Canine Oil Detection (K9-SCAT) following 2015 Releases from the T/V *Arrow* Wreck

E.H. Owens[1], H.C. Dubach[1], P. Bunker[2], S. MacDonald[3], Z. Yang[4], P. Lambert[4] and S. LaForest[4]

[1] Owens Coastal Consultants (OCC), 755 Winslow Way East, Suite 205, Bainbridge Island WA 98110, USA
[2] K2 Solutions Inc., Southern Pines NC, USA
[3]Triox Environmental Emergencies, Montreal QC, Canada
[4] Environment and Climate Change Canada, Ottawa ON, Canada

Abstract
The T/V *Arrow* sank in 1970, spilling Bunker C fuel oil into Chedabucto Bay, Nova Scotia. In the summer and fall of 2015, residual oil leaked from the sunken vessel and re-oiled shorelines in the Bay. A K9-SCAT field study, funded by Environment and Climate Change Canada (ECCC), was conducted in June 2016 to assess the capability of detection canines to locate stranded oil following the new releases. The canine detected small amounts of weathered surface oil that were barely visible, and in some cases, not visible, to the SCAT-trained observers, as well as subsurface oil on mixed- and coarse-sediment beaches. The average speed of a survey, in terms of the length of shoreline covered, varied depending on the shore type and the width of the survey band. The most challenging site was a steep bedrock shoreline with an alongshore survey rate of 0.2 linear km/hour. Typical alongshore coverage rates for the wide, mixed sediment were in the range 0.7 to 1.2 linear km/hour, and for both straight, wide sand beaches were 1.2 km/hour. The highest alongshore rate was 2.4 linear km/hour for the narrow beach on Janvrin Island. The successful detection of 2015 T/V *Arrow* cargo oil (both naturally stranded and intentionally planted) on selected Chedabucto Bay shorelines indicates that there is a low risk, high confidence level that the canine did not miss subsurface oil, although that possibility may exist. Where the canine made an alert and no surface oil was visible, chemical analyses of sediment samples indicated that weathered petroleum hydrocarbons were present at those locations and, therefore, the canine had made correct alerts. The results provide further "proof of concept" for K9-SCAT teams to support surface and subsurface oil detection during traditional shoreline assessment surveys.

Introduction
Program Objectives
The objective of the2016 K9-SCAT program was to conduct a shoreline survey to determine the capability of detection canines to locate stranded oil following the releases of oil from the T/V *Arrow* wreck into Chedabucto Bay, NS, during the summer and fall of 2015.The survey was conducted as part of a broader ECCC field study and sampling project on the shorelines of Chedabucto Bay, NS. This K9-SCAT component of the ECCC program provided an opportunity to participate in a "spill of opportunity" research study and to evaluate the capabilities of a K9-SCAT team in a real-world, oiled shoreline situation.

Background

Several trials and field tests have been conducted in recent years to evaluate the potential for canines to detect and delineate spilled oil (Brandvik and Buvik, 2009; API, 2016a; Owens et al., 2016). Only one post-spill oiled shoreline survey had been conducted prior to this study; in Norway, during November 2008 following the January 2007 M/V *Server* spill (Buvik and Brandvik, 2009).

The targets for this field study were residual Bunker C cargo oil that leaked during the summer and fall of 2015 from the T/V *Arrow*, which originally sank on Cerberus Rock in Chedabucto Bay, NS, in February 1970. Although a systematic ground SCAT survey was not conducted following the releases in 2015, some of that oil was observed by shoreline reconnaissance SCAT teams based on data from aerial observations and oil spill modeling results.

Survey Objectives and Priorities

The objectives of the K9-SCAT survey were to field test the ability and effectiveness of a detection-trained canine to locate and to communicate an alert for surface and/or subsurface oil on shorelines from a marine spill of Bunker C that had occurred approximately 9 months earlier.

The surveys were "double-blind", that is, neither the canine nor the handler knew where oil could be expected. One team member (SM) was involved in the 2015 SCAT surveys, and was familiar with locations where the team could find residual oil. However, this knowledge was not shared with the rest of the team until after the K9-SCAT survey for each location. The Indian Cove and Eddy Point surveys could be regarded as "triple-blind", as no-one on the team had any information concerning these beaches, other than the fact that they were in the potential affected area, but they had not been visited by the 2015 SCAT program.

Field Program

K9-SCAT surveys were conducted over four days, 31 May to 3 June 2016, on selected shorelines in Chedabucto Bay.

- A number of representative and accessible segments were chosen for the K9-SCAT surveys; some of which were known to have been oiled in 2015, some of which were known to have not been oiled in 2015, and some of which had not been surveyed in 2015.
- The survey team comprised a K9-SCAT Team Lead, Canine Handler and a Detection Canine. The project team comprised a project manager, canine technical advisor, and ECCC observers.
- The surveys were conducted during tides with predicted (and actual) water levels lower than+0.3m during daylight hours (maximum tidal range is 2m), to ensure that the full intertidal zone was surveyed by the canine team.
- The canine was initially imprinted on fresh (liquid) oil from the T/V *Arrow* bunker fuel cargo tanks collected from the vessel in 2015. The released 2015 oil had weathered significantly since it had stranded approximately 9 months prior to the survey. This project therefore tested the ability of the canine to recognize the odor of the 2015 weathered oil by associating components from the fresh, imprinted oil.

- Samples of fresh oil from the vessel and weathered oil collected from the shoreline were used to "plant" targets to calibrate and test the canine's ability to detect small quantities of the target oil. The planted targets were picked up once found by the canine.
- Search techniques and patterns identified during API canine oil detection field trails (API, 2016a) were used and adapted for Chedabucto Bay shorelines.
- The canine handler watched for "alerts", where the canine sits or lays down at the odor source, or for changes in behaviour of the canine, indicating that the canine has identified the target odor and is working to locate the source. A canine may also have change of behaviour in an area where s/he has detected the odor but has not pinpointed a point source; this may occur when the canine is in an area with multiple points of oiling, e.g. tar balls, splatters of oil, or subsurface oil deposits.
- Survey challenges for the canine, and for humans, included steep bedrock and backshore areas, steep beach-face slopes, large (cobble, boulder) sediments, slippery surfaces (e.g. boulders/cobbles covered with wet algae), and rough surfaces (such as barnacles).

