

4. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

This chapter summarizes useful background materials dealing with petroleum production and a range of common products derived from petroleum contaminants that could be documented through TPH testing at NPL sites. The chapter concludes with a discussion of acceptable disposal practices for petroleum products. In conjunction with materials in Chapter 5, the section on disposal summarizes special features of petroleum that set it apart from a variety of more highly processed petrochemicals. Under normal uses as fuels, lubricants, or paving materials, petroleum products are not considered hazardous materials. For instance, fuels are normally consumed through combustion processes to drive motors or provide space heating. Some combustion by-products (e.g., carbon monoxide) may be regarded as hazardous, but a variety of legal exemptions apply to the initial petroleum product, at least under federal law.

The special status of petroleum under normal use means that limited attention is given to monitoring of petroleum levels in the workplace or the environment. It is usually only in the case of accidental spills, pipeline breaks, or seepage from storage tanks that well defined legal requirements are in place that require record keeping and documentation. As a result, it is usually hard to make precise connections between the original petroleum products and the types of TPH materials encountered at NPL sites.

Especially at older dump sites, original petroleum product mixtures become even more complex mixtures. Over time, biotic and abiotic weathering processes alter the types of chemical fractions still present on-site. This means that even the most detailed knowledge of the various original petroleum products does not necessarily provide clear signals on the exposure risks affecting an NPL site with TPH contaminants. See Chapter 5 for discussion of environmental transport and potential human exposure. This chapter, therefore, highlights basic information relevant to the original petroleum products to provide a background for the discussion on environmental fate and transport issues in the next chapter.

Background on Primary Petroleum Products. Petroleum is a natural resource found in many types of sedimentary rock formations. Naturally occurring petroleum is a complex mixture of gaseous, liquid, and solid hydrocarbons. Entire industries have grown up around the activities

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required to produce the crude oil, transport it to refineries, and convert the natural petroleum into a variety of end products and chemical feedstocks. Processed petroleum products provide up to 50% of the world's total energy supply, major forms of transportation, electric utilities, and space heating. Petroleum is also used in lubricants, solvents, highway surfacing, and roofing and waterproofing materials, and as the source of the feedstocks used to make plastics and other modern petrochemicals.

Early refining techniques relied primarily on the separation of different fractions from the raw petroleum using distillation over different temperature ranges. For straight-chain, branched, and aromatic hydrocarbons, there is some degree of correlation between the number of carbon atoms in a compound and the boiling point. Many refined products were initially given simple technical definitions based on the temperature range at which a certain fraction was extracted from the crude oil. The very lightest fractions (e.g., C_4H_{10} or butane and other simple straight-chain compounds down through CH_4 or methane) were traditionally vented or flared since there was little apparent demand for these gaseous components. The most prized fractions were liquids at normal room temperatures that could be used as fuels in engines or as heating oils.

The petroleum refining industry has tried to find profitable uses for both the lighter and heavier crude oil fractions. Lighter gaseous fractions can now be used for space heating or fuels in the form of liquified petroleum gas (LPG). For the heavier fractions, a variety of technologies convert large hydrocarbon molecules from the distilled crude oil into lighter compounds that can be used as motor gasoline, aviation fuel, or fuel oil. In the process, large amounts of hydrocarbons are produced that can be isolated as relatively pure substances for use as solvents or petrochemical feedstocks. For instance, benzene was once derived from coal tars, but most supplies are now derived from oil. Ethane is easily converted into ethylene, a major petrochemical feedstock. Commercial techniques for producing xylenes, toluene, butadiene, butylenes, and propylene also involve simple adaptations of modern oil refinery technologies.

Some specific refinery-generated hydrocarbons are blended into gasolines or fuel oils to enhance some desired property. For example, commercially pure grades of toluene and benzene are added to modern gasoline to boost octane ratings. Similar enhancements in basic product qualities for combustion or viscosity are achieved through re-distilling products from the cracking process and blending them with fractions obtained from primary distillation. While the resulting products are still

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referred to as gasolines or fuel oils, the chemistry of the hydrocarbons in these mixtures often differs considerably from that of the hydrocarbons found in the original crude oil.

