

FOREWORD

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- Background (or naturally occurring) chemical concentrations (i.e., those typically found in unaffected areas)
- Analytical detection limits
- Concentrations that may be attainable if the most aggressive technologies were used for site remediation.

However, since none of these goals is directly tied to the actual risks posed by the chemicals of concern, there is no way to determine whether or not these goals actually protect human health and the environment.

TRADITIONAL APPROACHES MAY MISALLOCATE RESOURCES

There is no way to determine the cost/benefit associated with achieving the management goals listed above, since the benefit of the action cannot be determined. Without any knowledge of the benefit resulting from a given action, there is no way to prioritize actions to focus them on those problems where the greatest potential for risk reduction exists. This could conceivably result in a portion of the public being left at risk, and in the misallocation of both the technical and financial resources of this country. This represents a problem because there is a limit to the resources that the United States has available to solve the environmental problems in the oil and gas, or any other, industry.

RISK-BASED APPROACHES PERMIT COST-BENEFIT ANALYSES

In contrast, risk-based approaches to site management clearly describe the potential health benefits that might result from a particular environmental management decision. Consequently, the actions that are taken at a site can be evaluated and prioritized based on the actual reduction in risk that would be achieved and technical and financial resources can be allocated appropriately.

SHOULD IT BE USED AT ALL SITES?

Like all technical methodologies and protocols, risk-based decision-making is not necessarily applicable to every situation at every E&P site. For example, there may be instances where a risk-based assessment concludes that TPH concentrations at a specific site do not pose a health risk. However, these same concentrations may produce unsightly conditions that may influence site management decisions.

It is also important to think carefully about the assumptions that are made when using risk-based decision-making for site management. Since it is not uncommon to have limited data available to conduct a risk-based evaluation of a site, there is generally a need to make some

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At most E&P sites, it is likely that a tiered risk-based strategy will be the approach of choice. This is because E&P sites generally involve a known and very limited number of chemicals of potential concern (e.g., crude oil, gas condensates, selected additives), and they have relatively small operational footprints. Consequently, the lower tiers of risk analysis will often provide the most cost-effective site management approach.

Tiered risk-based strategies are appropriate for E&P sites since these sites:

- *Involve known and very limited number of chemicals*
- *Have relatively small operational footprints*

WHAT IS THE ROLE OF GENERIC SITE CLEANUP CRITERIA IN THE RISK-BASED DECISION-MAKING PROCESS?

Both generic and site-specific criteria have a potential role in the management of E&P sites. Generic site clean-up criteria, many of which are not explicitly risk-based, can be used as Tier 1 screening level criteria. E&P site managers can use these criteria for site management if the desire or need to generate a site-specific risk-based criteria is not present. For example, if a site in its current condition was already below the generic site clean-up criteria, there would be no need to incur the expense or spend the time to determine what the site-specific risk-based criteria would be. Similarly, for a given site, if the volume of impacted soil (or other environmental media) that exceeds the generic criteria is small, it may be more cost-effective to take the necessary remedial action to meet the generic criteria than to determine if the remedial action is really necessary by generating site-specific criteria. However, it should be recognized that those generic criteria that are not risk-based may or may not be protective of human health and the environment. One of the goals of the recent PERF research initiatives (i.e., PERF Project 97-08) was to derive a generic risk-based screening criteria against which existing, non risk-based criteria that are currently used for E&P site management could be compared.

Examples of generic site clean-up criteria for TPH in soils at E&P sites in North America (mg/kg)

- *Colorado:*
 - ♦ *1,000 (sensitive site)*
 - ♦ *10,000 (non-sensitive site)*
- *Louisiana: 10,000*
- *New Mexico: 100; 1,000; or 5,000*
- *Texas: 10,000*
- *Wyoming: 1,000 to 10,000*
- *Alberta (Canada): 1,000*

TIER 1 VERSUS TIER 2 OR TIER 3?

The development of tiered approaches for the risk-based analysis of sites was based on the premise that there are situations where conducting a detailed risk analysis may require more effort and time than immediate implementation of site remedial actions. For this reason, after every tier of risk analysis, the site manager must perform a cost/benefit evaluation to determine if it makes sense to proceed to the next level of risk analysis. Only if a clear benefit exists would the decision to move forward be made. For example, because the Tier 1 assessment is often based upon conservatively low, generic site clean-up goals, the extent of a site remedial action may be larger (and more expensive) than might be required if a more detailed site-specific Tier 2 analysis were conducted. However, additional time and expense will be incurred to complete the Tier 2 analysis. At this point, the site

Cost-benefit analysis will determine if the more detailed Tier 2 or Tier 3 analysis is warranted. Timing is also likely to be an important factor.

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PART III

CHARACTERISTICS OF CRUDE OILS, REFINED PETROLEUM PRODUCTS, CONDENSATES, AND E&P WASTES

An understanding of the chemical, physical, and toxicological characteristics of crude oils, refined petroleum products, condensates, and E&P wastes is required for the effective application of risk-based decision-making. However, most of the available analyses of these materials will not support a rigorous assessment of risk. Several recent studies have improved this situation by providing the necessary data to support risk analyses [TPHCWG, 1999; Kerr, et al., 1999a; Kerr, et al., 1999b; Magaw, et al., 1999a; Magaw, et al., 1999b; McMillen, et al., 1999a; McMillen, et al., 1999b]. A summary of these chemical, physical, and toxicological data is presented here.

CHEMICAL CHARACTERISTICS

WHAT ARE THE CHEMICAL CHARACTERISTICS OF CRUDE OIL AND ITS REFINED PRODUCTS?

