

HEAVY FUEL OIL DISCHARGE RESPONSE ACTIONS

**Florida Department of Environmental Protection (FDEP)
Division of Waste Management
Tallahassee, FL**

May 2016

HEAVY FUEL OIL DISCHARGE RESPONSE ACTIONS

Background

This guidance document outlines emergency response actions that may be followed to respond to heavy fuel oil discharges.

Heavy fuel oil includes American Society for Testing and Materials (ASTM) grades number 5 and number 6 residual oils, and intermediate fuel oils used for marine bunkering with a viscosity of 30 and higher. No. 6 fuel oil is far more common than no. 5, and is the principal fuel used by oil-fired power plants. Thus "heavy fuel oil" is frequently used as a synonym for no. 6 residual oil. Heavy fuel oil is a highly viscous oil that has a low propensity to flow. When discharged, it usually results in visual staining of the top 3 to 4 inches of soil in the vicinity of the discharge. The response actions in this guidance take into consideration the fuel's high viscosity, low propensity to flow, and the staining associated with a discharge.

Applicability

The response actions provided below can be applied to discharges of heavy fuel oil to a pervious surface. It cannot be applied to discharges of heavy fuel oil being addressed pursuant to the Clean Water Act. Heavy oil discharged onto impervious surfaces should be recovered.

Following this protocol, such that the heavy fuel oil discharge is remediated within 30 days, constitutes compliance with the de minimis discharge provisions of Chapter 62-780, F.A.C. In responding to heavy oil discharges, including those into or near waters of the state, responders should also comply with all other applicable laws and rules, including applicable notification requirements.

Response Actions

Heavy oil discharge response actions include two types of discharge categories: a new discharge and an existing discharge. For the purposes of this guidance document, a new discharge is defined as a discharge that is known to have occurred within the past 48 hours. An existing discharge is any other heavy oil discharge.

Response actions should be completed within 30 days of discovery of a new or existing discharge. To the extent response actions are not completed within that timeframe, the responder should contact the local county storage tank program office or Department of Environmental Protection ("Department") district office to develop an appropriate discharge response in accordance with Chapter 62-780, F.A.C.

A. New Discharge Response Protocol

1. New Discharge Not Resulting in Contact with Groundwater

The response actions for a new discharge of any quantity where the discharge did not result in contact with groundwater should be initiated within 48 hours after discovery. Once the source of the discharge is abated or otherwise secured, responders should initiate response actions, which should include immediate measures to control and abate the discharge.

Soil impacted by heavy fuel oil may be excavated through visual delineation of stained soil. This is typically done using shovels, a backhoe, a track hoe or other appropriate equipment. All visible traces of the heavy oil in the soil should be removed, including a one-foot lateral and vertical buffer, unless prevented by a physical obstacle such as a storage tank, building, etc. Excavated soil should be stockpiled on Visqueen or other similar impervious material until loaded into 55 gallon drums, roll-off dumpsters or similar containers. Excavated soil should be secured in a manner that prevents human exposure to contaminated soil and prevents soil exposure to precipitation that may cause surface runoff. All excavated soil should be disposed of or treated within 60 days of completion of field activities in accordance with applicable local, state, and federal regulations. Applicable disposal or treatment documents should be obtained and maintained with the response records.

2. New Discharge Resulting in Contact with Groundwater

The response actions for a new discharge of any quantity that resulted in contact with groundwater should be initiated within 48 hours after discovery. Once the source of the discharge is abated or otherwise secured, responders should initiate response actions, which should include immediate measures to control and abate the discharge.

In accordance with paragraph C. below, if a new discharge resulted in contact with groundwater confirmatory laboratory analysis should be conducted of the groundwater to ensure that levels of Polycyclic Aromatic Hydrocarbons (PAHs) applicable to heavy fuel oil as provided in Table A are below the corresponding groundwater cleanup target levels for those PAH constituents in Chapter 62-777, F.A.C., or alternative target levels agreed to with the Department.

To the extent such removal cannot be completed within 30 days, the responder should contact the relevant Department district office to develop an appropriate discharge response in accordance with Chapter 62-780, F.A.C.

