Advanced Notice of Proposed Rulemaking
Petroleum Cleanup Levels
November 2008

Introduction and Purpose

In September 2007 the Department of Environmental Conservation (DEC) solicited public comment on proposed revisions to the 18 AAC 75 site cleanup rules. As a result of stakeholder comments the department suspended proposed modifications to the petroleum cleanup levels pending further evaluation.

The purpose of this paper is to frame the policy and technical issues under consideration to help guide meaningful stakeholder input. Background information on the development of the current petroleum cleanup levels is provided, followed by a discussion of a number of germane policy and technical issues.

Interested parties are invited to provide comments, concerns, recommendations, or options on any of these or other petroleum-related issues. The goal is to maintain sound public policy reflective of the department's statutory obligations, while endeavoring to incorporate the most current scientific data to develop technically defensible cleanup levels.

Comments should be submitted to the department contacts below, either in hard copy or electronically, by April 30, 2009. A comment responsiveness summary will not be issued by DEC as part of this pre-rulemaking solicitation. However, future public workshops may be scheduled.

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To augment this pre-rulemaking solicitation, DEC plans to issue a professional services contract to research the most recent petroleum science in regards to petroleum soil and groundwater cleanup levels and present all relevant information for the department's consideration.

After all information is compiled in early 2009, DEC may either continue with pre-rulemaking solicitation or propose regulatory revisions under the formal rulemaking process.

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Background

Current regulations known as the "site cleanup rules" (18 AAC 75.325-390) allow for several methods to determine hazardous substance cleanup levels in soil and groundwater. Method 1 petroleum soil cleanup levels reflect simple "matrix" scores that account for depth to groundwater, mean annual precipitation, soil type, potential receptors, and volume of contaminated soil. Method 2 soil cleanup levels were determined using the equations in the 1996 EPA soil screening guidance (SSG). Method 3 alternative soil cleanup levels may be proposed by party undertaking a cleanup action by modifying site-specific variables in the cleanup level equations. Method 4 soil or groundwater cleanup levels may be proposed using the results of a site-specific risk assessment.

The cleanup standards comprise many chemicals, including a number of individual petroleum chemicals such as benzene, toluene, ethyl benzene, xylenes, and polycyclic aromatic hydrocarbons. Collectively, these are known as the petroleum "indicator" compounds. However, petroleum hydrocarbon mixtures consist of hundreds of individual chemicals, many of which have little or no toxicity data. This presented a challenge to DEC during the development of the cleanup regulations in the mid-1990s. As with the list of chemicals in Table B1, cleanup levels for petroleum mixtures (18 AAC 75.341, Table B2) were established for the various exposure pathways and climate zones. The development process was modified slightly, however, as explained below.

Building off the findings of the national Total Petroleum Hydrocarbon Working Group (TPHWG), DEC categorized petroleum hydrocarbon mixtures into hydrocarbon "fractions." The aromatic fractions include a class of chemicals characterized by the presence of the benzene ring as part of the molecule. The non-aromatic fractions are called aliphatic hydrocarbons.

The six fractions selected by DEC included three aromatic fractions and three aliphatic fractions corresponding to the three petroleum carbon ranges known as gasoline range organics (GRO), diesel range organics (DRO), and residual range organics (RRO). These carbon ranges were established by DEC for efficiency and simplicity, because they matched the Alaska methods for petroleum analysis, already in place at the time the regulations were developed. The TPHWG, however, recommended 13 carbon ranges.

DEC established cleanup levels for the six hydrocarbon fractions, which contain many chemicals, using toxicity information relevant to individual petroleum compound within the fraction. This is called a "surrogate" approach because the individual chemicals were assumed to represent the total fraction. DEC then set cleanup levels for the combined fractions (aliphatic component plus aromatic component).

For regulatory purposes, DEC defined the GRO, DRO and RRO compositions using the equivalent carbon ranges and aliphatic/aromatic splits shown in the table below.

Carbon Range	Percent Aliphatic	Percent Aromatic

Carbon Range	Percent Aliphatic	Percent Aromatic
GRO - C_6 - C_{10}	70	50
DRO - C_{10} - C_{25}	80	40
RRO - C_{25} - C_{36}	90	30

Because fuel constituents vary considerably, the default aliphatic/aromatic split was set at 120% of the total as a conservative measure. In other words, the actual aliphatic/aromatic split of a particular fuel blend may vary. This variation in fuel constituents is accounted for the overlapping percentage.

