USE OF GROSS PARAMETERS FOR ASSESSMENT OF HYDROCARBON CONTAMINATION OF SOILS IN ALBERTA

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Summary

Gross parameters describing hydrocarbon contamination of soils and sediments include: oil and grease, mineral oil and grease, total extractable hydrocarbons, light hydrocarbons, total petroleum hydrocarbons and total hydrocarbons. These terms denote fractions estimated by proximate chemical analyses that differ by jurisdiction, user group and even individual laboratory. An attempt to summarize and correlate terminology is presented. Regardless of what definition is chosen, gross parameters share the property of lacking any consistent relationship to biological hazard. This is because known toxic petrochemical components vary with hydrocarbon source and both biotic and abiotic environmental fate processes. Hence, no general statements based on biological effects can be made regarding "safe" levels of petroleum hydrocarbons. Despite the lack of a toxicological basis, gross hydrocarbon parameters can still be useful in contaminated site assessment. Three roles are identified: 1) as screening tools at contaminated sites, 2) as investigative surrogates on a site-specific basis, and 3) as remediation criteria when toxicological, organoleptic and groundwater protection concerns have previously been addressed.

Scope of Application of This Interim Guide

The technical discussion below pertains to observations on petroleum contamination of mineral soils and regolith materials. However, the discussion of guide values for assessment and remediation purposes is restricted to surficial soil materials -- roughly the first meter of surficial material which is biologically active and represents a direct exposure potential for humans. For deeper subsurface materials, the reader is referred to the MUST program administered by Alberta Environmental Protection's Groundwater Protection Branch.

Definitions

"Petroleum hydrocarbons" is a generic term applied to the various organic chemicals that comprise geological petroleum deposits or products refined from this source. Chemically, petroleum hydrocarbons are, in general, more reduced than organic molecules characteristic of living tissue and contain fewer and less complex bonding arrangements with elements other than carbon and hydrogen. A broad characterization of petroleum hydrocarbons based on a simple polar separation scheme (Fuhr et al. 1988, Pollard et al. 1992) is as follows:

Saturates. Mixture of straight-, branched-chain and cyclic alkanes and alkenes.

- *Aromatics*. Mono- and polycyclic aromatic hydrocarbons lacking heteroatoms. Examples include toluene, naphthalene, phenanthrene, benzo[a]pyrene, fluorene, chrysene, and substituted PAH such as 7,12-dimethylbenzanthracene.
- *Polars 1*. Relatively low molecular weight (compared to asphaltenes) amorphous polymers of various hydrocarbons including alcohols, acids and hydroxyacids; fatty acids.
- *Polars 2.* N- and S-rich heterocyclic aromatic compounds including pyrroles, quinolines, diazoles, carbazoles, thiophenes, benzothiophenes and thiazoles.
- *Asphaltenes.* Complex, highly condensed, high molecular weight, heterogeneous hydrocarbons including both aliphatic and aromatic structures. Very poorly characterized due to lack of appropriate purification and separation technology.

"Total Petroleum Hydrocarbons" is a gross characterization parameter that has been defined in several ways:

- Dichloromethane-extractable (EPA Preparation Method 3540A, EPA SW-846) hydrocarbons measured by gas chromatography (GC) or infrared spectrometry (IRS) after cleanup on silica gel to remove polar compounds (e.g. fatty acids from biomass).
- 2. Freon-113-extractable hydrocarbons measured by IRS after cleanup on silica gel to remove polar compounds (e.g. fatty acids from biomass)(EPA Method 9073).
- 3. Sum of extractable (GC or IRS) and purgeable (GC) petroleum hydrocarbons (Alberta MUST Program 1991). Purgeable hydrocarbons refers to volatile hydrocarbons released by EPA Preparation Method 5030 and generally quantified below C10 only. Detection is normally by GC equipped with a flame ionization detector (GC-FID). When monoaromatics or other low molecular weight unsaturates are expected to dominate the volatile fraction a photoionization detector (GC-PID) can be used and may be preferred.

For the purposes of the following discussion definition 3 applies unless otherwise specified.