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Crude Oil

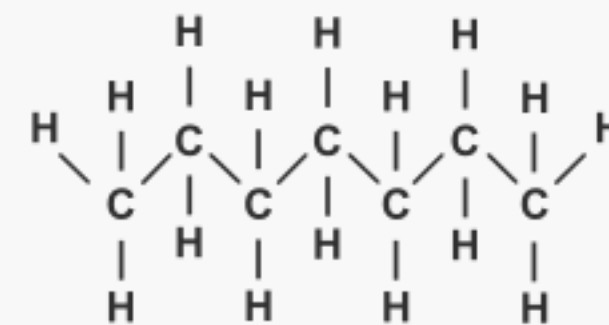
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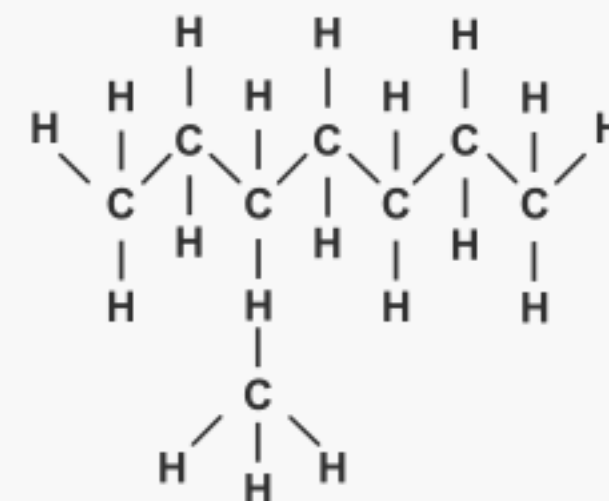
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Saturates: (alkanes or paraffins)

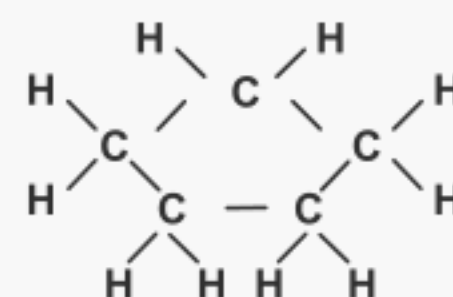
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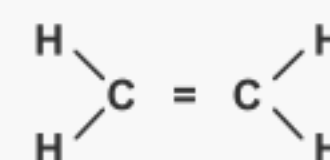


Cycloalkane:

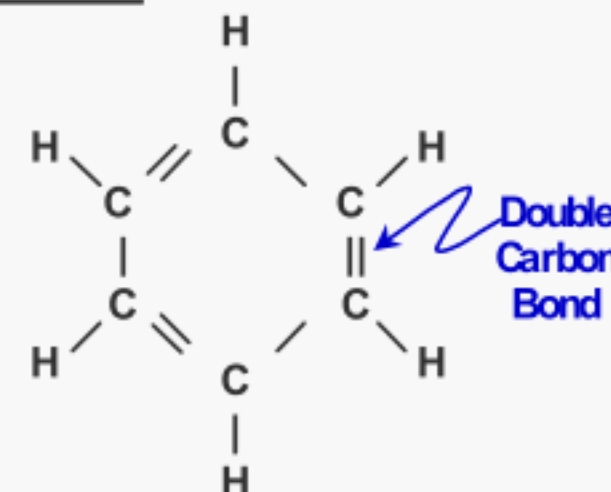


Unsaturates:

Olefins:



Aromatics:



PART III

CHARACTERISTICS OF CRUDE OILS, REFINED PETROLEUM PRODUCTS, CONDENSATES, AND E&P WASTES

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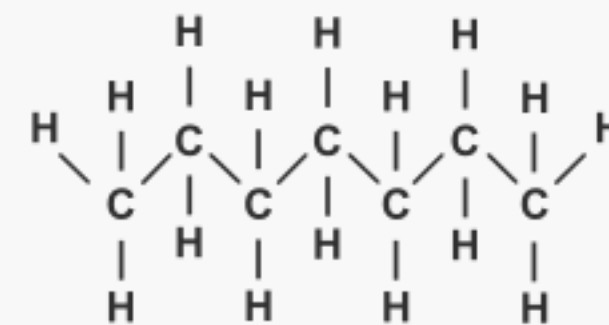
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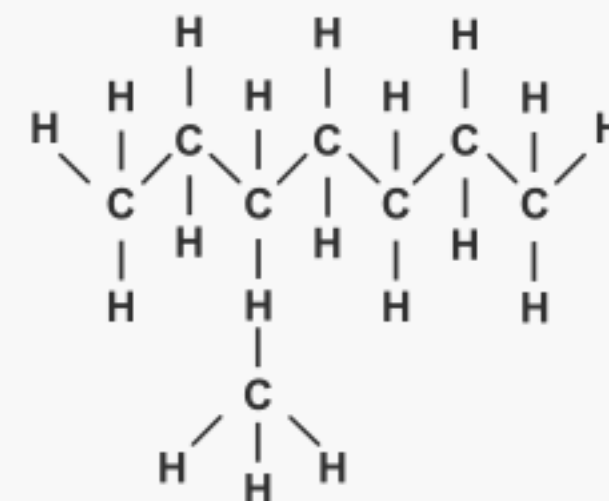
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Saturates: (alkanes or paraffins)

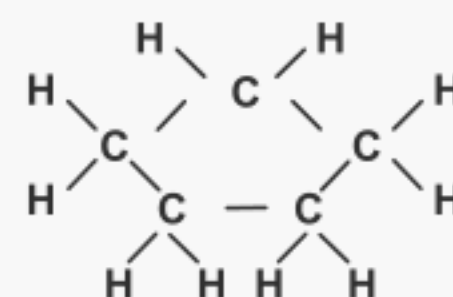
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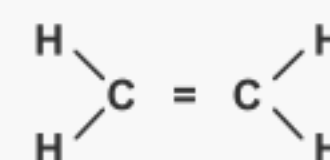