Environmental Setting

The shorelines of Chedabucto Bay are characterized by bedrock outcrops and mixed, coarse-sediment beaches (Owens, 1971; Owens, and Bowen 1977). The coastal environment experiences cold winter and cool summer, and ice forms on nearshore waters for 3-4 months each year.

Canines analyze the scent in odor plume to locate targets so that micrometeorological data collected during the study period are important. Table 1 summarizes the range of some of the key parameters that were measured at the shoreline, immediately adjacent to the work zones, for the duration of the K9-SCAT surveys.

Table 1 Summary of Micrometeorological Data during the K-9 SCAT Surveys

	Cross Wind (km/h)	**Alongshore Wind (km/h)**	**Air Temp. (°C)**	**Relative Humidity (%)**	**Barometric Pressure (bar)**
Maximum	7.9	14.3	13.8	69.7	1.0172
Average	5.6	6.7	12.6	68.3	1.0170
Minimum	2.1	0.2	11.2	65.9	1.0169

The tides of the area are mixed semidiurnal, ranging between 1.1 and 1.7m. The study was conducted immediately prior to a spring tide full moon (4 June 2016).

Survey Locations

Much of the coastline in Chedabucto Bay is not readily accessible or amenity shoreline. The K9-SCAT survey program covered selected accessible segments, including bedrock, coarse mixed-sediment beaches and boulder beaches (Figure 1, Table 2). These locations were selected based on the potential of surface and subsurface oil remaining from the 2015 T/V *Arrow* cargo spill. Sites also were selected that were unlikely to have oil remaining from either release, and which were intended for "clearance" survey missions to better understand the speeds at which such surveys can be completed.

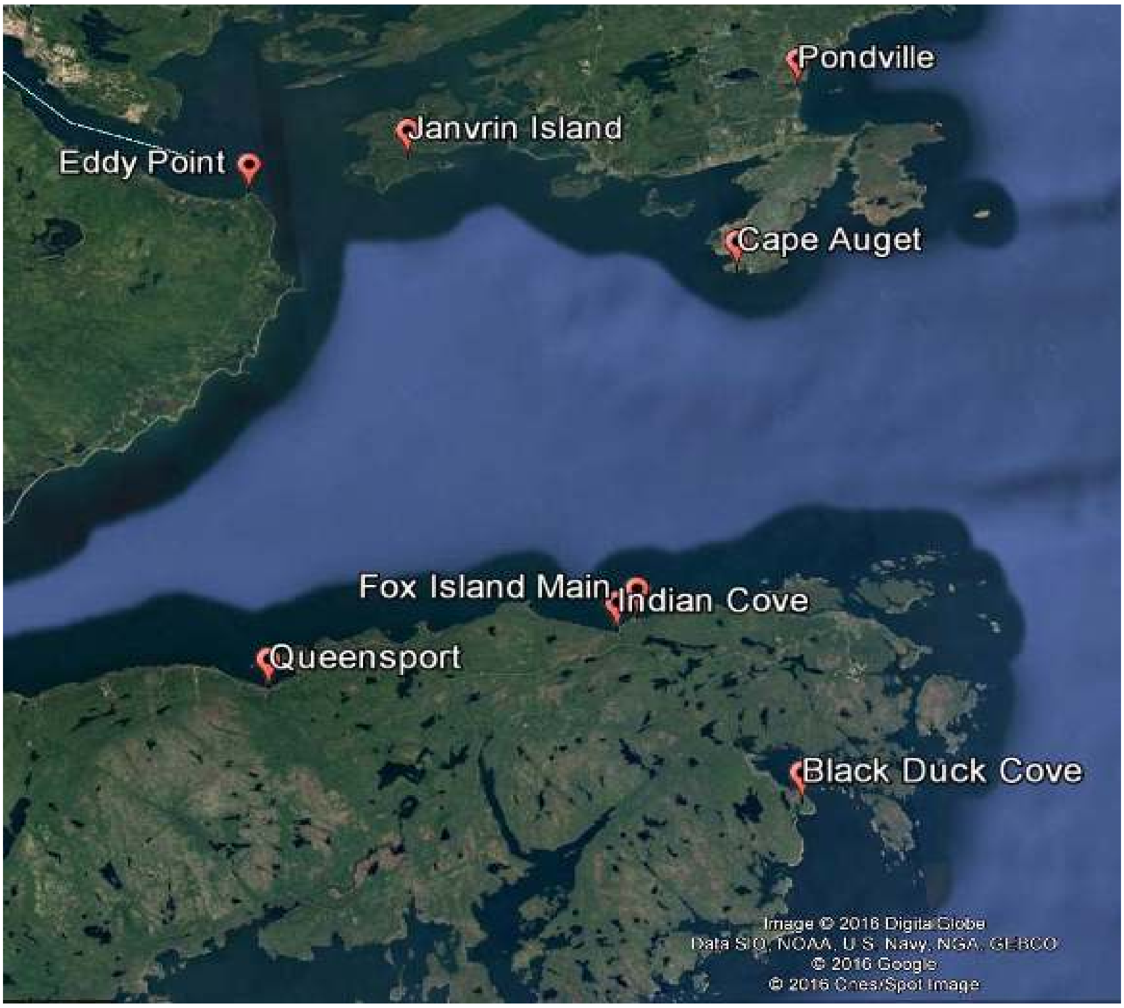

Figure 1 Map showing the K9-SCAT survey sites in Chedabucto Bay

Table 2 K9-SCAT Survey Locations

Location	Shoreline Type
Black Duck Cove	Wide, sand pocket beach
Cape Auget	Steep bedrock ramp; boulder, coarse (pebble/cobble) sediments
Eddy Point	Wide, mixed sand, pebble, cobble beach
Fox Island Main	Wide, mixed coarse-sediment (pebble/cobble) beach
Indian Cove	Wide, mixed coarse-sediment (pebble/cobble) beach
Janvrin Island	Narrow, mixed sand, pebble, cobble beach
Pondville	Wide, mixed coarse-sediment beach and boulder shoreline
Queensport	Mixed coarse-sediment beach and boulder shoreline

Target Oil Imprinting

A sample from the T/V *Arrow* cargo collected from the vessel in 2015 was provided to the team on the morning of the first day of the surveys (31 May) and the canine was imprinted in the field at the first site (Cape Auget). This sample was also used to test the canine intermittently during the field program by planting samples for the canine to detect. Weathered samples of stranded 2015 T/V *Arrow* oil were also collected from the shoreline and used to imprint and test the canine on the weathered oil.