Refining also dramatically increases the frequency of hydrocarbons in which carbon-hydrogen bonds have been replaced with double bonds between carbon atoms. The resultant chemicals are called olefins and include ethylene (C_2H_4), propylene (C_3H_6), and butylene (C_4H_8). While the lighter forms such as ethylene are relatively easy to remove for use as petrochemical feedstocks, a variety of heavier olefins wind up in the refinery gasoline or fuel oil products.

In addition to aromatics with benzene ring structures, modern refinery processes tend to increase the number of hydrocarbons with simpler types of carbon ring structures. Typical chemicals include cyclopentane, where the straight-chain pentane has been wrapped into a five-carbon ring. Other transformations of aliphatic hydrocarbons include cyclohexane and cyclopentane. These ring compounds are usually called naphthenes.

These complex alterations in the types of compounds generated from refinery operations have led to the development of a variety of technical nomenclatures to describe different petroleum fractions. Many commercial products still carry such traditional names as gasoline or heating oil. In terms of such basic physical and chemical properties as specific gravities and combustion performance, these traditional labels have held their meanings fairly well. New products, such as fuel oils derived from residuals, now join the original fuel oils derived from simple distillation, but the term "fuel oil" is still commonly used to organize data on petroleum imports, exports, and production. But the chemistry of these modern products is often considerably more complex than the chemistry of pre-World War II products with the same names.

Petroleum Production, Import/Export, and Use in the United States.

Petroleum Production and Use Statistics. Petroleum use and production statistics pooled from a variety of government and industry sources are available from the PennWell Publishing Company. A convenient printed compendium (also available on computer disk in a digitized form) is the *Energy Statistics Sourcebook* (PennWell 1994).

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During 1997, total U.S. crude oil production was 2,300,000,000 barrels (API 1998a). Using consistent estimation methods comparable to those employed over the last decade, it is often difficult to match current petroleum product statistics with historical statistics developed prior to 1978. For 1978, total U.S. crude production was 3,178,216,000 barrels. This represents a 27.6% decline in total production between 1978 and 1998. While total crude oil production in the United States has shown an overall downward trend, a comparison of statistics from 1993 and 1978 indicates that the total output from refineries based in the United States has remained remarkably constant. Table 4-1 summarizes total refinery output along with output estimates for major refinery petroleum products. Output for specific refinery products has changed: jet fuel kerosenes and LPG have increased, and fuel oils recovered from heavier refinery residuals and ordinary kerosene have decreased. Crude oil production levels and trends for selected states are summarized in Table 4-2.

Statistics on crude oil production or its processing into various petroleum fractions are generally presented using a standard barrel (42 U.S. gallons) as the basis of comparison. The barrel is still an international standard for crude oil statistics. While adjustments can be made for particular types of crude oil related to variations in their specific gravities (e.g., light oils versus heavy oils), 7.3 barrels of crude oil equal approximately 1 metric ton (1,000 kg or 2,204.6 pounds). Conversion factors are also available to make estimates of the barrel equivalents of other common petroleum products ranging from to liquified petroleum gas (LPG). Conversion factors for major petroleum fractions are given in Table 4-3.

Although crude oil production is the source of TPH exposures to certain occupational groups and people living near oil production sites, the releases in workplaces or to environmental media of more concern for this profile begin during the stage when crude oil is refined and transformed into a variety of petroleum products for fuels, lubricants, and petrochemical feedstocks.

In addition to the total production figures, percentage breakouts provide another way to summarize the major products stemming from U.S. based refineries. Table 4-4 presents 1993 product yields on a percentage basis.

