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Age Dating of Middle-Distillate Fuels Released to the Subsurface Environment

Gil Oudijk
Triassic Technology, Inc.
USA

1. Introduction

The term "age dating" is defined as: estimating the time frame of a contaminant release to the environment. Because of the high costs of environmental cleanups, age-dating studies have now become an integral part of environmental investigations. Knowledge of the local geology, hydrology and geochemistry are required to perform these studies and, therefore, geologists are commonly involved.

The "middle distillates" include products such as diesel fuel, heating oils, kerosene and jet fuels. Middle-distillate fuels are used throughout the world to power motors, heat residences, fuel jet engines and propel ships, among many other uses. Middle-distillate fuels are commonly stored in aboveground or underground tanks and these tanks are often unprotected and exposed to the elements. Because of corrosion, leaks from storage tanks are a severe environmental problem, especially in locations where groundwater is used for potable supplies. Numerous underground storage tanks (USTs) were installed in North America during the "boom" years following World War II and impacts from leakage are now being found in the subsurface.

An understanding of the problems associated with leaking petroleum USTs has been known since the 1950s (Kehoe, 1960). However, action was not undertaken until the late 1970s and in some places, even much later. For example, the US state of New Jersey did not pass UST regulations until 1986 (State of New Jersey, 1986).

The average non-leaking lifespan of unprotected steel USTs may be as little as 15 years (Robinson et al., 1988). The Canadian province of Nova Scotia requires that USTs older than 25 years be removed (Hankey-Masui, 1998). Thus, numerous leaking USTs existed over the years and many probably continue today. Because of costs, the number of people impacted and the large number of cases, releases of middle-distillate fuels from USTs are a serious problem in North America (Oudijk et al., 1999). In the US states of New Jersey and Maine, several leaks are reported daily to regulatory agencies (Pearson & Oudijk, 1993; McCaskill, 1999). Similar problems exist in Europe (Bennet, 1997).

Remediation costs can be high and cases exist where buildings were removed, razed or structurally supported to complete a cleanup. It is not uncommon for costs to exceed US$500,000 and many cases costing over US$1 million exist. Costs are often borne by insurance policies, although carriers may subrogate and obtain contribution from previous carriers or others responsible. For this reason, carriers and law firms commonly request information on the time frames of releases. Because of costs, many cases are litigated and,

consequently, a legally defensible method to age date releases is needed. Kanner (2007) provided the legal criteria needed to defend such methods.

Many methods exist to assess contaminant-release ages, such as UST corrosion models (Morrison, 2000), groundwater flow calculations (Morrison, 2000; Lee et al., 2007), isotope surveys (Oudijk, 2005), tree-ring investigations (Balouet et al., 2007), petroleum-weathering studies (Christensen & Larsen, 1993; Wade, 2001; Douglas et al., 2004; Hurst & Schmidt, 2005; Galperin & Kaplan, 2008; Oudijk, 2009a,b). The most common technique now in use, and normally the least expensive, is the Christensen & Larsen (C&L) method, a procedure employing petroleum-weathering rates. Hurst & Schmidt (2005), with additional data, expanded on the C&L method to date diesel-fuel releases, reporting a best-case precision of ±1.5 years.

2. Fuel composition

2.1 Diesel fuels and heating oils

In North America, diesel fuel and no. 2 heating oil have a similar composition. Diesel fuel may contain some additives during the winter and heating oil often contains a dye for tax purposes. These fuels normally have a density of 0.87 to 0.95 grams per cubic centimeter (g cm^{-3}) at 20°C and are lighter but more viscous than water (Schmidt, 1985; Wang et al., 2003) (Table 1). Heating oils and diesel fuels are composed of hydrocarbons, which are chains or rings of hydrogen and carbon. Hydrocarbons are classified by the number of carbon atoms present. For example, benzene is a C_6 molecule because it contains 6 carbon atoms.

Diesel fuels and no. 2 heating oils are composed predominantly of hydrocarbons in the range of about C_6 to C_{24} (but most of the hydrocarbons are heavier than C_8); sometimes hydrocarbons can be found up to C_{28}. The boiling range is from 150°C to 380°C (Song, 2000; Owen & Coley, 1995)(Figure 1). They contain aromatics (benzene, toluene, *o,m,p*-xylenes, naphthalenes, phenanthrenes), *n*-alkanes (such as *n*-heptadecane), *iso*-alkanes (such as the isoprenoids: pristane, phytane or norpristane), *cyclo*-alkanes and poly-aromatics plus sulfur-containing compounds such as dibenzothiophenes (Kramer & Hayes, 1987; Potter & Simmons, 1998; Bruya, 2001). The dominant hydrocarbons are the *n*–alkanes (straight-chain alkanes) and isoprenoids (methyl-substituted "*iso*-alkanes"). The aromatics include: mono-aromatics (such as benzene and toluene), alkyl-benzenes, naphthalenes, tetralins, biphenyls, acenaphthenes, phenanthrenes, chrysenes and pyrenes (Song, 2000). The predominant poly-aromatic hydrocarbons (PAHs) in no. 2 heating oil and diesel fuel are the napthalenes and phenanthrenes, whereas pyrogenic PAHs, such as chrysene and pyrene, may exist at reduced concentrations.

There can be variations in the composition of diesel fuels. For example, diesel fuels in colder climates tend to contain lighter hydrocarbons to prevent freezing problems (Figure 2).

2.2 Kerosene and jet fuels

Kerosenes are complex mixtures of hydrocarbons generally within a range of C_6 to C_{16} and a boiling range of about 145°C to 300°C (Table 1, Figures 3 & 4). Jet fuels are quite similar in composition to kerosene. The major components of kerosenes are *n*-alkanes, *iso*-alkanes and *cyclo*-alkanes. Aromatic hydrocarbons, predominantly alkyl-benzenes and alkyl-naphthalenes, normally comprise less than 25% of the volume (CONCAWE, 1995).

	Kerosene	Jet fuel (Jet-A)	Jet fuel (Jet-B)	Jet fuel (JP-5)	Jet fuel (JP-8)
Color	colorless, multiple dyes	colorless multiple dyes	colorless, multiple dyes	Clear and bright	Clear and bright
Carbon range	C_9 to C_{16}	C_9 to C_{16}	C_9 to C_{16}	C_9 to C_{16}	C_9 to C_{16}
Density	0.81@15°C	0.775 to 0.840 @15°C	0.751 to 0.802 @15°C	0.788 to 0.845 @15°C	0.775 to 0.840 @15°C
Boiling range (^{o}C)	145 to 300	205 to 300	145 to 245	150 to 290	150 to 290
Flash point (^{o}C)	62[b]	38	0	60	38
Kinematic viscosity[a] (mm^2 s^{-1})	1.5 to 2.5 @20°C	8 @-20°C	-	1.28 to 1.60 @40°C	1.05 to 1.58 @40°C
CAS No.	8008-20-6	8008-20-6	8008-20-6	70892-10-3/ 8008-20-6	70892-10-3/ 8008-20-6

	No.2 heating oil/Motor diesel fuel	No. 4 heating oil	No.6 heating oil/Bunker oil
Color	colorless to brown, often dyed red	colorless to brown, can be dyed red	colorless to brown
Carbon range	C_6 to C_{24}	C_{15} to C_{40}	C_{20} to C_{50}
Density	0.87 to 0.95 @ 20°C	0.876 to 0.979 @20°C	0.95 to 1.01 @15°C
Boiling range (^{o}C)	160 to 360	177 to 371	350 to 650
Flash point (^{o}C)	58	>60	>60
Kinematic viscosity (mm^2 s^{-1})	20 to 30 @ 20°C	4 to 50 @20°C	6 to 55 @ 20°C
CAS No.	68476-30-2	68476-31-3	68553-00-4

a One millimetre squared per second (mm^2 s^{-1}) equals one centistoke.
b Flash point is for US kerosene. Flash points for European kerosene are normally 40° to 45°C.

Table 1. General characteristics of middle distillate fuels. Sources: Bowden et al., 1988; CONCAWE, 1995;
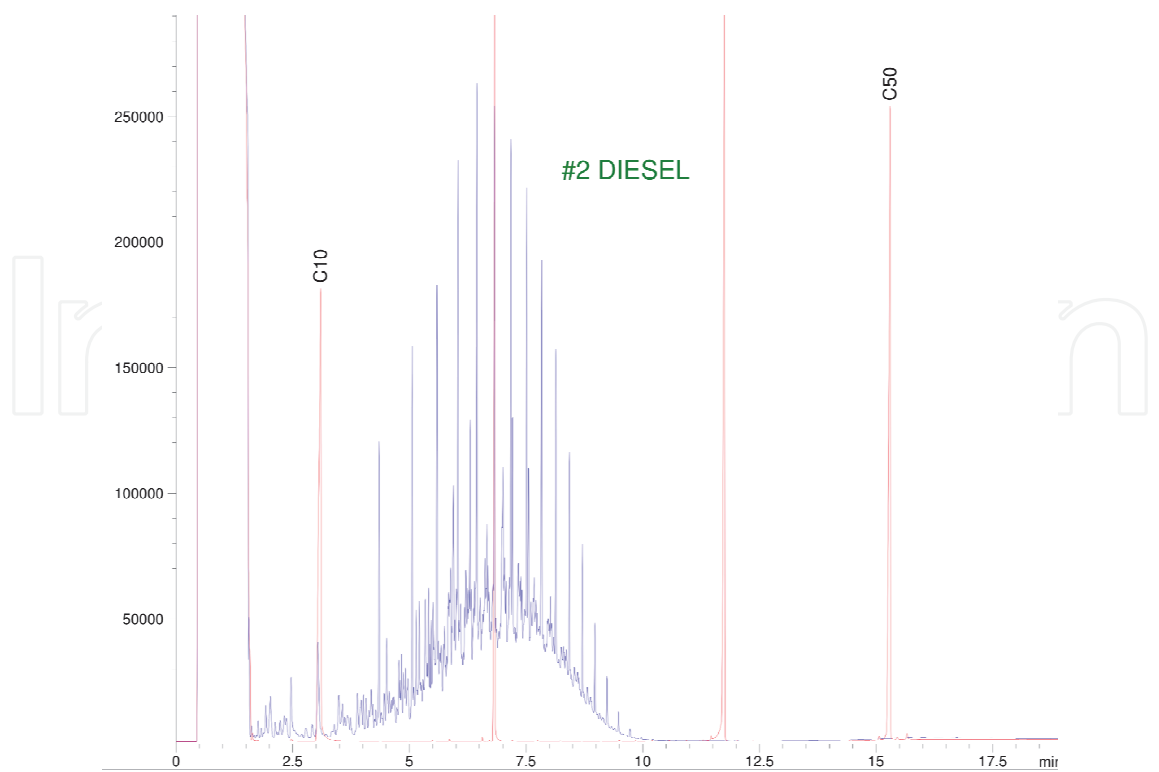
Fig. 1. A GC/FID chromatogram of a motor diesel fuel (2010). Source: Maxxam Analytics (Mississauga, Ontario, Canada).
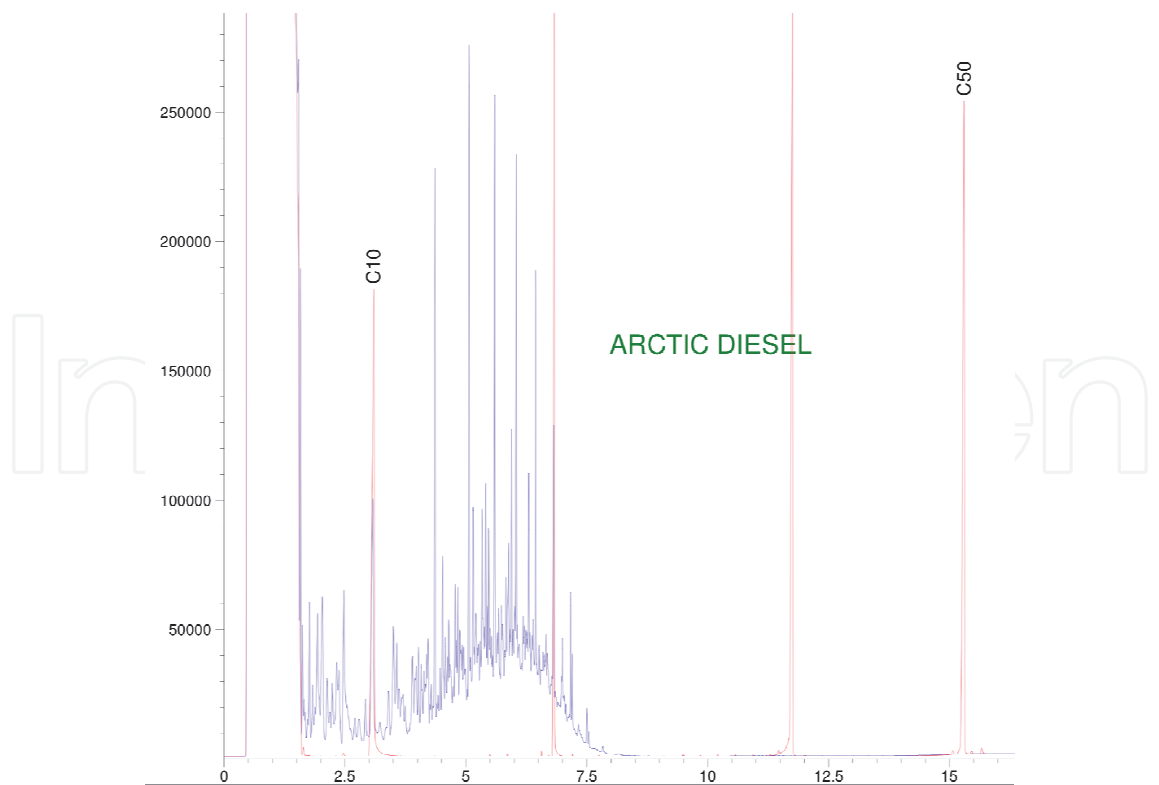