B. Existing Discharge Response Protocol

The response actions for an existing discharge should be initiated as soon as possible after discovery.

If the discharge is 25 gallons or less and did not result in contact with groundwater, the

response protocol for new discharges in paragraph A.I. may be followed.

If the discharge is 25 gallons or less and resulted in contact with groundwater, the response protocol for new discharges should be followed. Also, in accordance with paragraph C. below, potential groundwater impacts should be addressed.

If the discharge is greater than 25 gallons, or resulted in contact with groundwater (see paragraph C. below), all visible traces of the heavy fuel oil in the soil should be recovered including a one foot lateral and vertical buffer as provided in Section A above and confirmatory laboratory analysis of one composite sample of soil from the bottom of the excavation (unless the bottom is below the water table) and the walls or perimeter of the excavation should be conducted to ensure that all impacted soil has been removed. Also, where the existing discharge resulted in contact with groundwater, the provisions of paragraph C. should be followed.

Verification cleanup of the soil should be confirmed by ensuring that levels of PAHs applicable to heavy fuel oil as provided in Table A are less than the lower of the direct exposure or leachability soil cleanup target levels for those PAH constituents, or other alternative target levels agreed to with the Department. Removal should continue until applicable PAH constituent levels are below the aforementioned concentrations, unless prevented by a physical obstacle as previously mentioned.

To the extent such removal cannot be completed within 30 days, the responder should contact the relevant Department district office to develop an appropriate discharge response in accordance with Chapter 62-780, F.A.C.

C. Groundwater Contact

Heavy fuel oil removal activities in groundwater may include but are not be limited to the use of:

- a. Absorbent pads or booms;
- b. Pumps (skimmer, diaphragm, centrifugal, etc.) with mechanical, electrical or hand-bailed purging operations;
- c. Hand or mechanical bailing;
- d. Fluid vacuum techniques; or
- e. Other applicable techniques or technologies.

Recovered heavy fuel oil should either be burned for energy recovery or disposed of or treated in accordance with applicable local, state, and federal regulations.

If a new or existing discharge resulted in contact with groundwater, after heavy fuel oil removal activities in groundwater have been completed, confirmatory laboratory analysis should be conducted to ensure that PAH levels applicable to heavy fuel oil as provided in Table A are below the applicable groundwater cleanup target levels for PAH constituents in Chapter 62-777, F.A.C., or alternative target levels agreed to with the Department.

D. Documentation

The attached form should be completed by electric utilities for each discharge of heavy fuel oil on a pervious surface and kept on file for a period of five years and made available to the Department upon request.

Table A – PAH Constituents Applicable to Heavy Fuel Oil

Phenanthrene
Anthracene
Fluoranthene
Benz(a)anthracene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Chrysene
Indeno(1,2,3-cd)pyrene

Summary Document for Heavy Fuel Oil Discharge (on a pervious surface)

Location(s) of Spill (street address of discharge, if known, facility name and narrative description or illustration indicating where discharge occurred)	
Date of Spill	
Type of Product Discharged	
Volume of Product Discharged (in gallons)	
Volume of Free Product Recovered (in gallons)	
Volume of contaminated soil excavated (tons or cubic yards)	
Disposal or recycling methods for free product	
Disposal or recycling methods for excavated soil	
Disposal methods for other contaminated media or investigative related waste	
A site map or sketch showing location(s) of free product recovered and the area of soil removed.	
Narrative description or illustrations of the approximate dimensions of the excavation <u>-length, width and depth (all</u>	
Documentation confirming the proper treatment and/or disposal of the free product or contaminated soil. (Attach manifests to report)	
Narrative description or illustration of where samples were taken, screening methods used and analytical results. (Attach to report)	
Other applicable information such as a description of any physical obstacles, if any, preventing complete removal.	

Appendix 1

No. 6 Fuel Oil-PAH Analysis and Spill Response Recommendations

PAHs are ubiquitous in the environment, forming whenever organic substances are exposed to high temperatures. They can be broadly separated into three categories: biogenic (formed from natural biological processes including diagenesis); petrogenic (primarily associated with crude oil and natural oil seeps); and pyrogenic (formed in high heat or combustion processes, including incomplete combustion of fuels). PAHs derived from all three categories are likely to be found as contaminants in soils, particularly in urban or industrial areas, but also, for example, in areas where wood-burning stoves (biogenic) and high-volume vehicular traffic (pyrogenic) are present.