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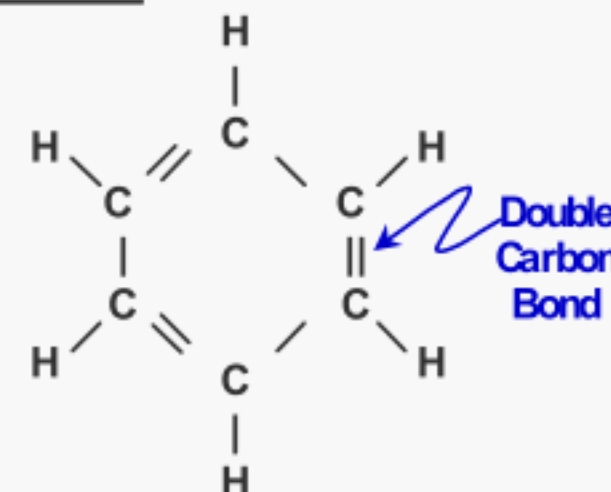


Unsaturates:

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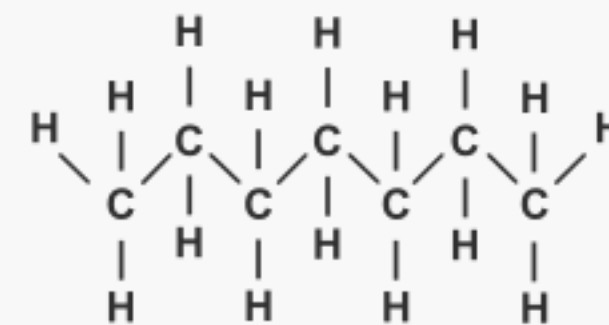
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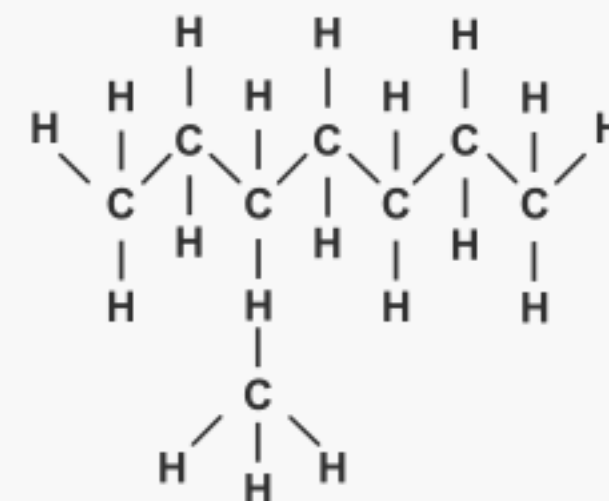
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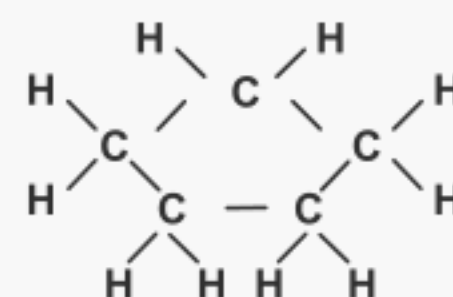
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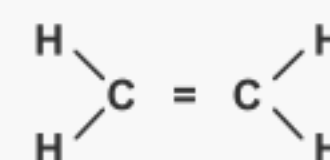


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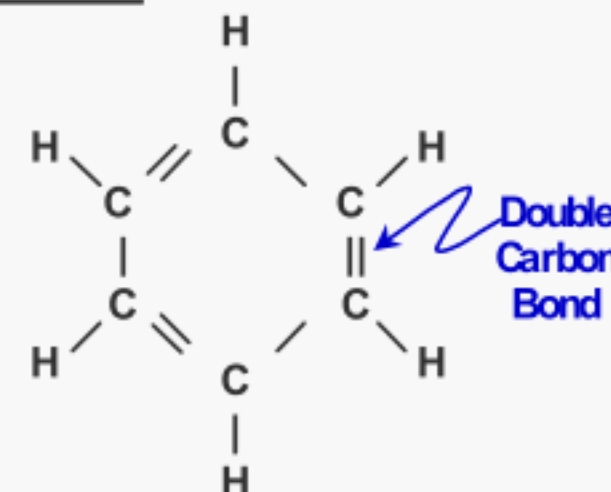


Unsaturates:

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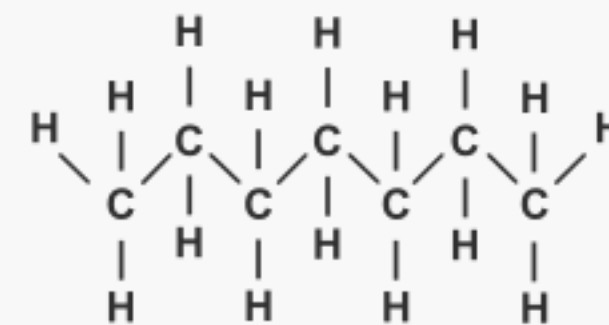
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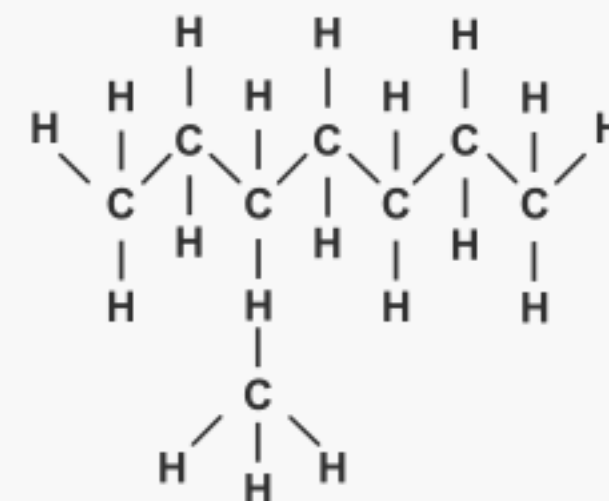
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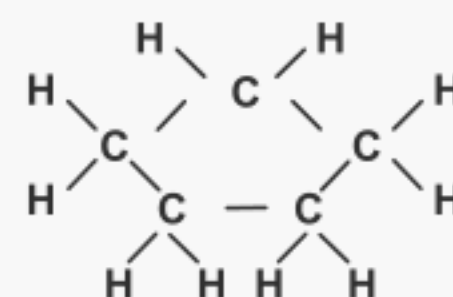
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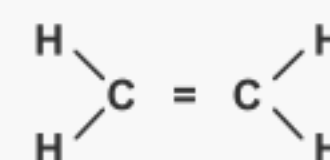