SurveySite Selection

Eight locations with 15 separate shoreline areas were selected to test different mission objectives:

a. <u>Wide Area Searches</u> in two locations that had no recent oiling history (Black Duck Cove Park, Pondville) and that were distant from the 2015 releases, and two that were potentially in the 2015 affected area but had not been surveyed at the time (Eddy Point, SE Janvrin Island),
b. <u>Detection Surveys</u> at three locations surveyed in 2015 that were known to have been oiled from the releases (Cape Auget, Fox Island Main, Queensport), and
c. <u>Detection Survey</u> on a pocket beach in the area known to have been affected by the 2015 releases but that had not been surveyed at that time (Indian Cove).

Survey Data

The unprocessed data from the field project include:

- Completed K9-SCAT survey forms
- Completed oiling verification forms (SOS forms)
- Canine collar GPS track line data
- Waypoints (start of segment, end of segment, alerts, pits)
- Photographs (showing segment information, environmental conditions, alerts, oiling)
- Videos
- Micrometeorological data

A total of 15 surveys were conducted during the four days of the project. Of these, 4 surveys involved planting a sample of the 2015 T/V *Arrow* oil from the vessel to imprint or test the canine (survey #s 2, 3, 5, and 13; survey #2 involved 3 planted targets). Table 3 summarizes the times, distances, and speeds for each survey. In this table, the Alongshore Distance is the length of the surveyed location, derived from GPS waypoints, and the Estimated Survey Band Width is the approximate across-shore width that was surveyed.

Survey Track Lines, Distances, and Speeds

The canine collar with a Garmin Astro 320 GPS unit tracked the search pattern (Figures 2, 3, 4 and 5; Table 3).

Table 3 Survey Times, Distances and Speeds

Date	Survey #	Location	Survey Time (mins)	Alongshore Distance Surveyed (m)	Estimated Survey Band Width (m)	Actual Track Length (km)	Track Line Speed (km/h)
31-May-16	1	Cape Auget	25	77	20	1,300	3.1
	2	Pondville West	23	456	20	2,200	5.7
	3	Pondville East	3	73	20	365	7.3
	4	SE Janvrin Is.	9	353	5	552	3.7
	5	SE Janvrin Is.	3	100	5	169	3.4
01-Jun-16	6	Black Duck Cove	13	250	25	1,400	6.5
	7	Fox Is. Main Central	20	175	25	1,300	3.9
02-Jun-16	8	Fox Is. Main West	34	200	15	1,800	3.2
	9	Fox Is. Main East	13	330	20	1,200	5.5
	10	Fox Is. Main West/Central	23	380	15	1,300	3.4
	11	Indian Cove	27	270	20	1,100	2.4
03-Jun-16	12	Queensport East	16	195	10	957	3.6
	13	Queensport East	12	175	10	576	2.9
	14	Queensport West	17	225	10	857	3.0
	15	Eddy Point	27	520	10	1,300	2.9

Figure 2 Plot of canine survey coverage –survey #7: the shoreline length is 175 m, the total track line is 1,300 m, and the total area surveyed is 4,375 m^2 (Map Data: Google, DigitalGlobe)

Figure 3 Calibrating the canine collar unit to a GPS

Figure 4 Off-leash survey on a wide, mixed coarse sediment beach, Fox Island Main (site # 8)

A detailed example of the raw data with GPS position fixes every 5 seconds is provided in Figure 5. In this example, on a steep bedrock shore at Cape Auget (Figure 6), the shoreline site alongshore length (thin yellow line) is 77m, the total length of the track lines (blue lines) is 1,300m^2, and the survey lasted 25 minutes. The data output includes 6 numbered waypoints (#1 through 6) taken by the K9-SCAT Team Lead. A close up of the track line data (Figure 5b) shows the actual position fixes by the GPS on the canine's collar and the direction of movement.

The canine enters the search area from the northeast (red arrow); initially sits while waiting for instruction to proceed from the Handler (the red circled area with approximately 10 square symbols: as the canine was stationary, the variance represents the GPS "drift"); and proceeds to search as recorded by the blue track line; the direction of movement is indicated by the blue arrows.

Micrometeorological Data

A portable micrometeorological station (with wind vane and tripod) was set up above the high-tide line immediately adjacent to the survey work area. The instrument height was set at approximately 100cm and the following data was recorded at each survey site for the duration of each work period: wind direction, wind speed, temperature, relative humidity, and barometric pressure.