The 18 AAC 75.341, Table B2 aliphatic/aromatic fractional cleanup levels were transformed into total GRO, DRO, and RRO levels by dividing the aromatic or aliphatic cleanup level by a corresponding aromatic or aliphatic default percentage and using the lesser of the two results.

For example, the C_{10}-C_{25} DRO "migration to groundwater" cleanup level for the over 40-inch zone was calculated by dividing the corresponding C_{10}-C_{25} aromatic level (90 mg/kg) by 0.40. The result, 225, was rounded to 230 mg/kg to account for two significant figures in the underlying mathematical equations.

This level was essentially viewed as a protective compromise between the higher aliphatic migration to groundwater cleanup level (6,400 mg/kg) and the lower aromatic migration to groundwater cleanup level (90 mg/kg). This cleanup level accounted for the 80/40 aliphatic/aromatic split. In other words, a site cleaned up to 230 mg/kg total DRO would obviously meet the 6,400 mg/kg aliphatic cleanup level, and would be assumed to contain no more than 90 mg/kg aromatics based on the percentage split.

Several petroleum soil cleanup levels listed in 18 AAC 75.341, Table B2 were based on what DEC termed "maximum allowable concentrations." In the mid-1990s it was DEC's intent to establish maximum allowable cleanup levels taking into account aesthetic and nuisance concerns such as odor and staining. After reviewing information provided in the American Petroleum Institute publication, *A Guide to the Assessment and Remediation of Underground Petroleum Releases* (API, 1996), DEC added footnote 14 to Table B2. Footnote 14 **allows** these so-called "maximum allowable" concentrations to be exceeded if a responsible person shows that contaminant migration will not occur and that no risk will be posed to human health and the environment.

POLICY ISSUES

1. DEC is considering repeal of the method 1 petroleum soil cleanup levels.

The method 1 matrix and soil cleanup levels (18 AAC 75.341, Tables A1 and A2) for petroleum hydrocarbons have been with the department for approximately 16 years. DEC believes the simple matrix and corresponding cleanup levels have outlived their usefulness, are not technically defensible, and to some degree conflict with the method 2

table levels. On the other hand they are conservative and offer an easy-to-use approach for persons conducting cleanups at petroleum-contaminated sites.

DEC is seeking stakeholder input as to whether the Method 1 tables are useful tools worth retaining and if so, how to resolve the conflicts with Method 2 petroleum cleanup levels.

2. DEC is considering repeal of the petroleum aliphatic and aromatic soil cleanup levels (18 AAC 75.341, Table B2). This modification would further clarify and simplify the regulations. As discussed earlier in this document, the current aliphatic/aromatic cleanup levels provide the technical foundation for the total GRO, DRO, and RRO soil cleanup levels. This basis would not change with the repeal. However, in themselves the calculated aliphatic/aromatic values have not been used as regulatory cleanup levels for site management decisions. The default values, chemical properties and assumptions used in the derivation would remain within the *Cleanup Levels Guidance*, adopted by reference in 18 AAC 75.

DEC is seeking stakeholder input on whether to retain the aliphatic/aromatic soil cleanup levels in 18 AAC 75.341, Table B2.

3. During the regulations development stage, so-called "maximum allowable" concentrations (18 AAC 75.341, Table B2) were used to "cap" a number of cleanup level pathways although calculated, risk-based concentrations were higher.

DEC is considering a modification to and use of the maximum allowable concentrations and is seeking stakeholder input on this issue.

Under one option the current maximum allowable concentrations for petroleum hydrocarbons in soil would be re-named "residual saturation levels" and revised to the following values: GRO – 1,000 mg/kg, DRO – 2,000 mg/kg, RRO – 5,000 mg/kg (from 1,400, 12,500, and 22,000 respectively). The modified levels are based upon values listed in the API 1628 publication and the API Soil & Groundwater Research Bulletin No. 9, *Non-Aqueous Phase Liquid (NAPL) Mobility Limits in Soil* (June 2000) for residual NAPL concentrations in coarse gravel.

