

Comparison of Emissions from Burning of Petroleum, Petroleum-Derived Fuels, and Common Vegetative Fuels

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Executive Summary

When accidental spills or releases of petroleum occur, decision-makers are faced with a variety of response options for cleanup of the spilled product, including mechanical recovery, *in situ* burning (ISB), or even allowing the petroleum to remain in the environment (i.e., natural recovery). Decision-makers must weigh the benefits, drawbacks, feasibility, and appropriateness of each response option. Often, these decisions must be made in a rapid fashion rapidly and are influenced by the circumstances particular to the spill, including the potential impacts that response options may have on the health and safety of response workers or individuals in nearby communities.

Emissions from spilled or burning petroleum may act as, or may be perceived as, inhalation hazards to both response workers and the public. This is particularly true for ISB, where the burning of oil produces large, black smoke plumes which are often considered a drawback for use of this oil spill response option. However, both mechanical recovery and natural recovery can also result in the release of airborne emissions that response workers and the public may come in contact with. Evaporation of volatile petroleum hydrocarbons (VPHs) is the primary inhalation hazard of concern for natural recovery and mechanical recovery. Particulate matter (PM) and polycyclic aromatic hydrocarbons (PAHs), some of which are considered probable human carcinogens, are the primary inhalation hazards of concern for ISB. Combustion gases such as carbon monoxide (CO), carbon dioxide (CO₂) and potential sulfur and nitrogen-containing oxides (SO₂ and NO_x) can also be produced by burning petroleum, but are of less concern in the context of potential inhalation exposures to response workers and the public.

This document is designed to provide decision-makers with an understanding of the types of constituents released into the atmosphere as a result of different cleanup options, and to compare emissions from ISB of petroleum to other anthropogenic and natural sources. The document opens with a general discussion of the chemical composition of petroleum, the process of natural weathering of petroleum by evaporation, and petroleum smoke. Emission factors (EFs) for PM and cPAHs from the burning of petroleum-derived fuels and vegetative fuels are identified, discussed, and compared to EFs from ISB of petroleum. The results indicate that emissions from ISB are similar in nature to emissions from burning vegetative fuels in a domestic, agricultural, or land management scenario.

This document closes with a general discussion of airborne emissions from spill response options, including natural recovery, mechanical recovery, and ISB. Overall, ISB can reduce emissions of VPHs emitted during natural weathering or during mechanical recovery operations. Emissions from ISB are relatively short-lived (minutes to hours) as compared to VPH emissions from natural weathering or mechanical recovery, processes that can last days. ISB can also eliminate or minimize the need for response workers to come into direct contact or be in close proximity to spilled petroleum for extended periods of time, and may also prove more effective in removing petroleum from the environment as compared to mechanical recovery. ISB also eliminates the need to collect, store, transport, and dispose of large amounts of recovered petroleum or contaminated soil and water, while also reducing atmospheric emissions of PM and cPAHs associated with the equipment, vehicles, and vessels needed to conduct mechanical recovery operations.

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I. Purpose and Objectives

When accidental spills or releases of petroleum occur, decision-makers are faced with a variety of response options for cleanup and must weigh the benefits, drawbacks, feasibility, and appropriateness of each option. Often, these decisions must be made rapidly and are influenced by the circumstances particular to a spill, including the potential impacts that response options may have on the health and safety of response workers or individuals in nearby communities.

ISB has been an option for petroleum spill response for many years. However, ISB results in the production of thick, black smoke plumes during the course of the burn. In the past, misconceptions about emissions from ISB have hindered the use of this method for oil spill mitigation. The perceived human health hazard associated with ISB emissions, both to response workers and the surrounding public, can be an obstacle for selection of ISB as a cleanup option, even in situations where it may be used effectively to remove oil from the environment.

This document is designed to provide decision-makers with an understanding of the types of constituents released into the atmosphere as a result of different cleanup options, and to compare emissions from ISB burning of petroleum to other anthropogenic and natural sources.

This document:

- provides general background on ISB, the chemical composition of petroleum, and weathering processes that influence emissions of constituents into the atmosphere;
- identifies the emissions released into the atmosphere that are associated with natural weathering of petroleum, mechanical recovery, and ISB;
- compares the emissions from ISB to emissions from burning vegetative fuels in residential, agricultural, and forest/land management scenarios;
- compares atmospheric emission profiles associated with cleanup options to address a petroleum spill.¹ These include:
 - natural recovery (i.e., weathering);
 - mechanical recovery;
 - *in situ* burning.

Additional health and safety guidance relevant to petroleum spills and ISB, including risk communication materials for the general public and personal protective equipment guidance for spill responders, are available through the American Petroleum Institute (API) (API, 2001, API, 2018; API, 2013).

¹ The effect of dispersants on volatile petroleum hydrocarbon emissions is a complex process and is beyond the scope of this evaluation.

II. Background

The following sections provide some basic background on ISB, the chemical composition of petroleum, weathering of petroleum by evaporation, and emissions associated with various petroleum spill response options, including ISB.

a. *In Situ* Burning as a Response Option

ISB is the controlled burning of spilled petroleum on or adjacent to the site of the spill (ASTM, 2014; API, 2005). ISB can also be used in situations where mechanical recovery is not a practical or effective option for removing spilled petroleum from the environment. Although ISB can be used to address spills on both land and sea (Fingas and Punt, 2000; API, 2004; API, 2005), it is typically conducted on open water using fire- or heat-resistant containment booms to concentrate floating oil to facilitate ignition and sustain burning. ISB can also be performed on broken ice without the use of containment booms or in wetlands and other onshore areas using artificial or natural barriers to concentrate floating oil.

Burning rapidly reduces the amount of spilled petroleum present in the environment. In some situations, ISB can be used as a preventative measure against continued spreading of the petroleum throughout the environment, particularly in the case of petroleum spills on water (Fingas and Punt, 2000). In comparison with mechanical recovery, ISB requires less resources and can eliminate the need to collect, transport, store, and dispose of large amounts of recovered petroleum (Fingas and Punt, 2000; API, 2005). Production of thick, black plumes of smoke, though controlled and transient, often present a degree of apprehension to using ISB as a response tool, especially with respect to the public's perception of the cleanup operation.

The benefits and drawbacks of ISB are often weighed against those of mechanical recovery as a cleanup option. Mechanical recovery also produces emissions that may pose a potential human health hazard to response workers or members of a surrounding community, and it may be less effective overall in removing petroleum from the environment. Equipment, vehicles, and vessels used in mechanical recovery operations are often powered by engines running on petroleum-derived fuels. Combustion of petroleum-derived fuels can produce many of the same emissions produced by ISB, albeit at different amounts, at different relative proportions, and at locations where emissions may be generated closer to workers and the general public than those from ISB. Atmospheric emissions from spilled petroleum and from engine exhaust produced during mechanical recovery operations is often overlooked as part of the decision-making process for response options.

b. Chemical Composition of Petroleum

Petroleum is a complex mixture of hydrocarbons of varying chemical structures and molecular weights. On a percentage basis, the elemental composition of crude oil is predominantly carbon (82–87%) and hydrogen (11–15%), as shown in **Figure 1**. Low concentrations of oxygen, nitrogen, and sulfur-containing compounds, as well as trace metals (nickel, iron, vanadium, copper, arsenic), are also commonly found in petroleum (API, 2005; API, 1999). The hydrocarbon composition of petroleum from different sources can vary widely. The composition of petroleum from the same source can even vary over time.

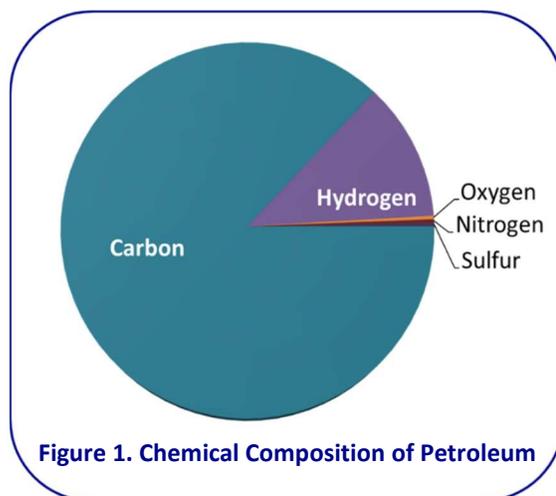


Figure 1. Chemical Composition of Petroleum

The major categories of hydrocarbons found in petroleum are paraffinic, naphthenic, and aromatic hydrocarbons (API, 2011), as illustrated in **Figure 2**.

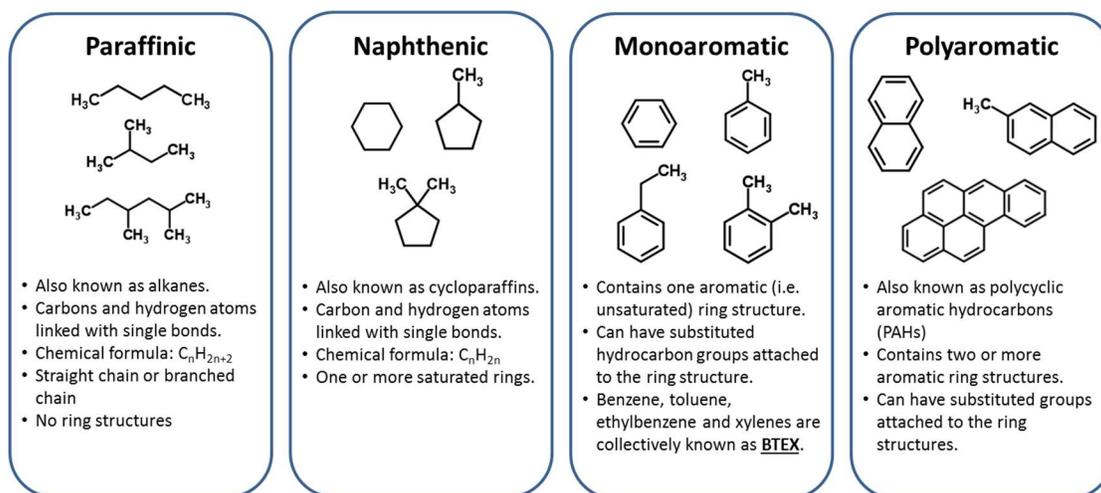
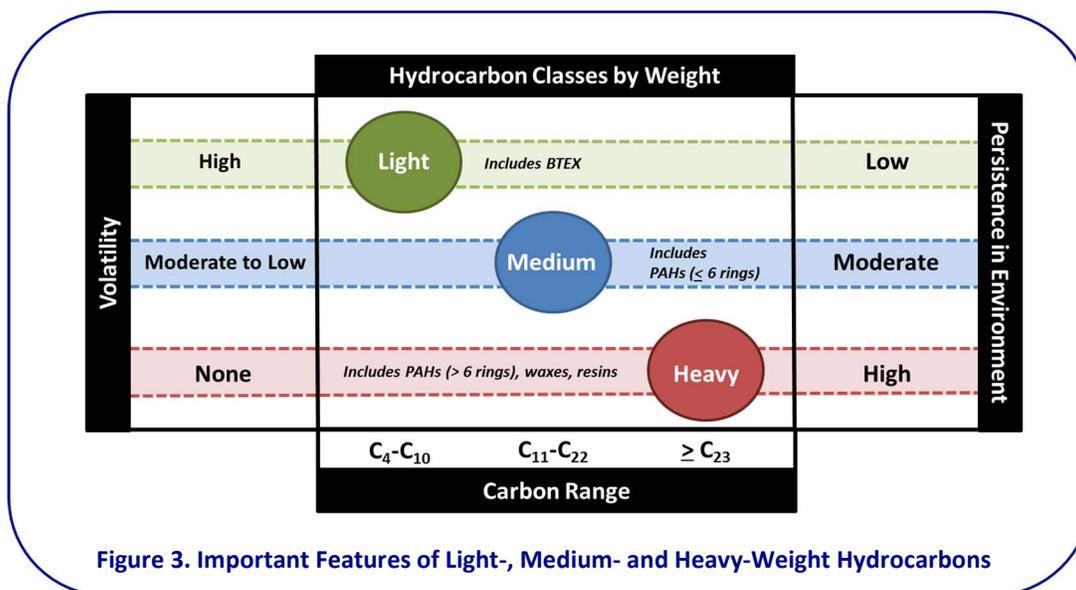


Figure 2. Major Types of Hydrocarbons Found in Petroleum

Petroleum hydrocarbons can be also categorized as either “light-weight,” “medium-weight,” or “heavy-weight” based on the number of carbons present in the molecule (API, 1999; API, 2005). The behavior and fate of individual petroleum hydrocarbons in the environment, as well as the toxicological properties of these chemicals, is influenced by the number of carbons present in the molecule’s molecular structure. An illustration demonstrating the relationship between carbon range, volatility, and persistence in the environment of light-, medium-, and heavy-weight hydrocarbons is presented in **Figure 3**. Light- and some medium-weight hydrocarbons are the constituents of petroleum that can readily evaporate and potentially create inhalation or flammability hazards close to a spill.



c. Weathering of Petroleum by Evaporation

When released into the environment, petroleum is subject to a number of weathering processes that change its chemical composition, physical appearance, and physical properties over time. For on-water spills, these processes include spreading, drifting, evaporation, dissolution, dispersion, emulsification, sedimentation, biodegradation, and photooxidation (API, 1999; API, 2001).² A lesser number of these weathering processes (i.e., evaporation, photooxidation, biodegradation) are pertinent to petroleum spills on land.

Evaporation is a natural weathering process that occurs during both water- and land-based spills. Evaporation is the transfer of volatile light- and medium-weight hydrocarbon components of petroleum to the vapor phase. This process results in the entry of volatile petroleum hydrocarbons (VPHs)³ into the ambient air above or surrounding a spill. Therefore, evaporation can produce airborne emissions of VPHs, which can be a concern to human health, particularly to workers located close to the spilled petroleum (Figure 4). VPHs also provide the fuel source for igniting and sustaining an ISB.

² A detailed discussion of how each of these weathering processes affects the behavior of spilled petroleum in the environment is beyond the scope of this document. For such information and in-depth discussion, the reader is referred to previous publications (API, 1999; API, 2005).

³ For the purposes of this report, “volatile petroleum hydrocarbons (VPHs)” is a general term used to refer to the mixture of hydrocarbons with sufficient volatility to be released into the ambient air from spilled petroleum under typical environmental conditions. “Volatile organic compounds (VOCs)” is also a term commonly used to refer to the same phenomenon.

Evaporation begins to occur immediately following a spill (API, 1999) and can last a few days to weeks following a spill depending upon oil type, weather conditions, or whether a continual release of petroleum is ongoing. Evaporation of VPHs occurs from both undisturbed oil and during the mechanical recovery process (Figure 4). Mechanical recovery operations may even have the potential to increase evaporation of VPHs due to manipulation of the spilled petroleum or, in the case of land-based spills, manipulation of soil containing spilled petroleum. Evaporation of VPHs will remain a health and safety concern as long as fresh petroleum continues to be spilled or soils contaminated with spilled petroleum are disturbed.



Figure 4. Exposure to VPHs May Occur During Mechanical Recovery

Evaporation of VPHs decreases the volume of liquid petroleum spills in the environment over time. The loss of volume will depend upon the VPH content of the spilled petroleum, which can vary substantially across petroleum types (IARC, 1989). A 20–40% loss of volume due to evaporation is typical for a crude oil spill (API, 1999; Mielke, 1990; Lewis and Aurand, 1997). Reductions in volume due to evaporation of up to 75% have been reported for light crude oils (API, 2001; Fingas, 1995), and higher losses (> 75%) have been reported for refined petroleum products with high VPH content, such as gasoline (API, 1999). Medium and heavy crude oils, which have less VPH content, have been reported to undergo reductions in volume between 10% and 40% as a result of evaporation (API, 2001).