Related gross characterization parameters include oil and grease, mineral oil and grease, BTEX and total extractable hydrocarbons:

- 1. Oil and grease -- Hydrocarbons extracted by various solvents including hexane, hexane/acetone, hexane/methyl-t-butyl ether, freon, n-pentane, and dichloromethane. Detection may be gravimetric or by IRS.
- 2. Mineral oil and grease -- Same as oil and grease except that the extract is cleaned up on a silica gel column to remove polar compounds.
- 3. Total extractable hydrocarbons -- Same as oil and grease except detection is usually by GC-FID.

These and some other gross hydrocarbon parameters are defined for comparative purposes in Table 1.

Relations Among the Gross Parameters

Because preparation, extraction, detection and quantification procedures vary among the methods it is expected that results for a given sample will depend on the method chosen. However, through consideration of what each method responds to and the expected hydrocarbon characteristics of the sample, some general statements can be made.

Properties of Petroleum Products

The chemical constituents of crude oil are extremely variable. In general, the five component classes listed above will be present but their relative abundances vary with factors such as the age and depth of the petroleum deposit (Schobert 1990), which affect primarily the extent of cracking and fate of heteroelements such as sulfur. In this scheme, end members are represented by young-shallow and old-deep crudes. The former will tend to have high aromatic and sulfur contents and mean molecular weight. Old-deep crudes, the most economically desirable type, are expected to have low aromatic and sulfur contents because cracking is maximal and most S will have been converted to H_2S .

Refining of crude oils generates industrial and consumer products with better defined, though still variable, properties. Patty's Industrial Hygiene and Toxicology (3rd Ed. Vol. 2B) summarizes the general properties and applications of the common distillate cuts as follows:

Fraction	Carbon Range	Boiling Range, °C	Uses
Natural gas	C ₁ -C ₃	-164 to -88	Fuel, chemical
Liquefied or bottled gas	C ₃ -C ₄	-44 to +1	Fuel, precursor for petrochemicals
Petroleum ether	C ₄ -C ₈	20 to 60	Solvents
Gasolines	C ₄ -C ₈ C ₅ -C ₁₀	32 to 149	Aviation fuel
		32 to 210	Automotive gasoline
Naphthas	C ₈ -C ₁₀	65 to 204	Cleaning fluids, solvents, refining stock
Kerosenes	C ₆ -C ₁₆	40 to 300	Jet and turbofuels
		350 to 550	Stove oil, tractor and gas turbine fuel
Gas oil	C ₉ -C ₁₆	204 to 371	Furnace oil, diesel
Lubricating stocks	> C ₁₇	204 to 400	White oils, lubricating oils and greases
Waxes	> C ₂₀	204 to 400	Sealing wax, food component
Bottoms	> C ₃₀	> 400	Heavy fuel oil, road oils, asphalts

Sensitivities of Laboratory Tests

Variations in recovery of hydrocarbon fractions in soils is affected by both preparatory and analytical detection procedures. Methods that do not attempt to conserve volatile fractions cannot reliably report on hydrocarbons of less than eight carbons atoms (see attached figure). For example, oil and grease measurements and total extractable hydrocarbon determinations that use Soxhlet extraction (EPA Method 3540A) are insensitive to BTEX species. Quantification of volatile organic compounds (VOCs) requires a purge and trap (e.g. EPA Method 5030) or headspace (e.g. EPA Method 3810) preparation.

VOCs may be detected and quantified to varying degrees by gas chromatography or infrared spectroscopy. GC-FID (EPA Methods 8015, 8100) is the most general method for determining hydrocarbons. FID is sensitive to most organic compounds and gives a linear response over a wide range of conditions. GC-PID (EPA Method 8020) is preferred for aromatic and unsaturated compounds but is insensitive to many other organics. GC/MS (mass spectrometry) is usually the method of choice for the most precise work (EPA Methods 8240A, 8250, 8260 and 8270A).

Infrared spectrometry differs from GC methods in that no attempt is made to isolate compounds. Rather, a spectrogram is obtained that indicates for the whole sample the types of carbon bonding patterns present. Integration of the IR spectrum, or keying on the C-H bond stretching frequency, can yield an estimate of the total hydrocarbon content of the sample. However, many assumptions are required to make this estimate and it is expected to be less accurate than a GC determination. Sources of both positive and negative bias in the IR approach are discussed and summarized by Douglas et al. (1992).

