Age significance of nC_{17}/Pr ratios in forensic investigations of refined product and crude oil releases

Richard W. Hurst and Gene W. Schmidt

ABSTRACT

Since the 1980s, several techniques have been developed to estimate the year a petroleum hydrocarbon release occurred. In this article, we evaluate and expand on the model of Christensen and Larsen, who proposed that the degradation of normal heptadecane relative to pristane (i.e., nC_{17}/Pr ratios) could be used to estimate the age of diesel fuels released into the environment. Linear regression analyses of nC_{17}/Pr ratios from known subsurface releases of crude oil, middle distillate, fuel oil, and lubricating oil in diverse climatic settings (Subarctic, temperate, and tropical) define a statistically significant, negative linear correlation termed the middle distillate degradation (MDD) model, in which, like the Christensen-Larsen model, nC_{17} is almost entirely degraded within about 20 yr. By comparison, our investigations indicate that degradation of nC_{17} relative to Pr in aerobic, surface environments is also systematic, following a first-order kinetic relationship in which nC_{17} degrades about 5–6 yr subsequent to the release. As observed by others, the timescale of degradation under aerobic conditions is accelerated.

We also present analyses of average initial $(nC_{17}/Pr)_o$ ratios of about 4500 worldwide crude oils and 90 domestic refined products (diesel jet A, fuel oils) to evaluate how variations in this parameter impact MDD model ages. As stipulated in debates surrounding the original Christensen-Larsen model, applications of the MDD model should be evaluated carefully on a case-by-case basis and not in an ad hoc fashion. Our results not only provide a database for evaluating the significance of geographic variations in $(nC_{17}/Pr)_o$ ratios but also allow experienced investigators to estimate MDD model age uncertainties (3–10-yr window of uncertainty under optimal to worst case conditions, respectively) at sites where it is determined that such models are applicable.

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INTRODUCTION

In 1993, Christensen and Larsen published a model (hereafter, the Christensen-Larsen [C-L] model), which they proposed could estimate the age of diesel releases to about ±2 yr. The C-L model was calibrated using measured ratios of n-heptadecane to 2,6,10,14-tetramethylpentadecane (i.e., n-C_{17} and pristane, Pr, respectively) extracted from soils impacted by diesel releases of known age (∼5–20 yr old) in Denmark. Christensen and Larsen observed a linear relationship between the nC_{17}/Pr ratio of weathered diesel and time elapsed since the release. The relationship, as approximated by Kaplan et al. (1997), is

$$T \text{ (years)} = -8.4(nC_{17}/Pr) + 19.8$$

The observed decrease in the nC_{17}/Pr ratio over time was attributed to the preferential degradation of the n-alkane, nC_{17}, relative to pristane, an isoprenoid hydrocarbon. Christensen and Larsen (1993) also analyzed 11 fresh diesel samples to assess variations in initial nC_{17}/Pr ratios (hereafter $(nC_{17}/Pr)_o$); they observed a range of 1.5–2.5 (95% confidence level standard error of the mean) and an average value of 1.98.

Given the importance of accuracy and scientific defensibility of models designed to estimate the age of petroleum hydrocarbon releases, it is not surprising that the applicability and scientific validity of the C-L model have been the subject of debate (Kaplan and Galperin, 1996; Schmidt, 1996, 1998; Kaplan et al., 1997; Morrison, 2000a, b; Smith et al., 2001; Wade, 2001; Alimi, 2002; Stout et al., 2002; Wade, 2002; Kaplan, 2003). These authors note that variations in $(nC_{17}/Pr)_o$ of diesel fuel released at a site and the rate of degradation of nC_{17} relative to Pr, the latter a function of local site conditions (Bossert and Bartha, 1984; Alvarez and Vogel, 1995; Alvarez et al., 1998), contribute to uncertainties in C-L model age estimates. Wade (2001, 2002) observed that investigations concerning the applicability of the C-L model to releases at sites where conditions differ significantly from those in Denmark have not been performed. The two extreme views regarding the applicability of the C-L model range from those of Smith et al. (2001), who conclude the C-L model is totally inappropriate in any situation, to those of Schmidt (1996, 1998), Wade (2001, 2002), and Alimi (2002), who suggest that the C-L model may be used, with caution, to estimate the age of middle distillate, heavy fuel oil, and crude oil releases in some areas of the United States and Europe.

In this article, we will address these uncertainties, providing data on variations in $(nC_{17}/Pr)_o$ and incorporating data from sites whose climatic conditions range from temperate to tropical to assess the impact on the rate of degradation and resultant C-L model age estimates. Measured $(nC_{17}/Pr)_o$ ratios of about 4500 worldwide crude oils and 90 domestic petroleum products are presented to provide constraints on the statistical variation in this parameter and its impact on resultant model ages. The original C-L model data (Christensen and Larsen, 1993) have been reproduced by transformation (scanning and scaling into a coordinate system; A. J. Skarnulis, 2003, personal communication), so that coordinates of each datum point could be determined. Their data have been integrated with data from Schmidt (1996, 1998), Wade (2001), Hurst (this study), and new data from documented middle distillate and crude oil releases from diverse geographic regions in the United States and the Caribbean to assess potential effects of subsurface temperature variations and spill location, i.e., subsurface vs. surface, on the degradation of nC_{17} relative to pristane.

The culmination of these data is a modified C-L model, the middle distillate degradation (MDD) model, for consideration as a tool to evaluate the age of middle distillate, heavy fuel oil, and crude oil releases up to about 20 yr old. The MDD model should be applied on a case-by-case basis, heeding the concerns noted (references above) regarding ad hoc applications of any model in environmental forensic investigations. A second article, Schmidt and Hurst (unpublished data) will focus on case studies in which the MDD model was used either independently or in conjunction with the anthropogenic lead archeostratigraphy model of Hurst (2000, 2002, 2003) to estimate ages of middle distillate and contemporaneous leaded aviation gasoline releases at sites in the United States.

HIGH-RESOLUTION GAS CHROMATOGRAPHY

Accurate and precise measurements of nC_{17}/Pr ratios require high-resolution gas chromatography (HRGC), in which individual peaks are identified and resolved, peak overlap and asymmetry are minimized, and signal-to-noise ratios are high. It is also imperative that standards are analyzed routinely to calibrate the gas chromatograph, assess baseline drift, and evaluate the reproducibility of the instrument (Dyson, 1995). For reference, representative HRGCs of fresh diesel and jet A are shown in Figure 1a and b, respectively; these can

be compared to chromatograms of weathered diesel and jet A (Figure 2a, b, respectively). Insets depict peak shape and baseline (dashed line) details at the retention times where nC_{17} and Pr elute from the column. The weathered products were sampled from releases that are in excess of 15 yr old.

As observed in the HRGC insets of both the fresh and weathered products, peak intensities of the noise (i.e., small peaks above the baseline in the valleys between the nC_{17}-Pr peaks) never exceed about 2 mV; hence, for fresh to moderately weathered free product, the signal-to-noise ratio is high; this ratio decreases as weathering proceeds. The nC_{17} and Pr peaks are well resolved, with negligible tailing and asymmetry even in the case of weathered product, where the intensity of the unresolved complex mixture has increased significantly relative to the peak heights of paraffins and isoprenoids (Figure 2a, b). When the nC_{17}/Pr ratio is approximately 0.1, resulting corrections to the nC_{17} peak caused by peak overlap produce a higher uncertainty in the nC_{17}/Pr ratio.

Measured $(nC_{17}/Pr)_o$ ratios of the fresh diesel and jet A (2.0 and 2.3; Figure 1a, b, respectively) are comparable to those measured on 92 domestic middle distillates and heavy fuel oils (2.0 ± 0.2; discussed later in this study). Peak intensities, and therefore concentrations, of nC_{17} and Pr are lower in jet A than in diesel (sample volumes injected for analysis are identical); however $(nC_{17}/Pr)_o$ ratios of jet A fuels analyzed in this study, like diesel, average approximately 2.0, reflecting those of their source crude oil (Schmidt, 1996, 1998; Morrison, 2000c; this study). Furthermore, although the boiling points of nC_{17} and Pr (302 and 296°C respectively [~570°F]; http://physchem.ox.ac .uk/MSDS) are similar to the cutoff temperature of jet A (~300°C; Kaplan, 2003), we have not observed any evidence for preferential fractionation of nC_{17} from Pr during refining of jet A that would result in higher variability in jet A $(nC_{17}/Pr)_o$ ratios relative to that observed in diesel fuels. Continued distillation of crude oil to about 400°C (~750°F), the cutoff temperature for diesel fuel, produces the higher concentrations of nC_{17} and Pr present in diesel fuels.

DEVELOPMENT OF THE MDD MODEL

The new nC_{17}/Pr ratios presented in this study were analyzed in soil and weathered product; ages of the hydrocarbon releases ranged from about 5 to 20 yr old.

In the case of soils, samples were collected at depths exceeding 4–5 m (13–16 ft), and residual total petroleum hydrocarbon concentrations were about 125–800 mg/kg (ppm).