The name change to "residual saturation level" is under consideration in order to be consistent with the referenced literature and to remove the connotation of "maximum"; in other words, that these levels shall never be exceeded. Text would be added to the regulations to clarify that these are screening levels only and indicate levels above which a risk of NAPL migration to uncontaminated soil may be present. These screening levels would apply only to a final department determination with conditions to control exposure; however, these levels would not imply they could not be exceeded. Residual contamination could remain on-site above these screening levels if it were shown to the department's satisfaction that there was no unacceptable risk of non-aqueous phase liquid (NAPL) migration or to human health and the environment. This would remain

consistent with the intent of footnote 14 in Table B2. Additional discussion on this issue may be found in the SOC report titled *Maximum Allowable Concentration, Residual Saturation, and Free Product Mobility Technical Background Document (GeoSphere, CH2MHill, 2005*[1]*).*

Another option would be to repeal footnote 14 and interpret the maximum allowable concentrations literally. That is, maximum allowable concentrations are thresholds above which anti-degradation and visual and olfactory concerns supersede actual risks. Additional discussion may be found in the SOC report titled *Maximum Allowable Concentration, Residual Saturation, and Free Product Mobility Technical Background Document (GeoSphere, CH2MHill, 2005*[2]*).*

3. Odor and taste thresholds may be exceeded for the petroleum fractions even though contaminant concentrations are below groundwater cleanup levels (18 AAC 75.345, Table C). However, the department's Drinking Water Program does not currently regulate GRO, DRO and RRO: odor is considered a secondary maximum contaminant level (MCL) for a public water system and only if the Drinking Water Program determines it is required. This creates an internal regulatory inconsistency.

DEC is seeking stakeholder input on whether odor and taste thresholds in 18 AAC.345 should remain in effect or be repealed.

TECHNICAL ISSUES

DEC recognizes that current soil and groundwater petroleum cleanup levels were adopted in 1999 with a number of technical discrepancies. **DEC recommends correcting these discrepancies and is seeking stakeholder input on the issues.**

1. Cleanup Level Approaches

   The first step in this process is a rigorous review of other possible petroleum cleanup level approaches. DEC intends to hire a contractor to research petroleum toxicity, phase modeling, alternative surrogates, and other information to help determine if existing petroleum cleanup levels are appropriate and defensible. The petroleum cleanup levels are being evaluated from risk, non-risk (aesthetic), and statutory/regulatory perspectives.

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1 This document is available from DEC upon request, and can also be found on the Contaminated Sites web page.

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There are a variety of approaches to the cleanup of petroleum contaminated sites. In some states site closure is "constituent based," an approach that targets individual compounds such as benzene. Other approaches require a risk assessment evaluation on a case-by-case basis. Some states may still subjectively assign cleanup levels. Other states have levels for total petroleum hydrocarbons (TPH) rather than the GRO, DRO, and RRO fuel fractions. In states with cleanup levels based upon fuel fractions, reported petroleum cleanup levels range from 10 to 2,000 mg/kg.

The variability in petroleum fraction cleanup levels at the national level, plus the other technical discrepancies discussed in this paper, have prompted DEC to re-evaluate Alaska's approach to determining its cleanup standards. Four-phase partitioning can be used to more scientifically identify risks on a site-specific basis. However, four phase partitioning is a site-specific tool and may not account aesthetic and nuisance concerns. Also, although the four-phase approach identifies potential water quality risks, it cannot address all issues with potential off-site transport and disposal of contaminated soil.

DEC is seeking stakeholder input to assist with this effort.

2. Alaska's migration to groundwater cleanup levels for the petroleum fractions are typically used by DEC to close a site without institutional controls. However, these cleanup levels, based on three-phase partitioning, may be overly conservative and may not accurately estimate risks. DEC is considering no longer applying the three-phase soil water partitioning equation to establish total petroleum fraction cleanup levels.

   Additionally, the Contaminated Sites program and regulations do not currently utilize leaching analyes, e.g. the Synthetic Precipitation Leaching Procedure (SPLP) EPA SW846 Method 1312, to evaluate migration to groundwater potential and risk. Other states' may include leaching analyses as part of their regulatory and/or policy framework for evaluating the migration to groundwater pathway.

   Petroleum hydrocarbons exist at a contaminated site in four phases: vapor, dissolved, adsorbed, and non-aqueous phase liquid (NAPL, or free product). The movement of molecules between these phases is continuous in the soil environment. Equilibrium is achieved when the movement into each phase equals the movement out of the phase. DEC's current regulations account only for the movement of molecules between the vapor, dissolved, and adsorbed phases.