Fig. 2. A GC/FID chromatogram of an Arctic diesel fuel (2010). Source: Maxxam Analytics (Mississauga, Ontario, Canada).
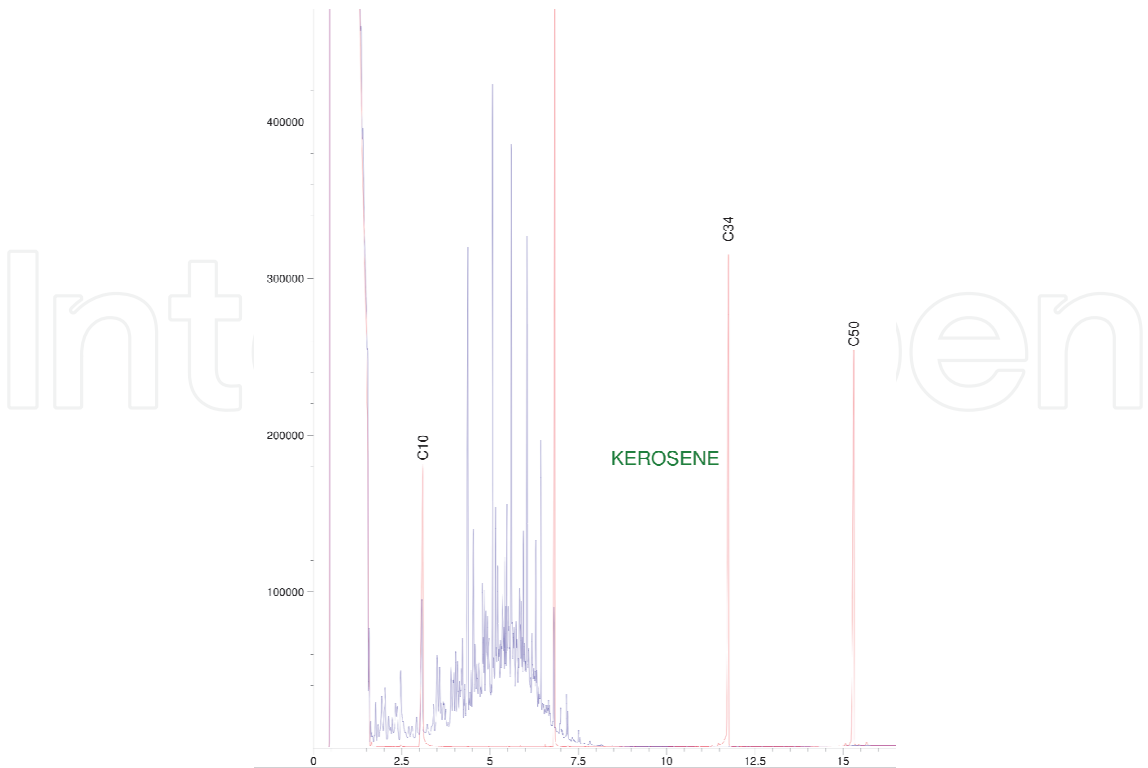
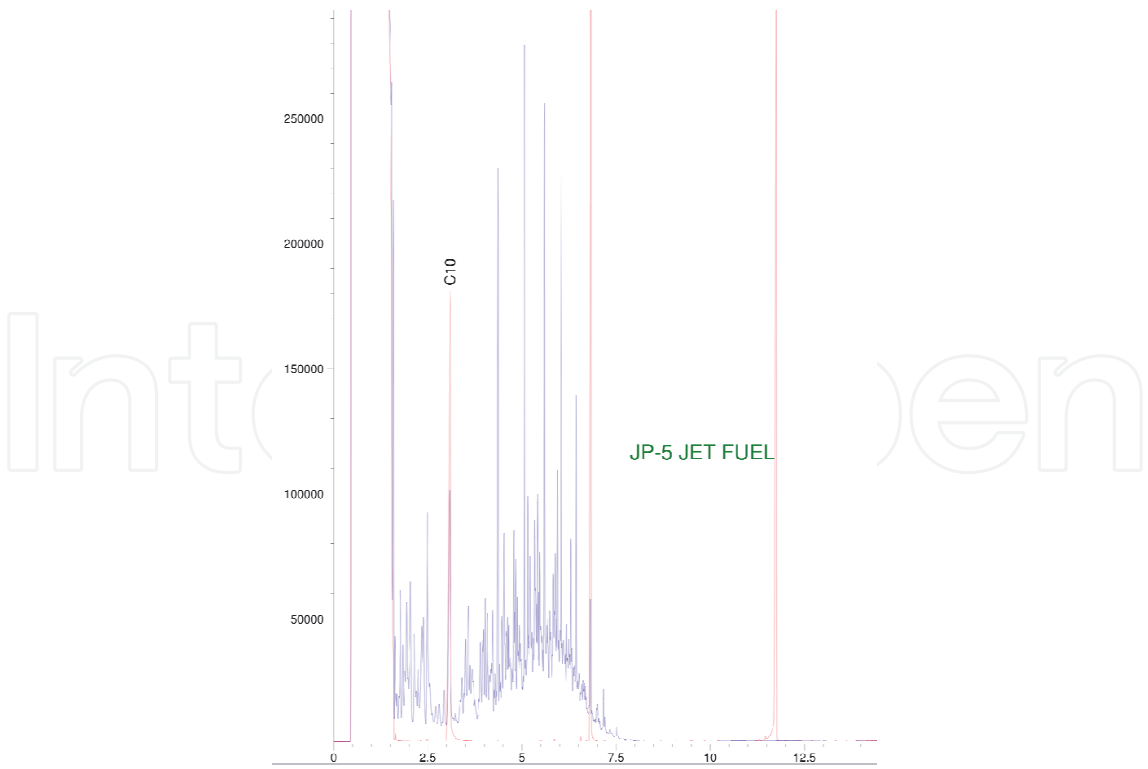Fig. 3. A GC/FID chromatogram of a kerosene (2010). Source: Maxxam Analytics (Mississauga, Ontario, Canada).

Fig. 4. A GC/FID chromatogram of a JP-5 jet fuel (2010). Source: Maxxam Analytics (Mississauga, Ontario, Canada).

2.3 No. 6 oils and bunker oils

No. 6 oil is a heating fuel, whereas bunker oil fuels ship engines. Both fuels are complex mixtures of hydrocarbons normally within a range of C_{15} to more than C_{30} (CONCAWE, 1998; Stout et al., 2002)(Table 1 & Figure 5). However, these fuels often differ greatly in composition. Furthermore, to prevent freezing problems during the winter, no. 6 oil is often mixed with lighter fuels such as kerosene or no. 2 heating oil.
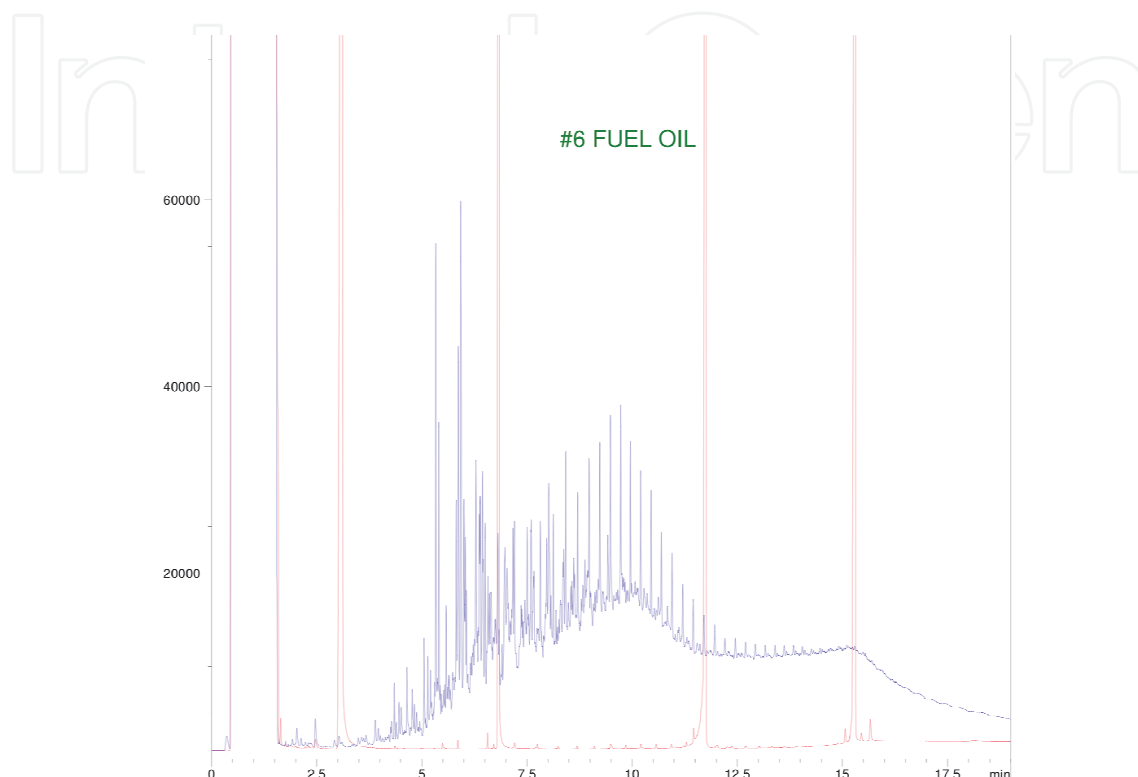

Fig. 5. A GC/FID chromatogram of a no. 6 heating oil (or "no. 6 fuel oil")(2010). Source: Maxxam Analytics (Mississauga, Ontario, Canada).

3. Middle distillate fuels in the subsurface

UST releases are normally slow and often prolonged. Corrosion of steel may be caused by many factors, such as contact with groundwater, ion exchange with clay minerals or stray electrical currents. Holes will begin as pin-sized openings and, with time, expand. Accordingly, petroleum in soil or groundwater is a mixture of ages and the ages will be skewed younger because leakage rates increase with time. The most downgradient portions of a middle-distillate plume are commonly the oldest and most age discrete. Moving closer to the source, for example towards an UST, the oil becomes progressively less age discrete (or less of a mix of ages)(Oudijk et al., 2006). To assess the maximum release age, sampling is needed within these downgradient areas.

4. Assessing a middle-distillate release

Over time, the chemistry of middle distillates placed into an UST may change because the crude-oil source for different refiners can be dissimilar. If the owner changed distributors or the distributor obtained its supply from different refineries, the initial composition of the

product will not be identical over the leakage time frame. Accordingly, to properly conduct an age-dating study, it is important to assess if the plume all originates from the same source and if the initial petroleum chemistry differed.

A test to assess different compositions is through isoprenoids ratios. These compounds are relatively resistant to degradation and their ratios may be used to determine if the initial chemistry varied across the plume (Wade, 2005). There are numerous other methods to fingerprint spilled hydrocarbons (Bruce & Schmidt, 1994; Douglas et al., 1996; Galperin & Camp, 2002; Wang & Fingas, 1995a; Wang et al., 2005; Galperin & Kaplan, 2008a). These methods include a comparison of compounds such as PAHs, dibenzothiophenes or bicyclic sesquiterpanes. However, use of pristane/phytane (pr/ph) ratios seems to be the easiest and least expensive.

The pr/ph ratio is dependent on the crude-oil source and may reflect the depositional environment during oil formation (Illich, 1983; ten Haven et al., 1987; Paul et al., 1994; Sun et al., 2004; Peters et al., 2005; Osuji et al., 2009). The refining process, whereby middle distillate are produced from crude oil, normally does not alter pr/ph ratios (Stout & Wang, 2007).