New Site Details

Summaries of specific details regarding the type of hydrocarbon release, year of the release, year(s) of sampling, nature of the matrix analyzed, and average (nC_{17}/Pr) ratios measured on five to seven samples are presented below. The range in measured (nC_{17}/Pr) ratios, as determined from the standard error of the mean at the 95% confidence level, is shown in parentheses next to each average value. These data are plotted in Figure 3 as either the continental United States or the Caribbean data points.

West Texas
Inventory records indicated that a supply line to a production pipeline had released crude oil at two different locations and on two separate occasions; distances between the locations of the releases and site remediation data indicated the presence of two distinct plumes. The older release dated back to late 1975, whereas the younger release occurred in 1990. Sampling of free product and analysis by gas chromatography were performed in 1994 to evaluate the extent of the contamination. Measured (nC_{17}/Pr) ratios of degraded crude oil from the 1975 release averaged 0.15 (0.08–0.19), whereas those associated with the 1990 release averaged 1.89 (1.85–1.91).

In a separate incident, a refueling station pipeline in El Paso, Texas, released diesel fuel into the subsurface in 1990. Soil samples collected in 1994 yielded an average (nC_{17}/Pr) ratio of 1.8 (1.7–1.87).

Maryland and Georgia
Diesel fuel releases were documented at a Maryland fuel terminal (1978) and from a pipeline in Georgia (1986). Samples of hydrocarbon-impacted soils were collected in 1993 and 1994, respectively. Average (nC_{17}/Pr) ratios from Maryland samples averaged 0.53 (0.35–0.60); samples in Georgia averaged 1.34 (1.25–1.41).

Pennsylvania
A machine shop had a release of lubricating oil in 1978 that permeated the porous soils that comprised the floor. The business was closed, but the structure
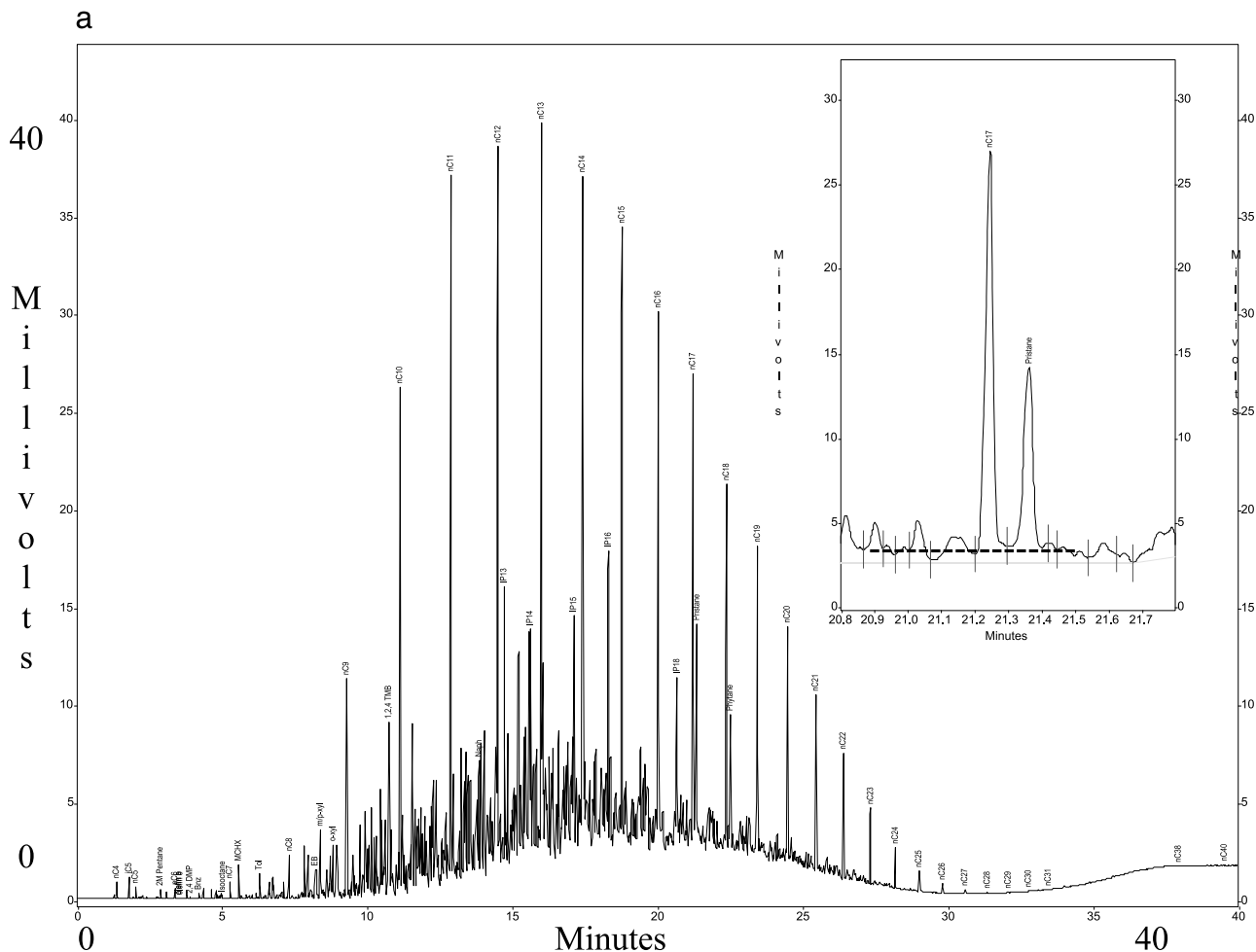
Figure 1. Representative high-resolution gas chromatograms of fresh (a) diesel and (b) jet A fuels. Note the excellent separation of nC_{17} from pristane (inset) and the high signal-to-noise ratio. Baseline is shown as a dashed line.

remained; no efforts were made at that time to remediate the release. In 1993, sampling of soils indicated the presence of lubricating oil whose measured (nC_{17}/Pr) ratios averaged 0.28 (0.24–0.35).

Caribbean

Diesel releases from damaged tanks and pipelines occurred as a result of severe hurricanes between 1982 and 1983. A part of the free product from disrupted subsurface pipelines migrated rapidly into the subsurface, impacting groundwater in the region. Free product samples were collected in 1997 and 2002 from the same monitoring wells to evaluate the extent of degradation of the diesel in the subsurface. Measured (nC_{17}/Pr) ratios of product collected in 1997 averaged 0.65 (0.44–0.72); results from the product in the same monitoring wells taken in 2002 average 0.13 (0.05–0.22).

Correlation of nC_{17}/Pr with the Age of the Release: Earlier Investigations

To evaluate the geographic applicability of the C-L model, comparative linear regression analyses of nC_{17}/Pr vs. T, the known age of a middle distillate release, were performed on each data set from the original Christensen and Larsen (1993) article, the work of Schmidt (1996, 1998), and recent results from Wade (2001). Each datum point plotted in Christensen and Larsen (1993) has been quantified through transformation to acquire specific coordinates, nC_{17}/Pr and release age, for each datum point. Linear regression analyses were performed using ISOPLOT, a program developed by the U.S. Geological Survey (Brooks et al., 1972; Ludwig, 1983) that accounts for analytical error in each datum point to produce the best-fit line; output from ISOPLOT includes the 95% confidence level
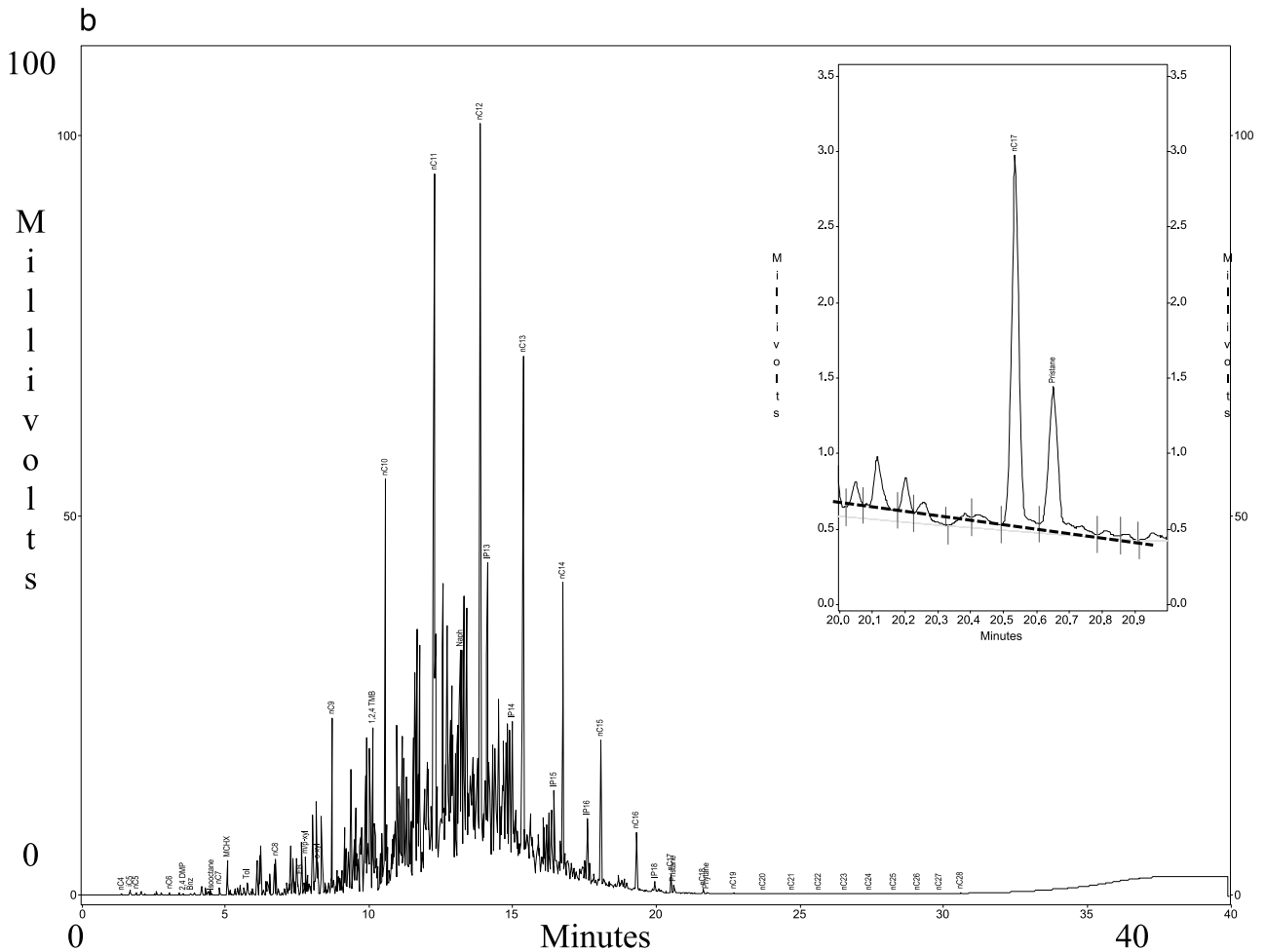
Figure 1. Continued.

