SILVERTIP PIPELINE SPILL

SUMMARY OF PURE AND WEATHERED CRUDE OIL SAMPLES

Sample ID	Date	Container Type and # Aliquots	Matrix	Analyses	Description
SPPR01	7/4/11	1 4-oz jar	Weathered Product (aqueous)	• VOCs • TEPH (Total, DRO & Oil) • SVOCs • Hydrocarbon ID	• Floating product layer collected from pooled crude oil along Thiel Road; submitted to Energy Laboratories. • One 40-mL VOA vial has been split for fingerprinting analysis at the USCG Marine Safety Laboratory (5mL).
SPPR02	7/4/11	1 4-oz jar	Weathered Product (aqueous)	• VOCs • TEPH (Total, DRO & Oil) • SVOCs • Hydrocarbon ID	• Floating product layer collected from pooled crude oil along Thiel Road; submitted to Energy Laboratories.
SPPR03	7/5/11	2 4-oz jars	Pure Product (crude oil)	• VOCs • TEPH (Total, DRO & Oil) • SVOCs • Metals (w/ Mercury) • Hydrocarbon ID • Sulfur Analysis	• Product sample collected from ExxonMobil pipeline; submitted to Energy Laboratories. • Originally thought to be source of release but later identified as incorrect location on pipeline. • Currently, EPA has 1 4-oz jar undergoing analysis at Energy Laboratories, 1 4-oz jar intact at laboratory.
SPPR04	7/9/11	6 40-mL VOA	Pure Product (crude oil)	• VOCs • TEPH (Total, DRO & Oil) • SVOCs • Metals (w/ Mercury) • Hydrocarbon ID • Sulfur Analysis • Massachusetts Method for Extractable Petroleum Hydrocarbons	• Product sample collected from ExxonMobil pipeline at Riverside Park, submitted to Energy Laboratories. • Currently, EPA has 1 40-mL VOA undergoing analysis at Energy Laboratories and 1 40-mL VOA that has been split for fingerprinting analysis at the USCG Marine Safety Laboratory (5mL). • EPA gave a split of this sample to MDEQ in 4 40-mL VOA vials for independent analysis at laboratories of their choosing.
SPPR99	7/4/11	1 4-oz jar	QA/QC Weathered Product (aqueous)	• VOCs	• Duplicate of SPPR01.

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Sampling Methodology:

The product samples were collected by contractor personnel for EPA. Samples were placed in 40 milliliter (mL) VOA vials, 4 ounce glass jars, or 8 ounce glass jars, as appropriate for the designated analysis. Samples were collected by filling sample bottles with a dedicated pipette, by directly immersing the sample bottles into the sample media, or from a valve on the pipeline itself. Sample descriptions were logged in the field log book and pictures were taken of the sampling events.

Analytical Methods:

Product samples were analyzed using the selected methods below:

- Method 8260B for Volatile Organic Compounds,
- Method 8270C for Semi-Volatile Organic Compounds,
- Method 8015B for Total Petroleum Hydrocarbons (DRO and Oil analyses),
- SW846 Method for Total Metals
- Hydrocarbon Identification by Simulated Distillation, and
- Sulfur Composition Analysis of Oils
- Massachusetts method for Extractable Petroleum Hydrocarbons (EPH)

Hydrocarbon identification (ASTM Method D2887) was performed using a simulated distillation method. The results are reported based on carbon chain length. The method performed on the samples is a quicker version of conventional distillation with the ability to define specific temperature controls. By defining temperature ranges, the method is quicker as unnecessary burn time is eliminated. The method employs a data logger capable of capturing data in 10 millisecond intervals and in turn producing more precise measurements (ASTM 2004).

Product samples were analyzed at the respective laboratories for Diesel Range Organics (DRO) and Oil Range Organics. A total extractable figure was also obtained through a total petroleum hydrocarbon (TPH). The TPH analysis is not the Montana-modified Massachusetts method TEPH. SPPR03 and SPPR04, which were the two samples collected directly from pipeline on the north and south side of the spill site, were analyzed for sulfur content of the oil samples, and SPPR04 was analyzed using the Montana-modified MA-EPH method because it is the most representative sample of the crude in the pipeline at the location of the break during the actual spill.