Evaporation of VPHs during actual spills occurs rapidly. The rate of VPH evaporation decreases in a logarithmic fashion over time (Fingas, 1995) (Figure 5). This means that evaporation rates are higher when the VPH content of the spilled petroleum is high (such as immediately following a spill) and decreases as the petroleum weathers. The evaporation of VPHs is influenced by temperature; the higher the temperature, the faster VPHs will be emitted. However, unlike water, the evaporation of VPHs is not influenced by wind speed or wind turbulence due to lack of boundary-layer effects. Even though the rate of VPH evaporation is not affected by wind speed or turbulence, the concentrations of VPHs in the ambient air would be influenced by these factors. Evaporation of VPHs under calm wind conditions would be anticipated to result in relatively higher airborne VPH concentrations, as opposed to windy conditions, where VPHs would be mixed and diluted with the ambient air at a higher rate.

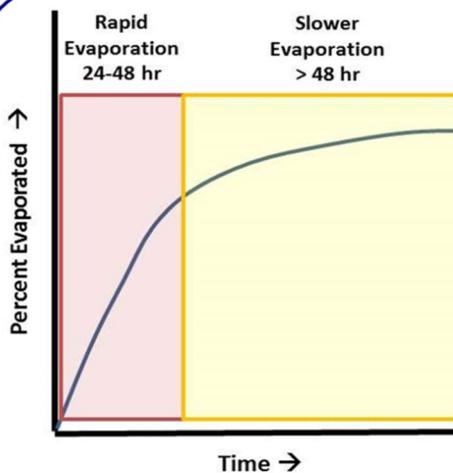


Figure 5. Evaporation Rates for Petroleum Decrease Over Time

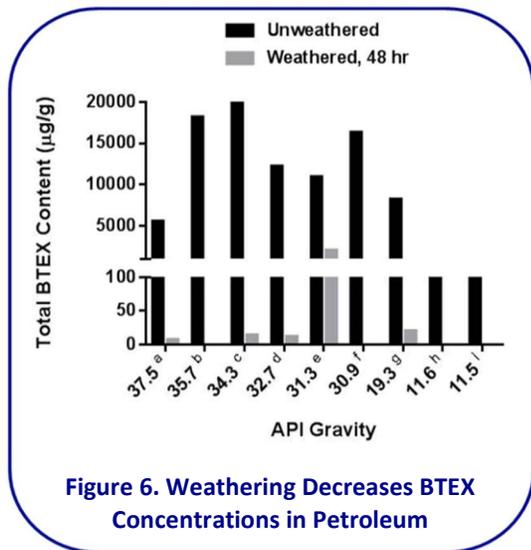


Figure 6. Weathering Decreases BTEX Concentrations in Petroleum

undetectable after 48 hours of weathering. The much lower concentrations of BTEX hydrocarbons in the weathered oils indicate that these hydrocarbons were emitted into the surrounding air due to evaporation. A similar effect is observed with paraffinic and naphthenic hydrocarbons consisting of 12 carbons or less (Wang et al., 2003).

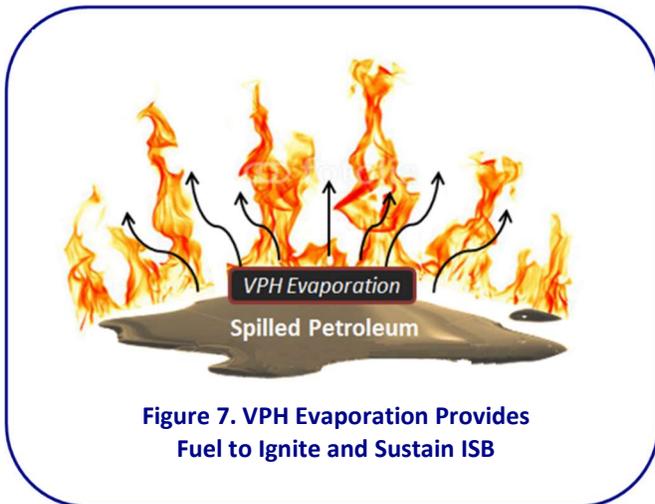


Figure 7. VPH Evaporation Provides Fuel to Ignite and Sustain ISB

Evaporation of VPHs is also critical to the process of ISB. VPHs provide the fuel source that allows for ignition of the spilled petroleum and sustains the burn (Figure 7). Weathered petroleum is more difficult to ignite due to the lack of VPHs being emitted.

The process of ISB results in much greater reduction in the volume of spilled petroleum (>97% under ideal conditions) as compared to evaporative weathering (Figure 8). However, residues⁷ will remain following ISB. Thus, mechanical recovery of residues remaining after

ISB would require less time and resources than collection of the larger volume of petroleum remaining after evaporative weathering.

⁴ BTEX = benzene, toluene, ethylbenzene, and xylenes

⁵ USEPA = United States Environmental Protection Agency.

⁶ The term “weathered oil” refers to the non-volatile petroleum hydrocarbons that had not entered the vapor phase following evaporation of VPHs. The physical properties and appearance of weathered oils are different from that of the freshly spilled oil. Weathered oil is thicker and more viscous than the original spilled products. Weathered oil contains a relatively higher percentage of heavy-weight hydrocarbons as compared to source oils.

⁷ The term “residue” refers to the material, excluding airborne emissions, remaining after oil stops burning. ISB residues have been described as thin, semi-solid, tar-like, and having a texture similar to peanut brittle.

The VPHs evaporating from petroleum provide the fuel source for ignition during the process of ISB. The VPH content of a particular petroleum product is therefore a key factor in initiating and sustaining ISB. Evaporation of VPHs begins immediately following a spill and can continue for days or several weeks during the response. Heat generated during ISB will further enhance VPH evaporation, such that heavier oils can be self-sustaining once ignited. The evaporation of VPHs represents a potential inhalation hazard to response workers or individuals located near the site of a spill. The rate of VPH evaporation decreases over time as the concentration of these constituents in the spilled petroleum is exhausted. Wind speed, wind turbulence, and the area of the spill will influence the concentrations of VPHs in the ambient air surrounding a spill. Calm wind conditions would result in potentially higher airborne VPH concentrations.

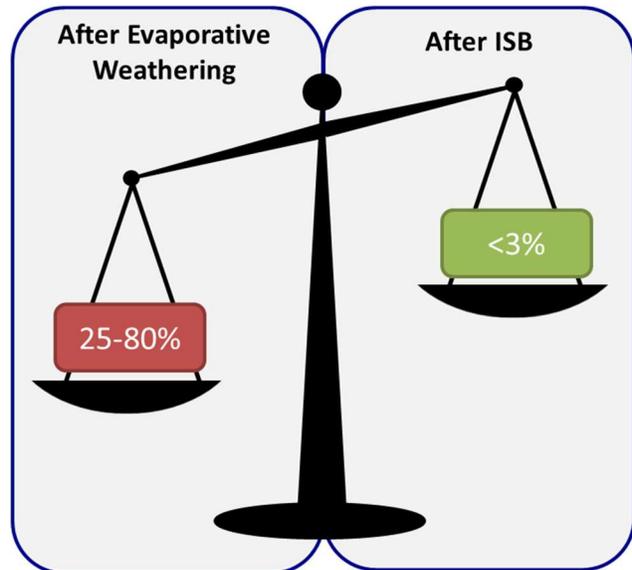


Figure 8. Petroleum Remaining in the Environment

d. Petroleum Smoke

Smoke is produced by the burning of petroleum. In a well-ventilated, oxygen-rich environment, complete combustion of petroleum would generate only water vapor, carbon dioxide (CO₂), and heat (Wakefield, 2010). However, petroleum fires are typically oxygen-starved, leading to the incomplete combustion and subsequent conversion of a portion of the petroleum into visible black smoke (Ferek et al., 1997). Smoke is defined as “the gaseous products of burning materials, especially of organic origin made visible by the presence of small particles of carbon” (Merriam-Webster, 2016). Smoke from a petroleum fire will include a heated combination of elemental carbon particulates (also known as soot), liquid droplets, and combustion gases. Often, one of the obstacles for selection of ISB as a petroleum spill response option are perceived health concerns regarding the production of petroleum smoke.

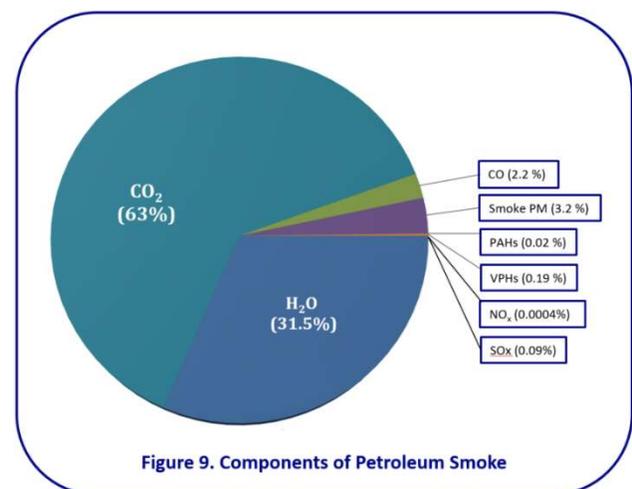


Figure 9. Components of Petroleum Smoke

Other than water, the predominant emissions from petroleum combustion are carbon dioxide (CO₂), carbon monoxide (CO), and smoke particulate matter (PM) (Booher and Janke, 1997; Ross et al., 1996) (Figure 9).

VPHs, aldehydes, and ketones, as well as nitrogen oxides (NO_x) and sulfur oxides (SO_x), may also be emitted when petroleum burns (Booher and Janke, 1997). Evaporating VPHs are

mostly consumed in petroleum fires, such as during responses where ISB is selected as the cleanup option. However, some VPHs, such as BTEX compounds, may escape combustion and be emitted into the atmosphere during the fire. Of note, significantly larger quantities of these VPHs are emitted from spilled or pooled petroleum and petroleum products due to evaporation as compared to ISB (Ross et al., 1996; Buist et al., 1999; Middlebrook et al., 2012).

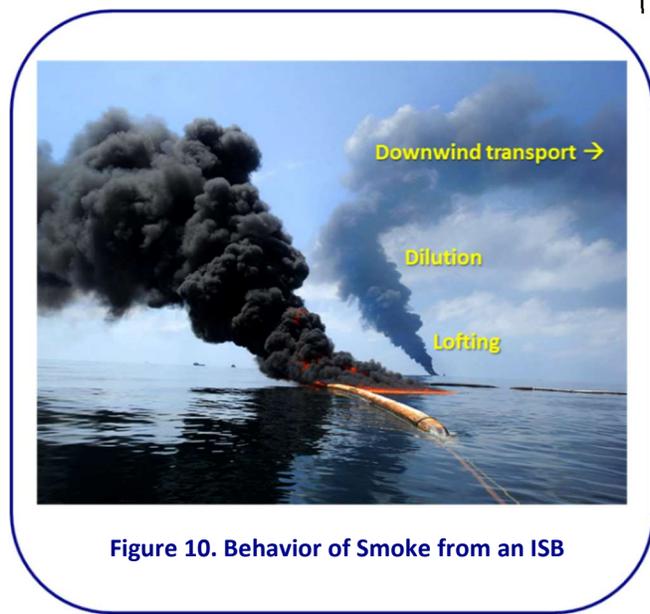


Figure 10. Behavior of Smoke from an ISB

The visibility of the black smoke that emanates from a petroleum fire (Figure 10) is due to the presence of PM, which is 80% to 90% elemental carbon particulates with only trace amounts of organic compounds (such as PAHs) adsorbed to the elemental carbon core (Booher and Janke, 1997; Fingas et al., 1996a). The absolute quantity of PM produced by burning petroleum will be influenced by the type of petroleum product burning and the availability of oxygen. In a review of published soot production studies, Fingas et al. reported that about 5% to 8% of the volume of burning diesel fuel is emitted as soot (i.e., PM), compared to 1% to 2% for burning crude oil (Fingas et al., 1996a).

e. Particulate Matter

Among the constituents released from the combustion of petroleum, exposure to PM represents the greatest health hazard to the general public. Due to the intense heat of a petroleum fire, PM will become entrained⁸ in the air and initially loft high into the atmosphere in a plume of black smoke (McGrattan et al., 1995; Middlebrook et al., 2012). Wind conditions will direct the movement of the lofted PM, diluting and dispersing the PM downwind from the source until it eventually reaches ground level and settles on cooler surfaces (Fingas et al., 2001) (Figure 10). PM can also pose a potential health hazard to response workers at elevated concentrations and under certain environmental conditions. For example, temperature inversions⁹ can act to prevent lofting of PM from a petroleum fire and increase the potential for workers in the immediate vicinity of the fire to be exposed to elevated concentrations of PM.

Airborne PM can be generated from a variety of sources, including combustion of various types of fuels. PM is generally classified according to its aerodynamic diameter¹⁰. PM from a petroleum fire consists of

⁸ Entrainment is a term frequently used in fire research to describe the mixing of combustion products with fresh air. Air turbulence generated by a petroleum fire will entrain a substantial fraction of PM, which is first step in transport and dispersion of PM away from the fire source (McGrattan et al. 1995).

⁹ A temperature inversion is an atmospheric condition where the normal decrease in temperature with height switches to the temperature increasing with height. This can act to trap entrained PM at lower heights in the atmosphere.

¹⁰ Individual particulates in PM can be irregularly shaped. The aerodynamic diameter is the diameter of an idealized spherical particle that corresponds to the volume that an irregularly shaped particulate may occupy as it moves through the air. Aerodynamic diameter is the most common measurement of particle size.

individual particulates that range in size from approximately 0.005 μm to 100 μm in aerodynamic diameter (Evans et al., 2001, Valavanidis et al., 2008). Classifications include total suspended PM having a diameter less than 100 μm ; coarse particulate matter with diameters ranging from 2.5 μm to 10 μm (i.e., PM_{10}); fine particulate matter with diameters that are 2.5 μm or smaller (i.e., $\text{PM}_{2.5}$); and ultrafine particulate matter with diameters less than 0.1 μm (i.e., $\text{PM}_{0.1}$) (Fingas, 2010; Valavanidis et al., 2008).