errors in the slope and intercept as shown in Table 1 and plotted in Figure 3. The value of R^2, as determined from standard linear regression programs, is also provided.

Linear regression analyses of each independent data set from Christensen and Larsen (1993), Schmidt (1996, 1998), and Wade (2001) produce significant negative correlations between nC_{17}/Pr ratios and T ($R^2 = 0.896$–0.979). Although resultant slopes and intercepts differ, they are statistically indistinguishable when 95% confidence level errors are considered. Maximum model age variations, as determined by inputting a specific (nC_{17}/Pr) ratio into the C-L, Schmidt, and Wade models (Table 1; previous investigations), range from 0.7 to 1.7 yr. The largest discrepancy is observed when (nC_{17}/Pr) equals 2; the Wade model yields an age of -0.1 yr compared to the C-L model age of 1.6 yr; given the uncertainties in these models (± 1.4 to ± 1.87 yr, respectively; Table 1), the 1.7-yr difference in model

ages is not significant. Theoretically, as nC_{17}/Pr approaches zero, variations among the model ages range from 0.3 to 0.9 yr, determined by differences in values of T_o. These variations, once again, lie well within the reported age uncertainty associated with the model, ± 2 yr, as originally proposed by Christensen and Larsen (1993) and corroborated by both Schmidt (1996, 1998) and Wade (2001).

It is significant that the slopes of the linear regressions, i.e., degradation rate of nC_{17} relative to Pr, from the independent investigations (Table 1), are statistically indistinguishable, given the different geographic locations of each study. Wade (2001) evaluated the C-L model, as originally published, at sites in the northeastern United States, New England (Connecticut, Massachusetts, Maine, New Hampshire, Rhode Island, and Vermont), where surface temperature ranges and precipitation are generally comparable to those of Denmark. Schmidt (1996, 1998) evaluated the C-L model
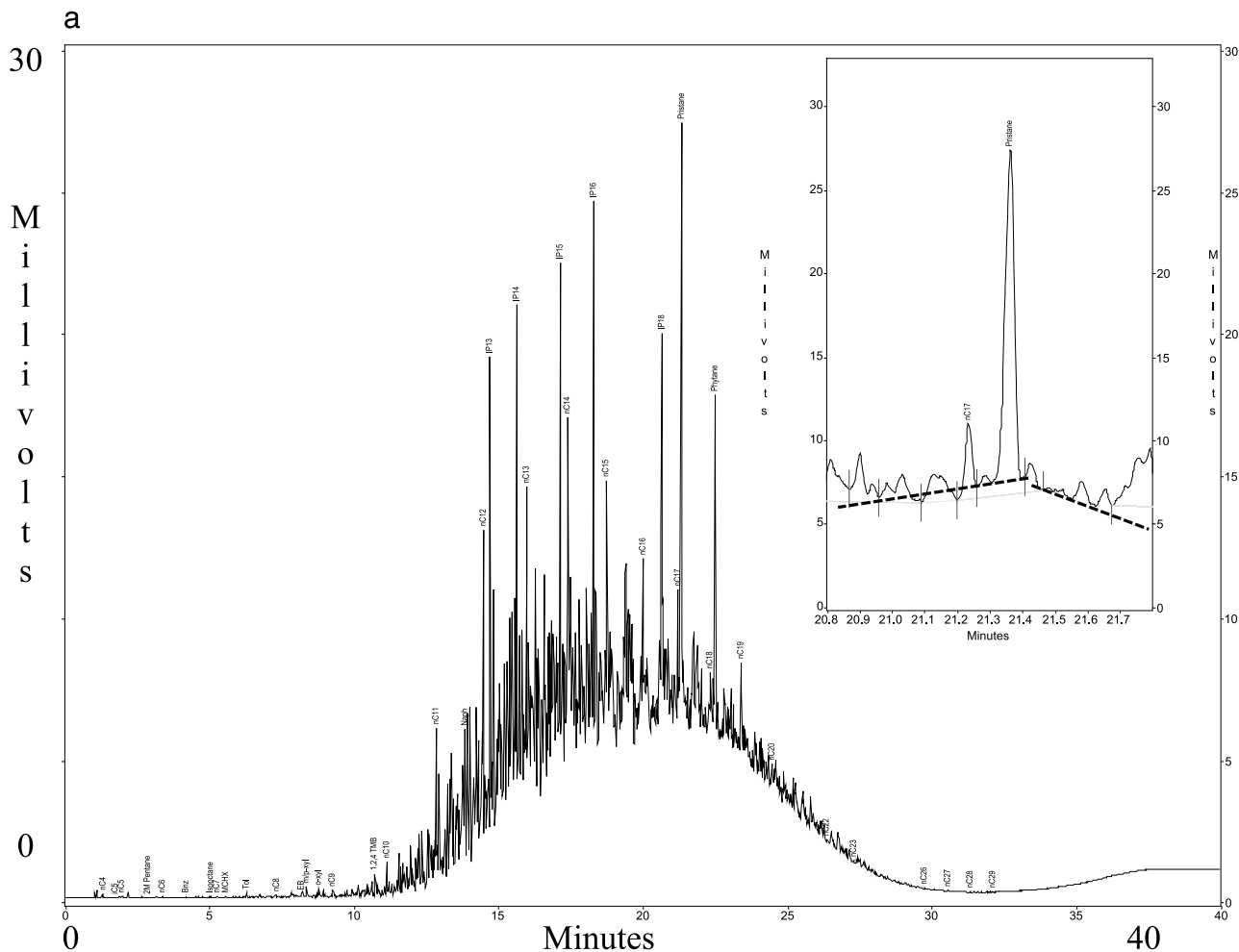
Figure 2. Representative high-resolution gas chromatograms of weathered (a) diesel and (b) jet A fuels. Although nC_{17}/Pr ratios are less than 0.4 in these products, nC_{17} and pristane are readily resolved from each other and the baseline (dashed line); note that peak overlap is now apparent because of the unidentified peak located between nC_{17} and pristane.

using domestic crude oil and diesel releases in areas where climate differs significantly from that of Denmark and the northeastern United States. Given good agreement between model ages determined by the C-L model and documented years of diesel and crude oil spills, both Wade and Schmidt concluded that the C-L model could potentially be applied to estimate ages of petroleum hydrocarbon releases in the United States.

Unified (MDD) Model: Subsurface Releases

Given the observed statistical concordance among the results of the linear regression analyses from the three independent studies, the three data sets and results from the new site analyses were combined and then regressed using ISOPLOT to generate the unified, MDD model (Table 1, Unified Model; Figure 3). Be-

cause the number of data points regressed has increased but the magnitude of scatter has not, the 95% confidence level errors in the MDD model slope and intercept decrease.