Petrogenic PAHs are characterized by low molecular weight compounds with 2 or 3 aromatic rings (i.e., six-carbon fused benzene rings) with a predominance of alkyl substitution (predominantly methyl groups attached to the ring structures). Conversely, pyrogenic PAHs are characterized by high molecular weight compounds typically with 4 to 7 aromatic rings, and much less alkyl substitution. An important toxicological distinction between the two categories is that all known carcinogenic PAHs fall into the high molecular weight, or pyrogenic, category. Atmospheric transport from point sources and the ever-increasing volume of mobile sources ensures the presence of pyrogenic PAHs in nearly all soils in the U.S. and elsewhere in the developed world.

Number (No.) 6 fuel oil, also known as Bunker C fuel, is a refinery by-product, principally the residue of processes in which light and medium crude oils are fractionally distilled and processed to produce gasoline, diesel fuel, and other products. Although derived from a predominately petrogenic source, No. 6 fuel oil may be substantially enriched in 3 to 5-ring PAHs formed in a number of high-temperature petroleum refining processes including catalytic and steam cracking, vacuum distillation, hydrodesulfurization, etc. PAHs in the high-viscosity residuum of the refining process are primarily petrogenic in origin; however, when necessary, low-viscosity blending stocks from the refining operations are blended with residuum to reduce viscosity and improve flowability. This occasional practice has the potential to introduce high-molecular weight pyrogenic PAHs in quantities that are both unpredictable and batch-specific, although the actual concentrations are low. This, along with the petrogenic PAH variability in parent crudes, are why PAH fingerprinting can be used to identify specific sources of fuel oil spills.

To develop a coherent approach to assessing risk from PAHs associated with a spill of residual fuel oil, as well as recommended cleanup criteria, all regulated PAH compounds have been compiled in Table 1. Those not found to be present in No. 6 fuel oil are shaded . Composition data for No. 6 fuel oil was compiled by the Total Petroleum Hydrocarbon Criteria Working Group (Potter and Simmons 1998). Data are presented as weight percentages for all fuel constituents reported from a comprehensive search of the literature, and from government, military and oil industry sources.

It is reasonable to assume that any PAHs with maximum reported levels less than 0.02 wt % in No. 6 fuel oil are unlikely to be present at detectable levels in soil or groundwater samples following a fuel spill. That is to say, if these PAHs are detected they would either be at a De Minimus level or derived from a source other than a heavy fuel oil spill, given the plethora of potential PAH sources described above. If this assumption is accepted, only the following PAHs found in soils subjected to a No. 6 fuel oil spill should be considered to be derived from that spill:

Anthracene	Chrysene
Benz(a)anthracene	Fluoranthene
Benzo(b)fluoranthene	Phenanthrene
Benzo(k)fluoranthene	

The threshold of 0.02 wt % eliminates inclusion of naphthalene; the remainder of PAHs reported to be present in fuel oil No. 6 (see Table 1) are less abundant in fuel oil #6 than naphthalene. (Some, like benzo(a)pyrene [reported only once in fuel oil No. 6], are an order of magnitude less abundant than naphthalene.) Naphthalene is the most soluble of binuclear aromatics, and orders of magnitude more soluble than PAHs with 3 or 4 aromatic rings. This is further justification for not including naphthalene in the above list since solubility is a major factor in determining the rate of biodegradation.

For decisions on remediation of PAHs in the environment it is also important to consider bioavailability. PAH bioavailability will not be discussed further here, but considerable literature information is available (e.g., National Research Council 2003, Stroo et al. 2005).

Recommendations

For response activities related to a No. 6 fuel oil spill to soil and/or groundwater, it is recommended, with respect to PAHs, to compare only the following PAHs and their respective regulatory criteria.

- Anthracene
- Benz(a)anthracene
- Benzo(b)fluoranthene
- Benzo(k)fluoranthene
- Chrysene
- Fluoranthene
- Phenanthrene

Bibliography

(Links verified as of May 24, 2016)

The following source were used in the development of this Appendix.