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Table 4-1. U.S. Annual Refinery Output (in 1,000s of Barrels)

Product	1978 Annual output	1998 Annual output
Total production	5,825,041	1,969,729
Motor gasoline	2,616,656	906,459
Jet naphtha	65,257	73
Jet kerosene	288,682	87,112
Kerosene	56,325	8,894
Distillate fuel oil	1,156,097	403,597
Residual fuel oil	608,634	92,639
Liquid petroleum gas and lighter fractions	129,526	79,388

Source: PennWell 1998

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Table 4-2. Crude Oil Production Trends by State

State trends	1978 Production 1,000s of barrels	1997 Production 1,000s of barrels	Percent change where more than 10%
Texas	1,074,050	594,103	-44.69
Alabama	19,829	14,831	-25.21
Alaska	448,620	472,949	28.73
Montana	30,467	15,527	-49.04
Arkansas	20,329	8,429	-58.54
Nebraska	5,862	3,337	-43.07
Utah	31,368	19,317	-38.42
Virginia	2	10	400
Arizona	418	82	-80.38
South Dakota	869	1,334	53.51
North Dakota	24,812	35,833	44.42
West Virginia	2,382	1,508	-36.69
Missouri	54	114	111.11
Pennsylvania	2,887	1,320	-54.28
New York	852	276	-67.61
Louisiana	532,740	488,784	-21.64
Florida	47,536	6,381	-86.58
Indiana	4,689	2,430	-48.18
Nevada	1,156	980	-15.22
Tennessee	593	367	-38.11
Kansas	56,586	39,836	-29.60
Kentucky	5,724	2,988	-47.8
Mississippi	42,024	21,037	-49.94
Colorado	36,797	25,616	-30.39
Michigan	34,667	10,052	-71.00
Illinois	23,362	16,115	-31.02
Oklahoma	150,456	83,365	-44.59
Ohio	11,154	8,593	-22.96
California	347,181	339,306	
Wyoming	137,385	70,176	-48.92
New Mexico	83,365	69,835	-16.23

Source: PennWell 1998

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Table 4-3. Barrel Oil Equivalents of Petroleum Liquid Fuels

Fuel	Thousands of barrels of oil equivalent	
	Per thousand metric tons	Per million U.S. gallons
LPG	11.6	23.8
Aviation gasoline	8.9	23.8
Motor gasoline	8.5	23.8
Jet fuel (gasoline types)	8.3	23.8
Naphtha	8.5	23.8
Kerosene	7.8	23.8
Jet fuel (kerosene types)	7.7	23.8
Distillate fuel oil	7.3	23.8
Residual fuel oil	6.7	23.8
Lubricating oil	7.1	23.8
Typical crude oil	7.3	23.8

Source: Stevens 1988

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Table 4-4. 1997 U.S. Refinery Output of Major Products as Percentages of Total Refinery Output

Product	Percentage of total output
Asphalt and road oil	3.2
Distillate fuel oil	22.5
Jet fuels	10.3
Kerosene	0.4
LPG and Ethane	4.6
Lubricants	1.2
Motor gasoline	45.7
Petrochemical feedstocks	2.9
Petroleum coke	4.6
Residual fuel oil	4.7
Other products (approximately)	5.0

Source: PennWell 1998

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With a long-term decline in the levels of domestic crude oil production, imports have increased to meet the demand for petroleum products and to sustain the fairly stable levels of U.S.-based refinery output. Tables 4-5, 4-6, and 4-7 summarize trends in petroleum product imports, exports, and levels of U.S. demand (use) for these products.

For the most common refinery products, statistics are available showing U.S. use patterns for sectors such as major industrial groups or residential demand. These statistics are presented in Table 4-8.

Disposal. An estimated 2.3 billion barrels of crude oil were produced in 1997 (API 1998a). From this crude oil, TPH waste may be generated in a number of ways that ultimately lead to either improper or acceptable disposal. Incineration is a primary method of disposal for wastes containing TPH. Oil spills are frequently captured and treated using various absorbents (e.g., straw, polyurethane foam, activated carbon, peat), gelling agents, dispersants, and mechanical systems. Biodegradation also has been used to treat contaminated soil (OHM/TADS 1985).

Sources of TPH waste include

- waste generated from crude oil production,
- waste generated from petroleum refining,
- used oil as a waste,
- used petroleum refining products as wastes, and
- accidental releases of crude oil, petroleum refining wastes, used oil, and petroleum refining products.