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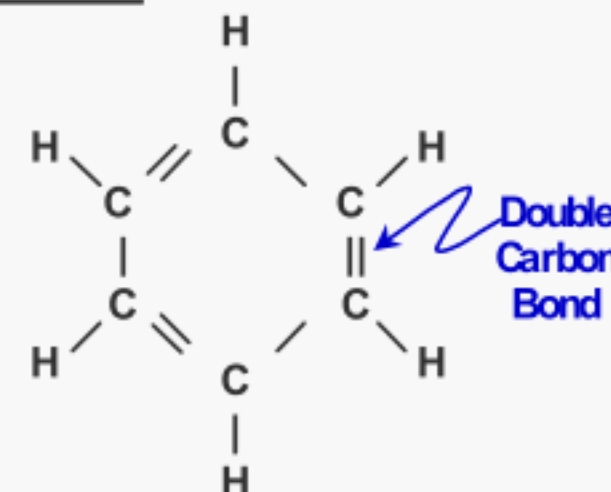


Unsaturates:

Olefins:



Aromatics:



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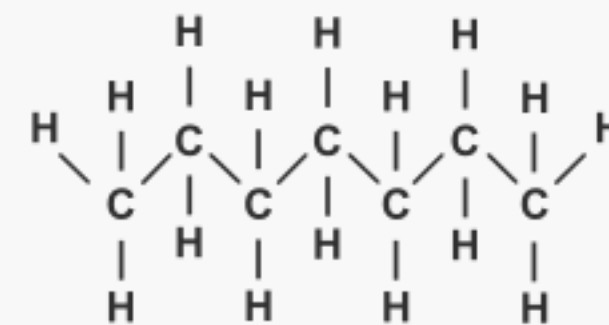
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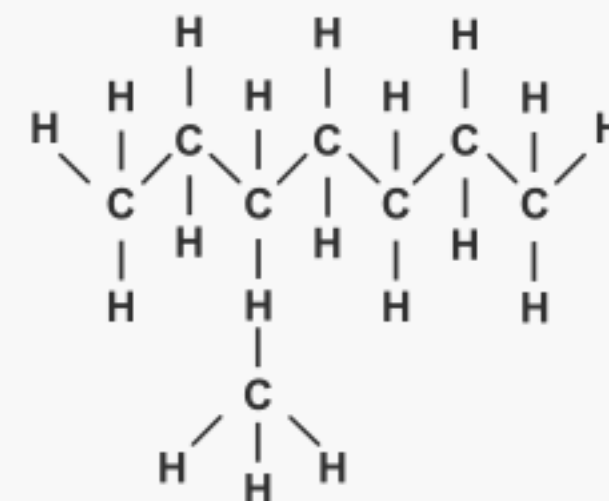
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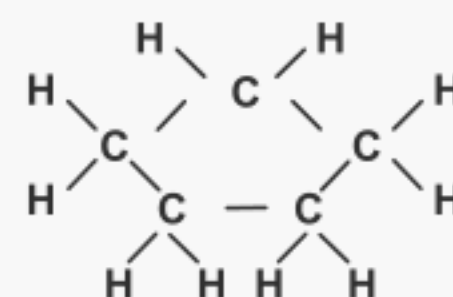
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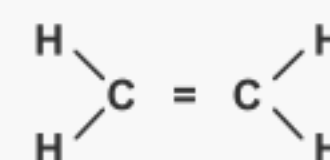


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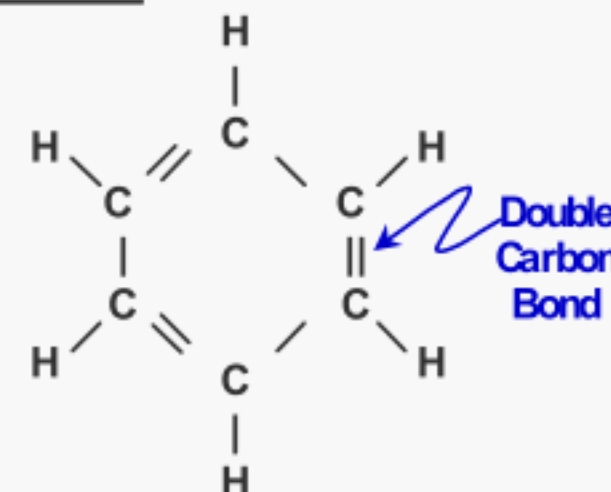


Unsaturates:

Olefins:



Aromatics:



Appendix A provides a discussion of RCRA exemption for E&P wastes and definition of "associated wastes."

API and GRI conducted studies to characterize "associated wastes" from wellhead production operations:

- API analyzed 12 wastes; GRI, 20 wastes. Five common waste types were analyzed by both organizations.
- Wastes were characterized for:
 - (1) VOCs
 - (2) Semi-volatile organic compounds
 - (3) Trace metals

Hydrocarbons Detected in E&P Wastes:

- VOCs: benzene, carbon disulfide, ethylbenzene, toluene, and xylene
- Semi-volatile Organic Compounds: phenol, naphthalene, methyl-naphthalene, methylphenol, chrysene, and phenanthrene

The wastes that are uniquely associated with exploration and production operations are currently exempt from regulation under the Resource Conservation and Recovery Act (RCRA) as "hazardous wastes." Produced water and drilling muds are the two wastes that are produced in the largest volumes. RCRA-exempt "associated wastes" include hydrocarbon-containing wastes such as soil impacted with crude oil, tank bottoms, and workover fluids. Other potentially significant associated wastes include the gas processing fluids that are used to dehydrate and remove sulfur from the gas (i.e., glycols and amines) as well as used exploration additives such as biocides, frac fluids, and drilling fluids. [See Appendix A for a discussion of the RCRA E&P regulatory determination and definition of "associated wastes"].