There is an increased concern for potential adverse health effects as the size of inhaled PM decreases. PM_{10} and $\text{PM}_{2.5}$ deposit at different locations in the respiratory tract (Figure 11), with PM_{10} having a higher probability of deposition in the upper airways and the bronchial tree, and $\text{PM}_{2.5}$ penetrating deeper into the airways (Valavanidas et al., 2008; Donaldson et al., 2001). As PM_{10} and $\text{PM}_{2.5}$ deposit in different locations in the lung, they are likely to cause injury through different biological mechanisms resulting in different health outcomes (WHO, 2013). The airborne smoke particles generated in a petroleum fire are on average

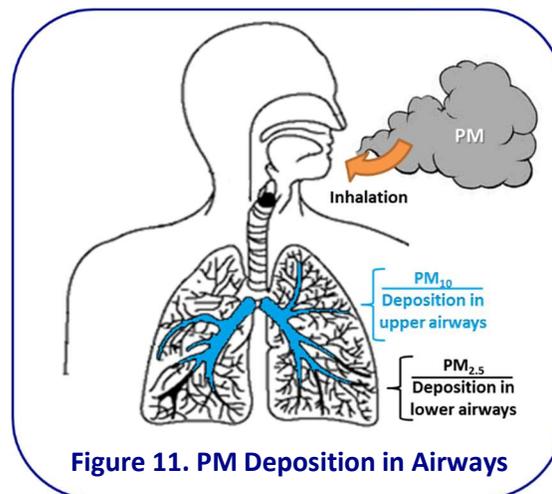


Figure 11. PM Deposition in Airways

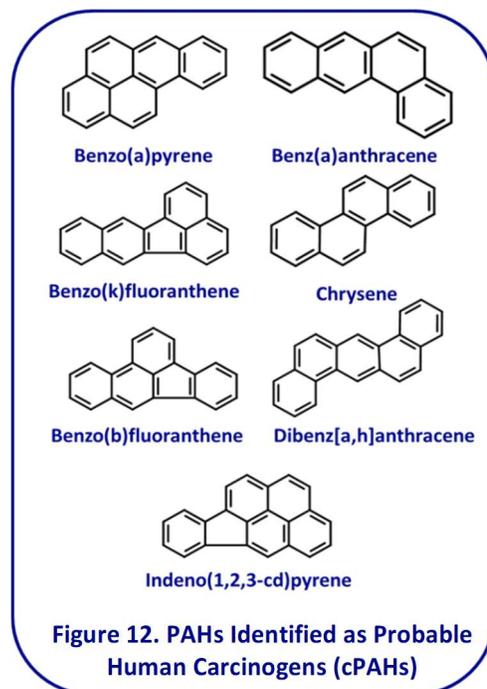
less than 1 micrometer (μm) in diameter, which is small enough to penetrate into the gas exchange regions of the lung (Ross et al., 1996; Buist et al., 1999). Measurements of PM_{10} and $\text{PM}_{2.5}$ include particulates in this size range, with measurements of $\text{PM}_{2.5}$ providing better estimates of the concentration of airborne particulates that may deposit in the deep airways of the lung. PM has consistently been identified as the primary human health safety hazard associated with ISB (RRT, 1996; NRT, 1998). Ambient air quality standards have been established for $\text{PM}_{2.5}$ as well as PM_{10} . ***The analyses presented in this report focuses on $\text{PM}_{2.5}$, given that $\text{PM}_{2.5}$ is capable of penetrating deeper into the lung and is associated with potentially more severe health effects.***

f. Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are a large class of organic hydrocarbons with diverse molecular structures, the common structural feature being the presence of multiple aromatic rings. PAHs are natural components of petroleum and are emitted from petroleum fires as a result of incomplete combustion. PAHs are also emitted from the incomplete combustion of numerous other fuel sources, including vegetative fuels (i.e., wood, leaves, grasses, underbrush), coal, garbage, and many others (USEPA, 2008). Much like the VPHs emitted from weathering petroleum, PAH emissions due to fuel combustion are produced as a mixture of different PAH species. A majority of the PAHs emitted as a result of combustion will primarily be adsorbed to particulate matter in petroleum smoke.

PAHs are typically not considered an acute inhalation hazard to humans (ATSDR, 1996), though it is proposed that long-term exposure to some PAHs can increase lifetime cancer risk. Not all PAHs are carcinogenic. The carcinogenic potential of a PAH

mixture is associated with PAH species within the mixture that act through a carcinogenic mode-of-action. As shown in **Figure 12**, USEPA has identified several PAHs as probable human carcinogens. These are referred to as cPAHs in this report. The carcinogenic potential of cPAH mixtures is evaluated using a benzo(a)pyrene (B[a]P) equivalence approach that relates the carcinogenic potency of a particular cPAH to a reference compound, B[a]P. Using the B[a]P equivalence approach, one can calculate a summed value of B[a]P equivalents that represents the carcinogenic potency for a PAH mixture. The seven cPAHs identified by USEPA provide a good indicator of the presence of the carcinogenic PAHs in a mixture, and are routinely measured as a component of particulate matter from combustion of various fuel types. Emissions of carcinogenic chemicals such as cPAHs may be perceived as a drawback to the use of ISB. However, a variety of sources have identified cPAHs as a minor human health hazard that may be associated with ISB (Barnea, 1995; RRT, 1996; NRT, 1998). ***The analyses presented in this report focuses on cPAHs using the B[a]P equivalents approach in order to determine if emissions of cPAHs from petroleum fires are similar to emissions observed during combustion of other fuel types¹¹.***



¹¹ Relative potency factors (RPF) used in this report are those listed in the USEPA Provisional Guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons (USEPA, 1993), as follows: benzo(a)pyrene = 1, benz(a)anthracene = 0.1, benzo(b)fluoranthene = 0.1, benzo(k)fluoranthene = 0.01, chrysene = 0.0001, dibenz[a,h]anthracene = 1, indeno(1,2,3-cd)pyrene = 0.1. Concentrations or emission factors for these individual constituents are multiplied by their respective RPFs, and the results are summed to provide a single value for B[a]P equivalents.

e. Summary of Emissions Associated with Petroleum Spill Response Options

Options for petroleum spill response activities in the immediate aftermath of a spill that are aimed at removing or reducing the amount of petroleum in the environment include:

- natural recovery;
- mechanical recovery;
- *in situ* burning.

The choice of the response option is dependent upon many factors, including protecting the health and safety of response workers and members of the public, effectiveness for preventing or reducing environmental impacts, technical feasibility, jurisdictional regulations governing the spill site, resource availability, and others (Fingas and Punt, 2000). Protection of human health is one of the initial and most important factors that is considered when making decisions regarding petroleum spill response options. The types of atmospheric emissions produced as a result of petroleum spill response activities will vary greatly depending upon which response option is chosen.

The emissions of primary and secondary concern to human health for petroleum spills and ISB are listed in **Table 1**.

Table 1. Summary of Key Emissions from Spilled and Burning Petroleum

Type of Emission	Emitted From	
	Spilled Petroleum	Burning Petroleum
Primary Emissions of Potential Concern		
Volatile Petroleum Hydrocarbons (VPH)	Yes	Reduced by burning
Smoke Particulate Matter (PM ₁₀ and PM _{2.5})	No	Yes
Polycyclic Aromatic Hydrocarbons (cPAHs)	No	Yes
Secondary or Situation-specific Emissions of Potential Concern		
Combustion Gases (CO, CO ₂ , SO ₂ , NO _x)	No	Yes
Hydrogen Sulfide (H ₂ S)	Yes; sour petroleum only	Reduced by burning

During natural recovery or during mechanical recovery of spilled petroleum, emissions of VPHs are the primary inhalation hazard. VPHs will be emitted as a complex mixture of different types of hydrocarbons (i.e., paraffinic, naphthenic, aromatic) of various carbon chain lengths. Of particular concern is benzene, a carcinogenic aromatic petroleum hydrocarbon whose concentration in the air surrounding a petroleum spill may be in excess of health protective exposure levels established for workers. VPHs are also emitted

during the burning of petroleum, but in much smaller quantities than from non-burning petroleum.^{12,13} The potential for hydrogen sulfide (H₂S) release following a “sour” petroleum spill can be reduced by burning. A consideration that must be accounted for is the generation of combustion products such as carbon monoxide (CO), carbon dioxide (CO₂), and, in the case of “sour” petroleum, sulfur dioxide (SO₂). Formed as an oxidation product during the combustion process, SO₂ is both toxic and irritating to the mucus membranes, where exposure to water facilitates the formation of sulfuric acid upon contact. However, the concentration of these products has been described as being well below any levels of concern due to widespread dispersal over the ISB site and not having apparent association with plume trajectory (Fingas et al., 1996b). During ISB, the emission of primary concern to human health is PM, which is small enough to penetrate into deep airways of the lung.¹⁴ cPAHs are also emitted (at lower concentrations than PM) from petroleum fires and are predominantly found adsorbed to the PM component of petroleum fire smoke.¹⁵ PM and cPAH would not be emitted from the spilled oil during natural recovery or mechanical recovery, but may be emitted from the engines of response vehicles, vessels, and equipment used during response.

III. Duration of ISB

ISB is a short-lived event. The spilled petroleum is consumed rapidly by the fire, and under typical conditions (and depending on the size of the spill), ISBs will last only a few minutes to a few hours. **Table 2** summarizes burn rates reported in scientific literature in terms of barrels per minute (bbl/min) and gives a range of plausible ISB durations based on different volumes of spilled petroleum. For example, based on the reported values, an ISB addressing 800 barrels of spilled petroleum is anticipated to last somewhere between 1 hour and 7 hours. The exact duration will vary depending upon environmental conditions at the site of the spill, as well as the type and thickness of the oil. The anticipated ISB durations in **Table 2** are consistent with anecdotal reports from the Deepwater Horizon oil spill, where ISB was used extensively as a remedial strategy. Out of 411 ISBs conducted during Deepwater Horizon, the average burn time was 58 minutes (Allen et al., 2011). Even the largest ISBs from that event did not last more than 12 hours (Mabile, 2012). It is notable that burn rates reported for actual ISB events are higher than those reported for test burns.

¹² For more information on exposure limits for benzene, BTEX hydrocarbons, and other VPHs, the reader is referred to ACGIH 2016, NIOSH 2010, and/or OSHA/NIEHS 2010.

¹³ For more information on exposure limits applicable to the public, the reader is referred to DOE/SCAPA 2016.

¹⁴ For information on action levels for PM that may be applicable to response workers or the public, the reader is referred to NIOSH, 2010; OSHA/NIEHS, 2010; and/or Lipsett, 2013.

¹⁵ For information on actions levels for airborne PAHs, the reader is referred to USEPA 2016.

Table 2. Anticipated Durations of ISB for Varying Volumes of Spilled Petroleum

Literature Source	Event/Study	Burn Rate (bbls/hr)	Barrels Spilled				
			100	200	400	600	800
			Anticipated Duration of ISB (minutes)				
McGrattan et al. (1997)	ACS ^a	115	52	104	209	313	417
	NOBE ^a	140	43	86	171	257	343
NOAA (2012)	NOBE ^a	200	30	60	120	180	240
Allen and Ferek (1993)	Kuwait Oil Fires ^b	715	8	17	34	50	67
Mabile (2012)	Deepwater Horizon ^b	750	8	16	32	48	64
Range of ISB Duration (minutes):			8 52	16 104	32 209	48 313	64 417
<i>ACS = Alaska Clean Seas Test Burn. NOBE = Newfoundland Offshore Burn Experiment. ^a Denotes staged test burns. ^b Denotes ISB or incidental oil fires in the field.</i>							

IV. Emission Profiles Associated with Petroleum Spill Response Options and Other Anthropogenic Sources.

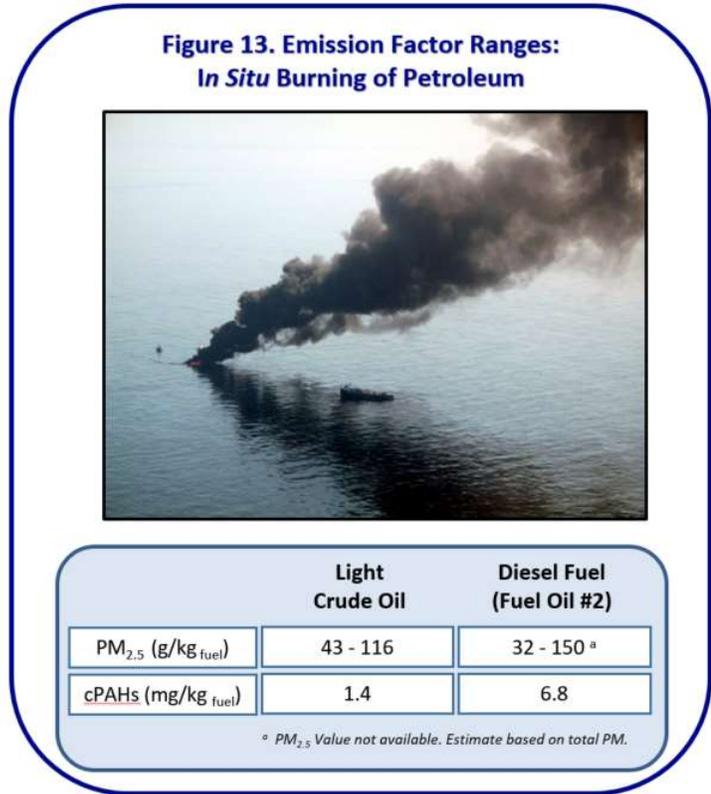
In the sections below, PM_{2.5} and cPAHs are used as the basis for comparison of emission profiles from ISB and from combustion of various types of petroleum-derived fuels and vegetative fuels. This section begins with a discussion of emission factors (EFs), followed by comparison of EF ranges from burning of various fuel types. The types of emissions that can be expected from ISB and burning of vegetative fuels is quite similar; therefore, the final portion of this section equates the emissions from ISB to those from burning of specific types of vegetative fuels, namely:

- woodstoves used in residential settings;
- prescribed burning of sugarcane fields in an agricultural setting;
- prescribed burning of pine forests in a land management setting.

a. Emission Factors

Ranges of EFs are used as the basis for the comparisons of PM_{2.5} and cPAH emission profiles between ISB and burning of other fuel types. In the context of this report, an EF is a ratio of the amount of a constituent generated as the result of combustion divided by the amount of source material (i.e., fuel) consumed during the combustion process. For example, if 2,000 grams (g) of PM_{2.5} were generated for every 10 kilograms (kg) of crude oil burned, the EF would be 200 g/kg (i.e. 2,000 ÷ 10 = 200). A range of EFs for petroleum and various other fuel types were determined through a survey of scientific literature, as discussed in Appendix A. Due to some degree of variability in the reporting of PM, conservative assumptions were prepared to calculate the EF associated with PM_{2.5}. In some instances, only a single EF estimate, as opposed to a range, was identified and used in the emission profile comparisons.

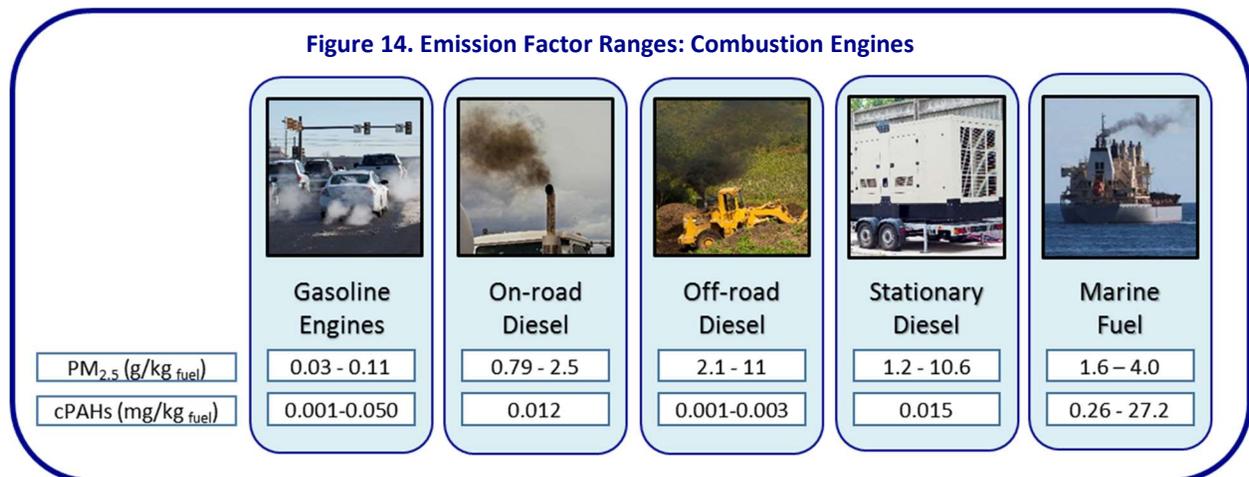
Figure 13 lists the range of EFs for PM_{2.5} and cPAHs for ISB of light crude oil and diesel fuel (Fuel Oil #2). The range of EFs were based on a literature survey of studies of petroleum combustion performed in laboratory settings, large-scale outdoor test burns, and field observations from studies of real-world events that involved the burning of petroleum (e.g., the Kuwaiti oil fires in the early 1990s and Deepwater Horizon ISBs in 2010). These sources are discussed in detail in Appendix A. Overall, burning of crude oil produces less PM_{2.5} and cPAHs per kg of fuel compared to burning of diesel fuel.