Organic compounds of more than eight carbon atoms can be determined as for VOCs by GC or IRS, or by gravimetric methods ("oil and grease" methods). Gravimetric methods require that the extraction residue be dried to constant weight. In this process further losses my occur, restricting such oil and grease measurements to compounds >C10. On the other hand, GC methods usually fail to resolve hydrocarbons beyond about C30 and therefore quantification in this region is very poor.

Whether an extract has had a cleanup treatment to remove polars will affect the magnitude of an extractable hydrocarbons determination. Surface soils high in organic

matter can contain a few hundred mg/kg extractable polar organics (probably mainly fatty acids) and these will contribute to the petroleum hydrocarbons estimate if not removed by silica gel cleanup (other solid phases for polar separation are also possible -- e.g. alumina). Elemental sulfur is also a positive interference. On the other hand, polar components of exogenous hydrocarbons will also be removed. Hydrocarbons with high heteroatom contents (e.g. sulfur) may be underestimated when silica gel cleanup is performed.

In general, one should expect $O\&G > mineral O\&G _ TEH$ by GC < TPH (when TPH is defined as the sum of purgeables and extractables as previously specified). When TPH and TEH are defined as differing only in the silica gel cleanup of a DCM extract then these two parameters can be expected to have the reverse relationship (i.e. TEH > TPH) in most cases. Regardless of what definition is applied to TEH, if TEH > O&G then it is likely that some gasoline range components are present and VOCs should be examined.

Toxicological Overview

Raw and refined petroleum products contain variable amounts of chemical substances toxic to humans and/or other organisms. For detailed treatment of this topic the reader is referred to Clayton and Clayton (1981), Sax (1989), Snyder (1987), and, Calabrese and Kostecki (1988-91). The brief discussion below describes only a few of the most common and best understood toxic responses.

Human Toxicology

Many compounds found in raw and refined petroleum products are toxic when administered at sufficiently high doses. Since, however, this guideline is concerned primarily with assessment and identification of conditions consistent with low residual risk, only highly toxic compounds with well-documented toxicology are discussed.

Few saturated compounds found in petroleum are documented as potently toxic to humans. Partial oxidation (unsaturation) increases reactivity and may lead to toxic properties of even simple, straight-chain precursors. For example, 1,3-butadiene, a component of light fuels and combustion exhaust, has recently been linked to cancers of the lymphatic and reproductive systems, stomach and other organs in both laboratory animals and humans (Mehlman 1992).

Certain aromatic compounds common in petroleum products and combustion trains are toxic to humans.

Acute, increasing exposures to benzene elicit dizziness, excitement, intoxication, coma and death Sax (1989). More important from a standpoint of managing contaminated soils is benzene's high cancer potency (Mehlman 1992). Benzene is classified as a confirmed human carcinogen in both Canada (HWC 1989) and U.S. (Mehlman 1992) and is identified principally with various leukemias, but roles in other cancers of both humans and laboratory animals have been described (Mehlman 1992).

Some polycyclic aromatic hydrocarbons (PAH) also are carcinogenic (ATSDR 1990). PAH shown carcinogenic in laboratory animals include: benzo(a)pyrene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenz(a,h)anthracene, indeno[1,2,3-cd]pyrene and chrysene (ATSDR 1990). These compounds share the property of having a nonlinear arrangement of fused benzene nuclei, which creates "bay regions". Oxidation of carbon atoms near bay regions generates epoxides which, through their alkylating ability, are thought to be responsible for mutagenic carcinogenesis (Levin et al. 1982, Thakker et al. 1985).

Carcinogenic PAH differ in their cancer potencies. Many agencies use benzo(a)pyrene as a reference for maximum potency. On this basis most carcinogenic PAH are 11 to 33 times less potent than benzo(a)pyrene, with the exception of chrysene which, on the basis of limited dermal exposure studies, may be of similar potency (Slooff et al. 1989).

Irritation of skin and membranes is caused by various compounds in the polar fractions of petroleum products including cresols, quinolines and substituted sulfur compounds. Chronic exposure can lead to dermatitis and/or respiratory disease. At very high doses vomiting, coma and death from cardiac or respiratory failure may occur (Clayton and Clayton 1981, Sax 1989). Low level, chronic exposures appear to have been studied little but indications from ecotoxicology (see below) suggest that such studies are needed.