API 1994. Transport and Fate of Non-BTEX Petroleum Chemicals in Soils and Groundwater. API Publication number 4593, American Petroleum Institute, Washington, D.C. http://www.techstreet.com/api/standards/api-publ-4593?product_id=25845

Davis, Jay. 2005. PAHs in the Estuary. San Francisco Bay Institute Regional Monitoring Program. http://www.sfei.org/rmp/rmp_news/Volume_2_issue_2#PAH

Massachusetts Department of Environmental Protection. 2005. Polycyclic Aromatic Hydrocarbons. <http://www.mass.gov/eea/agencies/massdep/toxics/reports/polycyclic-aromatic-hydrocarbons-pahs.html>

National Research Council. 2003. Current Use of Bioavailability in the Management of Contaminated Soil and Sediment, pp. 52-118. In: NRC. 2003. Bioavailability of Contaminants in Soils and Sediments: Processes, Tools, and Applications. 420 pp. National Academies Press, Washington D.C. <http://www.nap.edu/read/10523/chapter/4#53>

Neff, J.M., S.A. Stout and D.G. Gunster. 2005. Ecological risk assessment of polycyclic aromatic hydrocarbons in sediments: identifying sources and ecological hazard. Integrated Environmental Assessment and Management, 1(1):22-33. http://onlinelibrary.wiley.com/doi/10.1897/IEAM_2004a-016.1/epdf

Potter, Thomas L. and Kathleen E. Simmons. 1998. Composition of Petroleum Mixtures. Total Petroleum Hydrocarbon Criteria Working Group Series, Volume 2. Amherst Scientific Publishers, Amherst, Massachusetts.

Stroo, H.F. et al. 2005. Improving risk assessments for manufactured gas plant soils by measuring PAH availability. Integrated Environmental Assessment and Management, 1(3):259-266. <http://onlinelibrary.wiley.com/doi/10.1897/2004-009R.1/epdf>

Table 1. Compilation of Regulated PAHs, Occurrence in No. 6 Fuel Oil and Regulatory Characterization

Priority Pollutants PAHs ¹ (number of aromatic rings)	Reported weight % in No. 6 Fuel Oil ² (avg. and range)	USEPA Carcinogenic Potential ³
Naphthalene ⁴ (2)	4.2E-3 2.1E-4 – 1.5E-2	N/C
1-Methylnaphthalene (2)	N/R ⁵	N/A
2-Methylnaphthalene (2)	N/R	N/A
Acenaphthylene (2)	N/R	N/C
Acenaphthene (2)	N/R	N/A
Fluorene (2)	N/R	N/C
Phenanthrene (3)	2.1E-2 2.1E-3 – 4.8E-2	N/C
Anthracene (3)	5.0E-3	N/C
Fluoranthene (3)	2.4E-2	N/C
Pyrene (4)	2.3E-3	N/C
Benz(a)anthracene (4)	5.5E-2 2.9E-3 – 1.5E-1	B2
Chrysene (4)	6.9E-2 2.9E-3 – 3.1E-1	B2
Benzo(b)fluoranthene (4)	4.4E-2	B2
Benzo(k)fluoranthene (4)	4.4E-2	B2
Benzo(a)pyrene (5)	4.4E-3	B2
Indeno(1,2,3-cd)pyrene (5)	1.0E-2	B2
Dibenz(a,h)anthracene (5)	N/R	B2
Benzo(g,h,i)perylene (6)	N/R	N/C

1. Includes all reported constituents of No. 6 fuel oil (unshaded) that also are listed in Chapter 62-777 SCTLs.
2. Total Petroleum Hydrocarbon Criteria Working Group. Vol. 2, Composition of Petroleum Mixtures.
3. B2 - probable human carcinogen; N/C - not classifiable; N/A - not available, or Data are inadequate for an assessment of human carcinogenic potential
4. Naphthalene, although included in the Priority Pollutant list, is a di-aromatic and generally not considered in the same group as polynuclear aromatic hydrocarbons.
5. N/R (shaded) = Not reported in literature as occurring in No. 6 Fuel Oil.