As observed in Table 1, 95% confidence level uncertainties associated with the MDD model linear regression are improved, approximately by factor of 2, relative to those of previous investigations (Christensen and Larsen, 1993; Schmidt, 1996, 1998; Wade, 2001). Absolute age variations between MDD model ages vs. those determined using the Christensen-Larsen, Schmidt, or Wade regressions, as calculated for nC_{17}/Pr ratios of 2.0 and 0.2, range from 1.2 to 0.4 yr, respectively; all models yield identical results, 11 yr, when nC_{17}/Pr equals 1.0.

The MDD model age resolution could theoretically approach ±1 yr if all of the following conditions
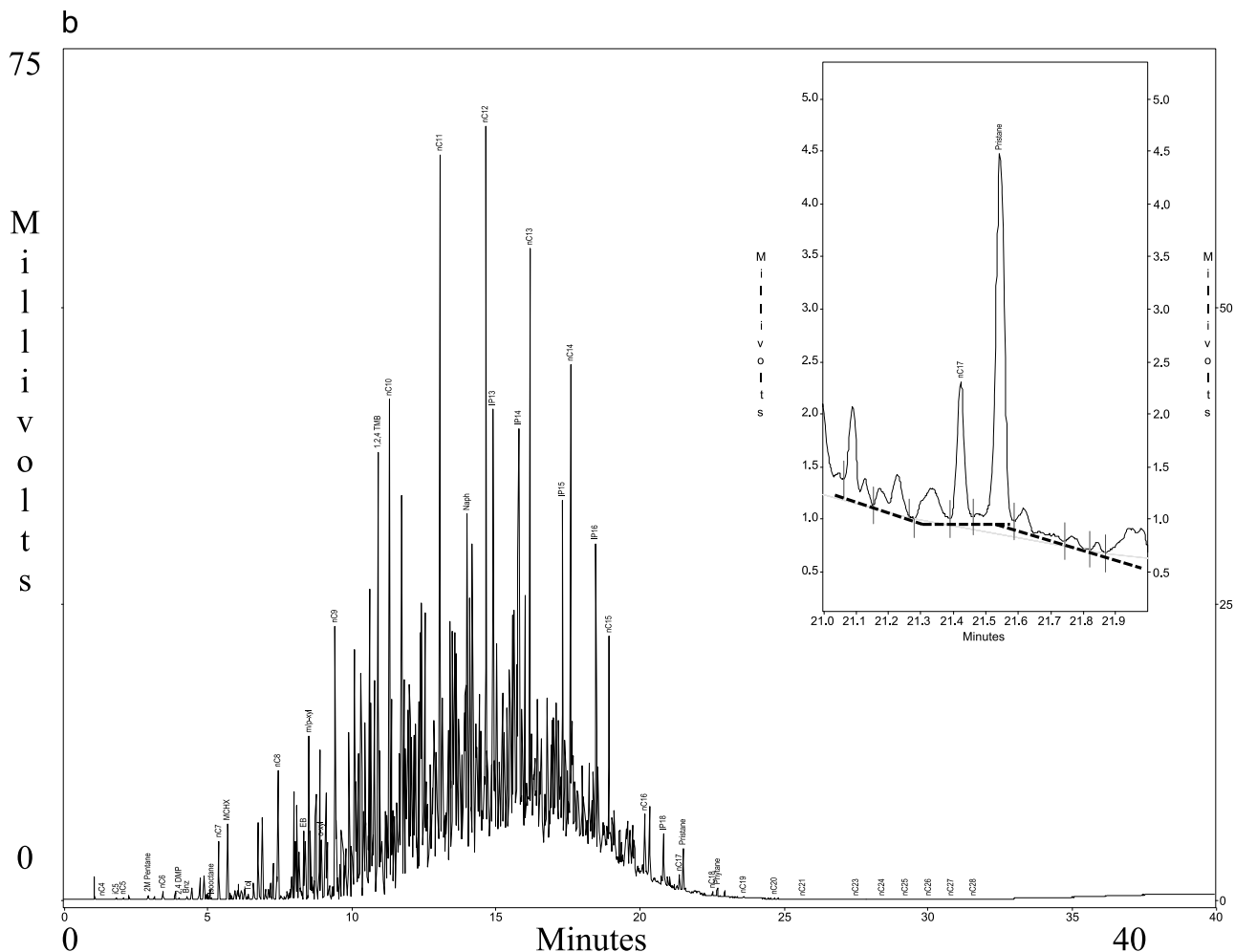
Figure 2. Continued.

were satisfied: (1) $(nC_{17}/Pr)_o$ ratios could be determined with reasonable certainty; (2) a sufficient number of statistically representative samples were analyzed; and (3) information pertinent to local environmental conditions were available. Being conservative, we recommend that the uncertainty be increased to ±1.5 yr, a 3-yr window, under optimal conditions. This increase also improves the statistical fit of the calibration data points to the MDD model regression shown in Figure 3; 31 of 35 (89%) calibration data points lie within the ± 1.5-yr confidence level interval as compared to 25 of 35 (71%), when the confidence level interval is ±1 yr. The effect of uncertainties in $(nC_{17}Pr)_o$ ratios on MDD model age resolution is discussed in the subsequent section.

The development of the MDD model implements the suggestion to evaluate the degradation of hydrocarbon releases in geographic regions where subsurface temperatures differ from those of Denmark (Wade, 2001, 2002); our work expands potential applications to estimating release ages for lubricating and crude oils, which have not been investigated (Kaplan, 2003). Because the degradation rate of nC_{17} relative to pristane observed in crude oil and diesel releases from Georgia, Texas, and the Caribbean is statistically indistinguishable from those determined in Denmark and the northeastern United States (Figure 3) (Christensen and Larsen, 1993; Schmidt, 1996, 1998; Wade, 2001; this study), we conclude that the observed temperature range in shallow soils and groundwater in a large part of the United States, about 8 to 20°C (Collins, 1925; Schmidt and Marsi, 1961; Heath, 1984; Hern and Melancon, 1986; van der Leeden et al., 1990), does not necessarily alter the degradation rate of nC_{17} relative to pristane in subsurface environments.
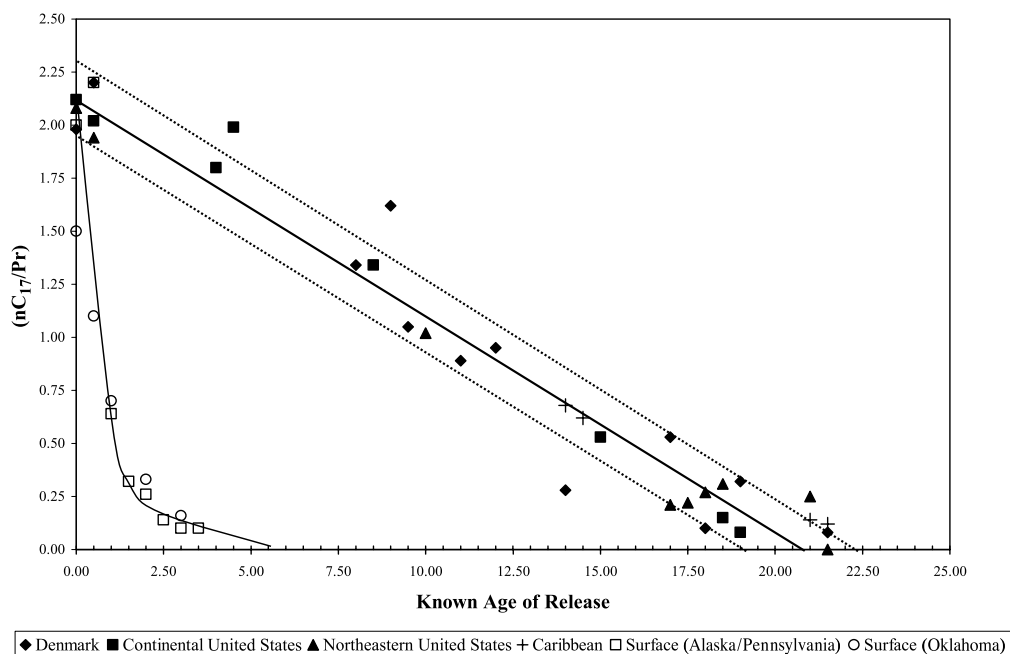
Figure 3. Middle distillate degradation model: nC_{17}/Pr vs. known ages of subsurface and surface releases of crude oil, diesel, jet A, and fuel oils. Data plotted are derived in part from the published literature (Denmark: Christensen and Larsen, 1993; northeastern United States: Wade, 2001; surface (AK/PA): Hostettler and Kvenvolden, 1994; Smith et al., 2001) as well as this work (all geographic locations except Denmark). The decrease in nC_{17}/Pr ratios as a function of time in crude oil and refined product releases in the subsurface define a well-correlated, linear trend (MDD model); the dotted error envelope around the best-fit linear regression indicates the 97.5% confidence level uncertainty, i.e., ± 1.5 yr. Surface releases of crude oil and middle distillate fuels (open symbols) define a first-order degradation curve in which nC_{17} is almost entirely degraded within approximately 5–6 yr.