Ecotoxicology

Biological health of soils may be affected both by specific toxic petrochemicals and/or general, physico-chemical alterations to the soil environment wrought principally by high MW hydrocarbons -- for example, hydrophobicity and inhibition of water and soil gas movements. In addition to these confounding constraints, ecotoxicological literature on petrochemicals is limited by 1) the enormous range of organisms that could be potentially

be affected, and 2) the preponderance of coarse-scale field studies that involve complex petrochemical mixtures. The following section thus addresses only a few of the better documented effects.

A toxic response in soil is a function of both the inherent toxicity of the contaminant and it's bioavailability. Bioavailability expresses the frequency and intensity of exposure, which, in turn, are regulated by the mobility of both the contaminant and the organism. Therefore, it is expected that factors regulating *in situ* toxicity of chemicals to soil-dwelling organisms will vary with the relative mobility of the organism. Creatures with limited capability for movement in soil (e.g. most microorganisms, plants) tend to be most susceptible to chemicals that can move in the vapour or dissolved phases. Thus toxic chemicals with high water solubilities or vapour pressures, for example, BTEX species; tend to affect poorly mobile soil organisms because 1) exposure may not occur, and 2) if exposure does occur, local detoxification is possible. On the other hand, toxicity to mobile soil organisms (e.g. microarthropods, earthworms) is less affected by contaminant mobility and more affected by structure-activity relationships such as lipid solubility, which is a strong determinant of a chemical's bioaccumulation potential.

Atlas (1981) and Leahy and Colwell (1990) describe factors affecting microbial activity in the presence of various hydrocarbon sources. The mobility and solvent properties of low molecular weight hydrocarbons, including BTEX, is thought responsible for the general toxicity of this group to microorganisms. Thus, light fuel spills are often followed by a period of inhibited microbial activity while low MW dissipate by physicochemical means (Bossert and Bartha 1984). Few data are available for soil invertebrates. Neuhauser et al. (1985) reported toxicity of various low MW hydrocarbons to the earthworm, *Eisenia foetida*, using contact and artificial soil media. They found LC_{50} values increased (toxicity decreased) in the order phenols < substituted aromatics < PAH < phthalates.

Low MW hydrocarbons also exhibit phytotoxicity. Toxic responses to various BTEX species are reported for row crops (Ivens 1952, Hung et al. 1992) and woody species (Keymeulen et al. 1991).

The water solubility of monoaromatics and low MW compounds found in aromatic and polar 2 fractions is of concern both in raising bioavailability to soil dwelling organisms and in increasing the frequency and intensity of exposure to aquatic and marine species at

or near hydrocarbon contaminated sites. BTEX toxicity to freshwater algae was related to bioconcentration factors by Herman et al. (1991). The toxicity of naphthalene and its derivatives to marine and aquatic organisms is well-documented (Verschueren 1983). Similar concerns exist for other more mobile substituted aromatics such as phenols, cresols, catechols and heterocyclic compounds including quinolines and thiophenes.

More complex hydrocarbon sources such as gas plant sludges, creosote, and flare pit sediments may 1) include combustion products and process by-products foreign to raw petroleum, or 2) have increased concentrations of toxic constituents normally found in only trace quantities in raw petroleum products. Recent investigations of these hydrocarbon sources has highlighted toxicity associated with the polars 2 fraction. Using the toxicity identification and evaluation (T.I.E.) approach Birkholz (1992) showed that most of the toxicity present in a diethanolamine (DEA) sour gas plant sludge could be traced to polycyclic aromatic sulfur heterocycles (PASH), particularly dibenzothiophene and substituted derivatives. Fedorak and Grblic-Galic (1991) and Saftic et al. (1992) have confirmed the resistance to degradation of many of the PASH by aerobic soil microbes. In general, the sulfur heterocycles appear to be degraded only by co-metabolic activities of a select group of bacteria. The toxicity and recalcitrance of this group of compounds has led to recommendations to target dibenzothiophene in GC scans of petroleum contaminated soils and sediments (Douglas et al. 1992).

The carcinogenic properties of certain PAH described above for humans have been identified and confirmed through both epidemiological studies and rodent laboratory studies. Therefore, there is reason to expect that neoplasia and carcinogenesis may also result in higher organisms (particularly mammals) exposed to sufficient concentrations of these PAH in contaminated environmental media -- including soils.