Discussion:

The responsible party, ExxonMobil, informed EPA of a crude oil batch change in the pipeline in the vicinity of the Yellowstone River crossing around the time of the spill, after the northern segment of the Silvertip Pipeline had been sampled near the Conoco Refinery (SPPR03). This sample represents the last portion of the crude oil batch immediately preceding the batch involved in the spill. As such, arrangements were made to collect a sample (SPPR04) of the product at the pipeline block valve on the south side of the Yellowstone River on July 9, 2011. The last sample was analyzed for all constituents to ensure that we have complete information about the crude oil that was released into the Yellowstone River during the pipeline break.

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Targeted comparison of the analysis of raw crude oil and weathered crude oil samples:

On July 4, 2011, samples SPPRO1 and SPPRO2 were collected near Thiel Road from an area of surface water with a floating product layer. These two samples represent the crude oil as it existed four days after the release and are indicative of the degree of breakdown in the environment due to evaporation, ultraviolet light degradation, and dissolution into the water.

Sample SPRRO4 was collected from a port above a block valve in the pipeline. Although it was collected on July 09, 2001, it is representative of the pure product as it existed in the pipeline during the release. The analysis of sample SPPR04 (collected from the crude oil in the pipeline) is indicative of a medium weight sour (containing greater than 0.5% by volume of sulfur) crude oil containing the full suite of organic compounds. Volatile organic compounds such as benzene (142 mg/kg), toluene (1060 mg/kg) and total xylenes (2530 mg/kg) are present at levels that are to be expected in raw crude oil. There is also a significant percentage (2.94%) of sulfur found in the crude oil, most likely present as hydrogen sulfide. Diesel range organic (DRO) are found at 369,000 mg/kg; oil range organics are found at 136,000 mg/kg; and total extractable hydrocarbons were found at 461,000 mg/kg. The metals analysis found only very low levels (parts per million) of iron, nickel, and vanadium, which are unlikely to pose any threat to human health or the environment. These results are also consistent with the information provided by the Responsible Party, ExxonMobil, regarding the assertions that the released oil was sour crude. Please refer to the analytical results table for additional information.

The analytical profile for samples SPPRO1 and SPRRO2 (both collected from near Thiel Road 4 days after the release) is representative of a weathered crude oil sample in the environment. The volatile organic compounds benzene, toluene, and total xylenes are no longer detected. These compounds have likely evaporated into the ambient air, been broken down by ultraviolet light, or dissolved into the water column and then released at lower levels further downstream. Additionally, the samples show that all the lighter aliphatic (straight-chain hydrocarbons) and semi-volatile constituents have been weathered.

During the evacuation conducted by local authorities, the air monitoring instruments used by emergency responders were used to measure these compounds in the ambient air. Volatile organic compounds were detected early on in areas immediately surrounding the spill site and precautionary decisions were made to conduct an evacuation in some areas. The sulfur present in the crude oil may have off-gassed as hydrogen sulfide and been an irritant, but was not detected by first responders at harmful levels in the ambient air. In addition the DRO, oil range organics and total extractable hydrocarbons levels also decreased appreciably as these larger compounds weathered in the environment.

These analytical results indicate that after the pure crude oil was released into the Yellowstone River, the lighter constituents of its hydrocarbon profile began to evaporate and weather immediately and this process has continued due to the high temperatures and daily exposure to hours of sunlight. Over the course of several days, the levels of volatile organic compounds decreased to levels where when sampled, the results were below laboratory method detection levels. As additional samples are collected and analyzed, the results should consistently show that no volatile organics are detected due to the weathering of the crude. Only the non-volatile, more durable compounds containing 10 or more carbon atoms will be present, but they too are being actively broken down.