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All but five of the wastes were characterized for volatile organic compounds (EPA Appendix IX of 40 *CFR*, Part 264: This Appendix of the *Code of Federal Register* presents a list of chemicals for groundwater monitoring at RCRA hazardous waste facilities. This list has also been

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- API analyzed 12 wastes; GRI, 20 wastes. Five common waste types were analyzed by both organizations.
- Wastes were characterized for:
 - (1) VOCs
 - (2) Semi-volatile organic compounds
 - (3) Trace metals

Hydrocarbons Detected in E&P Wastes:

- VOCs: benzene, carbon disulfide, ethylbenzene, toluene, and xylene
- Semi-volatile Organic Compounds: phenol, naphthalene, methyl-naphthalene, methylphenol, chrysene, and phenanthrene

The wastes that are uniquely associated with exploration and production operations are currently exempt from regulation under the Resource Conservation and Recovery Act (RCRA) as "hazardous wastes." Produced water and drilling muds are the two wastes that are produced in the largest volumes. RCRA-exempt "associated wastes" include hydrocarbon-containing wastes such as soil impacted with crude oil, tank bottoms, and workover fluids. Other potentially significant associated wastes include the gas processing fluids that are used to dehydrate and remove sulfur from the gas (i.e., glycols and amines) as well as used exploration additives such as biocides, frac fluids, and drilling fluids. [See Appendix A for a discussion of the RCRA E&P regulatory determination and definition of "associated wastes"].

Characterization Studies

Both API and GRI have conducted studies to characterize several of the associated wastes of oil and gas exploration and production. The API study [American Petroleum Institute, 1996] focused primarily on the characterization of the associated wastes from wellhead oil production operations. Complementing this effort, the GRI study [Gas Research Institute, 1993] emphasized the characterization of wastes from natural gas production associated with mainline compression/transmission, underground storage, and gas processing and conditioning. A common set of four samples from a single gas processing and conditioning facility were characterized in both studies.

The API study analyzed a total of twelve different associated wastes from oil and exploration and production sites. These wastes included:

- Tank bottoms
- Crude oil impacted soil
- Workover fluids (flowback from spent stimulation fluids)
- Produced sand
- Dehydration and sweetening materials (i.e., glycol waste, dehydration condensate water, spent molecular sieve, spent iron sponge, and used amine solutions)
- Pit and sump samples
- Rig wash waters
- Pipeline pigging materials

All but five of the wastes were characterized for volatile organic compounds (EPA Appendix IX of 40 *CFR*, Part 264: This Appendix of the *Code of Federal Register* presents a list of chemicals for groundwater monitoring at RCRA hazardous waste facilities. This list has also been

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WHAT IS THE EVIDENCE OF DIFFERENCES IN BULK HYDROCARBON COMPOSITION?

Carbon-Number Range

From a broad perspective, crude oil encompasses a wide spectrum of hydrocarbons compared to its refined products and most of the condensates. As mentioned, a typical carbon-number range for gasoline is only C₅ to C₁₀; diesel, C₁₂ to C₂₈; and condensate, <C₆ to C₃₀. Evidence of these differences can be seen by comparing the gas chromatograms of crude oil (Figure 3), gas condensates (Figure 5), and the refined products of gasoline and diesel fuel (Figure 6). These chromatograms reveal the narrower hydrocarbon distributions that are typical of the refined products and the condensates.

Refined products and condensates have narrower hydrocarbon distributions than crude oils.

Chemical Classes of Hydrocarbons

The gas chromatograms also provide evidence of the differences in hydrocarbon composition that can exist even within a single type of hydrocarbon mixture. The PERF Project 97-08 made a special effort to capture the differences among crude oils by collecting seventy samples of crude oils from all over the world. An indication of how representative these samples were of the general composition of a worldwide set of 636 crude oils is shown in Figure 7 [Tissot B. P. and D. H. Welte, 1978]. The individual data points shown represent the composition of the crude oil samples of the PERF project (51 separate crude oils and crude oil extracts from 6 soil samples). Every one of these data points fall within the 95% frequency distribution envelope that was delineated using the worldwide set of crude oil samples. The composition data points from the PERF project also uniformly cover nearly the entire area within the frequency distribution envelope shown in Figure 7.

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Once it has been determined who might be exposed to chemicals of potential concern, the next step is to determine **how** they might be exposed. This is a process in which potentially complete exposure pathways are identified. In identifying these complete exposure pathways, the sources of the chemicals at the site are determined and the ways in which they may move around in the environment and be transported to places at which receptors might realistically be exposed are considered. For example, if a crude oil is spilled on soil at a site, a worker in the area may be exposed by direct skin contact with the impacted soil. Alternatively, some of the components of the crude oil may vaporize into air and be inhaled by the worker or they may migrate through the soil into the groundwater and then be transported to a drinking water well at some distance from the site and subsequently ingested. The exposure assessment is important because it introduces site-specific factors into the characterization of the site risk.

The final step of the exposure assessment is to quantify the potential exposure to identified receptors. Standardized intake equations are used in this part of the analysis to answer the final question “To **how much** of the chemicals of potential concern is a receptor likely to be exposed?”

TOXICITY (DOSE-RESPONSE) ASSESSMENT

All chemicals have the inherent ability to cause adverse health effects of some sort, at some dose level; but only some chemicals have the ability to cause cancer.