Relations to Gross Hydrocarbon Parameters

contain Amounts of the toxic fractions or compounds discussed above present in a hydrocarbon contaminated soil will be influenced strongly by both hydrocarbon source (e.g. light vs heavy crude, gasoline, diesel, discarded lubricants, crankcase oils, gas plant sludge, flare pit residue) and environmental fate and behaviour of source components (e.g. mobility, volatility, biodegradability) as affected by time, edaphic factors (e.g. soil organic matter content, moisture and temperature regimes, pH, biological activity) and management (e.g. tillage, nutrient additions, moisture or thermal manipulations, biological enhancements). These factors interact so as to make prediction of toxics concentrations from gross parameters impossible on a generic basis. Only through sitespecific knowledge of contaminant and soil properties is it feasible to develop predictive relationships. For these reasons, soils contaminated by hydrocarbons will generally require analyses for suspected or target toxic compounds. Gross parameters alone convey no consistent toxicological information.

Implications for Analysis of Environmental Samples

Before selecting a petroleum hydrocarbons test the investigator should decide exactly what information is sought. Is the soil known to be contaminated by petroleum products? If so, is the chemical nature of the contamination known? Is the sampling exploratory or confirmatory? Answers to these questions should influence the choice of test.

It follows that when requesting analyses for hydrocarbon contaminated soils the investigator must decide, in consultation with the laboratory:

- 1) What will be the method of sample preparation (purge and trap, headspace sampling, extraction)?
- 2) Will cleanup of polars be done?
- 3) What method of detection will be used?

If a preliminary investigation (e.g. audit, shallow vapour survey) can *confirm* that low molecular weight hydrocarbons are not present, then hydrocarbon screening may be accomplished through an analysis of extractables. If the preliminary investigation shows no strong evidence for hydrocarbon contamination, a simple oil and grease test may be adequate in a screening mode. On the other hand, if evidence of hydrocarbon contamination exists, a GC-FID test will be more valuable because information is gained on the distribution of hydrocarbons by carbon number. This information can be helpful in identifying a potential hydrocarbon source, which may in turn suggest specific contaminants of concern, geographical pattern of contamination, or remedial strategy. An example of a phased, analytical procedure employing several types of chromatography and leading to tentative identification of hydrocarbon sources and contaminants of concern is given in Douglas et al. (1992).

Hydrocarbon analyses by GC presented *without an analysis of carbon number*, however, are likely not of greater value than a simple oil and grease determination.

If the general nature of hydrocarbon contamination is known, specific tests can be selected for the expected contaminants of concern. As examples, 1) leaks or spills of gasoline or aviation fuel indicate the need for BTEX analysis (EPA Method 8020), and 2) presence of combustion residues from hydrocarbon fuels indicates polynuclear aromatic hydrocarbon analysis (e.g. EPA Method 8100). Additionally, if a refined hydrocarbon source has been established, specialized analytical approaches may be applied that improve results and/or reduce costs. For example, intermediate range fuels may be quantified in a single step through elevated temperature purge and trap methodology (Chang et al. 1992).

Assessment of Petroleum Contaminated Soil in Alberta

Historical Use

Alberta MUST guidelines (Province of Alberta 1991) include TPH (TPH is here defined as the sum of purgeables and extractables without reference to cleanup of polars) as a remediation criterion. Criterion development depended on several assumptions: 1) the hydrocarbon source is diesel fuel, 2) the diesel fuel has a fixed benzene content, 3) a generic human exposure scenario includes a concrete basement pervious to benzene vapours, and 4) benzene exposure is managed to keep incremental cancer risk at or below 10⁻⁶. Under these assumptions MUST brought forward three TPH guidelines keyed to different site sensitivities -- for example, variations in soil texture on the site gives rise to different benzene diffusion rates.

The MUST soil guideline for TPH at the most sensitive sites is 40 ppm. Because the approach of the Soil Protection Branch is to provide criteria protective of flexible land use (recovery or preservation of equivalent capability) the 40 ppm value was brought forward for surface soils (Province of Alberta 1990).

Experience since the introduction of MUST has shown that, by posting a criterion for TPH with an attempted basis in toxicology, the expectation has been raised that all hydrocarbon contamination in soils can be dealt with via gross parameters. From the foregoing discussion of hydrocarbons types and measurement systems it is clear that gross parameters cannot completely meet this expectation nor regulatory needs. There is no reliable, general relationship between biological hazard and any gross hydrocarbon parameter.