Management of TPH wastes generated from the sources listed is discussed in the following sections, which address existing regulatory programs, quantities disposed (where data are available), waste management trends, recycling trends, and records of damage for each source.

Waste Generated from Crude Oil Production. EPA's Report to Congress, *Management of Wastes from the Exploration, Development, and Production of Crude Oil, Natural Gas, and Geothermal Energy* (EPA 1987a), reported that the American Petroleum Institute estimated that 361 million barrels of waste were generated from the drilling of 69,734 oil wells in 1985. This translates into about 5,183 barrels of waste per well. These wastes are not pure crude but can include petroleum hydrocarbons.

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Table 4-5. U.S. Petroleum Imports for 1978 and 1998

Product	1978 (1,000s Barrels)	1998 (1,000s Barrels)
Crude oil	2,261,026	974,667
All refined products	732,819	212,625
Motor gasoline	69,518	32,989
Jet naphtha	6,963	0
Jet kerosene	24,383	9,606
Kerosene	4,031	190
Distillate fuel oil	63,288	23,428
Residual fuel oil	494,640	24,331
LPG and ethane	44,827	26,988

Source: PennWell 1998

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Table 4-6. U.S. Petroleum Exports for 1978 and 1998

Product	1978 (1,000s Barrels)	1998 (1,000s Barrels)
Crude oil	57,728	20,621
All refined products	74,329	99,106
Motor gasoline	470	13,618
Jet naphtha	1	232
Jet kerosene	513	3,703
Kerosene	40	99
Distillate fuel oil	1,202	15,905
Residual fuel oil	4,634	16,624
LPG and ethane	7,238	5,562

Source: PennWell 1998

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Table 4-7. U.S. Petroleum Demand for 1978 and 1998

Product	1978 (1,000s Barrels)	1998 (1,000s Barrels)
Motor gasoline	2,705,309	943,156
Jet naphtha	72,546	-183
Jet kerosene	313,108	187,359
Kerosene	64,042	11,634
Distillate fuel oil	1,252,556	424,436
Residual fuel oil	1,103,233	101,591
LPG and ethane	511,598	256,941

Source: PennWell 1998

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Table 4-8. Petroleum Use Patterns by Sector for 1995

Sectoral use patterns for major petroleum products 1995 baseline Millions of barrels (percent of total sectoral demand)						
Product	Residential	Commercial	Industrial	Transportation	Electric utilities	Total
Motor gasoline	0 (0.0)	3 (<1.0)	38 (1.3)	2,801 (98.6)	0 (0.0)	2,842
Kerosene	13 (65.0)	4 (20.0)	3 (15.0)	0 (0.0)	0 (0.0)	20
Distillate fuel oil	152 (13.0)	79 (6.8)	184 (15.7)	740 (63.2)	16 (1.4)	1,170
Residual fuel oil	0 (0.0)	23 (7.4)	54 (19.9)	147 (47.3)	87 (28.0)	311
LPG and ethane	112 (16.2)	20 (2.9)	557 (80.4)	5 (0.7)	0 (0.0)	693

Source: PennWell 1998

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Wastes include drilling fluids and produced waters which are managed in pits, discharged to surface waters, or injected into the producing well or an aquifer (Charbeneau et al. 1995). Records of damage due to both improper and acceptable management of these wastes reflects the presence of constituents of concern found in crude oil such as benzene, phenanthrene, lead, and barium. Numerous damage cases are cited in this Report to Congress, including an estimated 425 reported spills on the North Slope of Alaska in 1986.

Current regulatory programs applicable to these wastes include a variety of state programs, the Underground Injection Control Program established under the Safe Drinking Water Act Part C (Class II wells are oil and gas-related), and the Bureau of Land Management regulations for the activities on federal and Indian lands.

Wastes Generated from Petroleum Refining. Petroleum refining wastes are regulated by EPA in several ways. There are approximately 150 active petroleum refineries in the United States. RCRA Subtitle C currently lists four characteristics as hazardous in 40 CFR 264.21 and .24 and five waste categories as hazardous in 40 CFR 261.31 and .32. When most of these wastes were listed beginning in 1980, there were 250-300 active refineries ranging in capacity from about 400,000 barrels (bbl) per day to only a few hundred bbl per day.