Key challenges associated with using toxicity data:

- (1) Extrapolating pure chemical test results to complex mixtures of chemicals*
- (2) Extrapolating pure chemical test results to situations where the chemicals are present in soil*
- (3) Extrapolating test results in animals to humans*

The toxicity assessment answers the question “What dose levels of the chemicals of potential concern may produce adverse health effects in people or other receptors?” In the toxicity assessment, chemicals are usually evaluated separately for their abilities to cause cancer and other adverse health effects. All chemicals can cause adverse health effects of some sort at some dose level, but only some chemicals have the potential to cause cancer. Most available toxicological data for both carcinogenic and non-carcinogenic chemicals have been generated in the laboratory using pure chemicals that have been added to the food or water of rats or mice. One of the major challenges is in extrapolating these results to situations in which mixtures of chemicals, such as crude oil, may be of concern. A second challenge is in extrapolating the laboratory results obtained in rodents treated with pure chemicals to situations in which people are exposed to chemicals in soil. In both cases, uncertainty factors are included to make certain that chemical toxicity is not underestimated.

RISK CHARACTERIZATION

The final step of the risk evaluation combines the results of the Exposure Assessment with the Toxicity Assessment to estimate the potential risks posed by the site. The result is a conservative risk estimate that is likely to overestimate the true risks posed by the site. In reality, the true risk is most likely to be much lower than the estimated risk, and may be as low as zero in some cases.

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The toxicity assessment answers the question “What dose levels of the chemicals of potential concern may produce adverse health effects in people or other receptors?” In the toxicity assessment, chemicals are usually evaluated separately for their abilities to cause cancer and other adverse health effects. All chemicals can cause adverse health effects of some sort at some dose level, but only some chemicals have the potential to cause cancer. Most available toxicological data for both carcinogenic and non-carcinogenic chemicals have been generated in the laboratory using pure chemicals that have been added to the food or water of rats or mice. One of the major challenges is in extrapolating these results to situations in which mixtures of chemicals, such as crude oil, may be of concern. A second challenge is in extrapolating the laboratory results obtained in rodents treated with pure chemicals to situations in which people are exposed to chemicals in soil. In both cases, uncertainty factors are included to make certain that chemical toxicity is not underestimated.

RISK CHARACTERIZATION

The final step of the risk evaluation combines the results of the Exposure Assessment with the Toxicity Assessment to estimate the potential risks posed by the site. The result is a conservative risk estimate that is likely to overestimate the true risks posed by the site. In reality, the true risk is most likely to be much lower than the estimated risk, and may be as low as zero in some cases.

The U.S. EPA has developed default values for each of these parameters that can be used if no other site- or chemical-specific data are available. Many state regulatory agencies have also made recommendations for their programs. Where appropriate, default values are available for several potential human receptors including workers, and adult and child residents.

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**Dried Oak Leaves
18,000 mg/kg**



Pine Needles — 16,000 mg/kg



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TPH measurements of several natural materials yield significant TPH concentrations:



Grass — 14,000 mg/kg



**Dried Oak Leaves
18,000 mg/kg**



Pine Needles — 16,000 mg/kg



**Petroleum Jelly
749,000 mg/kg**

Peoples, 1954; Udo, et al., 1975; Baker, 1970; deOng, et al., 1927; Plice, 1948; Chaineau, et al., 1997; and Saterbak, et al., 1999]. This work illustrated that >10,000 mg/kg TPH from crude oil did not adversely impact the growth of most plants nor pose a risk of leaching to groundwater. Some states adopted a TPH clean-up level of 10,000 mg/kg (1% by weight) based on these results. However, other states used TPH standards as low as 100 mg/kg in soil that are similar to those developed for gasoline leaks at underground storage tank sites for the protection of groundwater. This standard might be applied to an E&P site even though a heavy crude oil, with no potential to leach to groundwater, may have been the only onsite petroleum hydrocarbon. The current research initiatives seek to establish a more consistent technical approach for the management of petroleum hydrocarbons that emphasizes the protection of human health and determines if a TPH concentration of 10,000 mg/kg is indeed protective at E&P sites.

WHAT IS TOTAL PETROLEUM HYDROCARBON OR TPH?

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Conventional bulk measurements of TPH in a sample are sufficient for screening the acceptability of site concentrations, based upon a comparison with existing TPH regulations. However, these bulk measurements are not sufficient to support a human health risk assessment. To illustrate this point, high bulk TPH concentrations can be measured in items that clearly do not pose a risk to human health. For example, TPH concentrations have been measured in many items that can be found throughout nature including grass (14,000 mg/kg of TPH), pine needles (16,000 mg/kg of TPH), and oak leaves (18,000 mg/kg). It has also been measured in household petroleum jelly at concentrations of 749,000 mg/kg. Although these TPH concentrations are substantially greater than many existing TPH standards, none of these materials are considered a risk to human health.

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There are additional factors that must be considered when conducting the above calculations. For example, the summation of all of the mass fractions of the carbon number fractions must equal unity. Also, the concentration of any carbon number fraction in soil cannot result in hydrocarbon concentrations in pore water and soil vapor above saturation levels. The details regarding phase saturation have been reported elsewhere [TPHCWG, 1999] and are summarized briefly in Appendix C of this document. This detailed information should be consulted before any application of this methodology to a site is attempted.

Lastly, it should be understood that there are some key assumptions regarding the potential interactive toxicological effects of the individual fractions of a hydrocarbon mixture that are implicit in the calculation of the TPH RBSL for the whole crude oil. Specifically, the methodology of the TPHCWG assumes that each carbon-number fraction will affect the same target organ and that the toxic effects are additive. This assumption is considered appropriate for a screening level assessment since different hydrocarbon fractions often affect different target organs, rendering additivity of toxicological effects highly conservative.

WHAT EXPOSURE SCENARIOS AND PATHWAYS ARE IMPORTANT FOR CRUDE OIL AND WHAT ARE THE TPH RBSLS FOR THESE SITUATIONS?