Present Use

Gross hydrocarbon parameters are valuable in three primary roles:

- As gross screening parameters (investigation parameters, characterization parameters). These are used in the initial phases of site assessment to establish presence or absence of contamination, establish chemical nature, and identify affected areas. Positive results generally indicate the need for further investigation for contaminants of concern.
- 2. As investigative surrogates on a site-specific basis. It is often possible to correlate the concentration of contaminant of concern to a gross parameter in an area homogeneous with respect to contamination type. For example, in an area affected by a particular spill there may be a strong relationship between oil and grease and carcinogenic PAH. If such a relationship exists, it can be used to control costs during delineation and confirmation sampling steps.
- 3. In the case of hydrocarbon contamination low or lacking in toxic constituents, a gross parameter may be used as a remediation objective protective of aesthetic values (organoleptic considerations such as 1) nuisance odours encountered directly from soil off-gassing or from cross-contaminated water, 2) oily sheen in cross-contaminated water) and general soil quality issues such as water repellancy and structure.

For applications 1 and 3 above, a value of 1,000 mg kg⁻¹ oil and grease has been found useful. For example, in an initial assessment of a site, areas exceeding 1,000 mg kg⁻¹ oil and grease can immediately be identified as requiring further investigation and management. Furthermore, if 1) the hydrocarbon contamination is found to be sufficiently low in toxic contaminants, and 2) groundwater, general soil quality and aesthetic values are not at risk; then 1,000 mg kg⁻¹ oil and grease may function as a remediation criterion. However, in the absence of this toxicological, hydrological and organoleptic information, gross hydrocarbon parameters presently have no regulatory value as remediation criteria.

Expression of the above guide value as "oil and grease" does not constitute an endorsement of this parameter over other gross parameters. Indeed, oil and grease is the least sophisticated of the gross parameters. However, as a delineation tool, or as a

remediation criterion under the restrictive conditions given above, it is adequate and the least expensive of measurements. Hydrocarbon contamination investigations normally require a combination of gross parameter measurements for characterization and, subsequently, specific analyses for expected contaminants of concern.

Literature Cited

- Atlas, R.M. 1981. Microbial degradation of petroleum hydrocarbons: an environmental perspective. Microbiol. Reviews 45:180-209.
- ATSDR. 1990. Toxicological profile for polycyclic aromatic hydrocarbons. U.S. Department of Health and Human Services, Public Health Service. TP-90-20.
- B.C. Ministry of Environment. 1991. Draft, interim guidance for measuring hydrocarbon concentrations in soil and water.
- Birkholz, D.A. 1992. Isolation and identification of toxic substances present in gas plant wastewater pond sludge. *Prepared for* the Canadian Petroleum Association.
- Bossert, I., and R. Bartha. 1984. The fate of petroleum in soil ecosystems. <u>In</u>: R.M. Atlas (ed.), Petroleum Microbiology, MacMillan Publ., NY.
- Chang, D.Y., I. Lopez and S.G. Yocklovich. 1992. Determination of kerosene and #2 diesel in soil by purge and trap vs. extraction procedure. J. Soil Contam. 1:239-251.
- Clayton, G.D. and F.E. Clayton. 1981. Patty's Industrial Hygiene and Toxicology (3rd Ed. Vol. 2B), John Wiley and Sons.
- Douglas, G.S., K.J. McCarthy, D.T. Dahlen, J.A. Seavey, W.G. Steinhauer, R.C. Prince and D.L. Elmendorf 1992. The use of hydrocarbon analyses for environmental assessment and remediation. J. Soil Contam. 1:197-216.
- Fedorak, P.M. and D. Grbic-Galic. 1991. Aerobic microbial co-metabolism of benzothiophene and 3-methylbenzothiophene. Appl. Environ. Microbiol. 57:932-940.
- Fuhr, B.J., L.R. Holloway and C. Reichert. 1988. Component-type analysis of shale oil by liquid and thin-layer chromatography. J. Chromatogr. Sci. 26:55-59.
- Health and Welfare Canada. 1989. Exposure guidelines for residential indoor air quality. A report of the Federal-Provincial Advisory Committee on Environmental and Occupational Health. Rep. No. EHD-TR-156. Environmental Health Directorate, Ottawa.
- Herman, D.C., C.I. Mayfield and W.E. Inniss. 1991. The relationship between toxicity and bioconcentration of volatile aromatic hydrocarbons by the alga *Selanastrum capricornutum*. Chemosphere 22:665-676.
- Hung, P.E., V.A. Fritz and L. Walters. 1992. Infusion of *shrunken-2* sweet corn seed with organic solvents: Effects on germination and vigor. HortScience 27:467-470.