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Analytical Results Table

Analyte	Analysis	Units	SPPR04	SPPR01	SPPR02	SPPR03
Benzene	VOC	mg/kg	142	ND	ND	1,750
Ethylbenzene	VOC	mg/kg	335	ND	ND	312
Toluene	VOC	mg/kg	1060	ND	ND	3,220
m&p-xylenes	VOC	mg/kg	1800	ND	ND	1,780
o-xylene	VOC	mg/kg	728	ND	ND	462
Total xylenes	VOC	mg/kg	2530	ND	ND	2,240
2-methylnaphthalene	SVOC	mg/kg	ND	ND	ND	119
C19 to C36 Aliphatics	MA-EPH	mg/kg	121,000	NR	NR	NR
C9 to C18 Aliphatics	MA-EPH	mg/kg	139,000	NR	NR	NR
n-Decane	MA-EPH	mg/kg	2070	NR	NR	NR
n-Docosane	MA-EPH	mg/kg	1020	NR	NR	NR
n-Dodecane	MA-EPH	mg/kg	1780	NR	NR	NR
n-Eicosane	MA-EPH	mg/kg	1580	NR	NR	NR
n-Hexacosane	MA-EPH	mg/kg	821	NR	NR	NR
n-Hexadecane	MA-EPH	mg/kg	2050	NR	NR	NR
n-Hexatriacontane	MA-EPH	mg/kg	175	NR	NR	NR
n-Nonadecane	MA-EPH	mg/kg	1610	NR	NR	NR
n-Nonane	MA-EPH	mg/kg	2170	NR	NR	NR
n-Octacosane	MA-EPH	mg/kg	618	NR	NR	NR
n-Octadecane	MA-EPH	mg/kg	1620	NR	NR	NR
n-Tetracosane	MA-EPH	mg/kg	946	NR	NR	NR
n-Tetradecane	MA-EPH	mg/kg	2380	NR	NR	NR
n-Triacontane	MA-EPH	mg/kg	499	NR	NR	NR
C11 to C22 Aromatics	MA-EPH	mg/kg	141,000	NR	NR	NR
Diesel Range Organics	DRO	mg/kg	369,000	221,000	163,000	237,000
Oil Range Hydrocarbons (C28-C40+)	Oil Range	mg/kg	136,000	148,000	100,000	136,000
Total Extractable Hydrocarbons	TPH	mg/kg	461,000	365,000	261,000	431,000
Total Sulfur	Sulfur	Wt%	2.94	NR	NR	3.73
Nickel	Total Metals	mg/kg	8	NR	NR	ND
Vanadium	Total metals	mg/kg	48	NR	NR	1
C1-C5	Hydrocarbon ID	%	0.83	ND	ND	ND
C5-C6	Hydrocarbon ID	%	1.1	ND	ND	3.38
C6-C7	Hydrocarbon ID	%	2.19	ND	ND	5.55
C7-C8	Hydrocarbon ID	%	2.99	ND	ND	5.52
C8-C9	Hydrocarbon ID	%	3.69	ND	ND	2.87
C9-C10	Hydrocarbon ID	%	3.47	ND	ND	1.78
C10-C11	Hydrocarbon ID	%	3.75	ND	ND	1.80
C11-C12	Hydrocarbon ID	%	3.52	0.06	ND	1.83
C12-C13	Hydrocarbon ID	%	4.13	0.08	0.21	2.77
C13-C14	Hydrocarbon ID	%	3.88	0.99	1.68	2.70
C14-C15	Hydrocarbon ID	%	4.16	2.60	3.49	3.55
C15-C16	Hydrocarbon ID	%	3.93	3.73	4.31	3.37
C16-C17	Hydrocarbon ID	%	3.85	4.45	4.81	3.41
C17-C18	Hydrocarbon ID	%	3.71	4.68	4.89	3.36
C18-C19	Hydrocarbon ID	%	3.79	4.98	5.13	3.44
C19-C20	Hydrocarbon ID	%	3.73	5.07	5.11	3.70
C20-C21	Hydrocarbon ID	%	3.59	4.45	4.45	3.02
C21-C22	Hydrocarbon ID	%	3.25	4.59	4.48	3.46
C22-C23	Hydrocarbon ID	%	3.16	4.38	4.49	3.21
C23-C24	Hydrocarbon ID	%	3.10	4.29	3.84	2.89
C24-C25	Hydrocarbon ID	%	2.70	3.80	4.07	2.66
C25-C26	Hydrocarbon ID	%	2.69	3.84	3.96	2.71
C26-C27	Hydrocarbon ID	%	2.72	3.80	3.57	2.96
C27-C28	Hydrocarbon ID	%	2.46	3.87	3.84	2.45
C28-C29	Hydrocarbon ID	%	2.59	3.78	3.51	3.01
C29-C30	Hydrocarbon ID	%	2.57	4.03	3.91	3.33
C30-C32	Hydrocarbon ID	%	4.65	7.42	7.16	5.79
C32-C34	Hydrocarbon ID	%	4.64	6.79	6.53	5.22
C34-C36	Hydrocarbon ID	%	3.78	6.68	6.21	4.56
C36-C38	Hydrocarbon ID	%	3.26	6.57	5.60	3.78
C38-C40	Hydrocarbon ID	%	1.72	3.88	4.14	1.81
C40+	Hydrocarbon ID	%	0.42	1.17	0.63	0.11