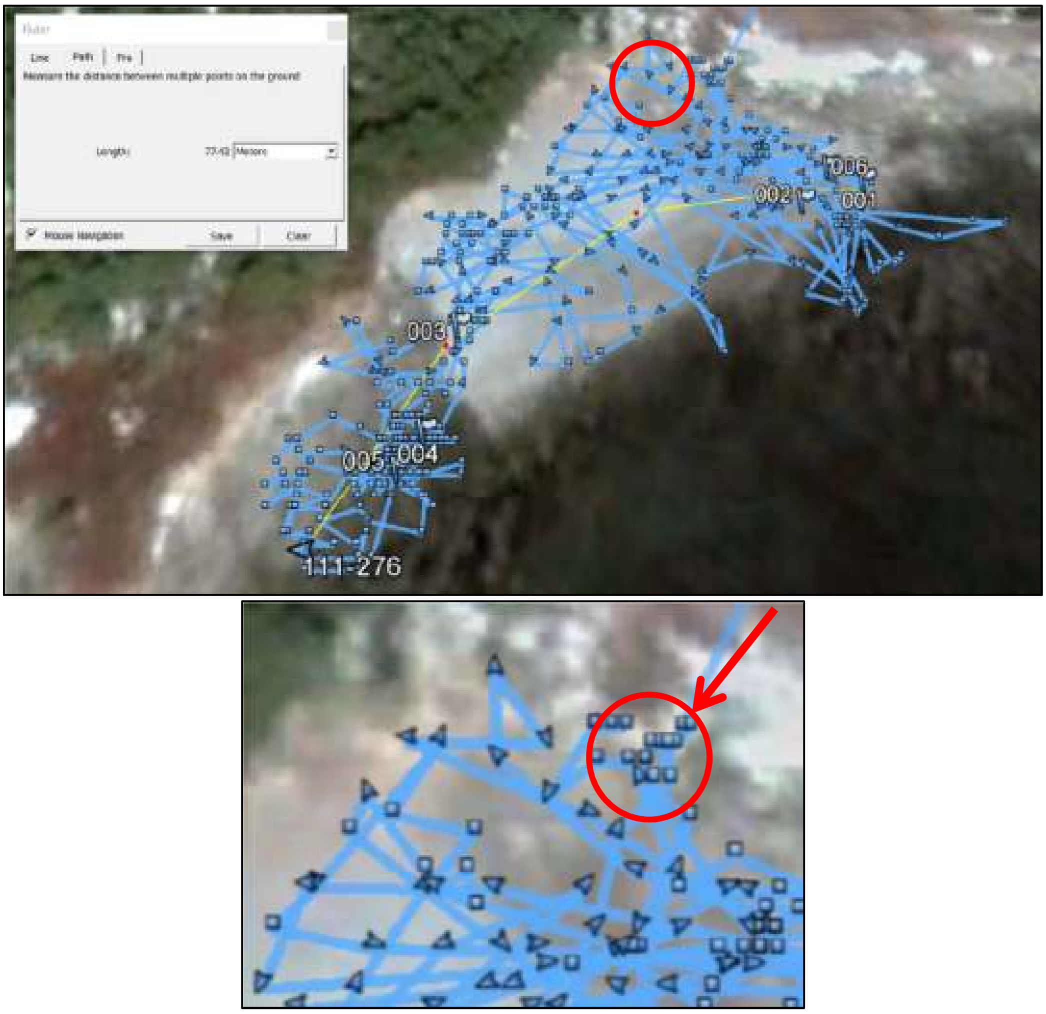

Figure 5 (a) compilation of track lines and waypoints, Cape Auget (Site # 1), 31 May 2016; (b) close up of upper central area with detail on the initial set up and survey fixes (Map Data: Google, DigitalGlobe)

Figure 6 Steep bedrock shoreline, Cape Auget (site # 1); note the canine is wearing protective footwear

Data processing provided with the station enables computation of a range of parameters that can assist understanding and interpretation of the behavior of odor plumes and a canine's actions at a study site. The computed data include: the shoreline "Cross Wind" and the "Alongshore Wind" speeds (Table 1); wind chill temperature; heat stress index; and dew point.

Weather and micrometeorological conditions did not negatively affect the planned program as the recorded temperatures during the surveys were mild (+10 to +14°C) and winds speeds typically above calm (0), but low (<10 km/h: 3 m/s) (Table 1).

K9-SCAT Detection Results

Clearance Survey Missions

Four missions were conducted at locations with no recent (2015) oiling history (Table 4):

- Pondville was outside the 2015 potentially affected area.
- SE Janvrin Island and Eddy Point and were within the 2015 potentially affected area, respectively northwest and north of the T/V *Arrow* spill site (Cerberus Rock), but not surveyed at that time, and
- Black Duck Cove Park was inspected as part of the 2015 T/V *Arrow* SCAT program with No Observed Oil at the time.

Cargo oil collected from the wreck in 2015 was used as near-surface (<5cm) targets at the Pondville and Janvrin Island locations. All planted near-surface targets were successfully detected.

Table 4 Summary of K9-SCAT Clearance Mission Results

Pondville Survey #s: 2 (east) 3 (west)	• Shoreline type: Wide, long sand beach • 2015 observations: Not surveyed • 2016 K9-SCAT: o survey #2: 2015 *Arrow* surface target oil planted at three locations; detected o survey #3: one 2015 *Arrow* surface target oil planted; detected
SE Janvrin Island Survey #s: 4 and 5	• Shoreline type: Sheltered, narrow (<5m), low-energy beach • 2015 observations: Not surveyed • 2016 K9-SCAT: o survey #4: No Detected Oil (NDO) o survey #5: one 2015 T/V *Arrow* near-surface target oil planted; detected
Black Duck Cove Survey #6	• Shoreline type: Sand pocket beach • 2015 observations: No Observed Oil (NOO) • 2016 K9-SCAT:NDO
Eddy Point Survey #15	• Shoreline type: Mixed sand, pebble/cobble, straight beach • 2015 observations: Not surveyed • 2016 K9-SCAT: canine alerted on 1cm COAT on pebble

Detection Survey Missions

Detection Survey missions were conducted at three locations where oil had been observed in 2015 and one (Indian Cove) that was not surveyed at the time but was adjacent to shorelines where oil had been observed (Table 5). The surveys at Fox Island Main and Queensport involved, respectively, four and three separate surveys due to the need to move between access points, and in part due to the low-tide windows. Sediment samples were collected by ECCC if the dog alerted and no surface oil was observed (NOO) by the survey team.

Survey Data

Survey data for each survey are summarized in Table 6.

Table 5 Summary of K9-SCAT Detection Mission Results

DETECTION SURVEYS ON BEACHES WITH OBSERVED OILING IN 2015	
Cape Auget Survey #1	• Shoreline: Small, coarse sediment, pocket beach with steep bedrock ramp (Figure 6) • 2015 observations: Oil observed • 2016 K9-SCAT: Very weathered ST/CV was observed on the bedrock
Fox Island Main Survey #'s: 7 (central) 8 (western) 9 (eastern) 10(west/central)	• Shoreline: Mixed sand, pebble/cobble beach (Figure 4) • 2015 observations: Oil observed • 2016 K9-SCAT: o survey #7: 2 alerts, NOO, sediment sample taken to verify alerts o survey #8: 5 alerts, surface oiling (SR and TB/P) detected, oil samples taken o survey #9: 2 alerts, NOO, sediment sample taken to verify alerts o survey #10: 1 alert, NOO, sediment sample taken to verify alerts
Queensport Survey #'s: 12 (east) 13 (east) 14 (west)	• Shoreline: Mixed sand, pebble/cobble beach • 2015 observations: Oil observed • 2016 K9-SCAT: o survey #12: 2 alerts, strong odor of oil in pit at 10cm, sediment sample taken to verify alerts and odor o survey #13: planted near-surface target; detected o survey #14: 2 alerts, surface tar balls detected
DETECTION SURVEY ON A BEACH WITHIN THE 2015 AFFECTED AREA, NOT SURVEYED AT THE TIME	
Indian Cove Survey #11	• Shoreline: Mixed sand, pebble/cobble pocket beach • 2015 observations: Not surveyed • 2016 K9-SCAT: 4 alerts, surface oiling (SR and TP) detected, oil samples taken