- Ivens, G.W. 1952. The phytotoxicity of mineral oils and hydrocarbons. Proc. Assoc. Appl. Biol.. pp 418-422.
- Keymeulen, R., H. Wan Landgehove and N. Schamp. 1991. Determination of monocyclic aromatic hydrocarbons in plant cuticles by gas chromatography-mass spectrometry. J. Chromatog. 541:83-88.
- Kostecki, P.T., and E.J. Calbrese (eds.) 1989-91. Petroleum contaminated soils, Vols. 1-3, Lewis Publ., Chelsea, MI.
- Leahy, J.G. and R.R. Colwell. 1990. Microbial degradation of hydrocarbons in the environment. Microbiol. Rev. 54:305-315.
- Levin, W., A. Wood, R.L. Chang et al. 1982. Oxidative metabolism of polycyclic aromatic hydrocarbons to ultimate carcinogens. Drug Metab. Rev. 13:555-580.
- Mehlman, M.A. 1992. Dangerous and cancer-causing properties of products and chemicals in the oil refining and petrochemical industry. VIII. Health effects of motor fuels: Carcinogenicity of gasoline - scientific update. Environ. Res. 59:238-249.
- Pollard, S.J., S.E. Hrudey, B.J. Fuhr, R.F. Alex, L.R. Holloway, and F. Tosto. 1992. Hydrocarbon wastes at petroleum- and creosote-contaminated sites: Rapid characterization of component classes by thin-layer chomatography with flame ionization detection. Environ. Sci. Technol. 26:2528-2534.
- Province of Alberta. 1990. Draft Alberta Tier I Criteria for Contaminated Soil Assessment and Remediation.
- Province of Alberta. 1991. Draft subsurface remediation guidelines for underground storage tanks. Alberta MUST Project, Departments of Environment and Labour.
- Saftic, S., P.M. Fedorak and J.T. Andersson. 1992. Diones, sulfoxides and sulfones form the aerobic co-metabolism of methylbenzothiophenes by *Pseudomonas* Strain BT1. Environ. Sci. Technol. 26:1759-1764.
- Sax, N.I. 1989. Dangerous Properties of Industrial Materials 7th Ed., Van Nostrand Rheinhold, NY.
- Schobert, H.H. 1990. The Chemistry of Hydrocarbon Fuels. Butterworth and Co. Ltd., Cornwall, England.
- Slooff, W., J.A. Janus, A.J.C.M. Matthijsen, G.K. Montizan and J.P.M. Ros. 1989. Integrated Criteria Document -- PAHs. National Institute of Public Health and Environmental Protection, Bilthoven, The Netherlands. Rep. No. 758474011.
- Snyder, R. 1987. Ethel Browning's Toxicity and Metabolism of Industrial Solvents (2nd Ed.), Vol. 1 Hydrocarbons. Elsevier Publ. Co., Amsterdam.