As previously noted, both the current and future land uses will play a role in establishing the exposure scenarios that are important at an E&P site. The TPH RBSLs for crude oil that are determined for the site will be different for these different exposure scenarios because of various assumptions that are made about the receptors and their frequency of contact with the site hydrocarbons. In general, residential exposure scenarios are not considered relevant to most E&P sites and the primary focus of site management is on commercial or other non-residential applications. However, in those instances where residential land use is of concern due to the past history of the site development, the conduct of a site-specific risk assessment to address this scenario may be warranted and should be considered.

Only exposure pathway for TPH that poses a significant risk of non-cancer health effects at E&P sites is direct contact with hydrocarbon-impacted soil.

With regards to non-residential land use, it has been determined that the only exposure pathway for TPH that poses a significant risk of non-cancer human health effects is direct contact with hydrocarbon-impacted soil (i.e., soil ingestion, inhalation of soil particulate, and dermal contact) [McMillen, et al., 199b]. Leaching to groundwater and volatilization to outdoor air can be important pathways for crude oil at non-residential sites but only under certain circumstances [Rixey, et. al., 1999]. This is because most crude oils have low concentrations of the low molecular weight aromatic hydrocarbons as compared to

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Texas Natural Resource and Conservation Commission recently issued draft guidance stating that conventional TPH measurements can be used to evaluate a site providing TPH RBSLs have been determined for the hydrocarbon mixture at the site using the fractionation approach.

WHEN IS IT NECESSARY TO USE THE RISK-BASED ASSESSMENT OF TPH RATHER THAN CONVENTIONAL TPH MEASUREMENTS OR ASSESSMENTS?

The use of conventional measures of bulk TPH is more than adequate for site management purposes providing that RBSLs have been determined for the specific hydrocarbon mixture at the site or for specific types of hydrocarbon mixtures, e.g., transformer mineral oil [TNRCC, 2000]. If it is suspected that multiple sources of different hydrocarbons may have been present at the site (e.g., chromatographic fingerprints of the bulk TPH changes across the site), then it may be necessary to calculate more than one RBSL for each exposure pathway of a site. However, in general, only one sample from each potential source area needs to be evaluated using the more advanced, risk-based assessment of TPH composition.

TABLE 5. NON-RESIDENTIAL TPH RBSLS FOR CRUDE OIL AND THEIR ASSOCIATED WASTES (MG/KG)

	Leaching to Groundwater	Vaporization to Outdoor Air	Surface Soils
Field #1			
Crude Oil	NL	NL	82,000
Tank Bottoms	NL	NL	84,000
Oily Soil	NL	NL	76,000
Oiled Road Material	NL	NL	96,000
Field #2			
Crude Oil	NL	NL	52,000
Cyclone Separator Sludge	NL	NL	59,000
Slop Oil	NL	NL	61,000
Field #3			
Crude Oil	NL	NL	63,000
Oily Soil	NL	NL	100,000
Field #4			
Crude Oil	NL	NL	64,000
Oily Soil	NL	NL	77,000
Field #5			
Crude Oil	NL	NL	61,000
Oily Soil	NL	NL	75,000

NL: Not limiting pathway.

In lieu of generating a mixture-specific RBSL for a site, the site manager can elect to use a pre-determined RBSL provided that it was generated using a petroleum mixture that is similar to the one of interest at his site. For example, the State of Texas has developed an RBSL specifically for transformer mineral oil [TNRCC, 2000]. This Tier 1 RBSL was based on actual data that were collected on hydrocarbon-impacted soils by the utility industry. Any owner of a site that has transformer mineral oil as a source of hydrocarbon impacts can now use this RBSL to conduct a Tier 1 screening of his site.

The TNRCC has invited other industries to generate similar data for gasoline, diesel, and other petroleum hydrocarbons. The objective of

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Polycyclic Aromatic Hydrocarbons

Similar to the analysis of metals in crude oil, an analysis of 70 crude oils revealed the presence of very low concentrations of priority pollutant PAHs including the seven carcinogenic PAHs (Table 7) [Kerr, et al., 1999a; Kerr. et al., 1999b]. A screening of the human health risk associated with the presence of the carcinogenic PAHs in crude oil-contaminated soil showed the risk was not significant at TPH concentrations up to 170,000 mg/kg at non-residential sites. Even when the more restrictive exposure and toxicity parameters of the State of California were used, the acceptable levels for crude oil in soil based on the potential human health effects of PAHs were determined to be well above 10,000 mg/kg. This indicates that the low levels of PAHs in crude oils are not likely to be a major risk management consideration at crude oil spill sites and that TPH RBSLs of 10,000 mg/kg will be protective of human health with a considerable safety factor. In cases where groundwater protection may be of concern, the potential for naphthalene to leach to groundwater may need to be evaluated separately. Overall, these results suggest that there is no compelling evidence to conduct routine PAH analyses at E&P sites.

Low concentrations of PAHs in crude oil are unlikely to be a major risk at E&P sites. These results suggest that there is no compelling evidence to routinely conduct PAH analyses at these sites.

Benzene

An understanding of the impact of benzene in terms of cancer risk on the management of residual hydrocarbons at E&P sites is continuing to evolve. Current work to examine this issue is building upon previous efforts that were focused on the management of underground storage tanks (UST). Since the UST programs usually dealt with refined petroleum products such as gasoline, the majority of the recent work has been to delineate the key differences that exist when crude oil is the petroleum hydrocarbon of concern.

Average benzene concentration in 69 crude oil samples was 1,340 mg/kg oil; in condensates, 10,300 mg/kg.

Presence of Benzene at E&P Sites. Benzene concentrations were measured in a total of 69 crude oils and 14 natural gas condensates [Rixey, 1999]. Its concentration in the crude oil ranged from non-detect (<1.4 mg/kg oil) to 5,900 mg/kg oil, with a mean concentration of 1,340 mg/kg oil. In contrast, the maximum concentration in the natural gas condensates was 35,600 mg/kg of condensate (3.56%) with a mean concentration of 10,300 mg/kg.

