The Detection of Underwater Oil by Oil Detection Canines

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Abstract

The current technology and capability for detecting sunken or submerged oil are very limited. Most techniques have either a low resolution or a slow survey coverage rate, or both. Observations during field deployments have demonstrated the ability of Oil Detection Canines to detect and alert to oil underwater held in the sediment of a river and coastal shoreline. The capability of Oil Detection Canines to detect and alert to the presence of oil held in the sediment of water sources such as rivers, lakes, and coastal water would bridge a gap in current capabilities. The limitation in developing the canine capability has been the inability to place training samples (oils) in water sources without causing contamination. If the ability to train Oil Detection Canines to detect underwater oil could be developed, then teams could be deployed on the front of boats and search significant water sources for the underwater oil efficiently, effectively, and at speed. They could detect and alert to the presence of the oil under the water or held within shorelines that have access constraints, such as large eroding banks or mangroves. Or they could walk a shoreline and respond to oil in the water's edge but obscured from view. In 2021 a research trial developed protocols supported by a commercially available canine training product and a specifically developed underwater training odor delivery device which resulted in the ability to train Oil Detection Canines without any risk of contaminating the environment. These protocols proved the concept for shoreline and offshore (in a boat) surveying by a canine team to support oil detection during a spill response.

1 Introduction

Oil Detection Canines (ODC) have proven their capability both in research and field deployments (API, 2016; API, 2020; Owens et al., 2018). Field deployments have provided an opportunity to observe the capabilities of the canines in real-world situations, as well as exposed the canine teams to a variety of scenarios that cannot be replicated in the research laboratory. One such experience is the ability of canines to detect oil on a river, lake, or sea bed or sequestered in sediment underwater.

In June 2016, an ODC team deployed to Chedabucto Bay, Nova Scotia, to conduct a proof-of-concept research trial in the capability of a canine to detect spilled oil. Nine months before the deployment, the T/V Arrow released Bunker C oil with the result that oil was stranded on adjacent beaches (Owens et al., 2017). During one shoreline survey conducted at high tide due to the deployment timeline, the canine was observed wading out into the sea and offering an

Bunker, P., S.R. Vaughan, L.E. DeGreeff, E.H. Owens, and S.G. Tuttle, The Detection of Underwater Oil by Oil Detection Canines, Proceedings of the Forty-forth AMOP Technical Seminar, Environment and Climate Change Canada, Ottawa, ON, Canada, pp. 192-203, 2022.

alert that oil was present. The canine had not been trained to detect oil in or underwater, and as the presence of oil could not be verified, the alert was noted but not confirmed.

Similarly, in 2017 four ODC teams were deployed on a spill response to Saskatchewan, Canada to support a Shoreline Cleanup Assessment Technique (SCAT) program. The author deployed with an ODC for four months, and during this time, the team had over 2,700 confirmed alerts. On several occasions the canine was observed entering the water and alerting that odor was present. On each occasion a Team Lead disturbed the sediment and oil sheen was observed to rise to the surface.

These experiences by the author led to the hypothesis that ODCs could reliably detect sequestered oil in water. Canine detection training for underwater targets is restricted due to the potential risk of environmental contamination of a water source (lakes, rivers) by training aids that contain oil so that canine teams cannot be exposed to potential oil target odors. To enable a canine to detect a target substance, it must be exposed to the odor of the target within a variety of operational scenarios. The development of the prototype device was intended to address this capability gap.

The use of Human Remains detection canines to locate bodies underwater is well known and has been a technique utilized for decades (Osterkamp, 2020). Detection canines have proven their ability to detect targets from the front of boats. The University of Washington trained canines to locate whale scat from the front of a boat in the Seattle area (UW, 2017). Therefore, the concept of using ODCs to search for underwater oil from the front of a boat is supported by previous detection canine deployment experience. Canines have demonstrated a capability to detect molecules in parts per trillion (DeGreeff, Singletary, & Lazarowski, 2022), well below the level of field-based detection technology.

The objective of this study was to develop a prototype device to enable the training of canines in the detection of underwater oils. In addition, the development of canine training protocols was required so that additional teams could replicate the capability of underwater oil detection.