- Standard Methods for the Examination of Water and Wastewater, 1992, 18th Ed., Amer. Publ. Health Assoc.
- Thakker, D.R., H. Yagi, W. Levin, A.H. Wood, A.H. Conney, and D.M. Jerina. 1985. Polycyclic aromatic hydrocarbons: Metabolic activation of ultimate carcinogens. <u>In</u>: Anders, M.W. (ed.) Bioactivation of Foreign Compounds. Academic Press, NY.
- U.S. EPA. Method 3540A. Soxhlet extraction. <u>In</u>: U.S. EPA SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods.
- U.S. EPA. Method 3630A. Silica gel cleanup. <u>In</u>: U.S. EPA SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods.
- U.S. EPA. Method 3810. Headspace. <u>In</u>: U.S. EPA SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods.
- U.S. EPA. Method 5030. Purge and trap. <u>In</u>: U.S. EPA SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods.
- U.S. EPA. Method 8015. Nonhalogenated volatile organics. <u>In</u>: U.S. EPA SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods.
- U.S. EPA. Method 8020. Aromatic volatile organics by gas chromatography. <u>In</u>: U.S. EPA SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods.
- U.S. EPA. Method 8100. Polynuclear aromatic hydrocarbons. <u>In</u>: U.S. EPA SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods.
- U.S. EPA. Method 8240A. Volatile organics by gas chromatography/mass spectrometry (GC/MS): packed column technique. <u>In</u>: U.S. EPA SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods.
- U.S. EPA. Method 8250. Gas chromatography/mass spectrometry for semivolatile organics: packed column technique. <u>In</u>: U.S. EPA SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods.
- U.S. EPA. Method 8260. Volatile organic compounds by gas chromatography/mass spectrometry (GC/MS): capillary column technique. <u>In</u>: U.S. EPA SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods.
- U.S. EPA. Method 8270. Semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS): capillary column technique. <u>In</u>: U.S. EPA SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods.

- U.S. EPA. Method 9073. Total recoverable hydrocarbons by infrared spectroscopy. <u>In</u>:
 U.S. EPA SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods.
- Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. Van Nostrand Rheinhold Co., NY.

oil and grease Dic	
gra bio	Dichloromethane- (DCM) or freon*-extractable hydrocarbons detected by gravimetric or infrared (IR) methods (EPA†, Standard Methods¥). May include polar biomass components.
mineral oil and grease DC afte	DCM- or freon-extractable hydrocarbons determined by gravimetric or IR methods after silica gel cleanup (EPA Method 3630A) to remove polars.
total extractable DC hydrocarbons (TEH) FID poli	DCM- or freon-extractablehydrocarbons determined by GC (usually GC- FID)(EPA?). In Alberta MUST program and some U.S. states implies cleanup of polars prior to gas chromatography.
total purgeables (TP) Vol pre Me	Volatile hydrocarbons determined by GC (usually GC-FID) (EPA Method 8015) preceeded by purge and trap (EPA Method 5030) or "headspace analysis" (EPA Method 3810). Usually limited to compounds < C10.
total petroleum (1) (EF hydrocarbons (TPH) (EF lab	(1) DCM- or freon-extractable hydrocarbons detected by GC after silica gel cleanup (EPA SW-846, State of New Jersey 1992), (2) mineral oil and grease by IR (various laboratories), (3) sum of total extractables as in (1) and total purgeables (Alberta MUST, several U.S. states).§
total hydrocarbons (TH) Sui gei	Sum of purgeable and extractable hydrocarbons cleanup not specified but generally assumed absent (various laboratories)
light (aliphatic) Vol hydrocarbons (LH or det LAH)	Volatile hydrocarbons determined by GC preceeded by purge and trap but detection extended to include up to ~ C18-C20 (B.C. MOE)
 U.S. EPA methods and revisions have specified freon-113 (1,1,2-trichlorr laboratory use of such chlorofluorocarbons should be reduced and, eventu hexanc/acctone, hexanc/methyl-t-butyl ether) are under investigation by U † The relevant general reference is U.S. EPA SW-846, Test Methods for Ev promulgated in 1986, there are many updates, revisions and new methods. ¥ Standard Methods for the Examination of Water and Wastewater, 1992, 1 § Because TP and TEH procedures both respond to intermediate chain length and TEH to vield an estimate of TPH. 	 U.S. EPA methods and revisions have specified freon-113 (1,1,2-trichloro-1,2,2-trifluorocthanc). Under the terms of the Montreal Protocol laboratory use of such chlorofluorocarbons should be reduced and, eventually, phased out. Alternate solvent systems (n-pentane, n-hexane, hexane/acctone, hexane/methyl-t-butyl ether) are under investigation by U.S. EPA and other regulatory agencies. The relevant general reference is U.S. EPA SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. Originally promulgated in 1986, there are many updates, revisions and new methods. Standard Methods for the Examination of Wastex and new methods. Because TP and TEH procedures both respond to intermediate chain length hydrocarbons, this overlap must be taken into account before summing TP and TEH to vield an estimate of TPH.