Between 2004 and 2007, pr/ph ratios were calculated from 141 petroleum-saturated soil samples collected from 48 sites in the US state of New Jersey (Oudijk, 2009a). The ratios were then compared to the apparent weathering for each sample, grouped into fresh, moderate, degraded and very-degraded classes (Table 2). Apparent weathering was based on review of chromatograms and dependent on depletion of specific hydrocarbon classes, such as *n*-alkanes, aromatics or *iso*-alkanes (Kaplan et al., 1996; Senn & Johnson, 1987). The data revealed that weathering did not alter pr/ph ratios until significant degradation occurred. Hence, pr/ph values in middle distillates are dependent on their crude-oil source and consequently, they can be a simple and effective fingerprint to assess the origin of relatively unweathered, middle distillates. Other helpful isoprenoid ratios include pristane/norpristane and pristane/farnesane. However, norpristane and farnesane are less resistant to weathering and ratios can be altered in the environment.

Magnitude of petroleum weathering in sample	Number of samples	pr/ph average	Standard deviation
Fresh	41	1.61	0.19
Moderate	39	1.73	0.21
Degraded	49	1.59	0.23
Very degraded	12	1.18	0.40

Table 2. Mean and standard deviation for pristane/phytane values from soil samples (contaminated with no. 2 heating oil or motor diesel fuel) collected in the US states of New Jersey, Pennsylvania and New York, 2002-2007. Source: Oudijk (2009a).

5. Factors influencing petroleum weathering

Petroleum degradation in soil is predominantly controlled by (Stout et al., 2002b):
- evaporation, occurring when petroleum is in contact with air, causing constituents to volatilize;

- dissolution, occurring when petroleum is in contact with water, causing constituents to dissolve, and
- biodegradation, the digestion of petroleum constituents by microbes.

Researchers found that normally, but not always, the predominant weathering process in the subsurface is biodegradation (de Jonge et al., 1997; Kaplan, 2003). With a subsurface leak, evaporation is often not a factor and the remaining processes dominate. Because hydrocarbons in middle distillates are relatively insoluble in water, especially the heavier ones, biodegradation often predominates over dissolution (Christensen & Larsen, 1993).

Many microbes can use hydrocarbons as a sole energy source in their metabolism (Zobell, 1946). Energy is obtained through transfer of electrons between donors such as organic carbon, although some reduced forms of nitrogen, iron and sulfur also play a role. Dissolved oxygen (O_2) produces the most energy per mole of organic carbon oxidized than any other commonly-available electron acceptor and it is preferred by subsurface microbes (McMahon & Chapelle, 2008).

Atlas & Bartha (1992) concluded that, in one environment, spilled petroleum could persist almost indefinitely, whereas under other conditions, the same hydrocarbons might be completely removed within a few hours or days. Therefore, each environmental setting is specific and significant differences could exist in the rates and types of biodegradation. In general, biodegradation depends on:

- presence of microbes with the metabolic capacity to degrade the petroleum;
- recalcitrance of compounds (in the middle-distillate mixture);
- growth and activity factors, such as temperature, nutrients, electron acceptors and pH, influencing the microbial-population dynamics; and
- bioavailability (de Jonge et al., 1997). Bioavailability is the amount of contaminant present in the soil or groundwater that is available for uptake by microbes (Harmsen et al., 2005).

Microbes with the potential to degrade hydrocarbons in soil and ground water include bacteria, fungi, and yeasts, although bacteria are normally the most plentiful, followed by fungi (Markovetz et al., 1968; Leahy & Colwell, 1990). The byproducts of microbial degradation of, for example *n*-alkanes, are normally alcohols, aldehydes, and then fatty acids and possibly ketones of similar chain length plus water, CO_2 or CH_4 (Klug & Markovetz, 1967; Atlas & Bartha, 1992). Dashti et al. (2008) found that bacteria prefer *n*-alkanes, whereas fungi prefer the oxidized byproducts; however, the same consortium of microbes could degrade both the original alkanes and the degradation byproducts.

For biodegradation to occur, electron acceptors, such as O_2 and NO_3^-, and nutrients, such as NH_4^+ and PO_4^{3-}, are needed. Aromatics can be mineralized in the absence of O_2 under denitrifying, iron-reducing, methanogenic and/or sulfate-reducing conditions, whereas *n*-alkanes can mineralize under sulfate-reducing or denitrifying conditions (Bregnard et al., 1996; Ehrenreich et al., 2000). However, biodegradation rates under anaerobic conditions may be slow. Under aerobic conditions, the *n*-alkanes and mono-aromatics are the first hydrocarbons to be depleted. They are usually followed by alkyl-benzenes, alkyl-naphthalenes, alkyl-*cyclo*-hexanes and then the isoprenoids, thiophenes and PAHs (Cerniglia, 1984; Singer & Finnerty, 1984; Hostettler & Kvenvolden, 2002). The lighter hydrocarbons in each series are commonly removed earliest. For example, the naphthalenes often degrade in series of methylnaphthalene to dimethylnaphthalene to trimethylnaphthalene (Garrett et al., 2003). According to Kaplan et al. (1996), the most

resistant isoprenoid is pristane, although our field data do not confirm this conclusion (Oudijk, 2009a)(Table 2).

In uncontaminated soils, hydrocarbon-degrading bacteria often constitute less than 1% of the microbial community. In polluted soils, hydrocarbon-degrading bacteria are often 10% of the community and, in some cases, may comprise 100% (Atlas, 1981; Atlas & Bartha, 1992). Furthermore, previously polluted environments, although remediated, tend to contain elevated percentages of hydrocarbon-degrading microbes (Leahy & Colwell, 1990). Therefore, microbial weathering may be accelerated in urban soils in comparison to pristine soils.

Environmental factors that may influence petroleum biodegradation, but are not always investigated or quantified in environmental investigations, include (Atlas, 1981; Leahy & Colwell, 1990):

5.1 Hydrocarbon physical state

The physical state of the spilled hydrocarbons, such as separate, dissolved, vapor or adsorbed phases, impacts biodegradation rates. Dissolved or vapor phases are often more susceptible to weathering processes.

The addition of large quantities of separate phase can suppress or completely stop bacterial growth. However, some researchers found that addition of large quantities to previously polluted environments increases bacterial growth (Colwell, 1978). At a previously pristine site, Hostettler & Kvenvolden (2002) found unweathered separate-phase crude oil almost 20 years after a spill. De Jonge et al. (1997) found that *n*-alkane biodegradation decreased significantly when petroleum concentrations exceeded 4,000 milligrams per kilogram (mg/kg). Lapinskiene et al. (2005) found that diesel concentrations in excess of 30,000 mg/kg were generally toxic to microbes in an aerated soil. Swindell & Reid (2006) found that, at total diesel concentrations of 20 mg/kg, 200 mg/kg and 2,000 mg/kg, phenanthrene was biologically removed from soil. However, at 20,000 mg/kg, phenanthrene removal was retarded.

The degree of separate-phase spreading will also influence biodegradation. A thick pool of separate phase will biodegrade slower compared to a pool that spread across the water table (Atlas & Bartha, 1992). The thinner pool will have more surface area in contact with ground water or the unsaturated zone, allowing increased dissolution and volatilization and hence more biological activity.

Concentrations of hydrocarbons in dissolved or vapor phases can have a strong influence on the petroleum-degrading microbes. Highly elevated dissolved petroleum concentrations may also limit biological alteration (Atlas, 1981).

5.2 Soil and groundwater chemistry

Factors such as pH or salinity can reduce biological activity. For example, elevated salt concentrations can prevent microbes from consuming petroleum. However, in some instances, salt-tolerant microbes exist and can accelerate biodegradation (Atlas, 1981; Diaz et al., 2002). The optimum pH for microbial activity is normally about 8 and soil water or groundwater commonly exhibits lower pH values (Atlas & Bartha, 1992). In some instances, soil with pH values greater than 6 can exhibit accelerated biodegradation. However, biodegradation often produces acids, allowing the pH to lower, often to as low as 3 or 4. A pH value in this range can often inhibit microbial degradation (Zaidi & Imam, 1999). The

presence of certain elements in the soil or groundwater, in particular heavy metals, is toxic to certain microbes and can reduce or prevent biodegradation.

5.2.1 Redox conditions

Under aerobic conditions, *n*-alkanes commonly degrade readily, whereas isoprenoids are generally recalcitrant. Bouchard et al. (2008) found that, based on isotopic studies, biological degradation of *n*-alkanes in aerobic, unsaturated sand was dependent on chain length with smaller molecules degrading quicker.   Isoprenoids, such as pristane, can weather under anaerobic conditions (Bregnard et al., 1997), whereas light *n*-alkanes may become recalcitrant compared to heavier *n*-alkanes (Hostettler & Kvenvolden, 2002; Siddique et al., 2006; Hostettler et al., 2008). In particular, Bregnard et al. (1997) found that pristane can weather under nitrate-reducing conditions. Hostettler & Kvenvolden (2002) found that under anaerobic conditions the degradation order is the same compared to aerobic conditions: *n*-alkanes are removed first followed by alkyl-*cyclo*-hexanes and *iso*-alkanes. However, anaerobic conditions can cause the order to reverse within each homologous series. Heavier *n*-alkanes may be removed first and the same is true for alkyl-*cyclo*-hexanes. Other researchers finding similar reversals include Setti et al. (1995)(and references therein). However, Davidova et al. (2005) did not find a reversal in the degradation order, at least under sulfate-reducing conditions, and Stout & Uhler (2006) and Galperin & Kaplan (2008b) contend that reversals are caused by other means. Also, *n*-alkane degradation up to C_{28} was observed under sulfate-reducing conditions (Caldwell et al., 1998). Therefore, use of *n*-alkane/isoprenoid ratios, as a measure of weathering under anoxic or sub-anoxic conditions, may be problematic.

Under nitrate-reducing or methanogenic conditions, nitrogen gas (N_2) or methane (CH_4) can form through degradation of aromatics. If the gas accumulates, it can limit groundwater flow and retard biological processes (Reinhard et al., 2000).

Fungi degrade long-chain *n*-alkanes (*n*-nonane to *n*-octadecane) in preference to shorter-chain varieties (Merdinger & Merdinger, 1970; Teh & Lee, 1973). Because fungi are dependent on oxygen for growth, depletion of long-chain *n*-alkanes may be indicative of fungi, instead of low redox. However, Jovancicevic̈ et al. (2003) found that an accumulation of heavier, even-numbered *n*-alkanes, such as *n*-C_{16} and *n*-C_{18}, may occur during biodegradation because of the presence of algae.

5.2.2 Temperature

Near-ground-surface temperatures fluctuate greatly, whereas underground temperatures remain somewhat constant. Biological alteration of spilled petroleum generally increases with temperature. Furthermore, volatilization of lighter *n*-alkanes at colder temperatures may decrease.

Atlas (1981) found that degradation was an order of magnitude greater at 25°C compared with 5°C, whereas Sexstone et al. (1978) found diesel contamination in Arctic soils 28 years after a spill. Ludzack & Kinhead (1956) found that motor oil rapidly oxidized at 20°C, but not at 5°C. Margesin & Schinner (2001) found that diesel degradation at a cold, high-altitude location occurred mostly during the summer and at a reduced rate. Man (1998) found that *n*-alkane depletion was similar regardless of temperature if the range was between 10°C and 22°C. Bonroy et al. (2007) found that heating-oil biodegradation rates in shallow soil almost doubled during the summer months compared to the winter.

Ground cover can impact the temperature of surface soils and consequently the temperature of percolating rainwater (Huang et al., 2008). Paved surfaces, such as asphalt or concrete, retain heat, whereas grass-covered or forested areas cool quicker during summer months. Increased temperature will decrease petroleum viscosity, allowing increased spreading, additional surface area in contact with groundwater, and enhanced biodegradation (Atlas & Bartha, 1992).

5.2.3 Contact with water

Many constituents of middle distillates exhibit low aqueous solubilities. Aromatics are more soluble than aliphatics of the same carbon number, whereas *cyclo*-alkanes tend to be slightly more soluble than *n*-alkanes (Bobra, 1992). Two compounds often used to represent petroleum weathering are the *n*-C_{17} alkane (*n*-heptadecane: $C_{17}H_{36}$) and pristane (2,6,10,14-tetramethylpentadecane: $C_{19}H_{40}$)(or "*n*-C_{17}/pr"). Bregnard et al. (1997) reported that pristane's aqueous solubility is less than 0.1 microgram per litre (µg/l), whereas Ritter (2003) found that solubility differences (in petroleum) between *n*-C_{17}, *n*-C_{18}, pristane and phytane are small. Middleditch et al. (1978) reported *n*-heptadecane concentrations in seawater ranging from 2 to 747 µg/l. Leahy & Colwell (1990) report that microbial degradation of long-chain *n*-alkanes ($\geq C_{12}$) occurs at rates that exceed the rates of hydrocarbon dissolution.