Table 6 Summary of Search Survey Data

	Total Survey Time (min)	Total Survey Alongshore Length(m)	Total Track Line Length (m)	Length: Track Line Ratio	Estimated Area Surveyed (m^2)	Average Alongshore Survey Speed (km/h)	Track Line Survey Speed (km/h)
CLEARANCE SURVEYS							
# 2 Pondville	23	456	2,200	4.8	9,120	1.2	5.7
# 3 Pondville	3	73	365	5.0	1,460	1.5	7.3
#4 Janvrin Island	9	353	552	1.6	1,765	2.4	3.7
#5 Janvrin Island	3	100	169	1.7	500	2.0	3.4
#6 Black Duck Cove	13	250	1,400	5.6	6,250	1.2	6.5
#15 Eddy Point	27	520	1,300	2.5	5,200	1.2	2.9
DETECTION SURVEYS							
#1Cape Auget	25	77	1,300	16.9	1,480	0.2	3.1
#7Fox Island Main	20	175	1,300	7.4	4,375	0.5	3.9
#8 Fox Island Main	34	200	1,800	9.0	3,600	0.4	3.2
#9 Fox Island Main	13	330	1,200	3.6	6,600	1.5	5.5
#10 Fox Island Main	23	380	1,300	3.4	5,700	1.0	3.4
#11 Indian Cove	27	270	1,000	4.1	5,400	0.6	2.4
#12 Queensport	16	195	957	4.9	1,950	0.7	3.6
#13 Queensport	12	175	576	3.3	1,750	0.9	2.9
#14 Queensport	17	225	857	3.8	2,250	0.8	3.0

Notes:

- Survey # 1 was the first survey, and was not a true search pattern as this involved many repeat sections.
- Survey # 8 repeated half of the survey area (i.e. covered approx. 1.5 times the survey alongshore length)

Sample Chemistry

The canine alerted in four locations where no oil was observed (NOO) by the field team. Sediment samples were taken for hydrocarbon analysis by ECCC at these alert sites. The oil samples underwent comprehensive laboratory analysis to identify and characterize the total gas chromatography detectable compounds, and individual n-alkanes, non-alkyalted polycyclic aromatic hydrocarbon, alkylated polycyclic aromatic hydrocarbon and biomarkers compounds by gas chromatography-mass spectrometer (Wang, 2015).

The Total Petroleum Hydrocarbon (TPH), n-alkane, biomarker, and PAH analysis results are provided in Tables 7, 8, 9 and 10. Note that two of the samples taken during the same survey were combined.

The processing and interpretation of the laboratory data to understand the composition of the oil itself is ongoing, however preliminary findings are discussed here:

- Weathered, petrogenic hydrocarbons were detected in all three of the samples.
- The TPH measured in the three sediment samples ranged from 10.7µg/g to 14,823µg/g, indicating a wide canine detection range, with a lower limit of 10µg/g TPH.
- The absence of n-C10 and low concentration of <n-C16 hydrocarbons in the samples indicate that the canine was able to detect weathered oil with a low volatile component.
- The ratios of total saturate hydrocarbon (TSH):TPH and total aromatic hydrocarbon (TAH):TPH is markedly different for the subsurface Queensport sample compared to the two surface Fox Island Main samples. This difference may indicate that the canine is able to detect oil that may have some variation in its chemical composition due to long term weathering.

For the individual samples:

- **Fox Island Main (Survey 7).** The source of the n-alkanes were predominantly from biogenic input, however biomarker results show the presence of notable and significant petroleum biomarkers in the two Fox Island Main samples. The presence of elevated presence of biomarkers may suggest that the oil contamination is historical at this site. A hypothesis is that over time, the long term weathering process may have caused the degradation of petroleum n-alkanes and polycyclic aromatic hydrocarbons, but the weathering resistant petroleum biomarkers (terpanes and steranes) remain.

- **Fox Island Main (Surveys 9 and 10)** was heavily contaminated by oil. It is notable that there is a heavy weathered pattern for alkylated polycyclic aromatic hydrocarbons and that the n-alkanes were non-detectable from C9 to C40.

- **Queensport (Survey 12)** had some subsurface oil contamination, and the APAHs pattern indicates a high degree of weathering. The presence of n-alkanes where the CPI index of the detected n-alkanes is high (up to 2.7) suggests a predominantly biogenic input for n-alkanes, however biomarker analysis results show minor petroleum biomarkers were detected in this subsurface sample.

Table 7 TPH Analysis Results

	Fox Island (Survey #7)	Fox Island (2 samples) (Survey #s 9&10)	Queensport (Survey #12)
	ug/g	ug/g	ug/g
TPH	10.7	14823	23.1
TSH	5.86	7483	1.53
TAH	4.85	7340	21.6
TSH/PHC (%)	54.7	50.5	6.63
TAH/PHC (%)	45.3	49.5	93.4
Resolved Peaks/PHC (%)	50.6	7.12	11.0
PHC range (%)			
<n-C10	0.00	0.00	0.00
n-C10-n-C16	1.94	1.39	0.64
n-C16-n-C34	50.1	66.0	52.2
>n-C34	47.9	32.6	47.2

Table 8 n-alkane Analysis Results

	Fox Island (Survey #7)	Fox Island (2 samples) (Survey #s 9&10)	Queensport (Survey #12)
Compounds	**ng/g**	**ng/g**	**ng/g**
n-C9	0.00	0.00	0.00
n-C10	0.00	0.00	0.00
n-C11	0.00	0.00	0.00
n-C12	0.00	0.00	0.00
n-C13	0.00	0.00	0.00
TMD	0.69	0.00	0.00
n-C14	3.36	0.00	1.16
n-C15	1.96	0.00	2.57
n-C16	1.25	0.00	0.74
TMP	0.00	0.00	0.00
n-C17	3.22	0.00	2.57
Pristane	1.10	0.00	0.40
n-C18	2.09	0.00	1.44
Phytane	1.04	0.00	0.46
n-C19	1.46	0.00	0.97
n-C20	1.89	0.00	1.17
n-C21	2.11	0.00	1.81
n-C22	1.63	0.00	1.32
n-C23	1.84	0.00	2.66
n-C24	2.74	0.00	2.11
n-C25	3.29	0.00	3.57
n-C26	2.44	0.00	2.28
n-C27	3.55	0.00	3.65

n-C28	2.24	0.00	1.79
n-C29	9.54	0.00	6.32
n-C30	2.03	0.00	1.29
n-C31	12.8	0.00	8.68
n-C32	1.33	0.00	1.04
n-C33	1.83	0.00	2.26
n-C34	0.96	0.00	0.00
n-C35	1.20	0.00	0.00
n-C36	1.23	0.00	0.00
n-C37	1.45	0.00	0.00
n-C38	1.24	0.00	0.00
n-C39	1.30	0.00	0.00
n-C40	1.35	0.00	0.00
Total n-alkanes (ng/g)	**74.1**	**0.00**	**50.3**
Diagnostic indexes			
n-C17/Pristane	2.93	/	6.44
n-C18/Phytane	2.00	/	3.13
Pr/Ph	1.05	/	0.86
Odd alkanes	45.5	0.00	35.1
Even alkanes	23.1	0.00	13.2
CPI	1.97	/	2.66