ODCs are imprinted (a method of associating the odor of an intended target to positive reinforcement) to various types of petroleum products. Imprinting involves the canines detecting the headspace of Volatile Organic Compounds (VOCs) and providing an alert. Environments to which this skill set would apply include riverbanks, shorelines, and pipeline Rights of Way (ROW). In these scenarios, the headspace presented to the canine is consistent. It can be practiced daily, allowing the canine to gain experience in the odor of the target in various environments and conditions. However, oil underwater would produce different odor profiles than the same oil exposed to the air, even if sub-surface on land. Therefore, this project developed a systematic protocol to ensure the canine detected the VOCs presented within a water source.

2 Method

The trials were observational and were not considered outside the normal biological functions of working dog training guidance. As such, the trials did not require review and approval by an Institutional Animal Care and Use Committee (IACUC) (NRC, 2011; NIH, 2019). The activities were conducted by a professional handler trained and certified in canines' care and ethical use. Training methods for these ODCs, handler responsibilities, and handler certification are described by Bunker (2017) and by the International Canine Spill & Leak Detection Association (ICSALDA, 2019).

The underwater device was developed using commercial off-the-shelf products. To ensure the safety of humans and canines, the paint spray tank had a 35lb pressure release valve fitted. The Pounds per Square Inch (psi) rating for the paint spray tank is 60psi. In addition, both air tanks and the paint spray tank are fitted with pressure gauges so that monitoring of air pressure can be maintained.

The canine and handler wore Personal Flotation Devices at all times when on the boat. Fresh drinking water was available at all times for the canine, and a Bimini cover was available for shade.

Initial canine training and testing was carried out at a laboratory at the canine training facility and described in a previously released report (Bunker, 2021a).

West Texas Intermediate (WTI) crude oil was used throughout the trial. The WTI was purchased from Texas Raw crude, Midland, Texas. Storage and handling of the samples and training equipment followed the protocols in the workbook, "Imprint Your Detection Dog in 15 Days" (Bunker, 2021b).

Two canines were utilized for the Laboratory phase:

- Chiron's Nika, a black female Labrador. Date of Birth: July 24, 2016. She is certified as an ODC through the International Canine Spill & Leak Detection Association. Nika has located oil underwater during oil spill response deployments. She has been utilized in ODC research trials and demonstrated the capability to detect targets below one part-per-million in vapor concentration (API, 2020). She has also been deployed and possesses field experience, including a proven ability to locate hydrocarbons within spill environments.
- Chiron's Poppy, a female English Springer Spaniel. Date of Birth: October 02, 2018. She is certified as an ODC through the International Canine Spill & Leak Detection Association. She has been utilized in ODC research trials and demonstrated the capability to detect targets below one part-per-million (API, 2020). Poppy has not deployed on a spill response and has no prior experience detecting oil underwater.

Once the canines detected and indicated the presence of oil underwater within a Training Aid Delivery Device (TADD) (SciK9, 2021) in a bucket of water, the training progressed to bubbled air in buckets (Fig. 1). A Vivosun Commercial aquarium air pump was connected to a GE Appliances in-line refrigerator carbon filter by 1/4" outer diameter, 3/16" internal diameter, Teflon tubing. The filter was used to remove ambient odors. The filter is connected to a stainless-steel three-way splitter with Teflon tubing. The three-way splitter is connected to three Kitchen Flower 3 L kimchi airtight stainless steel food containers. One of the containers contained oil in a 4oz size glass Mason jar, and the other two contained empty Mason jars. Each container was connected to a 5-gallon bucket by Teflon tubing, with the tubing going under the water within the bucket. A check valve was used on the tubing leading to the containers to prevent a backflow of any odors. Positive air was blown through the system and bubbled underwater in the buckets.

Figure 1. 5-gallon bucket bubbler device.

The canines were worked in a three-choice lineup while air bubbled through the buckets. Between each trial, the position of the buckets was moved around by an assistant. The handler was blind to the target bucket location when working the canines to prevent any conscious or subconscious cueing of the target location to the canine. The canines successfully demonstrated detecting the target headspace bubbled through the water.

3 Field Evaluation Phase

Due to time constraints, one canine, Poppy, was selected for the field evaluation phase. Poppy has no prior experience of underwater oil detection or working from a boat. Therefore, all training protocols and steps would be new to her and not influenced by previous experience. All field training was conducted at the City Public Service Energy of San Antonio Victor Braunig Lake, San Antonio, Texas.