*All results are preliminary, final results are expected on 7/30/2011 and will be posted to the EPA website.

mg/kg milligrams per kilogram

NR = Analysis not requested.

ND = Analyte not detected, or result was flagged with a “J” qualifier.

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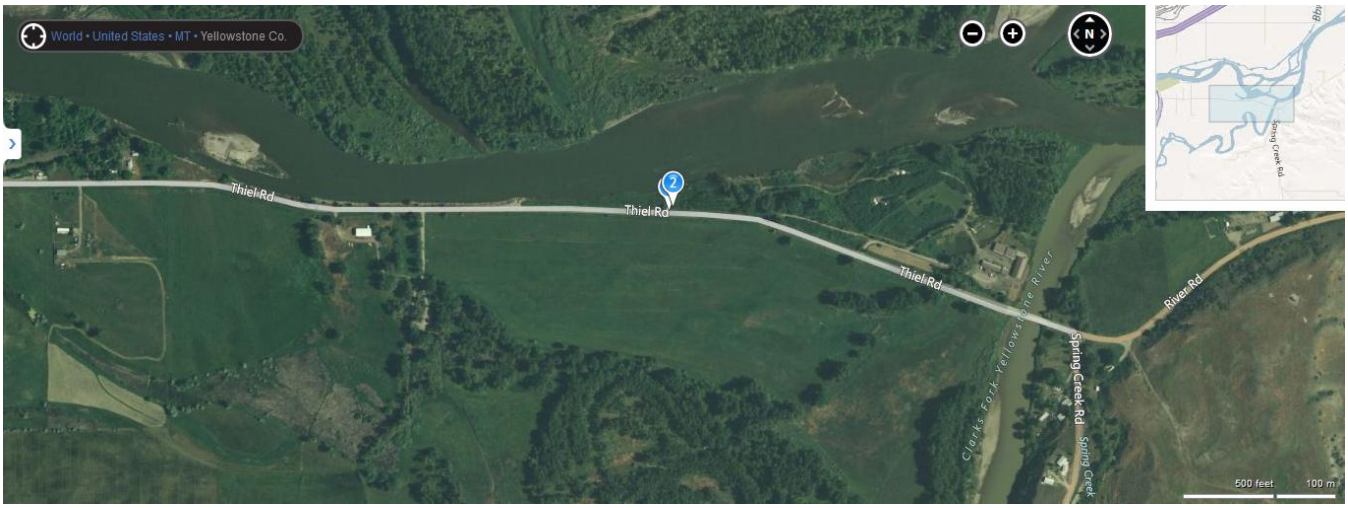
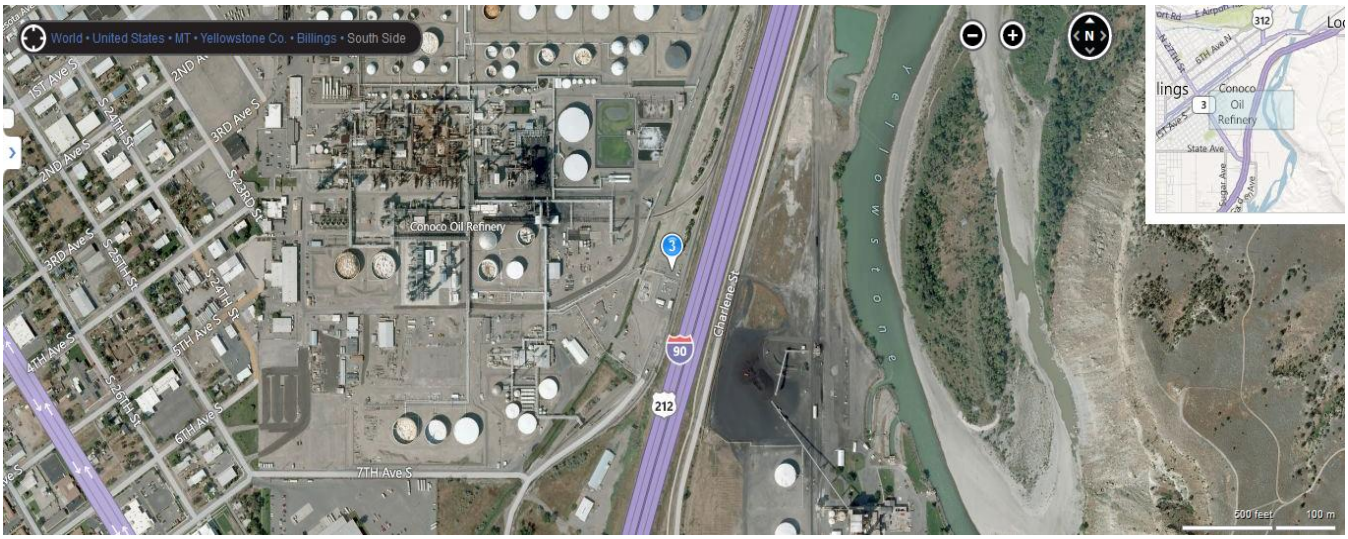
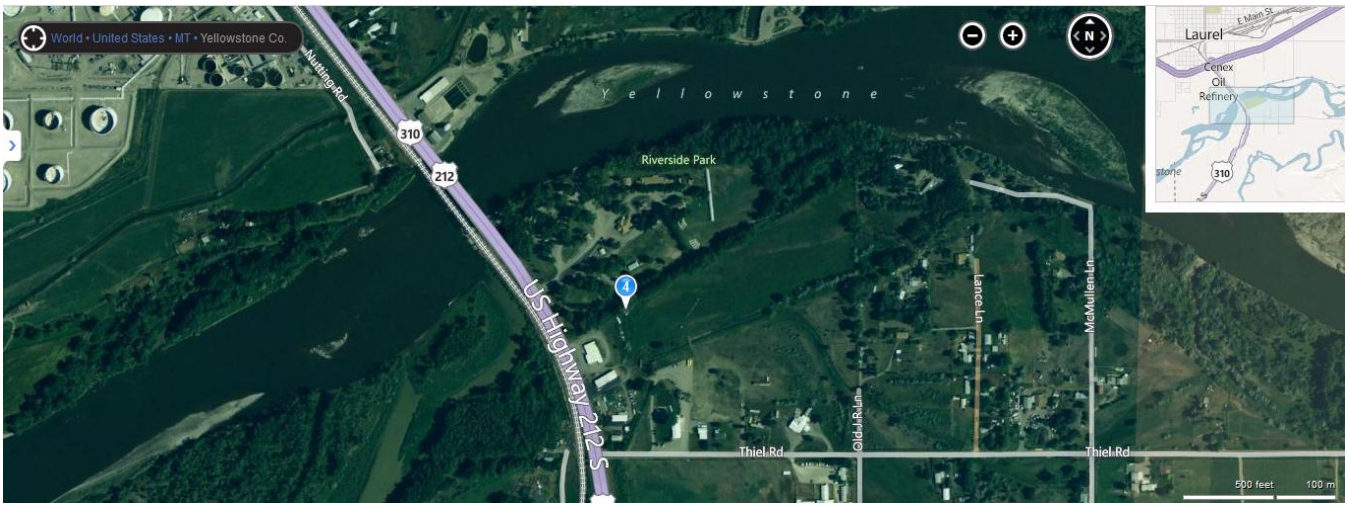