LaFargue & Barker (1988) found that *n*-alkanes lighter than C_{14} in crude oils were susceptible to dissolution, whereas the heavier *n*-alkanes were not. Isoprenoids heavier than C_{16} were not susceptible to dissolution, whereas the C_{13} through C_{15} isoprenoids were somewhat vulnerable.

For a given carbon number, ring formation, unsaturation, and branching cause an increase in aqueous solubility. Therefore, one could expect that when dissolution occurs, aromatics of a given carbon number would decrease first, followed by *cyclo*-alkanes, *iso*-alkanes and *n*-alkanes (Palmer, 1991).

Dissolution of hydrocarbons into groundwater or soil water may be impacted by:

- the surface area of hydrocarbons in contact with water, also known as the oil-water ratio. A higher ratio may impart greater dissolution; accordingly, geologic materials with a greater porosity may allow greater dissolution (Bobra, 1992);
- ambient groundwater chemistry and, in particular, temperature, pH and oxidation-reduction potential (ORP). The aqueous solubility of hydrocarbons often increases with temperature; however, the relationship between variables such as pH or ORP and solubility is often compound specific and possibly site-specific;
- the magnitude of precipitation and recharge. Recharge commonly increases dissolution, and
- the groundwater migration rate. Slow-moving groundwater will lessen transfer of hydrocarbons to a dissolved state, whereas the opposite occurs with rapidly migrating groundwater (Fried et al., 1979). In column experiments, Miller et al. (1990) found that the rate of mass transfer between a toluene separate phase and the aqueous phase was directly related to the groundwater migration rate.

As a result of mass transfer, dissolution and biodegradation are coupled processes because contact with water stimulates biological activity. Addition of petroleum to groundwater or soil water can allow indigenous bacteria to multiply and preferentially attack *n*-alkanes (Solević et al.,2003). Therefore, contact with groundwater may cause dissolution of lighter *n*-alkanes and isoprenoids and induce microbial degradation of lighter and heavier *n*-alkanes

and isoprenoids. Degradation can also begin inside an UST if sufficient water infiltration occurs (Gaylarde et al., 1999).

A rapidly fluctuating water table will foster emulsification and can enhance biological activity because of greater contact between the separate phase and water. Therefore, production of an emulsification can increase biodegradation rates (Atlas & Bartha, 1992).

5.2.4 Light

The rate of photochemical reactions is directly proportional to the number of photons absorbed by a chemical. Nearness to the Equator or an increase in altitude will accelerate the reactions (Sukol et al., 1988). Photodecomposition is not a significant process in the subsurface, although immediately adjacent to the ground surface, it may be important.

5.2.5 Oxygen and nutrients

Aerobic microbes need electron acceptors and nutrients to degrade petroleum. Lack of oxygen and nutrients may limit biological activity. Even though anaerobic microbes exist, anaerobic degradation is normally slower. For example, Bonin & Betrand (2000) found lowering oxygen contents could stop *n*-heptadecane mineralization. Numerous researchers found that oxygen availability is the most important factor in petroleum degradation (Raymond et al., 1976; Song et al., 1990). Factors affecting oxygen availability in soil include (Atlas & Bartha, 1992):

- *Drainage*: in water-logged soils, oxygen diffusion can be slow and bacterial movement restricted;
- *Soil texture*: coarse-grained soils have higher permeabilities and oxygen can be quickly replenished. Furthermore, coarser textures allow greater contact area between water and petroleum, increasing dissolution. However, for reasons stated earlier, medium-grained soils may exhibit the most biodegradation potential;
- *Proximity to the ground surface*: in laboratory column experiments, degradation was 3 to 5 times greater at the top versus the base (Atlas, 1981). This observation is related to proximity to greater oxygen abundance, temperature and recharge. Biological degradation can vary significantly over short distances in the horizontal and vertical directions. Variations will be dependent on nutrient and oxygen content and microbial diversity of geologic layers (Maila et al., 2005), and
- *Quantity of hydrocarbons*: Areas saturated with hydrocarbons may exhaust oxygen faster than it can be resupplied. Oxidation of 1 litre (L) of hydrocarbons can exhaust the dissolved oxygen in close to 400,000 L of water (Atlas & Bartha, 1992). Furthermore, large quantities of separate phase may decrease soil permeability with respect to water.

5.2.6 Bacteriocides

For biodegradation to occur, toxic concentrations of bacteriocides must not exist. Bacteriocides are elements or compounds toxic to bacteria. For example, H_2S may be toxic to some microbes (Prince & Walters, 2007). Under sulfate-reducing conditions, H_2S may form through biodegradation of aromatics.

5.3 Soil composition: Chemistry, lithology and texture

Coarser-grained soils permit freer movement of liquids such as soil gas, soil water and groundwater, allowing replenishment of oxygen, nutrients and microbes. Pore diameters of

less than 3 micrometres are an obstacle to bacteria, thereby limiting biodegradation (Aichberger et al., 2006). Zibiske & Risser (1986) found that medium-grained soil might have the most biodegradation potential: a combination of sufficient permeability and soil-surface area is the cause for increased biological activity. Increased surface area allows attachment of a greater number of microbes.

One cause for the persistence of spilled petroleum in the subsurface is a concept known as burial (Owens et al., 2008). If petroleum migrates into an enclosed area, for example, a sand layer sandwiched between clay, replenishment of nutrients and oxygen may be limited and petroleum could last for many years or decades.

5.3.1 Soil chemistry

The chemical composition of soil will impact conditions such as pH, redox and cation/anion exchange capacities (McVay et al., 2004). For example, soil derived from or overlying carbonate-type rocks will tend to exhibit higher pH values, whereas sandier soil (derived from sandstones, quartzites, etc.) will be less buffered and impacted more readily by acid rain. Higher organic carbon content tends to induce more biological activity in the soil. The organic carbon content commonly lessens in older soil and is often high in glacial sediments (Jobbágy & Jackson, 2000).

5.3.2 Soil moisture

Soils lacking moisture normally exhibit decreased biodegradation rates. The lack of moisture prevents influx of oxygen and nutrients and reduces contact between microbes and spilled petroleum. Waterlogged soils may retard biological processes. Laboratory studies performed by Schroll et al. (2006) showed a linear relationship between soil moisture and pesticide biodegradation. Bekins et al. (2005) reported on a crude-oil release where the shallowest soil samples exhibited the least petroleum degradation. The lack of degradation was attributed to reduced moisture within the shallow soil.

5.4 Petroleum chemistry

The chemical composition of petroleum products can influence weathering rates. Distillates derived from certain crudes can weather at varying rates, despite similar compositions (Atlas, 1981). Eganhouse et al. (1996) reports that certain petroleum constituents may inhibit degradation of others. For example, degradation rates of heavier *n*-alkanes may increase once lighter *n*-alkanes are removed.

Contaminant mixtures also impact biodegradation. In one study, *iso*-alkanes degraded individually, but when introduced with other hydrocarbons, degradation proceeded slowly. This finding suggests a competition effect (Kampbell & Wilson, 1991). However, there is evidence to the contrary, suggesting that degradation for some compounds is more rapid when in a mixture (Smith, 1990).

5.5 Distance from source

Distance from the source of the release will impact petroleum weathering. Because of the effects of source-area sequestration, increased surface area, and decreased contaminant mass, peripheral portions of the middle-distillate plume often weather at a faster rate than the core area (Parsons, 2003). It is unlikely that petroleum will weather at a uniform rate across the plume (Landon & Hult, 1991).

5.6 Hydrologic conditions

In areas with fluctuating water tables, separate phase can become engulfed by groundwater, forming an emulsion and enhancing biodegradation. Bekins et al. (2005) reports that in areas of significant recharge, enhanced degradation can occur because of increased contact with nutrient-rich water. At sites exhibiting rapid groundwater migration rates, mass transfer to the aqueous phase may increase, thereby enhancing hydrocarbon degradation.

5.7 Vegetation

Nearby plants and associated microbes can metabolize petroleum and convert it to harmless byproducts through a process known as phytoremediation. Microbial populations can be 5 to 100 times greater in the vicinity of roots, an area called the rhizosphere (Frick et al., 1999; Kechavarzi et al., 2007). McPherson et al. (2007) found that diesel removal in soil can be up to 40% greater when poplar trees exist. Hence, heavily vegetated areas may increase weathering of spilled petroleum.

Increased vegetation will also increase the number and density of roots in the subsurface. Because of transpiration, increased vegetation will lessen recharge and possibly decrease petroleum dissolution.

6. Sequence of biodegradation

The *n*-alkanes and aromatics (benzene, toluene, ethylbenzene and *o, m, p*-xylenes) are commonly the first compounds to be removed through biological processes (Chapelle, 2001). The *n*-alkanes are more readily converted to long-chain fatty acids (for subsequent beta-oxidation) compared to unsaturated or branched-chain hydrocarbons.

Because it has the highest solubility, benzene is commonly the first mono-aromatic to be depleted from a middle-distillate separate phase (Kaplan et al., 1996). However, Barker et al. (1987) found benzene to be the most persistent aromatic in ground water. Depletion is then normally followed by alkyl-benzenes and alkyl-naphthalenes. Alkyl-naphthalenes appear more resistant than alkyl-benzenes. Furthermore, homologues with longer alkyl chains will be more resistant to biodegradation (Kaplan et al., 1996). For example, a C_1-naphthalene (such as 1-methylnaphthalene) is normally less resistant than a C_4-naphthalene (such as diethylnaphthalene). Alkyl-*cyclo*-hexanes are commonly more resistant than *n*-alkanes and alkyl-benzenes and may be found in the environment much later in the life of a spill. In general, compound classes in order of decreasing susceptibility to biodegradation are *n*-alkanes > *iso*-alkanes (except isoprenoids) > low-molecular-weight aromatics > *cyclo*-alkanes (Leahy & Colwell, 1990).

Kaplan et al. (1997) found that weathering of petroleum products could be divided into seven progressive stages, which we term the *Kaplan Stages*. Similar weathering stages have been presented by Philp & Lewis (1987), Peters et al. (2005), Zytner et al. (2006) and Prince & Walters (2007). The *Kaplan Stages* are depicted on Table 4. Biodegradation including and beyond Stage 5 indicates substantial alteration and normally implies residence times greater than 20 years (Kaplan, 2003; Peters et., 2005).

7. Christensen & Larsen method

Microbes preferentially digest some hydrocarbons, leaving behind a biomarker (Christensen & Larsen, 1993). A biomarker is an organic compound that can be structurally related to its

precursor molecule, which occurs as a natural product in a plant, animal, bacteria, spore, fungi or petroleum (Philp & Lewis, 1987). Biomarkers are often resistant to degradation. For example, the isoprenoids: pristane, phytane, norpristane and farnesane, are resistant to microbial alteration, and their relative concentrations compared to n-alkanes, can be used as a proxy for weathering (Schaeffer et al, 1979). Therefore, ratios, such as n-C_{17} alkane to pristane (n-C_{17}/pr) or n-C_{18} alkane to phytane (n-C_{18}/ph) have been used as a measure of biodegradation. These n-alkanes and isoprenoids have similar solubilities and partitioning coefficients and the absence of n-alkanes is a result of biological activity and not transport or sorption (Bregnard et al., 1996).

Biodegradation of n-alkanes with molecular weights of up to n-C_{44} is known (Atlas, 1981). However, under aggressive conditions, isoprenoids may be susceptible to microbial oxidation; farnesane and norpristane are the most vulnerable (Pirnik et al., 1974; Pirnik, 1977; Nakajima et al., 1985).

The Christensen & Larsen (C&L) study reported a linear correlation between the n-C_{17}/pr ratio and the diesel-fuel age in soil from numerous spills where release dates were known. The n-C_{17}/pr ratio has been used as a measure of biodegradation for several decades (Atlas, 1981; Swannell et al., 1996), especially with marine spills. Christensen & Larsen (1993) report that statistical analysis of the correlation between the n-C_{17}/pr ratio and known spill ages can provide an age estimate to ± 2 years at a 95% confidence level, with some slight variability for releases <5 and >20 years old. Kaplan et al. (1996) provided an equation to calculate the C&L age where,

$$T(year) = -8.4(n\text{-}C_{17}/pr) + 19.8$$

According to Christensen & Larsen (1993), their method may be valid if several conditions are met:
- samples are collected from below an impervious cover such as asphalt or concrete;
- samples are obtained from at least 1 m below the ground surface;
- samples are acquired from at least 1 m above the water table;
- petroleum concentrations in the samples are at least 100 mg/kg, and
- the release is sudden.

Christensen & Larsen (1993) do not define a sudden release, but it can be assumed that a discharge lasting 1 year or less is implied. Most UST releases are slow and prolonged.

The C&L method dealt solely with contaminated soil samples. It did not apply to ground-water or separate-phase samples.