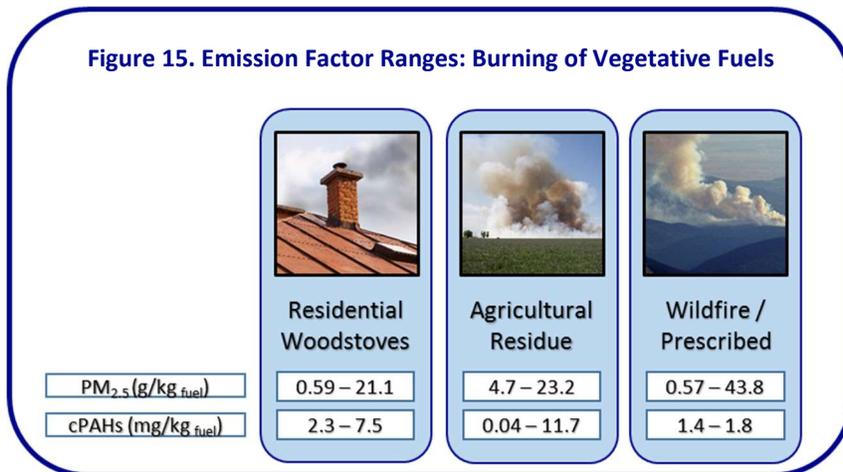
During petroleum spill response activities, a variety of vehicles, vessels, and equipment may be employed to assist in the cleanup efforts. These vehicles, vessels, or

equipment are commonly powered by combustion engines that use petroleum-derived fuels. Exhaust from these engines also contains constituents that are generated during ISB, including PM_{2.5} and cPAHs.

Figure 14 lists the range of EFs for PM_{2.5} and cPAHs associated with the exhaust from various combustion engine types. These values are derived from key studies present in scientific literature as detailed in Appendix A. The information available suggests that, under most conditions, combustion engines produce less PM_{2.5} and cPAHs per mass of fuel burned as compared to ISB of light crude oil and diesel fuel.



In comparison to the rare use of ISB, there are far more common practices that generate smoke. Petroleum is a naturally occurring organic substance. Large-scale burning of other types of natural organic material, such as vegetative fuels, occurs regularly in the United States and elsewhere. For example, burning of agricultural residue (the plant material remaining in fields after a crop harvest) is a common practice in many areas of the world, including the United States. Burning of crop residue is an efficient way to clear the land for the next growing season and help replenish nutrients taken up from the soil by recently harvested crops. Prescribed burning of brush and tree debris and wildfires are also relatively common occurrences that can produce large amounts of smoke. The burning of wood for residential heating using woodstoves and fireplaces is also quite common in the United States and elsewhere. Emissions from domestic burning of wood can be similar in nature to those that occur during wildfires and prescribed burning. **Figure 15** lists the range of EFs for PM_{2.5} and cPAHs for these types of combustion. As above, the EF values are based on a survey of scientific literature as detailed in Appendix A.



b. Comparison of Emission Factors

Figure 16 compares the EF range for PM_{2.5} from ISB with EF ranges for PM_{2.5} from different types of combustion engines, as well as the burning of vegetative fuels in various settings. The boxes represent the minimum and maximum EF values within the range for the various combustion types. The yellow shaded region represents the upper and lower end of the EF range for ISB of light crude oils. The EF range for PM_{2.5} for ISB of light crude oil are greater than the EF ranges for combustion of petroleum derived fuels in different engine types, as well as the EF ranges for residential woodstoves and burning of agricultural crop residue. There is minimal overlap between the lower end of PM_{2.5} EF range for crude oil and the upper end of the PM_{2.5} EF range for wildfire/prescribed burning. These comparisons indicate that ISB tends to produce more PM_{2.5} per amount of fuel burned as compared to either combustion engines that run on petroleum fuels or the burning of vegetative fuels.

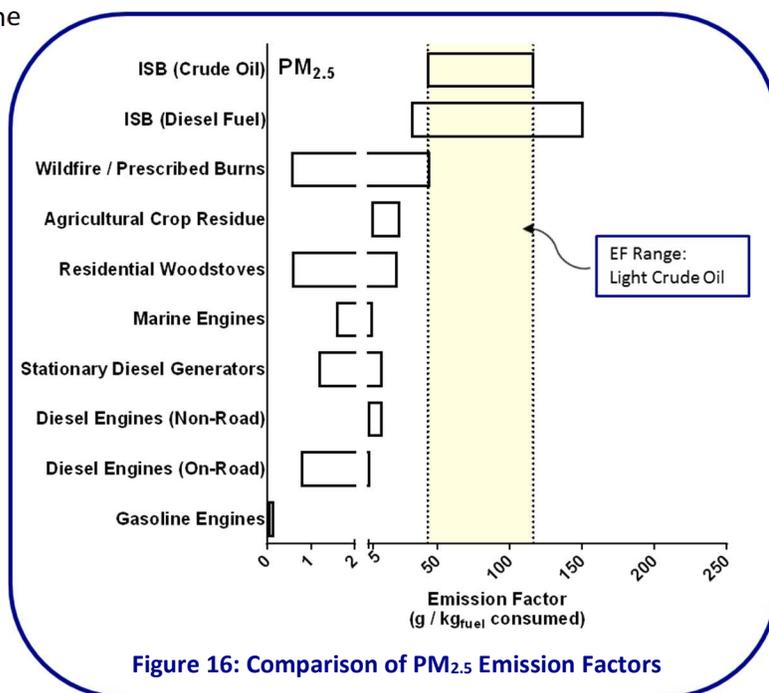


Figure 16: Comparison of PM_{2.5} Emission Factors

Figure 17 compares the EFs for cPAHs associated with ISB of light crude oil and diesel fuel with EF ranges from different types of combustion engines, as well as burning of vegetative fuels. As above, the boxes represent the minimum and maximum of the EF value range for the various combustion types. The EFs for ISB of crude oil and diesel fuel (denoted with an “X”) are composite values for cPAH emissions reported by USEPA (USEPA, 2002) and were derived from a variety of laboratory, mesoscale, and large field studies of petroleum combustion. To facilitate comparison, a vertical dotted line is

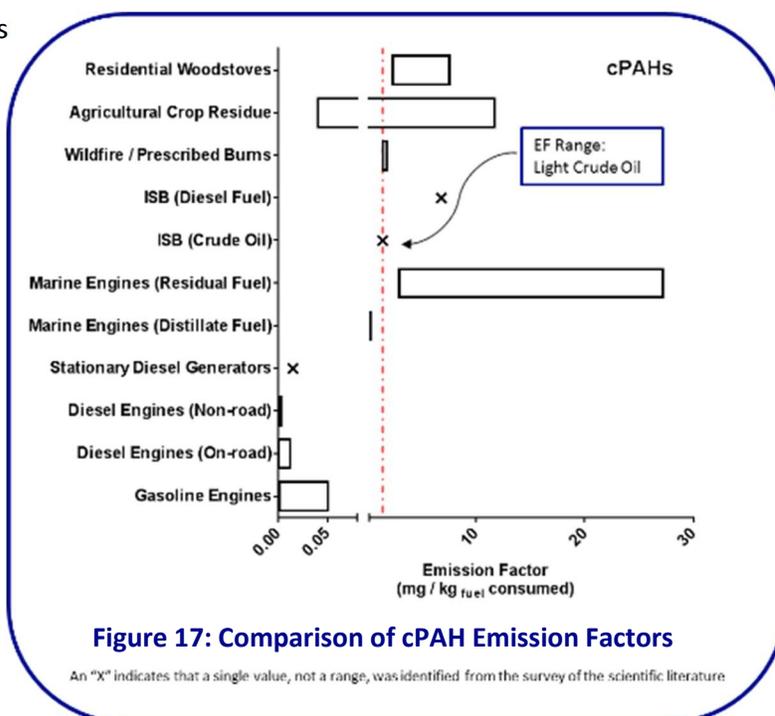


Figure 17: Comparison of cPAH Emission Factors

An “X” indicates that a single value, not a range, was identified from the survey of the scientific literature

shown in **Figure 17** that corresponds to the cPAH EF for ISB of light crude oil. The EF for cPAHs from ISB of light crude oil is greater than the EF ranges for gasoline engines, on-road and non-road diesel engines, and diesel generators, but lower than residual fuel marine engines and ISB of diesel fuel. The cPAH EF for ISB of light crude oil overlapped with the EF ranges for burning of agricultural residue and wildfire or prescribed burning, and was less than the EF range reported for residential woodstoves. Overall, the EF for cPAHs from ISB of light crude oil is within the range reported for large-scale burning of vegetative fuels.

c. Equating ISB Emissions with Emissions from Burning of Vegetative Fuels

The total amount of emissions produced during a fire will not just depend on the emission rate or the duration of the burn, but also on the amount of fuel consumed by the fire. In order to put ISB emissions into perspective, the amount of PM and cPAHs produced during ISB of various amounts of petroleum was compared to the amount of PM and cPAHs produced during large-scale burning of vegetative fuels. Three specific examples are used: 1) use of woodstoves in a residential setting; 2) burning of sugarcane in an agricultural setting; and 3) prescribed burning of slash pine forest debris in a land management setting. Each of these are common and familiar occurrences that involve intentional combustion of vegetative fuels. **Table 3** and **Table 4** provides a summary of this analysis, which is described in greater detail in Appendix B.

Table 3. Equating ISB Emissions to Emissions from Burning of Vegetative Fuels

Volume of Petroleum for ISB (barrels):	100	200	400	600	800
Time Scale for ISB (minutes):	8 - 52	17 - 104	34 - 209	50 - 313	67 - 417
ISB Emission Type:	Equivalent Number of Woodstoves ^a				
PM _{2.5}	752	1507	3008	4513	6017
cPAHs	63	127	253	380	507
	Estimated Number of Woodstoves in U.S.				1,793,000
	Equivalent Number of Sugarcane Fields ^b				
PM _{2.5}	0.9	1.7	3.4	5.2	6.9
cPAHs	1.6	3.3	6.5	9.8	13.1
	Estimated Number of Sugarcane Fields Burned Annually				12,000
	Equivalent Number of Pine Forest Wildlife Management Plots ^c				
PM _{2.5}	0.5	1.0	2.1	3.1	4.1
cPAHs	0.3	0.7	1.4	2.1	2.8
	Estimated Number of Pine Forest Wildlife Management Plots Burned Annually				122,000
^a For underlying assumptions, see Appendix B, Section a. ^b For underlying assumptions, see Appendix B, Section b. ^c For underlying assumptions, see Appendix B, Section c.					

Table 4. ISB Emissions Illustrated as a Percentage of Burning Vegetative Fuel Emissions

Volume of Petroleum for ISB (barrels):	100	200	400	600	800
Time Scale for ISB (minutes):	8 - 52	17 - 104	34 - 209	50 - 313	67 - 417
ISB Emission Type:		Percentage of Total Number of Woodstoves in U.S. ^a			
PM _{2.5}	0.04%	0.08%	0.17%	0.3%	0.3%
cPAHs	0.004%	0.007%	0.01%	0.02%	0.03%
		Percentage of Number of Sugarcane Fields Burned Annually ^b			
PM _{2.5}	0.008%	0.01%	0.03%	0.04%	0.06%
cPAHs	0.01%	0.03%	0.05%	0.08%	0.1%
		Percentage of Pine Forest Wildlife Management Plots Burned Annually ^c			
PM _{2.5}	0.0004%	0.0008%	0.002%	0.003%	0.003%
cPAHs	0.0002%	0.0006%	0.001%	0.002%	0.002%

^a For underlying assumptions, see Appendix B, Section a.
^b For underlying assumptions, see Appendix B, Section b.
^c For underlying assumptions, see Appendix B, Section c.

Overall, the amount of PM_{2.5} and cPAH emissions that would be produced by an ISB during an oil response event would only be a small percentage of the total PM_{2.5} and cPAH produced annually in the United States by the burning of vegetative fuels in domestic, agricultural, and land management settings.

d. Summary and Conclusions

In summary, these comparisons indicate that:

- EFs for PM_{2.5} and cPAHs from ISB of petroleum are similar to those observed for the burning of vegetative fuels for residential home heating or large-scale burning of vegetative fuels in common agricultural or land management practices;
- the amount of PM_{2.5} and PAH emission from occasional use of ISB in an emergency response setting would be equivalent to only a small percentage of the emissions produced by the burning of vegetative fuels in domestic, agricultural, or land management scenarios annually.

V. Emissions and Potentials for Exposure in the Context of Spill Response Options

The following sections contain a more detailed discussion of the key emissions associated with the various response options and how the potential for response workers and members of the public to be exposed to different types of emissions changes depending on what response option is selected. Information from previous studies regarding airborne concentrations and the migration of constituents from evaporating and burning petroleum is used to inform these discussions.

Additional health and safety guidance for response workers and members of the public, including risk communication materials and personal protective equipment guidance for responders, are available through the American Petroleum Institute (API) (API, 2001; API, 2018; API, 2013).

a. Natural Recovery

VPHs emitted from spilled petroleum due to evaporation would be the primary constituents of concern when natural recovery (Figure 18) is selected as an option. The VPHs would be emitted as a complex mixture of paraffinic, naphthenic, and aromatic hydrocarbons, including BTEX compounds.

Occupational exposure limits for most VPHs are designed to prevent acute nervous system effects (e.g., dizziness, motor incoordination, headaches, lethargy) and irritation of the eyes and upper respiratory tract. Benzene exposures should also



Figure 18. Natural Recovery

be limited, given that this chemical is a known human carcinogen. Evaporation from spilled petroleum would be expected to begin immediately after the spill and continue for the next 48 hours, if not longer (API, 1999; API, 2001). The rate of evaporation would decrease as the amount of VPHs in the spilled product becomes depleted (Fingas, 1995). Because no burning would occur in this scenario, PM and cPAHs produced as by-products of petroleum combustion would not be a concern to workers or the public.

Total VPH¹⁶ concentrations measured at sea level during the NOBE test burns **prior to ignition** of the spilled petroleum were less than 12 mg/m³ at stations several hundred meters downwind and approximately 150 meters crosswind of the spill location (Fingas et al., 1995). These concentrations are well below health protective exposure limits established for VPHs. Benzene concentrations were also well below health protective exposure limits at these sampling locations. In addition, worker exposure monitoring for VPHs and benzene during the NOBE burn experiments, which included periods prior to ignition of the test fuel, indicated that significant exposures to VPHs did not occur (Bowes, 1996). These data indicate that individuals downwind of a petroleum spill past a distance of 150 meters (and likely less) would not be exposed to concentrations of VPHs or benzene in excess of health protective occupational exposure limits. The potential for inhalation exposure to VPHs would increase with increasing proximity to the spilled petroleum. During Deepwater Horizon, NIOSH also performed area air sampling and personal breathing zone (PBZ) air sampling of workers aboard source control vessels tasked with containing, controlling, and stopping the release of oil from the damaged well (Ahrenholz and Sylvain, 2011). While VPHs were detected in each type of air sample, the concentrations were well below health protective exposure limits. Benzene was also detected in area air samples at concentrations below health protective exposure limits (benzene was not detected in PBZ samples). Air monitoring for VPH and

¹⁶ Measured as total volatile organic hydrocarbons (VOCs).

benzene during in-land spills have also demonstrated detections of the constituents in geographical areas up to 3 miles from the spill site; however, concentrations were below health protective limits (Dykema and Gray, 2015).