   The maximum holding capacity of soil for dissolved-, vapor-, and sorbed-phase hydrocarbons is described as the soil saturation concentration, which is abbreviated as Csat. Below Csat, the risk associated with the vapor-inhalation and migration-to-groundwater pathways increases linearly with increasing

concentration. At concentrations above Csat, the risk associated with the vapor-inhalation and migration-to-groundwater pathways does not increase, but rather remains relatively constant because the vapor and dissolved concentrations do not change as the mass of free product in the system increases. This is an important concept to understand because within the soil matrix, NAPL may be present at the generic GRO and DRO cleanup levels adopted by DEC using the three-phase partitioning approach. The result is that the current migration to groundwater soil cleanup levels for petroleum may overestimate actual risks.

The *Three- and Four-Phase Partitioning & Human Health Risk Calculations Technical Background Report* (Geosphere, CH2MHill, 2005[3]) prepared for the Alaska SOC Working Group proposes the use of a 4-phase partition model to address this issue. Four-phase partitioning is well documented in the technical literature and is used by the Washington State Department of Ecology and the Oregon Department of Environmental Quality to assess soil cleanup levels.

The primary difference between the SOC Working Group's proposed "four-phase calculator" and the existing DEC approach is that the partitioning equations in the four-phase calculator would apply either three-phase or four-phase partitioning equations based on site-specific conditions. The appropriate three- or four-phase distributions are then used to characterize the dissolved- and vapor-phase concentration in the contaminated soil source area.

The core four-phase equations are documented in a paper by Hun Seak Park and Charles San Juan (2000) and include the following variables within each phase:

- Contaminant mass within each phase
- Contaminant concentration within each phase
- Soil organic carbon to water partition coefficient within each phase
- Mass fraction of natural soil organic carbon
- Henry's Law constant
- Aqueous solubility
- Mole fraction in the NAPL mixture
- Total soil porosity
- Water filled porosity
- Air filled porosity
- NAPL filled porosity
- Molecular weight
- Weighted average of molecular weight of NAPL mixture
- Dry soil bulk density
- Density in liquid form
- Density of the NAPL mixture

3 This document is available from DEC upon request, and can also be found on the Contaminated Sites web page.

The four-phase calculator computes and displays risk taking into account the calculated phase concentrations. The phase concentrations are used to evaluate cumulative risk associated with all site-specific petroleum compounds; ingestion and inhalation exposure pathways; and the migration to groundwater fate and transport route.

Four-phase modeling is technically more robust than the current three-phase partitioning approach. However, it is important to understand that the use of four-phase modeling is likely to result in higher petroleum concentrations left on-site because risks have been documented to be within acceptable limits.

DEC is seeking stakeholder input on the use of three and four phase modeling approaches in regards to the migration to groundwater cleanup levels, as well as the utilization of leaching analyses to evaluate the fate and transport potential.

3. The basic surrogate approach currently used by DEC, although endorsed by the TPHWG, does not account for the recommended fractions.

The current DEC defined hydrocarbon range for DRO is C_{10} to C_{25} and RRO C_{25} to C_{36}. The ranges were selected during regulation and cleanup level development in the mid-1990s as a practical matter to allow for the continued use of the existing Alaska petroleum methods, AK102 and AK103. The ranges are not consistent with the TPHWG recommendations or available scientific data. For this reason, DEC is considering revising the DRO and RRO hydrocarbon ranges to C_{10} to C_{21} and RRO C_{21} to C_{36}, respectively. The revised C_{21} division between DRO and RRO is consistent with one of the thirteen TPHWG recommended fractions, as well as with other states' approaches (*e.g.* Washington, Massachusetts).

The revision is also supported by preliminary laboratory analysis of select Alaska fuels as discussed in the SOC paper *Hydrocarbon Characterization for Use in the 4-Phase Cumulative Risk Calculator and Example Characterizations of Selected Alaskan Fuels Technical Background Document* (Geosphere and CH2MHill, 2005).[4] The paper summarizes the analytical hydrocarbon fractionization results of select Alaskan diesel and jet fuels. The laboratory results indicate that approximately 92% of the analyzed fuels elute in the C_{10} to C_{21} hydrocarbon range and only approximately 2% in the C_{21} to C_{36} range. The remaining 7% elutes in the volatile GRO hydrocarbon range, C_5 to C_{10}. In conclusion, a hydrocarbon range revision would more accurately reflect the division point between diesel and residual range organics based on currently available scientific

4 This document is available from DEC upon request, and can also be found on the Contaminated Sites web page.

information. The Alaska Petroleum Methods for DRO and RRO, AK102 and AK103, would be updated to incorporate the hydrocarbon range revision.