There has been much discussion on the validity of the C&L method (Alimi, 2002; Kaplan, 2002; Stout et al., 2002a; 2002b; Wade, 2002; Galperin & Kaplan, 2008c). Several claim that the method is invalid (Bruya, 2001; Smith et al., 2001; Shepperd & Crawford, 2003; Zemo, 2007). For example, Hostettler & Kvenvolden (2002) found weathered products (crude oils and distillates) with n-C_{17}/pr ratios in excess of 3.0. Stout & Douglas (2007) presented a case study where the C&L method failed to accurately predict the age of a known and sudden release of diesel fuel. However, several recent studies conclude that the method is viable, although with limitations; for example, more than one sample is recommended and knowledge of the original n-C_{17}/pr ratio is needed (Wade, 2001; Hurst, 2003; Hurst & Schmidt, 2005; Oudijk et al., 2006; Hurst & Schmidt, 2007; Oudijk, 2007; Hurst & Schmidt, 2008). Galperin & Kaplan (2008d) recently provided a model based on different initial n-C_{17}/pr values.

As discussed earlier, de Jonge et al. (1997) found that biodegradation rates decreased significantly when petroleum concentrations exceeded 4,000 mg/kg. Accordingly, one

might argue that a window exists, only between 100 mg/kg and 4,000 mg/kg, where the C&L method might be valid.

To assess the validity of the assumption the C&L, nine samples of heating oil and motor diesel were collected from residential tanks and commercial service stations in the northeast United States in 2007. The samples were analyzed with a GC/FID to evaluate n-C_{17}/pr ratios. Furthermore, a literature review was conducted to establish n-C_{17}/pr ratios in middle distillates and crude oils (Palacas et al., 1982; Collins et al., 1994; Buruss & Ryder, 1998; Porter & Simmons, 1998; Wang et al., 2003; Chung et al., 2004; Environment Canada, 2004; Hurst & Schmidt, 2005; Blanco et al., 2006; Hwang et al., 2006; Stout et al., 2006; Røberg et al., 2007).

Christensen & Larsen (1993) claim that n-C_{17}/pr ratios for fresh diesel fuel range from around 2.0 to 2.4 (based on Figure 4 of their article). Based on 11 samples, they obtained an average n-C_{17}/pr value of 1.98 with a standard deviation (σ) of 0.83. Hurst & Schmidt (2005) conducted a search of n-C_{17}/pr ratios in fresh distillates and crude oil and found a mean value of 2.3±0.7. However, our samples revealed n-C_{17}/pr ratios ranging from only 0.95 to 1.54 with a mean of 1.15 and σ of 0.18 (Table 3). There are several potential reasons for the discrepancy between our findings and the others:

- n-C_{17}/pr ratios were previously around 2.0, but more recently lowered to the 0.95-to-1.54 range because of changes in crude-oil sources;
- lower n-C_{17}/pr ratios are an artifact of only northeast-US refineries, and
- C&L reveal a mean value of around 2.0, but data are highly variable. Assuming the cited σ value, a 95% confidence interval would be between 1.15 and 2.81.

Type	Town	State	n-C_{17}/pr	pr/ph
Heating oil	Frenchtown	New Jersey	1.25	1.87
Heating oil	North Bellemore	New York	1.10	1.69
Heating oil	Toms River	New Jersey	1.54	1.46
Diesel fuel	Morrisville	Pennsylvania	1.05	1.89
Diesel fuel	Millstone	New Jersey	1.11	1.74
Diesel fuel	North Brunswick	New Jersey	1.29	1.56
Diesel fuel	South Plainfield	New Jersey	0.95	1.62
Diesel fuel (1)	Trenton	New Jersey	1.00	1.66
Diesel fuel (2)	Trenton	New Jersey	1.04	1.85
		Average:	1.15	1.70
		Standard deviation:	0.18	

NOTES: Laboratory analyses performed by Precision Testing Labs, Inc., Toms River, New Jersey. Based on Hurst and Schmidt (2005), the origin of these heating oils and diesel fuels may be Venezuelan and Canadian crude oils, which have average n-C_{17}/pr ratios of 1.4 and 1.0, respectively. Because much of New Jersey's heating oil originates from the Hess Corporation refinery in Port Reading, New Jersey, and Hess obtains crude oil from Petroleo de Venezuela, SA (PDVSA), this conclusion seems probable. The Venezuelan crude oil is fairly immature and exhibits low n-C_{17}/pr values. Furthermore, as of 2008, much of the United States' East Coast crude oil comes from the oil sands of Alberta, Canada (Oudijk, 2009a), which also exhibit much low n-C_{17}/pr values.

Table 3. n-C_{17}/pristane (n-C_{17}/pr) and pristane/phytane (pr/ph) ratios in samples of fresh no. 2 heating oil and motor diesel fuel collected in the US states of New Jersey, Pennsylvania and New York in 2007. Source: Oudijk (2009a).

Stage	Description
1.	Abundant n-alkanes, dye still present
2.	Light-end n-alkanes removed (such as n-C_8 in diesel fuels)
3.	Middle-range n-alkanes (n-C_9 through n-C_{14} in diesel fuels), benzene, toluene removed
4.	More than 90% of n-alkanes removed
5.	Alkyl-*cyclo*-hexanes & alkyl-benzenes removed
6.	Isoprenoids, C_1-naphthalenes, benzothiophenes and alkyl-benzo-thiophenes removed, C_2-naphthalenes selectively reduced
7.	Phenanthrenes, dibenzothiophenes and other PAHs reduced

NOTE: In many North American localities, a dye is placed into no. 2 heating oil to distinguish it from motor diesel fuel for taxing purposes. Accordingly, fresh motor diesel fuel would not have this dye.

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Table 4. Stages of biodegradation of no. 2 heating oil or motor diesel fuel, known as the Kaplan Stages. Based in part on Kaplan et al. (1997) and Peters et al. (2005).

Our literature review showed that n-C_{17}/pr ratios for crude oil worldwide range from <1.0 to about 7.0. The n-C_{17}/pr ratio in diesel fuel or heating oil would not be significantly different from its crude source, although Stout & Wang (2007) report that if the fuel is blended with cracked components during refining, n-C_{17}/pr ratios may be altered.

Based on the crude-oil data and our findings, C&L ages for today's fresh diesel fuel are unreliable. Therefore, it is unlikely that n-C_{17}/pr ratios can presently assist in age-dating studies, especially if litigation ensues. Because original n-C_{17}/pr ratios have changed, the C&L method may no longer be appropriate for age dating, at a minimum in North America, and a new method is needed.

8. Age-dating methodology

Significant laboratory studies and/or field investigations have not been performed to determine specific weathering rates of spilled middle distillates. Furthermore, Chapelle & Lovely (1990) report that laboratory studies tend to overestimate biodegradation rates. Field studies with known spill time frames are not plentiful. Therefore, specific data on subsurface weathering rates are generally not available. To obtain such data may be an extremely cumbersome endeavor because of the numerous variables involved. Studies of this type would need to address all the different geological, hydrological and biological conditions, which are numerous.

Previous age-dating methods for spilled middle distillates have been based, for the most part, on the chemistry of the petroleum. These methods have, in general, used weathering or biodegradation rates as a proxy for age. Because weathering at and within each spill site could be different, such a method can be problematic. Cherry et al. (1984) found that "Because the proportion of each [microbial] species present at any point in space and time is environmentally dependent, predictions of actual organic transformation pathways and rates are all but impossible (p. 57)". In their study of a crude-oil spill, Bekins et al. (2005) concluded that ". . . techniques for dating the time of a spill on the basis of the degree of degradation may yield very different results. . . (p. 140)". Accordingly, the use of only degradation rates for age dating is not sound and a technique is needed that considers many

parameters, such as weathering, geology, site history and the numerous site-specific environmental factors.

Because a mix of historical and scientific data will be used for our age estimates, each with possibly a large error range, a purely quantitative method, such as the equation used by Kaplan et al. (1997) (equation 1), is not practical. For that reason, a semi-quantitative method is proposed. This technique is based on an evaluation of five major factors and 15+ sub-factors, some of which are used to select a site-specific, weathering-potential regime (Atlas, 1981; Atlas & Bartha, 1992; Providenti et al., 1993) (Tables 4 and 5).

With the technique described here, five site-specific weathering-potential regimes are proposed to describe each release site (Table 6). The regimes are: very weak, weak, moderate, aggressive and very aggressive, and they are based on site-specific environmental factors. To obtain the age-date range, the weathering regimes are compared through a matrix to the Kaplan Stages, as described in Oudijk (2009a) and Table 7.

Environmental conditions	Chemical conditions
Soil permeability & effective porosity	*n*-alkane depletion
Water-table depth/hydrologic setting	*n*-alkane distribution
Soil cover	aromatic content/depletion
Organic-matter content of soil	unresolved complex mixture (UCM)
Groundwater and soil-water	size and location
salinity & pH	Carbon range
Lithology/chemical composition of	Ratio of heavy versus light
geologic formation	hydrocarbons
Sulfide content of soil & groundwater	Depletion of:
Vegetation	*iso*-alkanes
Dissolved oxygen content of	PAHs
ground water/oxidation- reduction potential	alkyl-*cyclo*-hexanes
(aerobic v. anaerobic or oxic v. anoxic)	alkyl-benzenes
Moisture content of soil	thiophenes
Temperature	
Indigenous microbial community	
Co-presence of other contaminants	
Presence of electron acceptors	
Presence of emulsifying agents	
Distance from source	

Table 5. Examples of environmental factors impacting the weathering of middle-distillate fuels and resulting chemical responses

Regime	Examples and description
Very aggressive	Water-logged soils; areas prone to flooding; surficial or very shallow releases; moderate to high permeability and effective porosity; stray electrical currents, heavily vegetated; nutrient-rich soils and/or groundwater, moderate pH (7–8); high DO content (at or near saturation) and ORP in groundwater; lack of soil cover; high recharge rates, and history of environmental pollution (acclimated microbes).
Aggressive	High water table; highly-permeable and porous soils; lack of soil cover; shallow release; moderate pH (7–8); high oxygen content in soil and groundwater (>5 mg/L); high organic-matter content; stray electrical currents; high salinity content of groundwater; high soil sulfide content; high soil moisture; heavily vegetated, and urban environment (not pristine).
Moderate	Moderate water content in soil; moderate depth to groundwater; moderate permeability and porosity; moderate pH (5–9); moderate oxygen content in soil and groundwater (>2 mg/L); lack of stray electrical currents, and moderate vegetation.
Weak	Low moisture content in soils; water-logged soil (as per biodegradation); very high or very low pH; low oxygen content in soil and groundwater (<1 mg/L); deep water table; no stray electrical currents; low organic-matter content in soil; non-existent or sparse vegetation, and pristine environment.
Very weak	Extremely cold, hot or harsh environment; extremely high or extremely low pH; total lack of oxygen; pristine; no soil moisture, and sterilized environment (elevated bacteriocides).

Table 6. Site-specific weathering-potential regimes. Source: Oudijk (2009a)

9. Assessing petroleum weathering with chromatograms

Petroleum weathering may be assessed through collection of soil or separate-phase samples and laboratory analysis with a gas chromatograph (GC) equipped with flame-ionization (GC/FID) or mass spectrometry (GC/MS) detectors (Senn & Johnson, 1987).

To assess the magnitude of weathering in each sample, either the peak height or area for the *n*-alkanes and *iso*-alkanes (in particular, the isoprenoids) must be calculated. Calculation of the peak areas is preferred; however, peak heights are acceptable if there is a linear relationship between heights and areas (Wade, 2001). There are two methods to calculate the peak height: either directly from the base of the chromatogram, or from the base of the UCM. The UCM method is preferred (Hostettler et al., 1999).

Assessment of petroleum weathering is needed to determine into which *Kaplan Stage* a sample is placed. There are several factors to consider:

- *Compound depletion*: Specific compounds are more resistant to biodegradation and their presence or depletion can be used to assess weathering;
- *Carbon range*: No. 2 heating oil and diesel fuel are normally within a range of C_9 through C_{24}. Lighter hydrocarbons (less than C_9, but not the mono-aromatics) may be evidence of the presence or mixture with gasoline or kerosene. A heavier fraction may be evidence of increased weathering (Wang & Fingas, 1995b). In addition, heavier constituents (greater than C_{24}) may be evidence of a mixture with no. 6, lubricating or motor oils;
- *The n-alkane distribution*: The *n*-alkanes in middle distillates, such as diesel fuel, heating oils or kerosene, normally show an even distribution, evidenced by a bell-shaped

Weathering regime:	Very aggressive	Aggressive	Moderate	Weak	Very Weak
Fresh fuel	0	0	0	0	0
Kaplan Stages:					
1. Abundant *n*-alkanes	<0.25	0-2	0-4	0-8	0-10
2. Light *n*-alkanes removed, benzene & toluene removed	<0.5	2-4	4-8	8-16	10-20
3. Middle-range *n*-alkanes removed, ethylbenzene & xylenes removed	<1	4-6	8-12	16-24	20-30
4. More than 50% of the *n*−alkanes removed	<2	6-8	12-16	24-32	30-40
5. More than 90% of *n*-alkanes removed, alkyl-benzenes and alkyl-*cyclo*-hexanes begin to degrade	<3	8-10	16-20	32-40	40-50
6. All n-alkanes removed, alkyl-benzenes	<4	10-12	20-24	40-48	50-60
7. Isoprenoid removal significant	<5	>12	>24	>48	>60

NOTE: The age ranges cited above must be compared to site-specific information, such as underground storage tank (UST) age, UST condition and the extent of contamination, to assess their accuracy The age ranges provided in this table should be used solely as a guide. Accordingly, additional information is needed to estimate the actual age as described in the text herein. In some situations, however, these age ranges may not apply and should not be used at all. Such situations, for which an age estimate cannot be done with the method described herein, include but are not limited to the following: multiple releases as well as changes of environmental conditions since the release has occurred. Such conditions should be carefully evaluated and excluded before applying this age-dating method.