In addition, petroleum refining wastes are subject to evaluation as characteristically hazardous waste, including the toxicity characteristic (40 CFR 261, Subpart C) which labels wastes "RCRA hazardous" if a measured constituent concentration exceeds a designated maximum (e.g., a benzene concentration of 0.5 mg/L)

All Subtitle C hazardous wastes are prohibited from land disposal without prior demonstration that hazardous constituent concentration levels comply with regulatory limits or that prescribed methods of treatment are used. These two criteria are intended to reduce the toxicity of the waste or-substantially reduce the likelihood of migration of hazardous constituents from the waste, so that health and environmental threats are minimized. The primary method of treatment is waste combustion to destroy organic constituents.

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RCRA-classified listed hazardous wastes are also hazardous substances under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA), as amended. CERCLA hazardous substances are listed in 40 CFR 302.4 and have unique reportable quantities (RQs) which, when released, trigger emergency response and reporting measures.

Oil generated and recovered during petroleum refining has also been excluded from RCRA regulation. In 1994, EPA limited the exclusion to recovered oil from refining, exploration, and production that is inserted into the petroleum refining process prior to distillation and catalytic cracking. Recovered oil includes materials that are primarily oil and that are recovered from any phase of petroleum exploration, refining production, and transportation. It is considered by EPA to be equivalent to the raw materials normally used in refining in composition and management. In November 1995, EPA proposed to expand this exclusion to encompass all oil-bearing secondary materials that are generated within the petroleum refining industry and that are reinserted into the refining process (including distillation, cracking, fractionation, or thermal cracking).

Used Oil as a Waste. “Used oil means any oil that has been refined from crude oil, that has been used and as a result of such use is contaminated by physical or chemical impurities” (40 CFR 260.10). In 1992, there were approximately 700,000 commercial, industrial, and large farm used oil generators in the United States. The management of used oil has a statutory, regulatory, and judicial history dating back to 1978. Currently, used oil exhibiting any hazardous waste characteristics must be managed under RCRA Subtitle C as a hazardous waste. In turn, used oils contaminated with CERCLA hazardous substances are subject to RQs under 40 CFR 302.4. Disposal of nonhazardous used oil that is not recycled is regulated under 40 CFR 257 and 258 of RCRA Subtitle D. The recycling of all used oils is regulated under 40 CFR 279. These regulations include programs for generators, collection centers, transporters and transfer facilities, processors and re-refiners, burners, and marketers. An estimated 750 million gallons per year of used oil enter the commercial used oil recycling system according to EPA. In 1992, these recycling businesses consisted of independent collectors (383), minor processors (70), major processors (112), re-refiners (4), fuel oil dealers (25-100) and burners (1,155). Products of used oil processing and re-refining include specification fuel, reconstituted lubricating oils and fluids, distillate fuel, lube feedstock, asphaltic bottoms, and other non-fuel oil-derived products. Part 279 prohibits used oil use as a dust suppressant unless a state successfully petitions for authority to allow its use as a suppressant. As of 1992, 41 of 50

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states prohibited road oiling. No regulations exist for individuals who generate used oil through home or personal use of oil products.

Used Petroleum Refining Products as Wastes. Government regulations presume that petroleum refining products are consumed and not disposed. Therefore, there are no regulatory programs designed for the intentional disposal of petroleum products. However, RCRA can apply to disposed petroleum products. These products can be declared solid wastes and, possibly, hazardous waste as defined under 40 CFR 261. The only exemption from the definition of solid waste for petroleum products is when the material is recycled. There are no exemptions from the definition of hazardous waste for petroleum products declared to be wastes. Used oil, in particular, has a specific RCRA regulatory program, as described above.