VARIATIONS IN $(nC_{17}/Pr)_o$ RATIOS AND UNCERTAINTY IN MDD MODEL AGES

In this section, the uncertainties in MDD model ages that are dependent on the extent of our knowledge of $(nC_{17}/Pr)_o$ ratios at a particular site will be addressed through a series of scenarios. Conditions will range from those whose optimal $(nC_{17}/Pr)_o$ ratios are known or can be adjusted to account for variations in $(nC_{17}/Pr)_o$ to those where a broad range in $(nC_{17}/Pr)_o$ ratios, from about 1.6 to 2.6, might be used to estimate $(nC_{17}/Pr)_o$ in cases where sampling of the suspected source of a release is no longer viable.

Table 1. Comparative Linear Regression Analyses (nC_{17}/Pr vs. Time)

Name of Model	T (years) $= -\lambda\,(nC_{17}/Pr) + T_o$				
	Number of Data Points	λ (Slope)*	T_o	R^2	$(nC_{17}/Pr)_o$**
I. Previous investigations					
Christensen and Larsen (1993)	13	9.47 ± 1.87	20.5 ± 2.1	0.896	2.16 ± 0.22
Schmidt (1996, 1998)	9	9.36 ± 1.53	20.2 ± 2.4	0.967	2.16 ± 0.25
Wade (2001)	9	10.6 ± 1.40	21.1 ± 1.4	0.979	1.99 ± 0.13
II. Unified model					
MDD (this study)	35	9.76 ± 0.81	20.7 ± 1.0	0.952	2.12 ± 0.12

*Data have been fitted using ISOPLOT, a linear regression program that considers analytical errors associated with each datum point in the statistical fitting of the best-fit line (Brooks et al., 1972; Ludwig, 1983). The program calculates 95% confidence level errors in the resultant slope and intercept as shown.

**The $(nC_{17}/Pr)_o$ ratio is calculated from each linear regression model (i.e., the X-intercept when $nC_{17}/Pr = 0$).

Referring to Table 1, the MDD model regression (Table 1) is given by

$$T = -9.76 \, (nC_{17}/Pr) + 20.7$$

Setting T equal to zero, we obtain the following relationship between T_o and $(nC_{17}/Pr)_o$:

$$T_o = 9.76 \, (nC_{17}/Pr)_o$$

Based on the results of this study, the rate of degradation of nC_{17} relative to Pr in subsurface environments, i.e., the slope of the MDD model, appears to be constant. Thus, to adjust the MDD model regression for variations in $(nC_{17}/Pr)_o$ while maintaining the slope at 9.76, we use the relationship between T_o and $(nC_{17}/Pr)_o$ to calculate a new value for T_o. The value of T_o sets the upper limit to the oldest release that can be dated for a given value of $(nC_{17}/Pr)_o$. For example, if $(nC_{17}/Pr)_o$ of a release is known to be 1.5, T_o will equal 14.6 yr; for an $(nC_{17}/Pr)_o$ ratio of 4, T_o equals 39 yr. The latter example is interesting, in that it suggests that the age of hydrocarbon releases greater than 20 yr old might be modeled in cases where $(nC_{17}/Pr)_o$ of a release exceeds that of the MDD model (i.e., 2.12; Table 1). The data presented in this study do not allow us to evaluate dating releases greater than 20 yr old; in scenario 1 below, however, we provide an example using data from the northwestern United States plume discussed earlier, in which the MDD model age has been adjusted because the $(nC_{17}/Pr)_o$ of the diesel release exceeds that of the MDD model.

The scenarios are provided as suggested guidelines, providing limitations on the age resolution achievable using the MDD model given the variations in $(nC_{17}/Pr)_o$. Each scenario assumes that a statistically representative number of samples were analyzed, that sampling protocols are followed, and that site-specific environmental conditions have been evaluated.

Scenario 1: $(nC_{17}/P)_o$ is Known

If the $(nC_{17}/Pr)_o$ ratio of a hydrocarbon released at a site is known to be equivalent to that of the MDD model, 2.1 ± 0.1, the age uncertainty could theoretically approach ± 1 yr. As stated earlier, being conservative, an uncertainty of ± 1.5 yr, i.e., 3-yr window, would be reasonable under optimal conditions; no adjustment to resultant MDD model ages, as determined using the regression in Table 1, is required. As stated

above, what if $(nC_{17}/P)_o$ is known, but it is not equal to that of the MDD model? The northwestern United States plume discussed earlier provides an example of such a situation.

Case Study: Northwestern United States

Limitations on oxygen, water, and nutrients in the interior of a hydrocarbon plume have been suggested as inhibiting the rate at which hydrocarbons, including nC_{17} and Pr, degrade, thereby allowing hydrocarbons to persist in the environment for decades (Bossert and Bartha, 1984); we refer to these types of environments as conservative environments. Although such conservative environments may occur, the volume of literature published on hydrocarbon degradation indicates that such environments are not the norm. To address this issue in more detail, we investigated a large gasoline-diesel plume in the northwestern United States to (1) evaluate the effect of location within a free product plume on degradation rates; (2) study degradation of free product over a 13-yr interval; and (3) assess the impact of a significantly different $(nC_{17}/Pr)_o$ ratio on model ages (discussed later in this study).

The initial release of gasoline and diesel fuels is suspected to have started in the early 1970s as the result of a transfer line leak; the release continued until its detection in 1983 when remediation commenced. The dimensions of the about 10–15-yr-old release were 1350 m (4429 ft) in length, 125–400 m (400–1300 ft) in width, and up to 1.5 m (4.5 ft) in thickness. Given the plume length, 1350 m (4429 ft), and average groundwater velocity, about 0.45 m/day (1.5 ft/day), groundwater requires approximately 8 yr to migrate from the source of the release to the plume terminus. Although such inverse modeling is sometimes used to estimate the age of a release, contaminant plumes do not advect with groundwater, hence, inverse modeling commonly underestimates the age of a release (Morrison, 2000b; this study) as observed in this case.

A series of 12 free product samples were collected from groundwater monitoring wells at the following distances downgradient from the source: 250, 675, 1045, and 1350 m (820, 2214, 3428, and 4429 ft, respectively). Gas-chromatographic analyses were performed on each free product sample. The resulting nC_{17}/Pr ratios (samples from plume margins are italicized) and downgradient distance for each of the 12 samples are shown in Table 2.

The steady decrease in diesel-free product nC_{17}/Pr ratios correlates well with the distance from the source

Table 2. Downgradient (nC_{17}/Pr) Ratios in a Diesel Fuel Plume

Distance from Source	(nC_{17}/Pr) at the Plume	
	Margin	Interior
0		2.7; 3.0
250 m (820 ft)	2.5; 2.6	2.7
675 m (2214 ft)	2.0; 2.2	2.2
1045 m (3428 ft)	1.7; 1.7; 1.7	
1350 m (4429 ft)	1.3; 1.3	1.3

($R^2 = 0.998$) and, therefore, the time required for the free product to migrate from the point of the release.

As observed, nC_{17}/Pr ratios of the free product sampled from the interior of the plume 250 and 675 m (820 and 2214 ft) downgradient from the source are slightly higher than those at the plume margins; however, nC_{17}/Pr ratios of the free product from the plume interior vs. plume margins are equivalent in samples collected 1350 m (4429 ft) downgradient. The nC_{17}/Pr ratios of free product 1045 m (3428 ft) downgradient were all collected at the plume margin, yet the degradation of nC_{17} relative to Pr at this distance from the source remains consistent with that of the other samples. Variations in nC_{17}/Pr ratios of the product sampled at the plume margin vs. the interior do not exceed 10%, indicating similar, instead of vastly different, rates of degradation of nC_{17} relative to Pr in the hydrocarbon plume. Furthermore, our results and those of other investigators (Kaplan and Galperin, 1996; Schmidt, 1996, 1998; Kaplan et al., 1997; Smith et al., 2001; Wade, 2001; Alimi, 2002; Stout et al., 2002; Wade, 2002; Kaplan, 2003) concur, in that environmental conditions more commonly promote hydrocarbon degradation instead of long-term preservation. The study of this relatively large free product plume in the northwestern United States supports the conclusion by Schmidt (1996, 1998) that nC_{17}/Pr ratios of the free product, like residual diesel hydrocarbons in soil, decrease as a function of time.