Table 7. Matrix of *Kaplan Stages* and weathering-potential regimes providing potential age ranges in years for a release of a middle-distillate fuel. Source: Oudijk (2009b).

> envelope. In diesel and no. 2 heating oils, the envelope reaches a maximum at C_{14} to C_{17} (Kaplan et al., 1996). In kerosene and jet fuels, the maximum is normally between C_{10} and C_{12}. An uneven or jagged distribution is often evidence of weathering (Figure 6a through 6c);

- *Unresolved complex mixture (UCM)*: The UCM is the hump at the base of a GC/FID trace (Figures 6a through 6c) and a mixture of complex *cyclo-* and *iso*-alkanes that are unresolvable through gas chromatography (McGovern, 1999). UCMs are a typical appearance on chromatograms for crude oil and crude-oil distillates (Frysinger et al., 2003). The UCM normally increases in relative height and width as biodegradation proceeds (Wang & Fingas, 1995b). The presence of multiple UCMs is commonly evidence that more than one distillate is present, for example, a mixture of no. 2 and no. 6 heating oil, and

- *Heavy versus light n-alkanes*. Under aerobic conditions, lighter *n*-alkanes are normally removed quicker compared to the heavier *n*-alkanes (Mohantya & Mukherji, 2008). A comparison of heavy *n*-alkanes, such as n-C_{20} through n-C_{22}, versus lighter *n*-alkanes, such as n-C_8 through n-C_{10}, can demonstrate the magnitude of evaporation. Lighter *n*-alkanes are often more volatile (Wang & Fingas, 1995b). Experiments have shown that
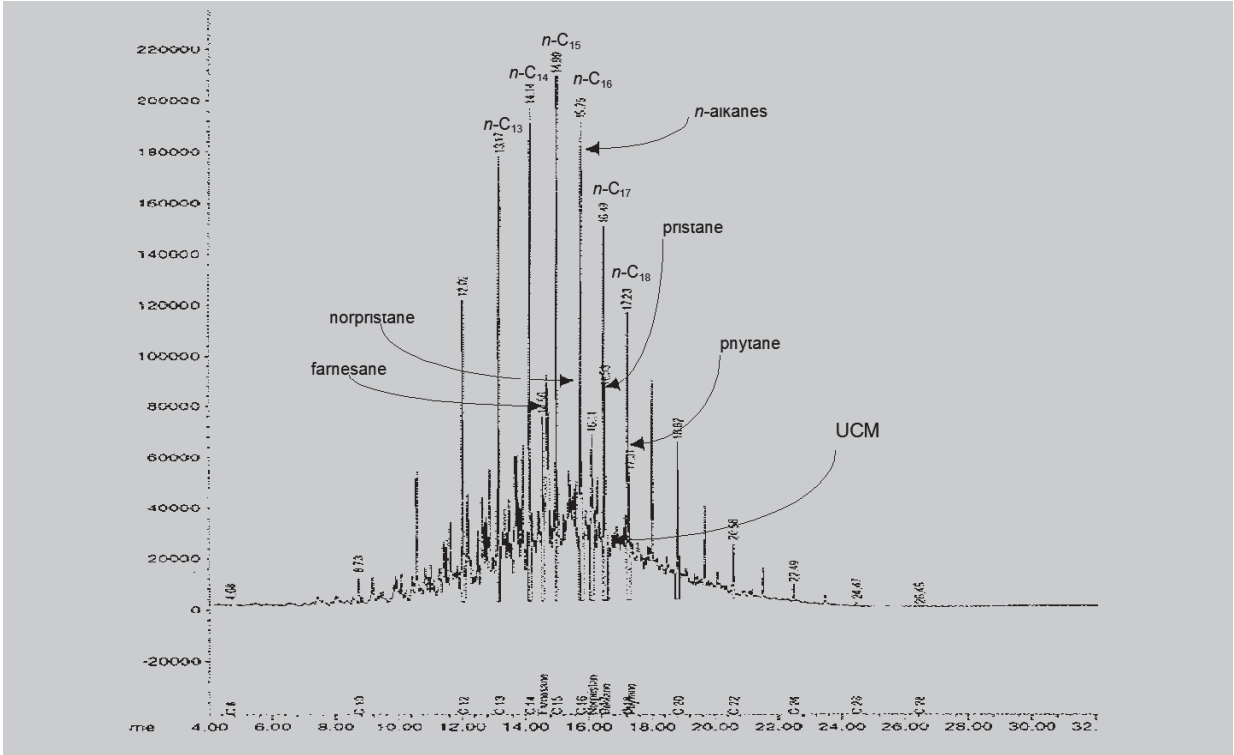
Fig. 6a. GC/FID chromatogram for a 2007 fresh motor diesel fuel from New Jersey (USA) showing the n-alkane peak envelope and the unresolved complex mixture (UCM). Source: Precision Testing Labs, Inc., Toms River, New Jersey (USA).
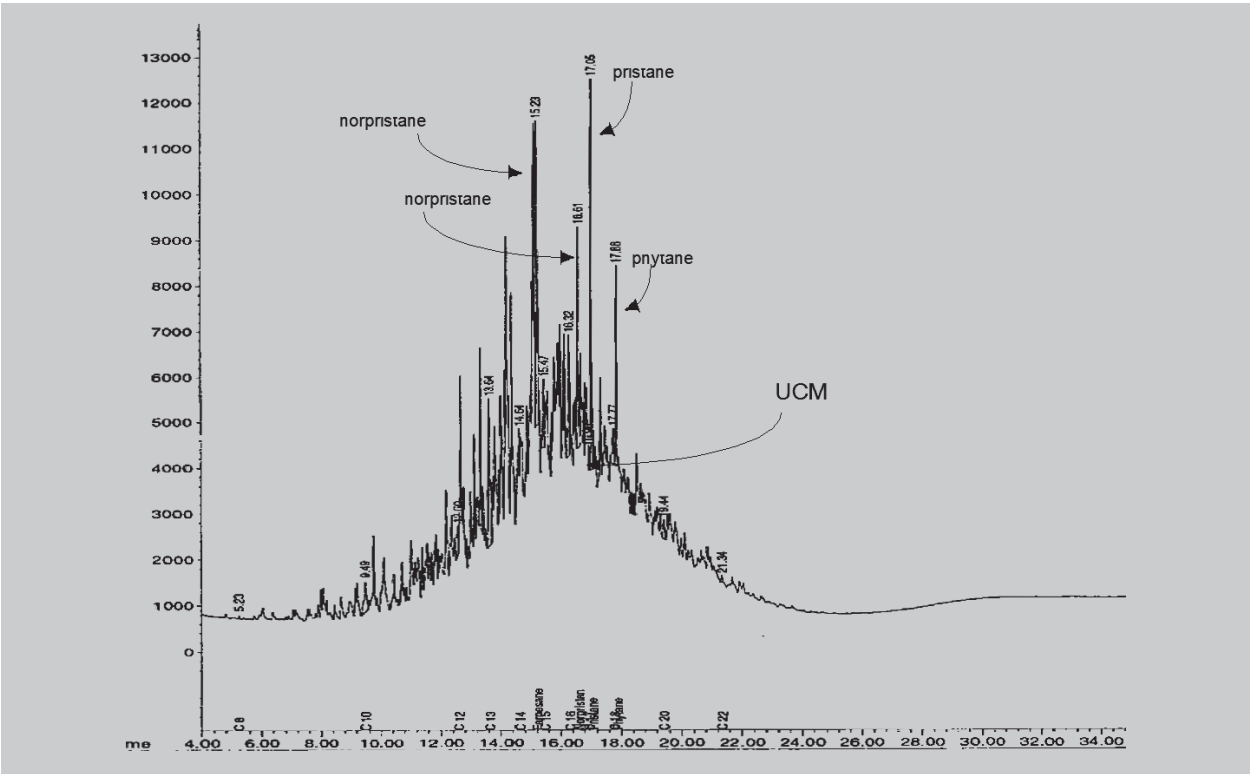

Fig. 6b. GC/FID chromatogram for a weathered motor diesel fuel obtained in 2007 from New Jersey (USA). Source: Precision Testing Labs, Inc., Toms River, New Jersey (USA).
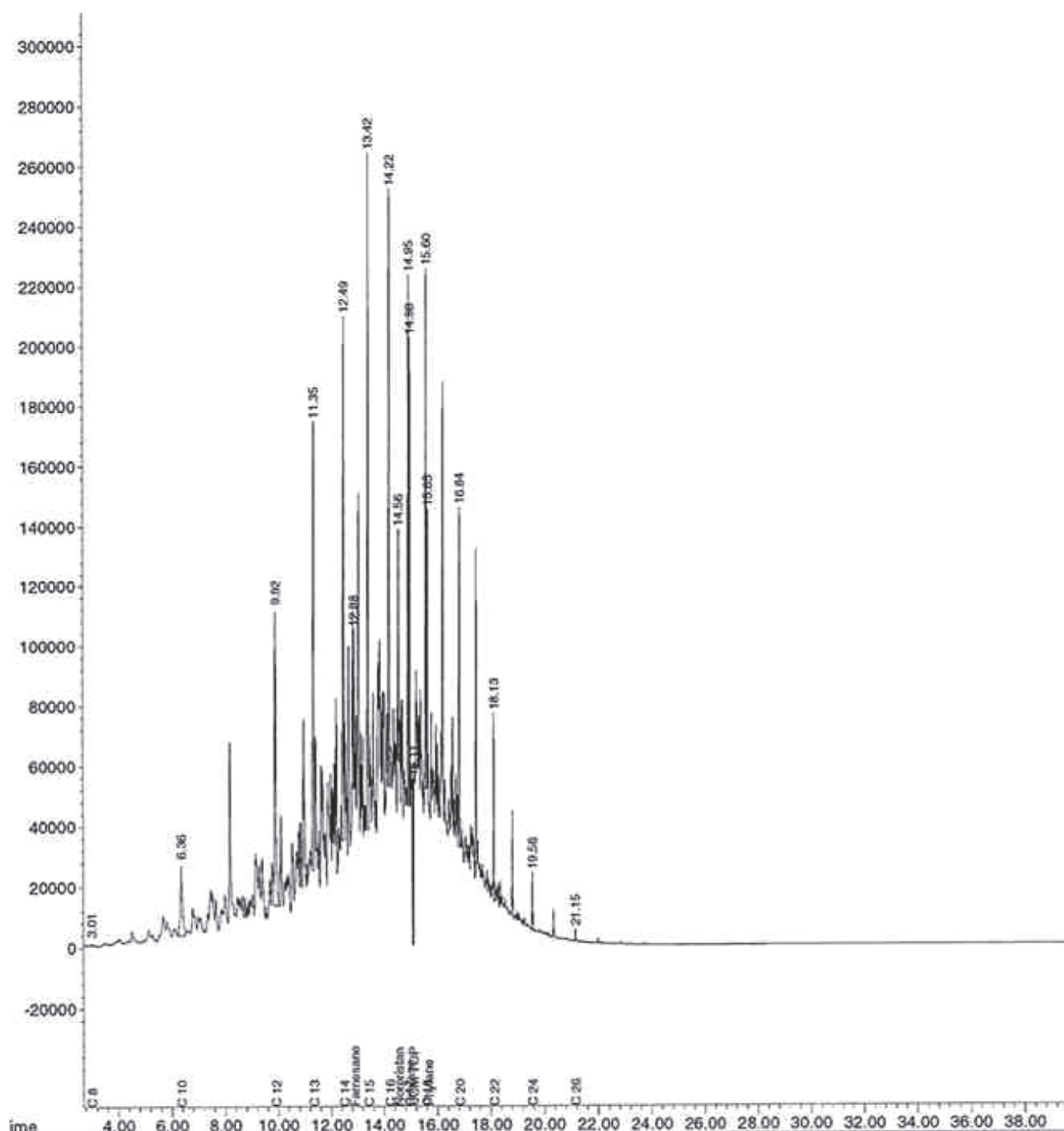
Fig. 6c. GC/FID chromatogram for a mixture of weathered and fresh motor diesel fuel obtained in 2011 from New Jersey (USA). Note the even distribution of *n*-alkane peaks and the relatively large unresolved complex mixture (UCM). Source: Precision Testing Labs, Inc., Toms River, New Jersey (USA).

n-alkanes lighter than $n\text{-}C_{11}$ can be lost within 9 days in a surface spill (Payne et al., 1991). In some cases, elevated salinity can increase evaporation rates and decrease dissolution (Oyewo, 1988). However, hydrocarbons heavier than C_{14} are only slightly impacted by evaporation or dissolution (Blumer et al., 1970). The ratio of $n\text{-}C_{10}$ to $n\text{-}C_{20}$ ($n\text{-}C_{10}/n\text{-}C_{20}$) is normally 0.5 to 1.5 in an unweathered diesel fuel, whereas evaporated diesel fuel often exhibits lower $n\text{-}C_{10}/n\text{-}C_{20}$ values. Therefore, $n\text{-}C_{10}/n\text{-}C_{20}$ values can help to assess the magnitude of evaporation and dissolution. Furthermore, a formula,

similar to the weathering index (WI*) suggested by Wang & Fingas (1995b), used to assess weathering for diesel fuels or no. 2 heating oil, is:

$$\text{WI*} = (n\text{-}C_8 + n\text{-}C_{10} + n\text{-}C_{12} + n\text{-}C_{14})/(n\text{-}C_{16} + n\text{-}C_{18} + n\text{-}C_{20} + n\text{-}C_{22})$$

Under aerobic conditions, lower WI* values are indicative of weathering, whereas higher values are evidence of less degradation.