Following laboratory testing, an underwater detection device was developed for field-based testing. The device comprises a 1-gallon Ryobi portable air compressor, an adapted Central Pneumatic 2 ½-gallon airtight paint tank for oil, and 100 ft of PVC hose (Fig. 2). One liter of WTI was placed inside the paint tank, and the tank remained unopened throughout the trial.

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Figure 2. Underwater Detection Device

The system was set up with the air/odor supply on the shoreline. The outlet pipe was deployed into the lake, and initially, the end of the pipe was weighted to deliver the odor into the water column just below the lake surface (Fig. 3). After several trials, the system was reconfigured to anchor the entire pipe to the lakebed (Fig. 4). The battery-operated air compressor had a 20-minute continuous operating time, allowing for up to six training sessions. Two batteries were used per day, which provided sufficient power for the day's training duration. In these shallow water depths (<5 feet), this did not affect successful detection by the canine.

After the field testing of the system was completed, a canine was trained to work from the bow of a small electric-powered boat to search for the odor source. The electric trolling motor was utilized for propulsion to ensure no air contamination of hydrocarbons by a fuel motor which may affect the canine's detection training.

Preliminary protocols for training canines in this technique were evaluated by a systematic approach and adjusted to provide an effective and efficient set of training steps for this detection application.

Initial stages focused on the acclimatization and orientation of the canine to traveling on a boat. A floating toy reward, KONG ball, was thrown into the water in sight of the canine. The boat was steered downwind of the ball, and the trainer gave the canine the cue to search. The boat was maneuvered into the scent plume of the ball, and the canine was encouraged to point at the source. The boat was steered to the source and the canine rewarded by retrieving the ball. The behaviors desired, such as pulling on the lead in the direction of the source, were reinforced with verbal encouragement.

Figure 3. A KONG ball being used in initial training of detection in water.

The boat was positioned downwind of the ball, and the canine cued to search. The boat was maneuvered in a zig-zag fashion across the wind, so the canine had an opportunity to detect the ball's scent plume as it was crossed. The process was repeated with the ball being deposited in the water without the canine knowing it had been placed out. This was repeated at further distances from the source and longer boat maneuvering before encountering the scent plume.

Once the canine demonstrated a searching behavior on cue and changes in behavior, sufficient for the trainer to recognize the canine had detected the scent, the ball was replaced with the underwater odor device.

Figure 4. Initial set up with a floating pipe and subsurface mid-level water column delivery.

The boat was positioned downwind of the submerged underwater device tube, which had no visual markers, and searches were conducted with zig-zag and linear patterns (Fig. 5). The trainer/boat operator observed the changes in the canine's behavior to steer towards the source.