Overall, the potential for inhalation exposures to VPHs at levels that would be an acute human health concern is low when natural recovery is selected as the response option. The use of natural recovery implies that workers would not actively be engaged in response operations around a spill site. Likewise, members of the public would be at low risk if they are located a sufficient distance away from the spill. The risk associated with VPH exposure would decline over time as natural evaporation occurs. While natural recovery may pose the least relative risk to response workers and members of the public, this option may not be acceptable due to potential ecological impacts and the potential negative public perception of visibly-impacted land (beaching of oil, for example).

b. Mechanical Recovery

VPHs emitted from spilled petroleum due to evaporation would also be the primary constituents of concern when mechanical recovery (Figure 19) is chosen as the response option. In contrast to the natural recovery option, selection of mechanical recovery as the response option places workers in close proximity to spilled petroleum. For both land- and water-borne spills, response workers would be engaged in work activities aimed at collecting and removing the spilled product. These activities place workers close to or in direct contact with the spilled petroleum. The equipment and clothing used by mechanical recovery workers will require decontamination or proper disposal, potentially exposing the personnel at decontamination stations to petroleum compounds.

Field studies of land-based crude oil spills indicate that many VPHs would be present in the air above or in proximity to freshly spilled (< 48 h weathering) crude oil at concentrations below occupational exposure levels. However, concentrations of benzene were detected above occupational health protective exposure limits in locations where oil spill response workers could be involved in mechanical recovery operations (Harrill et al., 2014).

Mechanical recovery operations on water often involve capturing or booming the spilled petroleum prior to removal of the petroleum from the water with a skimmer. This has the potential to enhance evaporation, thus increasing the likelihood of worker inhalation exposures. Similarly, for land-based spills, mechanical recovery can involve the use of heavy construction equipment such as



Figure 19. Mechanical Recovery

bulldozers, backhoes, and graders to remove petroleum-contaminated soil or beached oil. Disturbing petroleum-contaminated soil can also increase airborne concentrations of VPHs, including benzene, thereby increasing the likelihood of worker inhalation exposures. Volatilization of VPHs trapped in soil pore spaces may continue to occur even after complete evaporative weathering of petroleum on the soil surface has occurred. In such cases where fresh (unweathered) petroleum in subsurface soil is continually excavated, the potential for inhalation exposures to VPHs, including benzene, may be extended over days to weeks as remediation proceeds.

The potential for inhalation exposure of the general public to VPH emissions from mechanical recovery operations would be low, similar to that of the natural recovery option, especially if members of the public are more than 150 meters from the spill site. If a spill occurs in the middle of a populated area, such as that which may result from a pipeline release, an evaluation of potential inhalation exposure to residents in the immediate area should be considered and appropriate steps taken to limit exposure of the public to VPHs.

PM and cPAHs produced as by-products of petroleum combustion would not be a concern to workers or the public under the mechanical recovery response scenario. However, PM and PAHs would be emitted into the surrounding atmosphere by diesel- and gasoline-powered vehicles, heavy equipment, stationary combustion engines, and marine vessels used to execute the response. Mechanical recovery of spilled petroleum can be labor- and resource-intensive in that large volumes of spilled petroleum or contaminated water or soil must be collected, transported, stored, and disposed of properly. Each of these activities requires the use of equipment and vehicles that emit some of the same constituents (PM and PAHs) released during ISB.

c. *In Situ Burning*

The primary constituent of concern that results from ISB (Figure 20) as a petroleum spill response option is PM associated with the produced smoke plumes. The burning of petroleum reduces emissions of VPHs compared to natural weathering (Fingas and Punt, 2000). Except during atmospheric inversions, the smoke plume and PM associated with ISB lofts high into the air and disperses downwind of the fire (Fingas et al., 1996a). Dispersion in the air results in dilution of the PM within the atmosphere and a consistent decrease in the airborne concentration of PM as distance from the burn increases.



Figure 20. *In Situ Burning*

From a worker health and safety perspective, during ISB, response workers spend less time in close proximity to (within meters of) or directly contacting the spilled petroleum as compared to a mechanical recovery operation. Minimal worker contact with spilled petroleum further decreases potential exposure

to petroleum for decontamination station personnel. For water-borne spills, response workers may be located on the deck of a vessel during booming or collecting of petroleum that has been spread across the water's surface in order to facilitate ISB (Fingas and Punt, 2000; API, 2005). This type of job task provides less opportunity for close contact with the spilled petroleum as compared to operation of a skimmer or use of sorbents. A study of worker exposures during the NOBE test burns demonstrated that worker exposures to VPHs was minimal during job tasks associated with booming and ISB (Bowes, 1996). During the burn, worker exposures to PM would be limited if workers remain upwind and a sufficient distance from the burning oil.

Potential impacts to members of the public downwind of the burn site should be carefully assessed prior to selection of ISB as the response option.¹⁷ Measurements of PM at ground- or sea-level stations located varying distances downwind of burning petroleum were taken as part of the NOBE test burns and during several mesoscale burn experiments (Fingas et al., 1993; Fingas et al., 1994; Fingas et al., 1996a; Fingas and Punt, 2000). The amount of smoke PM from a petroleum fire is dependent upon the area of the burn. Large burn areas will produce more PM and the downwind concentrations of PM will be elevated at greater distances compared to burns that cover less area and consume less spilled oil. In a series of mesoscale crude oil test burns (Fingas et al., 1996a), the burn area ranged from 37.2 m² for spill volumes of 8–21 barrels to 231 m² for spill volumes of 74–88 barrels. The burns lasted between 15 and 20 minutes and consumed upwards of 90% of test oil. Particulate concentrations 30 meters downwind of test burn averaged 752 µg/m³, with a maximum value of 8,995 µg/m³. The PM concentration 60 meters downwind of the test burn averaged 299 µg/m³, with a maximum value of 3,075 µg/m³.

It is difficult to predict downwind concentrations of PM for specific sites given that wind speed and atmospheric turbulence will greatly affect how the particulates are dispersed in the air. Smoke modeling software such as ALOFT (A Large Outdoor Fire Plume Trajectory), developed by the National Institute for Standards and Technology and the U.S. Mineral Management Service, have been used to help predict safe distances for ISB based on site-specific data (McGrattan, 1997; Fingas and Punt, 2000). Prediction models have also been developed based on empirical data from ISB in an experimental setting. Empirical modeling of PM dispersion from burns of various sizes has been used to predict safe distances based on a maximum health protective action level of 150 µg/m³ for PM₁₀¹⁸ (Fingas and Punt, 2000; Fingas et al., 1999). For a 500 m² ISB of crude oil, these empirical models estimated that the PM₁₀ action level would be exceeded approximately 0.5 km (i.e., 500 meters or 0.3 miles) downwind of the burn site. This distance increased up to 19 km for crude oil burns of 1000 m² in area. Compared to crude oil, it was estimated that PM₁₀ action levels would be exceeded at greater distances away from an ISB of diesel fuel, due to the relatively higher PM emissions from burning diesel fuel.

Prior to use of ISB as a spill response option, these types of predictive models can provide general estimates of the PM concentrations that are expected to occur downwind of a burn and that may

¹⁷ The potential for atmospheric inversions to occur during the projected time frame of the burn should also be assessed prior to commencing an ISB. Atmospheric inversions can trap PM emissions near the water or ground surface and increase the likelihood of exposure to response workers and others near the burn site.

¹⁸ PM_{2.5} would be a more appropriate basis for predicting safe distances from an ISB as this size particle is generally considered more hazardous to human health than PM₁₀.

potentially impact downwind receptors such as members of the public. During ISB, it is advisable that real-time air monitoring for PM be conducted downwind of the burn site both within areas where potential receptors are located and upwind of the potentially impacted areas. Results should be communicated rapidly back to the burn site so that appropriate actions can be implemented to limit exposures if the downwind smoke particulate concentrations exceed a health protective action level. Actions may include shelter-in-place warnings, temporary relocation of downwind individuals, implementing fire control measures, or discontinuing the ISB.

ISB also results in emissions of some VPHs. However, the airborne concentrations of these chemicals during an ISB are much less than those that result from evaporative weathering of petroleum (Fingas and Punt, 2000; Fingas et al., 1995). The VPHs evaporating from weathering petroleum serve as the fuel source for ignition of the spilled oil (API, 2005). Thus, a majority of VPHs are consumed during combustion. Overall, the potential inhalation hazards associated with VPHs during an ISB would be less than that associated with natural weathering or mechanical recovery of the oil.

In summary, PM from ISB presents a potential inhalation hazard to both response workers and the public. The duration of ISB is on the order of minutes to hours; therefore potential exposures to workers and the public would be brief in duration. The likelihood of PM exposure in response workers can be limited by positioning workers upwind during burning. Potential exposures to members of the public downwind of the spill site should be carefully assessed prior to ISB and monitored during the burn. The airborne concentration of PM downwind of an ISB will vary according to wind speed, atmospheric turbulence, the type of oil being burned and the size of the burn area. Larger spills produce higher smoke concentrations at distances downwind of the spill site. The use of ISB results in a more efficient and complete removal of oil from the environment as compared to mechanical recovery, and requires the use of fewer pieces of particulate-emitting equipment and machinery, which can also contribute to the total emissions produced during an oil-spill response.

d. Summary of Emissions in the Context of Oil Spill Response

The response option selected following a petroleum spill will greatly influence the types of inhalation hazards that may potentially be present. For example, PM emissions may be a concern if ISB is chosen as the response option, but would not be a concern during mechanical recovery or natural weathering of spilled petroleum. The choice of response options can eliminate one hazard (i.e., combustion and potential inhalation of VPHs) while creating another (i.e., production of smoke).

Inhalation hazards may also be present for varying lengths of time depending upon the response option being used and the amount of spilled petroleum. The generation of combustion by-products from ISB would occur over a scale of minutes to hours, followed by dilution and dispersion in the atmosphere. Emissions from the natural weathering that occurs during mechanical recovery could last days or weeks depending upon site-specific circumstances, and would also be subject to dilution and dispersion in the atmosphere. The size and scale of a petroleum spill also dictates how long emissions associated with the various response options are generated. For example, if allowed to naturally weather, a relatively small petroleum spill (i.e., 100 bbls) would emit less VPHs than a relatively larger spill (i.e., 1000 bbls). Likewise, ISB and associated production of smoke from a relatively small spill would be of shorter duration than a relatively larger spill.

The weather, the surrounding environment, the type of spilled petroleum, and the disposition of the petroleum in the environment can also greatly affect what potential inhalation hazards may exist and the choice of an appropriate response option. In addition, the equipment, vehicles, or vessels used to execute a response can also contribute to the atmospheric emissions related to a petroleum spill. Each of these factors should be considered in the decision-making process for selecting a response option.

There are two general categories of people who may potentially be at risk for exposure to inhalation hazards following an oil spill: response workers and members of the public. The most important factor in considering the likelihood of an individual’s exposure to airborne constituents being emitted from spilled petroleum is proximity to the spill. The likelihood of exposure to some airborne emissions, such as VPHs, would be greater for response workers, who are typically working closer to the actual spill as compared to members of the public. On the other hand, in cases where ISB is used as the response option, migration of smoke constituents away from the spill site may be a concern to decision-makers and members of the public downwind of the spill.

Table 7 summarizes key emissions from petroleum spill response options and approximate durations of response activities. Brief comments on the potential of different receptors to be exposed to the key emissions are also provided.

Table 7. Key Emissions, Duration of Activity, and Potential Receptors Associated with Petroleum Spill Response Options.

Response Option	Key Emissions	Duration	Potential Receptors
Natural Recovery	VPH	Hours to weeks	Response: n/a Support: Possible migration of VPH downwind Public: Possible migration of VPH downwind. Concentrations would decrease with distance from spill. Lower likelihood of exposure compared to responder.
Mechanical Recovery	VPH	Hours to days	Response: Direct contact or close proximity to evaporating or recovered oil. Support: Possible migration of VPH downwind. Public: Possible migration of VPH downwind. Concentrations would decrease with distance from spill. Lower likelihood of exposure compared to responders.
ISB	PM _{2.5}	Minutes to hours	Response: Exposure minimized by staying upwind. Support: Exposure minimized by staying upwind Public: Potential migration of PM downwind. Concentrations would decrease with distance from spill. Potential for exposure less for those located upwind.
	cPAHs	Minutes to hours	Response: Exposure minimized by staying upwind. Support: Exposure minimized by staying upwind. Public: Potential migration of PAHs downwind. Not an acute inhalation hazard. Airborne concentrations would decrease with distance from spill. Potential for exposure less for those located upwind.
	Combustion Gases	Minutes to Hours	Response: Exposure unlikely due to operational safe distances from fire. Support: Exposure unlikely due to operational safe distances from fire. Public: Concentrations unlikely to pose inhalation hazard distance from ISB location.
<i>Response = Workers who are actively engaged in tasks relating to the capture of spilled petroleum that place them in direct contact or close proximity to the spilled petroleum. Support = Responders in the Command and Support Zones.</i>			

VI. Conclusions

Following a petroleum spill, the types of atmospheric emissions of potential concern to human health will vary according to which petroleum spill response option is selected. Information provided in this report is intended to help support decision-makers regarding the selection of different response options, including ISB, and provide information on the types of emissions that may be expected under each option. It also shows how exposure potentials for response workers and public to various emissions will change across response options.

During natural recovery or mechanical recovery, evaporation of VPHs will occur. VPHs, including benzene and BTEX compounds, are the primary inhalation hazard of concern for natural recovery and mechanical recovery response options. The potential for exposure to VPHs would be greatest for response workers who are in close proximity to the spill and actively engaged in mechanical recovery operations. The potential for the public to be exposed to VPHs during mechanical recovery is low, given that members of the public are typically located distant from the spill source and that airborne concentrations of VPHs will decrease with increasing distance from the spill.

In the process of ISB, VPHs are consumed as the fuel source for the fire. Thus, exposure potential related to VPHs is reduced. However, ISB results in the production of large smoke plumes that are primarily composed of PM containing elemental carbon and, to a much lesser extent, cPAHs adsorbed to the individual particulates. Emission of PM is the primary inhalation hazard of concern for ISB.¹⁹ The PM produced by ISB is similar in nature to that produced by the burning of vegetative fuels in a residential, agricultural, or land management setting, each of which is a common occurrence in the United States. Overall, the amount of PM and cPAH emissions produced by the occasional ISB of petroleum in an emergency response situation is only a small fraction of the total PM and cPAH emission produced routinely as part of normal domestic, agricultural, and land management practices. The potential for exposure to PM decreases with increasing distance from the ISB site due to mixing, dilution, and dispersion in the atmosphere. Positioning workers upwind from the ISB operations is an effective control measure for reducing the potential exposure of response workers to PM. Plume modeling prior to initiating an ISB and air monitoring in locations downwind of ISB can be effective tools for evaluating the potential for members of the public to be exposed to elevated levels of PM during an ISB.

Overall, ISB can be an effective means of removing large amounts of oil from the environment and, compared to mechanical recovery, eliminates the need for a large number of response workers to come into close proximity to spilled oil, while also eliminating the need to handle, store, transport, and dispose of large amounts of impacted media (e.g., soil, water, sorbants, etc.). Site-specific factors, such as weather conditions and the proximity of receptors downwind of a petroleum spill site, should be carefully considered before instituting an ISB. ISB can be the most effective response option for reducing the amount of spilled oil in the environment, limiting potential inhalation exposures to response workers while having minimal impacts on surrounding communities.

¹⁹ For a more detailed discussion of safety hazards specifically associated with ISB, the reader is referred to the API Technical Report 1254, *In-Situ Burning Guidance for Safety Officers and Safety and Health Professionals* (API, 2018).

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Appendix A

Emission Factors for PM and cPAHs from Burning of Petroleum, Petroleum-fueled Combustion Engines, and the Burning of Vegetative Fuel Sources

Below are descriptions and summaries of various studies that form the basis for particulate emission factor (EF) values presented in the main body of the document entitled *In-Situ Burning of Petroleum Comparison of Emissions from Burning of Petroleum, Petroleum-derived Fuels, and Other Fuel Types*.