GC/FID traces can show evidence of a mixture of fresh and weathered middle distillates. Evidence for this phenomenon is normally an enlarged UCM overlain with an envelope of evenly distributed *n*-alkanes. A mixture of highly weathered and fresh product is often evidence of two (or more) releases, although it does not necessarily reveal more than one source. Furthermore, a subsurface release could be superimposed by a surficial spill, overfill or piping failure (Figure _).

The above methods can be employed to assess the weathering characteristics of middle-distillate fuels such as kerosene, the jet fuels, diesel fuels (such as motor diesel or railroad diesel), heating oils (such as no. 2, no. 4 and no. 6) and bunker oil. In some cases, such as with no. 6 oil/bunker oil, quantifying the *n*-alkane/isoprenoid ratios may be difficult because of low concentration of the marker compounds. Furthermore, evaluation of ratios such as $n\text{-}C_{10}/n\text{-}C_{20}$ in the heavier oils may not be possible.

10. Site-specific environmental and non-environmental factors

A proper age-dating study will include information on the following five factors and several associated sub-factors: 1. site history; 2. on-site environmental conditions; 3. extent and magnitude of known impact; 4. condition (and age) of the UST (or other types of sources), and 5. other conditions. The environmental factors can be used to select a site-specific, weathering-potential regime (Table 5).

10.1 Site history

Historical factors include: 1) first date when petroleum was observed in the environment or when problems first began, such as a malfunctioning furnace; 2) age of the UST (or other types of sources, such as aboveground storage tanks or pipelines). Quite commonly, the UST age is not known and it must be assumed that it is the same as the site, service station or residence (although not always correct), and 3) known or calculated petroleum quantity in the subsurface.

It is assumed that the petroleum age will be less than the UST age, but older than the date of its first environmental appearance. Furthermore, trouble with the furnace, because of water or lack of oil, may be a clue surrounding the onset of UST failure in a residential case. The average lifespan of an UST may be as low as 15 years, whereas the commonly used "rule-of-thumb" is 25 years. The 15- to 25-year average lifespan should be kept in mind when estimating a release age. However, we have seen USTs develop leakage within days (because of improper installation) and USTs older than 75 years in close-to-perfect condition.

A calculation of the petroleum quantity in the subsurface may be helpful, although this result is often fraught with error. The calculation may be performed by: 1) computing the petroleum quantity through soil-sampling results and separate-phase-thickness measurements in wells, or 2) comparing the amount of fuel delivered versus average usage (with the use of "degree days" to estimate fuel usage). The calculated value may then be

divided by an estimated leakage rate to obtain the time frame. A minor leakage rate could be 0.01 L/day, whereas a high rate might be greater than 0.5 L/day.

10.2 Environmental conditions

Environmental factors impacting age-dating evaluations include: 1) depth to groundwater, 2) lithology and texture of geologic materials; 3) geochemical conditions of soil and groundwater, such as: a) pH; b) salinity; c) redox potential, and d) dissolved oxygen content; 4) biological conditions; 5) overlying soil cover, and 6) other factors.

10.2.1 Depth to groundwater

Petroleum in soil samples collected beneath the water table may experience increased dissolution, in particular, lighter *n*-alkanes. The hydrologic locality must also be considered. For example, in recharge zones, the water table may fluctuate several meters seasonally. Therefore, soil-sampling locations may have previously been within groundwater. To assess this problem, governmental agencies often have nearby observation wells with water-level data spanning decades and these data should always be consulted.

The amount of recharge is dependent on soil cover, vertical permeability and topographic location (such as within a hill or valley). Soil samples collected beneath a building may be subjected to less water contact. However, petroleum in samples collected beneath covers such as grass or bare ground may experience increased dissolution and, consequently, additional weathering.

10.2.2 Lithology and texture of geologic materials

Soil texture will impact drainage and permeability. Poor drainage and low permeability prevent oxygen and nutrient replenishment. Fine-grained soils, such as clays, more commonly exhibit anaerobic conditions. Soils exhibiting high cation-exchange capacities, such as silts or clays, or contain large organic-carbon contents, may adsorb petroleum readily. Adsorption decreases with increasing temperature and soil moisture and adsorbed petroleum is less available to microbes (Providenti et al., 1993). Hence, biological activity may be subdued and weathering minimized in fine-grained soils; however, large organic carbon contents could also induce greater microbial activity.

Inadequate soil hydration depresses microbial metabolism and movement. Furthermore, lack of moisture decreases nutrient replenishment (Providenti et al., 1993). However, waterlogged soils can also limit oxygen concentrations. Accordingly, soil-moisture extremes may decrease biological activity and weathering.

10.2.3 Geochemical and biochemical conditions of soil and groundwater

Subsurface geochemical conditions impact petroleum weathering. Extreme pH limits biological activity, whereas redox dictates if aerobes or anaerobes exist. Both microbes use middle distillates as substrates, but aerobic degradation is often quicker. The dissolved oxygen content and oxidation-reduction potential (ORP) of groundwater (if the water table is shallow) can help to identify these conditions.

10.2.4 Biological conditions

Microbes are a part of the geochemical framework of saturated and unsaturated zones. Populations may increase in response to petroleum releases and alter geochemical conditions.

Certain bacteria may increase or decrease mineralization rates of hydrocarbons. Furthermore, microbes can act as emulsifying agents, suspending petroleum in the aqueous phase and enhancing dissolution and biodegradation (Zajic et al., 1974). Additionally, vegetation impacts weathering, especially in the rhizosphere where microbial action is plentiful.

10.2.5 Overlying soil cover
The type and extent of soil cover will impact infiltration and potentially the magnitude of petroleum dissolution. This factor could have an impact on *n*-alkane depletion. Christensen & Larsen (1993) recommend that samples be collected at least 1 m below the ground surface. Petroleum located at shallow depths may be subject to increased volatilization or photodecomposition. Furthermore, shallow locations face greater temperature changes and increased weathering.

10.2.6 UST-related factors
In addition to affecting petroleum weathering, environmental conditions will also impact UST corrosion. These environmental factors include:
1. soil exhibiting low resistivity increases ion exchange between steel and soil minerals. Highly-corrosive soil is often composed of clay with elevated sulfide concentrations and low pH;
2. coarse-grained and/or angular-grained soil. The periodic filling of the UST can cause angular stones to puncture the UST;
3. increased recharge, such as an adjacent roof leader or a location within a low area, will increase UST contact with water, and
4. periodic or constant immersion in water, in particular acidic groundwater.
Anthropogenic conditions that can impact UST corrosion include:
*   quality of the UST materials, such as the steel thickness. Based on our field observations, North American USTs installed prior to the 1970s are often constructed of a thicker gage steel and, therefore, less susceptible to corrosion. In coastal areas, where the water table is shallow, aboveground tanks are often used underground. These tanks are commonly constructed with thin-gage steel and more susceptible to corrosion;
*   UST size. Larger diameter USTs will corrode at an accelerated rate, possibly because of the greater load on the steel (Holt, 1997);
*   improper installation procedures, such as use of jagged backfill;
*   lack of cathodic protection;
*   use of dissimilar materials in UST construction, such as a mix of galvanized- and stainless-steel, and
*   stray electrical currents from nearby buried power lines.
Many of these factors also apply to aboveground tanks (ASTs). Furthermore, ASTs are particularly susceptible to lightning strikes, which can cause immediate failure.

10.3 Extent and magnitude of impact
The extent and magnitude of impact can be measured by: 1) area of impacted soil and/or groundwater and the quantity of separate-phase-saturated soil; 2) vertical extent of impact, and 3) extent and thickness of separate phase on the water table.
It is assumed that a middle-distillate plume with a significant distance will also exhibit a significant age. If sufficient data are available, it may be possible to calculate the migration rate and back-calculate the time frame.

The volume of petroleum in the environment will have an impact on weathering. Samples collected within a large pool of separate phase may not exhibit any weathering many years after a release. Accordingly, samples collected within a highly contaminated location may not provide productive evidence.

10.4 UST condition

The UST condition can be assessed by: the number, size and location of corrosion holes. Corrosion often takes considerable time to develop. Metallurgists are commonly consulted to provide opinions on the UST release ages. However, soil conditions should be evaluated to determine their connectivity.

Stray electrical currents may have a significant impact on unprotected steel USTs. In particular, central air-conditioning units, which normally run on underground 220-volt currents, are often the culprits with newer buildings or homes. Unfortunately, USTs are commonly installed adjacent to these units and leakage can often initiate within 5 years.

10.5 Other considerations

There may be additional site-specific factors in addition to the five listed. For example, USTs are often abandoned in-place, possibly by a previous owner. The abandonment date might represent when a previous owner suspected leakage. Ecosystem responses may also need to be evaluated. For example, contamination may induce stressed vegetation or impacts to water bodies. The time needed to produce such impacts may be significant. Investigators need to evaluate these factors and determine if they are sufficiently important to consider in the matrix.

11. Recommended sampling and laboratory analyses

Oudijk et al. (2006) and Oudijk (2009b) provided guidelines for age-date sampling. Samples can be either impacted soil or separate phase, although soil samples are preferred. Samples as distant as possible from the source are needed to assess the maximum release age; however, a sufficient quantity of petroleum must be present to perform laboratory analyses. A hydrocarbon concentration of greater than 1,000 mg/kg is recommended.

An important decision is the sampling locations. It is assumed that locations distant from the source represent older ages. However, downgradient locations may be more susceptible to excessive weathering. Furthermore, petroleum in samples collected from within separate-phase pools may not weather as much as locations proximate or outside the pool. Accordingly, an understanding of sampling locations with respect to accumulations of separate phase is needed. As discussed by Wade (2001) and Oudijk et al. (2006), age dating based on one sample is unwise.

Field analyses of groundwater samples are needed (unless the water table is deep and inaccessible). The analyses should include pH, dissolved oxygen (DO), ORP, specific conductance, temperature and salinity. The samples should be laboratory analyzed by GC/FID. We have found that analyses for n-alkanes by GC/MS are often inaccurate. The GC/FID analyses must be conducted so that sufficient separation exists between peaks. For example, the n-C_{17} alkane and pristane elute very close to each other. To enhance peak separation, a run time of about 40 minutes is recommended. In some cases, some of the samples should be analyzed for aromatics such as benzene, toluene, ethylbenzene and o, m, p-

xylenes and base/neutral extractable compounds (B/Ns), also targeting C_1- and C_2-naphthalenes, alkyl-benzenes, alkyl-*cyclo*-hexanes and dibenzothiophenes. It is further recommended that a sample of fresh fuel be collected from each site for comparison purposes. However, it is possible that the fresh oil may be significantly different from the spilled oil.