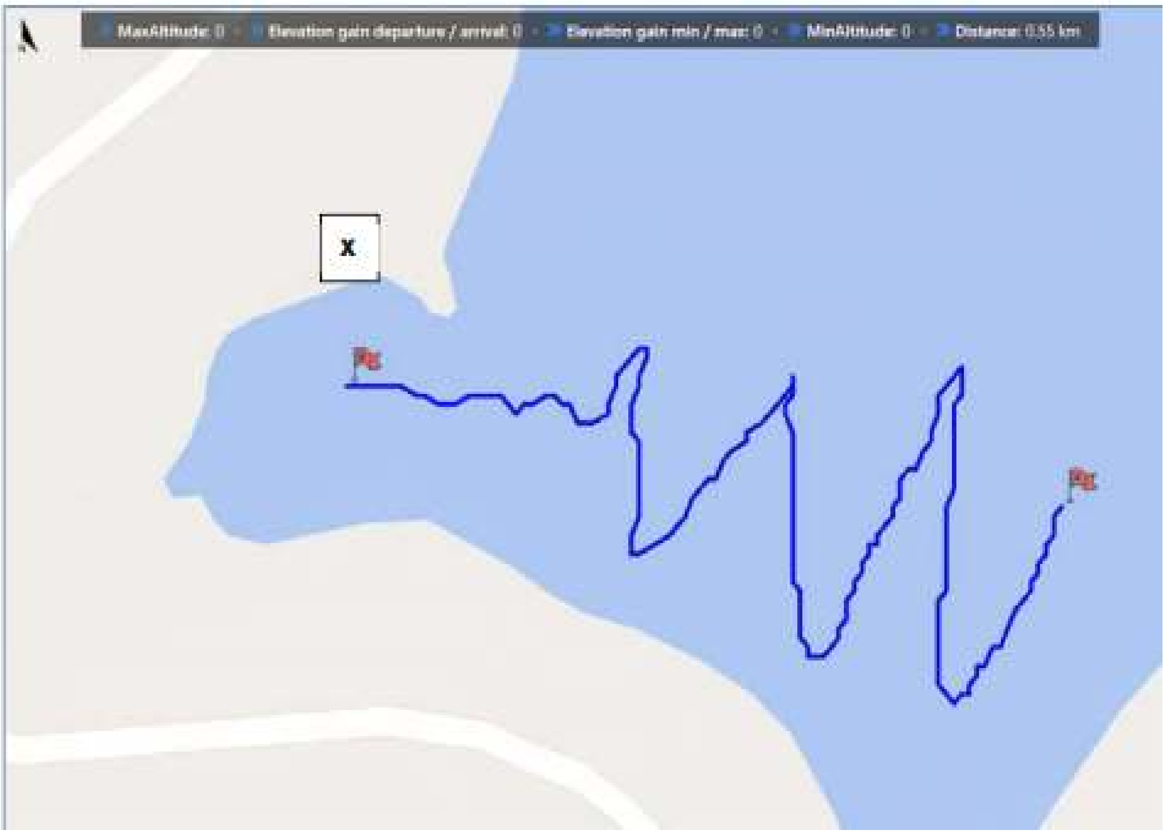

Figure 5. Example of zig-zag search pattern GPS track line: the total track line length is 550 m. The cross marks the location of the shore-side delivery system.

The compressor operation resulted in a humming noise from the device and visual bubbles. These could be cues to the canine. Through repeatition of training sessions the canine could learn that the start of the compressor (noise) and the bubbling are associated with the location of the odor. While this is not an issue in the early stages as it provides the canine information to search, it can become an established cue to the canine that odor is present. In a field deployment these clues would be absent and therefore mitigation is required. To resolve the potential issue of noise and bubbles the compressor was changed to a passive air tank. The battery-powered air compressor was replaced with a 5-gallon California Air Tools aluminum air tank. The air tank allowed for silent operation and, with a control value, allowed for the manual control of air supply. This provided a low level of bubbled air and intermittent flow as desired during the training steps. The tank provided approximately 15-minutes of continuous use airflow, which was sufficient for up to four training sessions.

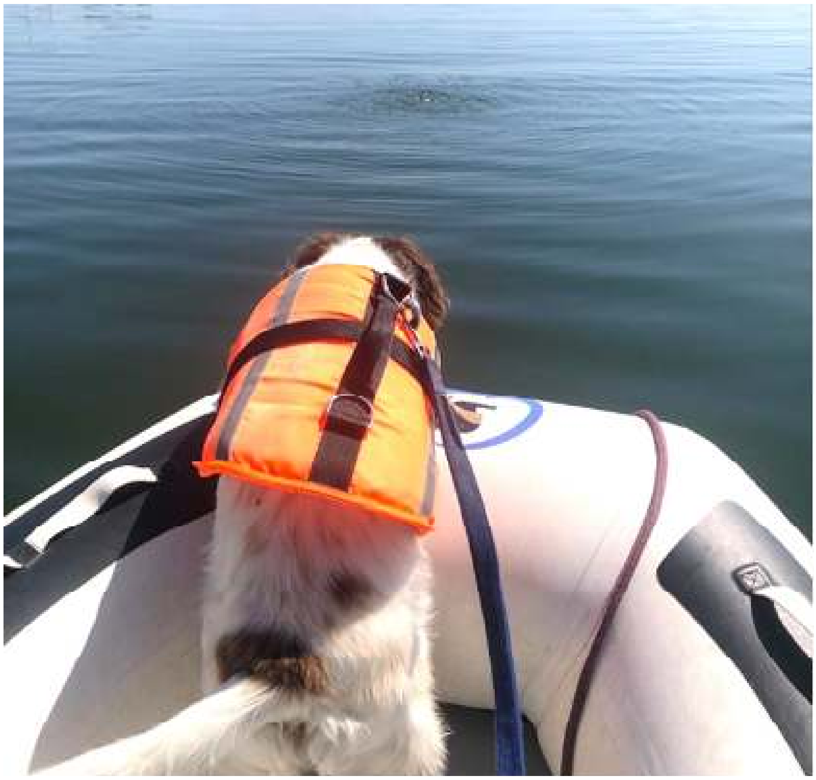

Figure 6. On-water subsurface oil odor detection training with the pipe anchored to the lakebed. Note: Odor bubbles can be seen surfacing directly ahead of the boat.