Petroleum products such as gasoline contain certain hazardous constituents including benzene, toluene, and xylene. However, the presence of such constituents in gasoline does not qualify it as a hazardous waste under RCRA or a hazardous substance under CERCLA. The management of petroleum products is, however, regulated under three programs: Underground Storage Tanks (UST) (40 CFR Part 280) to prevent tank leakage, Hazardous Materials Transportation (HMT) (49 CFR Chapter 1) for petroleum distillates with combustible and flammable properties, and the Occupational Safety and Health standards (29 CFR Part 1910.1000) for inhalation hazard. The UST and HMT programs are designed to prevent and respond to accidental releases of petroleum products. Both programs are discussed in the next section.

Accidental Releases of Crude Oil, Petroleum Refining Wastes, Used Oil, and Petroleum Refining Products

Oil Production Wastes. Numerous damage cases are cited in the 1987 EPA Report to Congress, including the estimated 425 reported spills on the North Slope of Alaska in 1986. However, EPA did not believe the impact of these releases warranted regulating these oil production wastes as RCRA hazardous. Rather, they are regulated under state programs.

Petroleum Refining Waste. The extent of mismanagement or accidental releases of petroleum refining wastes can be illustrated with the 1995 proposed RCRA listing determination for 16

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additional petroleum refining waste categories (of which 3 waste categories were determined to be RCRA hazardous and proposed to be listed in 40 CFR 261). A search of state and federal enforcement records, documented CERCLA-related activities at 10 sites and RCRA-related activities at 29 sites.

Accidental releases of RCRA-listed petroleum refining wastes are regulated in two ways. First, as part of the RCRA program, treatment storage and disposal facilities (TSDFs) that manage hazardous refinery wastes must obtain permits. A key component of the permit application is demonstration of an effective contingency plan for accidental releases, a preparedness/prevention plan, and a groundwater monitoring plan when wastes are managed in land-based units among other activities. Second, these wastes are also subject to the reportable quantity (RQ) requirements of CERCLA.

Used Oil and Other Waste Petroleum Refining Products. Used oil and other petroleum product mismanagement and related risks are controlled under other regulations and statutes; these include the 40 CFR Part 268 underground storage tank (UST) regulations, the 40 CFR Part 112 Spill Prevention, Control and Countermeasure (SPCC) program, the National Pollutant Discharge Elimination System (NPDES) storm water regulations, and the lead phase-down program. Section 311 of the Clean Water Act requires facilities to have an SPCC plan or contingency plan in place to ensure that oil spills are prevented, controlled via containment measures, and responded to when oil spills occur and reach navigable waterways. About 50% or more of the used oil generators, and most of the used oil transporters, processors/re-refiners, and off-spec used oil burners are covered by the SPCC program. Less than 10% of the used oil industry participants are excluded from the SPCC program because they are not in the vicinity of navigable waterways. The program includes non-transportation-related facilities located in proximity to navigable waters, USTs with capacities greater than 42,000 gallons, aboveground storage tanks with capacities greater than 1,320 gallons, and single tanks with capacities greater than 660 gallons.

The International Convention for the Prevention of Pollution from Ships (1973) as modified by the 1978 Protocol (MARPOL) focuses on preventing ship-generated ocean pollution. Annexes I-V of the MARPOL protocol address oil, noxious liquids, and other petroleum-related contaminants (MARPOL 1978).

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The Hazardous Materials Transportation Act regulates used oil and petroleum distillates if they meet the definitions of “flammable” or “combustible.” All used oil generators and transporters must comply with applicable Department of Transportation regulations for hazardous materials (49 CFR, Chapter I - Research and Special Programs Administration).

The Toxic Substances Control Act (TSCA) prohibits the use of waste oil containing any detectable polychlorinated biphenyls (PCBs) as a sealant, coating or dust suppressant. Any spill of material containing ≥ 50 ppm PCBs into the sewer, drinking water, surface water, grazing land, or vegetable gardens must be reported (40 CFR 761).

The UST program (40 CFR Part 280) focuses on control and prevention of petroleum leaks from underground petroleum storage tanks including petroleum products and waste oil tanks. The regulations currently exempt UST systems less than 110 gallons in capacity, machinery containing substances regulated under the UST program, farm or residential tanks less than 1,100 gallons in capacity, heating oil tanks where the heating oil is used on the premises, and flow-through process tanks, among others.