A.1. PM and cPAH Emission Factors from ISB of Petroleum

The primary emission of human health concern from the combustion of petroleum and refined petroleum products is PM. Several studies have reported emission factors (EF) for PM as a result of burning of petroleum. However, there is very little uniformity in the manner in which PM EFs are reported, particularly with respect to different particulate size ranges. **Table A.1.1** summarizes the estimated range of EFs for PM_{2.5} from ISB of light crude oil and diesel fuel (i.e., Fuel Oil #2). Several of the surveyed studies reported EFs for ISB of light crude oil were reported as either PM_{3.5} or PM₁. These values were assumed to be reasonable estimates of the amount of PM_{2.5} generated during ISB of crude oil and were used to define the PM_{2.5} EF range. EFs for PM_{2.5} for ISB of diesel fuel were not identified in the literature. However, EFs for PM_{Total} were reported in a small number of studies. In a conservative approach, it was assumed that 75% of the PM_{Total} from ISB of diesel fuel would be in the PM_{2.5} size range (Evans et al., 2001), and fractional adjustment was applied to the PM_{Total} values to provide an estimated PM_{2.5} EF range for ISB of diesel fuel. Future evaluations of ISB under various conditions are likely to improve the characterization of the EF for PM_{2.5} and reduce its range and uncertainty.

Table A.1.1. PM_{2.5} Emission Factors for ISB of Petroleum

Study	Oil Type	PM _{2.5} Emission Factor (g / Kg _{fuel})
Crude Oil		
Walton et al (1994)	Alberta Sweet Crude Oil (NOBE)	111–116 ^a
Ross et al. (1996)	Alberta Sweet Crude Oil	63–111 ^b
Laursen et al. (1992)	Kuwaiti oil fires	43–52 ^b
McGrattan (1997)	Composite values	75 ^c –87 ^b
Aurell et al. (2010)	Macondo Crude Oil (Deepwater Horizon)	44–110 ^c
		Range: 43–116
Diesel Fuel (Fuel Oil #2)		
Booher and Janke (1997)	Fuel Oil #2	150 ^d
Fingas et al. (1996a)	Diesel	32–65 ^d
		Range: 32–150
<p>^a In Walton et al. (1994), smoke yields ranged from 14.8% to 15.5% corresponding 148 g to 155 g / Kg fuel burned. Approximately 75% were below 2.5 μm in size. EF values for PM_{2.5} were calculated by multiplying the smoke yields by 0.75 respectively. ^b EF values reported as PM_{3.5}. For the purposes of this report, it is assumed that measurements of PM_{3.5} are a reasonable approximation of PM_{2.5} emissions. ^c EF values reported as PM₁. For the purposes of this report, it is assumed that measurements of PM₁ are a</p>		

reasonable approximation of PM_{2.5} emissions. ^d Values reported as PM_{total}. As in Walton et al. (1994), reported values were multiplied by 0.75 to provide an estimate of PM_{2.5} emissions.

The ISB of petroleum also results in airborne emissions of cPAHs. EFs for cPAHs from ISB of crude oil and diesel fuel are listed in **Table A.1.2**. These values are those specified by the USEPA in the document entitled *Emissions of Organic Air Toxics from Open Burning* (USEPA, 2002). The cPAH EFs are based upon a series of mesoscale experiments sponsored by the U.S. Minerals Management Service (MMS) and conducted at the U.S. Coast Guard Fire and Safety Test Detachment and Little Sand Island in Mobile Bay, Alabama (Fingas et al., 1996b; Fingas et al., 1993; Fingas et al., 1998; Fingas et al., 1999; Fingas et al., 2001b). The studies were designed to characterize emissions from the burning of pooled crude oils and heavier refined petroleum products in an open outdoor environment. Overall, ISB of crude oil emits less cPAHs per mass of fuel consumed as compared to the burning of diesel fuel.

Table A.1.2. cPAH Emission Factors for ISB of Petroleum

cPAH Species	cPAH Emission Factor (mg / kg _{fuel})	
	Crude Oil ^a	Diesel Fuel ^a
Benz(a)anthracene	1	5
Benzo(a)pyrene	1	5
Benzo(b)fluoranthene	2	7
Benzo(k)fluoranthene	2	7
Chrysene	1	9
Dibenz(a,h)anthracene	not reported	not reported
Indeno(1,2,3-cd)pyrene	1	5
Total	8	38
Total B[a]P Equivalents	1.4	6.8

^a Values from USEPA, 2002.

A.2. PM and cPAH Emission Factors from Gasoline-powered Engines

Gasoline is a petroleum-derived fuel composed of light petroleum hydrocarbons in the C₄ to C₁₂ range. Gasoline is the most common type of fuel used in light-duty highway vehicles and small, motorized equipment. Spark ignition engines are engines that run on gasoline and that rely upon an electrical discharge to ignite gasoline injected into the engine cylinders. Similar to ISB of petroleum, emissions from gasoline-powered engines include PM and cPAHs, albeit at a much lower amount per unit of fuel consumed. Gasoline engine emissions also contain a mixture of VPHs and combustion gases. Often, gasoline is blended with oxygen-containing additives (i.e., methyl tert butyl ether (MTBE), ethyl tert butyl ether (ETBE), or ethanol) in order to lower emissions of CO₂ and non-combusted VPHs in the engine exhaust stream. However, as these are not the primary human health concerns associated with ISB of petroleum, volatile organic compounds (VOCs), and combustion gas emissions from gasoline engines are not discussed in detail.

Table A.2.1. summarizes the range of PM_{2.5} EFs from various studies of mobile source gasoline engine emissions.

Table A.2.1. PM Emission Factors for Mobile Source Gasoline Engines

Study	PM _{2.5} Emission Factor (g / Kg _{fuel})
Miguel et al. (1998)	0.03 +/- 0.002 ^a
Kirchstetter et al. (1999)	0.11 +/- 0.01
Allen et al. (2001)	0.015 +/- 0.071 ^b
Grieshop et al. (2006)	0.031 +/- 0.044
Strawa et al. (2010)	0.07 +/- 0.02
	Range: 0.03 – 0.11
<i>^a Reported as PM_{1.3}. For the purposes of this report, it is assumed that measurements of PM_{1.3} are reasonable approximations of PM_{2.5} emissions. ^b Reported as PM_{1.9}. For the purposes of this report, it is assumed that measurements of PM_{1.9} are a reasonable approximation of the PM_{2.5} emissions.</i>	

Emissions from gasoline engines also contain cPAHs. The concentrations and emission rates of cPAHs will vary depending upon the type of gasoline engine, the type of gasoline used to power the engine, and the configuration of the exhaust system of the engine. In general, cPAH emissions from gasoline-powered engines are much lower than those of diesel and marine fuel engines. A range of EFs representative of cPAH emissions from gasoline-powered engines is listed in **Table A.2.2**. The range of EFs for individual cPAHs is variable, having approximately nine to 170 fold differences between minimum and maximum EF estimates for various cPAH species. Values in Table B.4 are from select studies examining cPAH emissions from gasoline-powered automobile traffic or automobile engines, and are representative of the amounts of cPAH emissions from gasoline-powered on-road, light-duty vehicles.

Table A.2.2. cPAH Emission Factors for Mobile Source Gasoline Engines

cPAH Species	cPAH Emission Factor (mg/Kg _{fuel}) ^a
Benz(a)anthracene	0.0019–0.0307
Benzo(a)pyrene	0.0002–0.0272
Benzo(b)fluoranthene	0.0010–0.0265
Benzo(k)fluoranthene	0.0002–0.0342
Chrysene	0.0012–0.0462
Dibenz(a,h)anthracene	0.0002–0.0115
Indeno(1,2,3-cd)pyrene	0.0055–0.0520
Total Mass	0.010–0.228
Total B[a]P Equivalents	0.001–0.050
<i>^a Ranges from Mi et al. (2001) and Miguel et al. (1998).</i>	

A.3. PM and cPAH Emission Factors from Diesel-powered Engines

Diesel is a petroleum-derived fuel composed of medium-weight petroleum hydrocarbons in the C₁₀ to C₁₅ range. Diesel fuel is commonly used in heavy-duty highway vehicles (i.e., semi-trailer trucks, buses), heavy construction equipment, railroad locomotives, some marine vessels, and certain types of stationary generators. Diesel engines are compression ignition engines that rely on compression and heating of air to ignite diesel fuel injected into the engine cylinders. Diesel engines are more fuel-efficient than gasoline engines.

Emissions from diesel engines include PM and cPAHs, as well as VOCs and combustion gases. The amounts of PM and cPAHs emissions can vary based on fuel type, engine type, and engine work load. In addition, diesel engines used in on-road vehicles, such as those found in semi-trucks, buses, and heavy-duty work vehicles, typically emit lower levels of PM and cPAHs than diesel engines used in heavy off-road vehicles (i.e., heavy construction equipment, heavy-duty military vehicles) or stationary diesel generators. Diesel-powered vehicles, equipment, and generators may be employed during petroleum spill response activities.

The emission profile for on-road diesel engines has changed markedly since the year 2000, with improvements and modernization of diesel engine exhaust systems (Hesterberg et al., 2011; IARC, 2013). A decrease in the mass of PM and cPAHs generated per unit mass of fuel consumed has occurred with the introduction of these new technologies in the on-road diesel vehicle fleet. Studies investigating PM emissions in highway traffic tunnels have calculated PM EFs attributed to emissions from on-road diesel engines.

Table A.3.1. summarizes the range of PM_{2.5} EFs from various studies of diesel engine emissions, including those for on-road and off-road diesel engines and stationary diesel generators.

Table A.3.1. PM Emission Factors for On-Road, Off-Road and Stationary Diesel Engines

Study	PM _{2.5} Emission Factor (g / Kg fuel)
On-road Diesel Engines	
Miguel et al. (1998)	1.44 +/- 0.16 ^a
Kirchstetter et al. (1999)	2.5 +/- 0.2
Allen et al. (2001)	0.79 +/- 0.33 ^b
Grieshop et al. (2006)	1.06 +/- 0.16
Strawa et al. (2010)	1.4 +/- 0.3
	Range: 0.79 – 2.5
Off-road Diesel Engines	
USEPA (2010)	2.1 – 11 ^c
Zhu et al. (2011); Watson et al. (2008)	0.36 +/- 0.21 ^d
	4.3 +/- 2.5 ^e
	Range: 2.1 – 11
Stationary Diesel Generators	
Watson et al. (2008) ^f	1.46 +/- 0.45
	1.64 +/- 1.0
	1.56 +/- 1.4
	2.73 +/- 1.2
	10.64 +/- 6.7
Zhu et al. (2009)	1.2 +/- 0.6
	Range: 1.2 – 10.64
^a Reported as PM _{1.3} . For the purposes of this report, it is assumed that measurements of PM _{1.3} are reasonable approximations of PM _{2.5} emissions. ^b Reported as PM _{1.9} . For the purposes of this report, it is assumed that measurements of PM _{1.9} are reasonable approximations of PM _{2.5} emissions. ^c Calculated by multiplying the reported PM ₁₀ range by 0.97 as recommended by USEPA (USEPA, 2010). ^d Value for military Medium Tactical Vehicle Replacement (MTVR) with 3.8 mpg fuel economy running on JP-8 fuel. ^e Value for military Logistics Vehicle Systems (LVS) vehicle with 2 mpg fuel economy running on JP-8 fuel. ^f Multiple PM _{2.5} EF ranges reported for different types/brands of diesel generators under various engine load conditions.	

EFs for cPAHs from mobile source diesel engines were calculated from values reported in the International Agency for Research on Cancer (IARC) monograph for diesel and gasoline engine exhausts. This document is a comprehensive evaluation of the potential carcinogenic health effects that may arise from chronic exposure to diesel engine exhaust. cPAH EFs representative of traditional on-road diesel engines (TDEs) and new technology diesel engines (NTDEs) are presented in **Table A.3.2**. According to these estimates, the EF for the total mass of cPAHs emitted per mass of diesel fuel consumed has decreased more than 3000-fold as diesel technologies have been improved. The ranges of cPAH EFs for non-road diesel engines and stationary diesel generators are similar to that of traditional on-road diesel engines. cPAH EF ranges estimated for off-road and stationary diesel engines are listed in **Table A.3.2**. The EF values listed for non-road diesel engines and stationary diesel generators are from field or laboratory studies of cPAH emissions from these types of engines.

Table A.3.2. cPAH Emission Factors for On-road, Off-road, and Stationary Diesel Engines.

cPAH Species	cPAH Emission Factor (mg / Kg fuel)			
	Stationary Diesel Generators ^a	Non-road Diesel Engine, Mobile Source ^b	2000 Traditional Diesel Engine, On-road Mobile Source ^c	2007 New Technology Diesel Engine, On-road Mobile Source ^c
Benz(a)anthracene	0.012	0.004–0.006	0.007	0.000002
Benzo(a)pyrene	< 0.005	0.0007–0.0015	0.005	0.000002
Benzo(b)fluoranthene	0.021	0.0013–0.0025	0.005	0.000002
Benzo(k)fluoranthene	0.004	0.0014–0.0018	0.005	0.000002
Chrysene	0.029	0.0108–0.0212	0.007	0.000002
Dibenz(a,h)anthracene	<0.007	0.0001–0.0001	0.005	0.000002
Indeno(1,2,3-cd)pyrene	<0.008	0.0002–0.0003	0.005	0.000002
Total Mass	0.085	0.019–0.034	0.039	0.000012
Total B[a]P Equivalent	0.015	0.001–0.003	0.012	0.0000039

^a From USEPA 1996a. ^b From Merritt et al. (2005). Values are for total (particulate + vapor phase) PAHs. Emissions factors were converted from ng/hp-hr using an equality of 1 hp*hr = 2.68 MJ and a high heating value of 45.575 for low-sulfur diesel fuel (Boundy et al., 2011). ^c From Khalek et al. (2011).

A.4. PM and PAH Emission Factors from Marine Engines

Engines on marine vessels are powered by either distillate fuels or residual fuels. Marine distillate fuels include marine diesel fuel (otherwise known as intermediate fuel oil) or marine gas oil. Similar to diesel fuels used in land-based equipment, marine distillate fuels contain hydrocarbon species in the C₁₁–C₂₀ range. Marine diesel can also be blended with heavier residual hydrocarbons (i.e., the hydrocarbon species that remain after distillation of lighter hydrocarbon cuts). Residual fuels are composed of residual hydrocarbons and are higher in non-petroleum impurities than distillate fuels.

Table A.4.1. summarizes the range of PM_{2.5} EFs from marine fuel engines. EF ranges are listed for marine distillate fuel engines and marine residual fuel engines. The data indicate that PM_{2.5} EFs for marine distillate and marine residual fuel engines overlap.