Scenario 2: $(nC_{17}/Pr)_o$ is not Known

If no information was available for a specific release and $(nC_{17}/Pr)_o$ could not be estimated using regional refinery oil-supply data, a worst case scenario results, in which, as discussed by Kaplan (2003), an experienced investigator may only be able to constrain the age of the release as being either older or younger than about 10 yr, unless other site-specific information were available to further refine the age. In the MDD

model, uncertainties in modeling the age of a release increase as our confidence in $(nC_{17}/Pr)_o$ ratios decrease. Specifically, differentiation of the relationship between T_o and $(nC_{17}/Pr)_o$ indicates that

$$dT_o = 9.76 \ d(nC_{17}/Pr)_o \approx 10 \ d(nC_{17}/Pr)_o$$

Hence, an uncertainty of ± 0.1 in $(nC_{17}/Pr)_o$ results in an uncertainty of ± 1 yr in the MDD model age. When $(nC_{17}/Pr)_o$ can only be assumed to lie in the range defined by the statistical analyses of domestic crude oil and refined product $(nC_{17}/Pr)_o$ ratios presented in this study, about 1.6 and 3.0 (2.3 $\pm$ 0.7), the uncertainty in the MDD model ages becomes ± 7 yr, which is the worst case scenario.

Scenario 3: $(nC_{17}/Pr)_o$ can be Calculated

If records are available, e.g., regional refinery oil supply data, that allow $(nC_{17}/Pr)_o$ to be calculated, the MDD model could be used and model ages adjusted as previously discussed. Depending on the resulting level of uncertainty in $(nC_{17}/Pr)_o$, concomitant model age uncertainties would range from about ± 2 to ± 7 yr, that is, an age uncertainty that lies between our best and worst case scenarios.

Surface Releases

At sites involving surface hydrocarbon releases (i.e., aerobic conditions), measured nC_{17}/Pr ratios have been shown to produce erroneous C-L model ages (Smith et al., 2001; Wade, 2001). However, this does not necessarily compromise the use of nC_{17}/Pr ratios as a means of estimating the age of surface releases of middle distillates. Although degradation rates may be accelerated, if the degradation rate is systematic, significant site-specific model ages can be determined. To assess degradation rates and systematics of middle distillate and crude oil releases in surface environments, data from the work of Smith et al. (2001), F. D. Hostettler and K. A. Kvenvolden (1994, personal communication), and Schmidt (this study) are evaluated; these data are plotted in Figure 3 (surface data points).

The case study employed by Smith et al. (2001) to question the validity of the C-L model involved a surface release of diesel fuel in Pennsylvania that occurred in October 1993. Although the release was less than 3 yr old, ad hoc application of the C-L model to estimate the age of six free product samples collected between 1993 and 1996 yielded erroneous ages that

ranged from about 1 to 18 yr, the majority exceeding the known age of the release. A reevaluation of the data presented by Smith et al. (2001) indicates that degradation of nC_{17} relative to pristane follows a well-defined ($R^2 = 0.923$) first-order kinetic reaction given by

$$(nC_{17}/Pr)_t = (nC_{17}/Pr)_o \ e^{-\lambda t}$$

The parameters in this equation and their calculated value as determined by the regression of the data from Smith et al. (2001) are as follows: $(nC_{17}/Pr)_t$ is the (nC_{17}/Pr) ratio of the degraded product t years after the release; $(nC_{17}/Pr)_o$, the nC_{17}/Pr ratio of the undegraded middle distillate at the time of the release ($T = 0$) is 2.01; and λ, the nC_{17}/Pr decay constant, is 1.14. The value of $(nC_{17}/Pr)_o$ as calculated, 2.01, is in excellent agreement with those observed, 2.0–2.2 (Smith et al., 2001); and the decay constant, 1.14 per year, yields a half-life, $t_{1/2}$, for nC_{17}/Pr of approximately 0.6 yr. The erroneous C-L model ages led Smith et al. (2001) to conclude that nC_{17}/Pr ratios could not be used to estimate ages of diesel releases, and that the C-L model was scientifically invalid. However, although C-L model ages are not correct, the degradation of nC_{17} relative to pristane with time is systematic but has been accelerated by the aerobic conditions.

Rapid degradation of organic compounds in aerobic environments, including compounds perceived as being recalcitrant (e.g., polycyclic aromatic hydrocarbons), has been observed in crude oil released into Prince William Sound, Alaska, as a result of the 1989 Exxon Valdez disaster (Hostettler and Kvenvolden, 1994). Degradation of nC_{17} relative to Pr in Exxon Valdez crude oil residues collected in 1990 follow a first-order law that is indistinguishable from that determined from the Smith et al. (2001) data (Figure 3). Collectively, the Pennsylvania and Alaska data suggest that the timescale of degradation of nC_{17} in diesel fuel and crude oil released at the surface is approximately 5–6 yr; hence, age estimates using the original C-L or MDD model would be erroneous.

Garden Experiment
To further investigate degradation rates of diesel fuel in an aerobic environment, Schmidt performed a garden experiment, in which a small volume of diesel fuel was buried approximately 0.6 m (2 ft) below the ground surface in nutrient-rich, sandy soil. Samples of the diesel fuel were collected quarterly over a period of about 2 yr and the (nC_{17}/Pr) ratio of the degraded diesel fuel present in the soil measured (Figure 3; Sur-

face OK). Although the $(nC_{17}/Pr)_o$ of the diesel fuel in the garden experiment differs from that observed in Pennsylvania and Alaska diesel fuels (1.5 vs. 2.1, respectively), the overall morphology of the (nC_{17}/Pr) time dependency curve is very similar to that observed in the Pennsylvania–Alaska studies and again, nC_{17} in the Oklahoma garden experiment will be totally degraded within 5–6 yr.

These results concur with those of previous studies (Bossert and Bartha, 1984; Alvarez and Vogel, 1995; Kaplan and Galperin, 1996; Kaplan et al., 1997; Alvarez et al., 1998; Morrison, 2000b; Smith et al., 2001), which suggest that the rate of degradation of organic compounds is accelerated in surface aerobic environments compared to those in the subsurface, where conditions are less aerobic. Although age estimates of middle distillate and crude oil releases in highly aerobic environments may be limited (≤ 5–6 yr), the results are neither meaningless nor do they necessarily invalidate age-dating models based on the degradation of nC_{17} relative to Pr in petroleum hydrocarbons.

MEASURED $(nC_{17}/Pr)_o$ RATIOS OF CRUDE OILS AND MIDDLE DISTILLATES

In the original Christensen and Larsen (1993) model, 11 fresh diesel samples were analyzed to evaluate variations in $(nC_{17}/Pr)_o$ ratios. Their results indicated an average $(nC_{17}/Pr)_o$ ratio of 1.98 with a 95% confidence level standard error of the mean of 0.50 (hereafter $2\sigma_{sem}$; calculated from their standard deviation of 0.83). As discussed later, an uncertainty of this magnitude in $(nC_{17}/Pr)_o$ alone doubles the uncertainty of ± 2 yr in C-L model ages proposed by Christensen and Larsen (1993; Hurst, 2003). Variations in $(nC_{17}Pr)_o$ and their potential impact on MDD model ages are best addressed by first examining measured ranges in $(nC_{17}/Pr)_o$ ratios of crude oils and refined petroleum hydrocarbons.

$(nC_{17}/Pr)_o$ Ratios in Domestic and Foreign Crude Oils

Between 1965 and 2000, HRGC analyses have been performed on thousands of foreign and domestic crude oils, the vast majority being compiled by the petroleum industry in unpublished studies (e.g., Amoco Crude Oil Analysis Program, 1965–1990; hereafter, COAP); segments of these studies have been published in the annals of special symposia (Schmidt, 1996, 1998). Results from the COAP investigation

have recently been released (G. W. Schmidt, unpublished data), and average $(nC_{17}/Pr)_o$ ratios from this extensive database are incorporated in this study. Our analyses of the COAP database included 4541 domestic and foreign crude oils, with the emphasis placed on 3549 crude oils from sources that provide about 85–90% of the crude refined in the United States (*Oil & Gas Journal*, 2002; hereafter OGJ, 2002). Note that average $(nC_{17}/Pr)_o$ ratios of domestic and foreign crude oils presented in Tables 3 and 4, respectively, are not

Table 3. Average $(nC_{17}/Pr)_o$ Ratios of Domestic Crude Oils

State	Production (thousands bbl/day)*	n*	(nC_{17}/Pr)
PADD 1: East Coast			
Florida	10	7	2.2
PADD 2: Midwest*			
Kansas	93	123	2.4
Oklahoma	188	151	2.2
North Dakota	87	45	6.5
PADD 3: Gulf Coast			
Louisiana	1621	600	2.4
Mississippi	54	8	1.8
Texas	1364	744	1.9
New Mexico	186	55	1.5
PADD 4: Rocky Mountain			
Colorado	45	221	2.0
Montana	44	135	3.4
Utah	42	125	1.8
Wyoming	157	308	1.8
PADD 5: West Coast			
Alaska	963	96	1.9
California	799	119	1.0
Grand mean**		2737	2.3 ± 0.7
Grand mean (North Dakota excluded)		2692	2.0 ± 0.3
Weighted mean**		2737	2.1

*Production figures given in thousands of barrels per day; n = number of crude oils analyzed; PADD = Petroleum Administration Defense District.