SPPR01 and SPPR02 Sampling Locations



SPPR03 Sample Location



SPPR04 Sample Location

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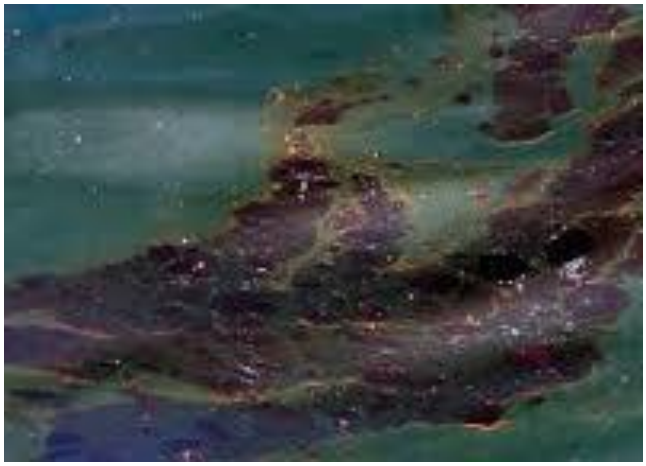
What Is Weathered Crude Oil?



On July 1, 2011, the Silvertip Pipeline ruptured at the point where it passes under the Yellowstone River just upriver from Billings, Montana. Preliminary indications are that the pipeline was damaged due to the swift current and flooding that was occurring on the river. Approximately 45,000 gallons of light crude oil was released directly into the water. ExxonMobil has accepted responsibility for the spill and is fully funding the cleanup effort. The State of Montana Department of Environmental Quality and the US Environmental Protection Agency have integrated into a Unified Command with ExxonMobil to manage and direct the cleanup efforts.

Crude oil is a mixture of more than 1000 chemical compounds, mostly containing carbon. Theses compound are called hydrocarbons, and can be grouped into chemical families based on the amount of carbon in each group. As the amount of carbon increases, the size and shape of each compound also increases. The chemical families represented in crude oil include (from smallest to largest) alkanes, cycloalkanes and aromatic hydrocarbons.

When crude oil is released and exposed to the environment, many of the smaller lighter hydrocarbons evaporate into the air within the first 24-48 hours. This process is also known as weathering. These light hydrocarbons, like benzene, xylene and toluene, are also among the most toxic and could present a health threat by inhalation. The potential for human exposure to these compounds was monitored by closely monitoring their presence in the air throughout the first weeks of the spill to ensure that all appropriate actions were taken to protect human health and the environment.

Evaporation of the lighter compounds leaves behind the medium and heavier portion of the oil that is now the focus of the cleanup effort. This remaining mixture is called **weathered crude oil**. It is thick, like motor oil or grease, and very sticky. It is also much less toxic than the raw crude oil that was initially released from the pipeline. These remaining compounds do not readily evaporate and are not generally an inhalation hazard. Studies have shown that toxicity decreases as the degree of weathering increases.

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