle cooler cryofocusing, and GC/MS analysis. Environ. Sci. Technol. 30 (6), 1939–1945. https://doi.org/10.1021/es9506317.

Rainey, C.L., Bors, D.E., Goodpaster, J.V., 2014. Design and optimization of a total vaporization technique coupled to solid-phase microextraction. Anal. Chem. 86 (22), 11319–11325. https://doi.org/10.1021/ac5030528.

Rinnan, R., Gierth, D., Bilde, M., Rosenørn, T., Michelsen, A., 2013. Off-season biogenic volatile organic compound emissions from heath mesocosms: responses to vegetation cutting. Front. Microbiol. 4, 224. https://doi.org/10.3389/fmicb.2013.00224.

Schnürer, J., Olsson, J., Börjesson, T., 1999. Fungal volatiles as indicators of food and feeds spoilage. Fungal Genet. Biol. 27 (2–3), 209–217. https://doi.org/10.1006/fgbi.1999.1139.

Shirey, R., 2007. Selecting the Appropriate SPME Fiber Coating-Effect of Analyte Molecular Weight and Polarity, vol. 28. Reporter EU. Retrieved from Millipore Sigma website: https://www.sigmaaldrich.com/technical-documents/articles/reporter-eu/selecting-the-appropriate.html.

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 bioelectric nose with human-like performance. Biosens. Bioelectron. 74, 199–206. https://doi.org/10.1016/j.bios.2015.06.053.

Spörle, J., Becker, H., Allen, N.S., Gupta, M.P., 1991. Occurrence of (-)-geosmin and other terpenoids in an axenic culture of the liverwort *Symphyogyna brongniartii*. Verlog der Zeitschrift für Naturforschung C. 46 (3–4), 183–188. https://doi.org/10.1515/znc-1991-3-404.

Stahl, P.D., Parkin, T.B., 1994. Purge-and-trap extraction of geosmin and 2-methylisoborneol from soil. Soil Sci. Soc. Am. J. 58 (4), 1163–1167. https://doi.org/10.2136/sssaj1994.03615995005800040022x.

Stahl, P.D., Parkin, T.B., 1996. Microbial production of volatile organic compounds in soil microcosms. Soil Sci. Soc. Am. J. 60 (3), 821–828. https://doi.org/10.2136/sssaj1996.03615995006000030020x.

Watson, S.B., Brownlee, B., Satchwill, T., Hargesheimer, E.E., 2000. Quantitative analysis of trace levels of geosmin and MIB in source and drinking water using headspace SPME. Water Res. 34 (10), 2818–2828. https://doi.org/10.1016/S0043-1354(00)00027-0.

Yu, S., Xiao, Q., Zhu, B., Zhong, X., Xu, Y., Su, G., Chen, M., 2014. Gas chromatography–mass spectrometry determination of earthy–musty odorous compounds in waters by two phase hollow-fiber liquid-phase microextraction using polyvinylidene fluoride fibers. J. Chromatogr. A 1329, 45–51. https://doi.org/10.1016/j.chroma.2014.01.002.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
October 2021	Final	

4. TITLE AND SUBTITLE

Solid-phase microextraction (SPME) for determination of geosmin and 2-methylisoborneol in volatile emissions from soil disturbance

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
601102

6. AUTHOR(S)

Morgan W. Conrady, Markus Bauer, Kyoo D. Jo, Donald M. Cropek, Ryan R. Busby

5d. PROJECT NUMBER
AB2

5e. TASK NUMBER
4

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Construction Engineering Research Laboratory
U.S. Army Engineer Research and Development Center
2902 Newmark Drive
Champaign, IL 61822

8. PERFORMING ORGANIZATION REPORT NUMBER

ERDC/ CERL MP-21-4

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U.S. Army Corps of Engineers
Washington, DC 20314

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

This article was originally published online in *Chemosphere* on 26 June 2021.
This research was funded by the U.S. Army Engineer Research and Development Center (ERDC) Basic Research Program.

14. ABSTRACT

A method is described here for the concentration and determination of geosmin and 2-methylisoborneol (2-MIB) from the gaseous phase, with translation to field collection and quantification from soil disturbances in situ. The method is based on the use of solid-phase microextraction (SPME) fibers for adsorption of volatile chemicals from the vapor phase, followed by desorption into a gas chromatograph-mass spectrometer (GC-MS) for analysis. The use of a SPME fiber allows simple introduction to the GC-MS without further sample preparation. Several fiber sorbent types were studied and the 50/30 μm DVB/CAR/PDMS was the best performer to maximize the detected peak areas of both analytes combined. Factors such as extraction temperature and time along with desorption temperature and time were explored with respect to analyte recovery. An extraction temperature of 30 ◦C for 10 min, with a desorption temperature of 230 ◦C for 4 min was best for the simultaneous analysis of both geosmin and 2-MIB without complete loss of either one. The developed method was used successfully to measure geosmin and 2-MIB emission from just above disturbed and undisturbed soils, indicating that this method detects both compounds readily from atmospheric samples. Both geosmin and 2-MIB were present as background concentrations in the open air, while disturbed soils emitted much higher concentrations of both compounds. Surprisingly, 2-MIB was always detected at higher concentrations than geosmin, indicating that a focus on its detection may be more useful for soil emission monitoring and more sensitive to low levels of soil disturbance.

15. SUBJECT TERMS

Solid-phase microextraction, Gas chromatography-mass spectrometry, Geosmin, 2-Methylisoborneol, Volatile organic compounds

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER *(include area code)*
Unclassified	Unclassified	Unclassified	UU	13	