**Grand mean calculated from the average $(nC_{17}/Pr)_o$ ratios of the 13 United States crude oils tabulated; error is 2σ standard error of the mean. Weighted mean is calculated using average 2001 production figures for each State (in thousands of barrels per day; *Oil & Gas Journal*, December 23, 2002).

determined from a single producing zone in one field. Instead, they were calculated using representative samples throughout active oil fields in regions either in the United States or overseas. Hence, although crude oils in a region may exhibit a range of $(nC_{17}/Pr)_o$ ratios, transport and storage of crude oil mixes the oil, reducing the observed range in $(nC_{17}/Pr)_o$ ratios of the resultant blended oil. Individual $(nC_{17}/Pr)_o$ ratios for about 3400 of the domestic plus foreign crude oils analyzed in our investigation are plotted in Figure 4.

Average $(nC_{17}/Pr)_o$ ratios of 2737 domestic crude oils, which account for about 90–95% of domestic crude produced in the United States (OGJ, 2002) are shown in Table 3. For reference, results have been grouped using their Petroleum Administration Defense District (PADD), i.e., regional, designations. The grand mean $(nC_{17}/Pr)_o$ ratio for domestic crude oil average $(nC_{17}/Pr)_o$ ratios is 2.3 ± 0.7 ($2\sigma_{sem}$; Table 3); the weighted mean, 1.9, which apportions each state's relative contribution to the total United States crude oil production, is calculated as follows:

$$(nC_{17}/Pr)_o^{WTD} = \sum_i [(p_i/P)(nC_{17}/Pr)_{o,i}]$$

where p_i is the crude oil production in thousands of barrels per day for a specific state (OGJ, 2002); P is the total United States crude oil production (from Table 3; $P = 2737 \times 10^3$ bbl/day); and $(nC_{17}/Pr)_{o,i}$ is the average $(nC_{17}/Pr)_o$ ratio for crude oil produced in a specific state. Weighted means reduce the impact of datum that could be considered as outliers, such as North Dakota crude oil (minor producer with an anomalously high crude oil $(nC_{17}/Pr)_o$ ratio). For comparison, the grand mean $(nC_{17}/Pr)_o$ ratio and related $2\sigma_{sem}$ for domestic crude oils, 2.3 ± 0.7, drop to 2.0 ± 0.3, if the North Dakota crude oil datum point is excluded (Table 3).

The grand mean $(nC_{17}/Pr)_o$ ratio of foreign crude oils produced by major importers, which account for approximately 75–80% of oil imported into the United States, is identical to that of domestic crude oils, 2.3 ± 0.5 ($2\sigma_{sem}$; Table 4). Average $(nC_{17}/Pr)_o$ ratios of Mexican and the Middle Eastern crude oils tend to exceed 3.0, with Saudi Arabian crude oil exhibiting the highest ratio, 5.1; $(nC_{17}/Pr)_o$ ratios of the 13 remaining foreign crude oils from Canada, South America, Africa, and Eurasia range from 1.0 to 2.2, with seven exceeding 1.8. Blending significant proportions of crude oil from a major importer, such as Saudi Arabia or Middle East in general, with domestic crude during refining increases the $(nC_{17}/Pr)_o$ ratio of both the blended crude

Table 4. Average $(nC_{17}/Pr)_o$ Ratios of Foreign Crude Oils

Location	Country	Import Volume (thousands bbl/day)*	n*	(nC_{17}/Pr)
North America	Canada	1856	287	1.9
	Mexico	1440	37	3.4
South America	Argentina	no data	51	1.8
	Venezuela (Organization of Petroleum Exporting Countries [OPEC])	1496	40	1.4
Middle East/Africa	Algeria (OPEC)	273	33	2.2
	Kuwait (OPEC)	248	3	4.4
	Nigeria (OPEC)	768	24	1.0
	Saudi Arabia (OPEC)	1622	17	5.1
	Abu Dhabi	no data	24	3.9
	Iran	no data	15	3.4
	United Arab Republic	no data	277	2.4
	Gabon	no data	49	1.3
	Libya	no data	33	1.9
EurAsia	England	384	248	1.8
	Norway	383	123	1.8
	Azerbaijan	no data	51	1.6
	Indonesia	no data	153	1.5
	Pakistan	no data	36	1.4
	Russia	no data	303	1.9
Imported crude oil grand mean**			1804	2.3 ± 0.5

*Imported crude oil volume given in thousands of barrels per day (bbl/day); n = number of crude oils analyzed. Average annual 2001–2002 import volumes are shown for nine crude oils for which data exist (*Oil & Gas Journal*, January 27, 2003).

**Grand mean calculated from the average $(nC_{17}/Pr)_o$ ratios of the 19 imported crude oils tabulated; error is 2σ standard error of the mean.
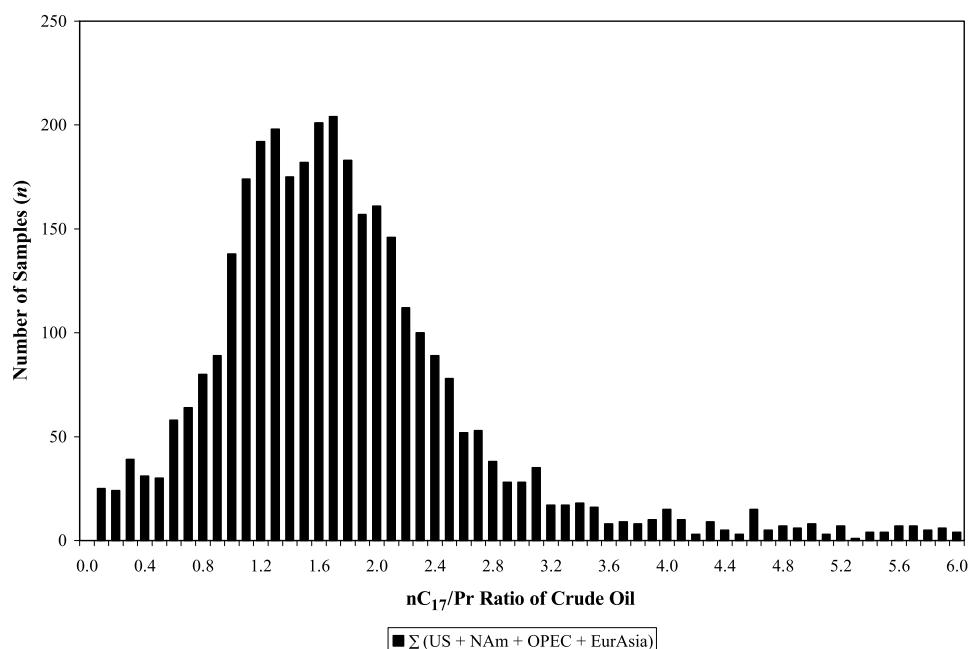

Figure 4. A histogram depicting 3401 $(nC_{17}/Pr)_o$ ratios of domestic and foreign crude oils from sources that provide about 80–85% of the crude oils refined in the United States. The data exhibit a normal distribution in which the mean, 1.9, is approximately equal to the mean 1.8. NAm = North America; OPEC = Organization of Petroleum Exporting Countries; EurAsia = Europe and Asia.

■ Σ (US + NAm + OPEC + EurAsia)

and refined product. Hence, drawing the conclusion that products refined in California will have exceptionally low $(nC_{17}/Pr)_o$ ratios, reflecting those of California crude, is not correct as discussed in the next section.

The worldwide crude oil data indicate the statistical averages, i.e., weighted and grand means, of domestic and foreign crude oil $(nC_{17}/Pr)_o$ ratios analyzed in this study range from 1.9 to 2.3. The overall range determined by incorporating the 95% confidence level standard error of the mean, $\pm2\sigma_{sem}$, is about 1.6 to about 3.0. These results are similar to $(nC_{17}/Pr)_o$ ratios calculated from the linear regression models of Christensen and Larsen (1993), Schmidt (1996, 1998), Wade (2001), and this study, which range from about 1.8 to 2.4 (Table 5, bottom) when the 95% uncertainty is considered.

Crude Oil Blending: The California Example

If middle distillates in California were refined entirely from California crude, the resultant $(nC_{17}/Pr)_o$ ratios of these products would be low, typically less than 1.5 and perhaps as low as 1.0. However, California refineries blend crude oils from several sources that include California, Alaska, and foreign crude. The effect of blending crude and the impact on $(nC_{17}/Pr)_o$ ratios of the blended crude oil and subsequent refined products can be demonstrated using data from the California Energy Commission (CEC; http://www.energy.ca.gov).