In the final phase of the training, the canine was encouraged to communicate the direction to the source to the trainer. The trainer would maneuver the boat in the zig-zag pattern across the scent plume to achieve this. As the canine demonstrated that it had detected the plume, the trainer would steer the boat to point at the source. At this point, the canine was at the front of the boat and within the scent plume. The boat was then steered to the right; the canine moved around to the left to remain in the plume. The boat was steered left, and the canine would move right to again, stay in the plume. As the boat passed the plume's center, the canine would continue to the right side of the boat. This process was repeated, so the canine developed the behavior of steering the boat by locating its body at the bow of the boat.

4 Headspace Analysis

Headspace analysis was accomplished using a previously optimized solid phase microextraction (SPME) coupled with gas chromatography and mass spectrometry (GC-MS) method. The headspace of WTI was generated and analyzed in the following environments: 1) 20 mL VOA vial, 2) Training Aid Delivery Device (Maughan, 2020) 3) TADD immersed in water, and 4) lab-based underwater training device. In each environment, 10 mL of WTI was placed inside the respective container and allowed to equilibrate for 20 minutes at 35 °C, with the exception of the lab-based underwater training device due to the large size of the bucket. Following equilibration, the headspace of each sample was extracted for 10 minutes using a 100 μm polydimethylsiloxane SPME fiber. The analytes were desorbed from the SPME fiber by injecting the fiber into the heated inlet (260 °C) of the GC followed by separation and detection of the analytes in the MS. An Agilent 7890A GC was used with a Rtx-Volatiles column (Restek

Co.) and a 10:1 split ratio with a flow rate of 40 mL/min. The oven method started at 40 °C, increased at 8 °C/min to 80 °C, followed by 5 °C/min to 200 °C, and ended with a 0.5 minute hold. The transfer line to the MS (Agilent 5975C) was set to 250 °C with a scan range of *m/z* of 30 – 300.

5 Results and Discussion

A practical training device for the environmentally safe underwater delivery of target oil odors has been developed and successfully field-tested in a shallow lake environment. The device and training protocols provided an opportunity to demonstrate the effectiveness of an ODC to be deployed from a boat to detect subsurface targets. In addition, training techniques were designed so that the canine developed the ability to communicate to the boat operator the direction to the source once the odor plume had been detected, rather than the handler relying on observed changes in canine behavior to steer the boat.

The headspace of WTI was generated in four different environments to first determine if an odor was readily available and then determine if the presence of water would affect this odor profile. Headspace analysis of WTI, WTI in a TADD, WTI in a TADD underwater, and WTI in lab-based underwater training device provided great insight on effects of water to the odor profile (Fig. 6). For instance, the headspace of WTI and WTI in a TADD were similar, which indicated that changing the containment did not affect the VOCs readily available in the headspace. In contrast, the headspace of WTI in a TADD compared to that of WTI in a TADD immersed in water was significantly different. In this regard, most of the odor was lost when immersed in water, and the few peaks seen in the chromatogram were due to siloxanes associated with the SPME fiber. Therefore, the presence of water significantly affects the headspace of crude oil. However, the headspaces of WTI in a TADD immersed in water and in the underwater device were extremely similar, which indicated that water has the same effect on the headspace of crude oil regardless of the containment size and that the device is working properly to deliver the available odor. It is acknowledged that a canine trained on the headspace of oil bubbled through water would have a different profile than actual spilled oil sequestered within the sediment. However, it is hypothesized that sequestered spill oil has a greater abundance of odor, than the bubbled headspace, due to the dispersion in the water column, rising to the surface and being available to the canine for detection. This is caused either through evaporation from the water surface or held within a footprint on the surface. The experience of canines detecting sequestered oil underwater despite not being trained to do so adds support to the hypothesis.