Table 9 Biomarker Analysis Results

	Fox Island (Survey #7)	**Fox Island (2 samples) (Survey #s 9&10)**	**Queensport (Survey #12)**
Biomarker compounds	**ng/g**	**ng/g**	**ng/g**
C21 terpane	0.59	1665	0.00
C22 terpane	0.37	467	0.00
C23 terpane	0.88	3169	0.00
C24 terpane	0.80	2166	0.00
C27 Ts	0.91	3008	0.10
C27 Tm	1.39	6269	0.15
C29 ab Hopane	4.86	23226	0.48
C30 ab Hopane	4.66	23946	0.37
C31(S) hopane	2.42	9085	0.23
C31(R) hopane	2.05	7212	0.19
C32(S) hopane	1.39	5804	0.00
C32(R) hopane	0.97	4300	0.00
C33(S) hopane	0.81	3924	0.00
C33(R) hopane	0.45	2483	0.00
C34(S) hopane	0.54	2913	0.00
C34(R) hopane	0.29	2038	0.00
C35(S) hopane	0.31	2117	0.00
C35(R) hopane	0.18	1545	0.00
C27aßß steranes	2.04	6766	0.00

C28aßß steranes	6.54	6815	0.00
C29aßß steranes	10.1	10659	0.35
Total	**42.6**	**129577**	**1.88**
Diagnostic Ratios			
C23/C24	1.10	1.46	/
C23/C30	0.19	0.13	0.00
C24/C30	0.17	0.09	0.00
C29/C30	1.04	0.97	1.30
C31(S)/C31(R)	1.18	1.26	1.19
C32(S)/C32(R)	1.43	1.35	/
Ts/Tm	0.65	0.48	0.66
C27abb/ C29abb	0.20	0.63	0.00
C30/(C31+C32+C33+C34+C35)	0.49	0.58	0.88

Table 10 PAH Analysis Results

		Fox Island (Survey #7)	**Fox Island (2 samples) (Survey #s 9&10)**	**Queensport (Survey #12)**
Alkylated PAHs		**(ng/g sample)**	**(ng/g sample)**	**(ng/g sample)**
Naphthalene	C0-N	0.47	19.3	0.51
	C1-N	1.67	26.4	0.64
	C2-N	3.46	95.6	2.35
	C3-N	1.38	1071	1.54
	C4-N	0.00	3587	0.91
	Sum	**6.98**	**4799**	**5.95**
Phenanthrene	C0-P	2.26	0.00	4.58
	C1-P	1.30	0.00	2.82
	C2-P	0.71	2732	1.78
	C3-P	0.65	9877	0.00
	C4-P	0.00	9160	0.00
	Sum	**4.92**	**21769**	**9.18**
Dibenzothiophene	C0-D	0.17	37.9	0.45
	C1-D	0.24	768	0.83
	C2-D	0.52	7484	1.97
	C3-D	0.49	19194	2.09
	Sum	**1.42**	**27484**	**5.34**
Fluorene	C0-F	0.33	0.00	0.46
	C1-F	0.00	0.00	0.72
	C2-F	0.00	1119	0.00
	C3-F	0.00	4634	0.00
	Sum	**0.33**	**5753**	**1.17**
Fluoranthene	C0-Fl	0.55	0.00	6.46
	C1-Fl	0.00	1537	3.28
	C2-	0.00	4078	4.20

	Fl			
	C3-Fl	0.00	6767	7.76
	C4-Fl	0.00	5873	6.39
	sum	**0.55**	**18256**	**28.1**
Benzonaphthothiophene	C0-B	0.00	621	1.77
	C1-B	0.00	6401	5.64
	C2-B	0.00	18779	8.18
	C3-B	0.00	23178	30.8
	C4-B	0.00	17073	40.4
	Sum	**0.00**	**66052**	**86.8**
Chrysene	C0-C	0.16	1283	3.20
	C1-C	0.00	2452	2.52
	C2-C	0.00	5986	4.78
	C3-C	0.00	7142	11.7
	Sum	**0.16**	**16863**	**22.2**
Total alkylated PAHS		**14.4**	**160976**	**159**
Other Priority PAHs				
Biphenyl (Bph)	Bph	0.25	0.00	0.35
Acenaphthylene (Acl)	Acl	0.05	0.00	0.48
Acenaphthene (Ace)	Ace	0.08	14.4	0.11
Anthracene (An)	An	0.11	0.00	0.64
Fluoranthene (Fl)	Fl	0.50	9.1	6.17
Pyrene (Py)	Py	0.33	508	5.33
Benz(a)anthracene (BaA)	BaA	0.06	0.00	2.55
Benzo(b)fluoranthene (BbF)	BbF	0.06	173	3.07
Benzo(k)fluoranthene (BkF)	BkF	0.02	0.00	1.11
Benzo(e)pyrene (BeP)	BeP	0.06	557	2.79
Benzo(a)pyrene (BaP)	BaP	0.03	105	2.51
Perylene (Pe)	Pe	0.30	72.9	0.88
Indeno(1,2,3-cd)pyrene (IP)	IP	0.00	18.5	1.36
Dibenzo(ah)anthracene (DA)	DA	0.00	67.9	0.45
Benzo(ghi)perylene (BgP)	BgP	0.08	88.2	1.83
Total EPA priority PAHs		**1.92**	**1614**	**29.6**
Total aromatic compounds		**16.3**	**162589**	**188**

Discussion

<u>Canine Detection</u>

The canine was able to detect small amounts of weathered surface oil that were barely visible (in some cases, not visible)to the SCAT-trained observers, as well as subsurface oil stranded from the 2015 *Arrow* releases. Specifically, the canine detected:

- small (<~1cm diameter) surface oil residues (SR) on sediments in situations where that oil was not immediately obvious to experienced SCAT observers;
- subsurface oil with an odor footprint on the order of 20m by 10m; and
- targets that had been intentionally planted.