The low $(nC_{17}/Pr)_o$ ratios of California crude oils, which average 1.0 but can range up to approximately 1.5 (Magoon and Isaacs, 1983; R. L. Ames, 2004, personal communication), would result in significant errors in MDD model ages if the model was applied without consideration for variations in $(nC_{17}/Pr)_o$. However, CEC statistics indicate that since about 1985, only about 45–50% of crude oil refined in California originates from California oil fields. Since 1985, foreign sources of crude oil refined in California have increased from about 5 to 25%, with the remaining 25–45% of the refined crude oil originating in Alaska. Mexican and Middle Eastern crude oils with high $(nC_{17}/Pr)_o$ ratios are predominant ($\sim$70%), which results in an average $(nC_{17}/Pr)_o$ ratio of about 3.2 for the foreign component of crude oil refined in California. Thus, the calculated average $(nC_{17}/Pr)_o$ ratios of crude oil refined in California, using CEC oil supply source statistical data and Amoco COAP Project results, has ranged from about 1.6 in the mid-1980s to about 2.1 in 2001. These values exceed those of unblended California crude oil yet are consistent with those of 16 western United States middle distillates analyzed in this study (1.8–2.0; Table 4). Concerns

Table 5. $(nC_{17}/Pr)_o$ Ratios: Refined Products and Calculated (Linear Regressions)

Location or State	Product	Number Analyzed	$(nC_{17}/Pr)_o$
PADD 1: East Coast			
Northeast	Diesel	29	2.1
PADD 2: Midwest			
Indiana	Blend oil	1	2.0
	Heavy naphtha	1	1.6
	JP-8	1	1.9
	Diesel	5	1.8
	Jet A	2	2.0
	Kerosene	1	2.1
	Motor/lube oil	6	2.6
	Fuel oil	2	2.1
	Furnace oil	2	1.9
Oklahoma	Kerosene	2	2.1
	Diesel	2	2.3
	Transmission oil	2	1.9
Michigan	Diesel	1	1.4
	Furnace oil	3	1.6
Minnesota	Diesel	1	1.9
Tennessee	Kerosene	1	2.0
PADD 3: Gulf Coast			
Louisiana	Kerosene	1	1.4
Texas	Jet A	1	1.7
	Diesel	5	1.8
PADD 4: Rocky Mountain			
Colorado	Diesel	1	2.5
Utah	Diesel	3	1.8
PADD 5: West Coast			
Arizona	Jet A	1	4.0
Western United States	Kerosene/jet A	2	1.8
	Diesel	8	1.9
	Fuel oil	6	2.0
United States petroleum product grand mean		90	2.0 ± 0.2

$(nC_{17}/Pr)_o$ calculated from linear regression models**

Christensen and Larsen (1993)	2.16 ± 0.22
Schmidt (1996)	2.16 ± 0.25
Wade (2001)	1.99 ± 0.13
MDD model	2.12 ± 0.12

*Grand mean calculated from the average $(nC_{17}/Pr)_o$ ratios of the 26 petroleum products tabulated; error is 2σ standard error of the mean (95% confidence level).

**For comparison, the $(nC_{17}/Pr)_o$ ratio is calculated from each linear regression model (see Table 1).
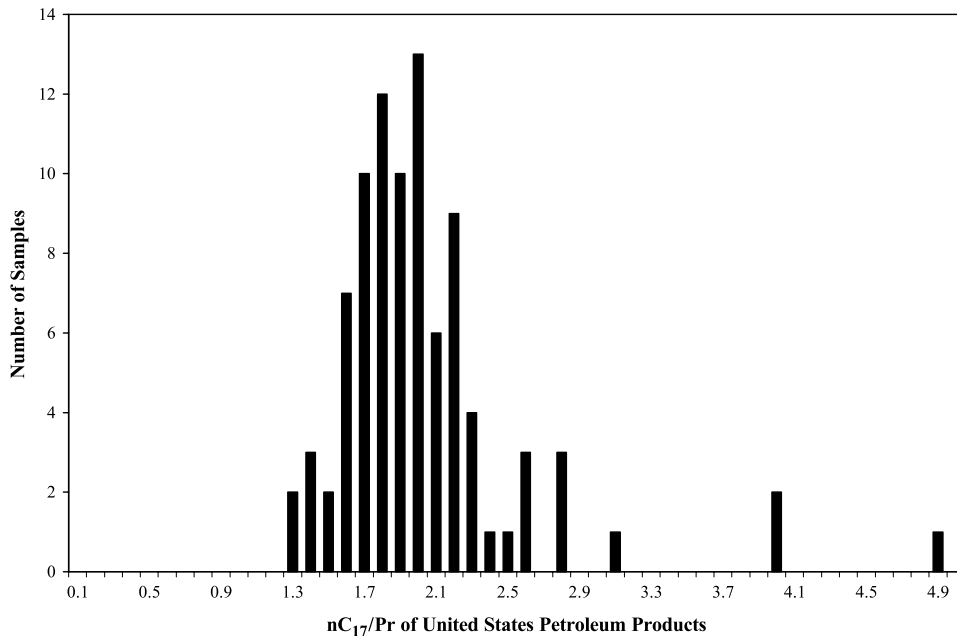
14

12

10

8

6

4

2

0
0.1   0.5   0.9   1.3   1.7   2.1   2.5   2.9   3.3   3.7   4.1   4.5   4.9

Number of Samples

nC$_{17}$/Pr of United States Petroleum Products

Figure 5. A histogram of (nC$_{17}$/Pr)$_o$ ratios for 90 domestic refined products. The data define a normal distribution in which the mean $\approx$ median, 2.0 and 1.9, respectively.

regarding ad hoc applications of the C-L model and the impact of uncertainties in (nC$_{17}$/Pr)$_o$ on model ages are well founded (Wade, 2001; Kaplan, 2003). However, in some cases, uncertainties associated with (nC$_{17}$/Pr)$_o$ ratios may be reduced by integrating the data presented in this study with region-specific oil supply statistics, when available (Hurst, 2003).

(nC$_{17}$/Pr)$_o$ Ratios of Domestic Middle Distillates and Fuel Oils

Analyses of 90 middle distillate and fuel oil average (nC$_{17}$/Pr)$_o$ ratios analyzed between 1970 and 1990 are presented in Table 5 and plotted as individual datum in Figure 5; PADD designations are again provided for reference. The average (nC$_{17}$/Pr)$_o$ ratio of these refined products, 2.0 ($\pm$ 0.2; 2σ_{sem}), and the median, 1.9, indicate a normal distribution; the average is also statistically indistinguishable from those observed in crude oils analyzed in this study, indicating that crude oil (nC$_{17}$/Pr)$_o$ ratios are passed conservatively to refined products (Schmidt, 1996, 1998; Morrison, 2000b; Murphy and Morrison, 2002). Of the 90 refined products analyzed, approximately 85% of the (nC$_{17}$/Pr)$_o$ ratios lie between 1.6 and 2.6. The range observed in (nC$_{17}$/Pr)$_o$ ratios of refined products, i.e., 1.3–4.9, when compared to that observed in crude oils, 0.1 to greater than 6.0 (Figures 4, 3, respectively) is again an indication that blending of crude oils during refining, as discussed previously, serves to reduce the overall variation in (nC$_{17}$/Pr)$_o$ ratios.

CONCLUSIONS

The degradation of nC$_{17}$ relative to Pr, the MDD model, has the potential to constrain the age of crude oil, diesel, jet A, and fuel oil releases, within certain limits, into the environment. However, we reemphasize the concerns stipulated in the scientific literature that due diligence and care should be exercised prior to the application of this, or any, model used to estimate ages of petroleum hydrocarbon releases.

In this study, we have integrated both published and new data from petroleum hydrocarbon releases to evaluate the Christensen and Larsen (1993) model at sites whose climatic conditions range from those of Denmark, where the C-L model was originally developed, to sites in the southern United States and the Caribbean with tropical climates. Our results indicate that subsurface releases of crude oils, diesel, and fuel oils do not degrade at a rate that is statistically distinguishable from that of the original C-L model, thereby allowing us to develop a unified model, the MDD model, as a potential tool to estimate ages of such releases.

Resultant age uncertainties associated with applications of the MDD model are dependent on local environmental conditions and variations in (nC$_{17}$/Pr)$_o$ ratios. Under optimal conditions, MDD model age uncertainties of $\pm$1.5 yr may be achieved; as our confidence in the value of (nC$_{17}$/Pr)$_o$ ratios of the product released and our knowledge of site conditions decrease, MDD model age uncertainties increase to $\pm$7 yr.

In aerobic environments, we observe that surface releases of petroleum hydrocarbons weather rapidly, with nC_{17} being totally degraded within about 6 yr. Under such conditions, ad hoc application of the MDD model is not appropriate given that erroneous ages result (Smith et al., 2001); hence, the MDD model is not applicable to surface releases. In the subsurface, if conditions are more anaerobic, MDD model age uncertainties can range from ±1.5 yr under optimal conditions to ±5 yr in a worst case scenario, where little information is available about the site and free product $(nC_{17}/Pr)_o$ ratios; in the latter case, it may only be possible to conclude that the release is older or younger than 10 yr.

Statistical evaluations of $(nC_{17}/Pr)_o$ ratios analyzed in approximately 4500 worldwide crude oils and 90 domestic refined products (diesel, jet A, fuel oils) were performed to evaluate the impact of variations in this ratio on MDD model ages as well as to provide a regional database for those who may wish to either apply the MDD model to estimate the age of a release or simply use the information in environmental forensic investigations.

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