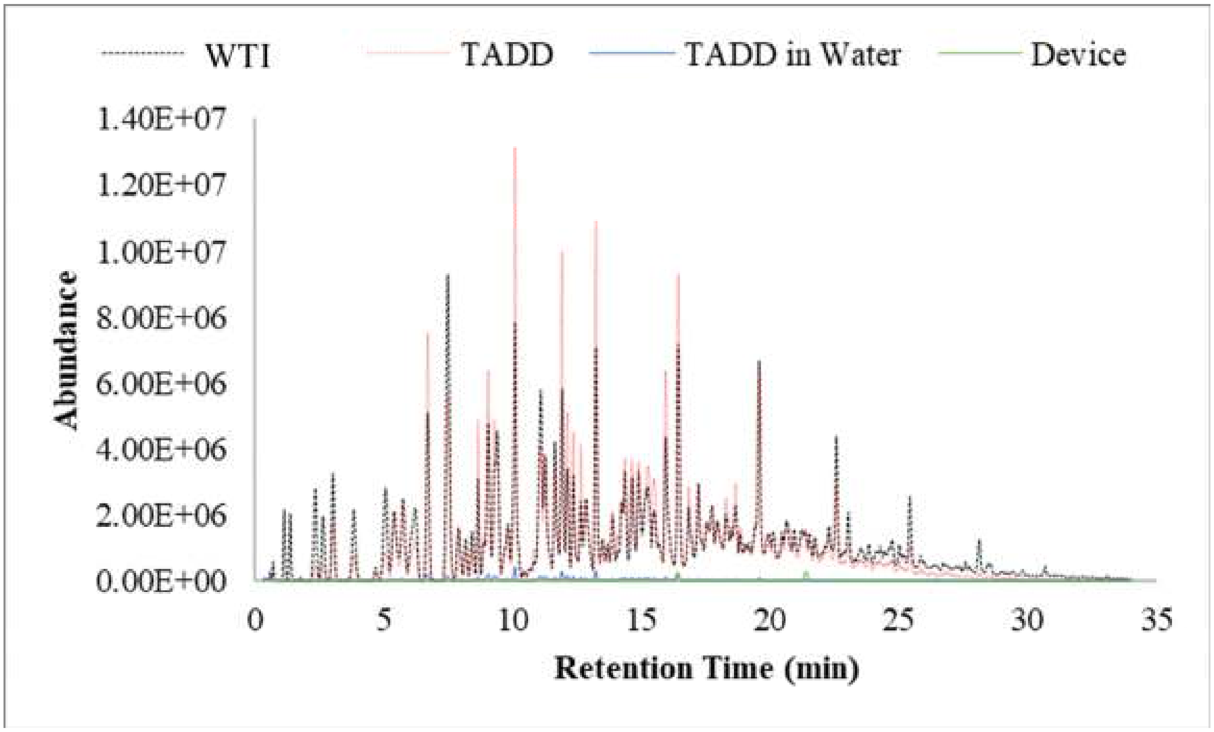

Figure 7. Overlaid chromatograms of WTI crude oil in different containments for comparison of extracted headspace.

Additionally, the device was developed to allow the training of a canine to search from the front of a boat and detect the target source within a water source. The techniques of searching from a boat, detecting a target plume, alerting the handler, and guiding the boat to the source are critical components in the detection sequence. Therefore, the headspace from the device not being the same as the headspace of sequestered oil is not a significant factor in the success of the proof-of-concept research trials. This demonstrates the sensitivity, in comparison to instrumentation, of trained ODCs.

ODCs have demonstrated generalizing capabilities to all variations of hydrocarbon, including fresh to heavy weathered and light, sour, and crude samples in training, research and field deployments (API, 2020; Owens & Bunker, 2022). It has been demonstrated that canines will respond to any presentation of a hydrocarbon despite never having been trained previously to that oil. This generalization capability suggests that the device headspace profile is not critical in field-deployed detection capability.

6 Conclusions and Future Work

The research project demonstrated the capability to utilze an underwater training device to train a canine in searching from both the shoreline and a boat. The device ensured there was no contamination of the water source providing an environmentally friendly system for canine training. The enhancement of an ODC capability provides another deployable tool in the oil spill response toolbox. Future research could include a series of controlled still-water and flowing-water field trials based on calculated parameters and models for (1) rise times for the gas, (2) the radii of the surface plume areas, and (3) current transport drift distances. Uncontrolled trials could be conducted to demonstrate the capability to transfer the detection capability of the canine from training to field deployments.

7 Acknowledgments

The author wishes to thank the Bureau of Safety and Environmental Enforcement (BSEE) for funding the project and the support of the Naval Research Lab (NRL).

8 Distribution Statement

U.S. Naval Research Laboratory (NRL) distribution statement A; Approved for public release: distribution unlimited.

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