Table A.4.1. PM Emission Factors for Marine Fuel Engines

Study	PM _{2.5} Emission Factor (g/Kg _{fuel})
Diesch et al. (2013) ^a	1.6 +/- 1.7 ^{d,i}
	2.6 +/- 1.5 ^{e,i}
	3.7 +/- 1.7 ^{f,i}
	4.0 +/- 3.2 ^{g,i}
	1.5 +/- 1.1 ^{h,i}
Beecken et al. (2014) ^{b,j}	2.53 +/- 1.30
	2.95 +/- 1.76
	3.12 +/- 5.48
	2.08 +/- 1.67
	2.14 +/- 1.29
Petzold et al. (2010) ^c	3.53 +/- 2.2
	2.41 +/- 1.8
	1.64 +/- 0.91
Agrawal et al. (2010) ^k	2.22 +/- 0.06
	2.43 +/- 0.12
	2.91 +/- 0.08
	3.18 +/- 0.05
Range: 1.6 – 4.0	
<p>^a Reported as PM₁. ^b Reported as PM_{<0.5}. ^c Reported as PM_{<0.1}. For the purposes of this report, it is assumed that measurements of PM₁, PM_{<0.5} and PM_{<0.1} are reasonable approximations of PM_{2.5} emissions. ^d Type 1 vessel with gross tonnage <5,000. ^e Type 2 vessel with gross tonnage of 5,000 to 30,000. ^f Type 3 vessel with gross tonnage > 30,000. ^g Top 10% of particulate emitters from Diesch et al. (2013). ^h Top 10% of elemental carbon particulate emitters from Diesch et al. (2013). ⁱ Survey study. The authors assume surveyed vessels were powered with marine diesel; however, specific fuel types were not reported. ^j Measurements taken using a remote sensor technology. Different EF ranges represent different distance ranges between the ship being surveyed and the remote sensor. ^k Values are for a container ship powered by a Hitachi 12k90MC 54,840 kW engine fuel with ISO 8217-compliant heavy fuel oil (HFO) with 3% sulfur content. Emission factors for PM_{2.5} are reported for engine loads of 25%, 50%, 75%, and 90%, respectively.</p>	

cPAHs are also emitted along with particulate matter from the combustion of marine fuels. **Table A.4.2** lists cPAH EF ranges for marine distillate and marine residual fuel engines. While the PM EF ranges for distillate and residual marine fuels are similar, there is a marked difference in the amounts of cPAHs produced by each of these fuel types. Marine residual fuel engines tend to produce more cPAHs per mass of fuel consumed.

Table A.4.2. cPAH Emission Factors for Marine Fuel Engines

cPAH Species	cPAH Emission Factor (mg / Kg _{fuel})	
	Marine Distillate Fuel Engines ^a	Marine Residual Fuel Engines ^b
Benz(a)anthracene	0.11–0.13	0.44–3.33
Benzo(a)pyrene	0.15–0.17	2.81–2.81
Benzo(b)fluoranthene	0.12–0.15	0.22–0.27
Benzo(k)fluoranthene	0.03–0.05	0.27–0.75
Chrysene	0.02–0.06	1.87–7.10
Dibenz(a,h)anthracene	0.08–0.09	0.01–22.87
Indeno(1,2,3-cd)pyrene	0.13–0.15	0.05–11.61
Total	0.64–0.79	5.67–48.74
Total B[a]P Equivalents	0.26–0.31	2.9–27.2

^a Ranges derived from Wu et al. (2010) and include four different types of marine diesel fuel: one low-sulfur and three high-sulfur fuels. Values converted from mg/bhp*hr using an equality of 1 bhp*hr = 2.68 MJ and high heating values of 45.575 and 45.766 for low- and high-sulfur diesel fuels, respectively. ^b Values derived from Agrawal et al. (2010) and Sippula et al. (2014).

A.5. PM and cPAH EFs from Burning of Vegetative Fuels

In order to provide perspective on the type and amounts of emissions produced by ISB of petroleum and refined petroleum products relative to other types of combustion, a literature survey was conducted to identify EF ranges for the burning of vegetative fuels. Large-scale burning of vegetative fuels is a relatively common practice in agriculture and land/forest management. Burning of agricultural residue— the plant material remaining in fields following a crop harvest—is an efficient way the clear the land for the next growing season, increase the efficiency of crop harvest, and help replenish nutrients taken up from the soil by recently harvested crops. Prescribed burning of vegetative matter is also commonly employed as a land management approach. The emissions produced by prescribed burning can be similar to those produced by uncontrolled wildfires. In addition, the burning of wood for residential heating using catalytic and non-catalytic woodstoves is also quite common in the United States and abroad. Emissions from the domestic burning of wood can be similar in nature to those that occur during wildfires and prescribed burning. Of note, the amount and type of emissions for the burning of vegetative fuels is influenced by oxygenation of the fire, moisture content of the fuel, and the fuel type (i.e., type of plant or wood). In an effort to capture this heterogeneity, **Table A.5.1** lists PM EFs for 1) the burning of agricultural residues; 2) wildfires and prescribed burning of forest land; and 3) use of woodstoves as a residential heating source in studies examining a variety of fuel types.

Table A.5.1. PM Emission Factors for Burning of Vegetative Fuels

Study	PM _{2.5} Emission Factor (g / Kg _{fuel})
Burning of Agricultural Crop Residue	
Akagi et al. (2011)	6.26–14.8
Pouliot et al. (2012)	4.72–23.23
All Studies	Range: 4.72–23.23
Prescribed Burning/Wildfire	
Radke et al. (1991)	5.5–43.8
Ottmar and Baker (2007)	0.57–9.08
Urbanski et al. (2013)	23.2 +/- 10.4
Akagi et al. (2011)	7.17–15.3
USEPA (1996b)	4–16
All Studies	Range: 0.57–43.8
Residential Heating, Conventional Woodstoves	
Houck et al. (2008)	0.59–21.1
Houck and Tiegs (1998)	1.9–14.2
Fine et al. (2004)	0.88–3.4
All Studies	Range: 0.59–21.1

Burning of vegetative fuels also produces cPAHs. Ranges for cPAH EFs from burning of agricultural residue, wildfire, prescribed burning of forest land, and residential use of woodstoves are listed in **Table A.5.2**.

Table A.5.2. cPAH Emission Factors for Burning of Vegetative Fuels.

cPAH Species	cPAH Emission Factor (mg / Kg _{fuel})		
	Burning of Agricultural Crop Residue ^a	Prescribed Burning/Wildfire ^b	Residential Heating, Conventional Woodstoves ^c
Benz(a)anthracene	0.06–1.30	3.09–6.32	1–12
Benzo(a)pyrene	0.01–9.56	0.74–0.75	2–3
Benzo(b)fluoranthene	0.04–4.66	2.57–2.57	2–3
Benzo(k)fluoranthene	0.04–2.85	1.3–2.57	1–1
Chrysene	0.08–1.43	3.09–6.32	5–6
Dibenz(a,h)anthracene	0.01–0.57	not reported	0–2
Indeno(1,2,3-cd)pyrene	0.06–9.67	1.2–1.7	0–10
Total Mass	0.3–30	7.6–11.3	11–37
Total B[a]P Equivalents	0.04–11.7	1.44–1.8	2.32–7.52

^aData are from USEPA, 2002; Jenkins et al., 1996; Lemieux, 2004; and Lutes and Kariher, 1996. ^b Data are from USEPA 1998; McMahon and Tsoukalas, 1978; Lemieux, 2004; and Versar, Inc, 1989. For McMahon and Tsoukalas (1978), data were reported as “total benzofluoranthenes” and “chrysene/benz[a]anthracene”, respectively, with no distinction made between cPAH species within these groups. For calculation of PAH EF ranges for total mass and total B[a]P equivalents, the EFs for benzofluoranthenes and chrysene/benz[a]anthracene were assigned to the PAH species with the highest relative potency factor. ^c Data from USEPA, 1998; USEPA, 2002; Downard, 2014; and Lemieux and Ryan, 1993.

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Appendix B

Equating ISB Emissions from Burning of Vegetative Fuels

The information presented in this appendix equates the emissions from varying sizes of ISB to emissions from three common types of vegetative fuel combustion: 1) use of woodstoves in a residential setting; 2) burning of sugarcane in an agricultural setting; and 3) prescribed burning of slash pine forest debris in a land management setting. Each of these are common and familiar occurrences that involve intentional combustion of vegetative fuels and the production of smoke.

B.1. Residential Woodstoves

Woodstoves have been used for many years in the United States and abroad as a means of heating homes (Figure B.1.1). In 2000, U.S. Census data indicated that 1.7% of 105,480,101 surveyed U.S. homes used wood as a primary fuel source for home heating (USCB, 2016). Census data from the U.S. in 2010 indicates that the popularity of using wood, either in woodstoves or fireplaces, for home heating has increased in recent years (Alliance for Green Heat, 2011). Recent surveys also indicate that households using woodstoves as a heat source use their stove 120 days a year, with an average of 3.7 hours per use for those using cordwood to heat their home (Wakefield, 2010). The wood used to generate heat from a woodstove could be representative of local trees found in a geographic area or commercially manufactured wax/sawdust logs



Figure B.1.1: Residential Woodstove

or wood pellets. There are a variety of factors that can influence the quantity and types of emissions from residential woodstoves, including the type of stove, the type of fuel (i.e., wood) used in the stove, fuel moisture, air circulation characteristics within a home, and damper setting on the stove (Houck et al., 2001). Individuals have a potential to be exposed to emissions from residential woodstoves that enter the ambient outdoor air through chimneys or stovepipes. Incorrect use or use of woodstoves with improper ventilation may also result in the potential for individuals to be exposed to emissions in the indoor air of their homes.

Table B.1.1 uses estimates of the amount of PM_{2.5} and cPAHs produced by ISB of varying volumes of petroleum (100 to 800 barrels) to calculate the equivalent number of woodstoves needed to produce the same amount of PM_{2.5} and PAH emissions, assuming one year of usage. Estimates are based on the average from the PM_{2.5} EF range for light crude oil (i.e., 77 g / kg_{fuel}), the point estimate cPAH EF for light crude oil (i.e., 1.4 mg/kg_{fuel}), and average PM_{2.5} and cPAH EFs determined from ranges of EFs from the scientific literature for woodstove combustion (Fine et al. 2004). It is assumed that one year of woodstove usage would entail 120 uses per year for 3.7 hours per usage and an average wood fuel consumption rate of 0.03 kg wood/minute (Fine et al. 2004)²⁰.

²⁰ In Fine et al. (2004), burn times for different wood fuels in a woodstove ranged between 112 and 148 minutes, and between 3 and 4.5 kilograms of wood was burned per test. An assumed average burn duration of 130 minutes (i.e., $[112 + 148] \div 2 = 130$ minutes) and an assumed average fuel consumption of 4 kilograms (i.e. $[3 + 4.5] \div 2 = 4$ kg) were used to calculate an average wood fuel consumption rate of 0.03 kg / minute.

Table B.1.1. Equating ISB Emissions to Emissions from Residential Woodstoves

Volume of Petroleum for ISB (barrels):	100	200	400	600	800
Time Scale for ISB (minutes):	8–52	17–104	34–209	50–313	67–417
Emission Type:	Equivalent Number of Woodstoves ^{a,b,c}				
PM _{2.5}	752	1507	3008	4513	6017
cPAHs	63	127	253	380	507
	Percent of U.S. Households Using Wood as Heating Source ^d				
PM _{2.5}	0.042	0.084	0.188	0.252	0.336
cPAHs	0.004	0.007	0.014	0.021	0.028

^a For each emission type, Equivalent Number of Woodstoves calculated as: $[(EF \text{ for ISB of light crude oil, g/Kg}) * (\text{barrels of oil}) * (137.4 \text{ Kg / barrel of oil})] / [(average \text{ fuel consumption rate, kg/min}) * (60 \text{ minutes/hour}) * (\text{Duration of woodstoves use, hours}) * (\text{number of uses per year}) * (EF \text{ for woodstoves})]$.

^b Assumed emission factors for ISB of light crude oil: PM_{2.5} [77], PAHs [1.4]

^c Assumed emission factors for woodstoves: PM_{2.5} [1.76], PAHs [0.38].

^d Assumed that 1,793,162 households use wood a primary heating source (either woodstove or fireplace) based on 2000 U.S. Census data.

ISB of 100 to 800 barrels of light crude oil would be expected to produce the amount of PM_{2.5} emissions equivalent to approximately 750 to 6,000 woodstoves. This is only a small percentage of the estimated total number of woodstoves used in the United States for home heating purposes.

The values presented in **Table B.1.1** are point estimates based on a single EF value for each emission type for each fuel source (i.e., ISB of light crude oil or woodstoves). There will likely be variability in the actual emission rates observed from the two different types of combustion being compared. The range of emission factors reported for ISB of light crude oil and use of residential woodstoves (Fine et al., 2004) were used to illustrate this potential variability in **Figure B.1.2**. This figure demonstrates that the emissions estimated for the equivalent number of woodstoves associated with ISB of various volumes of crude oil may vary, with greater variability observed with larger volumes of oil. **Figure B.1.2** also equates the emissions produced by ISB of various volumes of light crude oil to emissions from the estimated total number of U.S. households that use wood as a home heating fuel source (right y-axis). Even using the maximum EF for ISB (square symbols, **Figure B.2**), the PM_{2.5} and cPAH emissions from occasional use of ISB in an emergency setting would be only a small fraction of the total amount of emissions produced in the U.S. on an annual basis from the use of wood for home heating purposes.

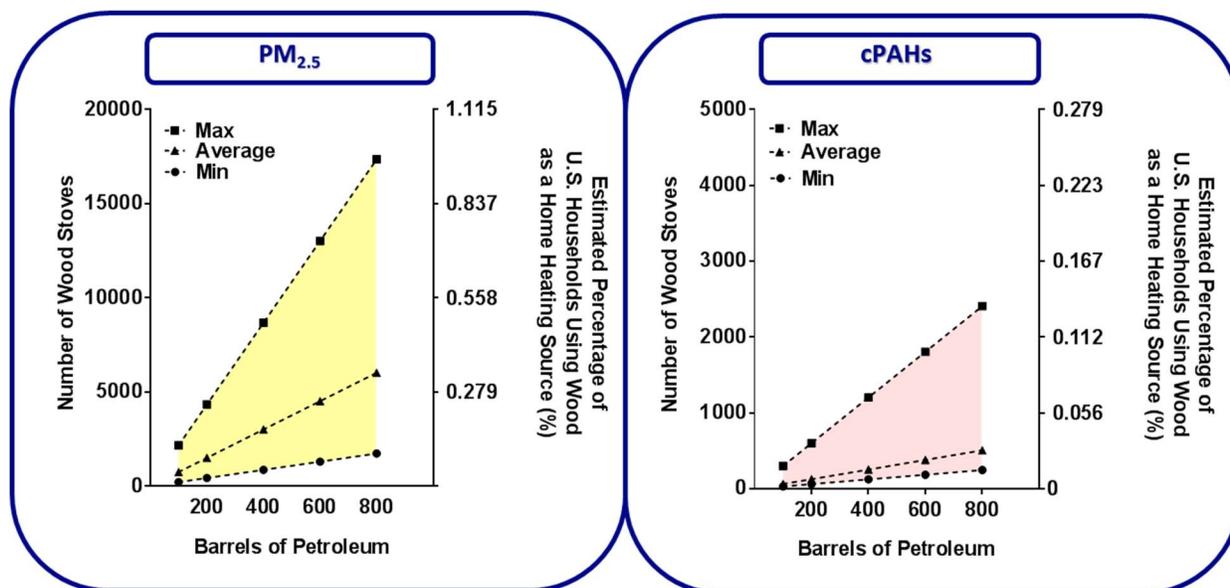


Figure B.2. Comparison of PM_{2.5} and cPAH Emissions: ISB and Residential Woodstoves

B.2. Agricultural Burning of Sugarcane Residue

Burning of sugarcane fields is a common agricultural practice in the United States (Figure B.2.1). Sugarcane fields are burned before harvesting to remove leafy material that makes up about a quarter of the sugarcane plant and makes the sugarcane itself more amenable to harvesting and processing (Darley and Lerman, 1975; HC&S, 2016). Approximately 850,000 acres of sugarcane fields²¹ are burned annually in the United States (HC&S, 2016; USDA, 1999). The burning produces similar combustion products to that observed during ISB of petroleum. Like ISB, burning of sugarcane is also a short-lived event. It is estimated that a 40-acre burn lasts approximately 15–20 minutes (Baucum and Rice, 2009) and that about 70 acres of sugarcane residue is burned at one time (HC&S, 2016). Studies of sugarcane burning have demonstrated that a sugarcane field may contain 4.46 tons of leaf residue per acre (Pouliet et al. 2012). Individuals have the potential to be exposed to emissions from burning of sugarcane fields in outdoor air in geographical areas where sugarcane burning is routinely used during harvest.