The successful detection of both naturally stranded and intentionally planted 2015 *Arrow* cargo oil on the beaches of Fox Island Main, Indian Cove, and Queensport indicates that there is a low risk, high confidence level that the canine did not miss subsurface oil, although that possibility exists. Oil may have been present both on the surface and in subsurface sediments, which may have confounded the canine and the handler. It is possible that the team may have missed some subsurface oiling in an area where there was also surface oil, due to the focus on the surface oil, which is likely to yield a stronger odor.

Where surface oil was not observed at a canine alert site, chemical analysis indicates that weathered petroleum hydrocarbons were present and that, therefore, the canine made correct alerts.

Further study is required to relate the capability of the canine to the detailed laboratory chemical analysis.

Survey procedures involve a close coordination and understanding between the K9-SCAT Team Lead and the Canine Handler. This relationship, as well as the communication link between the handler and the canine, is a key ingredient for a successful survey. As the survey progressed, the handler and the canine became more efficient, in terms of the search pattern, and the Team Lead became more aware of the changes in canine behavior that led to "alerts" and "changes of behaviour".

<u>Canine's Abilities and Canine/Handler Communication</u>
An important element of the study was for SCAT personnel to better understand how the canine and the handler operate and communicate. Some of the learning items include:

- The canine had not been trained to visually recognize oil deposits, only to detect the molecules in an odor plume that would match T/V *Arrow* cargo oil that had been collected from the vessel in 2015. In one instance (Indian Cove), it was evident that the canine did not see the oil, even though it was on the surface of a pebble. Rather, he detected a pocket of odor that had been trapped and pooled behind a branch about 1maway from the source of the odor. Once the canine detected this odor plume, which matched the imprint, he alerted this fact to the handler who flagged the location. The SCAT observers inspected the location and found the source.
- The handler is the crux of the investigation as s/he constantly reads the canine's behavior and watches for changes of behaviour and signals from the dog.
- The handler makes an initial assessment of the survey location prior to the search. During this phase s/he observes the wind direction, the boundaries of the search area, identifies any potential hazards or risks to the team, seeks likely productive search areas, and develops a mental search plan.

Other specific points related to the canine's ability that were learned include:

- An "alert" is a clear signal to the handler for point sources of oil.
- The communication is more subtle for area sources, such as a large odor footprint from subsurface oil, and the quality of this communication depends on an experienced and well-trained handler who knows the particular dog and can quickly recognize behavior signals. For example, a change of behavior when the canine has a heightened level of interest in an area, and typically increases the pace of movement, increases sniffing, and may lower his/her nose closer to the ground, and/or regularly look up at

the handler, indicates to the handler that there may be a large odor footprint, or several patches of oiling nearby.

- The canine quickly "learned" the basic desired search pattern on a beach, which reduced the amount of communication between the handler and dog, and allowed the canine to concentrate more on scenting rather than paying constant attention to the handler for directions.
- The canine appeared to work more efficiently when heading into the wind, and this enabled the canine to work with larger orbits or "boxes".
- Organic sheen was observed in the intertidal zone but was ignored by the canine.
- The canine ignored live birds, seaweed, dead fish and birds, and other potential distractions on the beaches.
- Throughout the survey, the canine handler and Team Lead continually assess the search area. Communication regarding changes in wind direction, observed hazards, and areas requiring detailed or concentrated attention, are passed between the handler and Team Lead.

<u>K9-SCAT Team Field Survey Techniques</u>

An important element of the study was to better understand how the team could improve survey techniques in terms of field coordination and communication. Some of the learning items include:

- Team members or other participants should walk behind the canine/handler, providing an operating space of at least 15 to 20m.
- Other participants should not talk to handler or the K9-SCAT Team Lead, or canine, while they are "active".
- Only the handler first praises the canine, as this communication is crucial in the reward process.
- The K9-SCAT Team Lead works with the handler, before and during a survey, to focus on potential oil accumulation areas. For example, the Team Lead suggested that the Indian Cove survey (#11) start at one end of the beach in the upper intertidal zone adjacent to a bedrock headland, and the canine found oil at that location within about 30 seconds.
- The K9-SCAT Team Lead typically would focus the survey on the upper half of the intertidal zone and up to storm high-water levels; in many instances, oil does not remain in, and is remobilized from, the water-saturated lower intertidal zone and the persistence of stranded oil in the middle and lower intertidal zones is shorter as sediments are subject to more reworking than those in the higher beach levels.
- During low tide, groundwater may leach odor molecules from subsurface oil so that the canine may provide a signal in the zone where the groundwater seepage intersects the beach-face slope.

<u>K9-SCAT Survey Challenges and Planning Issues</u>

- Bedrock outcrop and pebble-cobble-boulder beach surveys require more effort by the canine and involve a slower tracking pace when compared to sand beaches. For these shore types, the canine worked for up to 30 minutes before being rested by the handler.

- The longest “active” cumulative survey day was 97 minutes; the available survey time is controlled largely by the length of the appropriate low-tide window and also the need to reposition from different shore access locations.
- The average survey rate, in terms of the length of shoreline covered, varied depending on the shore type and the width of the survey band (Table 11).
    - the most challenging site was the steep bedrock of Cape Auget with an alongshore survey rate of 0.2 linear km/hour (Figures 5 and 6).
    - typical alongshore coverage rates for most of the wide, mixed sediment beaches were in the range 0.7 to 1.2 linear km/hour, and for both straight, wide sand beaches were 1.2 km/hour.
    - the highest alongshore speed was 2.4 linear km/hour for the narrow beach on Janvrin Island.