DEC is considering revising the DRO and RRO hydrocarbon ranges and the default aromatic/aliphatic compositional percentages used for calculating total GRO, DRO, and RRO (see #3 below) and is seeking stakeholder input on this issue.

4. As previously discussed in this paper, during the mid-1990s development of the petroleum cleanup levels DEC defined default aromatic/aliphatic compositional percentages for each hydrocarbon fuel range (GRO, DRO and RRO). Literature review indicated that fuel composition varied considerably; therefore, as a conservative measure the default aliphatic/aromatic composition sum was set at 120%. The above referenced SOC paper provides additional compositional data of select Alaskan gasoline, diesel and jet fuels.

   The DEC contractor will research available technical literature to evaluate if more accurate data is available for the aromatic/aliphatic composition of refined petroleum products. **DEC is seeking stakeholder input to assist with this effort.**

5. There is an inconsistency under current regulations in the way the petroleum soil and groundwater cleanup levels were derived. For gasoline range organics (GRO), the groundwater cleanup level, calculated according to the department's risk based equation, is 7.3 mg/L for aromatics and 182.5 mg/L for aliphatics. During the mid-1990s cleanup regulations development, DEC decided that as a conservative measure the GRO groundwater cleanup level, as listed in 18 AAC 75.345, Table C, would default to the calculated *solubility of the GRO aliphatic range* (1.3 mg/L) rather than using either the calculated aromatic or aliphatic level. This level was considered conservative because in addition to being less than the calculated aliphatic/aromatic groundwater levels, it addressed free product formation on the groundwater table.[5]

   The two assigned groundwater cleanup level fractions for GRO (7.3 mg/L aromatics and 1.3 mg/l aliphatics) were then used to calculate the aromatic/aliphatic soil migration to groundwater cleanup levels. As described earlier in this document, these cleanup levels were combined with the aliphatic/aromatic fuel composition percentages (70/50) to calculate the total GRO method 2 soil migration to groundwater cleanup levels for each climate zone. For example, the GRO aromatic cleanup level for the under 40 inch zone is 150 mg/kg. Divide 150 by 0.5 and the total GRO cleanup level is 300 mg/kg. The GRO aliphatic cleanup level for the under 40 inch zone is 270 mg/kg. Divide 270 by 0.7 and the cleanup level is 386 mg/kg. The more conservative of these

5 The requirements for addressing free product are documented at 18 AAC 75.325 (f)(1)B) and 18 AAC 75.380 (b)(7).

two calculations, based on the aromatic fraction, ultimately became the total GRO migration to groundwater cleanup levels in Table B2. Thus, the aliphatic solubility level for GRO had no effect on the migration to groundwater soil cleanup level.

Unlike the total GRO groundwater cleanup level, the calculated solubility of the DRO aliphatic range (0.1 mg/L) was not used as the total DRO groundwater cleanup level. Rather, the higher calculated aromatic risk based fraction (1.5 mg/L) was used. Although the basis was different, this groundwater cleanup level was similar to the GRO groundwater cleanup level (1.3 mg/L) and was selected in terms of both public acceptability and technical achievability.

The table below shows the differences in the cleanup levels depending on their basis.

	GRO	DRO
Current Groundwater Cleanup Level	1.3 (aliphatics)	1.5 (aromatics)
Solubility Based Groundwater Cleanup Level	1.3 (aliphatics)	0.1 (aliphatics)
Risk Based Groundwater Cleanup Level	7.3 (aromatics)	1.5 (aromatics)

In summary, the GRO migration to groundwater cleanup levels are slightly higher than the DRO although the gasoline fraction may represent more risk. For example, for the under 40-inch precipitation zone the most conservative GRO cleanup level in Table B2 is migration to groundwater at 300 mg/kg. The DRO migration to groundwater cleanup level for the under 40-inch zone, on the other hand, is 250 mg/kg. Recognizing that the BTEX indicator compounds are addressed independently in regulation, this is still counterintuitive because gasoline poses more risk than diesel due to its volatility and mobility in the environment. Also, there is minimal toxicity information related to many GRO fuel constituents; erring on the side of conservatism is therefore justified. **DEC is seeking stakeholder input on whether this inconsistency should be corrected, and if so, other options that may be available**.