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Polycyclic Aromatic Hydrocarbons

Similar to the analysis of metals in crude oil, an analysis of 70 crude oils revealed the presence of very low concentrations of priority pollutant PAHs including the seven carcinogenic PAHs (Table 7) [Kerr, et al., 1999a; Kerr. et al., 1999b]. A screening of the human health risk associated with the presence of the carcinogenic PAHs in crude oil-contaminated soil showed the risk was not significant at TPH concentrations up to 170,000 mg/kg at non-residential sites. Even when the more restrictive exposure and toxicity parameters of the State of California were used, the acceptable levels for crude oil in soil based on the potential human health effects of PAHs were determined to be well above 10,000 mg/kg. This indicates that the low levels of PAHs in crude oils are not likely to be a major risk management consideration at crude oil spill sites and that TPH RBSLs of 10,000 mg/kg will be protective of human health with a considerable safety factor. In cases where groundwater protection may be of concern, the potential for naphthalene to leach to groundwater may need to be evaluated separately. Overall, these results suggest that there is no compelling evidence to conduct routine PAH analyses at E&P sites.

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TABLE A-1. SUMMARY OF WASTES FROM OIL AND GAS EXPLORATION

Exploration	Drilling	Well Completion and Workover	Field Production	Gas Plant Operations
<ul style="list-style-type: none"> • Filters • Hydraulic Fluid • Mud/Cuttings from Shot Holes • Contaminated Soil • Solvents (Petroleum Naphtha) • Rig Washdown Water 	<ul style="list-style-type: none"> • Cement Returns • Completion Workover and Well Treatment Fluids • Drill Cuttings • Drilling Fluids • Filters • Hydraulic Fluid • Produced Sand • Produced Water • Contaminated Soil • Solvents • Hydrocarbon Spill Cleanup Waste • Rig Washdown Water 	<ul style="list-style-type: none"> • Cement Return • Completion Workover and Well Treatment Fluids • Pit Sludges • Produced Sand • Produced Water • Waste Crude • Oil/Condensate • Filters • Drill Cuttings • Drilling Fluids • Hydraulic Fluid • Naturally Occurring Radioactive Material • Packing Fluids • Paraffin • Contaminated Soil • Solvents • Hydrocarbon Spill Cleanup Waste • Rig Washdown Water 	<ul style="list-style-type: none"> • Boiler Blowdown • Catalyst • Process Equipment Cleaning Wastes • Completion Workover and Well Treatment Fluids • Cooling Tower Blowdown • Waste Crude Oil/Condensate • Filters • Hydraulic Fluid • Metallic Liquid Mercury • Mercury Solids • Naturally Occurring Radioactive Material • Pitting Wastes • Pipeline/Equipment Hydrates and Scale • Pit Sludges • Produced Sand • Produced Water • Hydrogen Sulfide Scrubber Liquid • Contaminated Soil • Solvents • Sulfur Dioxide Liquor • Sweetening/Dehydration Solids and Liquids • Tank Bottoms • Packing Fluids • Paraffin • Pitting Wastes • Pipeline/Equipment Hydrates • Rig Washdown Water • Hydrocarbon Spill Cleanup Wastes 	<ul style="list-style-type: none"> • Boiler Blowdown • Catalyst • Process Equipment Cleaning Wastes • Cooling Tower Blowdown • Waste Crude Oil/Condensate • Filters • Hydraulic Fluid • Metallic Liquid Mercury • Mercury Solids • Naturally Occurring Radioactive Material • Pitting Wastes • Pipeline/Equipment Hydrates and Scale • Pit Sludges • Produced Sand • Produced Water • Hydrogen Sulfide Scrubber Liquid • Contaminated Soil • Solvents • Hydrocarbon Spill cleanup Waste • Sulfur Dioxide Liquor • Sweetening /Dehydration Liquids and Solids

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- If, after mixing a non-exempt characteristic hazardous waste with an exempt waste, the resulting mixture does not exhibit any of the same characteristics as the hazardous waste, the mixture is exempt. Even if the mixture exhibits some other characteristics of a hazardous waste, it is still exempt.
- Generally, if a listed hazardous waste (i.e., a waste listed as hazardous in the Code of Federal Regulations under Subpart D of 40 *CFR* Part 261) is mixed with an exempt waste, regardless of the proportions, the mixture is a non-exempt hazardous waste.

Due to the complexity of the waste characteristics and the environmental regulations, it should be understood that these guidelines only provide a broad overview of possible waste management strategies. Before a final strategy is implemented for a given site, the site manager should consult the governing regulatory agency and/or an environmental expert in this area.

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EQUATION FOR SOIL RBSL: LEACHING TO GROUNDWATER

Groundwater RBSL

$$\text{RBSL}_{\text{gw}} \left[\frac{\text{mg}}{\text{L-H}_2\text{O}} \right] = \frac{\text{THQ} \times \text{RfD}_o \times \text{BW} \times \text{AT}_n \times 365 \frac{\text{days}}{\text{year}}}{\text{IR}_w \times \text{EF} \times \text{ED}}$$

where:

- THQ = Target hazard quotient for individual constituents [unit-less]
- RfD_o = Oral chronic reference dose [mg/kg-day]
- BW = Body weight [kg]
- AT_n = Averaging time for non-carcinogens [years]
- IR_w = Daily water ingestion rate [L/day]
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Soil RBSL Based on Groundwater RBSL

$$\text{RBSL}_s [\text{mg/kg-soil}] = \frac{\text{RBSL}_{\text{gw}} [\text{mg/L-H}_2\text{O}]}{\text{LF}_{\text{sw}}}$$

$$\text{LF}_{\text{sw}} = \frac{\rho_s}{[\theta_{\text{ws}} + k_s \rho_s + H \theta_{\text{as}}] \left(1 + \frac{U_{\text{gw}} \delta_{\text{gw}}}{IW} \right)}$$

where:

- LF_{sw} = leaching factor [mg/L-H₂O/mg/kg-soil]
- U_{gw} = groundwater Darcy velocity [cm/y]
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