Table 11 Summary of Average Alongshore Coverage Survey Rates by Shore Type

SHORE TYPE	LOCATION	Alongshore Coverage (km/h)	Track Line Speed (km/h)
Steep Bedrock	Cape Auget	0.2	3.1
Narrow Coarse Sediment Beach (<10m)	Queensport West	0.8	3.0
Wide Coarse Sediment Beach (>20m)	Fox Island, Queensport East, Indian Cove	0.7	3.2
Wide Mixed Sand Beach (>20m)	Eddy Point	1.2	2.9
Wide Sand Beach (>20m)	Pondville, Black Duck Cove	1.2	6.1
Narrow Mixed Sediment (<5m)	Janvrin Island	2.4	3.7

- The average canine working speed was relatively constant, with a work rate of around 3 km/hour. He worked twice the speed (6 km/hour) on the easier sand beach surfaces.
- The handler must be vigilant of wear and tear on the canine’s pads. This issue is less critical on sand beaches but can be very significant on coarse sediment or bedrock shores where the sediments or surfaces are angular, with potentially sharp edges. For example:
    - the surfaces of sandstone or similar bedrock outcrops typically are very abrasive,
    - shales or slates are very angular and often sharp,
    - attached shellfish (barnacles, mussels) may have sharp edges, etc.
- The boots that were used on this survey(Figure 6) provided only temporary protection, as the shape of canine’s feet makes it difficult for the shoes to remain in

place. Also, the material was rapidly frayed (on the order of 15 minutes). A boot made of stronger material, such as Kevlar, may be a mitigation option for shoreline surveys on rough surfaces. A protective cream applied to the canine's paws is also recommended for further protection.

- The mild weather during this study provided no environmental challenges, such as heat/cold stress conditions for the canine, and strong or gusty winds that would dissipate odors.

Conclusions

The objective of the 2016 K9-SCAT study was to conduct a shoreline survey to determine the capability of detection canines to locate stranded oil following the releases of oil from the T/V *Arrow* into Chedabucto Bay, NS, during the summer and fall of 2015. This field project provided further "proof of concept" of K9-SCAT to support surface and subsurface oil detection during shoreline assessment surveys.

The canine detected small amounts of weathered surface oil that were barely visible (in some cases, not visible)to the SCAT-trained observers, as well as subsurface oil stranded from the 2015 T/V *Arrow* releases. Specifically, the canine detected:

- small (<~1cm diameter) surface oil residues on sediments in situations where that oil was not immediately obvious to experienced SCAT observers;
- subsurface oil with an odor footprint on the order of 20m by 10m; and
- targets that had been intentionally planted.

The average speed of a survey, in terms of the length of shoreline covered, varied depending on the shore type and the width of the survey band:

- the most challenging site was a steep bedrock shoreline (Cape Auget) with an alongshore survey rate of 0.2 linear km/hour
- typical alongshore coverage rates for the wide, mixed sediment were in the range 0.7 to 1.2 linear km/hour, and for both straight, wide sand beaches were 1.2 km/hour
- the highest alongshore survey rate was 2.4 linear km/hour for the narrow beach on Janvrin Island
- the human team members (canine handler, K9-SCAT team lead) limit the speed at which the canine can work.

Overall, the average working speed of the canine was relatively constant; around 3 km/hour. He moved faster, twice the speed (6 km/hour), on the easier sand beach surfaces.

Survey procedures involve close coordination and understanding between the K9-SCAT Team Lead and the Canine Handler. This relationship, as we all as the communication link between the handler and the canine, is a key ingredient for a successful survey. As the survey progressed, the handler and the canine became more efficient, in terms of the search pattern, and the Team Lead became more aware of the changes in canine behavior that led to "alerts" and "changes of behaviour".

The successful detection of both naturally stranded and intentionally planted 2015 *Arrow* cargo oil on the beaches of Fox Island Main, Indian Cove and Queensport indicates that there is a low risk, high confidence level that the canine may not have missed subsurface oil, although that possibility exists. Where oil was not observed at a canine alert site, chemical analysis indicates that weathered petroleum hydrocarbons were present, and that, therefore, the canine made correct alerts.

References

API, 2016a. *Canine Oil Detection: Field Trials Report*. American Petroleum Institute, Technical Report 1149-3, Washington DC, 48 pp.

API, 2016b. *Canine Oil Detection (K9-SCAT) Guidelines*. American Petroleum Institute, Technical Report 1149-4, Washington DC, 81 pp.

Brandvik P.J. and T. Buvik, 2009.*Using dogs to detect oil hidden in snow and ice. Results from field training on Svalbard April 2008*. JIP-Report No: 14. SINTEF Report No. F12273, Trondheim, Norway, 19 pp.

Buvik, T. and P.J. Brandvik, 2009.*Using dogs to detect oil hidden in beach sediments. Results from field training on Svalbard, September 2008 and on the west coast of Norway. (Fedje/Austreheim), June 2009*. SINTEF Report No. F12274, Trondheim, Norway, 20 pp.

Furton, K.G. and L.J. Myers, 2001.The scientific foundation and efficacy of the use of canines as chemical detectors for explosives. *Talanta*, 54, 487-500.

Garner, K.L., L. Busbee, P. Cornwell, J. Edmonds, K. Mullins, K., Rader, J.M. Johnston and J.M. Williams, 2001. *Duty Cycle of the Detector Dog: A Baseline Study*. Report FAA Grant #97-G-020, Institute for Biological Detection Systems, Auburn Univ., AL, 49 pp.

K2 Solutions, 2016. *Canine Oil Detection Tasking Nova Scotia, Canada - Final Report*. Unpublished report byK2 Solutions, Inc. submitted to Environment Canada and Climate Change, Ottawa ON, 8pp.

Owens, E.H., 1971. *A Reconnaissance of the Coastline of Chedabucto Bay, Nova Scotia*. Marine Sciences Paper No. 4, Department of Environment, Ottawa ON, 24 pp. with map.

Owens, E.H., and Bowen, A.J., 1977. Coastal environments of the Maritime Provinces. *Maritime Sediments* 13(1): 1-31.

Owens, E.H., Bunker, P., Dubach, H.C. and Castle, R.W., 2016. Guidelines for Canine Oil Detection Teams to Support SCAT Surveys (K9-SCAT).*Proceedings of the Thirty-ninth AMOP Technical Seminar*, Environment and Climate Change Canada, Ottawa ON.

OCC, 2016. *K9-SCAT: T/V "Arrow" Survey Report*. Unpublished report by Owens Coastal Consultants (OCC) submitted to Environment Canada and Climate Change, Ottawa ON, 55 pp.

Wang, Z., Yang, C., Parrott, J.L., Frank, R.A., Yang, Z., Brown, C.E., Hollebone, B.P., Landriault, M., Fieldhouse, B., Liu, Y., Zhang, G. and Hewitt, L.M., 2015. Forensic source differentiation of petrogenic, pyrogenic, and biogenic hydrocarbons in Canadian oil sands environmental samples. *Journal of Hazardous Materials,* 271, 166-177.