12. Evaluating the age range

To evaluate the age, a Kaplan Stage is selected for each sample, whether soil or separate phase. Based on known environmental conditions, a weathering-potential regime is then chosen for the site. A matrix, comparing the Kaplan Stages to the weathering-potential regimes, is provided detailing potential release ages (Table 7). Compared to Kaplan et al. (1997), the Kaplan Stages on Table 7 were modified to include additional parameters. These potential age ranges are based on:

- under very aggressive conditions, *n*-alkanes can be completely removed in less than 5 years (Hurst, 2003). For example, in marine environments, which are very aggressive, *n*-alkanes can be removed in a matter of days (Colwell, 1978). In the 2002 *Prestige* tanker spill off the coast of Spain, the *n*-C_{17}/pr ratios in nearby sediments were cut in half after less than one year (Blanco et al., 2006). With marine spills, processes in addition to biodegradation, such as volatilization and dissolution, may cause the *n*-alkane depletion. Conversely, under these same aggressive conditions, PAHs may still last decades (DeLaune et al., 1990);

- under very-weak conditions, such as a Arctic environments, *n*-alkanes can persist in soil for decades (Sexstone et al., 1978a; Collins et al., 1994);

- high concentrations of nutrients and oxygen, indicative of aggressive environments, can allow complete middle-distillate degradation in soil within less than one decade (Bregnard et al., 1996). However, removal or lessening of oxygen and nutrients can effectively retard hydrocarbon removal (Bonin & Bertrand, 2000). Unless extreme conditions exist, such as permafrost or drought, complete or near-complete removal of hydrocarbons is normally accomplished within 20 to 30 years;

- benzene and toluene often biodegrade and dissolve quicker than ethylbenzene and *o,m,p*-xylenes (although not always)(Kaplan et al., 1996). Based on our field observations, these aromatics are removed rapidly at most sites, and under moderate weathering conditions, *iso*-alkanes, such as pristane and phytane, and the alkyl-naphthalenes are commonly the predominant compounds after about 20 years (Caredda et al., 2007).

The matrix was constructed with the following assumptions:

- the very-aggressive column represents a marine-spill situation. The *n*-alkanes degrade quickly in such environments. There are reports that *n*-alkanes may persist for two or three years (Colwell, 1978), but they will, in general, be gone within 4 years (and often much earlier). With regard to *n*-alkane depletion, time frames of weeks or months are more common than years (de Souza & Triguis, 2004). Accordingly, <4 years can be placed into the matrix for Stage 6 in an aggressive environment.

the very-weak column represents spills in an Arctic or Antarctic climate. The *n*-alkanes degrade slowly here (Sexstone et al., 1978a; Collins et al., 1994). Sexstone et al. (1978b) reported that biodegradation in tundra soil could be slow "with no major preferential utilization of classes of hydrocarbons during the period of exposure". The longer-chain *n*-alkanes (>C_{10}) are commonly solid at temperatures less than 10° C (Whyte et al., 1998). Kershaw & Kershaw (1986) found significant depletion at surface locations from a 35-year

old spill in the Canadian Northwest Territories, but with depth, up to 80% of the oil persisted. Collins et al. (1994) found only marginal depletion of *n*-alkanes in subsurface soils from a 12-year-old crude-oil spill in a permafrost region of Alaska. Gore et al. (1999) and Kerry (1993) also found minimal subsurface biodegradation in a similar Antarctic environment. A very weak environment is where microbes are dormant, cannot come in contact with hydrocarbons or have been removed because of toxicity. Accordingly, >60 years can be placed into the matrix for Stage 6 in a very-weak environment;

- under moderate conditions, *n*-alkanes are normally removed from subsurface soils in about 20 years (Christensen & Larsen, 1993; Kaplan, 2003). Accordingly, 20 to 24 years can be placed into the matrix for Stage 6 in a moderate environment;

- degradation follows a clear sequential pattern as depicted by Kaplan et al. (1996) and Table 4. This sequential pattern is normally the case. However, there are cases where different compounds of the same class degrade at significantly different rates. For example, Olson et al. (1999) found that components within the aliphatic fraction of diesel fuel degraded at different rates, although the aliphatic fraction, as a whole, degraded quicker than the aromatic fraction;

- removal of *n*-alkanes tends to be linear, instead of exponential (Christensen & Larsen, 1993; Hurst & Schmidt, 2005; Galperin & Kaplan, 2008c). Therefore, age ranges are extrapolated in a linear manner from Stage 6 to Stage 1 (zero-order kinetics). Chapelle (2001) explains that there is often a lag time between introduction of a contaminant to a soil or groundwater system and acclimation of microbes. However, in the first days or weeks after release and acclimation, once that acclimation has occurred, biodegradation rates may be significant. Díez et al. (2007) found that biodegradation rates of heavy oils can be slow, even in a marine environment. Accordingly, it can be assumed that as oil ages and becomes more viscous, the rate of biological consumption decreases. Colwell (1978) found that rates could initially be logarithmic for marine spills and later linear. Bonroy et al. (2007) reports that biodegradation rates will vary seasonally. Walker et al. (1976) found that the degradation rate of the alkane fraction of a crude oil was linear, whereas the rate for aromatics varied. Ostendorf et al. (2007) found that *n*-alkane degradation rates in unsaturated soil followed zero-order kinetics, whereas aromatics followed first-order. Bjorklof et al. (2008) found that petroleum degradation rates can be linear, but they are mass-transfer dependent. Therefore, rates will more likely be linear in a permeable soil where the petroleum can dissolve more easily. It is assumed that rates averaged across the years are linear, although it is understood that this assumption may not apply everywhere, and

- age ranges can then be extrapolated between the very-aggressive and very-weak environments and the moderate environments.

The matrix should only be used to provide potential ages and should not be the sole factor for an age-date opinion. The matrix is a method to lead the investigator towards the correct age, but it is not the final say.

13. Critiquing the matrix age range

Once a potential age range is obtained from the matrix, it must be compared to several factors to assess its reliability. Other factors that may impact the age are:

- age of the UST;

- time frames of known or possible pollution events, such as appearance of petroleum in waterways, furnace failures, excessive oil usage or abandonments. This process may entail a review of fuel bills to determine when excessive usage began;
- state of the UST, such as the number and sizes of corrosion holes and pitting;
- extent and magnitude of petroleum-impacted soil and groundwater, and
- miscellaneous factors such as high-voltage underground electrical lines.

With the date of petroleum appearance, such as when oil began seeping into a creek, the upper and lower ages can be constrained. For example, if it is known that an UST was installed in 1980 and the furnace began to take in water in 2004, we can conclude that UST failure occurred between 1980 and 2004.

If heating oil was released, the history of the heating system should be considered. The dates of repairs and service calls should be reviewed. The fuel company is often called when a furnace fails and causes for any failures should be determined. The date of any on-site work that included excavating should also be identified. Gardening is a common cause for severing feed and return lines.

Reports should be obtained on the UST condition. If one pin-sized hole is present, it is probable that the leak began within the last 1 to 2 years. However, if 25 coin-sized holes are found, it is more likely that the leak began 10 years ago or later.

Calculations of plume extent are important in assessing the reasonableness of estimated age ranges. A large and extensive plume is more indicative of an older release. However, care is needed in making such conclusions because aggressive biodegradation can greatly reduce plume sizes. If monitoring wells are available, groundwater migration rates may be calculated and time frames for plume movement assessed and compared to geochemical data.

Lastly, underground power lines should be assessed. Residential USTs are often adjacent to air-conditioning units and associated power lines can quickly instigate leakage. At a site in New Jersey, a power line produced a sequence of holes on the top and bottom of an underlying UST. The power line had only existed for 2 years.

Table 7 provides an age range, for example, of 4 to 8 years. This range could be interpreted as 6 years ±2 years. It is stressed that the values on Table 7 are only potential ranges and might contain significant error, if they are not verified through alternative means. Each release is different and on-site petroleum weathering may not necessarily fall within the confines of this technique.

An additional geochemical method to critique the age-date estimate is to establish the sulphur content of the oil. In many countries, the government limits sulphur contents in on-road diesel fuel (Table 8). By determining the sulphur content, the age of the diesel fuel can often be constrained.

14. Range of error

Error is the difference between an observed or calculated value and the true value. Usually, we do not know the true value, but can approximate error ranges from earlier experiments or theoretical predictions (Bevington & Robinson, 1992). The purpose of calculating error ranges is to evaluate the confidence of our results.

All geochemical data collected to assess some type of natural phenomenon contain error caused by sampling and analysis (Miesch, 1967). Subsurface modeling is plagued by uncertainties that are both epistemic (reducible through observations) and aleatory (irreducible because of inherent stochasticity) (Srinivasan et al., 2007). The amount of error

	Maximum sulphur concentration allowable (mg/l)	Regulated as of
Australia	10	2009
Canada	15	1997
	500	1994
China	2,000	2002
European Union	50	2005
New Zealand	10	2009
Singapore	50	2005
Taiwan	50	2007
USA	15	2007[a]
	500	1993

[a] Mandated year was 2006 in California and 2010 in Alaska.

Table 8. Maximum allowable sulphur concentrations allowable in motor diesel fuel in selected countries

often cannot be found in textbooks or with a formula. It is commonly based on a 'rule-of-thumb' or experience. Nevertheless, some calculations can be performed to provide insight into potential error ranges.

To assess error ranges in our calculations, we can use the C&L method as an example. C&L uses the $n-C_{17}$/pristane ratio as its basis and, to calculate the ratio, an analysis with a gas chromatograph is needed. This analysis generally has a precision of about 5%. Furthermore, the method assumes that $n-C_{17}$/pristane ratios for unweathered oil range from 2.0 to 2.2. Hence, the starting point has an error of about 10%. Therefore, errors are summed and the resulting error is about 15%. This exercise assumes that the C&L method perfectly reflects weathering processes in the subsurface. This, we know to be untrue. Consequently, we can assume that the method's error is at least 20% or ±2 years

In their article, Christensen & Larsen (1993) cite an error range of ±1 year or about 10%. Hurst & Schmidt (2005), employing a similar method, cite a minimum error of 15% or ±1.5 years. These cited error ranges seem optimistic and there are several references in the scientific literature arguing that the range is greater (Stout et al., 2002; Oudijk, 2007).

Because the age-dating method described herein is semi-quantitative, it may be difficult to assign an error range. Furthermore, there have not yet been experiments to test these techniques and evaluate what these error ranges may be. Nevertheless, one should assume that the range, under the best of scenarios, may be ±2 years and, under many circumstances, it may only provide a 5-year age window. In other circumstances, the method may only be able to constrain the age, wherein an example of an opinion might be 'less than 5 years' or 'greater than 10 years.'

One important limitation to this method is the presence of multiple, overlapping releases. It may be possible to distinguish the releases, but applying an age to each may be exceedingly difficult.

The limitations of the methods described herein need to be fully understood by its users and should be explained whenever an age-dating opinion is provided. As stated by Morgan & Bull (2007, p. 56),

"Fundamental differences exist between forensic geoscience and its sister disciplines, fundamental enough to make the unwary geoscientist succumb to philosophical and practical pitfalls which will not only endanger the outline of their report, but may well indeed provide false-negative or false-positive results leading to contrary or inaccurate conclusions. In the law, such outcomes have devastating and untenable consequences".

The need to apply age-dating methods cautiously cannot be understated. It must be noted that the methods described herein may not be applicable to all spill sites. It is certainly possibly that site-specific circumstances could exist to preclude these methods from consideration. The investigator will need to carefully consider each site individually and the possibility exists that other methods, such as tree-ring studies, isotopic analyses or groundwater migration rate calculations, may be more applicable or financially viable.

15. Conclusions

Because of costs associated with cleanups, many cases come to litigation. Age dating is often central to the litigation. For a plaintiff or defendant to be successful, a legally defensible age-dating method is needed. The C&L method, which is solely dependent on chemistry, has been strongly attacked inside and outside the courtroom. Hence, a revised method is needed and proposed here.

Each pollution site has specific characteristics that must be evaluated. Investigators need a thorough understanding of the geologic and hydrologic conditions, in addition to the nature of the release. Investigators also need to combine knowledge of chemistry, microbiology, and site-specific history to provide an opinion on the release time frame. Because scientific processes associated with releases are too complex to model through a simple formula, a qualitative or semi-quantitative technique is needed. The methods described herein are an effort to develop such an approach.

16. References

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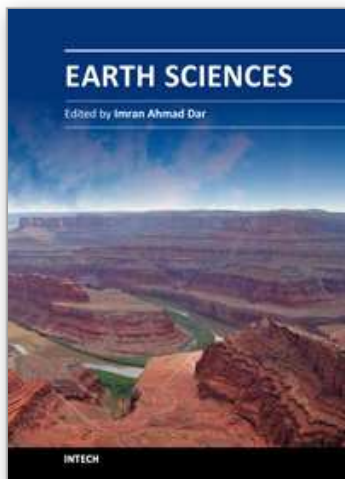
Earth Sciences

Edited by Dr. Imran Ahmad Dar

The studies of Earth's history and of the physical and chemical properties of the substances that make up our planet, are of great significance to our understanding both of its past and its future. The geological and other environmental processes on Earth and the composition of the planet are of vital importance in locating and harnessing its resources. This book is primarily written for research scholars, geologists, civil engineers, mining engineers, and environmentalists. Hopefully the text will be used by students, and it will continue to be of value to them throughout their subsequent professional and research careers. This does not mean to infer that the book was written solely or mainly with the student in mind. Indeed from the point of view of the researcher in Earth and Environmental Science it could be argued that this text contains more detail than he will require in his initial studies or research.

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