Figure B.2.1: Burning of Sugarcane

²¹ In addition to sugarcane, other crop residues are commonly burned in the United States. It is estimated that approximately 9,000,000 acres of crop residues (including sugarcane) are burned annually.

Table B.2.1 uses estimates of the amount of PM_{2.5} and cPAHs produced by ISB of varying volumes of petroleum (100 to 800 barrels) to calculate the equivalent acreage of sugarcane fields and number of typically-sized sugarcane fields needed to produce the same amount of these emissions. Estimates are based on the average from the PM_{2.5} EF range for light crude oil (i.e. 77 g / kg_{fuel}), the point estimate cPAH EF for light crude oil (i.e. 1.4 mg / kg_{fuel}), and average PM_{2.5} and cPAH EFs determined from ranges of EFs from scientific literature for the burning of sugarcane fields (Pouliot et al., 2012; Mugica-Alvarez et al., 2016).

Table B.2.1. Equating ISB Emissions to Emission from Prescribed Burning of Sugarcane Fields.

Volume of Petroleum for ISB (barrels):	100	200	400	600	800
Time Scale for ISB (minutes):	8–52	17–104	34–209	50–313	6 -417
Emission Type:	Equivalent Acres of Sugarcane Fields ^{a,b,c}				
PM _{2.5}	60	120	240	361	481
cPAHs	115	229	458	687	916
Emission Type:	Equivalent Number of Sugarcane Fields ^d				
PM _{2.5}	0.9	1.7	3.4	5.2	6.9
cPAHs	1.6	3.3	6.5	9.8	13.1

^a For each emission type, Equivalent Acres of Sugarcane Fields calculated as: $[(EF \text{ for ISB of light crude oil, g/Kg}) * (\text{barrels of oil}) * (137.4 \text{ Kg / barrel of oil})] / [(EF \text{ for prescribed burning of sugarcane, g/kg}) * (\text{Fuel Loading, tons / acre}) * (907.2 \text{ Kg / ton})]$.

^b Assumed emission factors for ISB of light crude oil: PM_{2.5} [77], PAHs [1.4].

^c Assumed emission factors for sugarcane: PM_{2.5} (4.35), PAHs [0.042].

^d Equivalent Acres of Sugarcane Fields divided by typical acreage of sugarcane fields burned in a single setting (i.e. 70 acres).

ISB of relatively small volumes of light crude oil (≤ 100 bbls) would be expected to produce the same amount of PM_{2.5} and cPAH emissions as the burning of approximately 1 to 1.5 typically-sized sugarcane fields. Naturally, the amount of emissions increases with the volume of light crude oil consumed by the ISB.

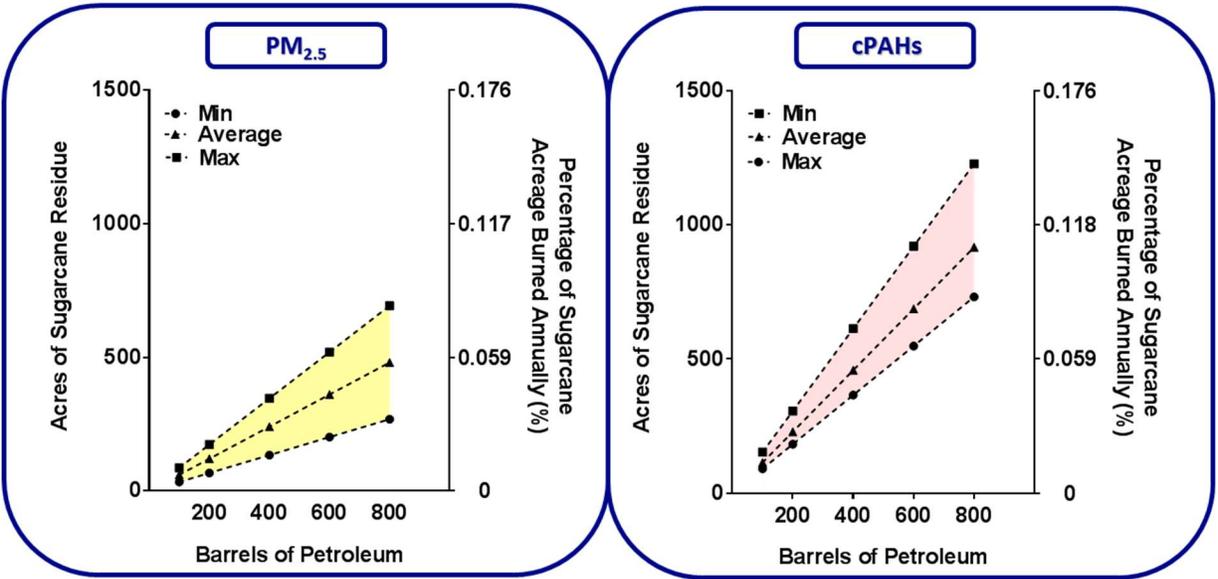


Figure B.2.2. Comparison of PM_{2.5} and cPAH Emissions: ISB and Burning of Sugarcane Fields

The values presented in **Table B.2.1** are point estimates based on a single EF value for each emission type for each fuel source (i.e., ISB light crude oil or burning of sugarcane). There will likely be variability in the actual emission rates observed from the two different types of combustion being compared. The ranges of EFs reported for the burning of light crude oil and sugarcane fields were used to provide an illustration of this variability in **Figure B.2.2**. This figure demonstrates that the emissions estimated for equivalent acreage of sugarcane associated with ISB of various volumes of crude oil may vary, with greater variability observed with larger volumes of oil. **Figure B.2.2** also equates the emissions produced by ISB of various volumes of light crude oil to emissions from the total acreage of sugarcane fields burned in the U.S. on an annual basis (right y-axis). Even using the maximum EFs for ISB (square symbols, **Figure B.2.2**), the PM_{2.5} and cPAH emissions from occasional use of ISB in an emergency response setting would be only a small fraction of the total amount of emissions produced in the U.S. on an annual basis from the burning of sugarcane fields. These data indicate that the occasional ISB of spilled oil would be a minor contributor to the overall PM_{2.5} and cPAH emissions associated with common agricultural practices.

B.3. Prescribed Burning of Pine Forests

A common practice in the United States is the use of prescribed burning²² as a land management tool for forestland, grasslands/prairies, and other types of terrain (Figure B.3.1). Prescribed burning of pine forests is a common practice in the Southeastern United States that removes pine litter, underbrush, and smaller plants from the forest floor without permanently damaging the larger pine trees. This common forest management practice, if performed properly, can be used to increase pine timber yield, improve habitat conditions for forest dwelling animals, control invasion of undesired tree types (i.e., hardwoods), increase biodiversity, increase visibility in the understory, and reduce the risk of unintentional wildfires (Thackston and Whitney, 2016; Gordon, 2016). Estimates of the total acreage in the Southeastern United States managed using prescribed burning ranged from approximately 6.5 million acres in 2011 to 6.1 million acres in 2014 (Melvin, 2015; Melvin, 2012), although information specifically relating to acreage of pine forests managed with prescribed burning could not be identified. It has been estimated that approximately 31.7 % of the total acreage of Southeastern forests are composed of either loblolly and shortleaf pines or longleaf and slash pines (Hanson et al., 2010). If performed properly, prescribed burning of pine forests is a short-lived event that can be completed in a standard workday (Wade and Lunsford, 1989). Individuals have the potential to be exposed to emissions from the prescribed burning of pine litter in the outdoor air in geographical areas where this land management practice is used.

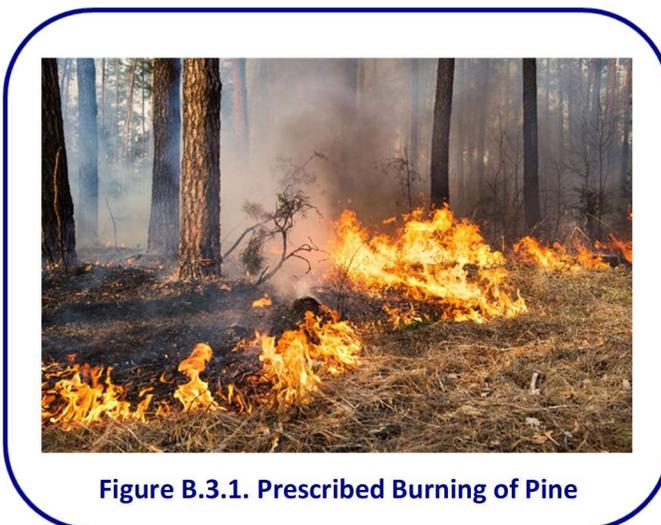


Figure B.3.1. Prescribed Burning of Pine

The acreage to be burned in a given time period will vary based on fuel loading (i.e., the amount, type, and characteristics of fuel on the forest floor) and can range from a few acres to around 1,000 acres (Wade and Lunsford, 1989; McNabb, 2001). Fuel loading in pine forests can vary depending on the density and age of the trees and the amount of time that has passed since a previous fire. In the analysis presented below, a fuel loading of 8 tons of pine litter per acre is assumed, although reported values can range between 3 and 14 tons per acre (SCFC, 2014). Wildlife habitat management strategies from several states suggest using 10- to 50-acre blocks for prescribed burns of pine forests (Thackston, 2002; Moorman and Sharpe, 2002; TWPD, 2016; Southern Regional Strategy Committee, 2016).

Table B.3.1. uses estimates of the amount of PM_{2.5} and cPAHs produced by ISB of varying volumes of petroleum (100 to 800 barrels) to calculate the acreage of pine forest and number of typically-sized wildlife management plots that would produce an equivalent amount of these emissions. Estimates are based on the average from the PM_{2.5} EF range for light crude oil (i.e., 77 g / kg_{fuel}), the point estimate

²² In forestry, prescribed burning is defined as the deliberate use of fire to achieve forest management objectives (Gordon, 2016).

cPAH EF for light crude oil (i.e. 1.4 mg / kg_{fuel}) and average PM_{2.5} and cPAH EFs determined from ranges of EFs from scientific literature for burning of pine litter (Hays et al. 2002; USEPA, 2001).

Table B.3.1. Equating ISB Emissions to Emission from Prescribed Burning of Southeastern Pine Forests.

Volume of Petroleum for ISB (barrels):	100	200	400	600	800
Time Scale for ISB (minutes):	8–52	17–104	34–209	50–313	67–417
Emission Type:	Equivalent Acres of Southeastern Pine Forests ^{a,b,c}				
PM _{2.5}	5.1	10.3	20.5	30.8	41.1
cPAH	3.4	6.9	13.8	20.7	27.5
Emission Type:	Equivalent Number of Wildlife Management Plots ^d				
PM _{2.5}	0.5	1.0	2.1	3.1	4.1
cPAH	0.3	0.7	1.4	2.1	2.8

^a For each emission type, Equivalent Acres of Southeastern Pine Forests calculated as: $[(EF \text{ for ISB of light crude oil, g/Kg}) * (\text{barrels of oil}) * (137.4 \text{ Kg / barrel of oil})] / [(EF \text{ for prescribed burning of pine forests, g/kg}) * (\text{Fuel Loading, tons / acre}) * (907.2 \text{ Kg / ton})]$.

^b Assumed emission factors for ISB of light crude oil: PM_{2.5} [77], PAH [1.4].

^c Assumed emission factors for pine forests: PM_{2.5} [28.4], PAH [0.77].

^d Equivalent Number of Wildlife Management Plots is calculated as Equivalent Acres of Southeastern Pine Forests divided by 10 acres.

ISB of volumes of light crude oil less than 400 bbls would be expected to produce the same amount of PM_{2.5} and cPAH emissions as the prescribed burning of between approximately 14 and 20 acres of Southeastern pine forests. This is roughly equivalent to 1.5 to 2 wildlife management plots, assuming that each block is 10 acres in size. As noted above, the amount of emissions would increase with the volume of light crude oil consumed by the ISB.

The values presented in **Table B.3.1** are point estimates based on a single EF value for each emission type for each fuel source (i.e., ISB of light crude oil vs. pine litter). As with the example of sugarcane fields, there likely will be variability in the actual emission rates observed with the two different types of combustion being compared. The ranges of EFs reported for ISB of light crude oil and prescribed burning of pine forests or pine litter were used to illustrate this variability in **Figure B.3.2**. This figure demonstrates that the emissions estimated for equivalent acreage of Southeastern pine forests associated with ISB of various volumes of crude oil may vary, with greater variability observed with larger volumes of oil. **Figure B.3.2** also equates the emissions produced by ISB of various volumes of light crude oil to emissions from the total estimated acreage of prescribed pine forest burned in the Southeastern U.S. in 2014 [i.e., 6,100,000 acres (Melvin, 2015) x 31.7 % (Hanson et al., 2010) = 1,933,700]. Even using the maximum emission factors for ISB (square symbols, **Figure B.3.2**), the PM_{2.5} and cPAH emissions from occasional use of ISB in an emergency response setting would be only a small fraction of the total amount of PM_{2.5} and cPAH emissions produced in the U.S. on an annual basis from prescribed burning of pine forests in a land management scenario.

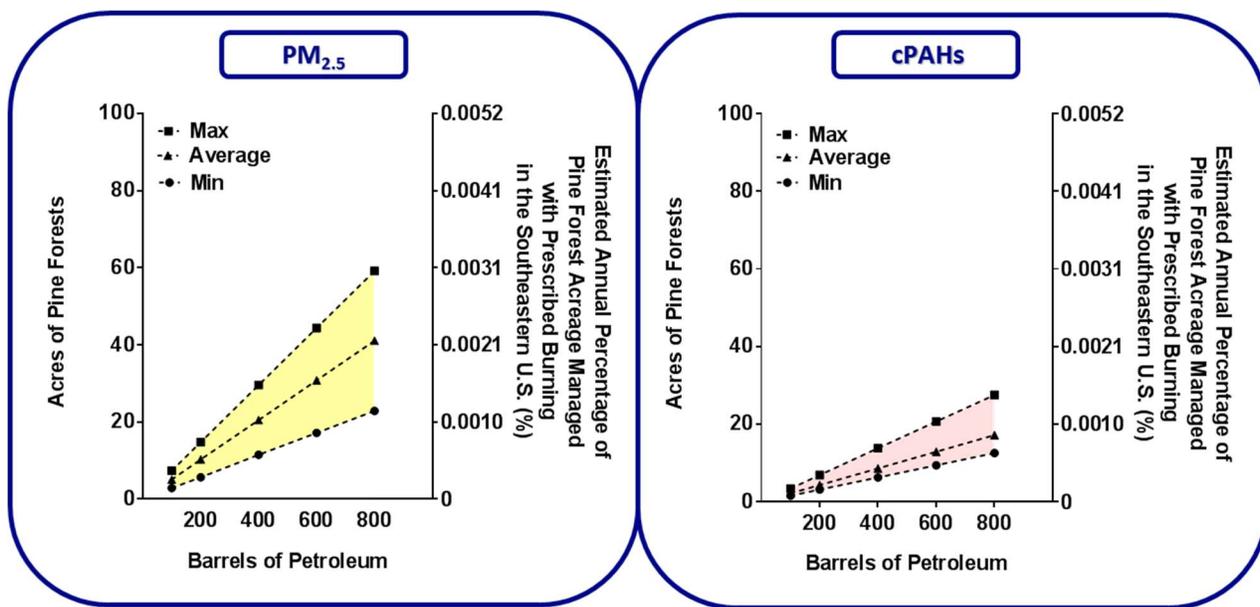


Figure B.3.2. Comparison of PM_{2.5} and cPAH Emissions: ISB and Burning of Pine Forests

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